INVESTIGATIONS ON THE PHENOMENON OF SORPTION-DESORPTION HYSTERESIS

A Thesis Submitted
in Partial Fulfilment of the Course work
for the Degree of Doctor of
Philosophy
to the
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

by

R. K. S. BHATIA, M. Sc.

DEPARTMENT OF CHEMISTRY
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)
MARCH, 1970.

INVESTIGATIONS ON THE PHENOMENON OF SORPTION-DESORPTION HYSTERESIS

A THESIS SUBMITTED
IN PARTIAL FULFILMENT OF THE COURSE WORK FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY
TO THE
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

BY
R.K.S. BHATIA, M.Sc.

DEPARTMENT OF CHEMISTRY
BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN)
MARCH, 1970.

Dr.S.L. Gupta, Ph.D., A.R.I.C., F.I.C.,
Head,
Department of Chemistry,

BIRLA INSTITUTE OF TECHNOLOGY & SCIENCE,
PILANI (RAJASTHAN)

Dated: March 30, 1970.

SUPERVISOR'S CERTIFICATE

This is to certify that the research work described in the thesis entitled "Investigations on the phenomenon of sorption-desorption hysteresis" was carried out by Shri R.K.S. Bhatia, M.Sc., during the period from August 1966 to March 1970 in the Department of Chemistry under my guidance and supervision.

S.L. GUPTA

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Professor S.L. Gupta, M.Sc., Ph.D., A.R.I.C., F.I.C., Head of the Department of Chemistry, Birla Institute of Technology and Science, Pilani, for his guidance and constant encouragement throughout these investigations.

My sincere thanks are also due to Dr. V. Shankar, Assistant Professor, Department of Chemical Engineering, B.I.T.S., Pilani, for instructive discussions and to fellow research workers in the department for their co-operation, in the work.

I am also thankful to Dr. K. Subba Rao, D.Sc., A.R.I.C., Retired Scientist (CSIR), Indian Institute of Science, Bangalore, for introducing me to the problem and guidance at the initial stages of the work. My thanks are also due to Mr. T.C. Gupta for typing the manuscript.

It is my pleasant duty to thank the authorities of the Birla Institute of Technology and Science, for providing research facilities and financial assistance.

R.K.S. BHATIA

CONTENTS

PAGE

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CONTENTS

PAGE

CHAPTER VI

CHAPTER VII

CHAPTER VIII

*****

***

*

CHAPTER I

INTRODUCTION

Sorption

Whenever the surface of a solid or a liquid is allowed to come into contact with a gas or the vapour of a liquid, there is usually increased concentration of the gas or the vapour molecules at the surface, regardless of the gas or the surface. This phenomenon of surface concentration is known as 'adsorption'. True adsorption or strictly surface concentration is a rarity in nature because of the rarity of ideally plane surfaces. Surfaces are generally non-uniform and contain cracks and capillaries. Porous adsorbents contain capillaries even in the interior. In such cases, in addition to surface concentration, the condensation of the liquid in the capillaries sets in. Infact, all cases of adsorption are generally accompanied by capillary condensation. Besides, other effects like absorption and chemisorption sometimes occur. In order to cover all these processes accompanying adsorption, the term 'sorption' was suggested by McBain (1,2).

The solid that takes up the gas or the vapour of liquid is called adsorbent while the gas or vapour adsorbed on the surface of the solid is termed adsorbate.

Types of Adsorption

Adsorption processes can be classified into two distinct types as physical adsorption and chemisorption, depending upon the nature of forces involved. In physical adsorption the surface concentration is due to weak interaction between adsorbent and adsorbate, similar to condensation. The gas molecules are bound to the surface by dispersion forces (3) and short ranged repulsion forces (4). Chemisorption is due to strong interaction between the adsorbent and adsorbate, similar to chemical reactions. The gas molecules are bound to the surface by a transfer or sharing of the molecules.

The term 'Van der Waals' adsorption is used as a synonym for the former while the term 'Activated' adsorption as a synonym for the latter.

All adsorption processes, whether physical or chemical in character, are accompanied by a decrease in free energy. Solid surfaces are similar to liquid surfaces in that there are unbalanced or unsymmetrical forces present. These forces are satisfied to some extent by the adsorption of the adsorbate. The free surface energy is therefore decreased. Because the adsorption of gases or vapours also involves a decrease in entropy. The equation

$$\triangle F = \triangle H - T.\triangle S$$

shows that $\triangle H$ will decrease when the sum of $\triangle F$ and $\triangle S$ decreased. Therefore,adsorption processes are always exothermic. Conversely, the corresponding desorption processes are endothermic. The decrease in the heat content of the system is termed as heat of adsorption.

Distinction between Physical and Chemisorption

One of the best known criteria for distinguishing between physical and chemisorption is the magnitude of the heat of adsorption. Physical adsorption involves relatively small heats of adsorption, similar in magnitude to heats of liquefaction. Chemisorption, however, is associated with high heats of adsorption, often in the neighborhood of heats of chemical reaction. Heats of physical adsorption of carbon monoxide and hydrogen were always less than about 6 and 2 K.cal/mole (5,6) respectively, whereas heats of chemisorption seemed always to exceed some 20 and 15 K.cal/mole (7,8). However, this distinction is in general valid, there are cases (9,10) in which the heat of chemisorption is considerably low.

Another contrast between physical and chemisorption lies in the rate of adsorption. Physical adsorption, being non-activated, proceeds at a fast rate even at very low temperatures. Chemisorption, being a chemical process, frequently requires activation energy and so, proceeds at a limited rate which increases rapidly with rise in temperature. Later work, however, with clean metal wires and evaporated films has shown that chemisorption is sometimes fast even at low temperatures (11,12).

Another important criterion concerns the thickness of the adsorbed layer. Physical adsorption, though monomolecular at lower relative pressures, becomes multimolecular at higher relative pressures whereas, chemisorption is always confined to a single atomic or molecular layer.

Physical adsorption is essentially non-specific with respect to the adsorbent and adsorbate, whereas chemisorption involves a high degree of specificity (13).

On the basis of these distinctions, it can be stated that physical adsorption is a surface condensation while chemisorption is a surface reaction. It is also useful to distinguish between chemisorption and chemical reaction. In chemisorption the adsorbate-adsorbent interaction involves only the surface layer, whereas in chemical reaction in the conventional sense there are bulk phase changes (14).

Different types of Adsorption Isotherms

For a given gas and a unit weight of a given adsorbent, the amount of gas adsorbed 'a' at equilibrium is a function of the final pressure 'p' and the temperature 'T', i.e.,

$$a = f(p, T)$$

When the pressure of the gas is varied and the temperature is kept constant, a plot of the amount adsorbed against the pressure is called the 'adsorption isotherm',

$$a = f(p) \quad \text{at constant 'T'}.$$

When the pressure is kept constant and the temperature is varied, a plot of the amount adsorbed against the temperature is the 'adsorption isobar'

$$a = f(T) \quad \text{at constant 'p'}$$

The plot of the variation of equilibrium pressure with temperature is the 'adsorption isostere'

$$p = f(T) \quad \text{at constant 'a'}$$

Adsorption isotherm proves to be the most convenient method for presenting adsorption data. The adsorption isotherms obtained with numerous adsorbates and adsorbents have a large variety of shapes. Brunauer, Deming, Deming and Teller (15) have classified these different isotherms into five typical categories (Figure 1). Type I represents monomolecular adsorption whereas others represent multimolecular adsorption.

Theoretical Aspects of Adsorption

A number of theoretical isotherms have been derived by many workers in the past. In deriving theoretical isotherms, three approaches are possible. (1) In kinetic terms, the condition for equilibrium is that the velocities of adsorption and desorption are equal, and isotherms may be obtained by equating these velocities. (2) In statistical terms, the equilibrium constant is given by a ratio of partition functions of vacant sites, adsorbed molecules and gas phase molecules, and isotherm may be obtained by equating this ratio to the corresponding ratio of concentrations. (3) In thermodynamic terms, the isotherm may be derived by using the condition that the change in free energy on transferring an infinitesimal amount of gas from the gas phase to the surface at constant temperature is zero, or alternatively, using the Gibb's adsorption equation.

Earlier Contributions

Current research in adsorption, both theoretical and applied, has been guided to a great extent by the early contributions of Langmuir, Freundlich and Polanyi. The work of these investigators represents three widely different approaches.

Langmuir's theory: One of the first and most important equations based on theory was that developed by Langmuir (16-18). It was pointed out by Langmuir that because of the rapid falling off of intermolecular forces with distance, it was probable that adsorbed layers were no more than a single molecule in thickness. Langmuir visualized adsorption in a unimolecular layer as a dynamic process. The gas molecules strike the surface, most of them get adsorbed and stay on the surface for a while, then they acquire enough energy to leave the surface. At equilibrium the amount adsorbed has a definite value; the rate of adsorption must therefore be equal to the rate of desorption. It was assumed by Langmuir that the forces of interaction between the adsorbed molecules themselves are negligible and only elastic collisions occur on the covered surface . If V_m is the volume of adsorbate required to complete the monolayer and V is the volume adsorbed at the measured pressure, p, then the fraction of surface covered is equal to V/V_m. Thus,

$$\frac{V}{V_m} = \frac{kp}{1+kp}$$

or

$$\frac{p}{V} = \frac{1}{kV_m} + \frac{p}{V_m}$$

This is the linear form of the Langmuir relationship that provides a method for obtaining the amount of adsorbate required to cover the surface.

Volmer (19) has derived the Langmuir equation thermodynamically whereas Fowler (20) has derived it by employing the statistical mechanical approach. Others (21,22) have also made the statistical derivation of the Langmuir equation.

Freundlich's equation: The classical Freundlich equation (23) described the behaviour of many systems in the slightly higher region of intermediate pressure:

$$V = kp^{1/n}$$

where V is the volume adsorbed, p is the pressure of adsorbate gas, k a constant, and n, a constant greater than unity. The Freundlich equation was introduced simply as an empirical relationship. It deals most successfully with adsorption at intermediate pressures, but many adsorption systems even in this region do not obey the Freundlich relationship. Nevertheless, theoretical considerations of Halsey and Taylor (24) and Sips (25) have shown that, if the Langmuir adsorption equation is applied to a series of sites the relative energies of which follow an exponential relationship, the Freundlich equation is obtained. Rideal (26) has shown that the Freundlich equation can be derived from the Gibbs adsorption equation by assuming that the surface layer obeys the change in free energy on adsorption of gas as proportional to the change in adsorbed volume and to the absolute temperature.

Frumkin (27,28) derived an adsorption isotherm by inserting in the Langmuir equation the condition that the heat of adsorption decreases linearly with coverage. Zeldowitsch (29) derived Freundlich isotherm on the basis of statistical mechanics.

Although Freundlich isotherm has been fairly widely used in the qualitative literature as an empirical equation, there does not seem to be any great significant theoretical basis for it. The chief use of the equation has been as an interpolation formula, though it is still frequently employed in connection with adsorption from solutions.

Polanyi's theory: At approximately the same time that Langmuir was developing his monomolecular theory for gas adsorption, Polanyi (30,31) was formulating an entirely different concept known as the potential theory. This concept in its original form dealt only with physical adsorption and implied the existence of films many molecules thick. According to Polanyi, the adsorbent exerts strong attractive forces upon the gas in its vicinity and these attractive forces give rise to adsorption. He further assumed that as the forces of attraction reaching out from the surface of the adsorbent are great, many adsorbed layers are formed on the surface. These layers are under compression as each layer is compressed by all the layers adsorbed on top of it.

The Polanyi theory, which has been considered in detail by Brunauer (32), is of limited utility because it does not yield an equation relating pressure and adsorption. It provides little information about the structure or extent of the surface or the thickness of the adsorbed layer. Nevertheless, it indicates that the adsorbed gases behave much like compressed gases and liquids and demonstrates the temperature dependence of adsorption. The early potential theory has been modified by Goldmann and Polanyi (33) and by others (34,32).

A polarization theory offered by de Boer and Zwikker (35) was also concerned with multi-layers. It attributes adsorption by ionic adsorbents to the dipoles induced in nonpolar adsorbate molecules. The induced dipoles in the first layer induce dipoles in succeeding layers. Polarization theory may have produced empirical relationships of some use but it is unlikely that the effect of induced dipoles even in a second layer could account for significant adsorption (32,36).

Capillary Condensation

Capillary condensation theory was put forward in its original form by Zsigmondy (37). It was long known that when a capillary is immersed in a liquid that wets its walls, the liquid rises in the capillary and forms a meniscus which is concave towards the vapour phase. The vapour pressure over the meniscus is lower than the normal vapour pressure of the liquid by an amount equal to the pressure exerted by the column of liquid in the capillary. The lowering of vapour pressure in a cylindrical capillary is given by the well known equation (38)

$$\ln p/p_o = - \frac{2\sigma V}{rRT} \cos \theta$$

where p is the equilibrium pressure, p_o is the normal vapour pressure, σ is the surface tension, V is the molecular volume of the liquid at temperature T, θ is the angle of wetting, R is the gas constant and r is the radius of the capillary. Zsigmondy assumed that in small capillaries condensation takes place at pressures considerably lower than the normal vapour pressure.

McGavack and Patrick (39) believed that the use of the Kelvin equation down to pore diameters of molecular magnitude was not justified and hence the volume of liquid condensed in the capillaries at the relative pressure p/p_o should be used instead of the volume of the gas adsorbed at pressure p. Capillary condensation plays an important role at higher pressures.

Later Developments

Later work has been concentrated on efforts to describe adsorption in terms of isotherms and to analyse different types of such isotherms. The equations developed give curves that closely approximate the contours of the isotherms throughout a wide range of pressure. In recent years the best known and most widely used of the multilayer adsorption theories is that developed by Brunauer, Emmett and Teller and now known as the BET theory (36). It was the first theory that attempted to describe more than one of the five types of isotherms. The BET theory was subsequently extended by Brunauer, Deming, Deming and Teller (15). In the extended form of the theory, all five types may be derived as special cases.

The BET theory: The BET multimolecular theory (36) is essentially an extension of the Langmuir interpretation of monomolecular adsorption. The derivation is based on the same kinetic picture and the assumption that condensation forces are the principal forces in physical adsorption. As in the Langmuir theory, the rate of evaporation of the molecules in the first layer is considered to be equal to the rate of condensation on the uncovered surface. It is then similarly argued that the rate of evaporation from each succeeding layer is equal to the rate of condensation on the preceding layer. A summation is then performed. It is assumed that the heat of adsorption in each layer, other than the first, is equal to the heat of liquefaction of the bulk adsorbate material, i.e., the Vander Waals forces of the adsorbent are transmitted to the first layer only. Expressions are obtained for adsorption on a free surface and on a restricted surface. If it is assumed that on a free surface an infinite number of layers may be adsorbed, the BET isotherm equation can be derived:

$$\frac{p}{V(p_o-p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c \cdot p_o}$$

where V is the total volume adsorbed at the measured pressure, p; V_m is the volume adsorbed in the monolayer; p_o is the saturation pressure of the adsorbate gas; and c is a constant related exponentially to the heat of adsorption and the heat of liquefaction of the adsorbate. Because the equation is linear, a plot of the data within limits will give a straight line from which the values of the two constants, V_m and c, may be obtained. The derivation of BET equation by a statistical mechanical approach is discussed by Hill (40).

The BET multilayer theory yields another adsorption expression if the adsorption is not on a free surface but is limited in amount by the walls of pores having very small diameters. When the number of layers on each pore wall is restricted to n, then the limited summation leads to the equation:

$$V = \frac{V_m c x}{1-x} \cdot \frac{1-(n+1)x^n+nx^{n+1}}{1+(c-1)x-cx^{n+1}}$$

where x is the relative pressure, p/p_o. This general equation reduces to the Langmuir relationship when n = 1.

Refinements and New Approaches

Several defects in the multilayer theory of Brunauer, Emmett and Teller have been pointed out by the authors themselves and others (41-45). One difficulty is the assumption that the heat of vaporization is the same for all layers following the first and is equal to the heat of vaporization for the bulk liquid. A common subject of criticism is based on the erroneous belief that the authors did not consider lateral interaction effects of adsorbed molecules.

Detailed analysis of adsorption theory by means of statistical and thermodynamic methods has been undertaken by Cassie (46), Everett (47), Halsey (48), Harkins and Jura (49) and Hill (50). The more rigorous treatments include detailed consideration of horizontal interaction effects. Hüttig (51, 52) proposed an adsorption theory which was somewhat similar to the BET theory (36, 53). The principal point of difference between the BET and Hüttig theories is that the Hüttig theory holds that molecules covered by succeeding layers may evaporate with the same facility as exposed molecules. The Huttig equation can be written in the form:

$$\frac{x(1+x)}{V} = \frac{1}{V_m c} + \frac{x}{V_m}$$

where the various terms have the same meaning as for the BET equation. According to Hill (40), the Hüttig derivation (52) contains all the shortcomings that can be attributed to the derivation of the BET equation plus a few additional ones.

Hill (55,56) has developed his statistical mechanical treatment in part by careful consideration of the horizontal interactions of the adsorbed molecules in the monolayer. Cassell has also considered horizontal interactions in a thermodynamic development of adsorption theory (59). Specific application of thermodynamic functions has been discussed by Hill, Emmett and Joyner (57) and Kemball et al (58).

Refinements of the BET theory as well as independent derivations of adsorption isotherm equations have been presented by Halsey (60,61) and by Frenkel (62). These arguments involve the concept of cooperative adsorption which implies that adsorbate molecules influence each other during the adsorption process (63).

Isotherm equations developed by Harkins and Jura (64,65) are closely related in certain respects to those derived by Halsey (60). Harkins and Jura, in developing their thermodynamic theory, observed an analogy between the relationship for monomolecular films on water and those for the physical adsorption of gases on solids. Similar observations have been presented by Gregg and Maggs (66). The following isotherm equation was derived:

$$\log p/p_o = B - A/V^2$$

where V is the volume of gas adsorbed at the measured pressure, p, p_o is the saturation pressure, and A and B are constants.

Other Contributions

Anderson and Hall (67,68) have endeavoured to correct the BET theory for the difference in free energy of adsorption for the second and succeeding layers and of liquefaction of the bulk material. Pickett (69) has dealt with the multilayer adsorption concept in the high pressure region. Carman and Raal (70) have argued that capillary condensation cannot be ignored and must be considered along with multilayer phenomenon. A'dual surface adsorption theory' has been offered by Walker and Zettlemoyer (71,72). Pierce and Smith have also criticised the BET theory to its application to systems having small pores and large areas (73-75).Experiments tending to support the application of the BET theory to small pore systems have been presented by Johnson and Ries (76).

A new approach to a theory for physical adsorption has been proposed independently by Wheeler (77,78) and Ono (79). Discussions of the BET theory and its modifications have been presented by Keenan (80,81) and Cook (82).

* * *

References

(1) McBain, J.W., Phil. Mag. 1909, 6, 18, 916.

(2) McBain, J.W., Z.Physik. Chem., 1909, 68, 471.

(3) London, F., Z. Physik, 1930, 63, 245; Z. Physik. Chemi., 1930, 11, 222.

(4) Born, M., and Meyer, J.E., Z. Physik., 1932, 1, 75.

(5) Beebe, R.A., and Stevens, N.P., J. Am. Chem. Soc., 1940, 62, 2134.

(6) Taylor, H.S., and Williamson, A.T., J. Am. Chem. Soc., 1931, 53, 2168.

(7) Beebe, R.A., Trans. Faraday Soc., 1932, 28, 761.

(8) Beebe, R.A., and Taylor, H.S., J. Am. Chem. Soc., 1914, 46, 23.

(9) Beebe, R.A., and Dowder, D.A., J. Am. Chem. Soc., 1938, 60, 2912.

(10) Trapnell, B.M.W., Proc. Roy. Soc. 1951, 39, A206.

(11) Roberts, J.K., Proc. Roy. Soc., 1935, A152, 445.

(12) Hayward, D.C., and Trapnell, B.M.W., Chemisorption, Butterworth, London, 1964, p.75.

(13) Emmett, P.H., and Brunauer, S., J. Am. Chem. Soc., 1937, 59, 310.

(14) Ries, H.E. Jr., Catalysis, Ed. P.H. Emmett, Reinhold Publishing Corporation, N.Y. 1954, p.2.

(15) Brunauer, S., Deming, L.S., Deming, W.E., and Teller, E., J. Am. Chem. Soc., 1940, 62, 1723.

(16) Langmuir, I., J. Am. Chem. Soc., 1916, 38, 2221.

(17) Langmuir, I., J. Am. Chem. Soc., 1917, 39, 1848.

(18) Langmuir, I., J. Am. Chem. Soc., 1918, 40, 1361.

(19) Volmer, M., Z. Phys. Chem., 1925, 115, 253.

(20) Fowler, R.H., Proc. Camb. Phil. Soc., 1935, 31, 260.

(21) Brunauer, S., The adsorption of gases and vapours, Princeton University Press, Princeton, 1943, p.66.

(22) Young, D.M., and Crowell, A.D., Physical adsorption of gases, Butterworths, London, 1962, p.108.

(23) Freundlich, H., Kapillarchemie, Akademische Verlagsgesellschaft M.B.H., Leipzig, 1923.

(24) Halsey, G.D., and Taylor, H.S., J. Chem. Phys., 1947,15,624.

(25) Sips, R., J. Chem. Phys., 1948, 16, 490.

(26) Rideal, E.K., Surface Chemistry, Cambridge University Press, 1930.

(27) Frumkin, A., and Slygin, A., Acta Physico. Chim., U.R.S.S. 1935, 3, 791.

(28) Brunauer, S., Love, K.S., and Keenan, R.C., J. Am. Chem. Soc., 1942, 64, 751.

(29) Zeldowitsch, J., Acta Physico. Chim., U.R.S.S., 1934,1,961.

(30) Polanyi, M., Verhandl. deut. physik. Ges. 1916, 18, 55.

(31) Polanyi, M., Z.Elektrochem., 1920, 26, 370.

(32) Brunauer, S., The adsorption of Gases and Vapours, Vol.1, Princeton, N.J., Princeton University Press (1943).

(33) Goldmann, F., and Polanyi, M., Z. Physik., Chem., 1928, 132, 321.

(34) Emmett, P.H., and Brunauer, S., J. Am. Chem. Soc., 1935, 57, 2732.

(35) de Boer, J.H., and Zwikker, C., Z. Physik. Chem., 1929, B3, 407.

(36) Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 1938, 60, 309.

(37) Zsigmondy, R., Z. anorg. Chem., 1911, 71, 356.

(38) Thompson, W., Phil. Mag. 1871, 4, 42, 448.

(39) McGavack, J. Jr. and Patrick, W.A., J. Am. Chem. Soc., 1920, 42, 946.

(40) Hill, T.L., Advances in catalysis. Ed. W.G. Frankenburg, V.1, Komarewsky and E.K. Rideal, Vol.4, p.211, New York, Academic Press, Inc. 1952.

(41) Band, W., J. Chem. Phys., 1951, 19, 435.

(42) Cassie, A.B.D., Trans. Faraday Soc., 1947, 44, 575.

(43) Gregg, S.J., and Jacobs, J. Trans. Faraday Soc., 1948, 45, 615.

(44) Hill, T.L., J. Chem. Phys., 1947, 15, 767.

(45) McMillan, W.G., and Teller, E., J. Chem. Phys. 1951,19,25.

(46) Cassie, A.B.D., Trans. Faraday Soc. 1945, 41, 450.

(47) Everett, D.H., Trans. Faraday Soc. 1950, 46, 453.

(48) Halsey, G.D., Advances in Catalysis, Ed. W.G. Frankenburg, V.I. Komarewsky, and E.K. Rideal, Vol.4, p.259, New York, Academic Press, Inc. 1952.

(49) Harkins, W.D., and Jura, G., J. Am. Chem. Soc., 1944,66,1366.

(50) Hill, T.L., J. Am. Chem. Soc., 1950, 72, 5347.

(51) Huttig, G.F., Monatsh, 1948, 78, 177.

(52) Huttig, G.F., Monatsh, 1948, 78, 155.

(53) Ross, S., J. Phys. and Colloid Chem., 1949, 53, 383.

(54) Emmett, P.H., Annual Review of Physical Chemistry Edited by G.K. Rollefson and R.E. Powell, Vol.2, p.287, Annual reviews, Inc., Stanford, California (1951).

(55) Hill, T.L., J. Chem. Phys. 1949, 17, 775.

(56) Hill, T.L., J. Chem. Phys. 1950, 18, 246.

(57) Hill, T.L., Emmett, P.H., and Joyner, L.G., J. Am. Chem. Soc., 1951, 73, 5102.

(58) Hill, T.L., and Kemball, C., J. Am. Chem. Soc., 1952, 74, 3946.

(59) Cassell, H.M., J. Phys. Chem., 1944, 48, 195.

(60) Halsey, G.D., J. Chem. Phys., 1948, 16, 931.

(61) Halsey, G.D., J. Am. Chem. Soc., 1951, 73, 2693.

(62) Frenkel, J., Kinetic Theory of Liquids, Oxford University Press, Oxford, 1946.

(63) Rhodin,T.N.,Jr., J.Am.Chem.Soc., 1950, 72, 4343.

(64) Jura, G., and Harkins, W.D., J. Chem. Phys. 1943, 11,430.

(65) Jura, G., and Harkins, W.D., J. Am. Chem.Soc. 1946,68,1941.

(66) Gregg, S.J., and Maggs, F.A.P., Trans. Faraday Soc., 1948, 45, 615.

(67) Anderson, R.B., J. Am. Chem. Soc., 1946, 68, 686.

(68) Anderson, R.B., and Hall, W.K., J. Am. Chem. Soc., 1948, 70, 1727.

(69) Pickett, G., J. Am. Chem. Soc. 1945, 67, 1958.

(70) Carman, P.C., and Raal, F.A., Nature, 1951, 167, 112.

(71) Walker, W.C., and Zettlemoyer, A.C., J. Phys. and Colloid Chem., 1948, 52, 47.

(72) Walker, W.C., and Zettlemoyer, A.C., J. Phys. and Colloid Chem., 1948, 52, 58.

(73) Pierce, C., and Smith, R.N., J. Phys. and Colloid Chem., 1948, 52, 1111.

(74) Pierce, C., and Smith, R.N., J. Phys. and Colloid Chem., 1948, 52, 1115.

(75) Pierce, C., Wiley, J.W., and Smith, R.N., J. Phys. and Colloid Chem., 1949, 53, 669.

(76) Johnson, M.F.L., and Ries, H.E., Jr., J. Am. Chem. Soc., 1950, 72, 4289.

(77) Wheeler, A., paper presented before the Division of Physical and Inorganic Chemistry, Am. Chem. Soc. Atlantic City, 1949.

(78) Wheeler, A., paper presented before the Division of Colloid Chemistry, Am. Chem. Soc., New York, 1951.

(79) Ono, S., J. Chem. Phys., 1950, 18, 397.

(80) Keenan, A.G., J. Am. Chem. Soc., 1948, 70, 3947.

(81) Keenan, A.G., J. Chem. Education, 1948, 25, 666.

(82) Cook, M.A., J. Am. Soc. 1948, 70, 2925.

***

CHAPTER II

EARLIER AND PROPOSED WORK

Sorption-desorption Hysteresis

Adsorption, in the ideal case, is a reversible process; the amount adsorbed at a given pressure is independent of the way the equilibrium has been approached, i.e., by adding the gas or vapour to the adsorbent (sorption) or by subtracting the gas or vapour from it (desorption). In practice, however, the sorption and desorption curves frequently do not coincide and this phenomenon of the non-coincidence of sorption and desorption curves is known as "Hysteresis". The loop formed by sorption and desorption curves is known as the hysteresis loop. It follows from the study of hysteresis loop that the adsorbent retains for the same vapour pressure, more of the adsorbate during desorption than during sorption (Figure 1). If the difference between sorption and desorption curves is reproducible, the hysteresis is said to be reversible, if the difference is temporary, the hysteresis is irreversible. In physical adsorption hysteresis is usually reversible.

Sorption-desorption hysteresis, which has been established to be real and reproducible, is a puzzling phenomenon. The exact cause of this phenomenon has still remained a vexed and unsolved problem for which there is still no generally accepted explanation though a number of fruitful suggestions have been put forward to explain the difference which exists between the states of adsorbate along the two sides of the hysteresis loop.

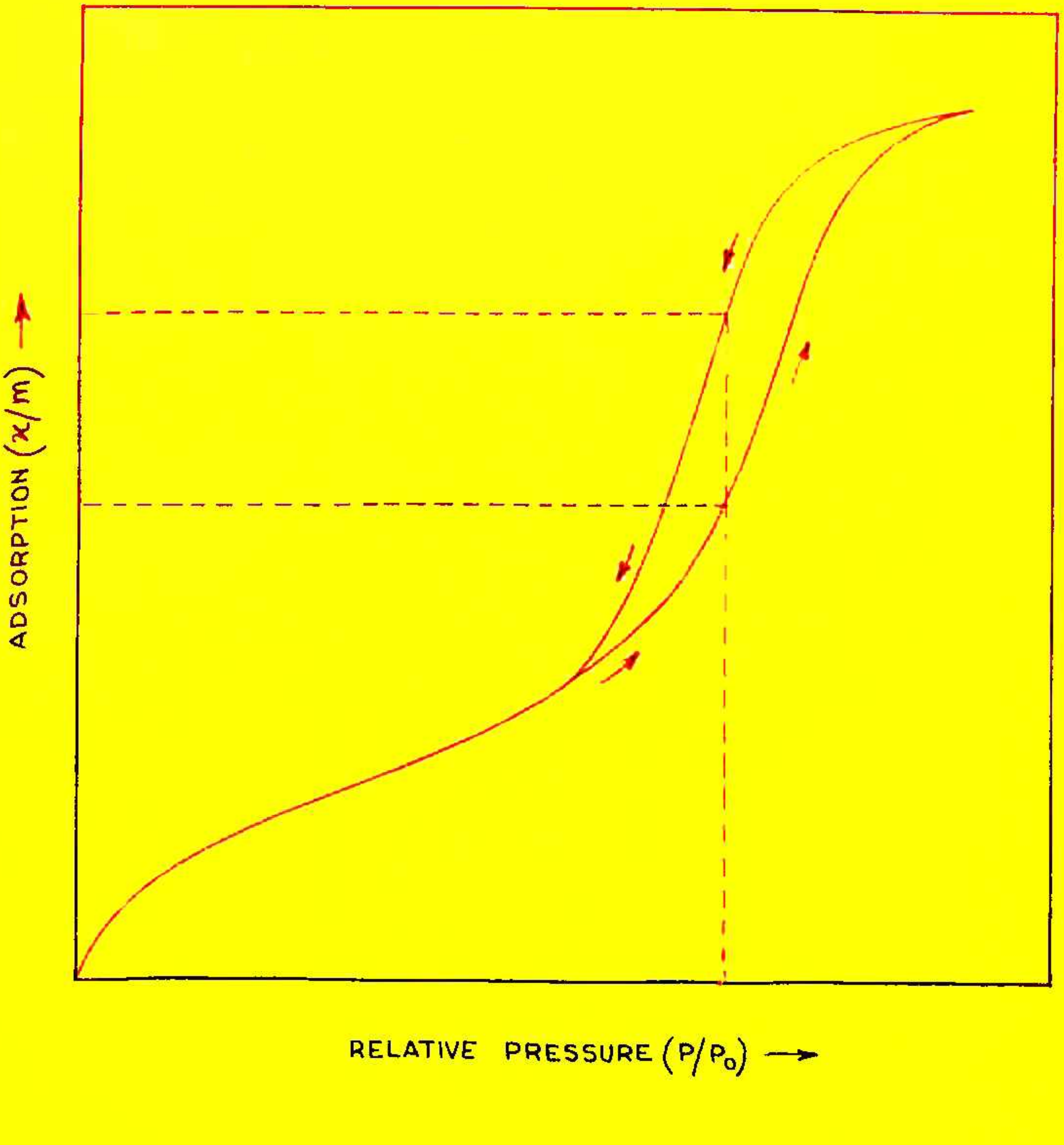


FIG. 1 SORPTION-DESORPTION HYSTERESIS.

[illegible] of Sorption-desorption Hysteresis

Since the relative pressure corresponding to a given adsorption is lower along the desorption branch, it follows, on general thermodynamic grounds that the chemical potential of the adsorbate is likewise lower; the desorption branch is accordingly more likely to correspond to a condition of true equilibrium. There have been a number of attempts to explain the difference which obviously exists between the state of the adsorbate along the two side of the loop. The earlier attempt at an explanation was that by Zsigmondy (1), who explained hysteresis in terms of a difference of contact angle during adsorption and desorption. Later developments of capillary condensation hypothesis ascribed hysteresis essentially to some difference between the mechanisms of adsorption and desorption. Cohan (2), and independently Coelingh (3), reverted to the view that capillary condensation occurred along both branches of the loop, and explained hysteresis in terms of the different shape of the meniscus during adsorption and desorption respectively. Along the desorption branch the Kelvin mechanism is assumed - the meniscus being hemispherical - but along the adsorption branch the meniscus is supposed to be cylindrical in shape, the pore being open at both ends. In the Kraemer-McBain(4) theory of hysteresis, a 'bottle neck' pore having a narrow orifice and a relatively large body is assumed. The difference lies in the radius of the pores in which condensation and evaporation respectively occur; the Kelvin mechanism being retained for both processes.

As pointed out earlier, no mechanism has so far been proposed that fits all the experimental data. Theories that have been advanced to explain sorption-desorption hysteresis are based on capillary condensation which is governed by the well known Kelvin equation (5).

$$\ln p/p_o = - \frac{2V\sigma}{rRT} \cos \theta$$

where, p_o = normal vapour pressure

p = observed pressure

V == molar volume of the adsorbate

σ = surface tension of the adsorbate

r = radius of the capillary

R = gas constant

T = absolute temperature

θ = angle of wetting.

The incomplete wetting theory

Zsigmondy assumed that during adsorption, the vapour does not wet the walls of the adsorbent completely and hence angle of wetting θ is not zero. The equilibrium pressure will be given by the Kelvin equation (5)

$$\ln p_a/p_o = - \frac{2V\sigma}{rRT} \cos \theta \qquad (1)$$

where p_a is the observed pressure on the adsorption branch of the curve and other symbols having the usual meaning. He also emphasised that incomplete wetting was caused by the impurities, mostly air, adsorbed on the walls of the capillary. As the pressure is raised, these impurities get displaced by the adsorbate and finally at saturation pressure complete wetting takes place, thereby giving zero wetting angle, i.e.,

$$\ln p_d/p_o = - \frac{2V\sigma}{rRT} \qquad \text{(ii)}$$

hence, on comparing equations (i) and (ii)

$$p_a > p_d$$

This indicates that pressure along adsorption branch is greater than that along desorption branch thus, accounting for hysteresis.

Zsigmondy's interpretation, which would apply only to irreversible hysteresis, was subsequently disapproved by the work of Rao and coworkers (56-69).

<u>Ink bottle or cavity theory</u>

The ink bottle or cavity theory was suggested by Kraemer (6) and developed by McBain (4), Katz (7) and Rao (8). A cavity is a capillary with a narrow neck like an ink bottle (Figure 2). A cavity may have two or more necks. During

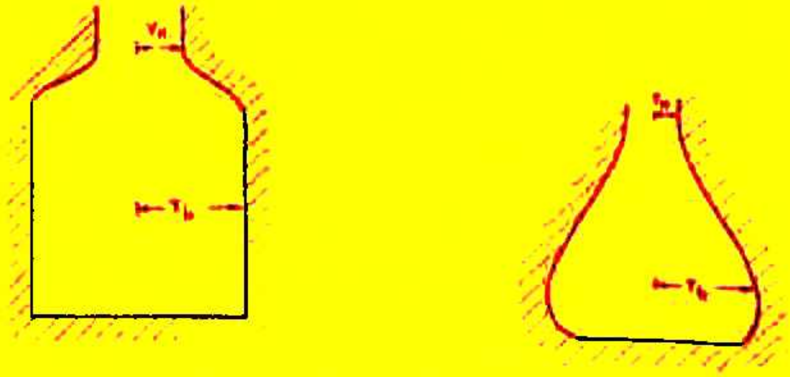


FIG 2 INK BOTTLE PORES.

sorption, neck or necks get filled up with the liquid and the liquid meniscus advances into the interior of the cavity as the vapour pressure increases until the cavity is completely filled. During desorption, the cavity remains filled until the vapour pressure is lowered than the value corresponding to the neck radius when the cavity is suddenly emptied. Thus, the process of filling (sorption) is progressive and emptying (desorption) is sudden and abrupt. The two processes are not identical, certain amount of sorbate is entrapped in the cavity during desorption which accounts for hysteresis. Mathematically, on adsorption side

$$\ln p_a/p_o = -\frac{2V\sigma}{r_b \cdot RT} \qquad (i)$$

where r_b is the radius of the body and all other symbols have their usual meaning (5). On desorption side,

$$\ln p_d/p_o = -\frac{2V\sigma}{r_n \cdot RT} \qquad (ii)$$

where r_n is the radius of the pore.

Since r_n is smaller than r_b, $p_a > p_d$. Thus, accounting for hysteresis.

In addition to the cavities which are present mainly in the interior of the porous adsorbent, there are also V shaped pores, present mostly on the surface. According to 'ink bottle' hypothesis, V shaped pores oriented with their large openings to the surface would not exhibit hysteresis because the filling and emptying of these pores are reversible.

The argument was developed further by Barrer et al (9), they associated hysteresis with re-entrant angles within the pores, i.e., spheroidal cavities or ink bottles, but not with V-shaped pores. They also emphasized that hysteresis can arise from causes other than capillary condensation, i.e., structural changes in the adsorbent.

The 'ink bottle' or cavity theory of hysteresis has been successful in explaining reversible hysteresis and the phenomenon associated with it such as disappearance, drift, scanning and permanence. However, it can explain all cases of hysteresis in a qualitative way. So far, no quantitative formulation of the theory has been made by anybody.

Cohan's theory

Cohan (2) explained hysteresis in terms of the different shapes of the meniscus during sorption and desorption. Cohan formulated his theory with Foster's idea (10) that a delay in the formation of meniscus during adsorption is responsible for the phenomena of hysteresis. Cohan assumed that the shape of the meniscus being hemispherical in desorption and cylindrical in shape, pore being open at both side, during sorption., In desorption Kelvin's equation of evaporation of liquid from capillary is assumed but in sorption a cylindrical film of liquid is first formed and next the capillary is filled with liquid as the pressure increases. Assuming this mechanism, Cohan has shown that for a capillary of particular radius, capillary condensation along the sorption branch occurs at a high relative vapour pressure than capillary evaporation along the desorption branch; thus accounting for hysteresis. Further, he has shown that hysteresis cannot occur in capillaries narrower than four molecular diameters of the adsorbate. This immediately explains why certain vapours exhibit hysteresis on a given adsorbent while other vapours show no hysteresis on the same adsorbant.

Enderby (11,12) and Everett et al (13-16) attributed hysteresis to the existence of a very large number of independent domains in a system and at least some of which can exist in meta stable states.

Summing up, the ink bottle theory has been successful in explaining the hysteresis effect and all its allied phenomenon but the theory accounts for all the phenomenon in a qualitative way. A quantitative formulation of the theory would be probably difficult, because it involves information about the number, shape, size, the neck and body diameter of the cavity in any system.

Classification of hysteresis loops

Barrer et al (9) discussed various shapes of capillaries

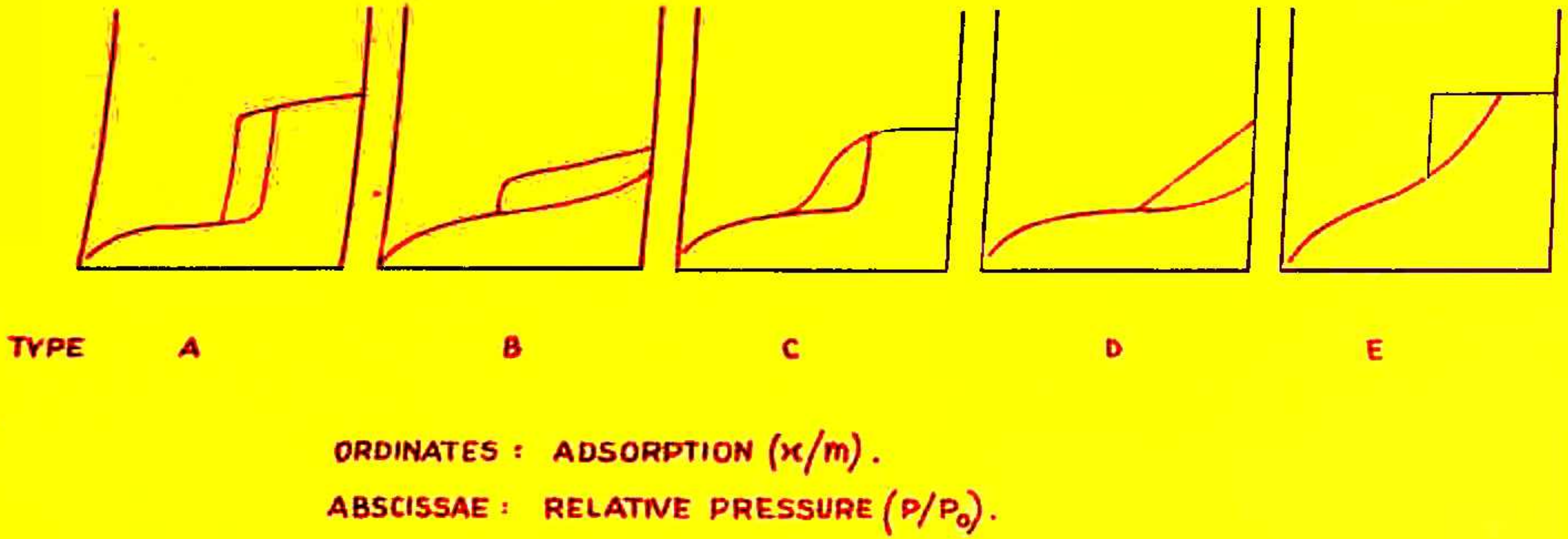


FIG.3 FIVE TYPES OF HYSTERESIS LOOPS.

and their influence on the form of the sorption and desorption. But deBoer (17) has adopted the reverse procedure and classified hysteresis loops into five typical categories (Figure 3).

Type (A) Both adsorption and desorption branches are steep at intermediate relative pressures.

(B) The adsorption branch is steep at saturation pressure, the desorption branch at intermediate relative pressures.

(C) The adsorption branch is steep at intermediate relative pressures, the desorption branch is sloping.

(D) The adsorption branch is steep at saturation pressure, the desorption branch is sloping.

(E) The adsorption branch has a sloping character, the desorption branch is steep at intermediate relative pressures.

Earlier work

The classical researches Van Bemmelen (18), Zsigmondy et al (1) and Anderson (19) revealed the existence of hysteresis effect in sorption of water by gels and jellies. Gustaver (20) and Coolidge (21,22) showed the presence of hysteresis with charcoal. Winning and Williams (23) have shown that glyptal resins exhibited hysteresis in sorption of organic vapours. Shiels (24-26) has reported the complete absence of hysteresis effect in the sorption of sulphur dioxide on platinised asbestos, whereas in the sorption of sulphur dioxide on platinum black, hysteresis was observed. Further, working with active charcoal in the sorption of sulphur dioxide, carbon monoxide and nitrous oxide, he obtained hysteresis effect in carbon-sulphur dioxide system. He stated that preliminary evacuation of adsorbent and its history during experimental work was important in considering hysteresis effect.

McGavack and Patrik (27) obtained the hysteresis effect in the sorption of sulphur-dioxide on silica gel, whereas, on keeping the gel over night in contact with sulphur dioxide, subsequent sorptions and desorption showed no hysteresis. Richardson (28) has shown that the hysteresis in coconut charcoal-carbon dioxide system disappeared at temperatures above 55°C.

King and Lawson (29) observed hysteresis effect in the sorption of heavy water on charcoal. The hysteresis effect was attributed to rise in pressure of evacuation during studies. McBain and Fergussion (30) also noticed hysteresis effect in the sorption of water vapour on Gatton stone. Burrage (31) studied the sorption of carbon tetrachloride, methyl alcohol, ethyl alcohol, propyl alcohol and Formic acid on charcoal and obtained hysteresis effects in all cases. Foster (32) obtained the reproducible hysteresis loops on the sorption. of methyl alcohol and ethyl alcohol on silica gel. Whereas Pidgen (33) obtained hysteresis effect only in case of water while studying the sorption of water, benzene and ethyl alcohol on silica gel.

Allmand and coworkers (34) provided strong evidences for the fundamental nature of the phenomenon and established, beyond doubt, the reality of the phenomena. While studying the sorption of vapours of water, ethyl alcohol and benzene on gels of silica and ferric oxide, Lambert and Foster (35) showed that hysteresis effect was real and it persisted even after drastic degassing of the gel surface.

Urquhart and coworkers (36-40) reported the hysteresis effect on the sorption of water on cellulose. Sheppard and Newsome (41) on the other hand observed that the hysteresis loop becoming smaller in three consecutive sorptions and desorptions in the study of water sorption on cellulose and its derivatives. They stated that yet there is no complete explanation of the hysteresis effect. Wahba and Nashed (42) have also noticed that the adsorption regain and hysteresis effect becoming smaller in successive sorption-desorption cycles. According to their interpretation of hysteresis, the water molecules are more tightly held on the desorption side, so that the vapour pressure on the desorption side is lower than that on the adsorption side, for the same amount of water adsorbed.

Seborg (43) studied the hysteresis in water sorption by paper making materials and attributed hysteresis to some physical or molecular characteristic of cellulose molecule connected with sorption mechanism. Walker and Collaborators (44) studied the influence of air on hysteresis of water vapour sorption on cellulose. Recently, Rao and Das (45) have studied the influence of variety of the adsorbent on the sorption-desorption hysteresis with water vapour. Carman and Raal(46), Kiselev (47), Zwietering (48) and Barrer (49) have studied the effect of compaction of the adsorbent on hysteresis but the most appropriate explanation was provided by Thorp (50).

Jeffries (51) has reported hysteresis effect in the sorption of water vapour on cellulose and eight other textile polymers below and above 100°C. The main object of Jeffrie's work was to find a treatment which would stabilise the samples, i.e., to make them independent of further sorption treatments. Similar studies with paper have been reported by Houtz and McClean (52).

Fugassi (53) obtained hysteresis effect in the sorption of methyl alcohol vapours on cellulose. Barkas (54) obtained marked hysteresis in cellulose water vapour systems and explained the hysteresis effect in terms of plastic deformation of cellulose surface brought about by water vapour during sorption. The work of Archer (55), on the sorption of non-aqueous vapours on cellulose exhibited hysteresis and the hysteresis effect increased with increasing vapour pressure of the adsorbate.

Although, sorption-desorption hysteresis has been observed by many investigators in the past, the status of the phenomenon has been frequently challanged. It was claimed, for example, that hysteresis arose from the presence of impurities on the surface of the adsorbent, the failure to allow sufficient time for the attainment of equilibrium, from the ash content of the adsorbent, etc. However, by the extensive work of Rao and his school (8,56-69), in India, on a large number of variety of systems, the hysteresis effect has been established to be real and the only satisfactory explanation for hysteresis and allied phenomenon such as permanence and reproducibility (56,61,64), drift (56,59), scanning (56,58, 63, 64) and disappearance (56,57,60,65,67) of hysteresis loop has been based on the cavity concept (4,6) thus, disapproving all earlier explanations.

Recently, Bhatia (70,71) and Gupta and Bhatia (72) reported permanent and reproducible hysteresis in cellulose and other swelling systems and they have also supported the cavity theory of hysteresis. A recent private communication by McIntosh (73) suggested that the hysteresis of dielectric values might be related to the presence of water-soluble matter in the gel but Petrie's examination of ethyl alcohol in porous glass (74) shows no evidence of this phenomenon.

Proposed Work

Although, very many major studies of synthetic polymers, cellulose, starch, gums and resins with water and organic liquids as sorbates have been carried out, there are still many aspects, in particular hysteresis and sorption capacity, which need detailed and systematic investigations. This thesis, therefore, contains the results obtained in a systematic and detailed study of the following investigations on which very little or no data are available in literature. It is expected that such studies will further enhance the present knowledge in the elucidation of the structures of the porous systems, resins and organic natural colloids.

(1) Studies in sorption-desorption hysteresis with starch

This includes the results obtained on a series of sorptions and desorptions of water and organic liquids on starch. The influence of certain modifications of starch caused by factors such as temperature, denaturation, compaction, removal of fat, swelling, etc., has been studied from the point of view of hysteresis and sorption capacity. The role of polarity and molecular volume of sorbate in sorption mechanism is discussed.

(2) Sorption-desorption hysteresis with cellulose and cellulose derivatives

Detailed sorption-desorption studies of water, aliphatic normal alcohols and carbon tetrachloride on cellulose and some carefully selected cellulose derivatives have been carried out. For the first time in this field of research, 'Ink bottle' or cavity theory has been applied to explain the permanent and reproducible hysteresis effect exhibited by these systems. The mode of adsorption in the monolayer region, calculated by the application of BET theory, has also been investigated.

(3) Sorption-desorption hysteresis in natural gums

The natural gums - Karaya, Sudan, Guar and Sandarac gums have been used in sorption-desorption studies with water and ethyl alcohol. All the gums show decrease in size and disappearance of the hysteresis loop on successive sorptions and desorptions of the sorbate. This behaviour is related to the structure of gums. The effect of particle size on sorption mechanism has also been investigated.

(4) Studies in sorption-desorption hysteresis in cellex resins and some other swelling systems

Four cellex resins - cellex T, cellex P, cellex E and cellex D and some other swelling systems - Agar, plantago ovata, methyl cellulose, etc., have been used. All the resins and the swelling systems show decrease in size and disappearance of hysteresis loop on successive cycles of sorptions and desorptions of water. The results are explained on the basis of the cavity theory in conjunction with the properties of swelling and shrinkage of the resins and other swelling systems. The BET surface areas are calculated and the applicability of F-H-H equation is discussed.

* * *

References

1. Zsigmondy, A., Z. anorg. Chem., 1911, 71, 356.

2. Cohan, L.H., J. Am. Chem. Soc. 1938, 60, 433.

3. Coelingh, M.B., Thesis, Utrecht, 1938.

4. McBain, J.W., J. Am. Chem. Soc. 1935, 57, 699.

5. Thompson, W., Phil. Mag. 1871, (4), 42, 448.

6. Kraemer, E.C.In H.S. Taylor's, "A treatise on Physical Chemistry", New York, 1931, p.1661.

7. Katz, S.M., J. Phys. Chem., 1949, 53, 1166.

8. Rao, K.S., J. Phys. Chem., 45, 500, 1941.

9. Barrer, R.M., McKenzie, N. and Reay, J.S.S., J. Colloid. Sci. 1956, 11, 479.

10. Foster, A.G., Trans. Faraday Soc. 1932, 28, 645.

11. Enderby, J.A., Trans. Faraday Soc. 1956, 52, 106.

12. Enderby, J.A., Trans. Faraday Soc. 1955, 51, 835.

13. Everette, D.H., and Whitton, W.I., Trans. Faraday Soc., 1952, 48, 749.

14. Everette, D.H., and Smith, P.W., Trans. Faraday Soc., 1954, 50, 187.

15. Everette, D.H., Trans. Faraday Soc. 1954, 50, 1077.

16. Everette, D.H., Trans. Faraday Soc. 1955, 51, 1551.

17. de Boer, J.H., "The structure and properties of porous material", Butterworth, London, 1958, p.68.

18. Van Bemmelen, J.M., Die adsorption, Theodor, Stem Kopff, Dresdon, 1910.

19. Anderson, J.S., Z. Physik. Chem. 1914, 88, 212.

20. Gustaver, B., Kolloid. Chem. Beihfte, 1921, 15, 248.

21. Coolidge, A.S., J. Am. Chem. Soc. 1924, 46, 596.

22. Coolidge, A.S., J. Am. Chem. Soc. 1927, 49, 708.

23. Winning, C.H., and Williams, J.W., J. Phys. Chem., 1932, 36, 2915.

24. Shiels, D.C., J. Phys. Chem. 1929, 33, 1167.

25. Shiels, D.C., J. Phys. Chem. 1929, 33, 1175.

26. Shiels, D.C., J. Phys. Chem., 1929, 33, 1386.

27. McGavack, J. Jr., and Patrik, W.A., J. Am. Chem. Soc. 1920, 42, 946.

28. Richardson, et al., J. Phys. Chem. 1929, 33, 1386.

29. King, A., and Lawson, C.G., Trans. Faraday Soc. 1936,32,478.

30. McBain, J.W. and Fergussion, J., J. Phys. Chem., 1927,31,564.

31. Burrage, L.J., Trans. Faraday Soc., 1934, 30, 317.

32. Foster, A.G., Proc. Roy. Soc. 1934, A146, 129.

33. Pidgeon, L.M., Can. J. Res. 1934, T13, 10.

34. Allmand, A.J., Hand, P.G.T., and Manning, J.E., J. Phys. Chem. 1929, 33, 1694.

35. Lambert, B., and Foster, A.G., Proc. Roy. Soc., 1932, A136, 363.

36. Urquhart, A.R. and Eckersall, N., J. Text. Inst. 1930, T499, 21.

37. Urquhart, A.R., J. Text. Inst. 1929, T20, 125.

38. Urquhart, A.R., and Williams, J. Text. Inst. 1925, T158,16.

39. Urquhart, A.R., and Williams, J. Text. Inst. 1924, T133,15.

40. Urquhart, A.R., and Williams, J. Text. Inst. 1924, T559,15.

41. Sheppard, S.E., and Newsome, P.T., J. Phys. Chem. 1929, 33, 1817.

42. Wahba, M., and Nashed, S., J. Text. Inst. 1957, T1, 48.

43. Seborg, C.O., Ind. Eng. Chem. 1937, 29, 169.

44. Walker, W.C. , Campbell, C. , and Maass, O., Can. J. Res. Sect. B; Chem. Sci., 1937, 15, 340.

45. Rao, K.S., and Das, B., J. Phys. Chem. 1968, 72, 1223.

46. Carman, P.C., and Raal, F.A., Proc. Roy. Soc. 1951,59,209A.

47. Kiselev, A.V., "The structure and properties of porous materials", Butterworth, London, 1958, p.195.

48. Zwietering, P., "The structure and properties of porous materials", Butterworth, London, 1958, p.287.

49. Barrer, R.M. et al., Proc. Roy. Soc., 1955, 52, A231.

50. Throp, M., and Nair, N.K., Trans. Faraday Soc. 1965,61,962.

51. Jeffries, R., J. Text. Inst., 1960, 51, T399.

52. Houtz,C.C., and McClean, D.A., J. Phys. Chem., 1945, 45, 111.

53. Fugassi, P , Fuel, 1959, 38, 259.

54. Barkas,W.W. , Trans. Faraday Soc., 1942, 38, 194.

55. Archer, W.L., Can. J. Chem., 1959, 37, 1655.

56. Rao, K.S., Curr. Sci., 1939, 8, 256.

57. Rao, K.S., Curr. Sci., 1939, 8, 468.

58. Rao, K.S., Curr. Sci., 1939, 8, 546.

59. Rao, K.S., Curr. Sci., 1940, 9, 19.

60. Rao, K.S., Curr. Sci., 1940, 9, 68.

61. Rao, K.S., Curr. Sci., 1940, 9, 70.

62. Rao, K.S., Proc. Ind. Acad. Sci., 1942, A16, 296.

63. Rao, K.S., Proc. Ind. Acad. Sci., 1942, A16, 301.

64. Krishnappa, T., Rao, K.S., and Rao, B.S., Proc. Ind. Acad. Sci., 1947, A25, 162.

65. Rao, G.N.S., Rao, K.S., and Rao, B.S., Proc. Ind. Acad. Sci., 1947, A25, 221.

66. Rao, K.S., Rao, M.B., and Rao, B.S., Curr. Sci., 1948,17,334.

67. Rao, K.S., Rao, M.B., and Rao, B.S., Proc. Nat. Inst. Sci (India), 1949, 15, 41.

68. Rao, K.S., Rao, M.B., and Rao, B.S., Proc. Nat. Inst. Sci. (India), 1949, 15, 51.

69. Rao, K.S., Rao, M.B., Murthy, A.R.V., and Rao, B.S., Proc. Nat. Inst. Sciences, 1950, 1, 16.

70. Bhatia, R.K.S., J. Inst. Chem., 1969, XLI, 125.

71. Bhatia, R.K.S., Chem. Age India, 1969, 20, 2, 119.

72. Gupta, S.L., and Bhatia, R.K.S., Ind. J. Chem., 1969, 7, 1231.

73. McIntosh, R.L., In the solid-gas Interface, Ed., E.A. Flood, Vol. 2, Marcel Dekker, Inc., New York, 1967, p.538.

74. Petrie, S.E., Ph.D. Thesis, Univ. Toronto, Toronto, Canada, 1957.

*****

CHAPTER III

EXPERIMENTAL TECHNIQUE

Outgassing

For measurement of adsorption isotherm the adsorbent should be in the highest state of purity. It should be free as far as possible from gases already adsorbed on the surface. In order to remove previously adsorbed gases (especially water vapour) from the adsorbent surface "outgassing" is considered to be most essential. Outgassing signifies the exposure of the adsorbent to high vacuum. With adsorbent containing fine pores, the process of outgassing is accelerated by raising the temperature of evacuation. Adsorbents exposed to air often hold chemisorbed oxygen, water or carbon dioxide on their surfaces. The removal of these gases is difficult, requiring long continued evacuation at high temperatures. Even sometimes it becomes impossible to get rid of them completely without permanently injuring the surface of the adsorbent.

For physical adsorption, a vacuum of the order of 10^{-5} torr is in general sufficient while ultra-vacuum, of the order of 10^{-10} torr, is necessary for measuring chemisorption with evaporated metal film adsorbents. Vacuum, in case of physical adsorption, is generally produced by a mercury or oil diffusion pump backed by a rotary vacuum pump, preferably of the gas ballast type. If the adsorbent is a fine powder, it may spurt badly when evacuated and invade other parts of the apparatus, and to avoid this the rate of pumping must be carefully controlled. A small plug of glass wool may usefully be placed in the neck of the adsorbent bulb or one may employ one of the various types of special bulbs (1-3). To guard against impurities that may get to the surface of adsorbent from stop cock grease vapour, only those greases must be used which have very low vapour pressures.

The adsorption of gases on solids can be generally determined by either the volumetric method or by the gravimetric method. The former, although simple and versatile, includes errors due to dead space, from which the gravimetric method is free.

Volumetric method

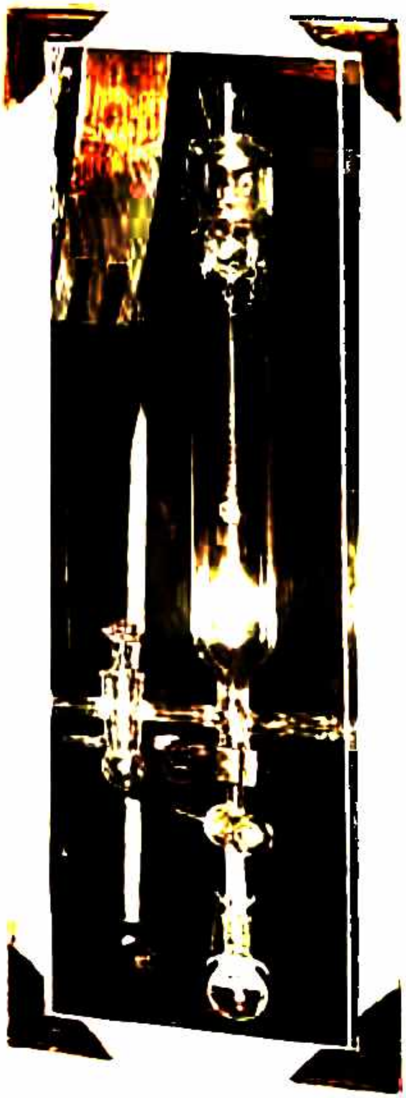
This is by far the most usual method of carrying out adsorption measurements. The adsorbent is contained in a bulb connected to the necessary manometers, pressure gauges, etc., and after the preliminary outgassing a known quantity of adsorbate is admitted. The pressure in the dead space is read when equilibrium is reached, and knowing the volume of the dead space, the quantity of unadsorbed gas can be calculated. By subtracting this from the total quantity admitted, the amount adsorbed can be obtained. The volume of the dead space is best determined in presence of the adsorbent by a blank experiment in which helium is used instead of the adsorbate. Helium is assumed to have negligible adsorption except at very low temperatures.

Successive admissions of gas or the vapour are made to get the adsorption isotherm, successive withdrawals will then give points for desorption isotherms. After each admission or withdrawal, successive readings of pressure are taken until there is no further detectable change. This state is usually assumed to represent the equilibrium.

The description of various types of apparatus used for different adsorbates have been illustrated by Gregg and Sing (4), Young and Crowell (5) and Brunauer (6).

Gravimetric method

In view of the dead space difficulty attached to the volumetric method, attempts have been made to estimate the amount adsorbed by direct weighing. There are two methods to record the increase in weight of the adsorbent. The first involves the use of an adsorbent bulb (furnished with a tap) which can be detached from the main apparatus at a ground glass joint. Errors are liable to arise owing to the unavoidable use of grease or wax necessary for keeping the joint vacuum tight and the consequent variation in the residual amounts of such grease left on at successive weighings. The other method involves the use of quartz fibre spring balance which was first introduced by McBain and Bakr (7) into studies



PHOTOGRAPH FIGURE 1

in sorption. It consists essentially of a quartz fibre spring, on the end of which is hung a bucket, preferably of platinum, containing the adsorbent, and the whole placed in a glass tube. Increase in weight are followed by measuring the increase in the length of the spring.

The Quartz fibre spring balance

The quartz fibre spring technique was employed in all the investigations presented in this thesis. The helical quartz fibre spring (Photograph figure 1) ends in two hooks. The upper hook is attached to a glass sphere which rests on three hinges at the top of the pyrex glass tube. The lower hook holds the bucket that contains the adsorbent. The balance is built into a glass tube having a mercury manometer and a glass bulb at the bottom to have the adsorbate. The balance is connected to a vacuum system and it is completely sealed off before starting the experiment.

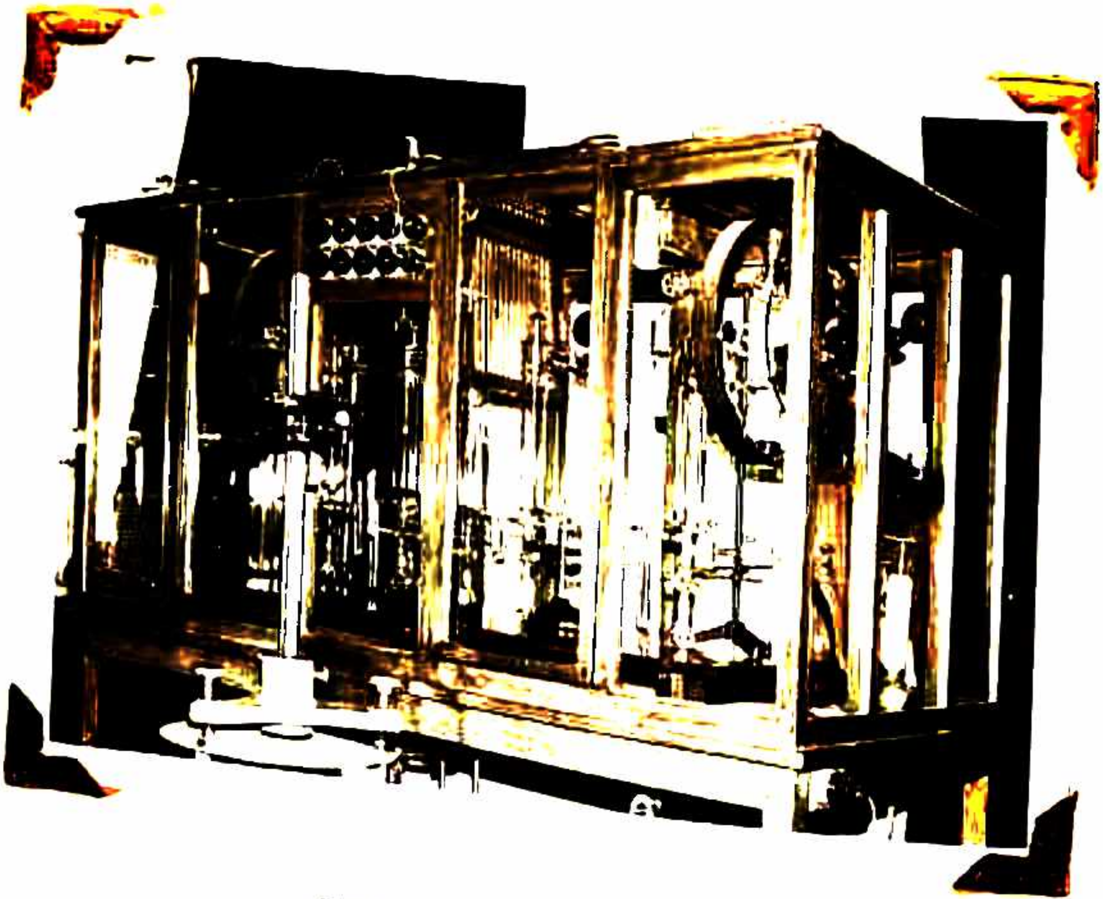
The quartz fibre springs are extremely delicate and brittle. A number of techniques for the fabrication of quartz spirals have been given in the literature (8-10). These springs are now available commercially. Some workers recommended springs of pyrex (11-12), beryllium copper alloy (13,14) and molybdenum (15) because of easy fabrication but have not been used probably on account of lack of dimensional stability. The automatic recording type of apparatus have been discussed by Hooley (16) and Klevens et al (17).

Advantages and disadvantages of spring technique

The spring technique is an excellent instrument for studies involving a series of successive sorptions and desorptions of the vapour of a liquid on the same sample of the adsorbent in vacuum. Measurements with the spring balance is quick and extraordinarily simple. The Quartz springs can be used at moderately high temperatures as its elastic coefficient is not affected. It is non-corrodible by most of the organic liquids and its sorptive capacities for the same is negligibly small.

The spring balance is very handy for determining the adsorption of vapours at high pressures (18). It is very useful in comparative studies because a number of balance tubes can be connected to the same manometer and the adsorptive properties of several solids measured under identical conditions (19,20).

The main disadvantage of the technique is bioyancy correction at high pressure (21); but at low pressures the correction is very small. Another disadvantage of the balance is that if it is desired to carry a large total load on the spring, it is necessary to increase the diameter of the quartz fibre, in which case the sensitivity is correspondingly diminished unless the number of turns of the spring is made inordinately great.



PHOTOGRAPH FIGURE 2

Air thermostat for constant temperature

The maintenance of a constant temperature is necessary in the study of sorption-desorption hysteresis. This can be achieved by keeping the sorption apparatus in a thermostat. In the present studies an air thermostat was constructed similar to one built by Vernon (22) and is shown in the photograph Figure 2. The thermostat chamber was built of wooden frame and glass panels. It was fitted in a wooden table. The external dimension of the chamber are 96" long, 39" wide and 43" high. The four door (two in the front and two in the rear) open by sliding vertically upwards.

The working floor is provided by a rectangular wooden platform placed 3" above the base of the chamber. Between the ends of the platform and the walls of the chamber there is a gap of about 6". To facilitate free and continuous circulation of air inside the chamber by the electric fans, two square holes, 9" apart and 4" edge are provided in the middle of the platform.

The four bladed fans are kept on brackets, one at each end of the thermostat, and the two facing each other. The heating lamps are of the usual tungsten filament type. They are arranged in two groups of four, each group being disposed symmetrically in a circular wooden frame, 15" in diameter and suspended from the roof in front of the fans. The centre of the frame is in line with the centre of the fans. In each set of lamps only two horizontal lamps are connected by the relays, the other two are auxiliary lamps operated upon by switches outside. The heating capacity of the four controlled lamps is arranged according to the outside temperature. In cold weather, the lamps are replaced by nichrome wire heaters.

The two operating streams of air originate from the fans. After passing over the heating elements, they meet in the middle of the thermostat where the toluene thermoregulator is fixed and then pass down. On reaching the platform it divides into two streams each of which passes through the square hole, next beneath the platform and finally to the rear of the fan. The air in each half of the thermostat is thus thoroughly stirred.

The thermoregulator consists of a network of pyrex glass tube, 1.2 cm bore. It is filled with toluene. The open and is fitted with mercury ending in a capillary in which the electrical contact is made with the platinum wire. The heating elements are controlled by the thermoregulator through an electronic relay. The thermoregulator is suspended (23) from the roof of the chamber, so that it is in the middle of the thermostat and directly in front of the two fans.

The temperature of the thermostat was maintained at 35°C in all the present investigations. The constancy of temperature in different portions inside the thermostat was measured by means of a sensitive thermometer and was found to be 35 ± 0.05°C. The periods of heating and cooling were adjusted to be approximately equal. The chamber is illuminated by bulbs kept at the ceiling and rear of the chamber. In summers, the temperature of the room was brought down with the aid of a room cooler. The fouling of mercury inside the mercury capillary owing to electric spark was prevented to a certain extent by the use of liquid paraffin.

Sorption apparatus

Sorption apparatus was fabricated as per design shown in the photograph Figure 1. Interchangeable ground glass joints were used. The apparatus consists of a pyrex tube 10" in length and 2" in diameter. At the bottom of it is connected a bulb for the adsorbate with a B-10 ground glass joint and a B-19 high vacuum stop cock. A U-tube mercury manometer is connected to the sorption apparatus with B-10 ground glass joint. Just on the opposite side of it a B-19 stop cock connects the apparatus to vacuum line. To the upper end of the tube a B-50 ground glass joint is joined, there are three projections on which the glass sphere support for the spring rests.

The manometer tube had a bore diameter of 1.2 cm. The mercury used in the manometer was purified by first passing it through a 10% nitric acid in Meyer's column, then distilling in air and finally distilling in vacuum.

A 'speedy vac' high vacuum pump which produces a pressure of 10^{-2} mm was used. For sealing the ground glass joints the

Corning silicone high vacuum grease was used. Pressure readings and elongation of the quartz helix were determined with a cathetometer, reading correct to 0.01 mm. Quartz fibre springs used in these studies had sensitivities ranging from 20 to 45 cm of stretch per gram of load. The springs were obtained from M/s British Thermal Syndicate, London. The buckets to hold the sorbent were made out of pyrex glass according to the method of Cameron (24).

Calibration of Quartz fibre spring balance

First the spring balance was calibrated by adding and removing known weights and measuring the corresponding extension of the spring. The spring balance was kept inside the air thermostat at 35°C. The results of calibration of a spring of the following specifications have been presented.

Maximum load	1.0 gm.
Extension	28.8 cm.
Sensitivity	25.1 cm/gm.

The observed and calculated stretch for the dimensions are shown under:

Weight of the bucket = 0.18950 gm.

Initial length of the spring with bucket = 3.603 cm.

Weight in gms.		Observed length in cms.	Stretch Observed in cm for 0.05 gm.	Calculated stretch in cm for 0.05 gm.
While adding weights	0.05	4.855	1.252	1.255
	0.10	6.109	1.254	1.255
	0.15	7.352	1.253	1.255
While removing weights	0.10	6.113	1.257	1.255
	0.05	4.858	1.255	1.255

The above results show that spring obeys Hook's Law.

Sorption-desorption procedure

The sorption tube was thoroughly evacuated and then kept for about a month for vacuum tightness. During this period there was no measurable variation in the manometer readings, thus ensuring complete vacuum tightness of the sorption apparatus.

Double distilled water was taken in the bulb and made air free by allowing it to evaporate in vacuum for an hour. The vapours of water were allowed into the tube having spring with bucket to see whether there is any measurable adsorption of water vapour on the spring and bucket. Negligible variation in the length of the spring was noticed even after the vapour was in contact with spring for about a month, thus showing the absence of measurable adsorption of water vapour on the quartz spring.

The spring with bucket was placed inside the tube. The length of the spring was measured using a reference rod (25). The reference rod, which is a glass fibre suspended within the spring coils from the same hook from which the spring is suspended, simplifies the manipulation of the cathetometer by reducing the distance between the fixed end and the moving end of the spring to be measured in each reading. Next, the spring is taken out, the bucket is filled with the adsorbent and spring is placed again inside the tube. The upper end of the sorption tube was covered with the ground glass stopper and the system was thoroughly evacuated. After evacuation the pump was disconnected from the sorption apparatus by closing the stop cock. The spring reading and the zero pressure reading of the manometer were taken with the cathetometer. Next, the lower stop cock was slightly opened and small quantity of the vapour of the air free liquid was introduced. After the equilibrium was reached, the pressure difference on the manometer and spring extension were noted. Similarly at different equilibrium pressures, corresponding stretches were noted till saturation pressure reached. The readings give sorption curves. After the saturation is reached, the lower stop cock was closed and a small amount of vapour was removed from the tube by using vacuum pump. Spring length and corresponding pressure was noted after equlibrium was attained. The process is continued until sufficient number of points on the desorption curve is obtained and zero pressure is reached.

Knowing the stretch of the spring for the evacuated adsorbent at zero pressure, the percentage of adsorbate taken or retained can be calculated. By plotting percentage sorption and desorption, against the corresponding vapour pressure of the adsorbate, the sorption and desorption isotherms are obtained. From these, the existence or non-existence of the hysteresis effect is obtained.

***

References

1. Russell, A.S., and Cochrane, C.N., Ind. Eng. Chem. Anal. 1950, 42, 1332.

2. Carman, P.C., and Malherbe, P. R., J. Soc. Chem. Ind. 1950, 69, 134.

3. Anderson, R.B., Ind. Eng. Chem. Anal. 1946, 18, 156.

4. Gregg, S.J., and Sing, K.S.W., Adsorption, surface area and porosity, Academic Press, London and New York, 1967, P.310.

5. Young, D.M., and Crowell, A.D., Physical adsorption of gases, Butterworth, London, 1962, p.279.

6. Brunauer, S., The adsorption of gases and vapours,Oxford University Press, 1945, p.32.

7. McBain, J.W., and Bakr, A.M., J. Am. Chem. Soc., 1926, 48, 690.

8. King, A., Lawson, C.G., Tapp, J.S. and Watson, G.H., J. Sci., Instrum. 1935, 12, 249.

9. Doss, K.S.G., and Rao, B.S., Proc. Ind. Acad. Sci. 1936, 4, 11.

10. Kirk, P.L., and Schaffer, F.L., Rev. Sci. Instrum. 1948, 19, 785.

11. Chipalkatti, V.S., and giles, C.H., Nature, 1950, 165, 735.

12. Sing, K.S.W., and Maddey, J.D., J. Appl. Chem., 1954, 4, 365.

13. Sawyer, F.G., and Othmer, D.F., Ind. Eng. Chem., 1944, 36, 894.

14. Wade, P., J. Sci. Food. Agri., 1955, 1, 1,.

15. Makolkin, I.A., Chem. Abs. 1950, 44, 996G.

16. Hooley, J.G., Can. J. Chem. 1957, 35, 374.

17. Klevens, H.B., Carriel, J.T., Fries, R.J. and Peterson, A.R., Proc. Second Inst. Congr. Surface Activity, Butterworth, London 1957, p.169.

18. McBain, J.W., and Brittin, G.T., J. Am. Chem. Soc. 1930, 52, 2198.

19. Morris, H.E., and Maass, O., Can. J. Res. 1933, 9, 240.

20. Lawson, C.G., Trans. Faraday Soc. 1936, 32, 473.

21. Morris, H.E., and Maass, O., Can. J. Res., 1933, 9, 240.

22. Vernon, W.H.J., Trans. Faraday Soc., 1931, 27, 24.

23. Rao, K.S., J. Phys. Chem., 1941, 45, 500.

24. Cameron, A.E., J. Am. Chem. Soc., 1931, 53, 2646.

25. Lawson, C.G., Trans. Faraday Soc., 1936, 32, 473.

****

CHAPTER IV

STUDIES IN SORPTION-DESORPTION HYSTERESIS WITH STARCH

PART I

SORPTION OF WATER AND ORGANIC VAPOURS ON STARCH AT 35°C

SORPTION OF WATER AND ORGANIC VAPOURS ON STARCH AT 35°C

Abstract

A series of sorption-desorption studies, at 35°C, of water, methyl alcohol, ethyl alcohol, and carbon tetrachloride vapours have been carried out on starch, employing the quartz fibre spring technique. The polar sorbates yielded sigmoid isotherms with linear hysteresis effect. The hysteresis effect increases as the molecular weight of the sorbate increases. The sorptive capacity of starch shows the following trend in binding these vapours: water > methyl alcohol > ethyl alcohol > carbon tetrachloride. Time-adsorption curves, constructed for the polar sorbates, showed that the rate of adsorption follows the order: methyl alcohol > ethyl alcohol > water. Starch-alcohol systems exhibited the phenomenon of 'bound alcohol'. The results have been explained in the light of the 'cavity theory' of hysteresis and the role of polarity and molecular volume of the sorbates in the sorption mechanism has been discussed. A reasonably good fit for the BET equation has been obtained for starch-water and starch-methyl alcohol systems. Specific surface area of starch for

the two sorbates and the number of molecules in the monolayers have also been calculated.

Introduction

The interaction of adsorbates, particularly water, with polymers, celluloses, proteins and cereals is different from that of gel and rutile systems. In the former systems very strong interaction between the adsorbate and adsorbent is normally observed. The interaction is so strong that major changes of structure are normally observed (1). More information about the interaction between sorbed vapours and these systems may be obtained by the study of simpler systems.

The sorption of adsorbates, particularly water, with starches has been reported by many workers (2-14), but in many cases the isotherms are incomplete and the data are conflicting. Bushuk and Winkler (7) have studied the sorption of water vapour on wheat flour, glutin and starch up to relative humidity 0.85. According to these authors, at higher relative humidites the adsorbents were physically altered and the sorption was no longer reversible.

Hellmann and Melvin (6) have reported that moisture sorption by ten corn starches was not affected by origin, condition, preparatory procedure, method of drying and time of storage while other investigations (9-13) covering the sorption of water by starches have shown that starches of different origin vary markedly in sorptive capacity - a result contrasting with that found for raw cellulose, free from non-cellulosic materials (17).

Sair and Fetzer (4) have studied the water sorption by maize and potato starches. They agreedwith Katz (12) that water was held by physical adsorption between relative humidities of 20 and 90%, thus contradicting Freeman (8) who stated that sorbed water in starch was in the bound form. Ulman (15) believes that water sorbed by starch was held by binding and two unspecified kinds of association. Winkler et al (16) from heat of adsorption data found that starch retains water by adsorptive forces alone.

Shotton and Harb (18) found that considerable caking was observed in starch at 75% relative humidity while Bushuk and Winkler (7) reported that no caking was observed in starch at 80 - 90% relative humidities. In both cases incomplete sorptions and desorptions were presented.

The aim of present studies is to help make good this deficiency, i.e., to provide complete sorption and desorption data for many sorbates on starch. These studies were initiated to gather more information about the nature of interaction of various polar and non-polar vapours with starch from the point of view of hysteresis and time dependence. Among the polar sorbates, water, methyl alcohol and ethyl alcohol were studied while carbon tetrachloride was included as an example of non-polar sorbates.

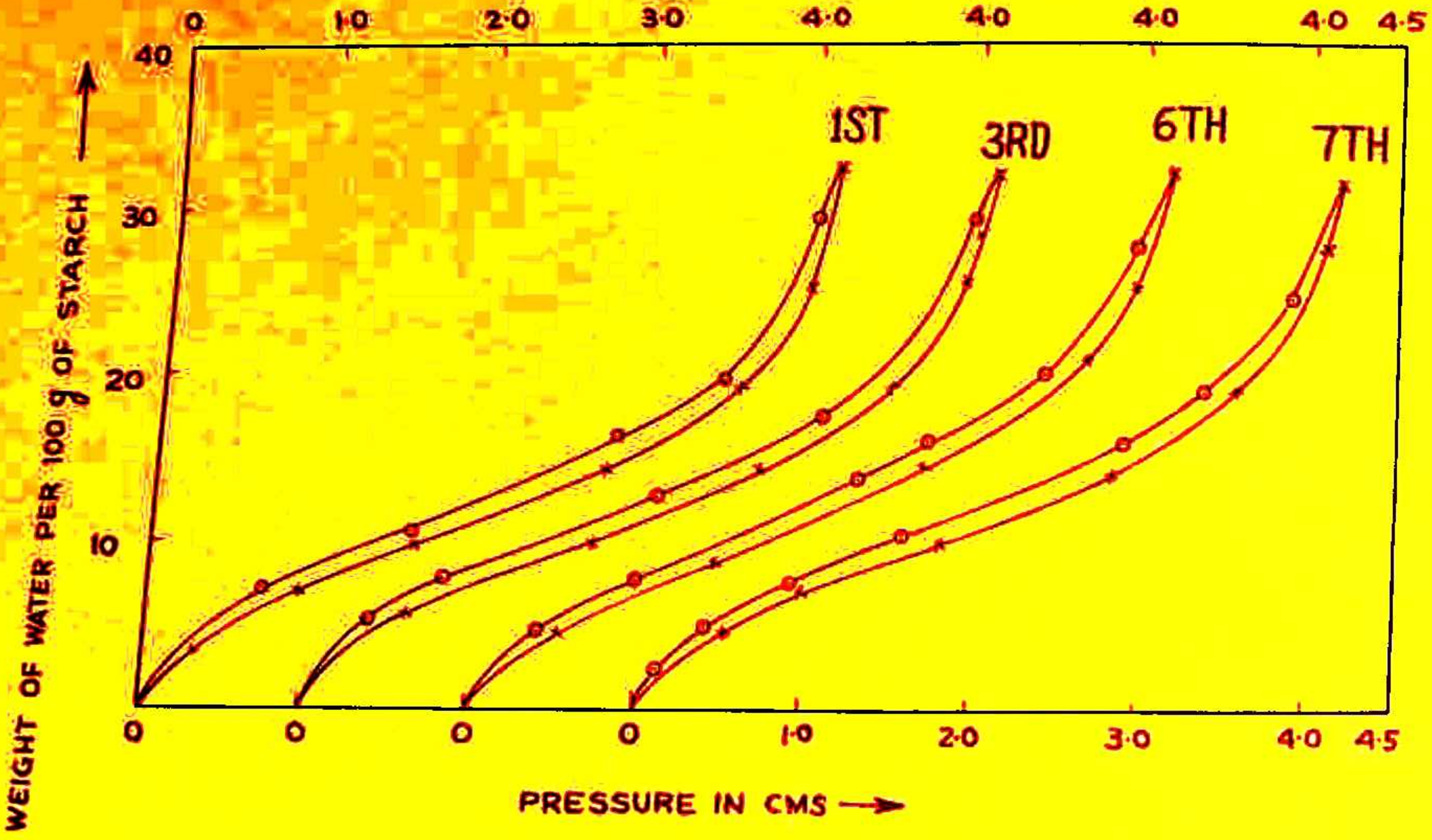


FIG. I SORPTION-DESORPTION HYSTERESIS OF WATER VAPOUR ON STARCH AT THE 1ST, 3RD, 6TH, AND 7TH CYCLES.

Adsorbent and adsorbates

Starch powder (Schmidt & Berg Hamburg Fu.1 Germany) was used as adsorbent in all the experiments.

Double distilled water; redistilled methyl alcohol, B.D.H. (A.R.); carbon tetrachloride, (A.R.), "Reanal"(Budapest) and absolute alcohol distilled over Ca metal were used as sorbates. These sorbates were distilled in an all-glass apparatus.

Results

The hysteresis loops obtained with water, methyl alcohol and ethyl alcohol are presented in Figures 1-3.

Starch-water vapour system

Permanent and reproducible hysteresis effect has been exhibited by starch-water vapour system. The sorption and desorption studies were continued up to 7th cycle. The loops obtained in the 1st, 3rd, 6th and 7th cycles are shown in Figure 1. The amounts of water taken at saturation pressure of water in each of these cycles are 32.5, 32.0, 32.0 and 31.5 c.c., respectively.

Starch-alcohol systems

Hysteresis loops obtained with methyl and ethyl alcohols on starch are presented in Figures 2 and 3 respectively. The nature of first cycle of sorption and desorption is interesting. At the end of the first cycle starch retains "irreversibly" certain amount of alcohol which cannot be removed even by drastic evacuation for 10 to 12 hours. After the first cycle of sorption and desorption, these systems exhibit permanent and almost reproducible hysteresis effect. The amounts of "bound" methyl alcohol and ethyl alcohol are 3.2 cc. and 6.6 cc. per 100 grams of starch respectively.

With methyl alcohol, the sorption-desorption studies were continued up to 6th cycle. The loops of 1st, 2nd, and 6th cycles are presented in Figure 2. The values at saturation pressure of methyl alcohol are 26.8, 25.4 and 24.6 ccs respectively. The hysteresis loops obtained with ethyl alcohol are shown in Figure 3. The amount of ethyl alcohol taken at saturation pressure of ethyl alcohol in the 1st, 2nd and 6th cycles are 16.5, 16.3, and 16.4 ccs respectively.

Starch-carbon tetrachloride system

With carbon tetrachloride, sorption-desorption studies were continued up to 3rd cycle. It was not possible to obtain accurate data for adsorption of carbon tetrachloride with this technique owing to very low sorptive capacity of starch for this sorbate. The sorption capacities in the 1st, 2nd and 3rd cycles are 0.3, 0.3 and 0.2 ccs per 100 gms. of starch.

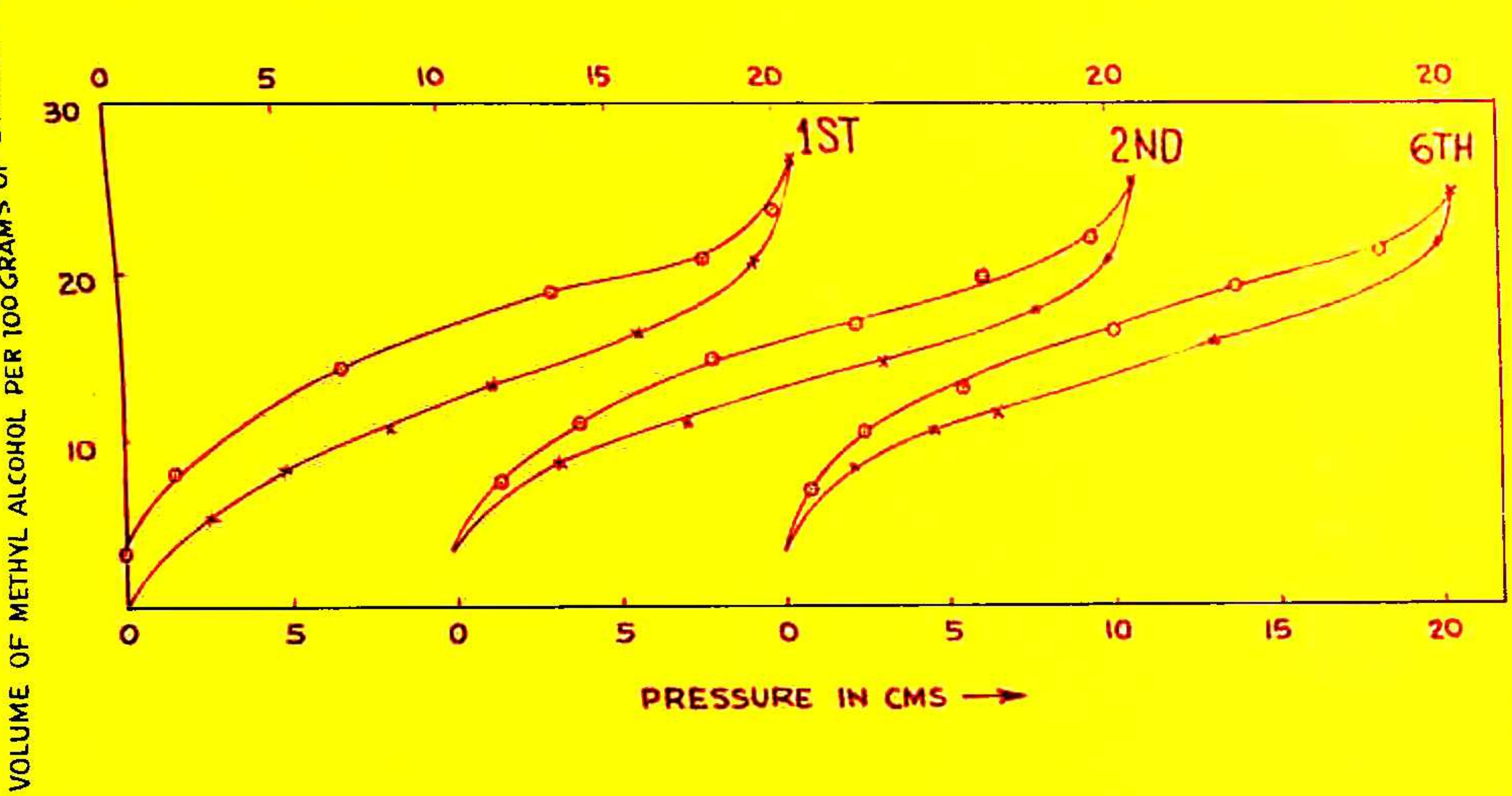


FIG 2 SORPTION-DESORPTION HYSTERESIS OF METHYL ALCOHOL ON STARCH AT THE 1ST, 2ND, AND 6TH CYCLES.

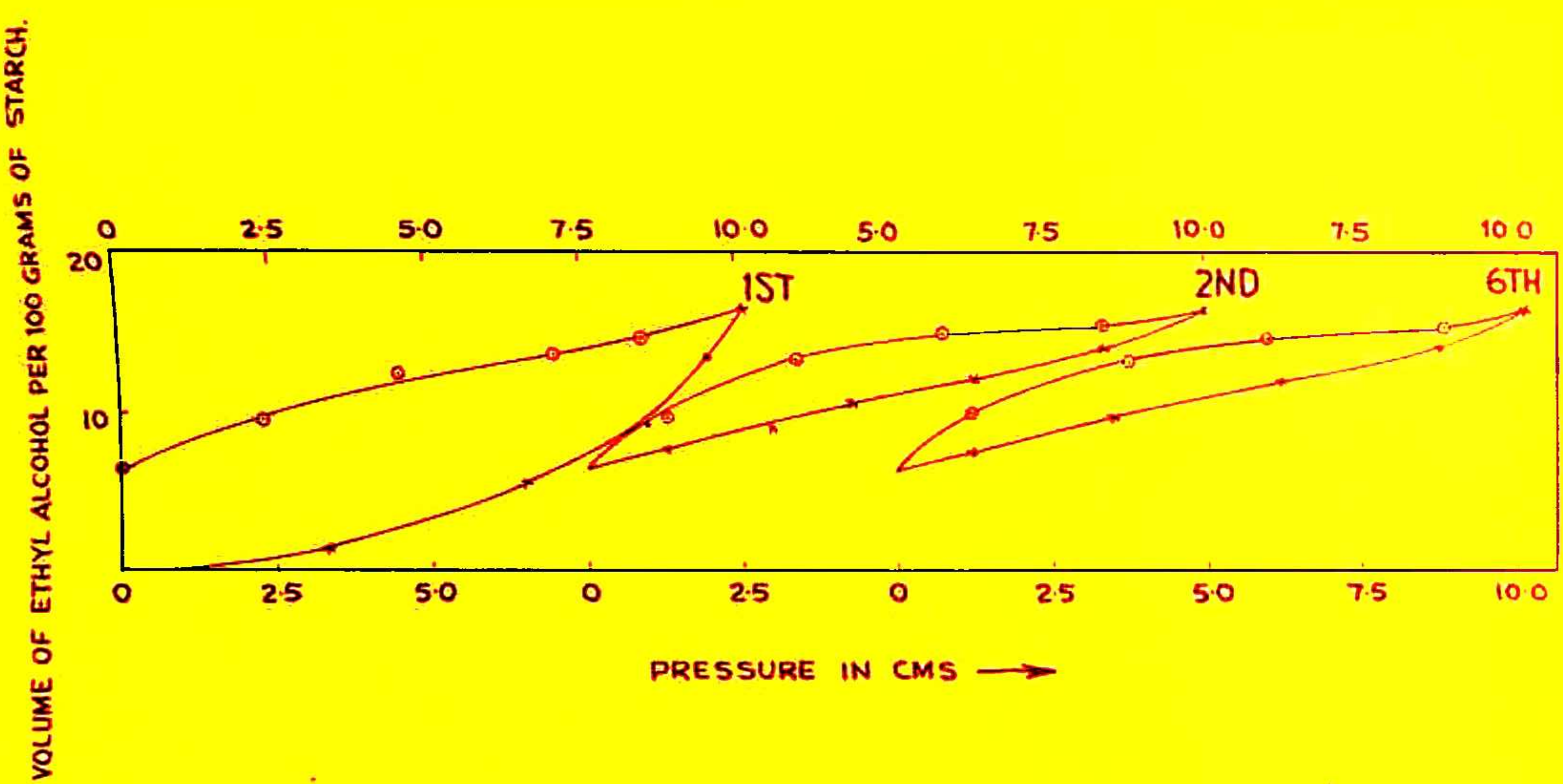


FIG.3 SORPTION - DESORPTION HYSTERESIS OF ETHYL ALCOHOL ON STARCH AT THE 1ST, 2ND, AND 6TH CYCLES.

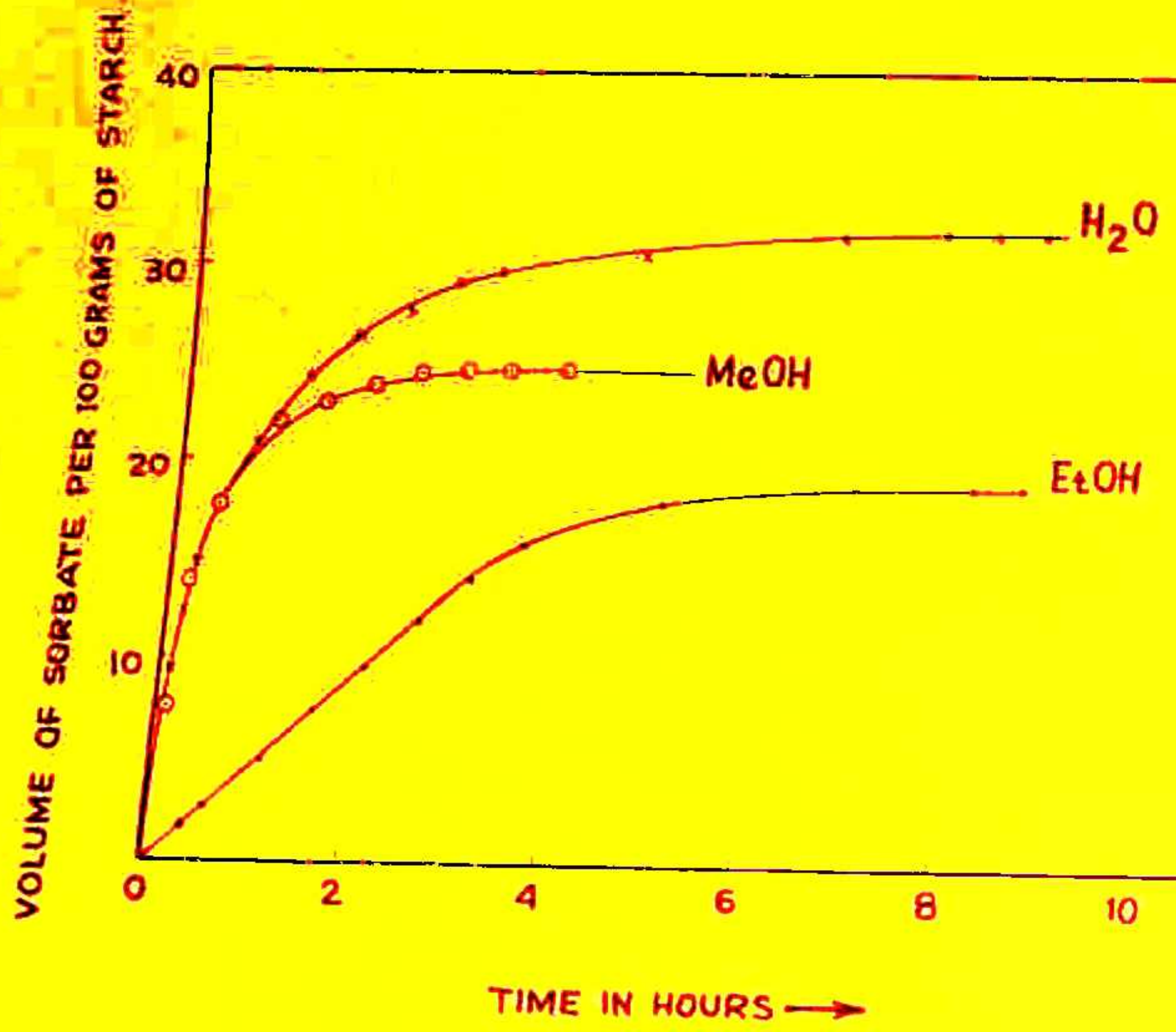


FIG. 4 TIME — SORPTION CURVES FOR WATER METHYL ALCOHOL AND ETHYL ALCOHOL AT THEIR SATURATION PRESSURES AT 35°C ON STARCH.

The sorptive capacities of starch at saturation pressure for different sorbates are summarized in Table I.

Table I

Sorptive capacities of starch for different sorbates.

Sorbate	Sorptive capacity cc/100 g.
Water	31.5
Methyl alcohol	24.6
Ethyl alcohol	16.4
Carbon tetrachloride	0.2

Time-adsorption curves

Starch, like other organo gels swells when it sorbs water. In all the swelling systems water sorption is a slow process. Incomplete equilibrium during sorption and desorption can cause hysteresis. To eliminate this,sufficient time was allowed till equilibrium is attained. Figure 4 compares the time-adsorption curves for the adsorption of water, methyl alcohol and ethyl alcohol vapours at 35°C. The rate curves reveal that under similar experimental conditions, methyl alcohol is adsorbed on starch much faster than either ethyl alcohol or water.

Discussion

Characteristics of sorption isotherms

The sorption isotherms, plotted in the standard manner, for water, methyl alcohol and ethyl alcohol on starch, at 35°C, are essentially sigmoid in shape, although the isotherms for ethyl alcohol show a little concavity to the pressure axis in the low pressure region. The sigmoid shape is characterized by three relatively distinct regions: (1) an initial region concave to pressure axis, (2) an intermediate almost linear region and (3) a final region convex to pressure axis. Except ethyl alcohol, the other two sorbates exhibit these three regions quite clearly. The low concavity of the sorption isotherm of ethyl alcohol to the pressure axis, at low relative pressure, may be due to the fact that some of the sorption sites are inaccessible because of the large molecular volume of the sorbate.

The extent of sorption of carbon tetrachloride is too small to show up the characteristics of the isotherms obtained with other sorbates. There is also a possibility that the carbon tetrachloride might represent a chemical interaction of carbon tetrachloride with some components of starch rather than sorption.

Sorption-desorption hysteresis

In addition to the sigmoid shape, the polar sorbates exhibit the linear hysteresis effect, i.e., the hysteresis loop extending over the entire pressure range.

Earlier, investigations of the series of sorptions and desorptions of water vapour on proteins (19), gums(20) and cereals (21) have revealed the common phenomena of the disappearance of the hysteresis loop initially exhibited. The disappearance of the hysteresis loop has successfully been explained on the basis of cavity theory (22,23) of hysteresis by the following: the organo colloid swells on the imbibition of water, the cavities collapse, the entrapping effect is lost, and the hysteresis disappears.

In the present studies, starch has exhibited permanent hysteresis loops with different sorbates. The size of the hysteresis loops shows the following trend:

Ethyl alcohol $>$ Methyl alcohol $>$ Water.

The different behaviour shown by starch may be attributed to the rigidness of the molecular structure of starch.

Structure of starch

Starch is known to be composed of two types of molecules, one, amylose consisting of linear chains of α-glucose units, connected at 1 and 4 positions by oxygen bridges and the other type amylopectin, is similar except that there are frequent branches. Rudle (24) from X-ray data suggested the structure of starch in terms of a unit cell, through which pass four extended molecular chains with extension of 10.6 Å per two glucose residues. The extension, which is greater than that present in cellulose (10.3 Å), suggests that it would be impossible for the glucose residues to have the puckered arrangement of ring atoms. It is possible, however, that the ring atoms have the boat form of the structure with carbon 3 and oxygen atom 5 in the median plane of the boat. Another possibility (25) in apparent confirmity with X-ray data is that there are only two molecular chains passing through each unit, each chain being coiled helically, with about four glucose residues per turn in a hydrogen bonded structure.

Explanation of sorption-desorption hysteresis

In the natural state, starch exists in the form of discrete microscopic granules, held together by extended helically coiled miceller network of associated molecules. The network possesses submicroscopic cracks and cavities as demonstrated by Whistler et al (26) under electron microscope. In the light of cavity theory of hysteresis these cavities are responsible for the effect.

During sorption, the filling of cavities is progressive and proceeds from the neck to the body of the cavity. At the end of each sorption, starch swells with the sorbate taken up at saturation pressure and the network of starch expands. The extent of swelling depends on the accessibility of the sorption sites to the sorbate molecules. During desorption, the swollen sorbent shrinks. The cavities entrap the sorbate molecules and cause hysteresis. The process of entrapping is sudden and abrupt. At the end of each desorption, the network of starch shrinks but does not collapse. It appears to be rigid but elastic, thus accounting for reproducible hysteresis effect.

The increase in the size of hysteresis loops with increasing molecular volume follows directly from the assumption that the hysteresis is due to physical trapping of the molecules within the adsorbent. The same degree of shrinkage would produce a greater effect with the larger sorbate molecules. Also, for the polar sorbates, the molecular volume and dipole moment seem to be main factors upon which the extent of sorption depends; the dipole moments (27) and the molar volumes for the four sorbates are given in Table II to facilitate discussion of results on the basis of these two physical properties. The sorptive capacities of starch for these sorbates are also presented in the last column.

Table II

Dipole moments, molar volumes and sorption capacities of water, methyl alcohol, Ethyl alcohol and carbon tetrachloride.

Sorbate	Dipole moment (Debyes)	Molar Volume* c.c.	Sorption capacity cc/100 g.
Water	1.87	18.79	31.5
Methyl alcohol	1.69	42.74	24.6
Ethyl alcohol	1.70	62.28	16.4
Carbon tetrachloride	0.00	103.11	00.20

* Molecular weight/density at boiling point.

It seems apparent that once the sorbate molecules reach the sorption sites, the number of molecules that can be accommodated within the region of influence surrounding the sorption sites (i.e. extent of adsorption) would be dependent upon the molecular volume. The effect of molar volume is exhibited particularly by the isotherms of two alcohols. The two alcohols have essentially the same polarity but differ markedly in their sorption capacities, so the decrease in the extent of sorption may be attributed to an increase in the molar volume.

Bound alcohol

At the end of the first cycle of sorption and desorption, starch irreversibly retains small amount of the sorbate alcohol. The amount of bound methyl and ethyl alcohols are 3.2 and 6.6 cc. per 100 gm. of starch. The alcohol appears to have been adsorbed in the fine pores and interstices of starch without changing the outer surface or the cavity volume of starch.

Applicability of BET equation

Excepting ethyl alcohol, the sorption isotherms of polar sorbates yielded sigmoid isotherms showing clearly defined "knees". According to BET, theory (28) the knee signifies the transition from monomolecular to multimolecular adsorption. The BET-equation has been applied to isotherms of water and methyl alcohol (Table III).

Table III

BET plots for the sorption of water and methyl alcohol on starch.

Relative vapour pressure p/p_o	Adsorption x cc/g	$\frac{p}{x(p_o-p)}$
Water		
0.024	0.013	1.89
0.052	0.024	2.27
0.072	0.030	2.59
0.120	0.042	3.28
Methyl alcohol		
0.024	0.046	0.54
0.048	0.062	0.82
0.097	0.080	1.34
0.121	0.090	1.53
0.169	0.100	2.04

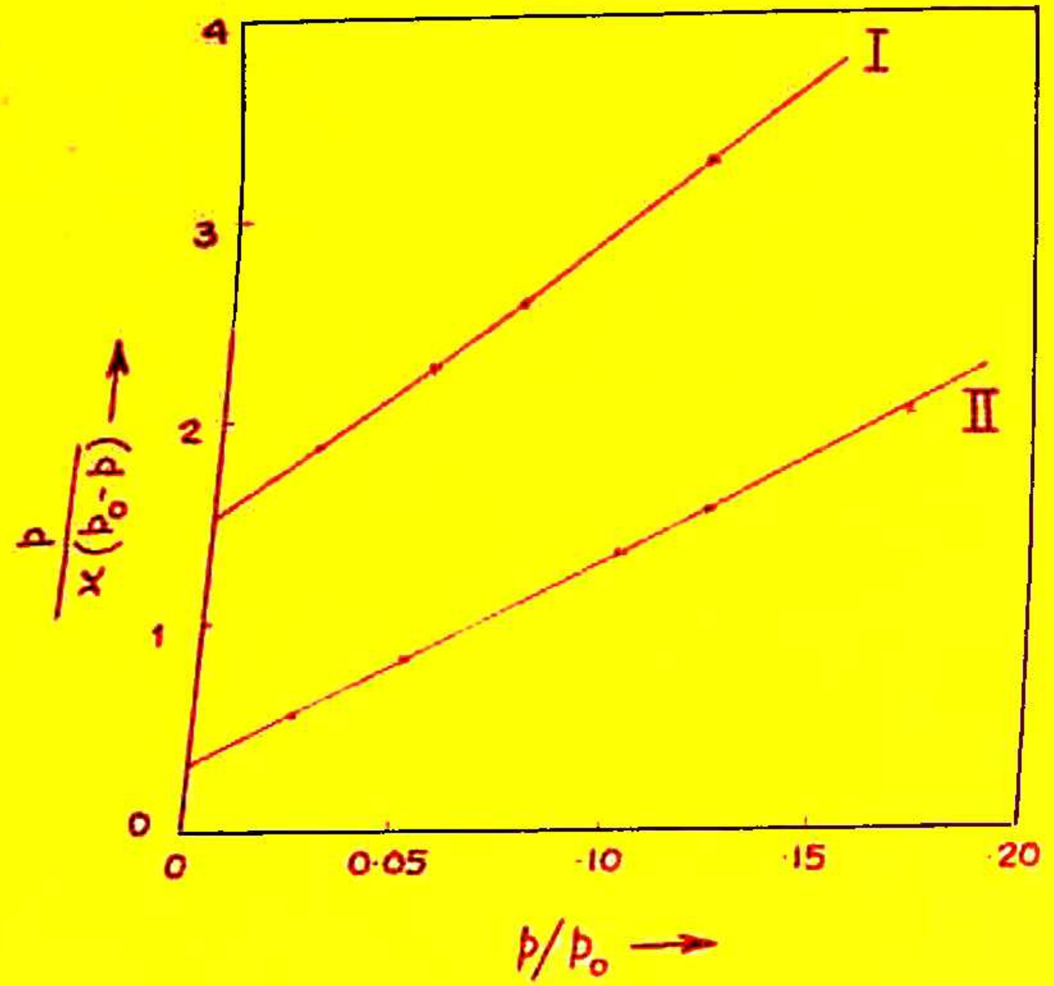


FIG. 5 BET PLOTS FOR WATER (I) AND METHYL ALCOHOL (II) ON STARCH.

The BET plots yielded straight lines (Figure 5). From the slope and intercept of the lines, the monolayer capacity x_m has been calculated. The value of monolayer capacity was also read out directly from the isotherms with reasonable accuracy (30,31) and this is denoted by x_B. The values of monolayer capacities x_m and x_B for the two sorbates and the relative vapour pressures at which the monolayers are fully formed are presented in Table IV.

Table IV

Monolayer capacities x_m and x_B in g. per g. of sorbent and the corresponding relative vapour pressures:-

Sorbate	x_m	x_B	p/p_o
Water	0.060	0.062	0.197
Methyl alcohol	0.097	0.100	0.194

The agreement is good between the values of x_m and x_B. This illustrates the success of the mathematical form of BET theory of sorption.

Knowing the monolayer capacity and the molecular weight of the sorbate, the total number of alcohol molecules (N_o) contained in the monolayer on the surface of one gram of starch can be calculated by the expression:

$$N_o = \frac{x_m . N}{M}$$

where N is the Avegadro's number.

The total number of water and methyl alcohol molecules, contained in the monolayer are presented in Table V.

Table V

Total number of molecules of water and methyl alcohol contained in the monolayer.

Sorbate	Mol. wt. M	Monolayer capacity x_m	No. of molecule N_o
Water	18	0.060	20.1×10^{20}
Methyl alcohol	32	0.097	18.3×10^{20}

Table V reveals that the number of molecules in the monolayer decreases as the molecular weight of the sorbate increases.

Specific surface area of starch

From the monolayer capacity, the specific surface area of the sorbent can be calculated according to the following equation (31)

$$S = \frac{x_m}{M} . N . A_m . 10^{-20}$$

where, S = Specific surface in m^2/gm. of sorbent

x_m = Monolayer in gm. of sorbate/gm. of sorbent,

M = Molecular weight of sorbate,

N = Avegadro's No.

A_m = Molecular cross-section of the sorbate molecules.

Assuming the water molecules to be spherical ($A_m = 10.6 \mathring{A}^2$), the specific surface of starch has been calculated and found to be 210.0 m^2/gm.

In case of methyl alcohol sorption, the specific surface of starch depends upon the mode of adsorption. Assuming the alcohol molecules to be spherical ($A_m = 21.2 \mathring{A}^2$) the specific surface comes out to be 333.4 m^2/gm. This value is higher than that obtained from water sorption. There can also be a possibility of oriented adsorption if the molecules are considered linear. In that case, the adsorbed molecules can be held either perpendicular or parallel to the surface of the adsorbent. Knowing the cross-section and the area of the side (32) the specific surface is calculated and found to be 378.2 m^2/gm and 390.7 m^2/gm respectively. Each of these values is higher than the value obtained from water sorption. However, if Am for water is arbitrary adjusted to 14.8 $\mathring{A}^2$, as suggested by Harkins and Jura (33), the specific surface of starch comes out to be 303.4 m^2/gm, which is in moderately good agreement with the value obtained for methyl alcohol sorption, considering the methyl alcohol molecules as spherical.

PART II

INFLUENCE OF CERTAIN MODIFICATIONS OF STARCH ON ITS SORPTIVE PROPERTIES WITH WATER VAPOUR

INFLUENCE OF CERTAIN MODIFICATIONS OF STARCH ON ITS SORPTIVE PROPERTIES WITH WATER VAPOUR

Abstract

A series of sorption and desorption isotherms, at 35°C, of water vapour have been carried out on modified starch, employing the quartz fibre spring technique. The influence of certain modifications caused by factors such as temperature, denaturation, compaction, removal of fat, swelling, etc., has been studied from the point of view of hysteresis and sorption capacity. Unmodified and heat treated starch exhibited permanent hysteresis extending over the entire pressure range while denatured and compacted starch showed hysteresis only in the lower pressure region. In case of defatted and aqueous swollen starch no hysteresis was observed. These interesting results have been explained in the light of 'cavity theory' of hysteresis in conjunction with the nature of changes brought about by such modifications.

Introduction

The interaction of adsorbates, particularly water, with starch has been reported by many workers over the past thirty years (2-14) but in many cases the isotherms are incomplete and the data are conflicting. Recently, Gupta and Bhatia (34) studied complete sorptions and desorptions of water and organic

INFLUENCE OF CERTAIN MODIFICATIONS OF STARCH ON ITS SORPTIVE PROPERTIES WITH WATER VAPOUR

Abstract

A series of sorption and desorption isotherms, at 35°C, of water vapour have been carried out on modified starch, employing the quartz fibre spring technique. The influence of certain modifications caused by factors such as temperature, denaturation, compaction, removal of fat, swelling, etc., has been studied from the point of view of hysteresis and sorption capacity. Unmodified and heat treated starch exhibited permanent hysteresis extending over the entire pressure range while denatured and compacted starch showed hysteresis only in the lower pressure region. In case of defatted and aqueous swollen starch no hysteresis was observed. These interesting results have been explained in the light of 'cavity theory' of hysteresis in conjunction with the nature of changes brought about by such modifications.

Introduction

The interaction of adsorbates, particularly water, with starch has been reported by many workers over the past thirty years (2-14) but in many cases the isotherms are incomplete and the data are conflicting. Recently, Gupta and Bhatia (34) studied complete sorptions and desorptions of water and organic vapours on starch and reported two effects: firstly, there was an irreversible adsorption of alcohol on starch after preliminary contact with the vapour and secondly, sorption-desorption isotherms exhibited permanent and almost reproducible hysteresis effect. They also discussed the role of polarity and molecular volume of the sorbate in the sorption mechanism.

Inspite of the voluminous data which have been published on the sorption of water by starch, there appears to have been almost no attempt to account for the sorptive capacity of starch on the basis of its physical and chemical structure. The structure of starch can be modified by factors such as temperature, compaction, denaturation and swelling, etc., and these modifications can have marked influence on the sorptive properties of starch. The aim of the present investigations is to study the effects of certain modifications of starch caused by heat treatment, aqueous swelling, compaction, removal of fat, bound alcohol and denaturation on a series of sorptions and desorptions with water vapour at 35°C.

Experimental

Starch powder of soluble grade (reffered hereafter as unmodified starch) supplied by Schmidt & Berg., Hamburg,Fu.1, Germany was used as adsorbent in all the experiments.

Heat Treatment

Different portions of the unmodified starch were heated, in air, at different temperatures, i.e., 110°C, 150°C, 160°C, 170°C, and 180°C. The heating time was 6 hours in each case.

Bound Alcohol

A portion of the unmodified starch was evacuated for 4 hours at a vacuum of 10^{-2} mm. in the adsorption apparatus, kept inside an air thermostat, at 35°C. The evacuated sample was subjected to integral sorption of methyl alcohol vapours, kept in contact for one day and then alcohol was desorbed. The system was evacuated, at 35°C, for 12 hours. The amount of bound methyl alcohol was 3.6 c.c. per 100 g. of modified starch.

An exactly similar procedure was adopted for obtaining modified starch having bound ethyl alcohol. The amount of bound ethyl alcohol was 6.4 cc./100 g. of modified starch.

Removal of fat

Fat was removed from unmodified starch by extracting it, for 12 hours, in the soxhlet apparatus with 80% dioxane as solvent. The fat free starch was dried in an oven at 105°C.

Aqueous Swelling

Unmodified starch was swollen by submerging it in boiling distilled water for 30 minutes and then was allowed to cool and remain in the water overnight at room temperature. The swollen sample was allowed to dry, at room temperature, for two weeks. The swollen mass was made to fine powder (particle size less than 100 mesh).

Denaturation

A sample of unmodified starch was denatured by heating in boiling absolute alcohol for one hour and then drying in an oven at 60°C for 4 hours.

Compaction

Starch was compacted into a tablet (diameter 3/8", thickness 1/8") at a pressure of 5000 Kg/sq.inch.

A series of sorptions and desorptions of water vapour on these modified samples was carried out at 35°C.

Results and Discussion

Effect of 'Bound Alcohol'

With modified starch samples retaining irreversibly adsorbed methyl alcohol (A) and ethyl alcohol (B), the sorption-desorption studies were continued up to the 4th cycle. The loops of 1st, 2nd and 4th cycles are presented in Figures (6) and (7). The values of water sorption at the

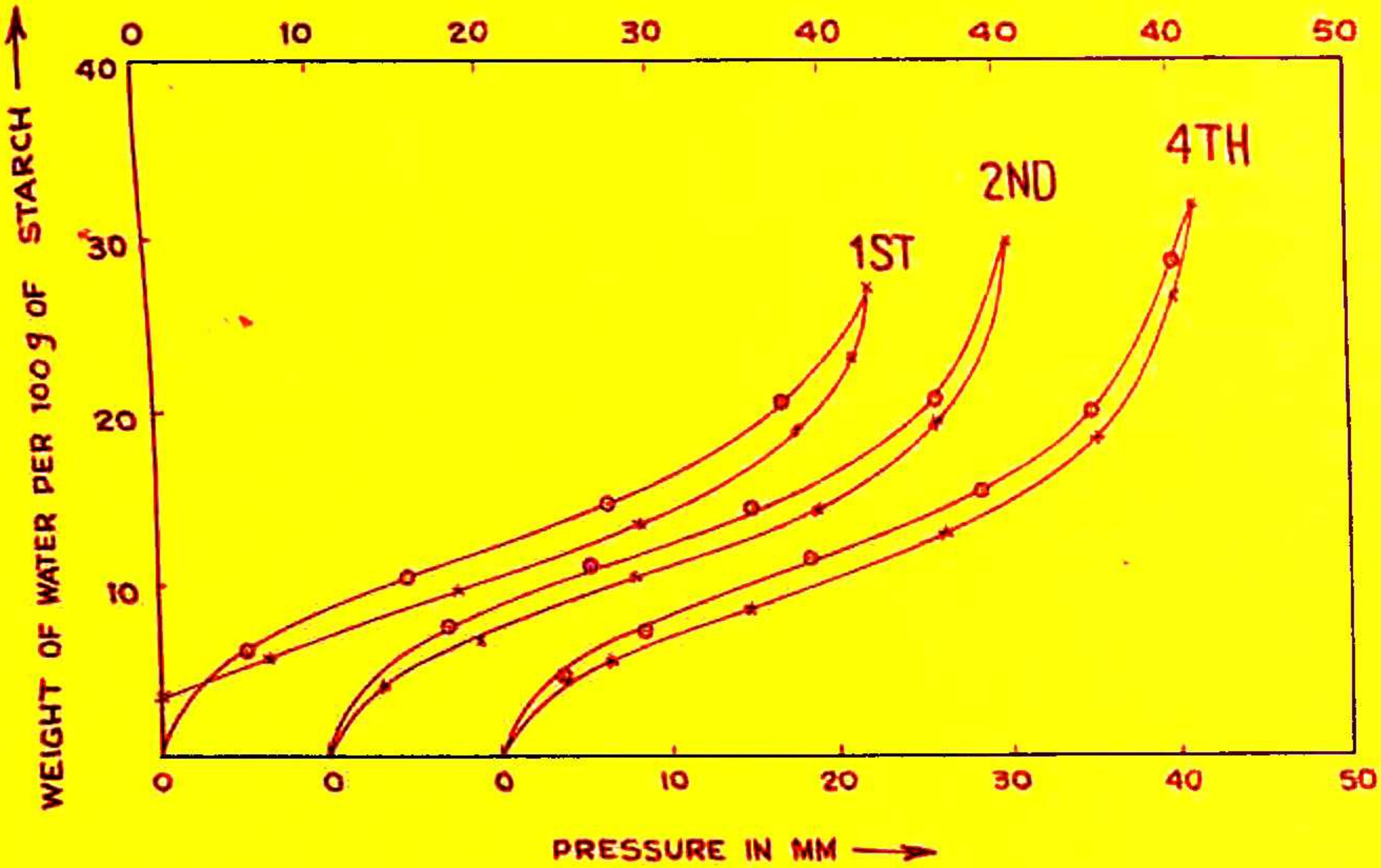


FIG. 6 SORPTION - DESORPTION HYSTERESIS OF WATER ON MODIFIED STARCH RETAINING BOUND METHYL ALCOHOL AT THE 1ST, 2ND, AND 4TH CYCLES.

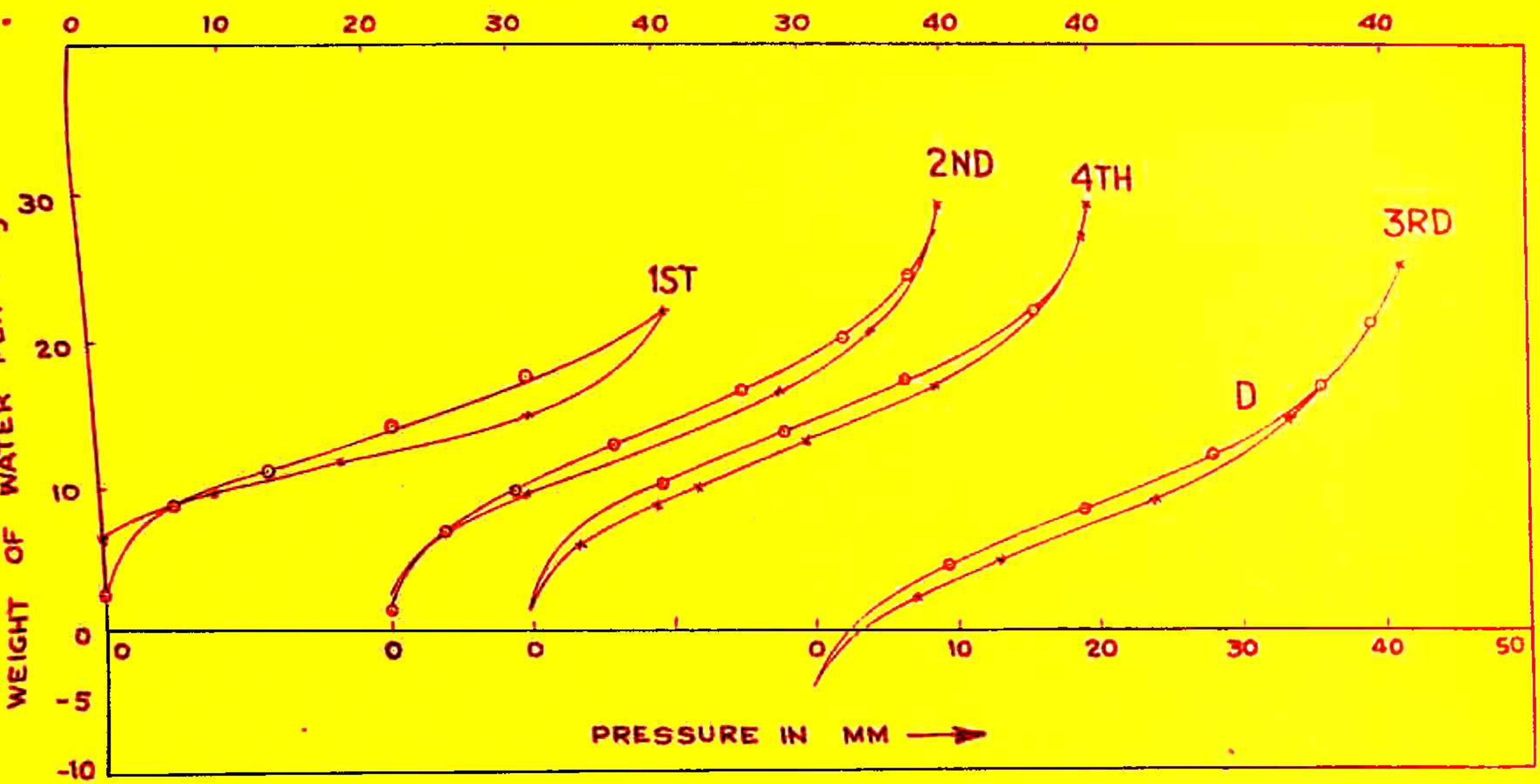


FIG.7 SORPTION-DESORPTION HYSTERESIS OF WATER ON MODIFIED STARCH RETAINING BOUND ETHYL ALCOHOL AT THE 1ST, 2ND, AND 4TH CYCLES.

CURVE D: SORPTION-DESORPTION HYSTERESIS OF WATER ON DENATURED STARCH AT THE 3RD CYCLE.

saturation pressure of water at 35°C are 26.8%, 30.0% and 31.6% in case of (A) and 22.0%, 28.9% and 29.0% in case of (B).

The nature of the 1st cycle of sorption and desorption is interesting. At the end of first cycle modified starch suffers a loss in weight which must be due to the residual alcohol retained by it even at vacuum of 10^{-2} mm. (B) continues to loose weight even at the end of the 2nd cycle but the weight remains constant in all the subsequent cycles.

The bound methyl alcohol has not altered the surface of modified starch which is evident from the same sorptive capacity and the area enclosed in the hysteresis loop as that of unmodified starch (34). The alcohol molecules appear to have been locked in the fine pores and interstices of starch granules, without changing the outer surface or the cavity volume of starch. At the end of the 1st cycle, all the bound methyl alcohol is completely removed by water, by preferential adsorption in interstices, and modified starch behaves in a manner exactly similar to that shown by unmodified starch (34).

Bushuk and Winkler (35) have observed in their studies on the sorption of organic vapours on wheat flour that complete removal of alcohols could be achieved by swelling the flour by sorbing water vapour on the same sample and then desorbing the alcohols and water by evacuation. It is, however, observed by the authors, that, irreversibly adsorbed methyl alcohol can be removed by such a treatment but the situation is different in case of bound ethyl alcohol. The interaction between ethyl alcohol vapours and unmodified starch appears to be quite strong and complete removal of ethyl alcohol is not possible by such a treatment. Even after 4th cycle,modified starch retains 1.2 c.c. of ethyl alcohol per 100 grams of modified starch.

Ethyl alcohol seems to have changed the surface of modified starch. Modified starch is rendered less hydrophilic and less swellable. The sorption and desorption isotherms are coincident in the higher vapour pressure region. In order to study the nature of changes brought about by ethyl alcohol, a series of sorptions and desorptions were carried out with denatured starch. The curve D of Figure(7) shows the nature of results. The loop obtained at the 3rd cycle is only presented. The denatured starch also lost about 4 c.c. of ethyl alcohol at the end of 1st cycle.

A comparison of 4th loop and the D loop reveals that both are almost identical. Hence, it is reasonable to assume that bound alcohol has the same effect on sorption of water vapour as denatured starch. Probably,this effect is caused as result of compression of starch surface by bound ethyl alcohol.

The results obtained on the compacted starch (Figure 10) also support such a possibility.

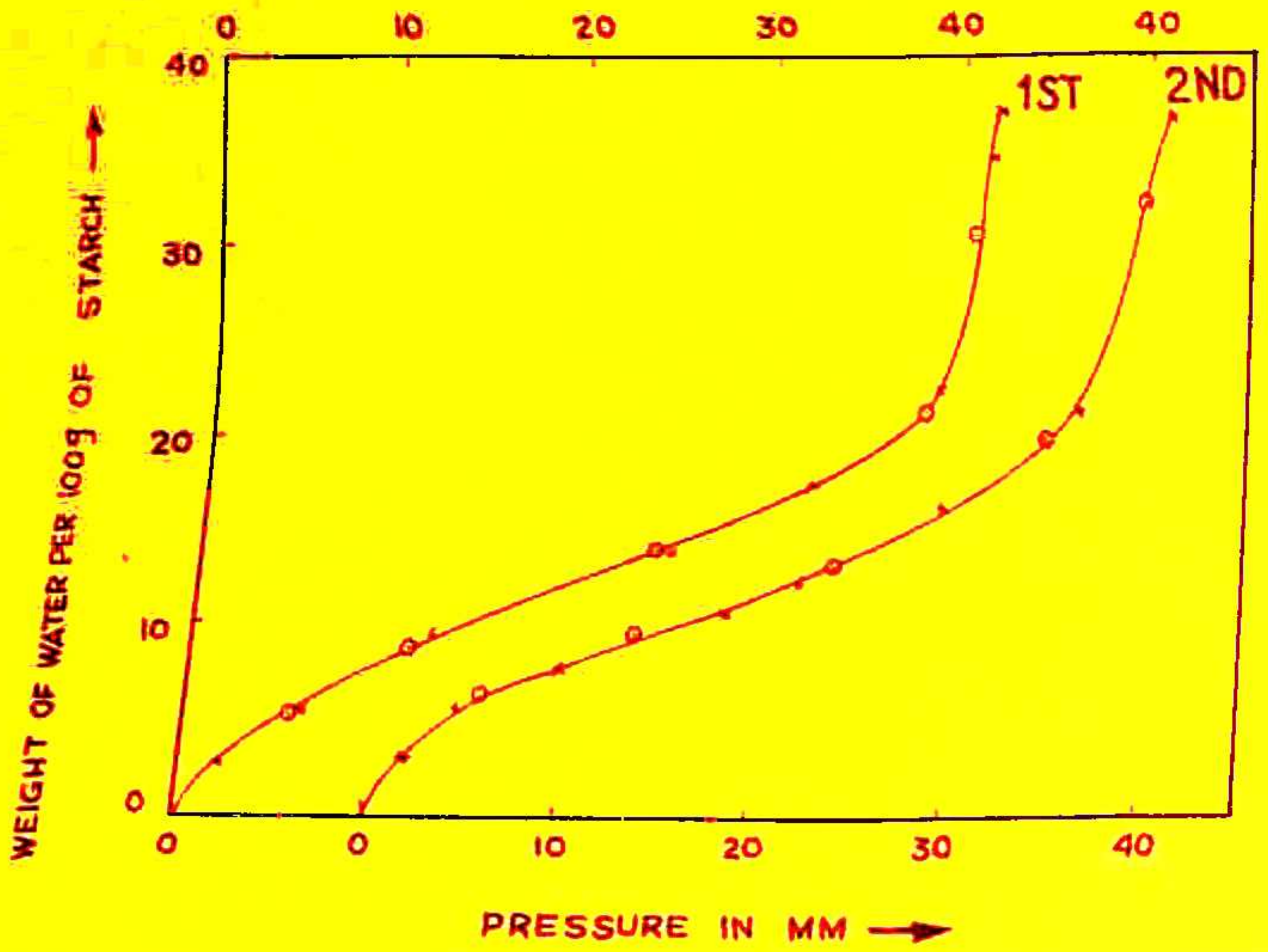


FIG. 8 SORPTION - DESORPTION HYSTERESIS OF WATER ON DEFATTED STARCH AT THE 1ST, AND 2ND CYCLES.

Effect of fat removal

Starches available commercially are isolated from botanical sources by an extraction process and encompass minor amounts of non-carbohydrate constituents. Of these fat materials are most important. Little is known about the detailed chemical composition of the proteinaceous substance and fat materials embedding the starch granule. Although, fat materials are present in small amounts (less than 1%) (36-38) their influence on the sorptive properties of starch is remarkable.

Figure (8) gives the results of water vapour sorption and desorption on fat extracted starch. The loops obtained at the first two cycles are presented. There is an increase in sorptive capacity from 31.5% to 41.6%. The coincidence of sorption and desorption isotherms indicates the absence of hysteresis effect.

The realization that the granule structure could be disrupted by hydrolysis led to the belief that the fatty materials occur in an esterified form, attached to carbohydrate substances (39-41). This concept was challenged by Schoch (42), who considered the fatty materials as extraneous impurity distributed throughout the starch granule.

Lehrman (43) thought that the fatty materials might be present as an adsorption complex with carbohydrate.

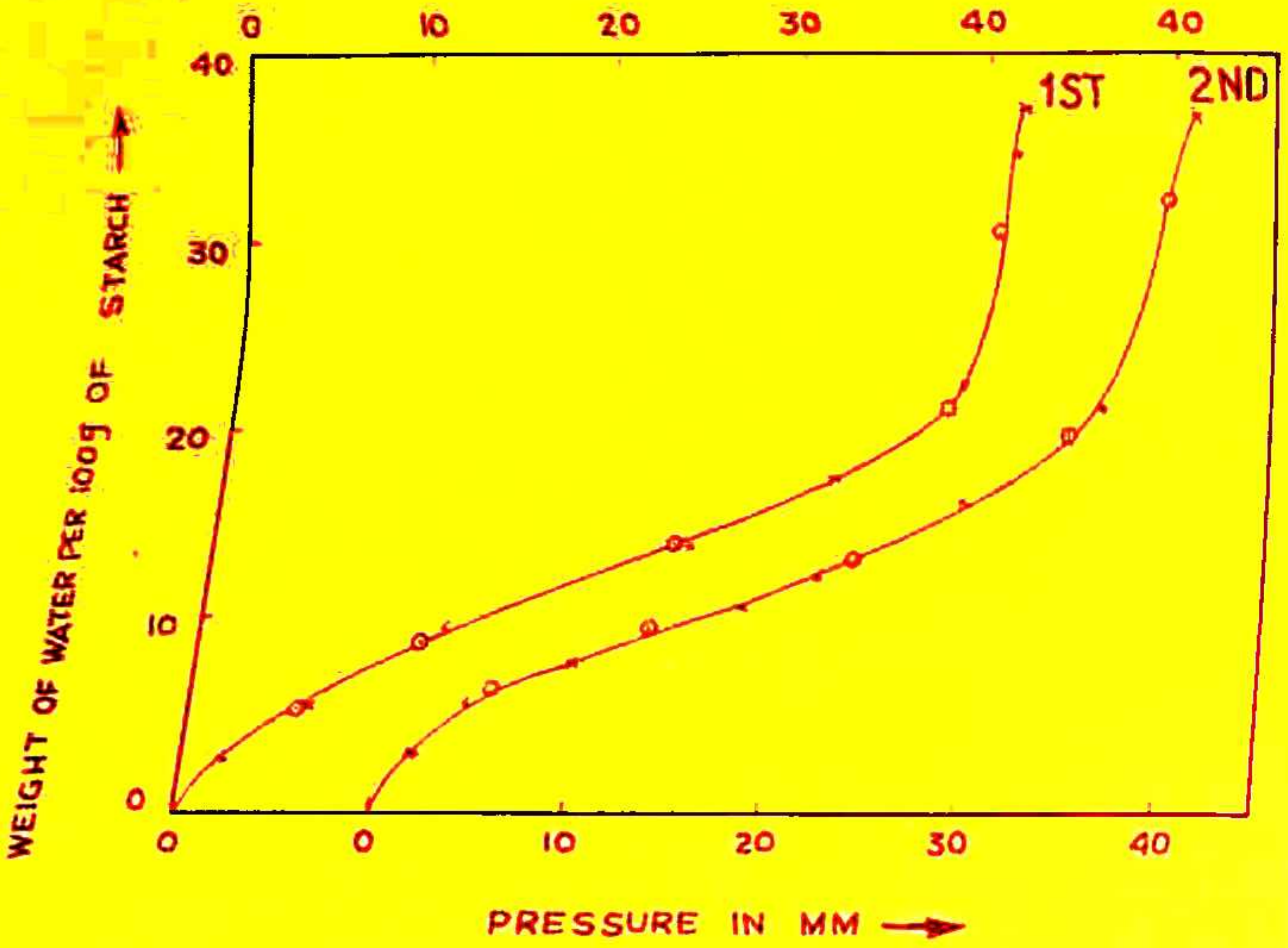


FIG. 8 SORPTION-DESORPTION HYSTERESIS OF WATER ON DEFATTED STARCH AT THE 1ST, AND 2ND CYCLES.

Effect of fat removal

Starches available commercially are isolated from botanical sources by an extraction process and encompass minor amounts of non-carbohydrate constituents. Of these fat materials are most important. Little is known about the detailed chemical composition of the proteinaceous substance and fat materials embedding the starch granule. Although, fat materials are present in small amounts (less than 1%) (36-38) their influence on the sorptive properties of starch is remarkable.

Figure (6) gives the results of water vapour sorption and desorption on fat extracted starch. The loops obtained at the first two cycles are presented. There is an increase in sorptive capacity from 31.5% to 41.6%. The coincidence of sorption and desorption isotherms indicates the absence of hysteresis effect.

The realization that the granule structure could be disrupted by hydrolysis led to the belief that the fatty materials occur in an esterified form, attached to carbohydrate substances (39-41). This concept was challenged by Schoch (42), who considered the fatty materials as extraneous impurity distributed throughout the starch granule.

Lehrman (43) thought that the fatty materials might be present as an adsorption complex with carbohydrate.

Neither the concept of extraneous impurity nor the 'adsorption complex' theory can account for the rigidity of starch granules as far as hysteresis is concerned. These concepts are, obviously, specific and cannot account for reproducible and permanent hysteresis exhibited by starch-water system (34). The authors are of the view that fat material is present in starch in the form of a 'coating membrane' around each starch granule. This membrance is tough and resists the collapse of cavities during desorption.

The removal of fat by extraction results in the removal of this coating membrane. Now when the fat free starch is exposed to water vapour, the network swells, granules coalase with each other and since the rigidity is lost, the cavity walls become elastic. During desorption all the cavities collapse and no hysteresis is exhibited even in the 1st cycle.

Effect of Aqueous Swelling

The starch granule is composed of linear and branched starch molecules,associated by hydrogen bonding either directly or through water hydrate bridges to form radially oriented micells or crystalline areas of various degrees of order. The overall strength of the network controls the behaviour of starch in water.

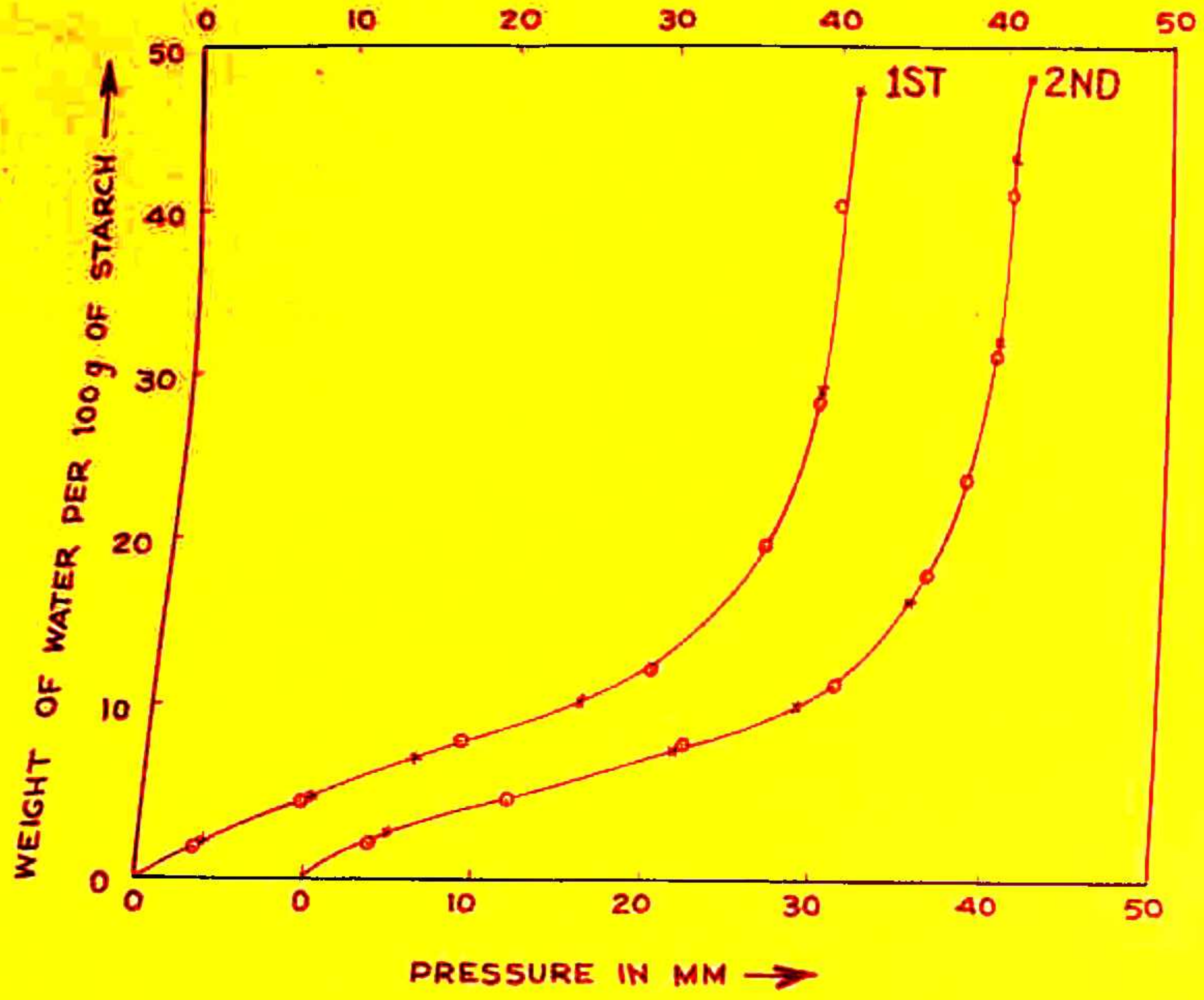


FIG. 9 SORPTION-DESORPTION HYSTERESIS OF WATER ON AQUEOUS SWOLLEN STARCH AT THE 1ST, AND 2ND CYCLES.

The subjection of an aqueous suspension of starch to the influence of heat weakens this miceller network within the granules by disrupting hydrogen bonds. The individual granules undergo a series of physical changes of which swelling is the most important.

The swollen starch behaves in an interesting manner. There is an increase in the sorptive capacity of starch from 31.5% to 48.1% (Figure 9). This may be due to the expansion of the starch network owing to swelling. The sorption and desorption isotherms are coincident, indicating the absence of hysteresis. The disappearance of hysteresis reveals the role of elasticity of the network of starch on the imbibition of water which is a solvating liquid for starch.

Effect of compaction

In the natural state, starch exists in the form of discrete microscopic granules, held together by extended miceller network of associated molecules. The network possesses sub-microscopic cracks and cavities as demonstrated by Whistler et al (26) under electron microscope. In the light of cavity concept (22,23), these cavities are responsible for the hysteresis effect.

In order to examine the cavity theory of hysteresis crucially, a series of sorptions and desorption were performed

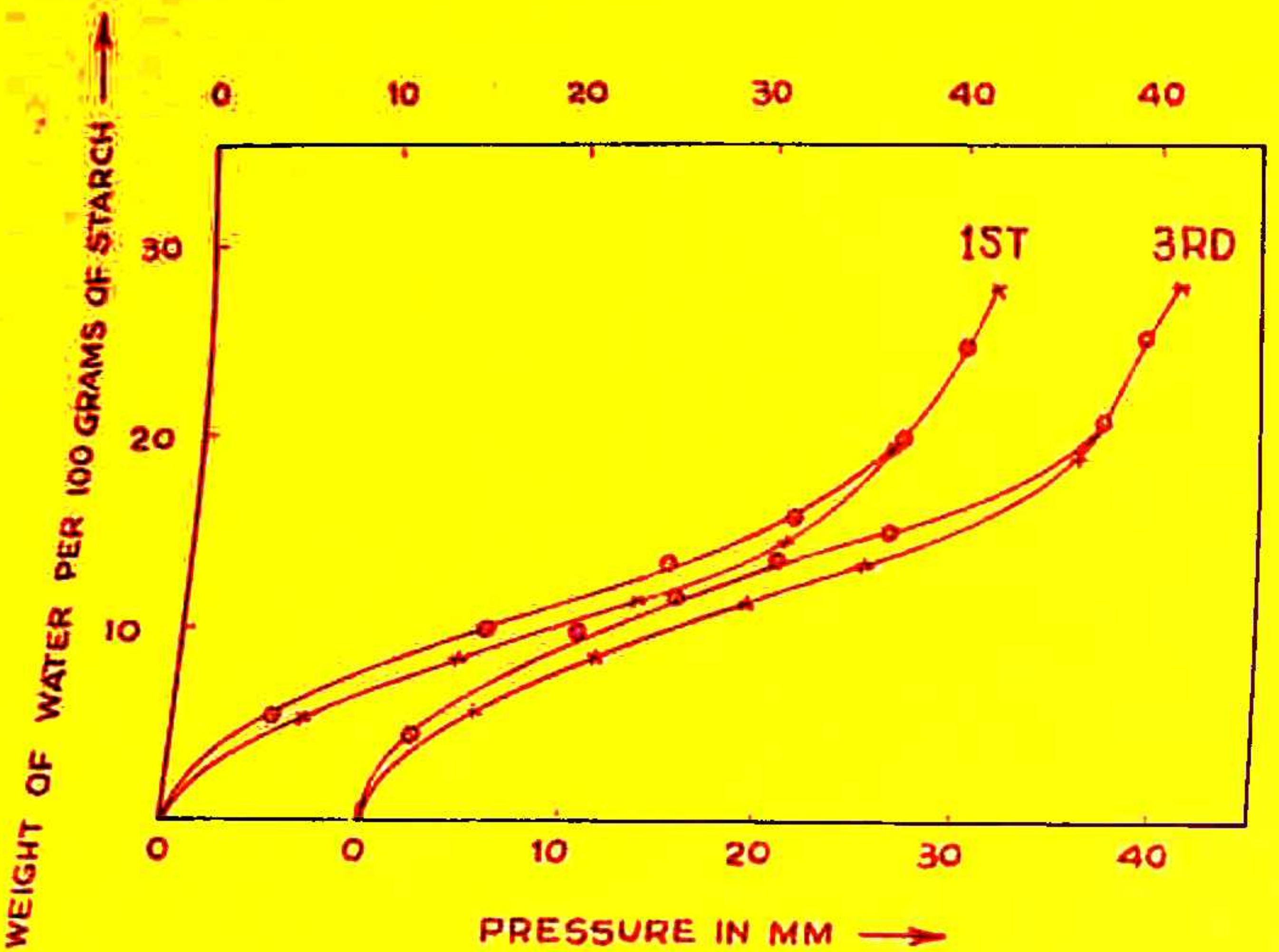


FIG. 10 SORPTION - DESORPTION HYSTERESIS OF WATER ON COMPACTED STARCH AT THE 1ST AND 3RD CYCLES.

on compacted starch. The results are shown in Figure (10). The experiment was continued up to 3rd cycle.

Compacted starch exhibited a degree of relaxation or irreversible length change when alternate conditions of sorptions and desorptions of water vapour were cycled a number of times but it did not disintegrate when exposed to saturated water vapour.

There is a slight decrease in the total sorptive capacity of starch which can be attributed to the contraction in surface area by adhesion of neighboring particles. Earlier (44,45), it has been reported that the monolayer region virtually remains the same both before and after compaction. A similar observation has also been made by the authors in the present studies.

There is no hysteresis effect in the region of higher humidities, i.e., above $p/p_o = 0.85$. In this region, the relationship of moisture content to volume change is mainly influenced by the geometry of the pore system. It is obvious that compaction has merely diminished the interparticulate gaps. The cavities disappear and no hysteresis appears in the primary region. The authors thus believe that if higher pressures for compaction were used, the hysteresis effect would have been completely removed.

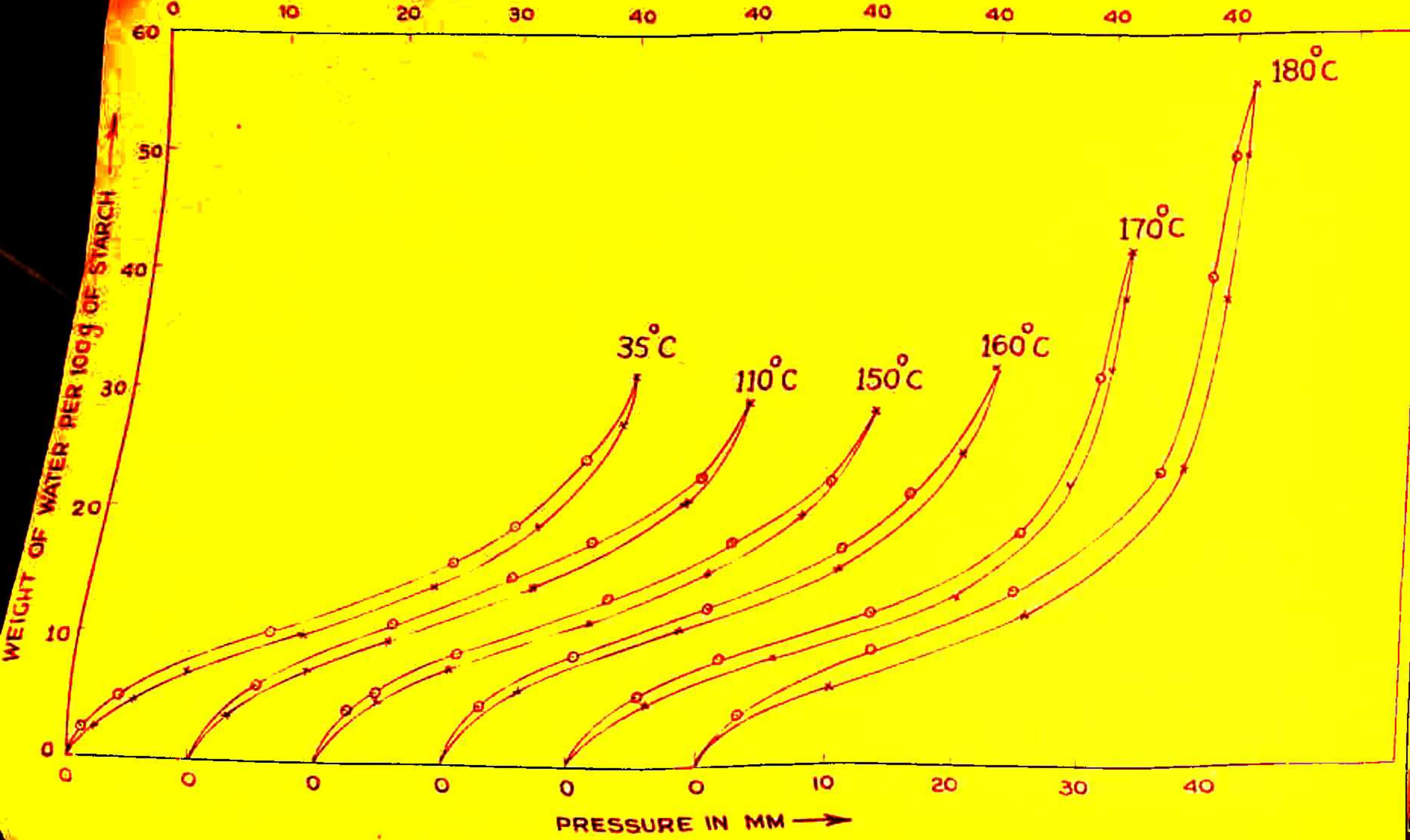


FIG.11 SORPTION - DESORPTION HYSTERESIS OF WATER ON STARCH

Effect of heat treatment

Figure (11) gives the results obtained on successive sorptions and desorptions of water vapour on starch modified by heat treatment. The sorptive capacities of modified starch are presented in Table VI.

Table VI

Sorptive capacities of modified starch at different temperatures.

Temperature °C	35	110	150	160	170	180
Sorptive capacity %	31.5	29.0	28.2	32.0	41.9	55.9

Linear hysteresis, i.e., hysteresis effect extending over the entire pressure range has been exhibited by modified starch at all the temperatures studied.

The nature of loops is very interesting. There is a slight decrease in the sorptive capacity and in the size of the loop up to 150°C. Starch, when heated, undergoes a progressive series of irreversible changes. These changes are not very predominant up to a heating temperature of 150°C. The slight decrease in the sorptive capacity and the size of hysteresis may be attributed to the shrinkage of the network of modified starch owing to the removal of residual water as a consequence of heat treatment.

In a detailed investigation, Katz (46) reported that no observable difference in the X-ray pattern occurs with heating temperature below 120°C. Above this temperature, the moisture uptake of heated starch, when allowed to rehydrate, becomes less. Katz and Weidinger (47) reported that heating temperatures up to about 140°C have little effect on the solubility properties of granule starch.

Heating temperatures above 150°C, affect the sorptive properties considerably. At about 170°C, when the colour of starch becomes yellow, a profound change takes place. At still higher temperatures both the sorptive capacity and the size of the hysteresis loop increase with temperature. This is a unique and significant finding.

It is evident from these results that heat has caused modifications in the polymer network of starch. It is reasonable to assume that the network has disintegrated into products capable of taking up large amount of water. It was reported by Puddington (48) that, when potato starch was heated to temperatures in the range of 180-210°C gaseous products, CO_2, CO, H_2O and traces of volatile solids were librated. The unique behaviour exhibited by starch at higher temperatures can be attributed to the formation of some new products as pyrodextrins. The pyrodextrins are typically amorphous, soluble in water and are capable of adsorbing large quantities of water. It has also been reported that granule starches heated

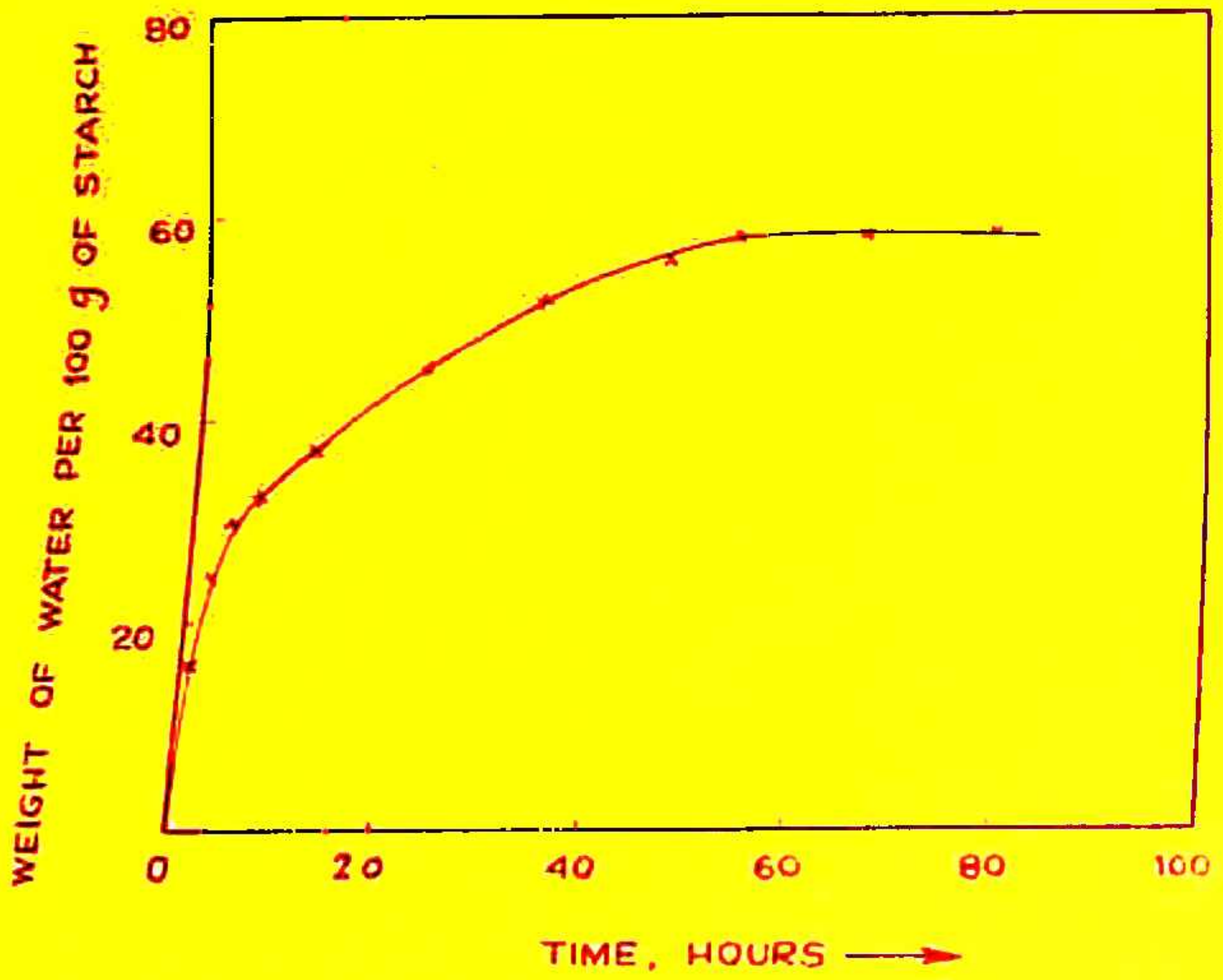


FIG.12 TIME-SORPTION CURVE FOR STARCH SAMPLE HEATED AT 180°C AT THE SATURATION PRESSURE OF WATER AT 35°C.

to 1[illegible]0-210°C no longer show the swelling properties in water that are characteristics of the unmodified granules. Instead, they undergo dissolution by sloughing off the concentric layers (49,50). A similar effect has been observed in the present studies which accounts for the increase in sorptive capacity of starch at higher temperatures.

The widening of the hysteresis loop may be due to an increase in the formation of cavities. This agreement is further supported by the findings of Whistler et al (26) who reported that heating starch, especially at elevated temperatures promots the formation of cavities in starch and the cavities are all open to the granule surface.

The time sorption curve (Figure 12) constructed for 1[illegible]0°C heated sample reveals that the time required for the attainment of equilibrium is about 55 hours. The time required for the attainment of equilibrium with unmodified starch was about 8 hours. This result further supports the formation of more cavities in starch heated at higher temperatures.

***

References

1. [illegible], in "The solid gas interface", Ed. E.A. Flood, Marcel Dekker, Inc., New York, 1967, p.540.

2. Goto, H., J. Chem. Soc., Jap., Pure Chem. Sec., 1951, 72, 790.

3. Ubertis, B., and Roversi, [illegible], Die Starske, 1953, 5, 266.

4. Sair, L., and Fetzer, W.R., Ind. Eng. Chem., 1944,36,205.

5. Browne, C.A., Ind. Eng. Chem., 1922, 14, 712.

6. [illegible], and Melvin, [illegible], Cereal Chem., 1948, 25, 146.

7. [illegible], and Winkler, C.A., Cereal Chem., 1957, 34,2,73.

8. Freeman, [illegible], Arch. Biochem., 1942, 1, 27.

9. [illegible], Koll. J. (U.S.S.R.) 1937, 3, 121.

10. Farrow, F.D., and Swan, [illegible], Shirley Inst. Mem., 1923,2,329.

11. Rakowski, A., Kolloid-Z., 1911, 9, 225; 1912, 10, 22.

12. Katz, J.R., Kolloid Chem. Beihefte, 1917, 9, 65.

13. Swan, G., Shirley Inst. Mem., 1926, 5, 167.

14. [illegible], J.D., and Harris, R.H., Cereal Chem., 1952, 29, 132.

15. Ulman, M., and Schierbaum, F., Ernaehrungs fur Schuing, 1958, 3, 65.

16. Winkler, C.A., and Geddes, W.F., Cereal Chem., 1931, 8, 455.

17. Urquhart, A.R., and Williams, A.M., J. Text. Inst., 1926, 17, T136.

18. Shotton, E., and Harb, N., J. Pharm. Pharmacol., 1965, 17, 504.

19. Rao, G.N.S., Rao, K.S., and Rao, B.S., Proc. Ind. Acad. Sci., 1947, 25, 221.

20. Elworthy, P.H., and George, T...., J. Pharm. Pharmacol., 1964, 16, 258.

21. Rao, [illegible], J. Phys. Chem., 1941, 45, 531.

22. [illegible], J. Am. Chem. Soc., 1935, 57, 699.

23. Brunauer, S., "The adsorption of gases and vapours" Oxford University Press, London, 1945, p.396.

24. Rundle, R.E., Daasch, L., and French, D., J. Am. Chem. Soc., 1944, 6[illegible], 1[illegible].

25. Huggins, M.L., in "Physical chemistry of high polymers", John Wiley & Sons Inc., New York, 1958, p.1[illegible]1.

26. [illegible]istler, [illegible], Spencer, [illegible], [illegible], J.L., and Mikuni, Z., Cereal Chem., 195[illegible], 35, 331.

27. Partington, J.R., "Advances physical chemistry", Vol.V, Longmans Green, New York (1955).

28. Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 1938, 60, 309.

29. Emmett, P.H., and Brunauer, S., J. Am. Chem. Soc., 1937, 59, 1553.

30. Gregg, S.J., and Sing, K.S.W., "Adsorption, surface area and porosity", Academic Press, London and New York, 1967, p.54.

31. Gregg, S.J., and Sing, K.S.W., "Adsorption, surface area and porosity", Academic Press, London and New York, 1967, p.65.

32. Rao, K.S., and Das, B., Curr. Sci., 1968, 21, 5.

33. Harkins, W.D., "The physical chemistry of surface films", Reinhold (1952), p.235.

34. Gupta, S.L., and Bhatia, R.K.S., Ind. J. Chem., 1969, 7, 1231.

35. Bushuk, W., and Winkler, C.A., Cereal Chem., 1957, 34, 2, 87.

36. Taylor, T.C., and Nelson, T.H., J. Am. Chem. Soc., 1920, 42, 1726.

37. Lindemann, E., Staeke, 1951, 3, 141.

38. Fukuba, H., Nippon Nogeik Kagaku Kaigen, 1954, 28, 38.

39. Taylor, T.C., and Sherman, R.T., J. Am. Chem. Soc., 1933, 55, 258.

40. Taylor, [illegible], and Iddles, H.A., Ind. Eng. Chem., 1926, 18, 713.

41. Taylor, [illegible], and Werntz, J.H., J. Am. Chem. Soc., 1927, 49, 1584.

42. Schoch, T.J., J. Am. Chem. Soc., 1938, 60, 2824.

43. Lehrman, L., J. Am. Chem. Soc., 1939, 61, 212.

44. Carman, P.C., and Raal, F.A., Proc. Roy. Soc., 1951, 59, 209A.

45. Kiselev, A.V., in "The structure and properties of porous materials", Butterworth, London, 1958, p.128.

46. Katz., J.R., Rec. Trav. Chim., 1934, 53, 555.

47. Katz, J.R., and Weidinger, A., Z. Physik. Chem., 1939, A184, 100.

48. Puddington, I.E., Can. J. Res., 1948, B26, 415.

49. Sjostrom, O.A., Ind. Eng. Chem., 1936, 28, 63.

50. Brimhall, B., Ind. Eng. Chem., 1944, 36, 72.

*****

CHAPTER V

ADSORPTION HYSTERESIS IN CELLULOSE AND CELLULOSE DERIVATIVES

PART I

SORPTIVE PROPERTIES OF CELLOBIOSE

SORPTIVE PROPERTIES OF CELLOBIOSE

Abstract

Making use of the quartz fibre spring balance technique, a series of sorptions and desorptions, at 35°C, of water, methyl alcohol, ethyl alcohol and carbon tetrachloride vapours have been carried out on cellobiose. The extect of adsorption was considerably small in every case and there was no hysteresis effect. The low sorptivities of cellobiose for these vapours and the absence of hysteresis effect have been related to the structure of cellobiose.

Introduction

Glucose is the building brick of cellulose. Two molecules of β-glucose combine to give one molecule of cellobiose. In an exactly similar way, two molecules of cellobiose combine, spilling off another molecule of water, giving a longer chain. This process of condensation goes on continuously in nature and results in the formation of cellulose.

Sorption of water and other liquids on cellulose has already been studied and reported earlier(1-9) but the nature of interaction is not fully understood. Little systematic work appears to have been done on the vapour phase sorption and desorption on cellobiose. There is an indication that more

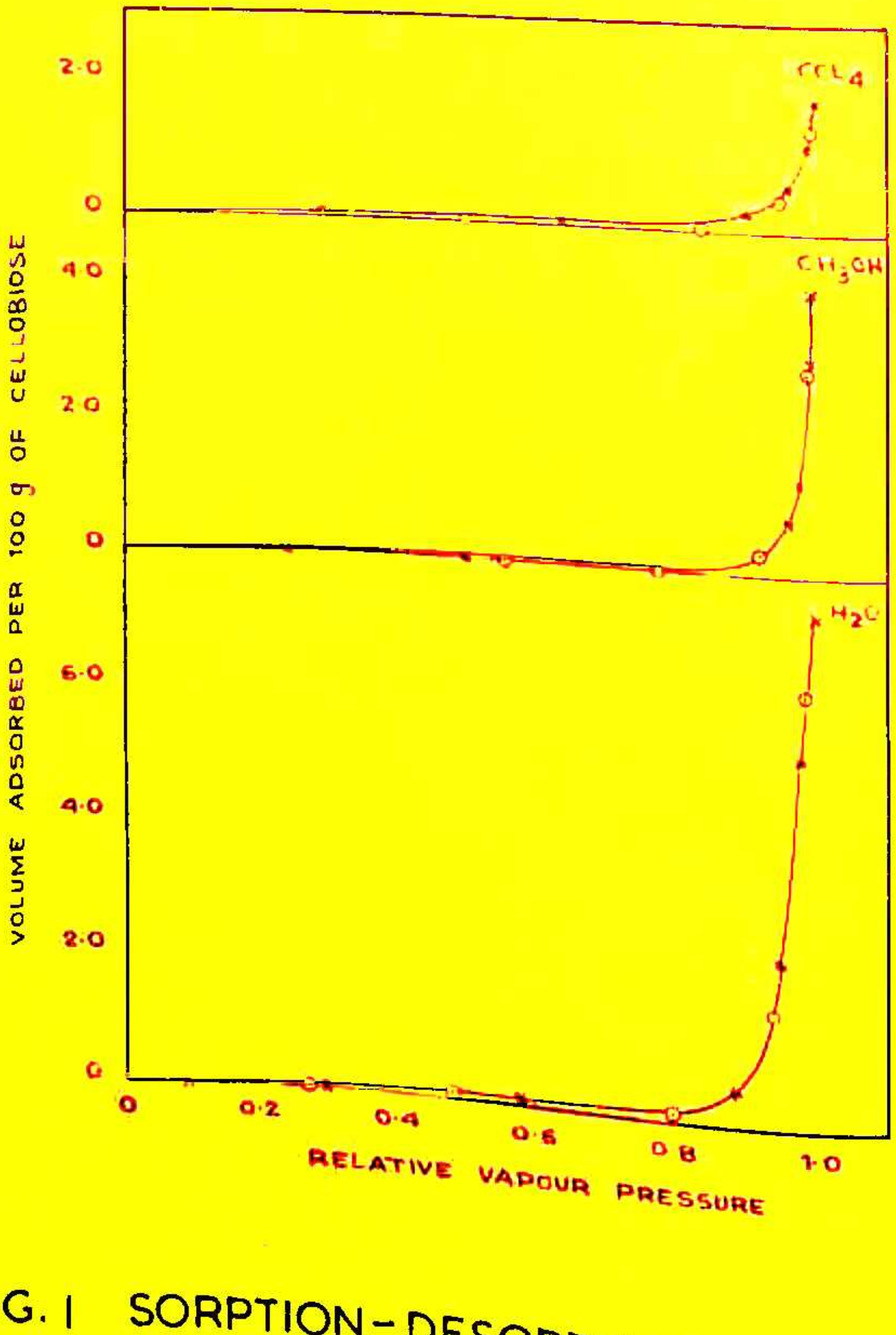


FIG. I SORPTION-DESORPTION HYSTERESIS OF H_2O, CH_3OH AND CCL_4 ON CELLOBIOSE information about the nature of interaction can be achieved by the study of such simple systems.

Experimental:

Cellobiose (B.D.H.), Biochemical grade, moisture content less than 0.5%, sulphated ash less than 0.2% was used as adsorbent in all the experiments while redistilled methyl alcohol, ethyl alcohol and carbon tetrachloride and double distilled water were used as sorbates.

Results and Discussion

The isotherms obtained with different sorbates are presented in Figure (1) in which the volume of sorbate adsorbed per 100 grams of cellobiose is plotted against the relative vapour pressure of the sorbate. The equilibrium sorption and desorption of various sorbates on cellobiose have been presented in Table I.

Table I

Equilibrium sorption and desorption of water, methyl alcohol and carbon tetrachloride on cellobiose.

Relative vapour pressure	Sorption cc/100 g	Relative vapour pressure	Desorption cc/100 g
Water			
0.09	0.00	0.99	6.3
0.29	0.04	0.94	1.67

Table I (contd..)

Relative vapour pressure	Sorption cc/100 g	Relative vapour pressure	Desorption cc/100 g
Water			
0.58	0.16	0.92	0.40
0.89	0.54	0.81	0.16
0.95	2.40	0.48	0.08
0.98	5.40	0.27	0.04
1.00	7.50		
Methyl alcohol			
0.24	0.00	0.99	3.00
0.495	0.10	0.92	0.40
0.77	0.20	0.78	0.10
0.97	0.84	0.56	0.00
0.98	1.40		
0.99	3.20		
1.00	4.20		
Carbon tetrachloride			
0.29	0.00	0.99	1.51
0.64	0.05		
0.90	0.25	0.95	0.51
0.96	0.60	0.84	0.10
0.99	1.20	0.49	0.00
1.00	1.90		

Cellobiose exhibited considerably low sorptive capacities for these sorbates. It showed the following trend in binding these vapours:

water > methyl alcohol > carbon tetrachloride

The sorption of ethyl alcohol was practically negligible. Table II shows the sorptive capacities of cellobiose for different sorbates.

Table II

Sorptive capacities of cellobiose

Sorbate	Sorptive capacity cc/100 g.
Water	7.5
Methyl alcohol	4.2
Ethyl alcohol	0.2
Carbon tetrachloride	1.9

Except ethyl alcohol, type III isotherms of BET classification (10) were obtained in every case. The isotherms were practically horizontal and showed no appreciable increase in sorption up to relative pressure of about 0.85. In the light of capillary condensation theory of sorption, this indicates the absence of micropores and even the transitional pores as per Dubinin's classification (11).

The low sorptive capacity of cellobiose for carbon-tetrachloride is a measure of the pore space and this is very small as compared with its saturation capacity.

In all the systems, no hysteresis effect was observed i.e., the sorption and desorption curves were coincident. In the light of cavity theory of hysteresis (12,13) the absence of hysteresis is due to the elasticity of the cavity walls of cellobiose. Sorption and desorption of vapours on cellobiose cause swelling and shrinkage and these are associated with the development of internal stresses and strains. Cellobiose has a very low sorptive capacities for water, methyl alcohol, ethyl alcohol and carbon tetrachloride, the stresses and strains are least. Therefore, cavities collapse easily and no hysteresis is exhibited even in the first cycle. On the contrary, cellulose showed high sorptive capacities for these sorbates and exhibited permanent hysteresis effect (14). The present results indicate that, as the chain length increases, the structure becomes more rigid and uncollapsable. The cavity walls become tough, entrap liquid sorbate and cause permanent and reproducible hysteresis effect.

***

PART II

SORPTION-DESORPTION STUDIES OF WATER, ALIPHATIC NORMAL ALCOHOLS AND CARBON TETRACHLORIDE ON RAW AND MODIFIED COTTON

SORPTION-DESORPTION STUDIES OF WATER, ALIPHATIC NORMAL ALCOHOLS AND CARBON TETRACHLORIDE ON RAW AND MODIFIED COTTON

Abstract

A series of sorptions and desorptions of water, aliphatic normal alcohols and carbon tetrachloride have been carried out at 35°C on raw cotton, employing the quartz fibre spring technique. Permanent hysteresis effect has been observed with all the sorbates. Raw cotton water vapour system exhibits remarkable reproducibility of the hysteresis effect. The hysteresis loop has been reproduced up to 24 cycles of sorptions and desorptions. The sorptive capacity of raw cotton for various polar sorbates follows the trend: water $>$ methyl $>$ ethyl $>$ n-propyl $>$ n-butyl alcohols. The extent of adsorption becomes practically negligible with n-butyl alcohol. Raw-cotton - alcohol systems exhibited the phenomena of 'bound alcohol'. The size of the hysteresis loop decreases as the molecular weight of the sorbate alcohol increases. The sorption data have been compared with the data obtained by earlier workers.

The influence of certain modification of raw cotton, brought about by factors such as activation, dewaxing and

aqueous swelling towards water sorption has also been studied. An attempt has been made, for the first time to explain the results in the light of the cavity theory of hysteresis in conjunction with the nature of changes brought about by such treatments.

Introduction

Cellulose and cellulose derivatives are hygroscopic and when surrounded by an atmosphere containing the vapour of water or certain organic liquids, are capable of taking up vapour from the atmosphere while undergoing considerable swelling. The property of swelling is, by far, the most important fundamental characteristic of cellulosic fibres. Attempts to relate the extent of swelling to the dielectric constant (15,16), the dipole moment (17) and the surface tension of the sorbate (15,18) have been only partially successful. The tendency for hydrogen bonding appears to be important (17). Swelling in organic liquids as well as in water, leads to a decrease in strength properties.

The take up (sorption) of water by cellulose has been extensively studied and the published literature is large; this is because the presence of sorbed liquid changes the chemical behaviour, mechanical properties and chemical characteristics of cellulose and the results of research in this field are of obvious technical as well as scientific, interests. Much of the previous work has been outlined by Howsmon(1).

Of the recent publications (2-8) on the sorption of water by cellulose, stress is laid either to the kinetics of sorption or to the thermodynamic properties of cellulose. Sorption hysteresis, which is a characteristic of the adsorbent has not been discussed and interpreted. Earlier (9,19-22) many attempts have been made to provide a suitable explanation for sorption hysteresis shown by cellulose and its derivatives but the explanations were specific and could not account for the permanence and reproducibility of hysteresis loop. Sorption-desorption hysteresis has still remained an unsolved problem.

The present comprehensive investigations describe complete sorptions and desorptions, at 35°C, of water, aliphatic normal alcohols and carbon tetrachloride on raw and modified cotton. The effect of temperature on hysteresis has been studied over a wide range of temperature and is also presented. An attempt has been made, for the first time, to explain these results in the light of "ink bottle" theory of hysteresis (12,13).

Experimental section

Raw cotton, taken from a mature cotton boll, was used as adsorbent in all the experiments. Cotton bolls were obtained from the botanical gardens of B.I.T.S.

Raw cotton was subjected to following modifications:-

(1) Aqueous swelling

Cotton fibres were swollen (23) by submerging them into boiling distilled water for 5 minutes and then allowed to cool and remained in the water overnight at room temperature. Then fibres were dried in air till they attained a constant weight. The complete drying took about ten days.

(2) Dewaxing

Cotton fibres are a purer form of cellulose and have a simpler morphological structure than wood. They consist of a wall which surrounds a central cavity called Lumen. The wall consists of a secondary part and a primary part. The primary part is very thin and contains wax and cellulose. Several methods (24-27) have been described for the extraction of wax. In the present studies, a two step operation for the removal of wax was employed as follows:

A weighed amount of raw cotton was extracted with 95% ethyl alcohol in a soxhlet apparatus for six hours. Wax-free cotton was washed 2-3 times with chloroform and finally washed several times with distilled water and dried in air.

The total wax content of the raw cotton sample was 2.746%.

Activation

Raw cotton was activated by heating, in vacuum, for four hours, at 60°, 95°C, 125°C, 150°C, 175°C and 200°C.

The moisture content of raw cotton, as determined by heating it at 110°C for 4 hours, was 5.56%.

Redistilled methyl alcohol (BDH, AR), n-propyl alcohol (BDH, LR), n-butyl alcohol (BDH, LR), carbon tetrachloride (AR, Reanal, Budapest) and double distilled water were used as sorbates while ethyl alcohol was kept in contact with Ca metal for 24 hours and then distilled.

Results

Sorption-desorption of water vapour on raw and modified cotton

The sorption and desorption isotherms, at 35°C, of water vapour on raw, dewaxed and aqueous swollen cotton are presented in Figures 2-4.

In the sorption and desorption of water vapour raw cotton exhibits permanent and almost reproducible hysteresis loops (Figure 2). The experiment was continued up to 6th cycle of sorption and desorption. The loops obtained at the 1st, 2nd and 6th cycles are presented in the figure. The sorptive capacities of cotton in each of these cycles is 39.6%, 35.3% and 32.0% respectively. As the number of cycles increases the sorption isotherms show a tendency to drift towards the vapour pressure axis. The sorption-desorption isotherms are coincident in very low pressure regions.

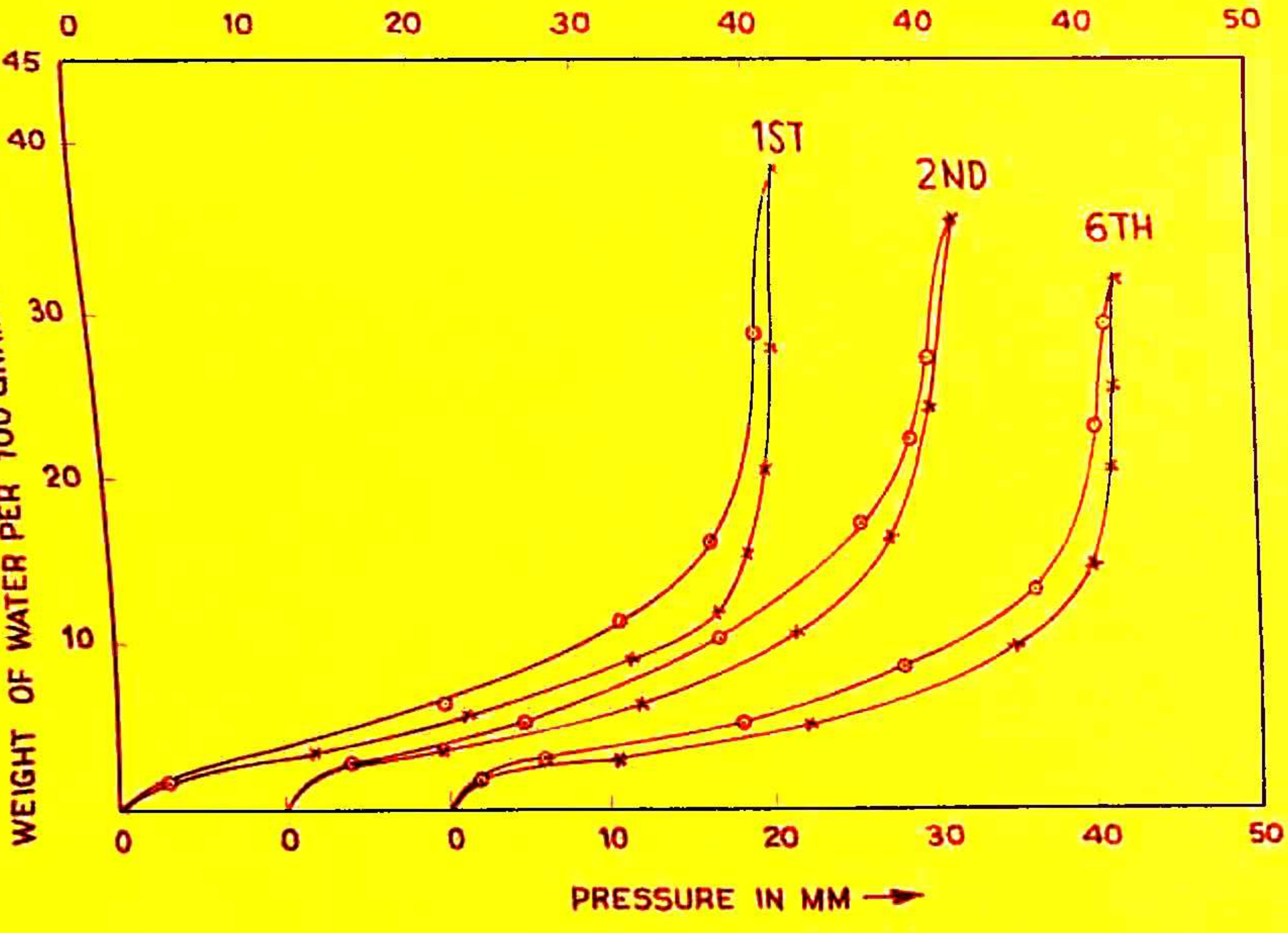


FIG.2 SORPTION - DESORPTION HYSTERESIS OF WATER ON RAW COTTON AT THE 1ST, 2ND, AND 6TH CYCLES.

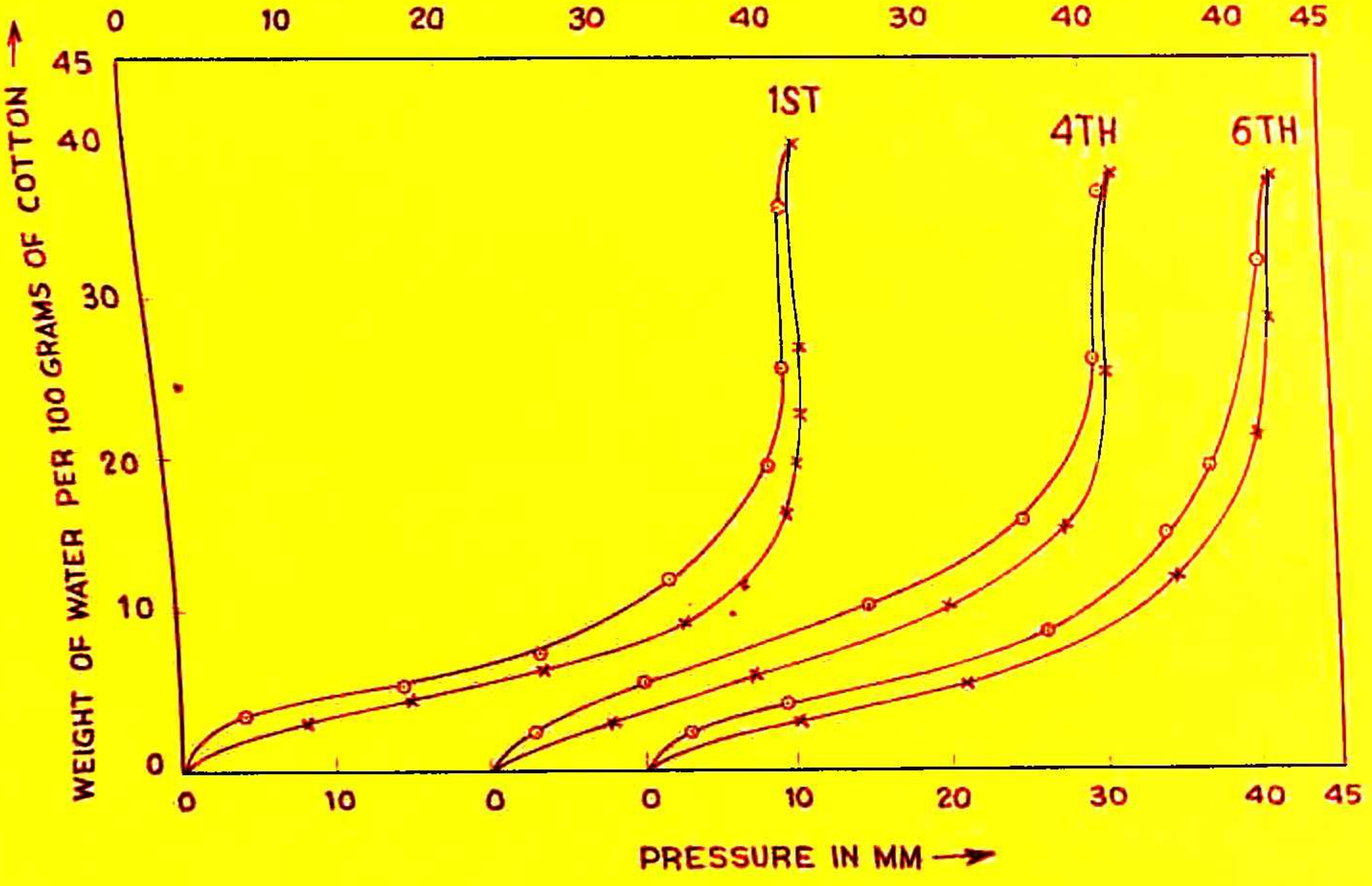


FIG. 3 SORPTION-DESORPTION HYSTERESIS OF WATER ON DEWAXED RAW COTTON AT THE 1ST, 4TH, AND 6TH CYCLES.

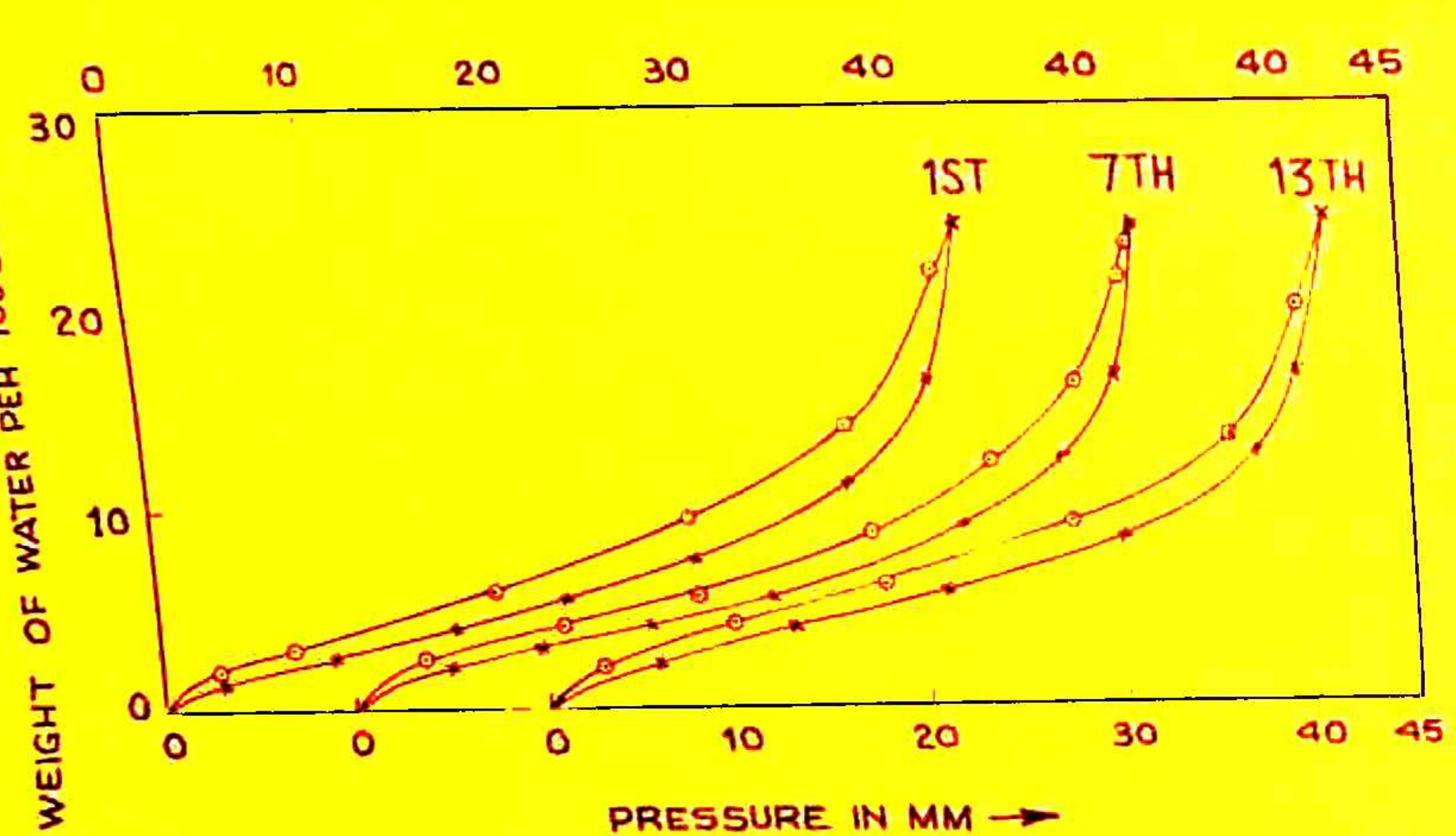


FIG. 4 SORPTION-DESORPTION HYSTERESIS OF WATER ON AQUEOUS SWOLLEN RAW COTTON AT THE 1ST, 7TH, AND 13TH CYCLES.

Figure 3 presents the sorptions and desorptions of water vapour on dewaxed cotton. The loops are permanent after the first cycle. The experiment was continued up to 6th cycle and the loops of 1st, 4th and 6th cycles are shown in the figure. There is a tendency of hysteresis loop to decrease in size with increasing number of cycles. The hydration capacities of dewaxed cotton are 39.2%, 37.5% and 37.5% in 1st, 4th and 6th cycles respectively. The tail end of the hysteresis loop extends up to zero pressure.

The sorption desorption studies with aqueous swollen cotton have been continued up to 13 cycles, Figure 4. Permanent but slightly decreased hysteresis loops are obtained. The sorptive capacities of swollen cotton remains almost the same throughout the 13 cycles studied. The sorptive capacities at the 1st, 7th and 13th cycles are 24.2%, 24.0% and 24.5% respectively. Linear hysteresis, i.e., hysteresis loops extending over the entire vapour pressure range have been obtained.

The effect of activation temperature on hysteresis has been presented in Figures 5-10. Permanent hysteresis loops are obtained with cotton activated at different temperatures ranging from 60° to 200°C. There is a tendency for the hysteresis loops to decrease in size with increasing temperature and the tendency is more dominant at higher temperatures. Table II presents the equilibrium moisture regains by cotton at different activation temperatures.

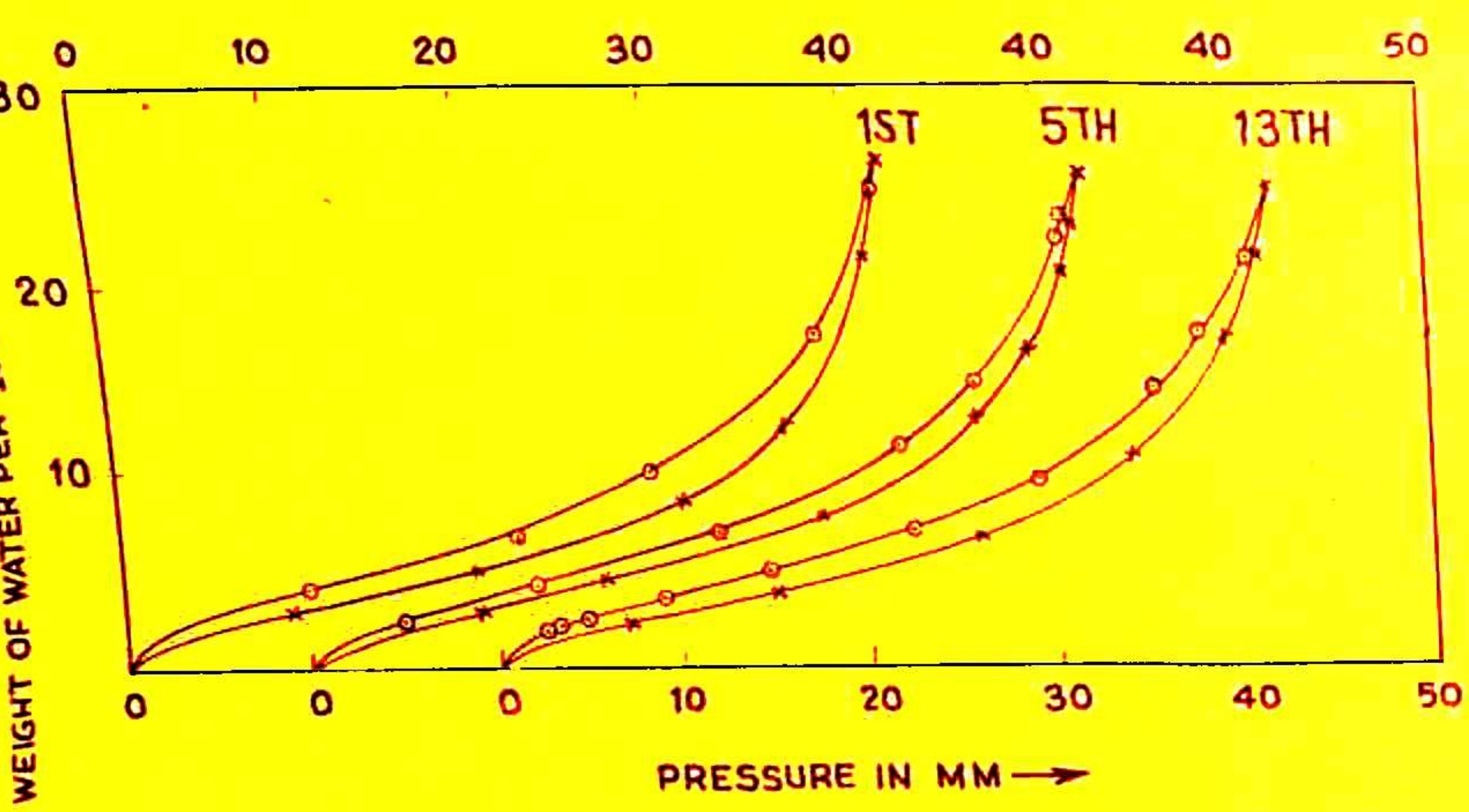


FIG. 5 SORPTION-DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 60°C) AT THE 1ST, 5TH, AND 13TH CYCLES.

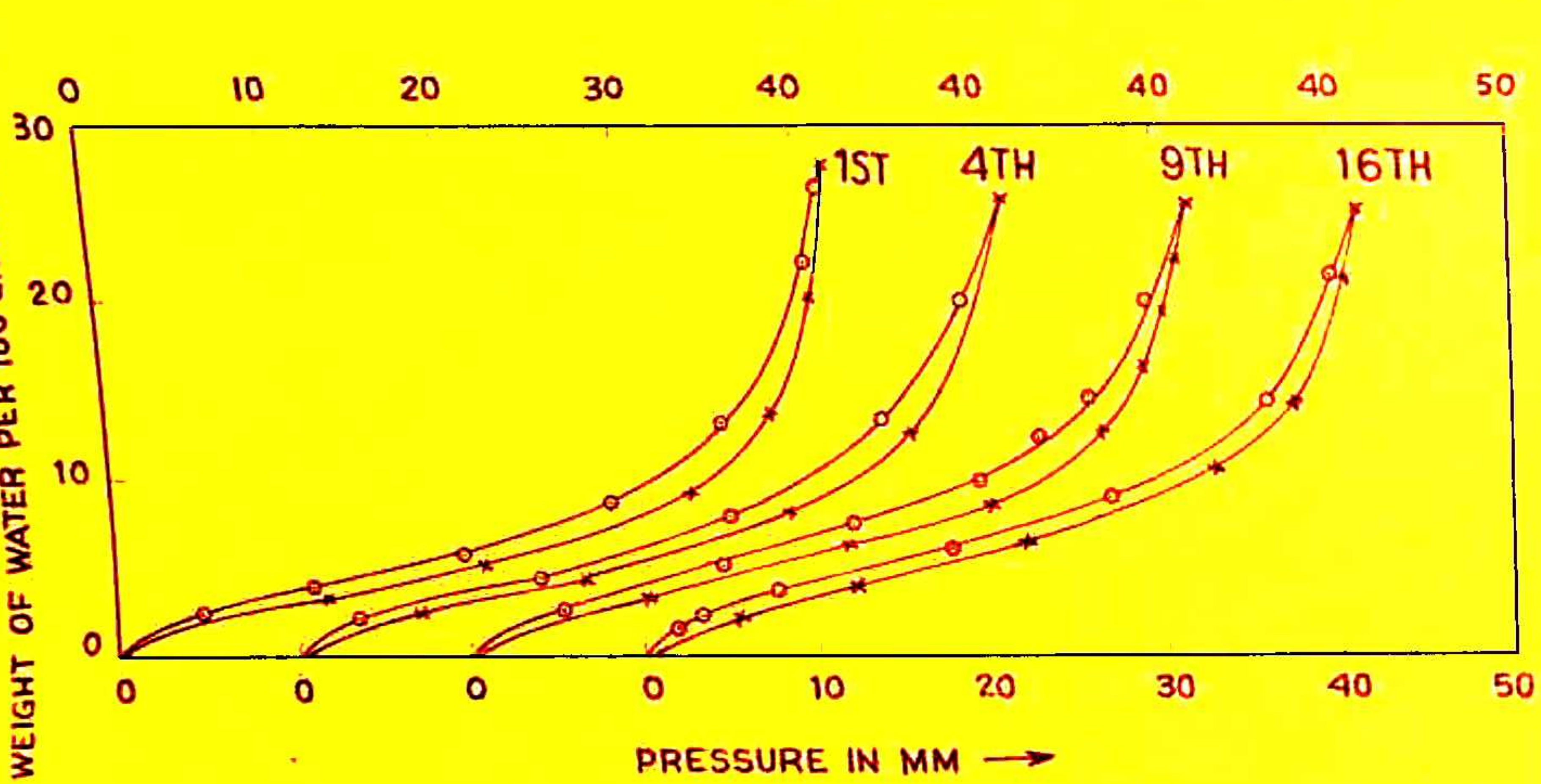


FIG.6 SORPTION - DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 95°C) AT THE 1ST, 4TH, 9TH, AND 16TH CYCLES.

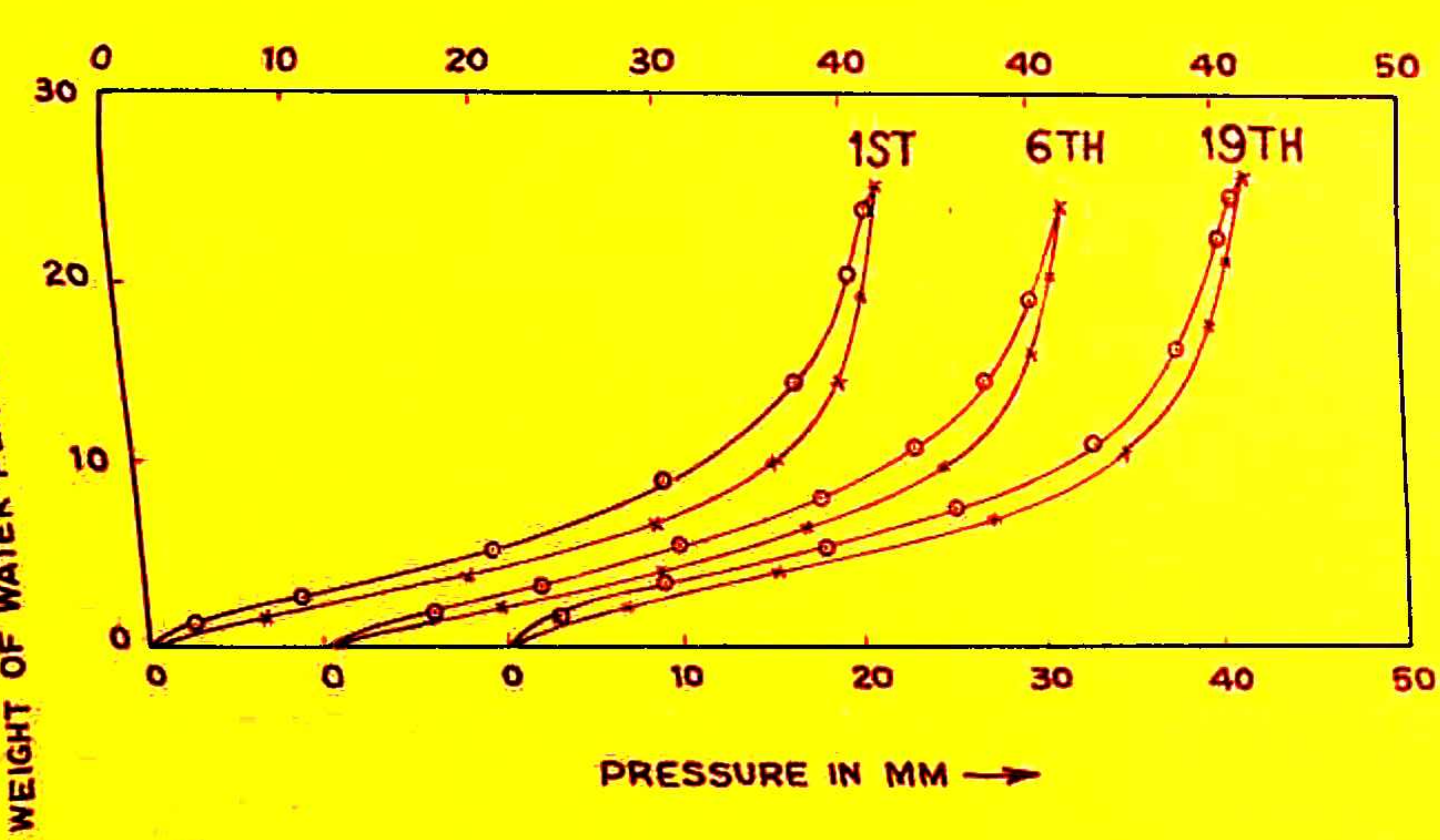


FIG.7 SORPTION-DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 125°C) AT THE 1ST, 6TH AND 19TH CYCLES.

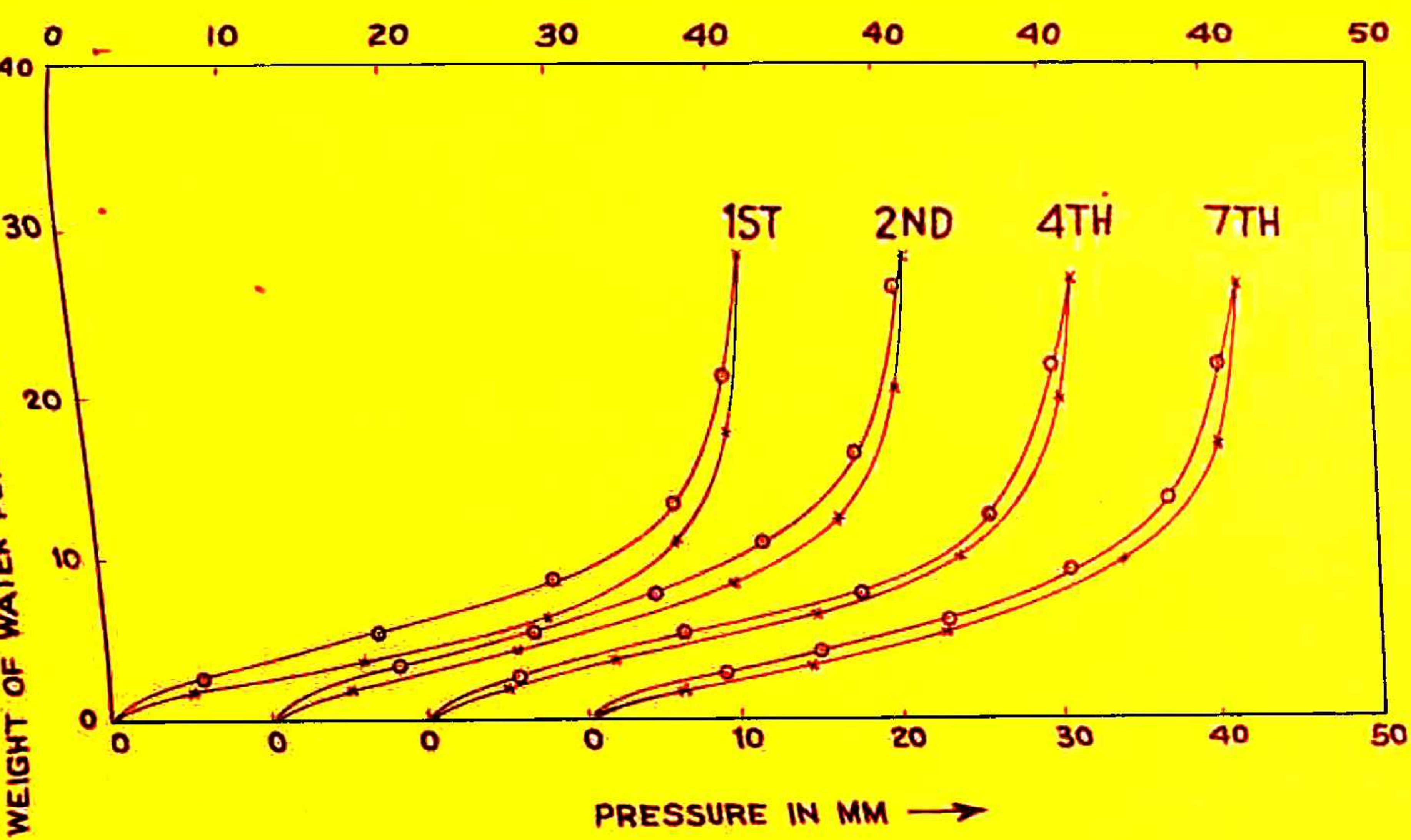


FIG. 8 SORPTION-DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 150°C) AT THE 1ST, 2ND, 4TH AND 7TH CYCLES.

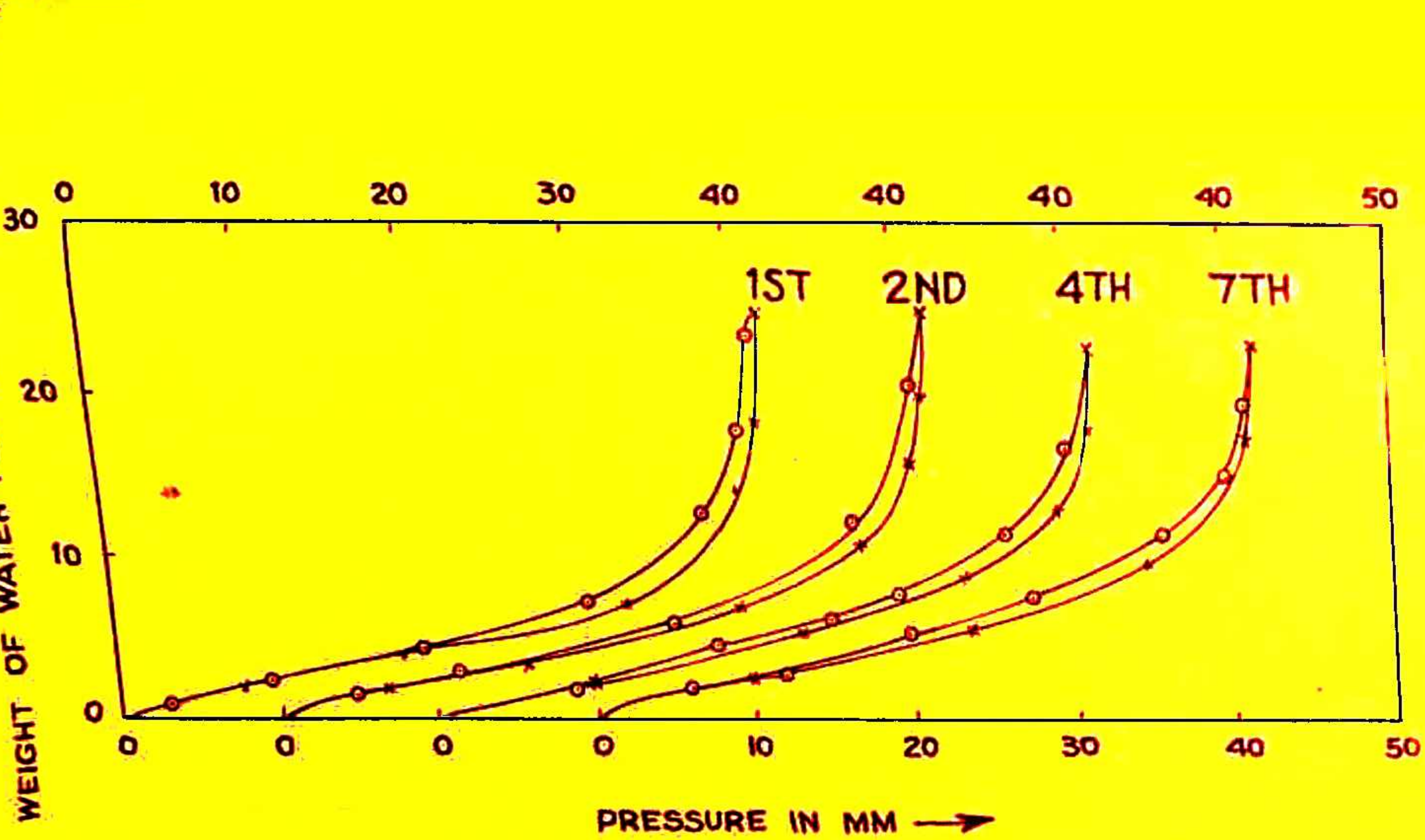


FIG. 9 SORPTION - DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 175°C) AT THE 1ST, 2ND, 4TH AND 7TH CYCLES.

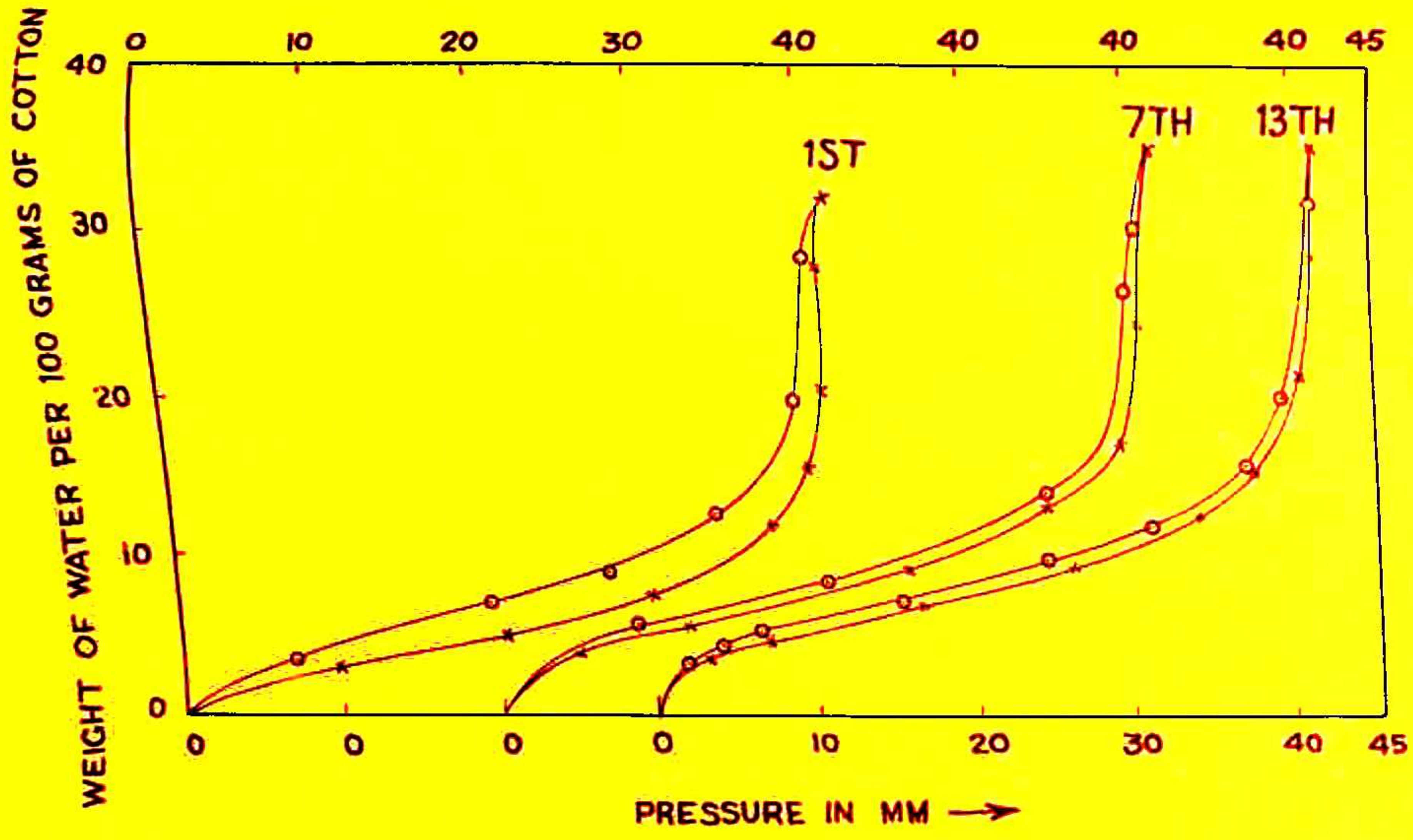


FIG.10 SORPTION-DESORPTION HYSTERESIS OF WATER ON RAW COTTON (ACTIVATED AT 200°C) AT THE 1ST, 7TH AND 13TH CYCLES.

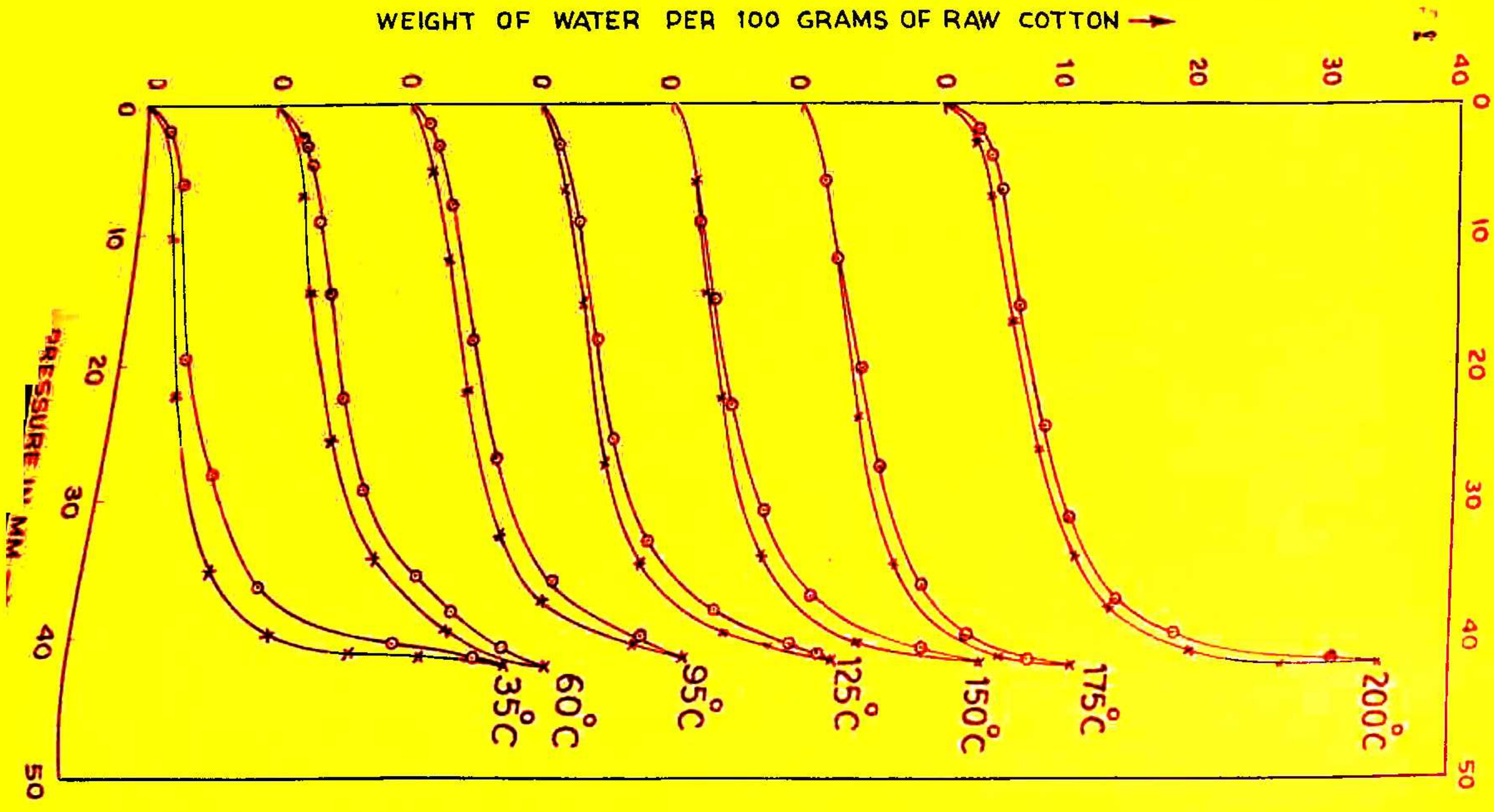


FIG.11 SORPTION-DESORPTION HYSTERESIS OF WATER ON RAW COTTON ACTIVATED AT 60°C (13TH CYCLE), 95°C (16TH CYCLE), 125°C (19TH CYCLE), 150°C (7TH CYCLE), 175°C (7TH CYCLE), AND 200°C (13TH CYCLE).

Table II

Sorptive capacities of raw cotton, activated at different temperatures.

Activation Temperature °C	Physical Appearance	No. of cycles studied	Saturation value g/100 g of cotton
60	White	13	26.0-25.2
95	White	16	25.0-24.8
125	Ligh yellow	19	24.8-25.3
150	Light brown	7	28.8-26.6
175	Brown	7	24.7-23.0
200	Dark brown	13	32.0-35.0

Figure 11 presents a comparative study of the hysteresis loops.

Sorptions and desorptions of organic liquids on raw cotton

The sorptions and desorptions of methyl and ethyl alcohols on raw cotton are presented in Figures 12 and 13 respectively. The maximum up-take of methyl alcohol, at its saturation pressure, at 35°C, is 22.2, 17.8 and 18.1 c.c.s per 100 grams of cotton at the 1st, 3rd and 5th cycles, respectively. The sorption capacities of ethyl alcohol are 10.4, 9.50, 9.55 and 10.2 c.c. per 100 grams of cotton at the 1st, 2nd, 5th and 8th cycles

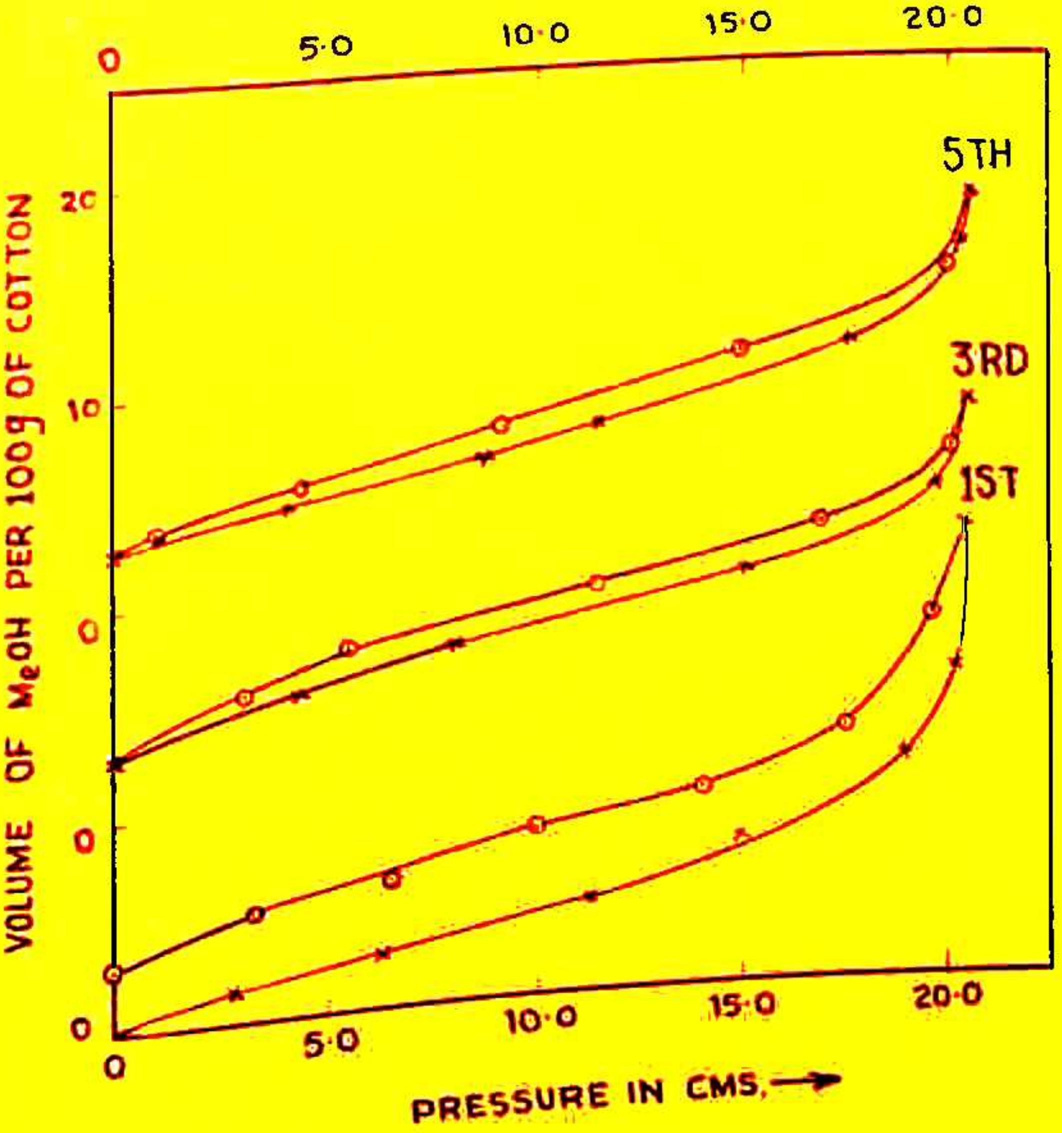
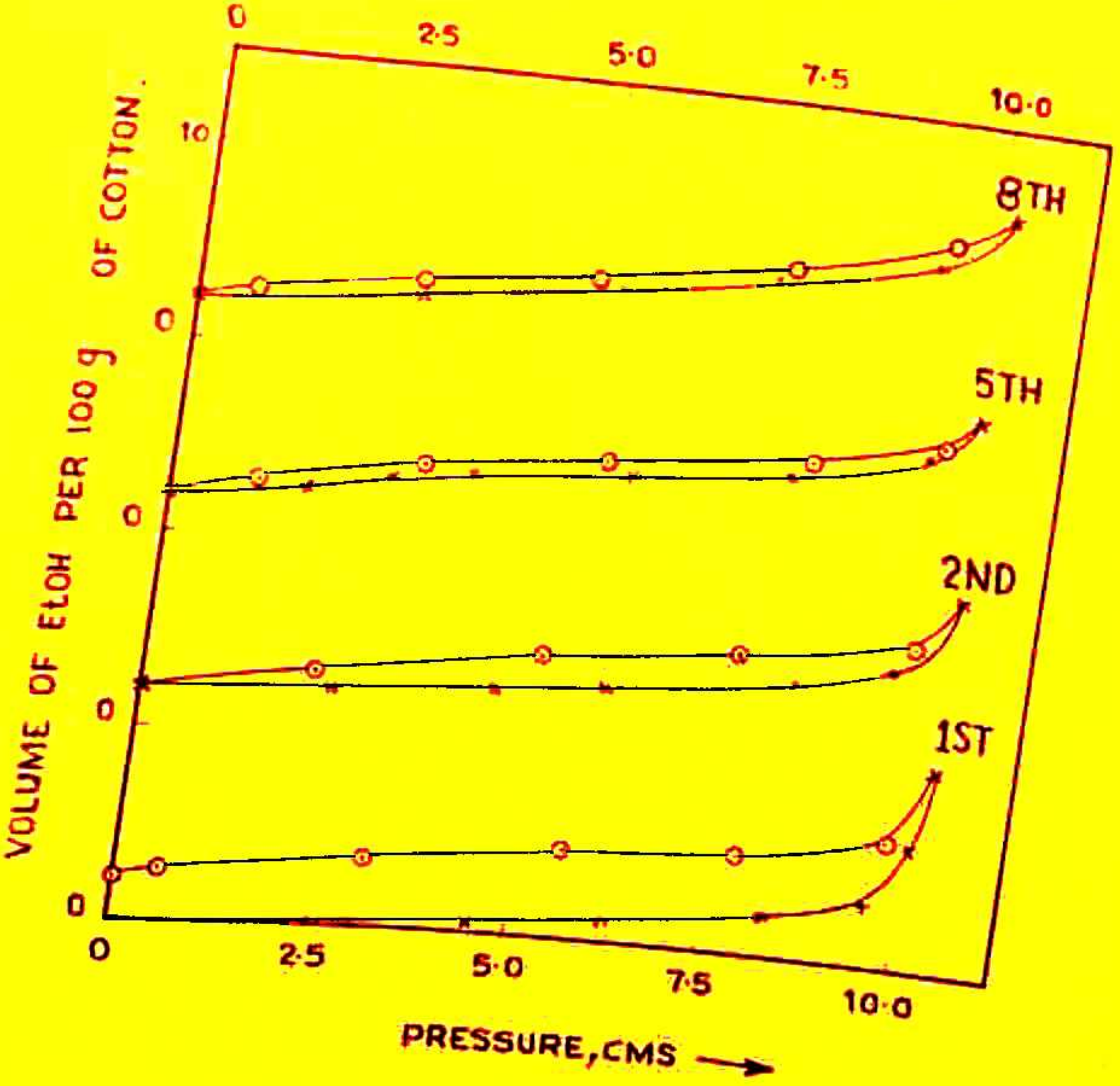


FIG.12 SORPTION-DESORPTION HYSTERESIS OF METHYL ALCOHOL ON RAW COTTON AT THE 1ST, 3RD, AND 5TH CYCLES.



.13 SORPTION-DESORPTION HYSTERESIS OF EtOH ON RAW COTTON AT THE 1ST, 2ND, 5TH, AND 8TH CYCLES.

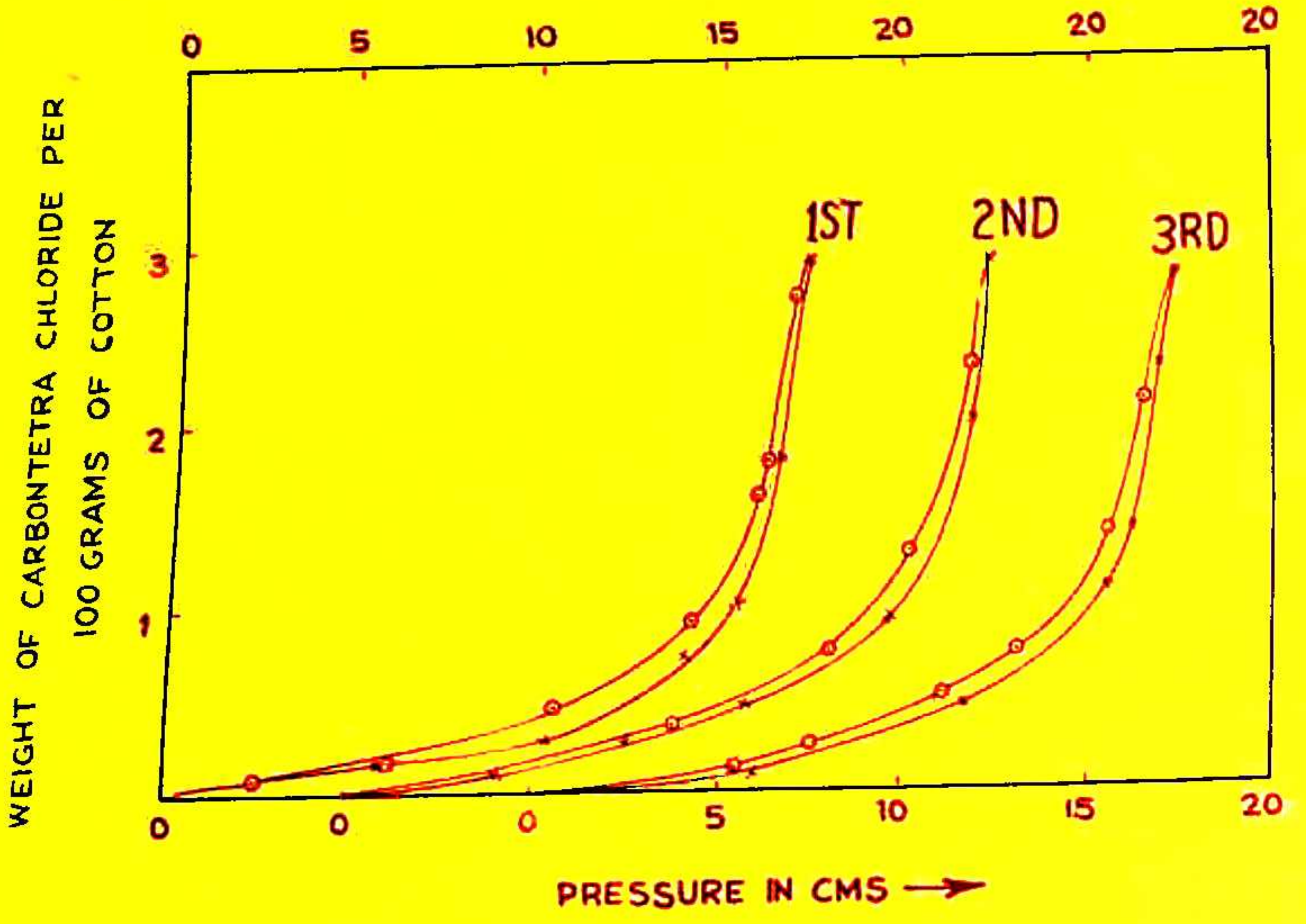


FIG 14 SORPTION- DESORPTION HYSTERESIS OF CARBON TETRA CHLORIDE ON RAW COTTON AT THE 1ST, 2ND, AND 3RD CYCLES

respectively. At the end of the 1st cycle, cotton irreversibly retains certain amounts of alcohol which could not be removed by drastic evacuation at a pressure of 10^{-2} mm even after 8 hours of evacuation. This irreversibly retained alcohol is termed as 'bound alcohol'. The amounts of bound methyl and ethyl alcohol are 2.92 and 2.20 c.c.s. per 100 grams of cotton respectively.

The extent of sorption of normal propyl alcohol and normal butyl alcohol was so small that it was not possible to obtain accurate data with this technique. The sorption was practically negligible with normal butyl alcohol.

Figure 14 shows the sorption-desorption hysteresis of carbon tetrachloride on raw cotton. Permanent and reproducible hysteresis loops are obtained over the three sorption-desorption cycles. The amount of carbon tetrachloride sorbed is 2.9%, 2.9% and 2.8% in the 1st, 2nd and 3rd cycles, respectively.

Duplicate experiments were performed in each case which also yielded similar results.

Discussion

Structure of cellulose

The present knowledge regarding the structure of cellulose has been contributed by a large number of workers over a period of many years. Detailed surveys of most of the early work have been published elsewhere (28,29).

Cellulose is in part crystalline and yields X-ray diffraction diagrams corresponding to a monoclinic unit cell. The first unit cell dimensions were calculated by Polanyi (30) who postulated a rhombic unit cell with dimensions 7.90 x 8.45 x 10.2 A°. Sponsler (31) postulated an orthohombic unit cell with dimensions 6.10 x 5.40 x 10.25 A°. Meyer and coworkers (32,33), after a series of investigations, led to the postulation of a monoclinic unit cell $a = 8.35$ A°, $b = 10.3$ A° (fibre axis), $c = 7.90$ A°, $\beta = 84^{\circ}$ in which the molecular chains lie parallel to each other. Each microfibril consists of bundles of such chains in parallel crystalline array clothed in a cortex in which cellulose chains lie intermixed with chains of sugar residues other than glucose; the chains in this region are parallel but not regularly spaced and are said to be paracrystalline.

Cellulose microfibrils are usually specifically oriented with respect to cell axis but the mechanism of orientation is not known. In thicker secondary walls they often lie helically arround the cell in lamellae in which the helical angle varies from one lamella to the next. Cellulose is considered to be bonded in cell walls in hydrogen bonds. The structure has been confirmed by Gross and Clark (34) and is still generally accepted.

Recently (35) Lamporte has shown that the cell walls of higher plants contain a specific protein which contains hydroxy prolene and the possibility has been recognised that -S-S- bonds of this protein are significant for the cell wall growth. It is not known whether this protein is linked with cellulose, but the probability is that the linkage is through hemicellulose and not through cellulose itself.

The physical interpretation of the sorption process must account for the phenomena of swelling, sorption and hysteresis. The cell wall of a cellulosic fibre behaves towards water as a swelling gel and the structure is distended as the sorption takes place. Only the non crystalling regions enter into sorption and swelling processes, the crystallites of cellulose are not penetrated by water and only their surface can participate in the sorption phenomena.

Phenomena of swelling

Swelling in water is one of the most important characteristic of cellulosic fibres. According to Katz (36) a solid is said to swell when it imbibes a liquid, becomes soft and flexible, its dimensions are enlarged but it does not lose its apparent homogeinity. Cellulosic fibres, on sorbing water swell longitudinally as well as transversely. The extent of longitudinal swelling is very small as compared with the transverse swelling. The penetration of water in cellulose depends upon the surface tension of water. It has been shown that a significant quantity of water is held by surface forces (37). Steinburger has also emphasised the dependence of swelling on the degree of micellar or crystal orientation. Morton (1962) believes that swelling is akin to solutions in that there is an exchange of positions between fibre molecules and water molecules (38). According to Hartley (39) swelling is a diffusion phenomena in which there is an exchange of positions of molecules of water moving into and occupying spaces previously held by fibre molecules. In a fibre swollen in water the chain molecules are oriented more or less parallel. At some places they are packed in a tight and orderly manner and so juxtraposed as to form a lattice, and at some places there is less order; water can penetrate into the fibres to form a homogeneous solid solution. A monolayer of water molecules is tightly packed against the chains and forms a true chemical hydrate.

The extent of swelling depends upon the availability of accessible groups, temperature, relative humidity, tension and cross linking.

Organic liquids, in general, swell cellulose less

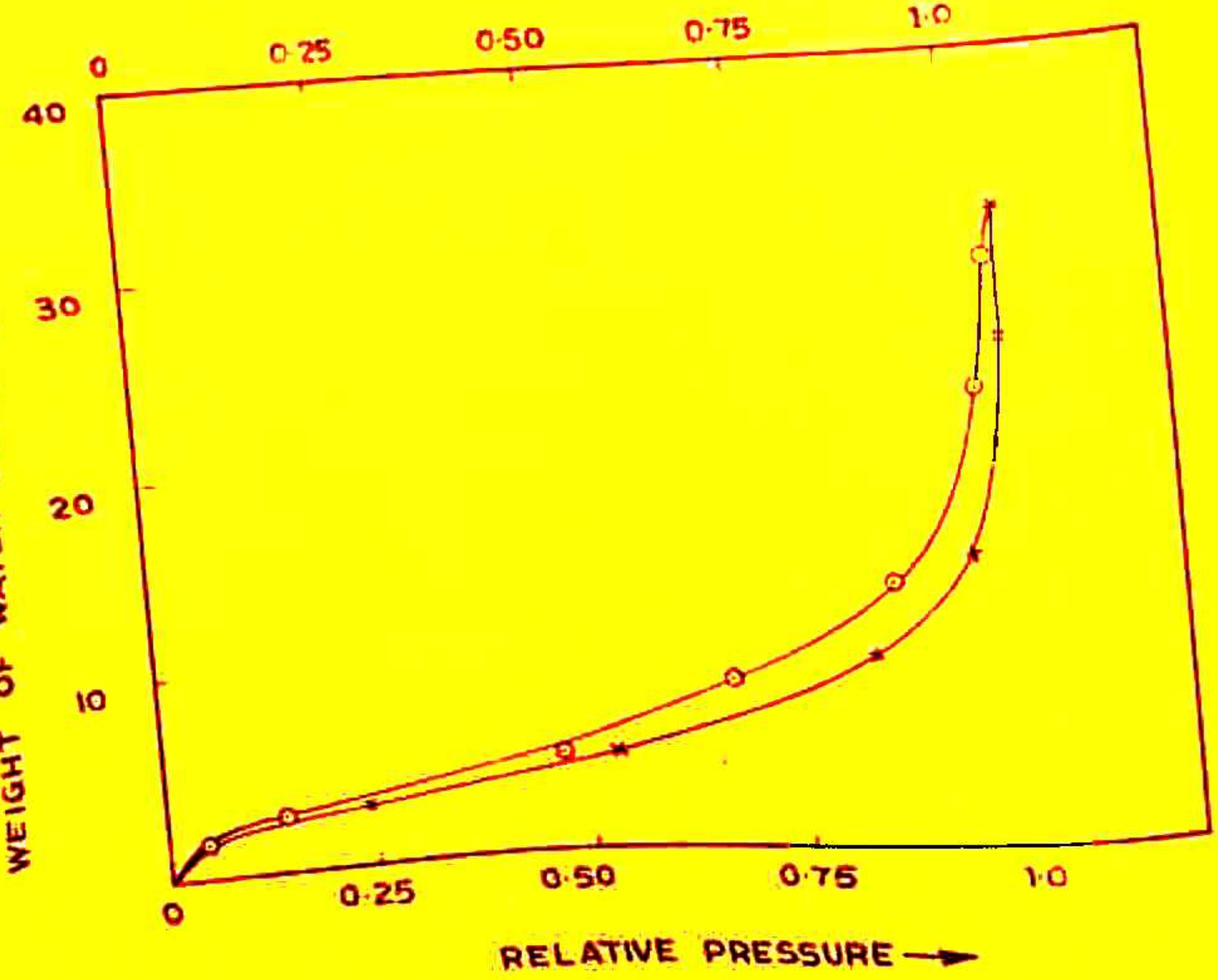


FIG.15 SORPTION-DESORPTION HYSTER
OF WATER VAPOUR ON RAW COTT
AT THE 6TH CYCLE.

than water, the swelling being chiefly dependent upon the polarity and molecular volume of the sorbate. Organic molecules which have high molecular weights do not penetrate the cellulose fibre or, at least, only superficially. Little or no swelling of cellulose takes place in relatively non polar liquids such as Benzene. The swelling is inversely proportional to the molecular weight of the solvent in a homologous series. The sorbates which produce significant swelling are those which are capable of forming hydrogen bonded complexes with cellulose molecules (40,41), this is to be expected as hydrogen bond must be ruptured before swelling can occur.

Sorption isotherms

The sorption isotherms obtained with water and organic sorbates can be looked upon as composite of three regions: first, surface sorption (or Langmuir adsorption region), second, intermediate sorption (or multilayer or solid solution region) and third, condensation (or capillary condensation region). The shape of the isotherm is determined by the range of pressure in which these regions successively become dominant.

The initial adsorption from the dry state, up to a relative pressure of about 0.2 represents the first rising portion of the isotherm (Figure 15). It is considered that in this region the sorbed water contributes towards formation of a monomolecular layer of water molecules on the assessable surface. As the assessable surface of dry cellulose is only a small fraction of that produced upon adsorption of water, the adsorption in this region occurs only by the breaking of the hydrogen bonds between the -OH groups of the cellulose with simultaneous surface development.

The following long, nearly linear portion of the isotherm extends from relative pressure of about 0.2 to 0.75. In this region it is supposed that multimolecular layer of water molecules are built up successively on the monolayer first formed.

At relative pressures above 0.6 the water content increases further with an increase in relative pressure and isotherm rises rapidly as the saturation pressure is approached. In this region it is considered that water is taken up primarily by a process of condensation. The mechanism has often been attributed to capillary condensation but it has also been suggested that the water is disposed as a mobile surface that differs from the underlying immobilised layers (8).

The energy considerations suggest that initial strong sorption at low relative pressures results from the linking

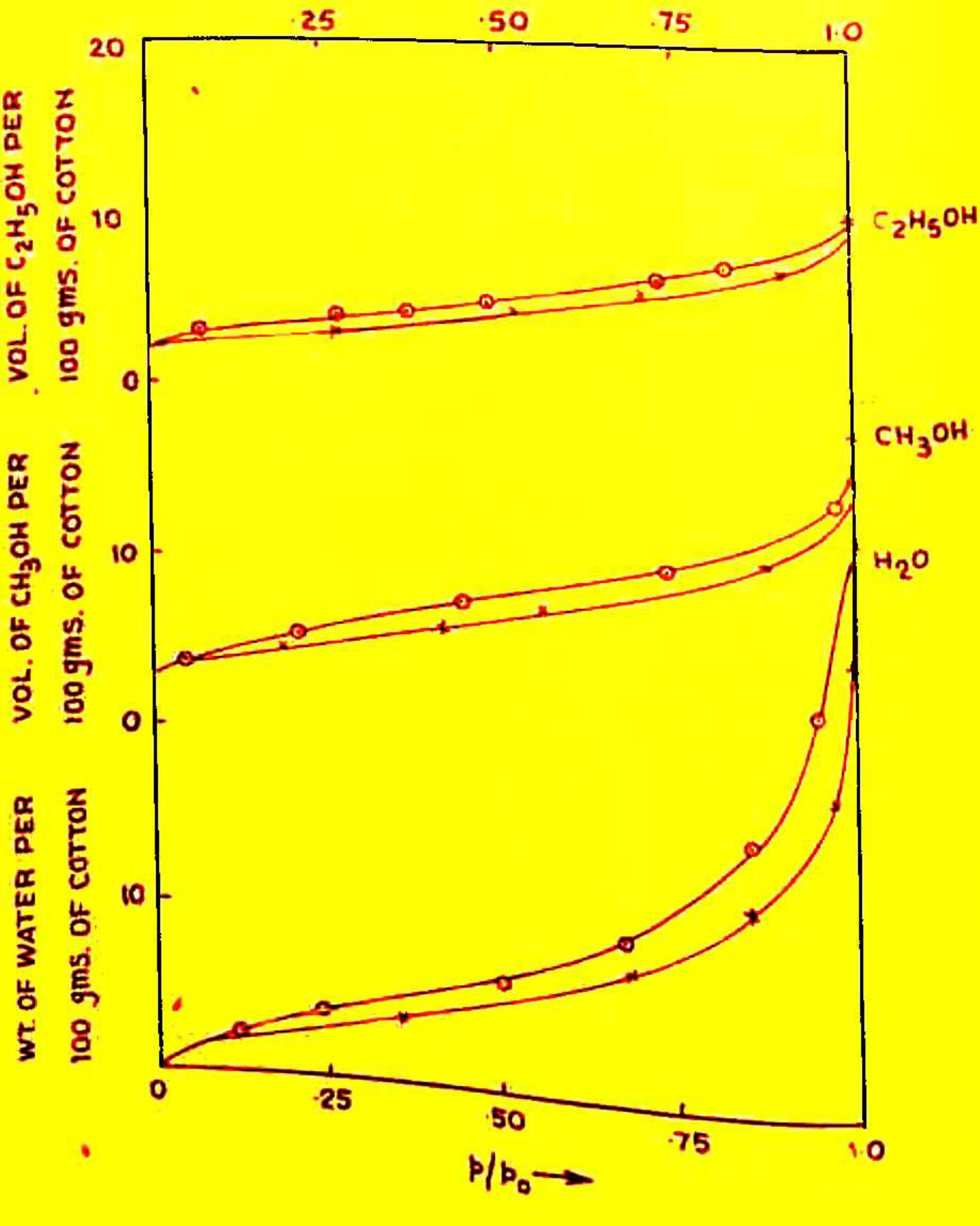


FIG.16 SORPTION–DESORPTION HYSTERESIS OF WATER, CH_3OH, AND C_2H_5OH VAPOURS ON RAW COTTON.

of one water molecule to two adjacent hydroxyl groups, whereas further sorption leads to combination to single -OH groups and to oxygen atoms (42).

One noteworthy feature of the sorption isotherms obtained with polar sorbates is that the sorption isotherm of water rises asymptotically to the saturation pressure ordinate while the isotherms of methyl and ethyl alcohols cut the saturation pressure ordinate at an angle (Figure 16). This gradual variation in the shapes may be attributed to the increasing contact angles, from water to ethyl alcohol. The observations of Fox and Zisman (43) also support this possibility. However, the effect of contact angle on the shape of isotherms has been considered in detail in cellulose acetate - aliphatic normal alcohols system.

Extent of sorption

Very few data on the sorption of nonaqueous liquids by cellulose fibres are available, and in many cases the data given by various investigators are in consistent. These inconsistencies probably arise from the fact that sorption of nonaqueous liquids is strongly dependent on the moisture content of the sample and is, therefore, extremely sensitive to small variations in sample history and drying methods. The most comprehensive studies are those of Kanamaru and Chao (44) and Lauer (45) whose results are given in Table III, and are compared with the results obtained by present investigations.

Table III

Sorption of vapour by cotton

Sorbate	Maximum vapour sorbed per 100 g of cotton			
	Lauer's data		Present data	
	Relative pressure		Relative pressure	
	20%	90%	20%	90%
Water	2.2	10.1	2.6	11.6
Methyl alcohol	0.6	7.5	1.6	8.9
Ethyl alcohol	0.5	4.7	0.3	3.0
n-Propyl alcohol	0.2	0.85	0.0	0.50
n-Butyl alcohol	0.0	0.0	0.0	0.0
Carbon tetrachloride	1.0	1.2	0.1	1.2

The extent to which a given liquid penetrates cotton fibres is dependent upon the molecular volume of the liquid and its ability to form hydrogen bonds with cellulose hydroxyl groups. Thus, small molecules which form hydrogen bonds will be strongly sorbed by cellulose fibres and this sorption will decrease with increasing molecular volume or other steric effects.

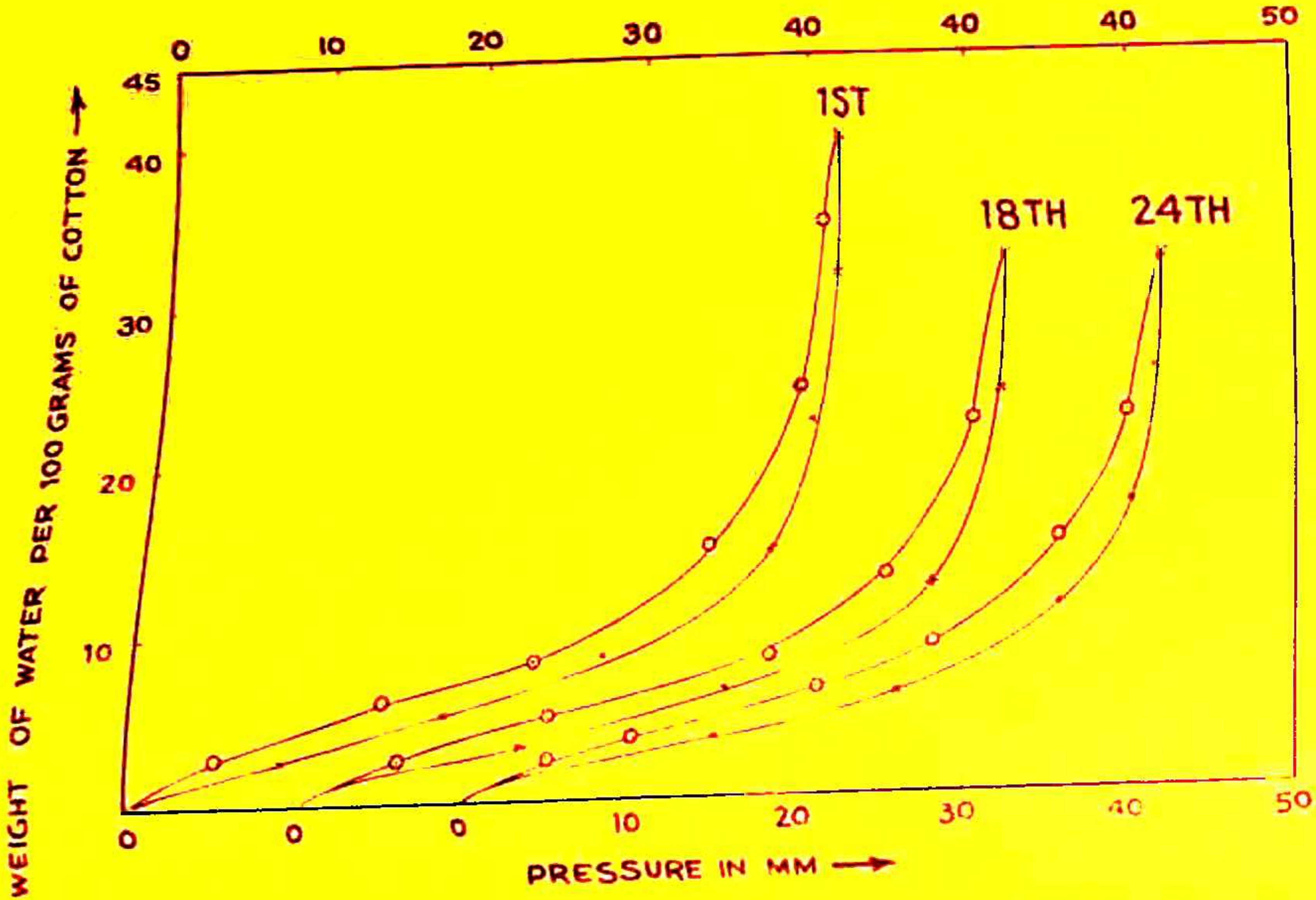


FIG.17 SORPTION-DESORPTION HYSTERSIS OF WATER ON RAW COTTON AT THE 1ST, 18TH, AND 24TH CYCLES.

Sorption-desorption hysteresis

Permanence of the hysteresis loops

One striking feature, in all the systems investigated is the remarkable permanence and reproducibility of the hysteresis loop. In raw cotton - water vapour system, the loop remains permanent and almost reproducible after 6 sorptions and desorptions. In a separate experiment (Figure 17), the loop has been reproduced up to 24 cycles of sorption and desorption (14). Similarly, permanent hysteresis loops have been obtained at the 5th cycle in cotton methyl alcohol system, 8th in cotton - ethyl alcohol and 3rd cycle in cotton - carbon tetrachloride system. In spite of drastic degassing of the gel surface and flushing with the vapour of the liquid as a result of successive sorptions and desorptions, the hysteresis loop still persists. There is a absolutely no doubt about the reality of the hysteresis.

Different explanations of hysteresis

Different explanations have been offered by various workers for the phenomena of sorption-desorption hysteresis. Urquhart and collaborators (9) have attributed hysteresis in the sorption of water vapour on cellulose to the reversible orientation of the molecules on the surface of cellulose. McBain and Fergusion (46) attributed hysteresis effect to the uncoupling of certain linked particles through the addition of water molecule to each valency bond broken and exposed. According to Wabba and Nashed (47) hysteresis is due to the fact that water molecules are more tightly packed on the adsorption side than on the desorption side for the same amount of water sorbed. Barkas (21) and Benson (48) attribute hysteresis to plastic deformation of sorbent on the sorption of water. Arnell and McDermot (49) explain hysteresis in terms of steric effects in swelling systems.

The explanation based on the reversible orientation of the molecules on the surface of cellulose, is obviously specific. The uncoupling of certain linked particles by the addition of water molecules is in nature of an irreversible change. The explanation of the hysteresis effect based on this, is specific and fails to account for the reproducibility of the effect a large number of times. The ideas of deformation and steric effect cannot explain a permanent and reproducible hysteresis as in raw cotton-water vapour system. It can explain the hysteresis loop which decreases in size and finally disappears, because when the deformation and steric effect cease, the hysteresis effect should cease to exist. The cavity concept (12,13) alone has been found to explain the permanence and reproducibility of hysteresis in cotton-water or cotton-organic liquid systems. Cavity concept postulates hysteresis due to entrapping of sorbate in cavities with constricted necks.

Explanation of hysteresis in the light of cavity or ink bottle theory of hysteresis

Cellulose and other fibrous materials possess chain structures. The number of cellulose units in a chain may be as high as 2000. The structure of these chains are partly crystalline and partly amorphous. The chain molecules are arranged in an orderly manner and tightly packed in the former while in the later the molecules are arranged in a less orderly manner and not tightly packed. It is, therefore, obvious that the amorphous region should contain more empty spaces than the crystalline region. The empty spaces are also called pores or capillaries. X-ray diffraction studies have revealed that these pores range from 10 to 25 A° in cellulose. With the existence of pores established in cellulose, the cavity-entrapping effect inevitably follows.

In cellulose there may be two distinct classes of capillaries, namely, the open pores (50)and cavities having narrow necks (50). Sorption and desorption are mainly the filling and emptying of these open pores and cavities. The filling and emptying of an open pore are reversible but in the case of cavities it is not so. For the same vapour pressure the cavities can retain larger amount of adsorbate during desorption than during sorption, thus causing hysteresis. The filling (sorption) and emptying (desorption) of capillaries can be tried any number of time and a permanent and reproducible hysteresis loop even at the 24th sorption and desorption (14) can be thus satisfactorily explained.

Seborg (51) has shown that the ratio of the adsorption to the desorption regain was essentially constant at all relative humidities except at the ends of the hysteresis loops. The present investigations also show similar behaviour. The sorption-desorption ratio for raw cotton-water vapour system is presented in Table IV.

Table IV

Sorption desorption ratio of raw cotton-water vapour system:

Relative vapour pressure	Sorption g/100g of cotton	Desorption g/100 g of cotton	Ratio
0.20	2.8	3.4	0.82
0.25	3.0	3.7	0.81
0.40	3.9	4.8	0.81
0.50	4.7	6.0	0.79
0.60	5.8	7.3	0.79
0.75	8.0	10.0	0.80
0.90	12.0	15.5	0.77

Drift of the hysteresis loop

Raw cotton has shown a unique and interesting behaviour in the sorption of water (Fig. 2). With progressive sorptions and desorptions, cotton suffers continuous decrease in sorptive capacity and the hysteresis loop suffers drift away from the axis other than the pressure. These indicate slight decrease in the total capillary volume and the widening of the cavities and their necks. Infra red studies (52) have also provided evidence of a slight decrease in the amount of amorphous region during repeated sorption-desorption treatments.

Summarizing, the permanent and reproducible hysteresis effect has been satisfactorily explained on the basis of the cavity theory in conjunction with the structure of cellulose.

***

PART III

STUDIES IN SORPTION-DESORPTION HYSTERESIS WITH CELLULOSE ACETATE

STUDIES IN SORPTION-DESORPTION HYSTERESIS WITH CELLULOSE ACETATE

Abstract

Complete sorption-desorption isotherms for methyl, ethyl, n-propyl and n-butyl alcohols on cellulose-acetate have been obtained, at 35°C, employing quartz fibre spring technique in conjunction with a high vacuum technique. Characteristic sigmoid isotherms showing marked hysteresis effect were obtained. The hysteresis effect extended over the entire vapour pressure range of the different alcohols. The size of the hysteresis loop increases as the molecular weight of the sorbate alcohol increases. However, the sorptive capacity decreases in the order:

methyl $>$ ethyl $>$ n-propyl $>$ n-butyl alcohol.

The time-adsorption curves, obtained for each alcohol indicate that the rate of adsorption increases as the molecular size of the sorbate increases. A reasonably good fit for BET equation was observed for all the alcohols. BET surface areas have been calculated by considering the alcohol molecules as spherical and linear. The mode of adsorption in the monolayer region and the role of contact angle in

sorption mechanism have been discussed.

Detailed results have also been presented on the equilibrium sorptions and desorptions of water vapour by cellulose acetate in the range of 0 - 100% r.h. and 35 - 200°C. Permanent hysteresis effect has been exhibited at all temperatures. However, the size of the hysteresis loop and the total sorptive capacity decreased as the temperature of activation was increased. The rate curves, obtained for activated samples indicated that the rate of adsorption increased as the temperature of activation was raised. These interesting results have been explained on the basis of 'cavity theory' of hysteresis. The influence of relative humidity and temperature on relative hysteresis have also been discussed.

Introduction

The effect of acetyl content on the sorption of water vapour by cellulose acetate has been studied by Beever and Valentine (53,54). These authors reported that the extent of adsorption decreased as the acetyl content increased. Majury (55) measured the absorption by acetate from both aqueous solutions and from vapour phase. Marsden and Urqhart (56) have studied the swelling of acetate in aqueous solutions of phenol. In a detailed study on the diffusion of acetone into cellulose acetate, Bagley and Long (57) presented the equilibrium sorption values at 30°C. Jeffries (58) studied the complete sorption and desorption values of water vapour at temperature ranging from 30 to 90°C on cellulose acetate, cellulose triacetate and other textile polymers.

Ray and Bartell (59) studied the wetting characteristics of cellulose acetate and other cellulose derivatives. Jeffries (60) reported the thermodynamic properties of secondary cellulose acetate and its solvents and observed marked hysteresis effect at all temperatures studied. Park (61) carried out radio active studies of sorption and self diffusion in the acetone-cellulose acetate system and obtained marked hysteresis. The researches of several investigators (62-64) have lead to the conclusion that the diffusion of organic vapours into cellulose acetate is anomalous in the sense that Fick's Law does not apply.

Wiegerink (65), Urquhart et al (66), Wahba and Nashed (67) and Jeffries (60) have studied the effect of heat on the sorption of water vapour by cellulose, and observed that, heat had, in some respects, a more degrading effect on cellulose than mild acids or mild oxidising agents. The effect of heat was principally due to dehydration, which if carried far enough, would result in an appreciable loss in hygroscopicity and the swelling ability of the cellulose fibres. One observation which was common to all of them was that, equilibrium water content decreased steadily with increasing temperature for both sorption and desorption. Kataocka (68) also reported that swelling rate and swelling values in organic solvents decreased with increasing temperature of treatment.

Cellulose acetate is a thermoplastic, it melts at about 230°C with decomposition (69). Little detailed information is available in literature on the effect of heat on this compound. Earlier, secondary cellulose acetate (65) and ethyl cellulose (70) have only been studied over a wide range of temperatures. The published data on cellulose triacetate (53,54) is restricted to small range of temperature,i.e., from 20 to 40°C. Detailed results on cellulose acetate over a wide range of temperatures are very few indeed.

Cellulose acetate, being an important textile material, its swelling and sorption properties are, therefore, of considerable interest. Sorption of water (71,72) and non aqueous liquids (57,73) on cellulose acetate have been studied and reported earlier. However, sorption-desorption hysteresis has not been discussed and interpreted. The aims of the present work are:

(1) To study the sorption-desorption hysteresis of aliphatic normal alcohols on cellulose acetate at 35°C.

(2) To study the role of contact angle in sorption mechanism

(3) To study the mode of adsorption in the monolayer region and to calculate the specific surface of the adsorbent.

(4) To study the effect of activation temperature of cellulose acetate on sorption-desorption hysteresis with water vapour.

(5) To study the influence of relative humidity and temperature on relative hysteresis.

Experimental

Cellulose acetate, supplied by Riedel De Haen, Germany, was used as adsorbent in all the experiments. The particle size used was between 30 and 50 mesh British Standard Sieves.

Activated samples were obtained by heating, in vacuum, at temperatures 90°C, 150°C, and 200°C. The heating time was 4 hours in each case.

The following adsorbates have been used.

Water	Double distilled	
Methyl alcohol	BDH (AR)	Redistilled at 64.5°C
Ethyl alcohol	Distilled over Ca metal at 78°C	
n-Propyl alcohol	BDH (LR)	Redistilled at 97°C
n-Butyl alcohol	BDH (LR)	Redistilled at 116°C.

All the studies were performed at 35°C.

Results and discussion

Sorption-desorption hysteresis of aliphatic normal alcohols on cellulose acetate

Complete sorption-desorption isotherms, at 35°C, of different alcohols on cellulose acetate have been presented in Figures 18 to 21.

Figure 18 shows the sorptions and desorptions of methyl alcohol on cellulose acetate. The experiment was continued up to 4th cycle of sorption and desorption. The loops obtained at the 1st, 2nd and 4th cycles are only shown in the figure. The sorptive capacities of cellulose acetate, at the saturation pressure of methyl alcohol, at 35°C, are 45.5 c.c., 44.7 c.c., and 44.0 c.c.respectively. A permanent hysteresis effect has been obtained throughout the pressure axis. The area enclosed in the hysteresis loop decreases slightly with successive sorption-desorption cycles.

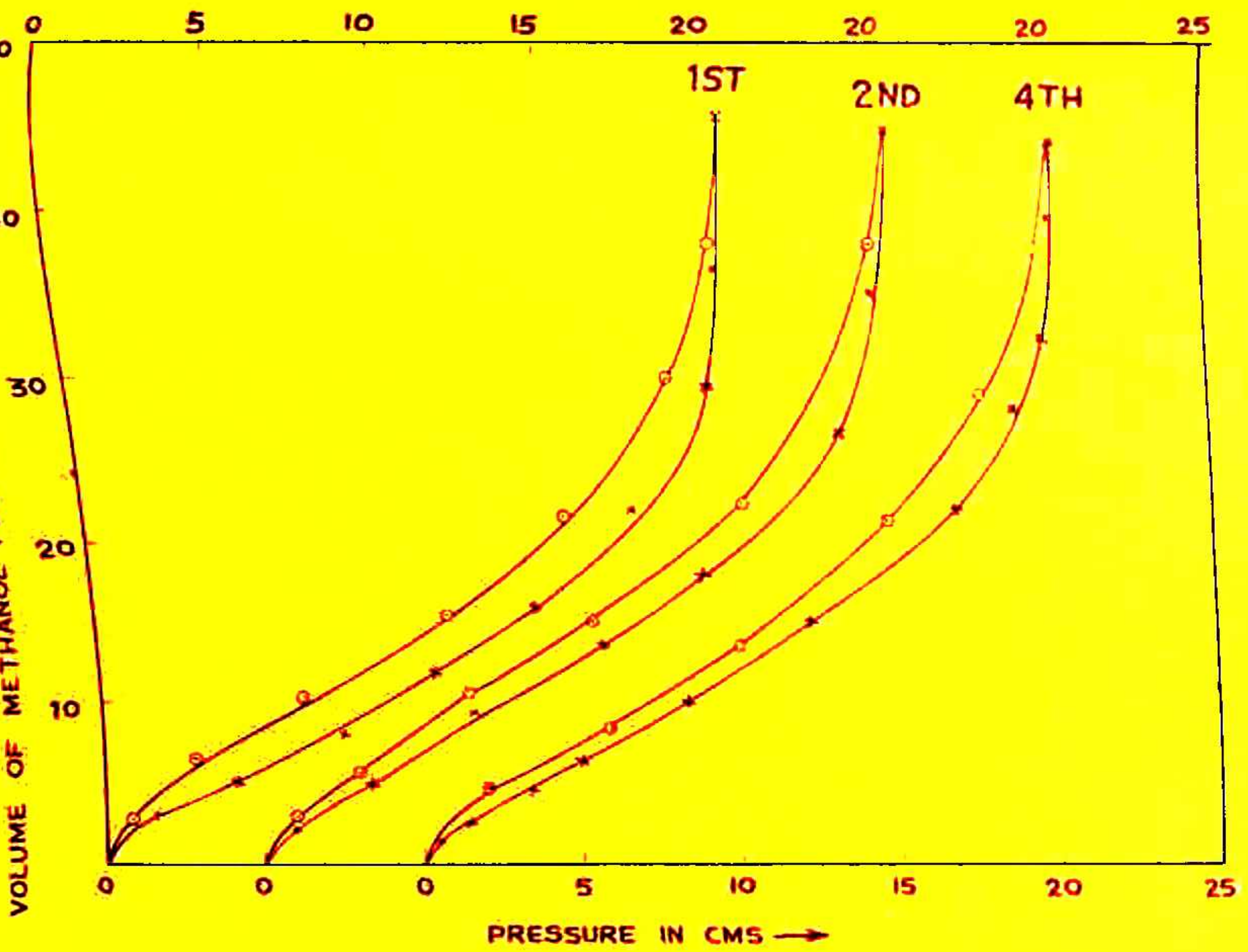


FIG.18 SORPTION-DESORPTION HYSTERESIS OF METHANOL ON CELLULOSE ACETATE AT THE 1ST, 2ND, AND 4TH CYCLES.

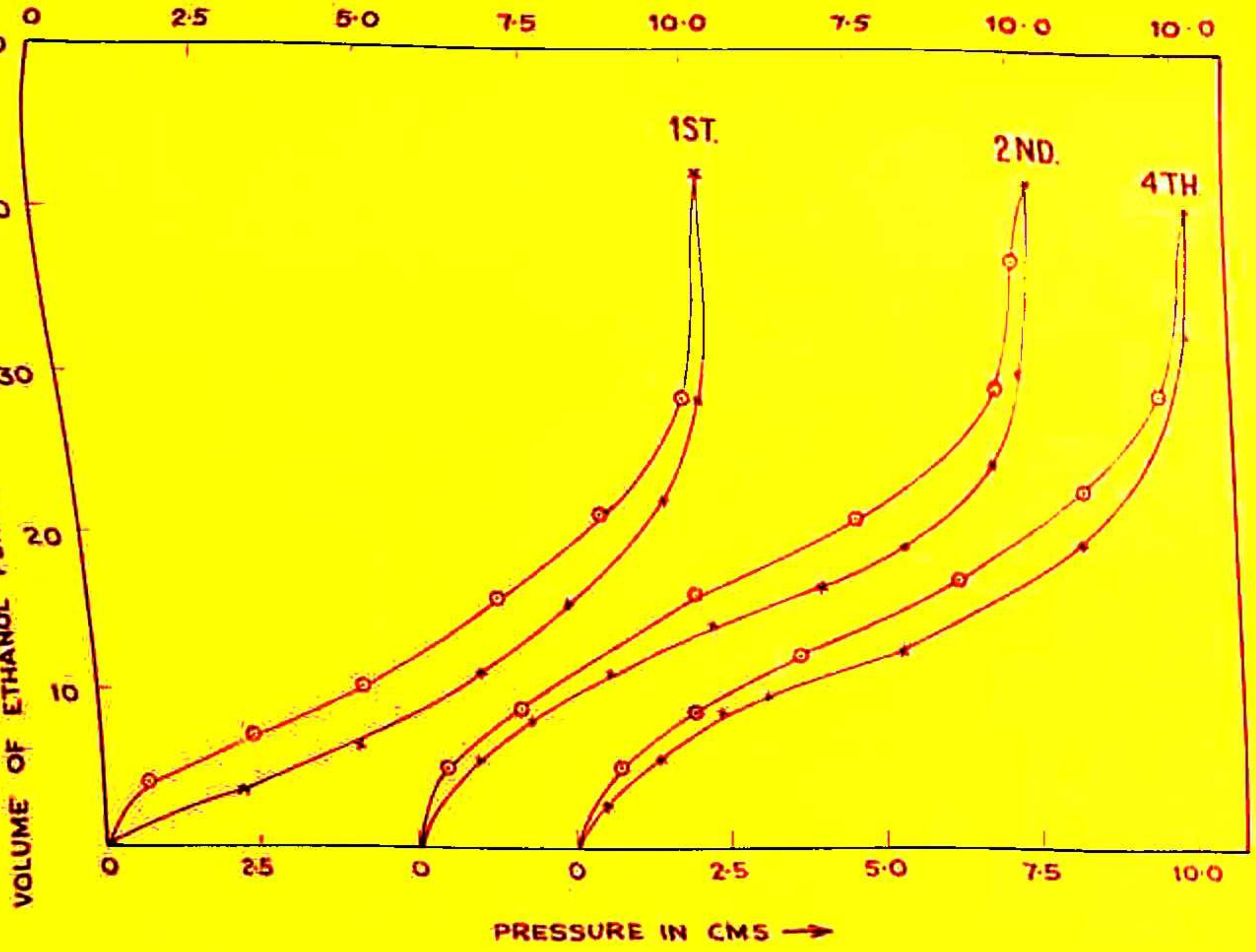


FIG.19 SORPTION-DESORPTION HYSTERESIS OF ETHANOL ON CELLULOSE ACETATE AT THE 1ST, 2ND, AND 4TH CYCLES.

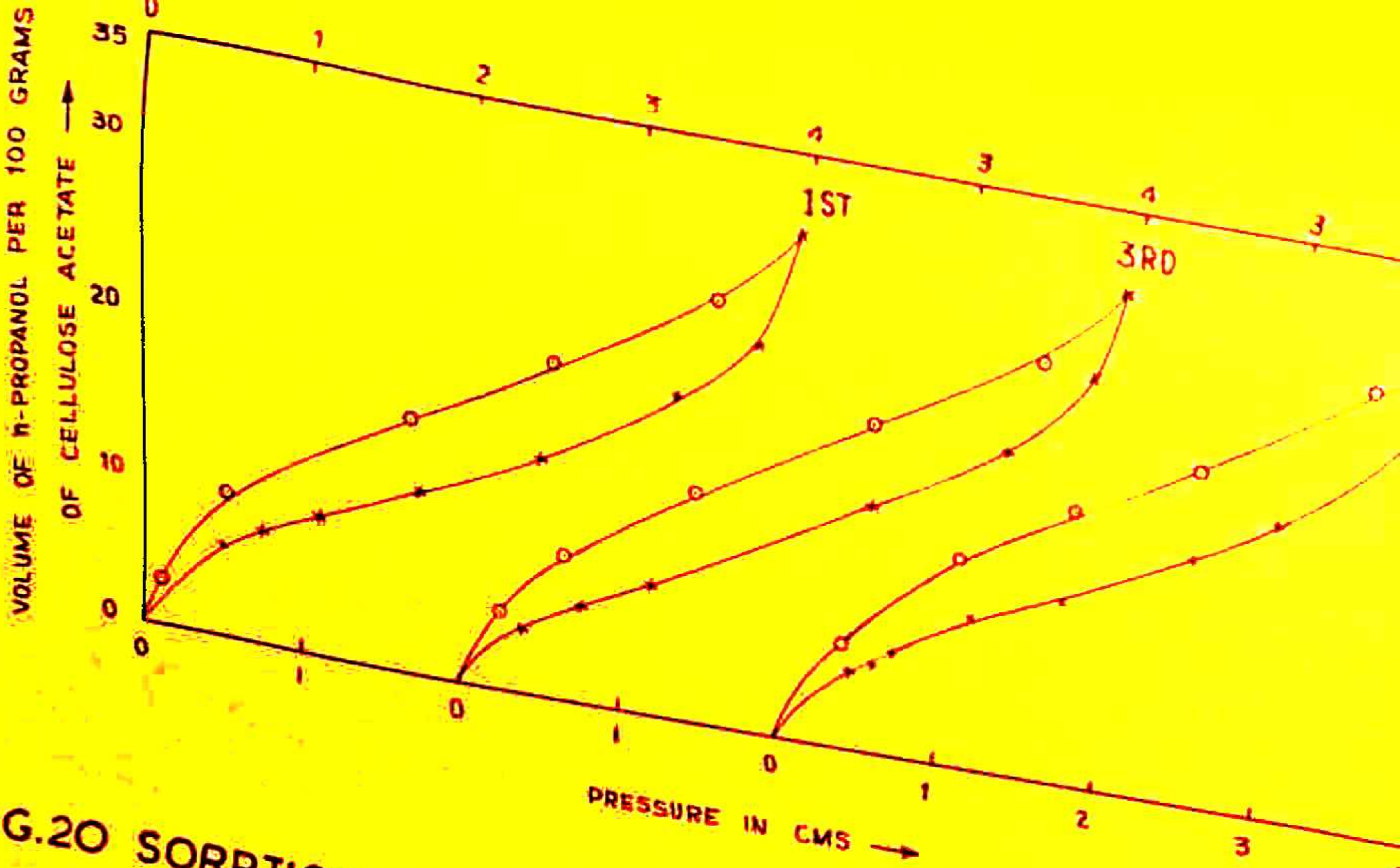


FIG.20 SORPTION - DESORPTION OF n -PROPANOL ON CELLUL
ACETATE AT THE 1ST ,3RD, AND 4TH CYCLES.

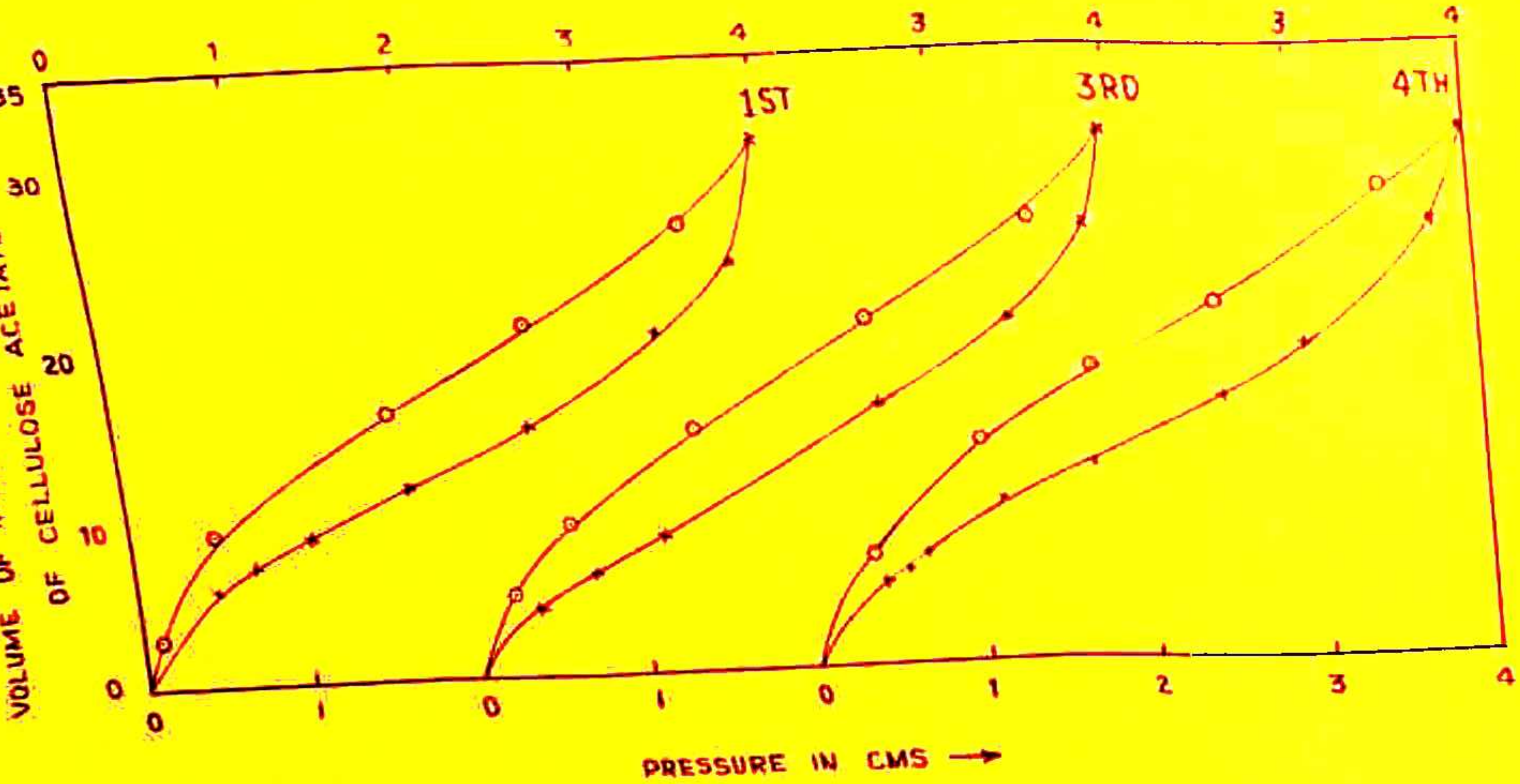


FIG.20 SORPTION-DESORPTION OF n-PROPANOL ON CELLULOSE ACETATE AT THE 1ST, 3RD, AND 4TH CYCLES.

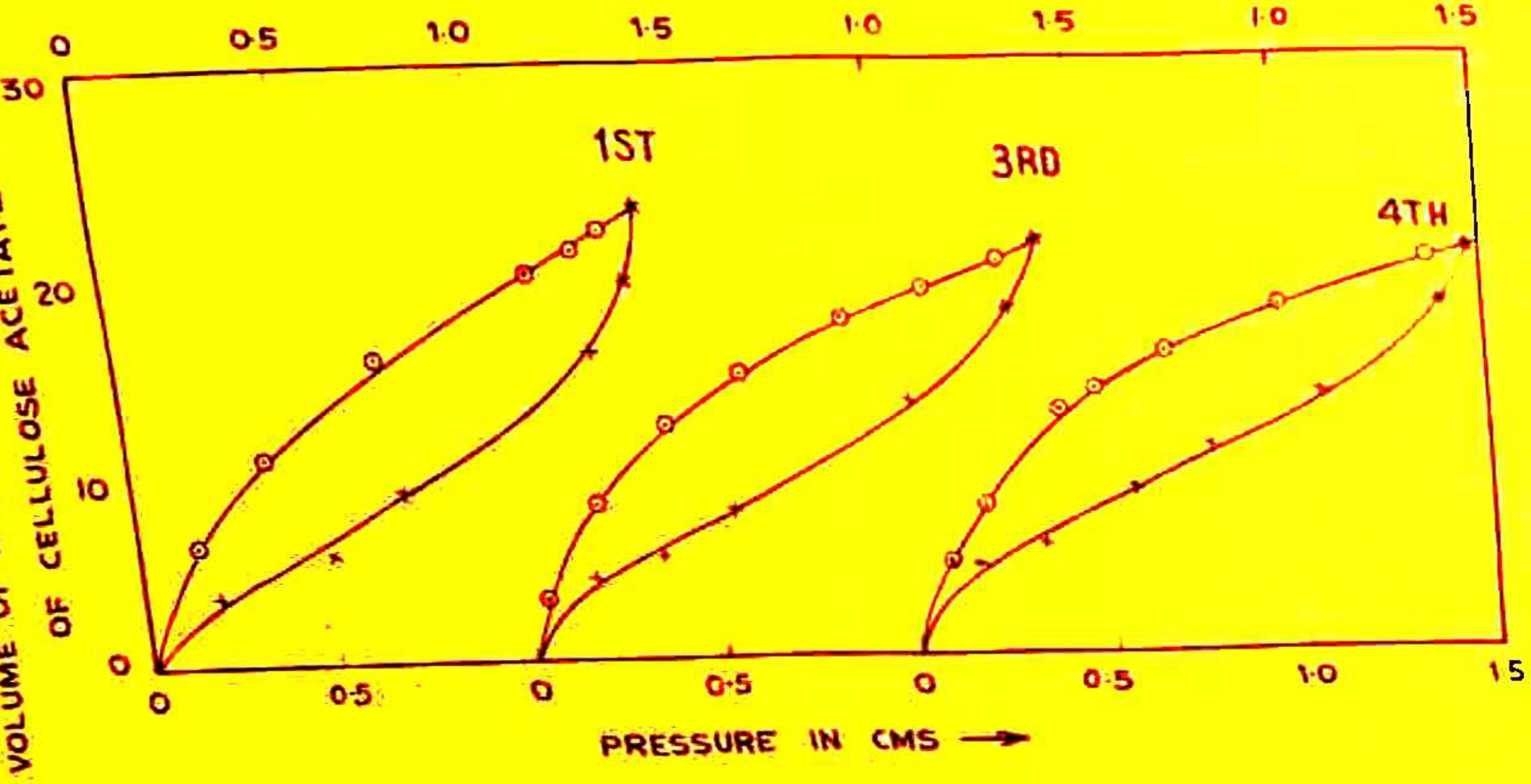


FIG.21 SORPTION-DESORPTION HYSTERESIS OF n-BUTANOL ON CELLULOSE ACETATE AT THE 1ST, 3RD, AND 4TH CYCLES.

The hysteresis loops obtained with ethyl alcohol are presented in Figure 19. The amounts of ethyl alcohol taken at the saturation pressure of ethyl alcohol are 42.2 c.c., 41.8 c.c. and 40.0 c.c. at the 1st, 2nd and 4th cycles respectively. The loops are almost reproducible after the first cycle. It indicates that all the irreversible changes have occurred in the 1st cycle and after the end of the 1st cycle, the adsorbent behaves in a reversible manner.

Figure 20 presents the successive sorptions and desorptions of n-propyl alcohol on cellulose acetate. The maximum uptake of n-propyl alcohol at its saturation pressure is 30.6 c.c., 30.5 c.c. and 30.2 c.c. at the 1st, 2nd and 4th cycles respectively. The hysteresis loops are permanent and almost reproducible.

Figure 21 shows hysteresis loops of n-butyl alcohol on cellulose acetate. The size of the hysteresis loop has increased considerable. The tail end of the hysteresis loop stretches up to zero pressure. The amounts of n-butyl alcohol at the saturation pressure are 23.0 c.c., 21.0 c.c. and 20.2 c.c. at the 1st, 2nd and 4th cycles respectively.

Scale

The sorptive capacities of cellulose acetate, at 35°C, for the four aliphatic normal alcohols have been presented in Table V.

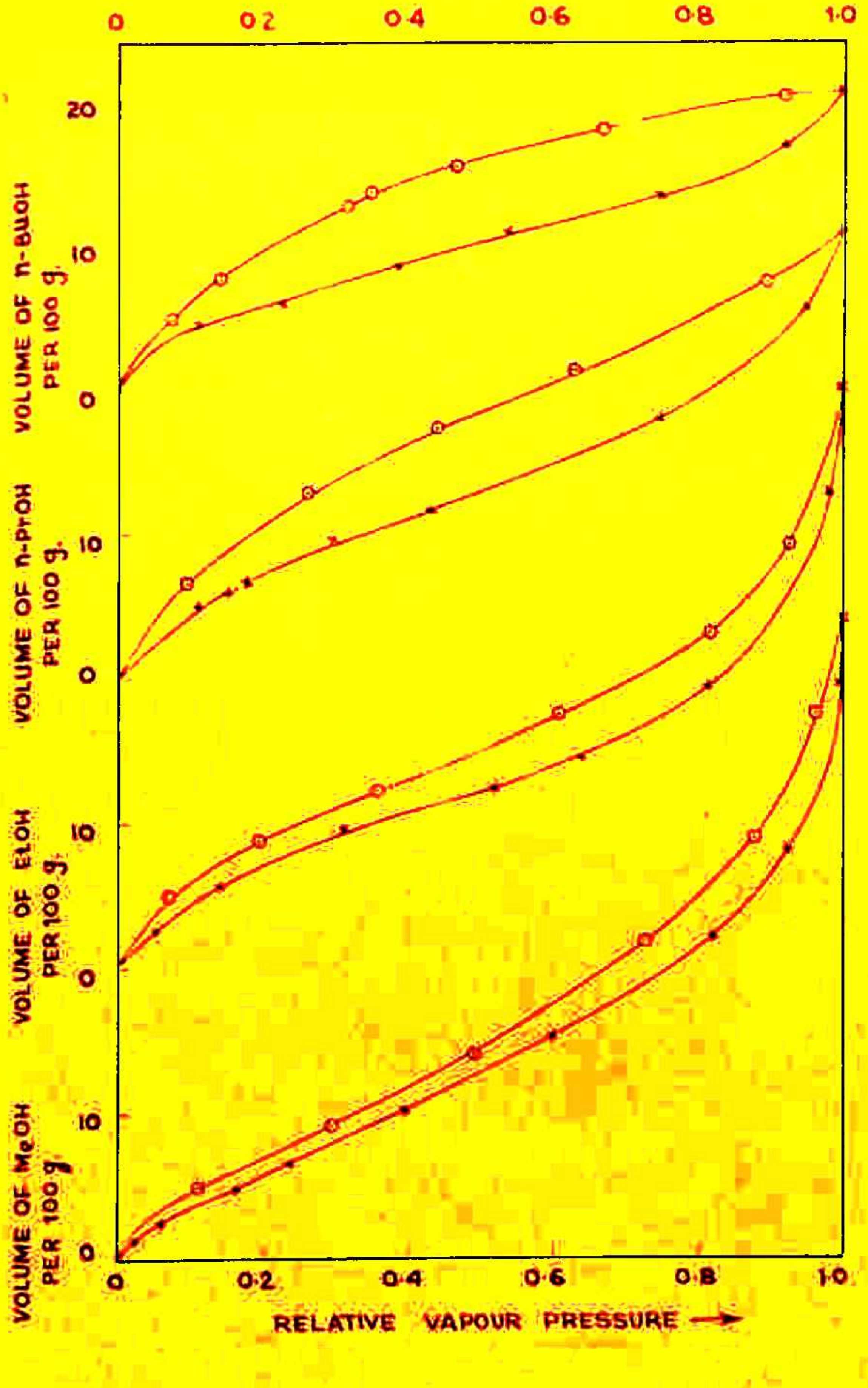


FIG.22 SORPTION-DESORPTION HYSTERESIS OF ALIPHATIC NORMAL ALCOHOLS ON CELLULOS ACETATE.

Table V

Sorptive capacities of cellulose acetate for methyl, ethyl, n-propyl and n-butyl alcohols, at 35°C.

Sorbate	Sorptive capacity cc/100 of cell. acetate
Methyl alchol	44.0
Ethyl alcohol	40.0
n-Propyl alcohol	30.5
n-Butyl alcohol	21.5

To facilitate a comparative study of the hysteresis loops obtained with different alcohols, the sorptive capacities of cellulose acetate have been plotted against the relative vapour pressure, p/p_o, instead of the actual vapour pressure of each alcohol, Figure 22.

Earlier, Newns (74) has considered the structural changes during sorption and desorption to be responsible for the hysteresis effect. Ray and Bartell (59) attributed hysteresis to the variation of contact angles during sorption and desorption, and Urquhart et al (75) explained hysteresis, shown by cellulose-water systems, on the basis of reversible orientation of water molecules on the surface of cellulose. None of these explanations can satisfactorily account for the permanence and reproducibility of the hysteresis effect

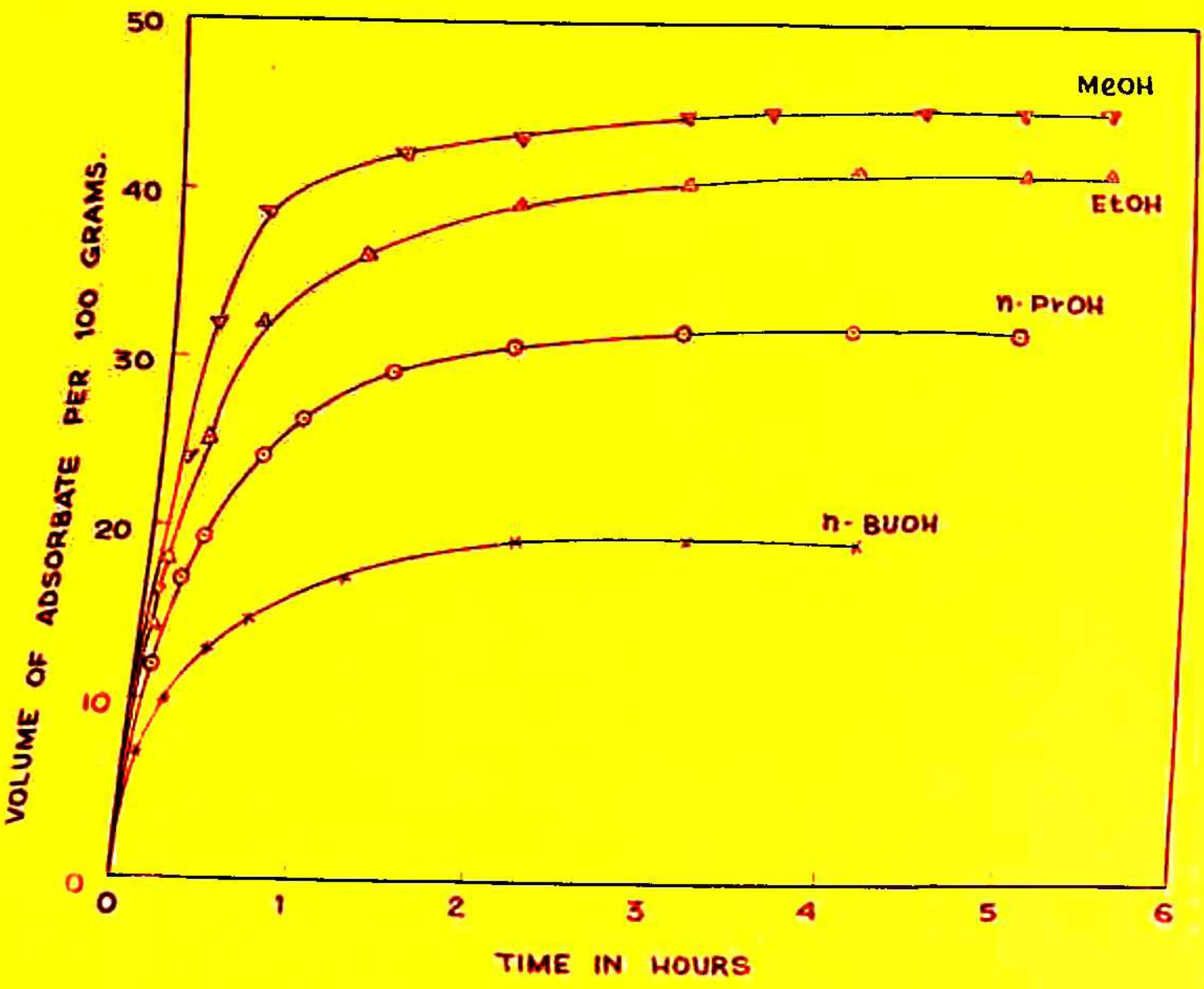


FIG.23 TIME-ADSORPTION CURVES FOR ALIPHATIC NORMAL ALCOHOLS ON CELLULOSE ACETATE AT 35° C.

exhibited by cellulose acetate - n-aliphatic alcohol systems. The only explanation which can account for the permanence and reproducibility of hysteresis effect exhibited by these systems is based on the cavity theory of hysteresis (12,13). The cavity theory postulated that sorption-desorption hysteresis is due to the physical trapping of the liquid sorbate by cavities with constricted necks.

The widening of the hysteresis loops with increasing molecular volume of the sorbate indicates that the entrapping effect of the cavities goes on increasing progressively. Probably, with increasing molecular size of the sorbate, the necks of the cavities become more and more constricted than the bodies. As to why the necks become more and more constricted than bodies with increasing molecular size of the sorbate is still an open question and needs explanation.

Time-sorption studies

Figure 23 compares the time-sorption curves for equilibrium sorption of methyl, ethyl, n-propyl and n-butyl alcohols, at their saturation pressures, at 35°C, on cellulose acetate. The times required for the attainment of equilibrium with methyl, ethyl, n-propyl and n-butyl alcohols are about $4\frac{1}{2}$, 4, 3 and 2 hours respectively. The time-sorption curves reveal that under similar experimental conditions, n-butyl alcohol is adsorbed on cellulose acetate much faster than either methyl, ethyl or n-propyl alcohols. In other words, time required for equilibrium sorption varies inversely with the vapour pressure of the sorbate alcohol.

The rate of sorption is the rate at which the liquid condensed in the neck creeps into the interior of the cavity. This is dependent on the difference between the outside pressure, i.e., the saturation pressure of different alcohols, at 35°C, and the pressure of the vapour in the interior of the cavity. Hence, with decreasing vapour pressure of the sorbate, the time for equilibrium sorption follows the trend:

methyl > ethyl > n-propyl > n-butyl alcohols.

Role of contact angle in sorption mechanism

The isotherms of all four alcohols have quite clearly defined "knees". The shapes of adsorption isotherms are significant. After the initial adsorption due to the formation of monolayer, the extent of adsorption increases steadily with increasing vapour pressure up to about $p/p_o = 0.80$. Above this there is a steep rise. In the region of high relative vapour pressure (above $p/p_o = 0.80$), there is a gradual variation in the shapes of isotherms from methyl to n-butyl alcohol. The isotherm of methyl alcohol rises asymptotically to the saturation pressure ordinate while the isotherm of n-butyl alcohol cuts the saturation pressure ordinate at an angle. This variation in the shapes of isotherms can be attributed to the variation in contact angles of the four alcohols on the surface of cellulose acetate.

The angle of contact (Ø) may be regarded as a measure of the difference in molecular arrangement between the adsorbed film and the bulk sorbate. If Ø = 0, the film is indistinguishable in structure from the bulk sorbate. As Ø increases from zero, the state of the film differs increasingly from that of the bulk.Gregg (76) has discussed the effect of contact angle of the sorbate on the shape of the sorption isotherm. In the application of Kelvin equation to sorption isotherm, the contact angle is ordinarily assumed to be zero, provided the surface is free from impurities. This is true with liquids like water whose contact angle is zero and whose isotherm is asymptotic to the saturation pressure ordinate. But, with liquids having definite contact angle, the isotherm intersects the ordinate at an angle.

The asymptotic nature of methyl alcohol isotherm indicates almost indefinitely large uptake of the sorbate at saturation pressure. From this, the contact angle of methyl alcohol on cellulose acetate surface may be assumed to be zero. The interception of the n-butyl alcohol isotherm at an angle with the saturation pressure ordinate indicates the existence of a definite contact angle.

From the gradual changes in the shapes of sorption and desorption isotherms, the hysteresis loops, and the total sorption values at saturation pressure of the four alcohols - methyl, ethyl, n-propyl and n-butyl - on cellulose acetate, it follows that there is steady increase in contact angle from methyl to n-butyl alcohol. A survey of the literature on contact angle was made and values of contact angles of the four alcohols could not be obtained. However, Fox and Zisman (43) have shown that for many of liquids on solids, the contact angle decreases with decreasing surface tension of the liquid. The values of surface tension (77,78) of the methyl, ethyl, n-propyl and n-butyl alcohols are presented in Table VI.

Table VI

Surface Tension of aliphatic normal alcohols at 35°C

Alcohol	Surface Tension dynes per cm.
Methyl	21.10
Ethyl	21.45
n-Propyl	22.55
n-Butyl	23.35

In the light of Fox and Zisman's conclusion, these values indicate that the contact angle increases from that of methyl alcohol to n-butyl alcohol.

The mode of adsorption in the monolayer

As stated earlier, the isotherms of the four alcohols show clearly defined 'knees' (10) which signify the transition from monomolecular to multimolecular adsorption. The BET equation (10) has been applied to the isotherm (Table VII).

Table VII

BET plots for the sorption of n-aliphatic alcohols on cellulose acetate.

Relative vapour pressure (p/p_o)	Sorption (x) cc/g	$\frac{p}{x(p_o-p)}$
Methyl alcohol		
0.024	0.013	1.90
0.048	0.021	2.45
0.073	0.027	2.90
0.098	0.032	3.40
Ethyl alcohol		
0.024	0.015	1.66
0.073	0.036	2.20
0.098	0.045	2.40

Table VII (contd..)

Relative vapour pressure (p/p_o)	Sorption (x) cc/g	$\frac{p}{x(p_o-p)}$
Ethyl alcohol		
0.120	0.052	2.67
0.146	0.060	2.85
0.195	0.072	3.36
n-Propyl alcohol		
0.025	0.016	1.62
0.051	0.028	1.90
0.075	0.039	2.10
0.100	0.048	2.34
0.125	0.055	2.63
0.150	0.062	2.87
n-Butyl alcohol		
0.034	0.020	1.81
0.068	0.034	2.22
0.103	0.043	2.66
0.120	0.047	2.88

The BET plots yielded straight lines which are presented in Figure 24. From the slope and the intercept of of the lines the monolayer capacity x_m has been calculated for each alcohol. Also, the values of monolayer capacity

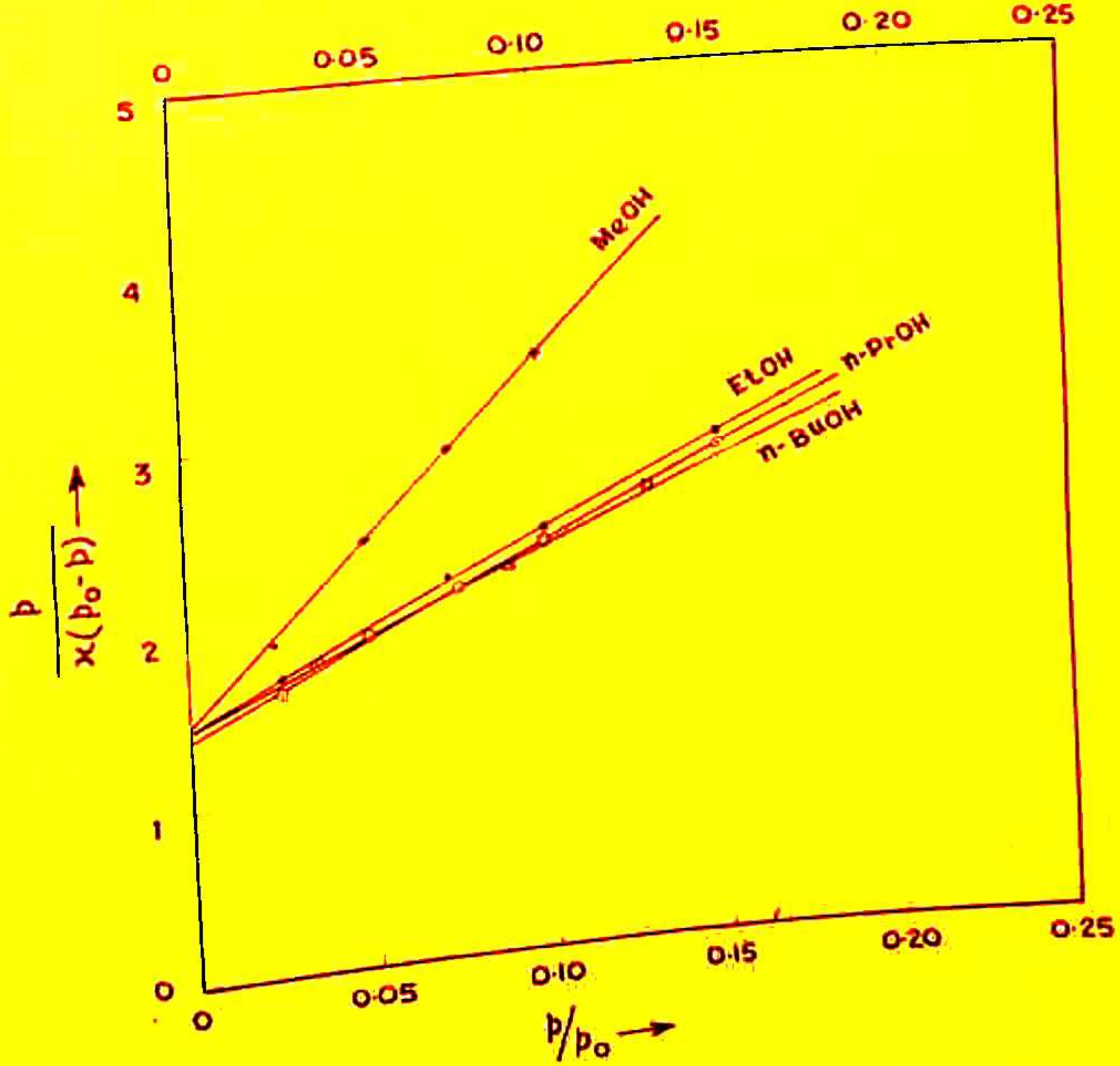


FIG. 24 BET PLOTS FOR THE SORPTION OF ALIPHATIC NORMAL ALCOHOLS ON CELLULOSE ACETATE.

can be read directly from the isotherms with reasonable accuracy (79) and is denoted by x_B. The values of monolayer capacities x_m and x_B for the four alcohols and the relative vapour pressure at which the monolayers are fully formed have been presented in Table VIII.

Table VIII

Monolayer capacities x_m and x_B in g/g of sorption and the corresponding relative pressures.

Sorbate	x_m	x_B	p/p_o
Methyl alcohol	0.075	0.071	0.268
Ethyl alcohol	0.086	0.086	0.268
n-Propyl alcohol	0.094	0.092	0.277
n-Butyl alcohol	0.097	0.077	0.278

Excepting n-butyl alcohol, the coincidence between the values of x_m and x_B for each alcohol is quite good. This illustrates the success of the mathematical form of BET equation.

Specific surface of the adsorbent

From the monolayer capacity (x_m) and knowing the cross-section area of the alcohol molecules, the specific surface (S) of cellulose acetate can be calculated by means of the following equation -

$$S = \frac{x_m}{M} \times N \times Am \times 10^{-20}$$

where N is the Avogadro's number.

There are three possible values for the cross-section, depending upon the shape of the molecule and mode of adsorption. If the molecule is assumed spherical, the molecular diameter (D) can be given by (80)

$$D = 1.33 \times 10^{-8} \times V_m$$

where V_m is the molecular volume. Knowing D, the molecular cross-section (Am) can be obtained from its molecular weight and density. Considering the alcohol molecule as linear, there can be two modes of oriented adsorption - perpendicular and parallel to the surface. The cross-section of the linear molecule is $(4.55)^2$ Å^2. Knowing the total volume of the molecule D^3 spherical, the length of the molecule and also the area along the length of the molecule can be calculated. The values of the three different cross-sections are shown in Table IX. The values of the specific surface calculated for these three cross-sections are also shown.

Considering the molecules as linear and assuming oriented adsorption perpendicular to the surface, the calculated specific surface areas are not the same. The value of specific surface goes on decreasing from methyl

Table IX

Specific surface of cellulose acetate considering alcohol molecules as spherical and linear

	Molecules as spherical		Molecules as linear		Specific surface in m^2 per gm. of sorbent		
	Diameter D spherical in $\AA^o$	Cross-section in $\AA^{o2}$	Cross-section in $\AA^{o2}$	Area of side in $\AA^{o2}$	Molecules as spherical	Linear molecules perpendicular to surface	Linear molecules parallel to surface
Methyl alcohol	4.6	21.2	20.7	21.4	299.6	292.5	302.5
Ethyl alcohol	5.2	27.0	20.7	30.9	304.1	233.3	348.3
n-Propyl alcohol	5.6	31.4	20.7	38.5	296.6	169.4	363.5
n-Butyl alcohol	6.0	36.0	20.7	47.5	283.0	163.3	375.5

to n-butyl alcohol. Assuming the oriented adsorption parallel to the surface, the specific surface areas obtained are again different. The value increases from methyl to n-butyl alcohol. However, assuming the alcohol molecules to be spherical, the specific surface area are almost the same.

It follows from these results that the mode of adsorption of four linear aliphatic normal alcohol molecules is not of oriented type, the molecules are held spherical to the surface of cellulose acetate. Evidences of oriented adsorption of molecules on solid surfaces are not many, though oriented adsorption of molecules in films on liquid surface is well known and well established.

The foregoing studies reveal the existence of adsorption of alcohol molecules as spherical in the monolayer on the surface of cellulose acetate and the effect of contact angle of the alcohols on the shapes of the isotherms and the hysteresis loops.

Number of molecules in the monolayer

The total number of alcohol molecules contained in the monolayer on the surface of one gram of the adsorbent have been calculated from the mathematical expression

$$N_O = \frac{x_m \cdot N}{M}$$

and are presented in Table X.

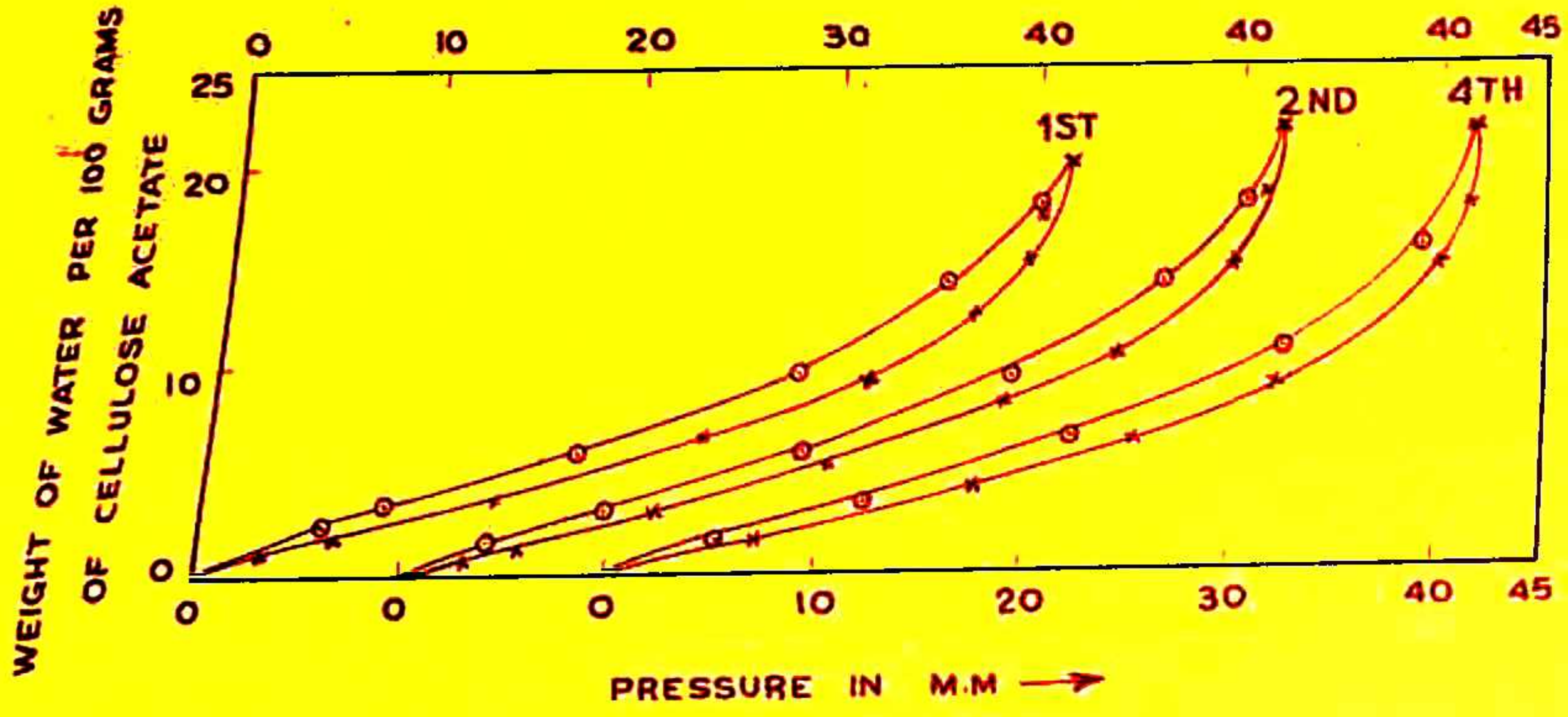


FIG.25 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLULOSE-ACETATE AT THE 1ST, 2ND, AND 4TH CYCLE.

Table X

No. of alcohol molecules in the monolayer

Sorbate	No. of molecules
Methyl alcohol	14.1×10^{20}
Ethyl alcohol	11.3×10^{20}
n-Propyl alcohol	9.50×10^{20}
n-Butyl alcohol	7.90×10^{20}

The decrease in the number of alcohol molecules is due to the increasing molecular sizes of alcohols from methyl to n-butyl.

Effect of activation temperature

Hysteresis effect has been exhibited in both activated and unactivated cellulose acetate.With unactivated sample, sorption-desorption studies have been carried up to 4th cycle. The loops obtained at the 1st, 2nd and 4th cycles are shown in Figure 25. The percentage of water taken at the saturation pressure 20.2, 21.8, 21.8 respectively.

The hysteresis loops obtained with 90°C activated samples are presented in Figure (26). The studies were continued up to 8th cycle of sorption and desorption. Loops

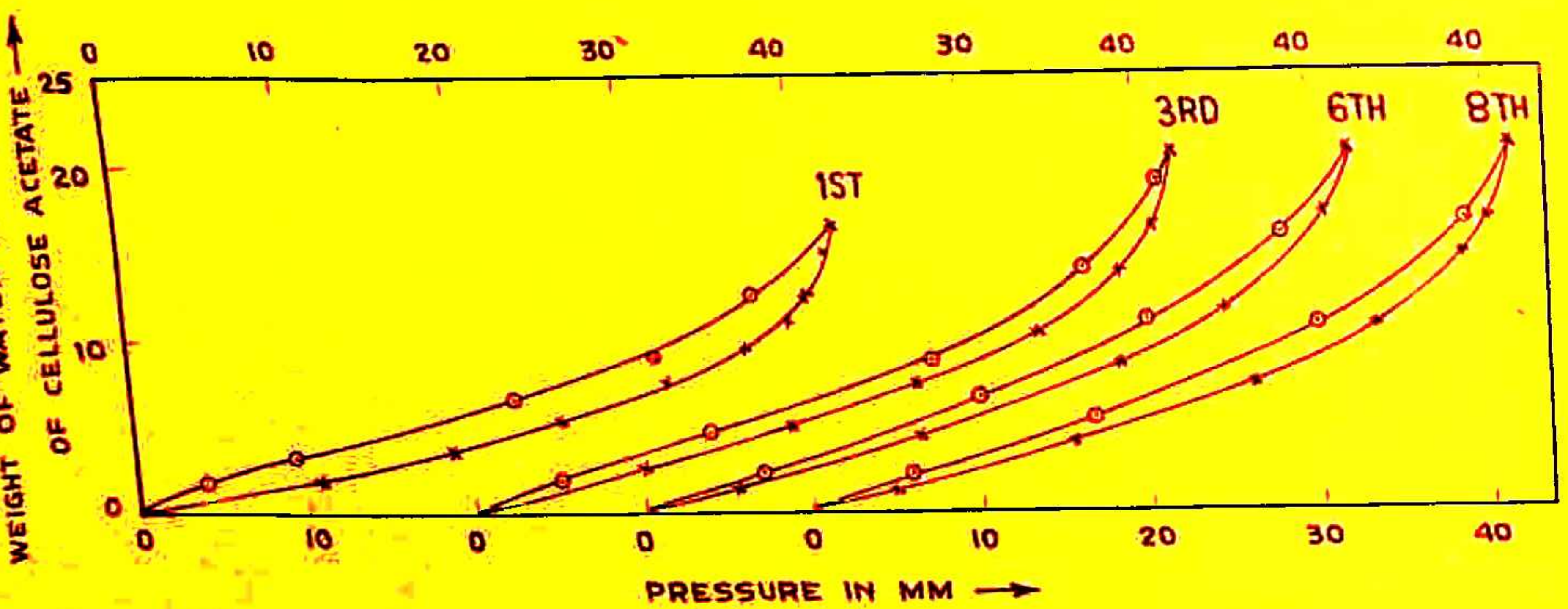


FIG.26 SORPTION-DESORPTION OF WATER VAPOUR ON CELLULOSE-ACETATE (ACTIVATED AT 90° C) AT THE 1ST, 3RD, 6TH, AND 8TH. CYCLES.

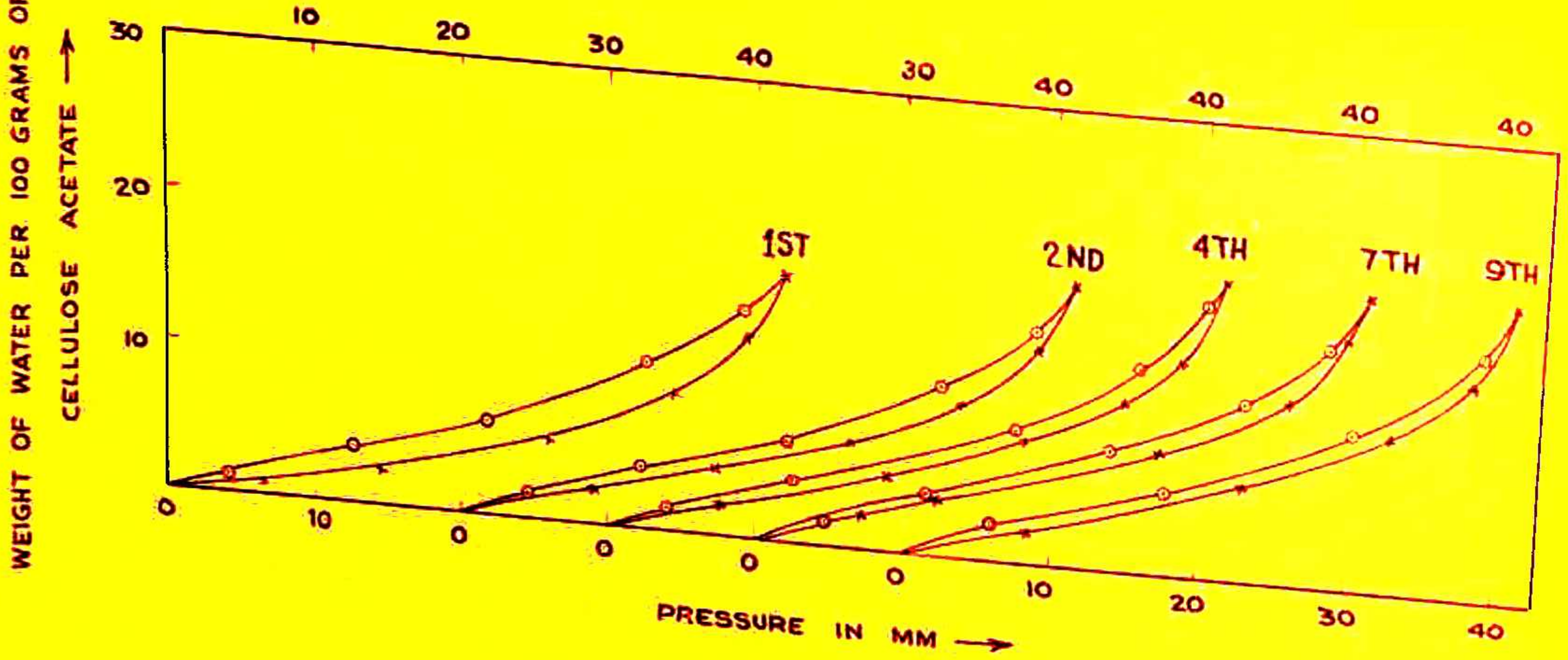


FIG.27 SORPTION - DESORPTION HYSTERESIS OF WATER VAPOUR ON CELLULOSE ACETATE (ACTIVATED AT 150°C) AT THE 1ST, 2ND, 4TH, 7TH, AND 9TH CYCLES.

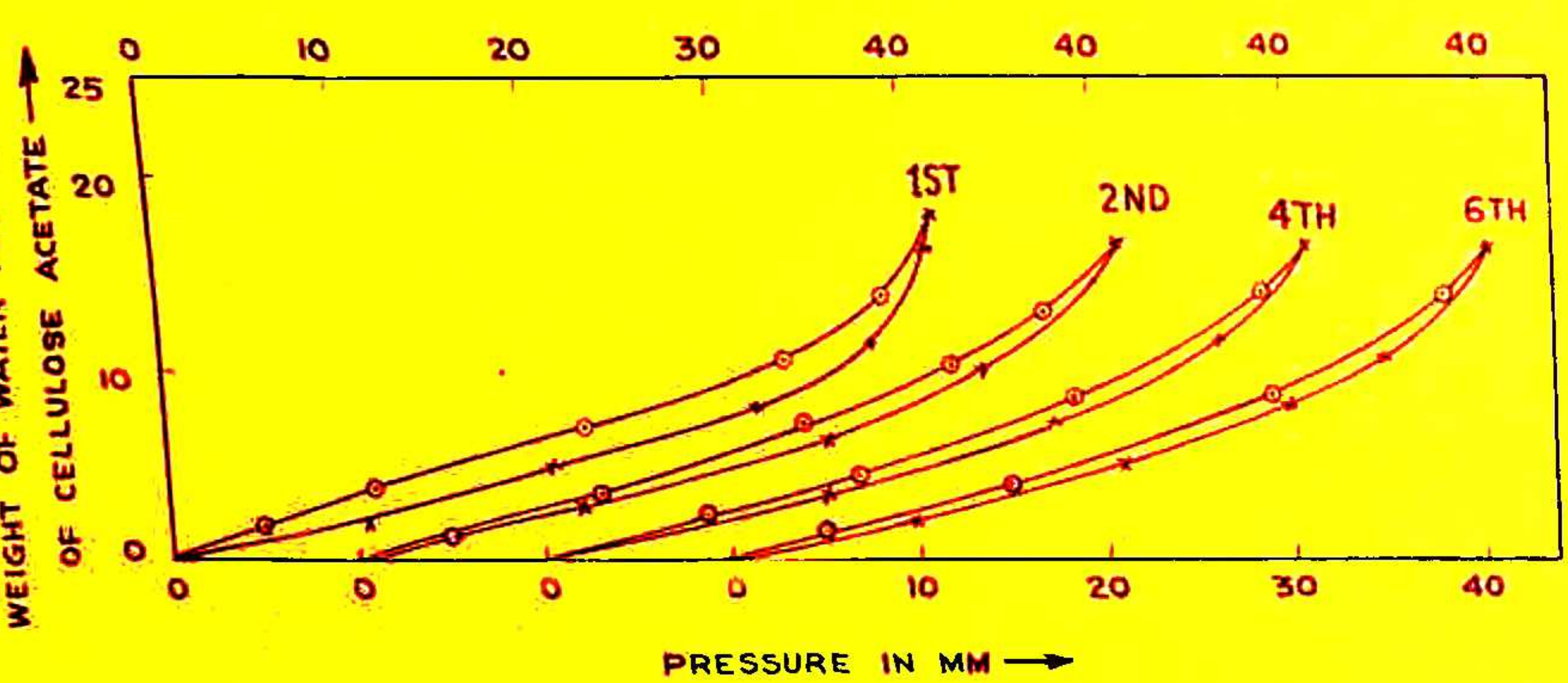


FIG.28 SORPTION-DESORPTION HYSTERESIS OF WATER VAPOUR ON CELLULOSE ACETATE (ACTIVATED AT 200°C) AT THE 1ST, 2ND, 4TH, AND 6TH CYCLES.

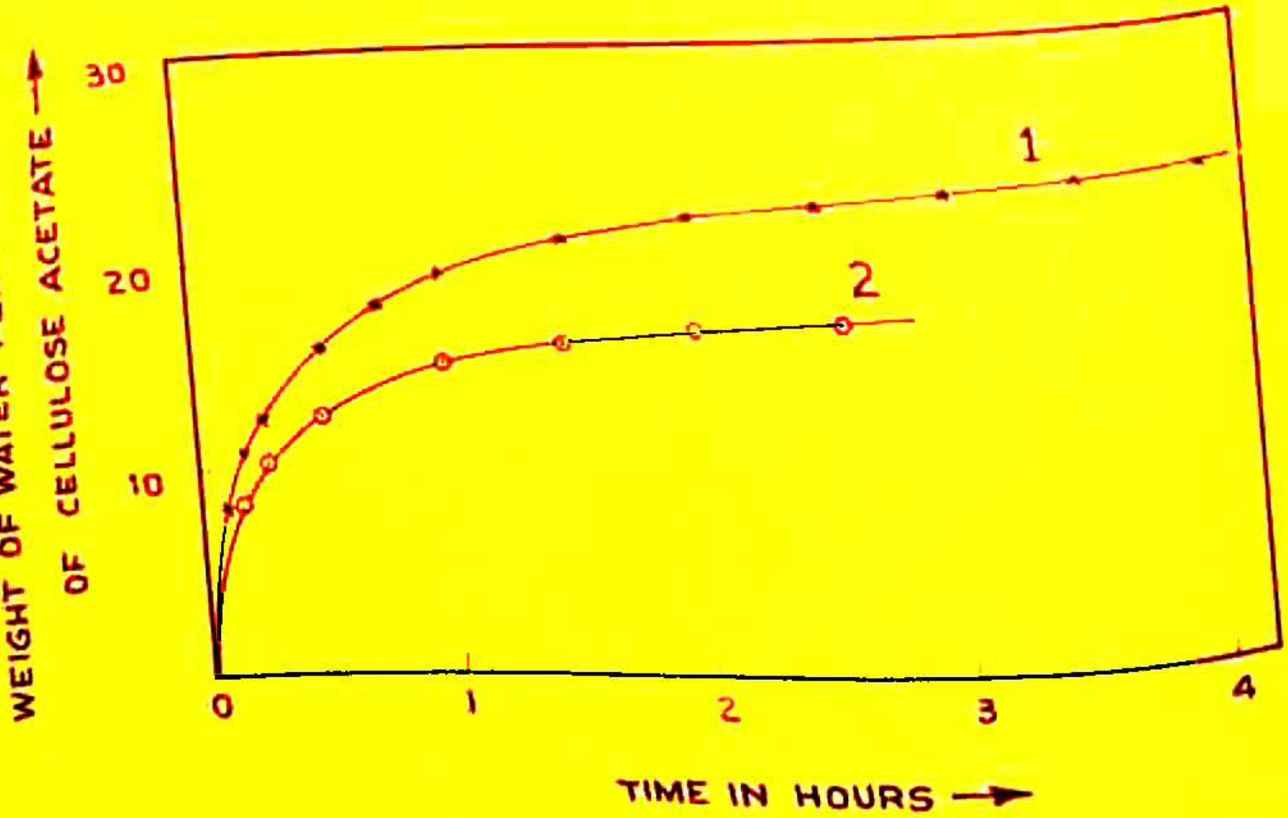


FIG.29 TIME-SORPTION CURVES AT 35°C FOR CELLULOSE ACETATE (UNACTIVATED) 1 AND (ACTIVATED AT 200°C)-2.

Figure 29 reveals the results of time-sorption curves constructed for unactivated and 200°C activated samples of cellulose acetate.

Hysteresis loops obtained during sorption and desorption of water vapour on cellulose acetate have shown some interesting characteristics. With unactivated cellulose acetate there is a tendency for the decrease in the size of the hysteresis loop from 1st to 4th cycles; the activated samples also have shown similar tendency but the tendency is more marked. In every case hysteresis loop type C of de Boer classification (81) is obtained which extends over the entire pressure range. The sorptive capacity of cellulose acetate also decreases as the temperature of activation is raised. This decrease in the total sorptive capacity is probably due to the shrinkage of the network of the sorbent owing to heat and vacuum.

As it has been pointed out earlier, the only probable explanation which can satsifactorily account for almost all cases of hysteresis is the one based on the 'cavity concept' (12,13) which postulates that hysteresis is due to entrapping of the liquid sorbate by cavities with small necks and wide bodies. The difference between the neck radius and the body radius is a measure of the amount of hysteresis.

In the light of the cavity concept it is reasonable to suppose that during activation, drastic evacuation at 90°C, 150°C and 200°C, not only removes the adsorbed permanent gases but also a part of the water content of the adsorbent; which changes the adsorbent structure by reducing the diameter of cavities present in the network. As the diameters of the cavities decrease the difference between the neck radius and the body radius of the cavities also decrease which results in decreased entrapping effect and hence in smaller hysteresis loops.

This explanation is further confirmed by the rate studies. The rate of sorption is the rate of filling of the cavities with water. The sorptive capacities of unactivated and 200°C - activated samples are not much different but the time intervals for complete filling are markedly different. The 200°C - activated sample is filled more quickly than unactivated sample. It follows that 200°C activated sample contains a large number of comparatively small cavities than the unactivated sample. Filling of smaller cavities is much quicker than those of bigger ones (82); indicating that rate of sorption varies directly with increasing temperature of activation.

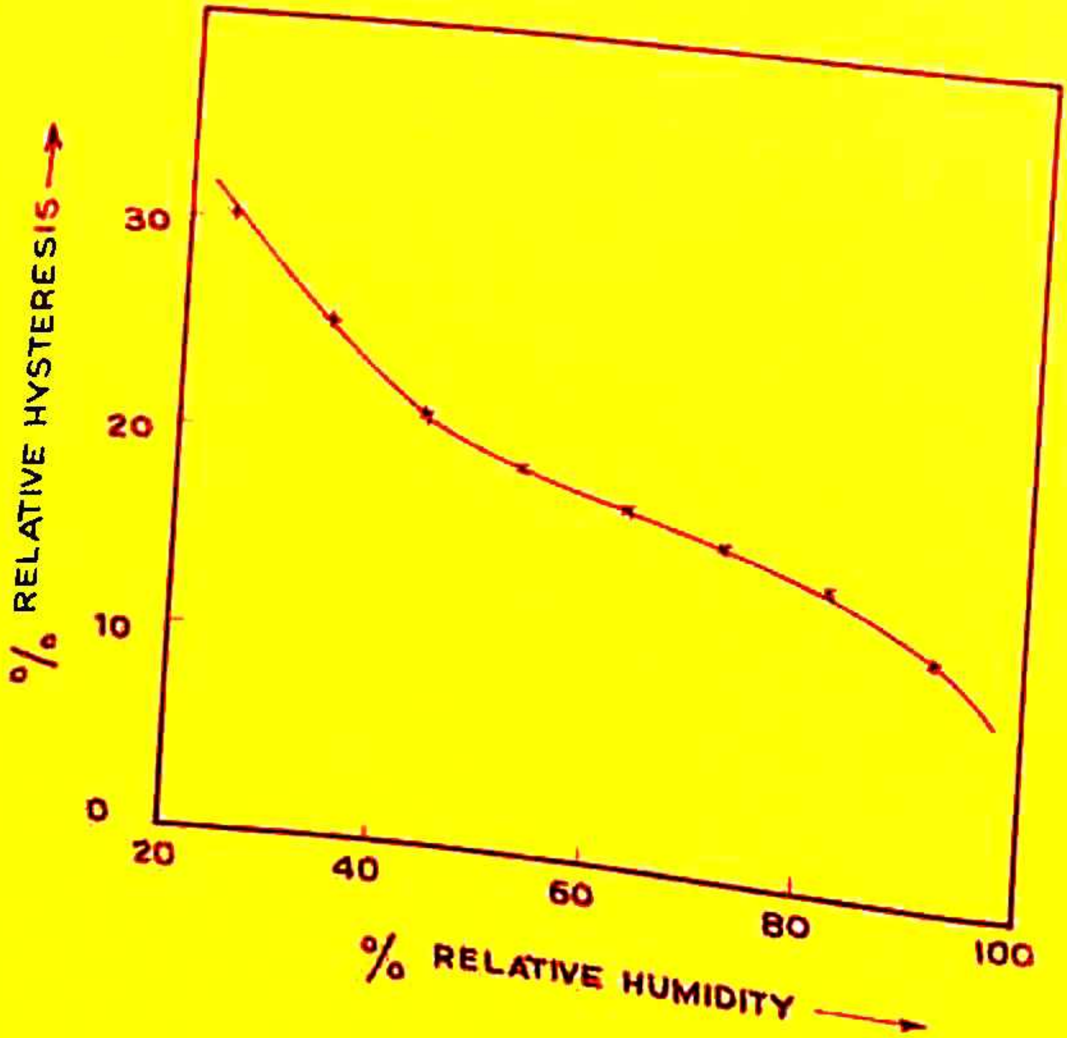


FIG. 30 RELATIVE HYSTERESIS (AVERAGE FROM 35 - 200°C) AS A FUNCTION OF RELATIVE HUMIDITY.

Hysteresis and the effect of relative humidity and temperature

Figures 30 and 31 present the effect of relative humidity and temperature on relative hysteresis. Relative hysteresis, which has been employed as a qualitative measure of the amount of hysteresis at a particular temperature or relative humidity, can be defined as:

$$\text{Relative hysteresis} = \frac{\text{Desorption regain-sortion regain}}{\text{sorption regain}} \times 100$$

In dealing with the effect of relative humidity on the amount of hysteresis, the relative hysteresis values concerned are, at each particular relative hysteresis, the average values at the various temperature. Similarly, in considering the effect of temperature, the relative hysteresis values employed are, at each particular temperature, the averages of the values at 10% relative humidity intervals in the range 20-90% relative humidity inclusive; values outside this range were not considered in the averages partly because the error was greater outside this range, and partly because the relative hysteresis must for all samples decrease towards zero at approaching 100% relative humidity.

Effect of relative humidity on relative hysteresis (20-90% r.h.) Figure 30.

Figure 30 shows that as the relative humidity increases

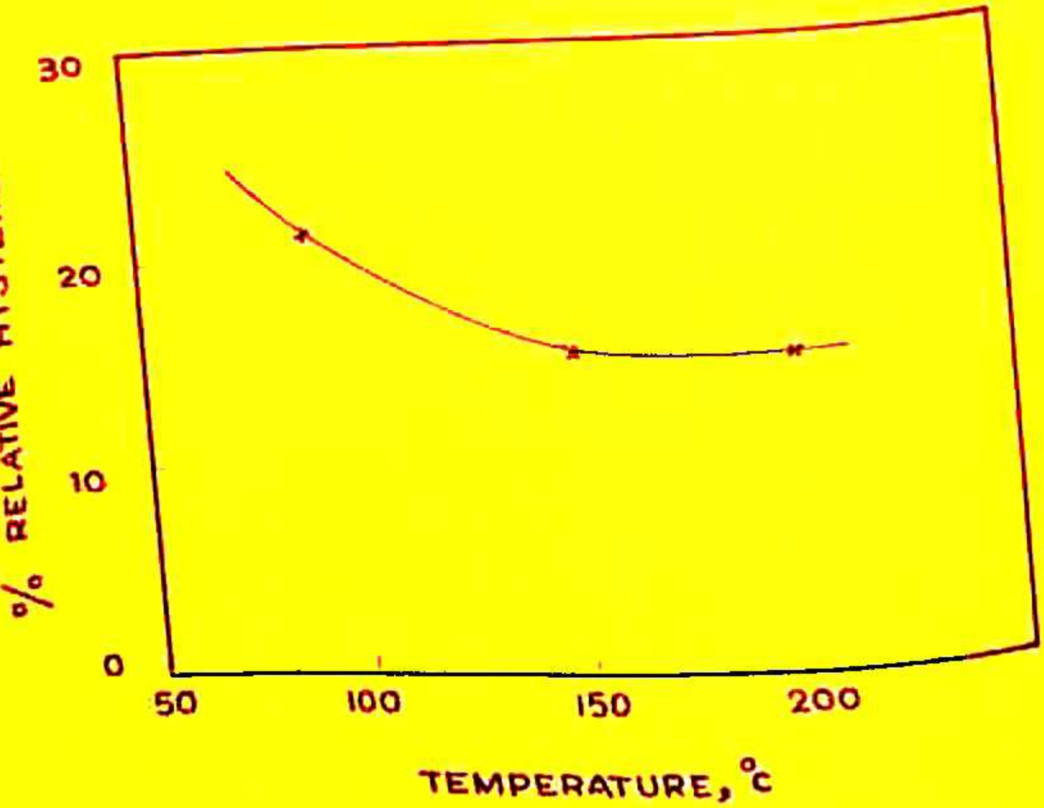


FIG.31 RELATIVE HYSTERESIS (AVERAGE FROM 20-90% Rh) AS A FUNCTION OF TEMPERATURE.

from 20 to 90%, the relative hysteresis of cellulose acetate decreases; the decrease being marked in the range 20 to 50% r.h. Earlier results on cellulose and other textile polymers (58) have also revealed a similar behaviour. The present results are in excellent agreement with the results of Jeffries (58) who studied secondary cellulose acetate and triacetate. The 100% r.h. regain values, at 35°C, are also in good agreement with most of the previous values (58).

Effect of temperature on relative hysteresis (Fig. 31)

With cellulose acetate activated at different temperatures (90°C, 150°C and 200°C), the relative hysteresis decreases with increasing temperature (Figure 31); the decrease being very marked between 90°C to 150°C; above 150°C the relative hysteresis appears to be independent of temperature. Previous results show that with all the celluloses studied, the relative hysteresis decreased with increase in temperature in the 30°C-60°C range. Jeffries (58) studied the sorptive properties of cellulose secondary acetate and triacetate up to 150°C and reported similar observations. The behaviour of cellulose acetate in the range of 150°C to 200°C is very interesting, the relative hysteresis decreases by about 6% in the range 90-150°C and then remains almost constant from 150°C-200°C. The reason for this unusual behaviour at high temperatures, however, is not clear.

***

PART IV

STUDIES IN SORPTION-DESORPTION HYSTERESIS WITH CELLOPHANE

STUDIES IN SORPTION-DESORPTION HYSTERESIS WITH CELLOPHANE

Abstract

Making use of the quartz fibre spring balance, a series of sorptions and desorptions of water and organic vapours, at 35°C, have been carried out on (1) commercial cellophane (2) commercial cellophane, washed with water (3) commercial cellophane, washed with water, and next with different organic liquids and (4) cellophane activated at temperatures varying from 35°C to 200°C. Commercial cellophane showed no hysteresis loop at all in the first two cycles. Commercial cellophane, washed with water, showed hysteresis effect in the first cycle and it disappeared in the 2nd and 3rd cycles. Commercial cellophane, washed with water, and next with different organic liquids showed permanent and almost reproducible hysteresis loops.

Commercial cellophane has no pores and cavities and therefore showed no hysteresis effect. On washing with water, glycerine which is normally present in cellophane as a plasticiser is removed. Pores are created, the hysteresis effect is produced in the first cycle and it disappears in subsequent cycles owing to swelling of cellophane. Washing with organic liquids makes cellophane less swellable

and less hydrophilic. The cavities are not collapsable and the hysteresis effect persists over a large number of cycles.

With activated cellophane, it appears that the molecules of regenerated cellulose undergo thermal vibration at elevated temperatures and cellophane tends to acquire a more stable conformation which results in readjustment of position, shape and size of capillaries within the solid. The readjustment appears to be ultimately responsible for the appearance or disappearance of hysteresis effect.

The water-vapour sorption data have been plotted according to BET and FHH equations and BET surface area for cellophane has also been calculated.

Introduction

The remarkable extent to which the properties of textile fibres, protective films and many plastics are modified by the sorption of water vapour has long maintained an interest in the subject (83-86). The extensive work on the sorption of water vapour by high polymers led Smith (87) to believe that hysteresis in sorption was a consequence of variation in the fraction of bound water present in the sorption and desorption processes; the bound fraction being always larger on desorption than on sorption. Hauser and McLaren (88) studied the permeation through and sorption of water vapour by high polymers and suggested a mechanism which was in accordance with Pauling's consideration (89) for Nylon and proteins. Simril and Smith (90) obtained sorption-desorption hysteresis in cellophane-water vapour system at temperatures ranging from 16.5 to 49.5°C. They interpreted hysteresis on the basis of the entropy of the sorbed water. Stamm (91,92) studied the diffusion of water into uncoated cellophane. Usmanov and Park (93) obtained sigmoid isotherms during sorption and desorption of water on cellophane at 25°C. Their results indicated a change in the structure of cellulose during the process of water sorption.

Glycerol free, non moisture proofed cellophane is a desirable subject for research in the field of physics and chemistry of cellulose because this material is pure regenerated cellulose in the form of a thin film which lends itself readily to experimental conditions. A fairly comprehensive study of the cellophane - vapour equilibrium was undertaken with the hope that some of the film properties which show marked dependence on the vapour content might be correlated. Also, the effect of activation temperature of cellophane on water sorption has been studied over a wide range of temperatures. No data of this kind are available in literature.

Experimental

Commercial cellophane, supplied by E.I. du Pont de Nemours & Co. Inc. has been used in all experiments. in the form of strips 6 cm x 4 cm. These strips are clear and transparent because the holes are too small to scatter much light(94).

Commercial cellophane usually contains about 18% glycerine (95) which functions as a plasticiser in cellophane.

Extraction of glycerine: Cellophane was kept in contact with distilled water for 24 hours and washed several times to remove glycerine (92). The washed cellophane was dried in air. Glycerine free cellophane is referred hereafter as cellophane while unwashed cellophane is referred to as commercial cellophane.

Treatment with organic liquids: Cellophane was treated with different organic liquids: methyl alcohol, ethyl alcohol and acetone,kept overnight. The organic liquid was changed six times during intervals of four hours and the treated cellophane was dried in air.

The following sorbates have been employed:

Water	Doubled distilled	
Methyl alcohol	BDH (AR)	Redistilled at 64.5°C
Ethyl alcohol	Bengal Chemicals	Redistilled over Ca at 78°C

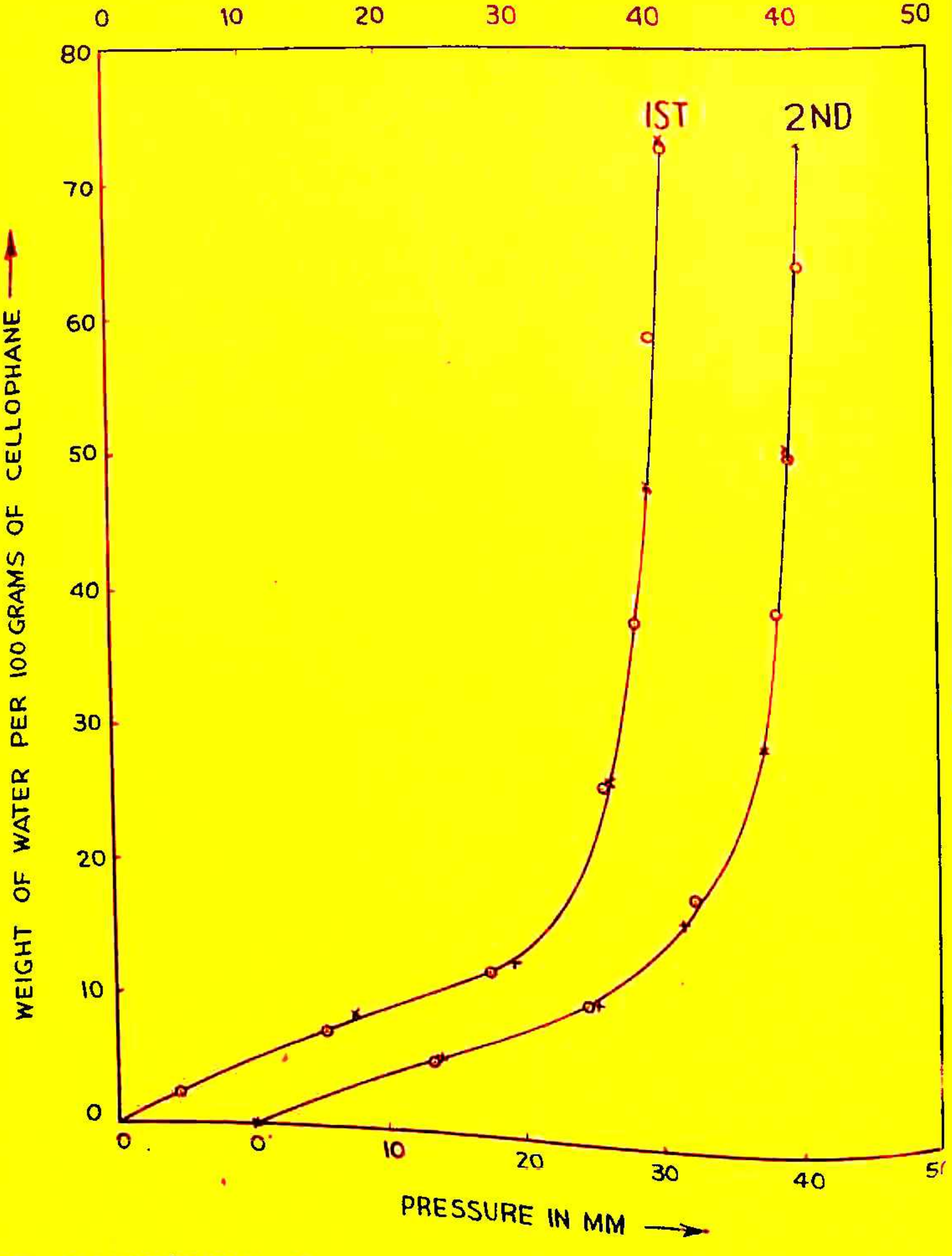


FIG. 32 SORPTION-DESORPTION HYSTERESIS OF WATER ON COMMERCIAL CELLOPHANE AT THE IST AND 2ND CYCLES.

n-Propyl alcohol	BDH (LR)	Redistilled at 97°C
n-Butyl alcohol	BDH (LR)	Redistilled at 116°C
Carbon tetrachloride	German (LP)	Redistilled at 76°C.

All the sorption-desorption studies have been carried out at 35°C.

Results

Commercial cellophane - water vapour system

In the sorptions and desorptions of water vapour, the commercial cellophane has shown no hysteresis effect, Figure 32. The sorption and desorption curves are coincident in the first two cycles. Commercial cellophane has taken 73.2% and 73.0% water in the 1st and 2nd cycles, respectively. Attainment of equilibrium was complete in about one hour but actually two to four hours were allowed before taking each point. The isotherms show no clearly defined knees.

Cellophane - water vapour system

Glycerol-free cellophane has shown very interesting behaviour towards water sorption and desorption. There was hysteresis loop in the first cycle and it disappeared in the 2nd and 3rd cycles, Figure 33. The sorptive capacities of cellophane in the 1st, 2nd and 3rd cycles are 52.0%,

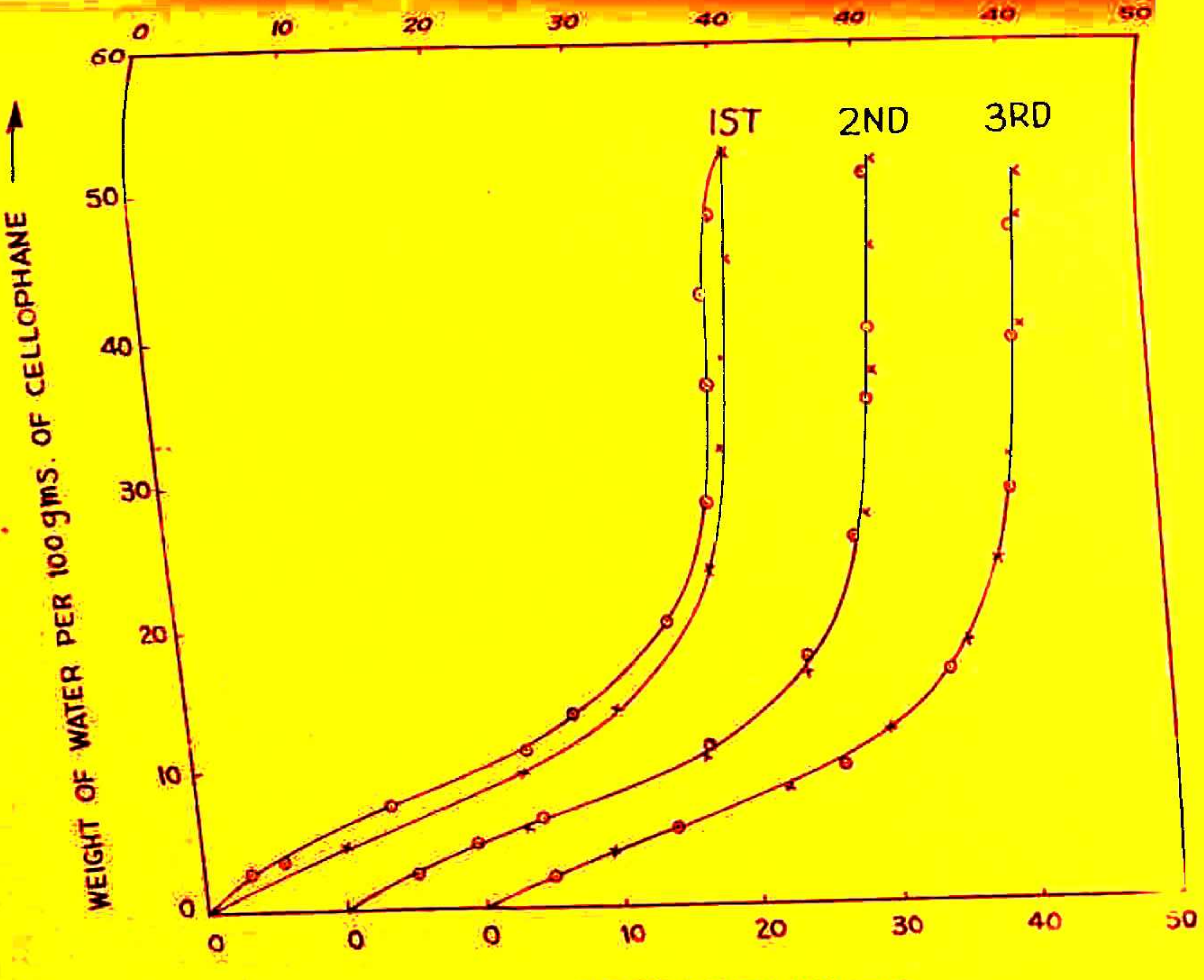


FIG. 33 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELOPHANE WASHED WITH WATER AT 1ST, 2ND, AND 3RD CYCLES.

51.3% and 50.1%, respectively. The study of these cycles lasted over 20 days. Duplicate experiment also yielded similar results.

Organic liquid treated cellophane - water vapour system

Cellophane, treated with different organic liquids, was used as adsorbent in an another series of experiments. The organic liquid used were methyl alcohol, ethyl alcohol and acetone. The study in each case was extended up to 6th cycle. There have been permanent hysteresis loops in each case, Figures, 34, 35, 36. At the end of 1st cycle of sorption and desorption, the ethyl alcohol treated cellophane lost about 6% of its initial weight while acetone treated cellophane lost about 2% of its initial weight. There was no loss in weight in case of methyl alcohol treated cellophane. The sorptive capacities of organic liquid treated cellophane have been presented in Table XII.

Table XII

Sorptive capacities of organic liquid treated cellophane for water vapour.

Adsorbent	Sorptive capacities g/100g of cellophane Sorption-desorption cycles					
	1st	2nd	3rd	4th	5th	6th
Methyl alcohol treated cellophane	30.0	34.9	-	-	35.2	35.8
Ethyl alcohol treated cellophane	39.7	-	51.5	-	50.0	50.0
Acetone treated cellophane	36.0	49.5	49.5	-	-	49.5

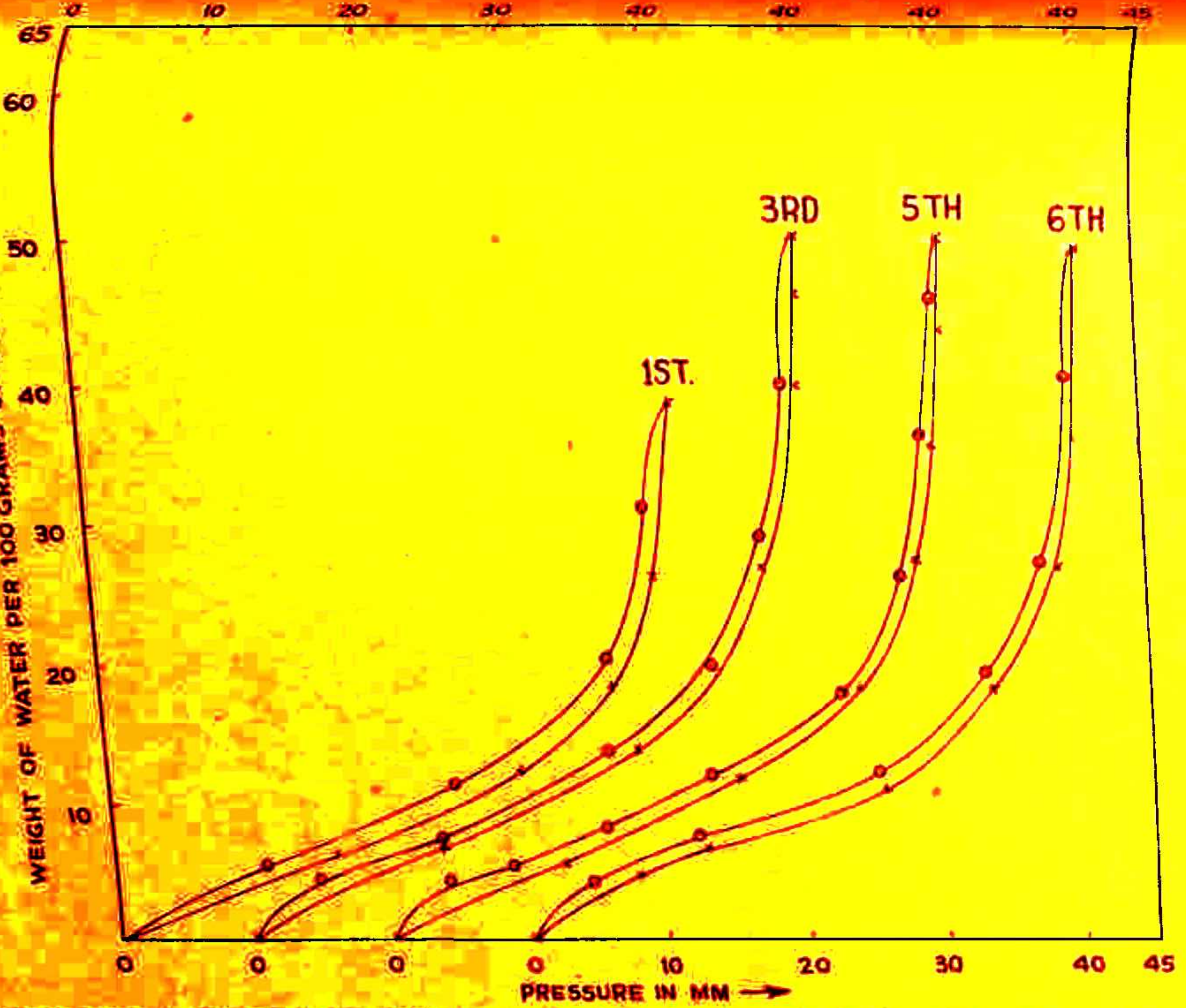


FIG.34 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE WASHED WITH WATER AND NEXT WITH METHYL ALCOHOL AT THE 1ST 3RD, 5TH AND 6TH CYCLES.

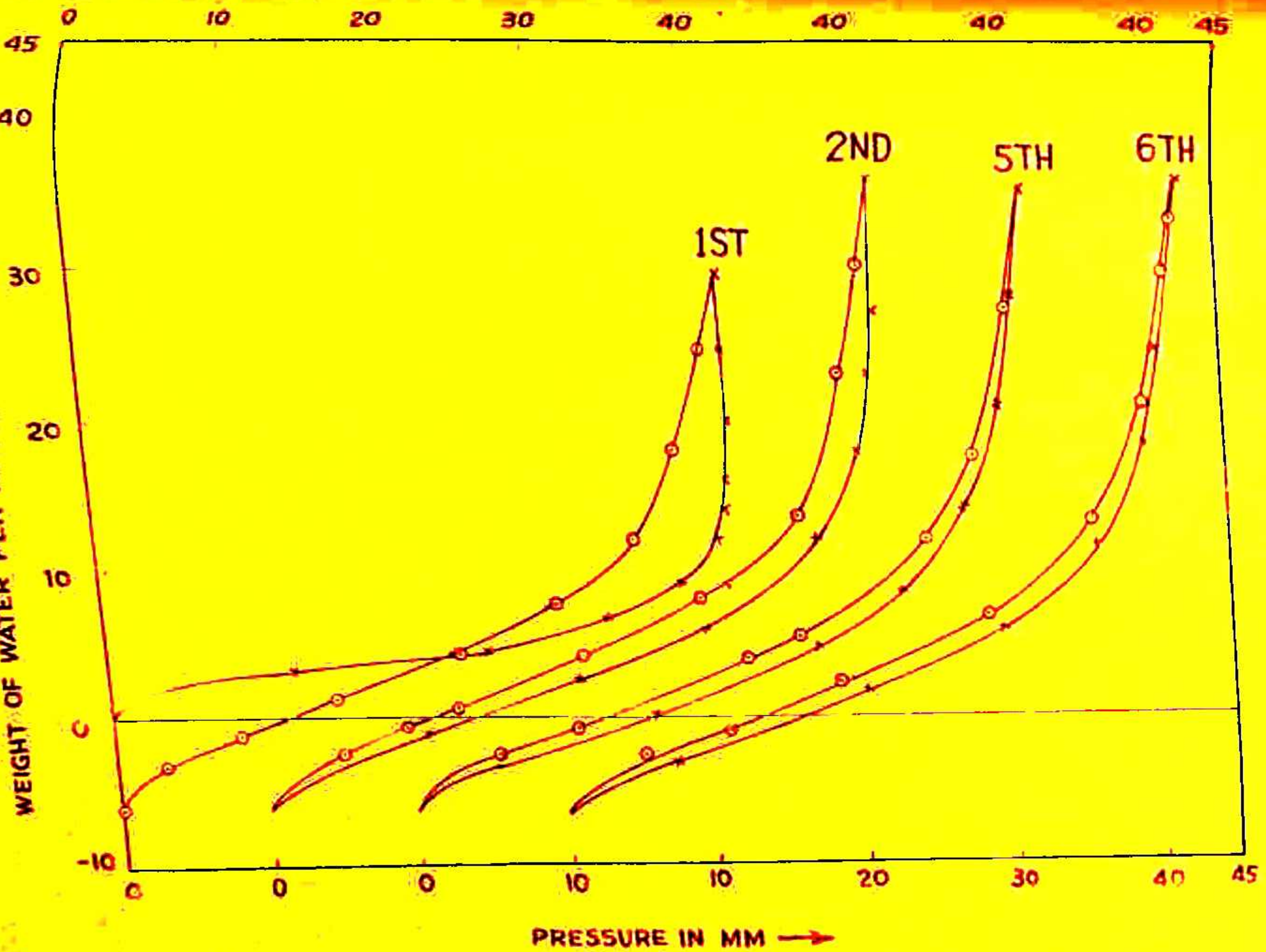


FIG. 35 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE WASHED WITH WATER AND NEXT WITH ETHYL ALCOHOL AT THE 1ST, 2ND, 5TH, AND 6TH CYCLES.

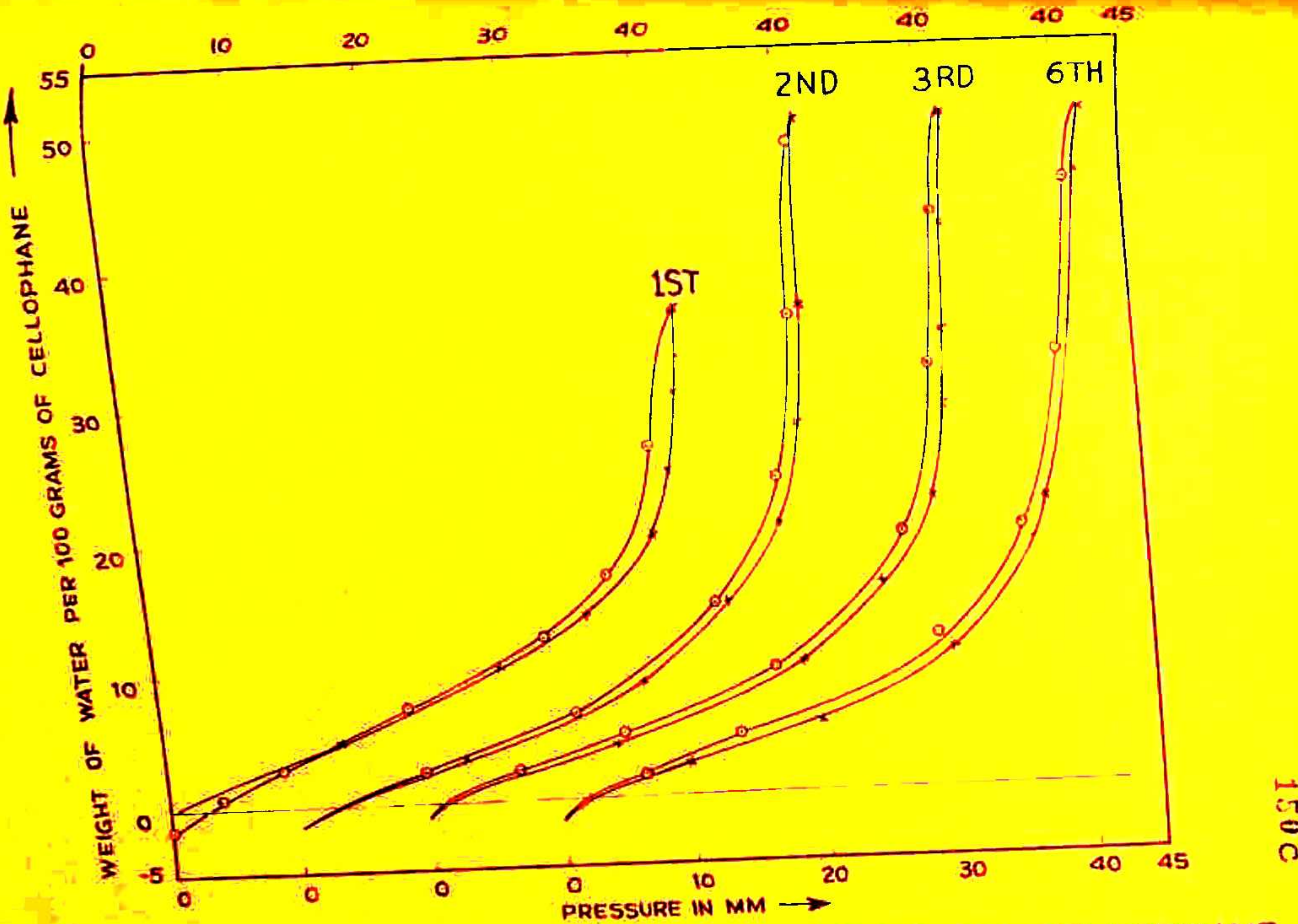


FIG.36 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE WASHED WITH WATER AND NEXT WITH ACETONE AT THE 1ST, 2ND, 3RD AND 6TH CYCLES

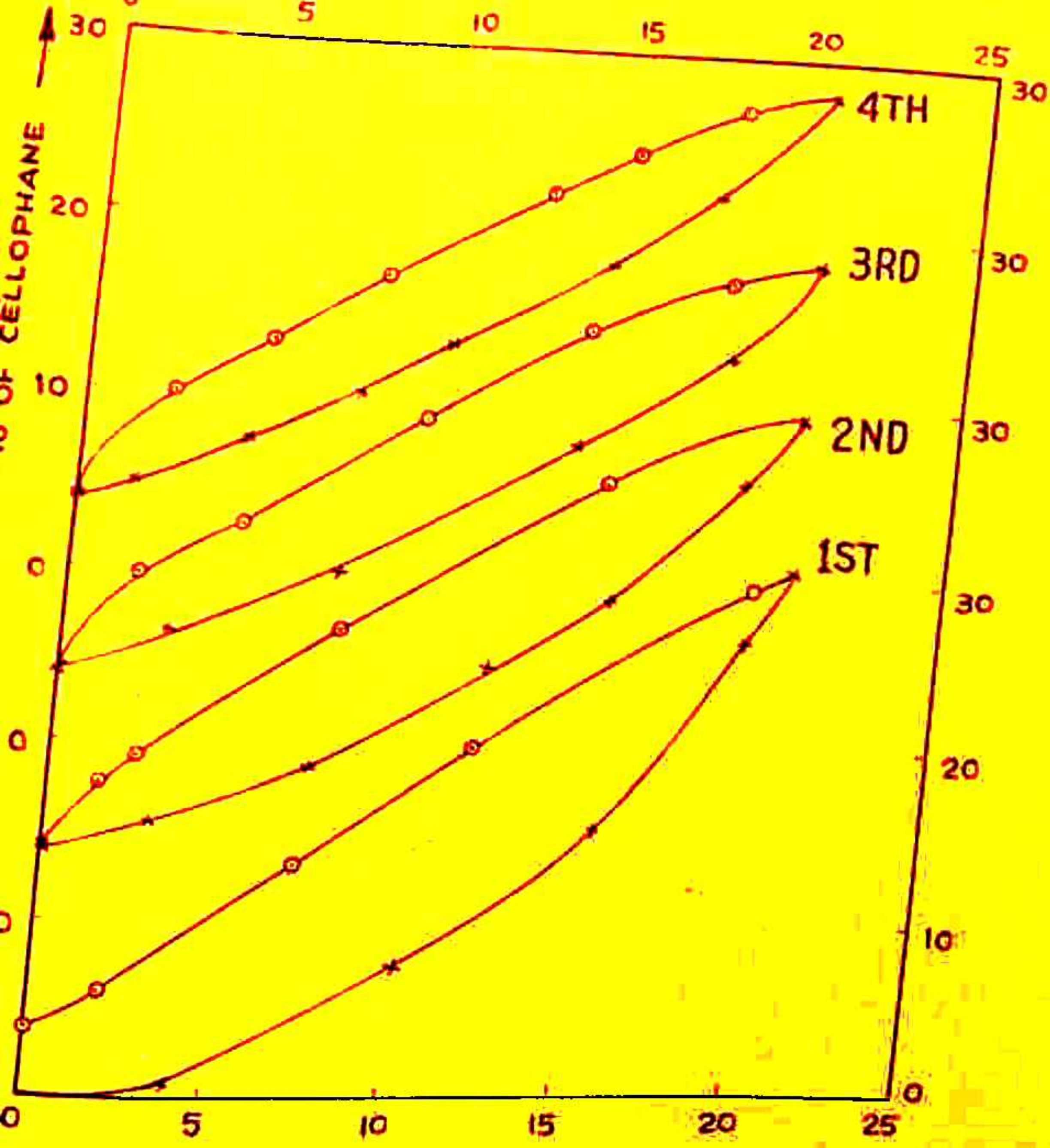
Sorption of organic vapours on cellophane

In another series of experiments, cellophane was subjected to complete sorptions and desorptions of polar sorbates like methyl alcohol, ethyl alcohol, n-propyl alcohol and n-butyl alcohol, and non-polar sorbates like carbon tetrachloride.

The sorptions and desorptions of methyl and ethyl alcohols have been presented in Figures 37 and 38, respectively. The amounts of methyl alcohol taken at its saturation pressure, at 35°C, in the 1st, 2nd, 3rd and 4th cycles are 30.6, 29.4, 28.3 and 28.0 c.c. per 100 grams of cellophane respectively. The sorption capacities of ethyl alcohol are 36.8, 35.3, 34.3, 34.5 and 34.6 c.c. per 100 grams of cellophane in the 1st, 2nd, 3rd, 4th and 5th cycles respectively.

At the end of the 1st cycle of sorption and desorption, cellophane retained, irreversibly, about 4.0 and 5.5 c.c. of methyl and ethyl alcohols respectively. This 'bound' alcohol is retained by cellophane inspite of several hours of evacuation, at 35°C, at a vacuum of 10^{-2} m.m. of Hg.

In the sorption of n-propyl and n-butyl alcohols, the extent of adsorption was very small. It was of the order of 0.2%. It is thus, reasonable to assume that the adsorption of these alcohols is negligible on cellophane.



ORPTION-DESORPTION HYSTERESIS OF METHYL

LCOHOL ON CELLOPHANE (WASHED WITH

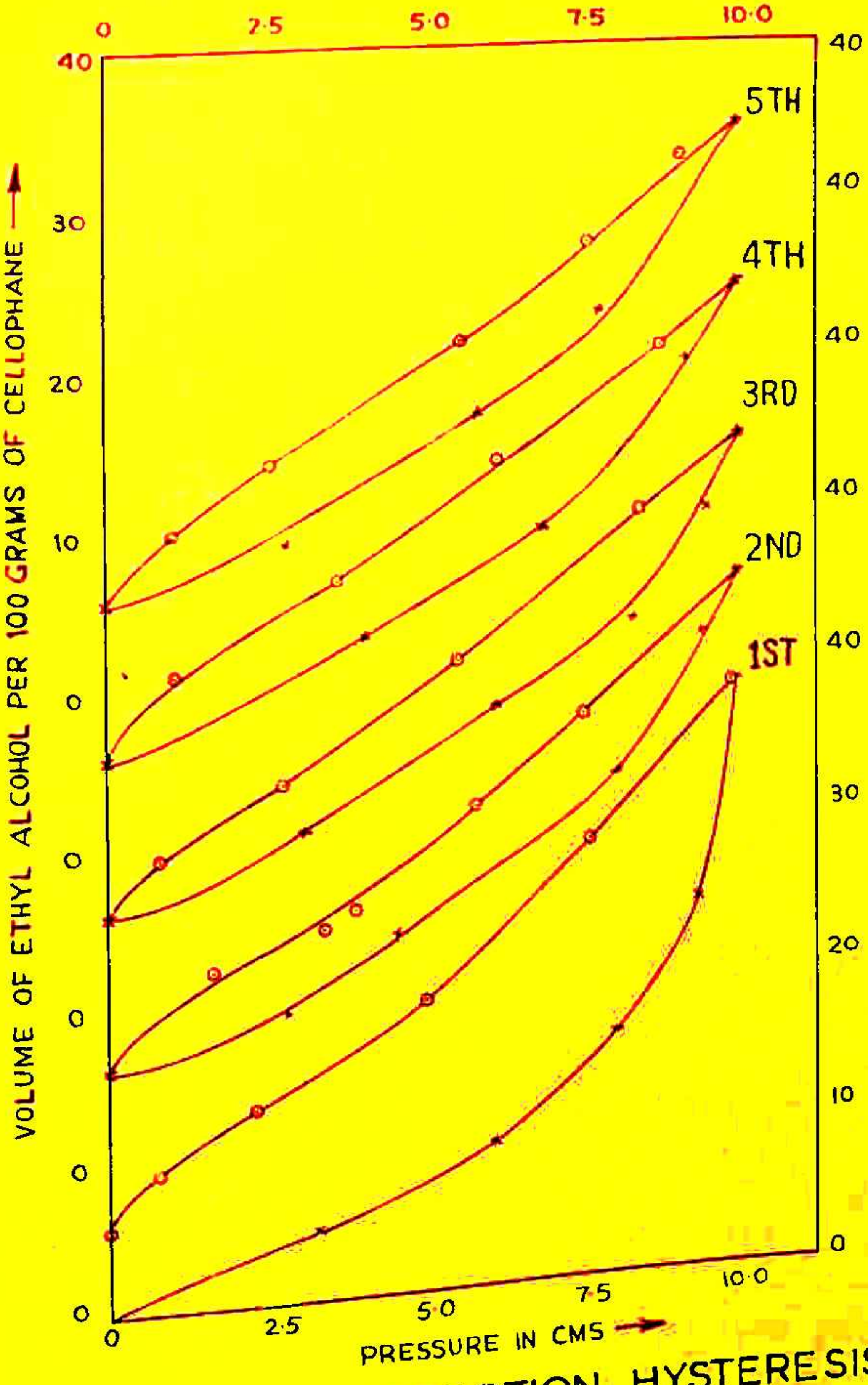


FIG. 38 SORPTION-DESORPTION HYSTERESIS OF ETHYL ALCOHOL ON CELLOPHANE WASHED WITH WATER AT 1ST, 2ND, 3RD, 4TH, AND 5TH CYCLES

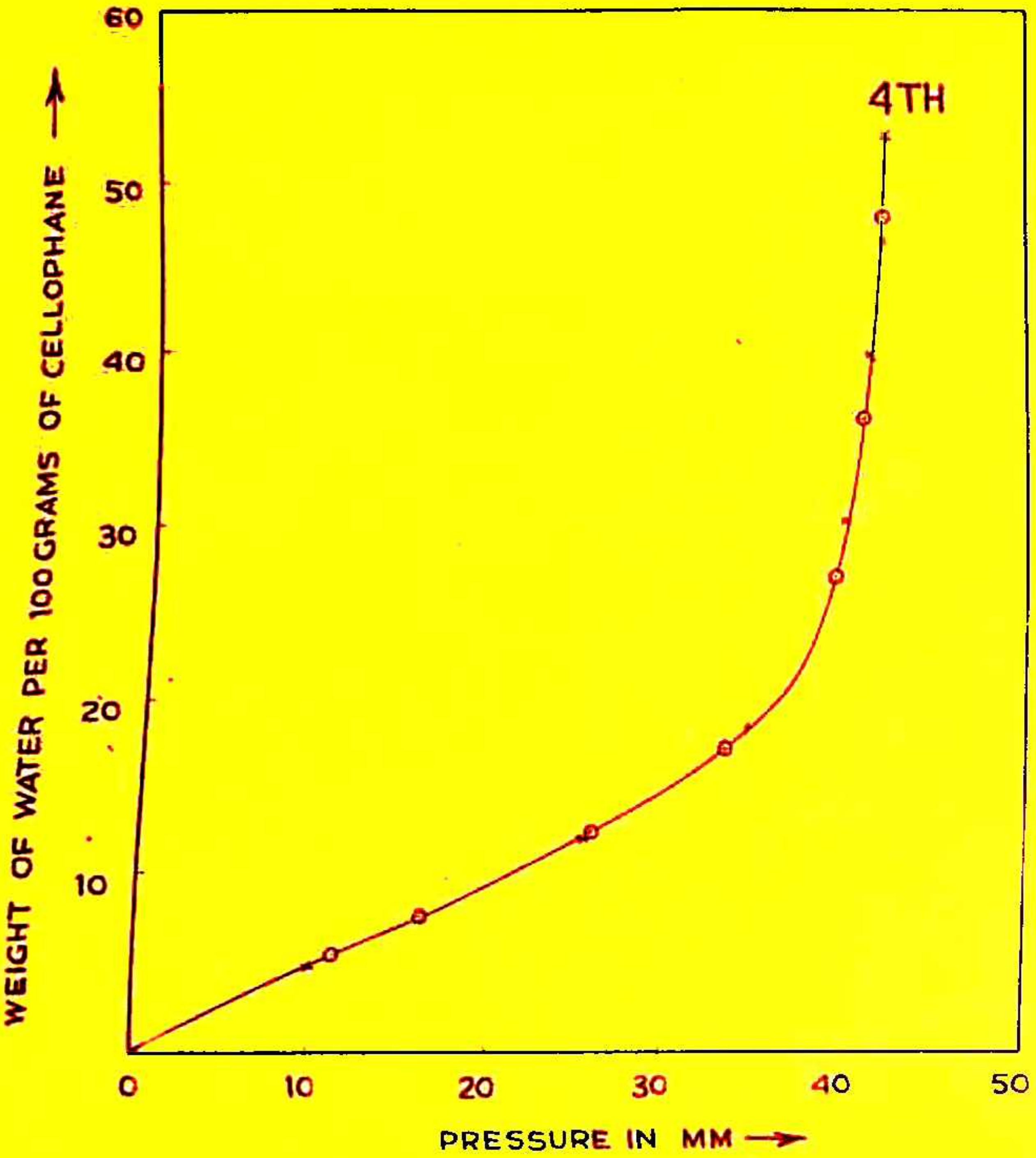


FIG. 39 SORPTION-DESORPTION HYSTERESIS OF WATER ON

The extent of adsorption, in case of **carbon tetrachloride**, was also considerably small. Cellophane was subjected to three integral sorption of carbon tetrachloride vapours. The extent of adsorption was about 0.25%. After three sorptions and desorptions of carbon tetrachloride, the same cellophane film was exposed to water vapour sorption. The sorption-desorption curves obtained at the 4th cycle have been presented in Figure 39. The nature of the 4th cycle of Figure 39 is almost similar with the 3rd cycle of cellophane - water vapour system, Figure 33. This treatment was given to cellophane with a view that water sorption treatment might increase the pore diameters in cellophane, as water is a solvating liquid for cellophane, and consequently cellophane might take up more of carbon tetrachloride vapours. After completing four cycles of sorptions and desorptions with water vapour, cellophane was once again subjected to carbon tetrachloride vapours, but the amount of carbon tetrachloride taken was still small i.e., 0.2 to 0.25%.

Sorption of water vapour on activated cellophane

Figures 40 to 46 present the effect of activation temperature of cellophane on the sorption-desorption hysteresis with water vapour. The sorptive capacities of activated and also unactivated cellophane have been presented in Table XIII.

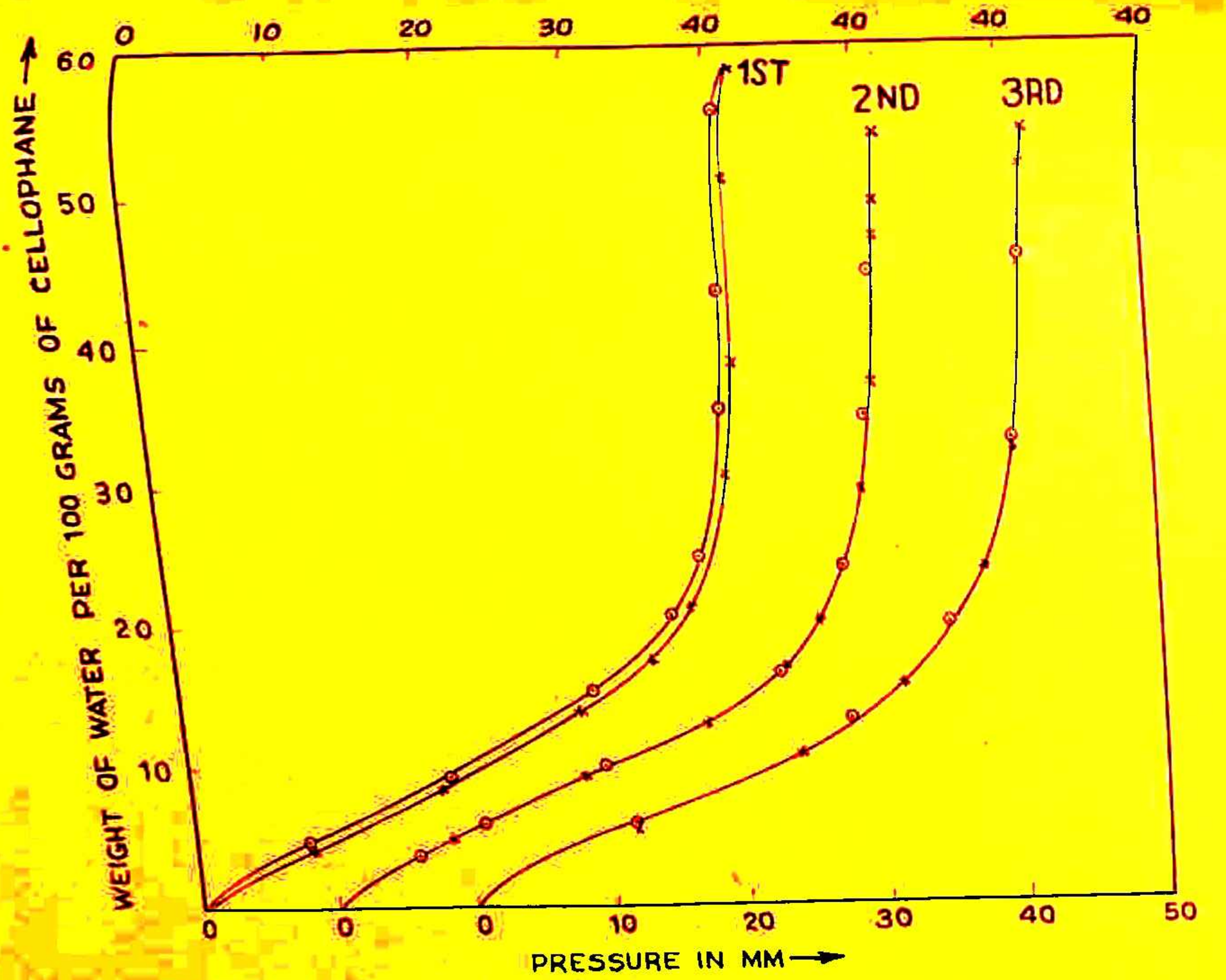
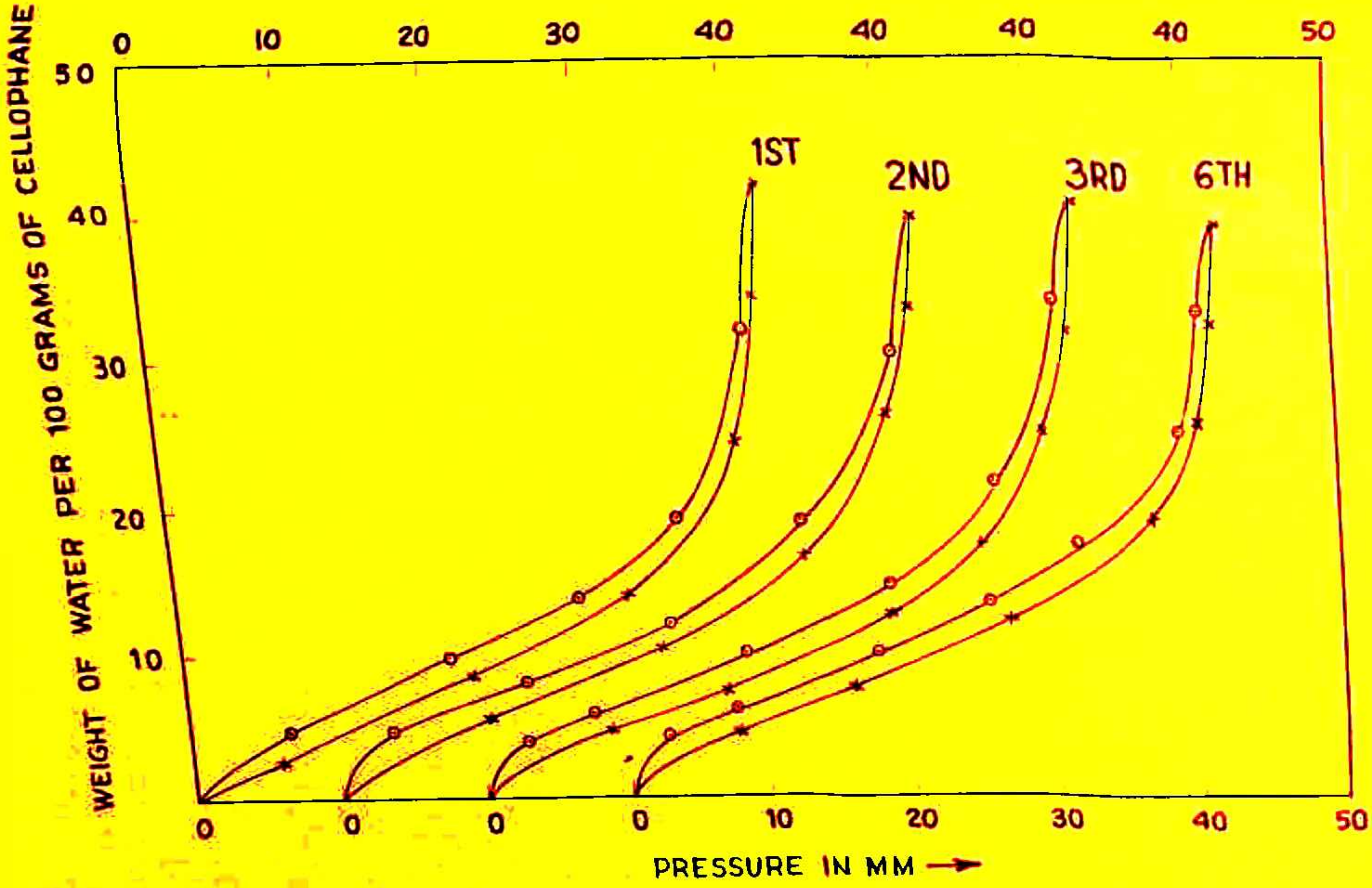


FIG 40 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 60°C) AT THE 1ST, 2ND, AND 3RD CYCLES.



IG41 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 95°C) AT THE 1ST, 2ND, 3RD, AND 6TH CYCLES.

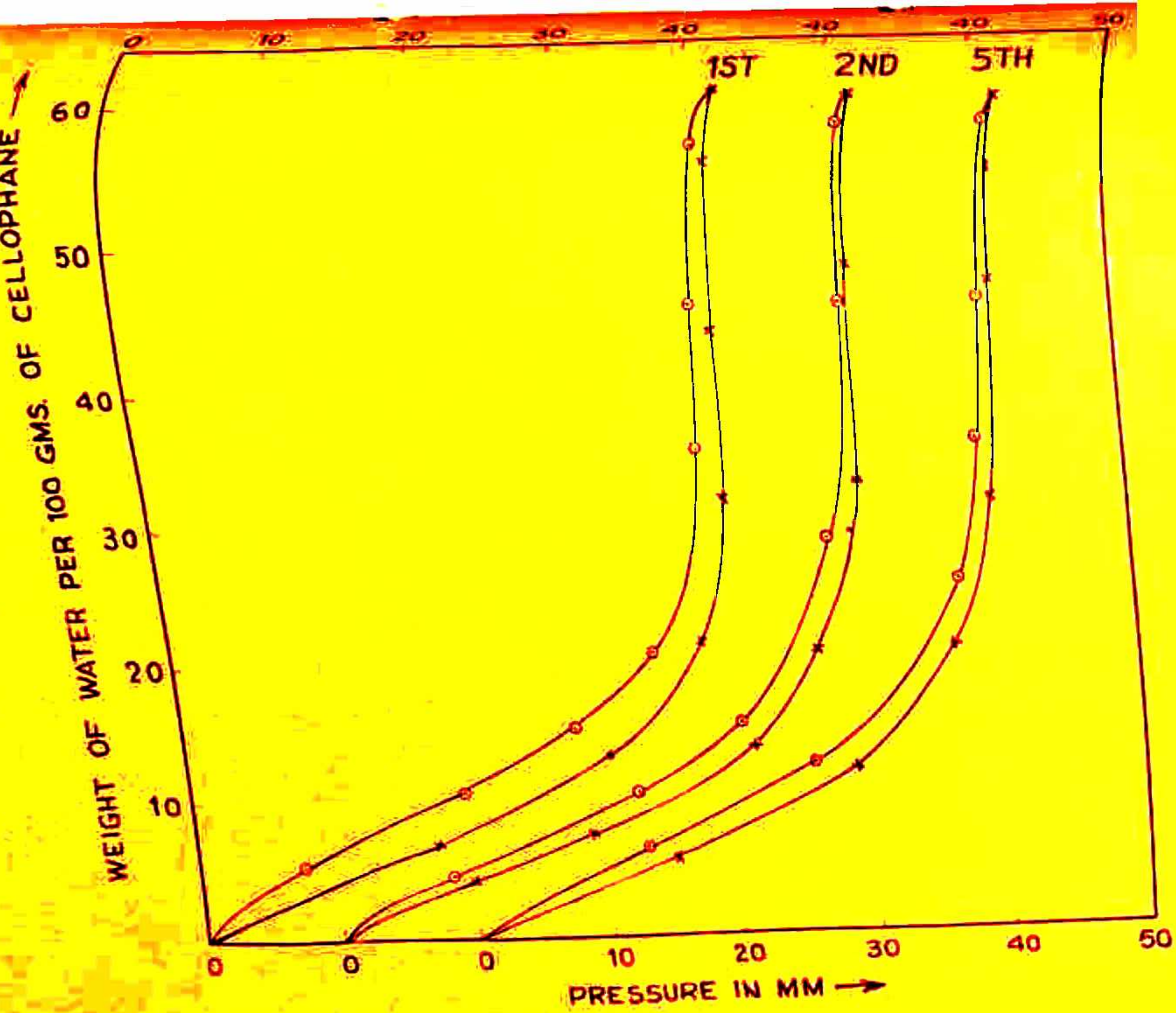


FIG.42 SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 110° C) AT THE 1ST, 2ND, AND 5TH CYCLES.

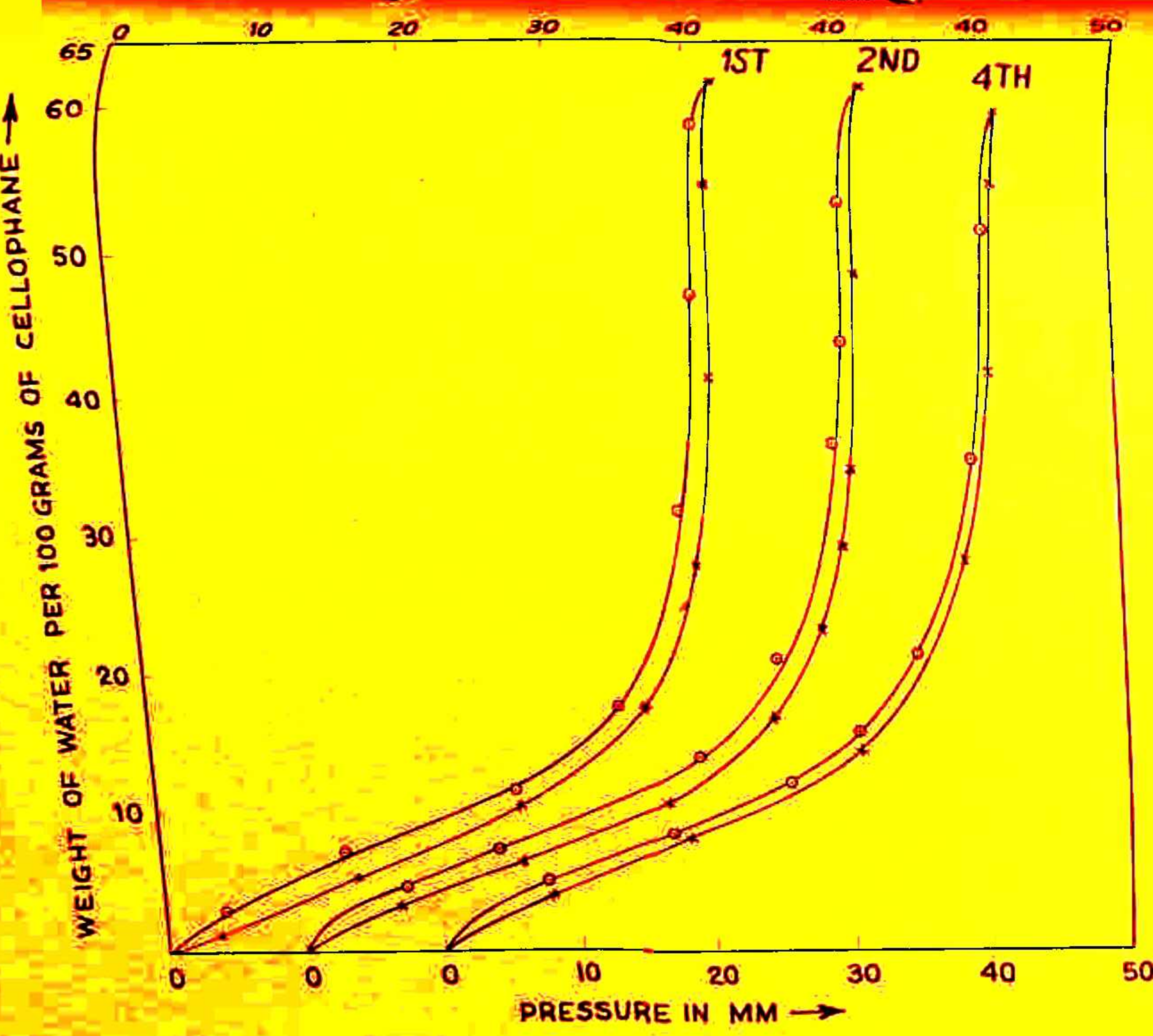


FIG43SORPTION-DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 125°C) AT THE 1ST, 2ND, AND 4TH CYCLES.

RPTION - DESORPTION HYSTERESIS OF WATER ON CELL

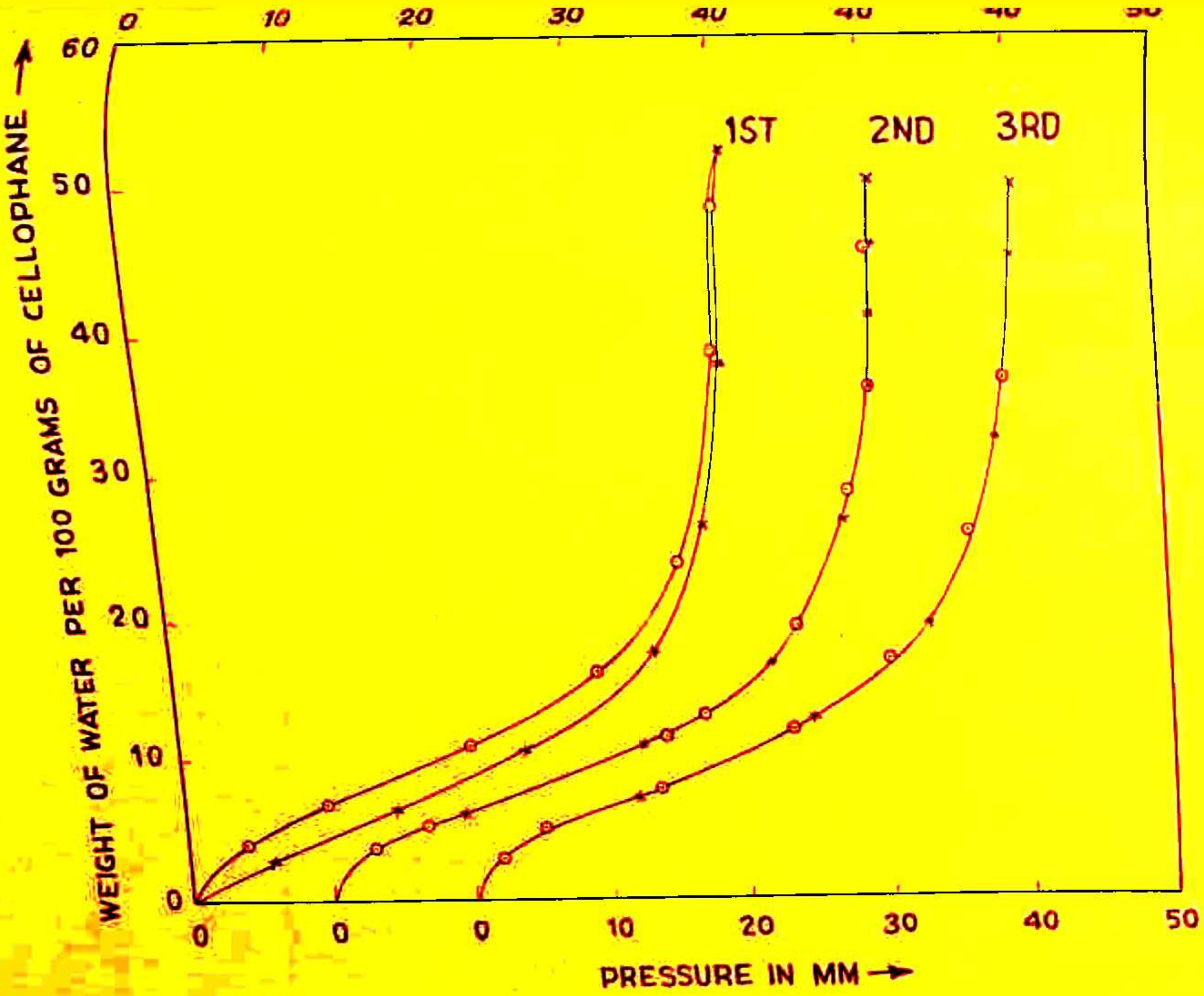


FIG.45 SORPTION - DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 175°C) AT THE 1ST, 2ND, AND 3RD CYCLES.

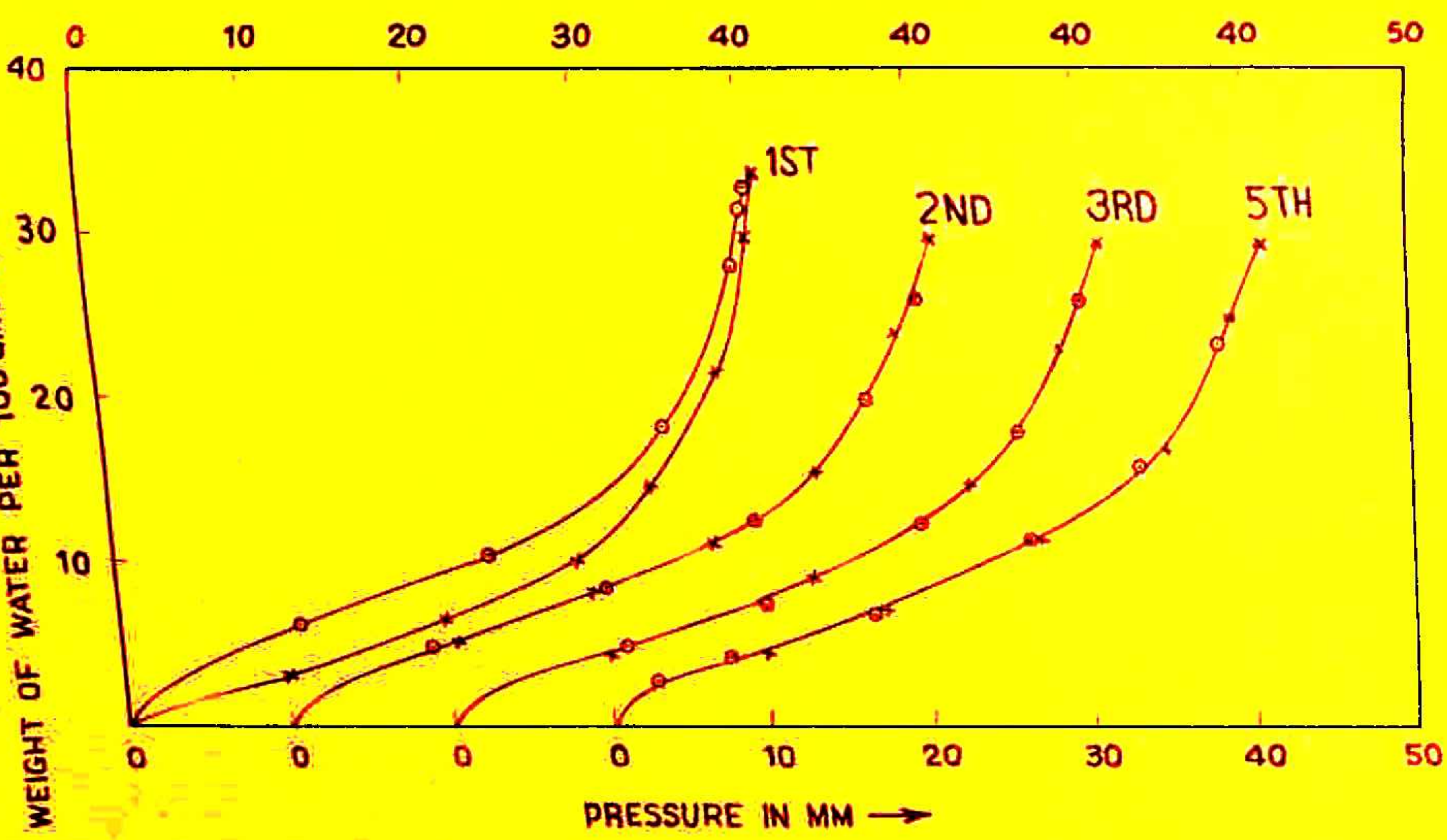


FIG.46 SORPTION - DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (ACTIVATED AT 200°C) AT THE 1ST, 2ND, 3RD, AND 5TH CYCLES.

Table XIII

Sorptive capacities of cellophane activated at different temperatures

Temperature of Activation	No. of cycles	Sorptive capacities
Unactivated(35°C)	3	52.0 - 50.1%
60°C	3	58.2 - 54.0%
95°C	6	42.0 - 39.1%
110°C	5	60.5 - 59.8%
125°C	4	62.0 - 59.5%
150°C	7	67.0 - 66.0%
175°C	3	52.0 - 50.0%
200°C	5	33.5 - 29.5%

Excepting 95°C activated sample, the sorptive capacity of cellophane increases as the activation temperature increases from 35°C to 150°C. After 150°C, the sorptive capacity gradually decreases as the activation temperature increases from 150°C to 200°C. The behaviour of hysteresis loops is very interesting. At lower activation temperatures (35°C to 60°C) the loop shows the tendency to disappear after 1st cycle whereas, at higher activation temperatures (95°C - 150°C), there are permanent hysteresis loops. At still higher activation temperatures (175°C - 200°C), the hysteresis loop again shows the tendency to disappear after the first cycle of sorption and desorption.

Discussion

Sorption of water and organic liquids on cellophane

In the light of the cavity theory (12,13) of hysteresis in conjunction with the swelling property of cellophane, the results obtained on successive sorptions and desorptions of water vapour, lead to interesting conclusions. The commercial cellophane has obviously no pores and cavities as indicated by the absence of the hysteresis effect. Probably, the pore space is all filled with the glycerine. On washing with water, the glycerine is removed and the pore space containing the cavities produce the hysteresis effect in the sorption and desorption of water vapour. As the cellophane can swell in water which is a solvating liquid for cellophane, the cavities disappear and the hysteresis loop disappears in the 2nd and 3rd cycles. There is decrease in the sorption capacity from 73.0% to 50.1%. This is probably due to shrinkage of the network of cellophane owing to the removal of glycerine.

The commercial cellophane, washed with water, was kept soaked in different organic liquids. As a result of this treatment, the swelling property of cellophane was probably affected. Consequently, a permanent and reproducible hysteresis loop even in the 6th cycles of sorption and desorption with water vapour was obtained.Excepting the 1st loop, others are practically identical.

Methyl alcohol, ethyl alcohol and acetone seemed to have altered the nature of the surface of cellophane. Cellophane was rendered less hydrophilic and less swellable. Consequently, the cavity walls have become fairly stable and the entrapping effect persisted. There was a reproducible hysteresis effect in each case. The decrease in the total sorptive capacity is also indicative of the above change.

Excepting methyl alcohol treated cellophane, the nature of the 1st cycle of sorption and desorption was quite interesting. At the end of the 1st cycle,cellophane had suffered a loss in weight which was 5.6% in case of ethyl alcohol and 1.5% in case of acetone treated cellophane. This must be the residual liquid retained by the cellophane even at vacuum of 10^{-2} m.m. This liquid has been displaced by water, by preferential sorption. There was a shift of the zero point at the end of the 1st cycle of sorption and desorption and it remained the same in all subsequent cycles.

The sorption-desorption isotherms of water, methyl and ethyl alcohols showed that the tail end of the hysteresis loops stretched up to the zero pressure in each case. It is indicative of the fact that there are necks of molecular dimension in the pore structure of cellophane. With sorbates of high molecular weights, the extent of adsorption became very small. In fact, there was negligible adsorption of carbon tetrachloride, n-propyl alcohol and n-butyl alcohol. The difference in the amounts of the adsorbate taken up by cellophane can be attributed to the varying accessibilities of the pores present in cellophane.

As stated earlier, cellophane retains, at the end of first sorption and desorption, small amount of 'bound' alcohol which could not be removed even after long evacuation. The amounts of 'bound' sorbates retained by cellophane are presented in Table XIV.

Table XIV

Amounts of 'bound' sorbates retained by cellophane.

Sorbate	Molecular size A°	Bound sorbate cc/100 g
Water	3.5	0.0
Methyl alcohol	4.6	4.0
Ethyl alcohol	5.2	5.5

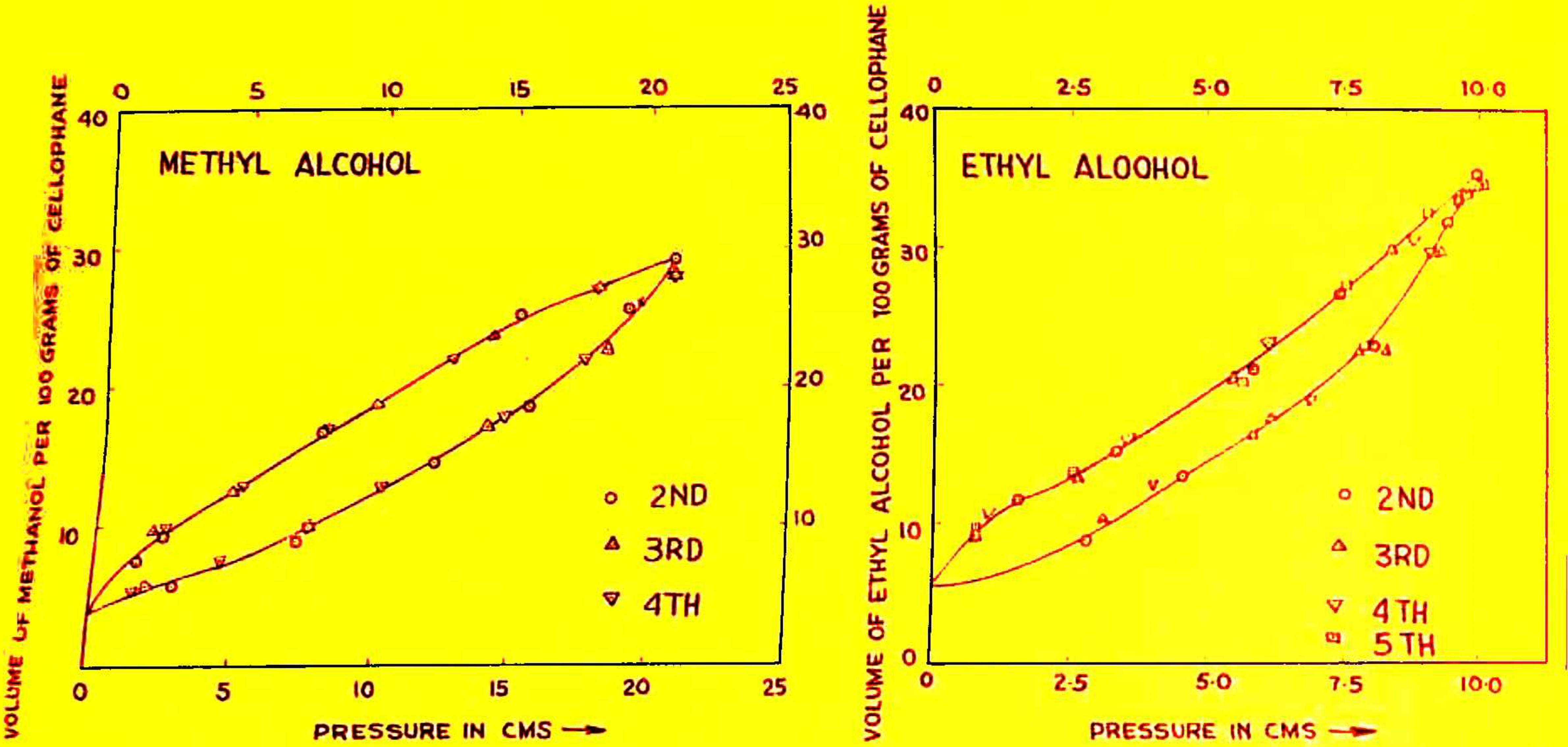


FIG. 47 REVERSIBILITY OF HYSTERESIS LOOPS IN CELLOPHANE-ALCOHOL SYSTEMS.

The above table reveals that the amount of 'bound' sorbate varies directly with the molecular size of the sorbate.

One noteworthy feature of the cellophane - alcohol systems is the remarkable reproducibility of the hysteresis loops after the first sorption and desorption, Figure 47. It indicates that all the irreversible changes have occurred during the first cycle and in subsequent cycles, cellophane behaves reversibly towards further sorptions and desorptions.

Effect of activation temperature

To facilitate discussion, the hysteresis loops obtained at different activation temperatures of cellophane are presented in Figure 48.

The changing pattern of the hysteresis loop indicates the change in the structure of cellophane under the influence of heat. As has been discussed earlier, the size and the shape of the hysteresis loop are dependent on the size of pores, their distribution and shape.

Macromolecules, in general, tend to coil up under the influence of heat - by thermal motion. This behaviour is more pronounced in the case of elastomers, where there is a free rotation of C-C bonds. It appears that molecules of regenerated cellulose undergo thermal vibration at elevated temperatures and the solid tends to acquire a more

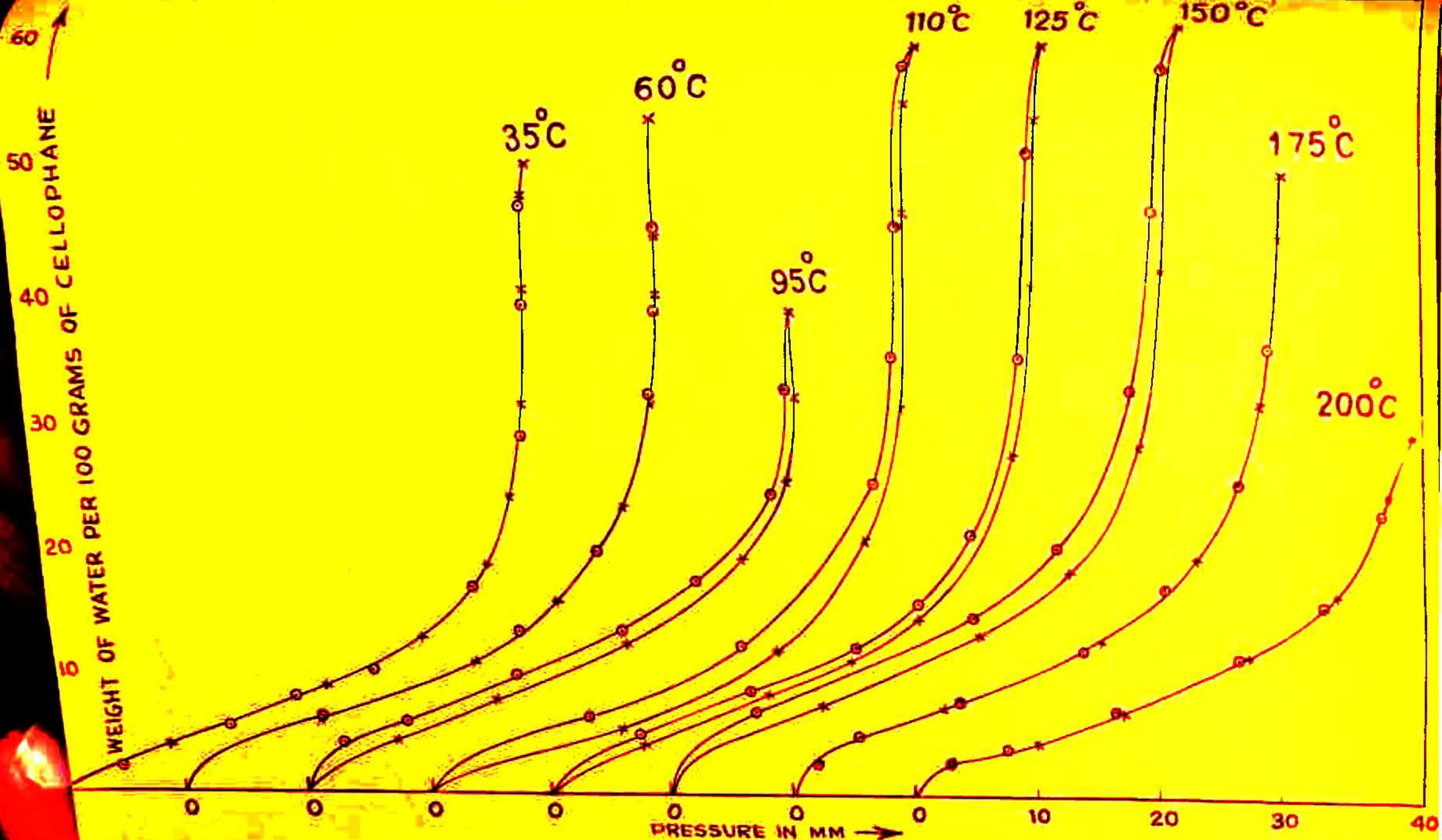


FIG. 48

SORPTION - DESORPTION HYSTERESIS OF WATER ON CELLOPHANE (WASHED WITH WATER) ACTIVATED AT 35°C, 60°C, 95°C, 110°C, 125°C, 150°C, 175°C AND 200 stable conformation. This results in readjustment in the size and shape of micro pores and capillaries within the solid which is ultimately responsible for the hysteresis phenomenon.

From Figure 48, it is apparent that this kind of change occurs in cellophane above activation temperature of 60°C. From 60°C to 150°C activation temperatures, cellophane appears to have acquired a rigid pore structure, the walls of the capillaries and pores have become tough and uncollapsable; they entrap water and thus, are responsible for the permanent hysteresis effect which persists over repeating sorption-desorption cycles.

Another change seems to occur beyond activation temperature of 150°C, due to which the hysteresis loop disappears in second and subsequent cycles. It can be simultaneously noted that total amount of water sorbed also reduces. Reduction in total sorption value at elevated temperature may be either due to crystallization or due to breaking of chains to smaller fragments which result in the close packing of the material. Cellophane was observed to have acquired a slight brownish colour at elevated temperatures which supports the possibility of breaking of the chains. It is expected that at still higher temperatures the sorption value will rise as has been observed in activated starch-water vapour system(page85).

It has been observed earlier (96), that a change in the dimension of cellulose derivatives occurs with increasing temperatures, confirming the fact that with increase in temperature the chains become more freely orienting. In case of elastomers, the internal hinderance to free orientation is small and the type of observations obtained with cellophane should be more pronounced with rubbery materials like polybutadiene or natural rubber.

Diffusion and reorientation of molecules in solid polymeric bodies is a time dependent process. At higher temperatures the rate of diffusion is higher and a stable conformation is achieved in lesser time. At lower temperatures also the stable confirmation can be achieved but will need more time. It is likely, if the activation time is increased at 60°C, the solid will acquire a stable conformation and permanent hysteresis loops like 110°C activated sample (Figure 48) will be obtained. Also, the loops between 60°C and 150°C should all be almost identical if sufficient time is allowed for activation treatment.

Applications of BET and FHH equations

The water vapour isotherms of cellophane (Figure 33) show not very clearly defined "knee". This suggests that the adsorption is co-operative in nature. BET equation has been applied to calculate the monolayer capacity (x_m)

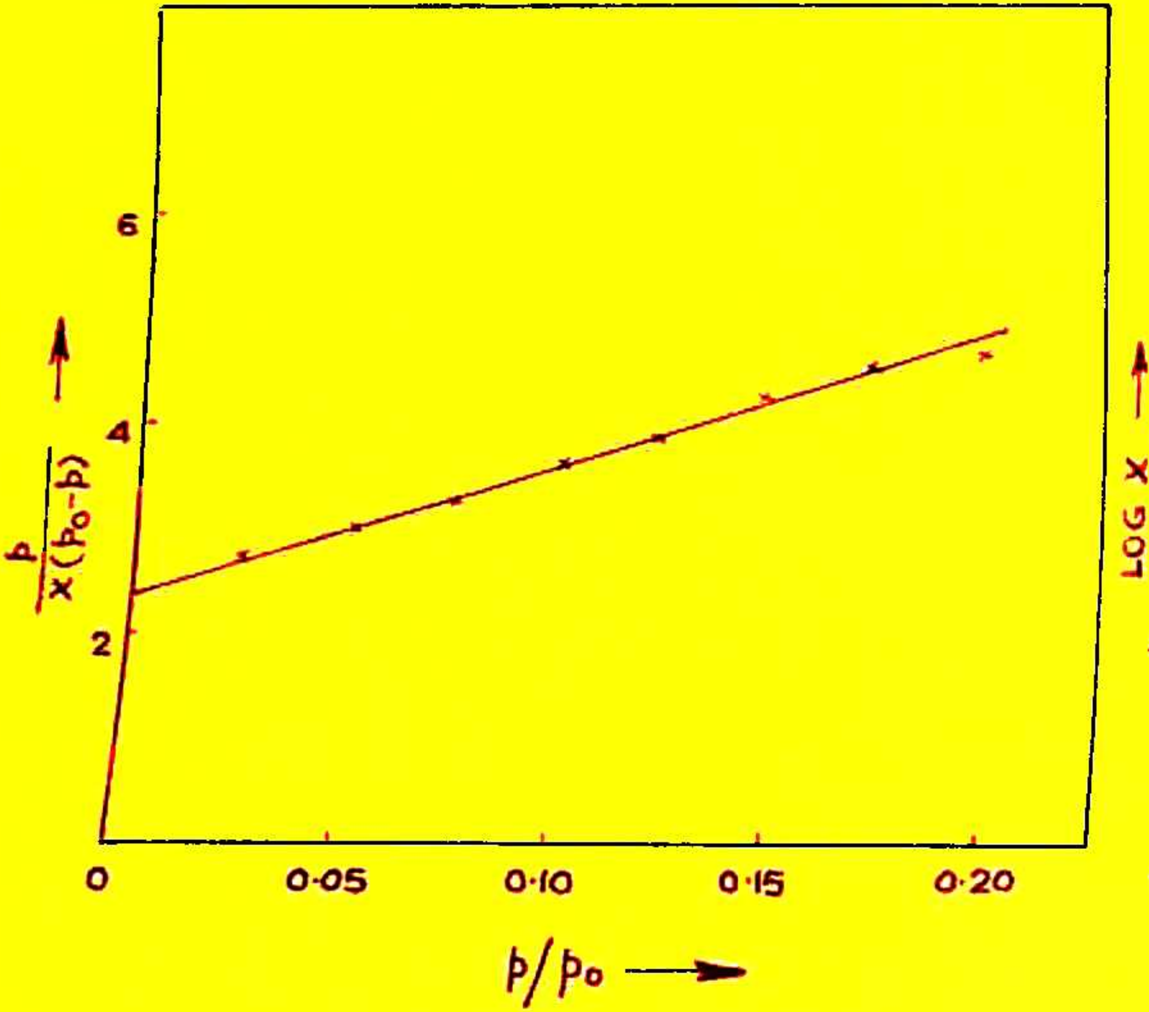


FIG 49 BET PLOT FOR WATER VAPOUR SORPTION ON CELLOPHANE.

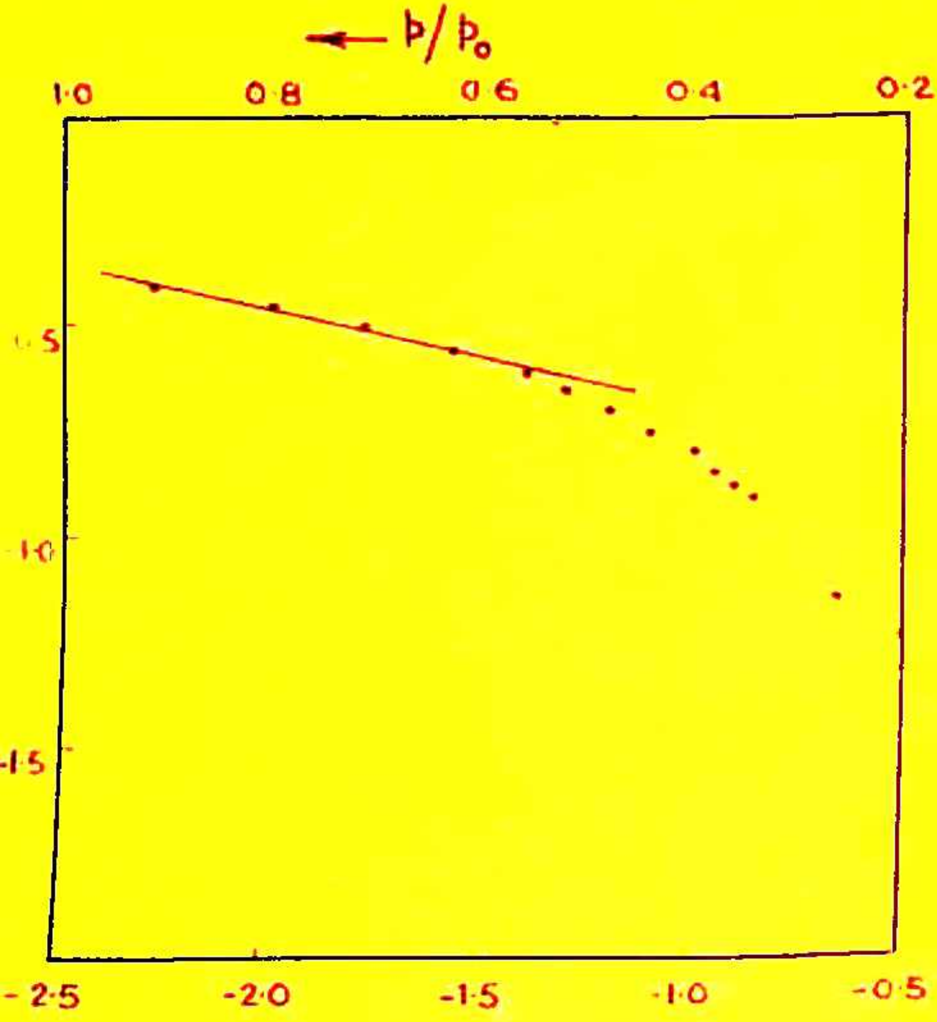


FIG.50 F-H-H PLOT FOR WATER VAPOUR SORPTION ON CELLOPHANE.

in a manner analogous to that applied to type II isotherms. The BET plot (Table XV) yielded straight line, Figure 49.

Table XV

BET plot for the sorption of water vapour on cellophane.

Relative vapour pressure p/p_o	Sorption g/g x	$\frac{p}{x(p_o-p)}$
0.024	0.0065	3.79
0.048	0.0120	4.20
0.072	0.0170	4.58
0.096	0.0210	5.00
0.120	0.0260	5.27
0.145	0.0300	5.60
0.169	0.0330	6.14
0.193	0.0370	6.45

From the slope and intercept of the line, the specific surface area (S) of cellophane was calculated as usual (10). The monolayer capacity and specific surface area were found to be 0.052 and 184.4 m^2/g respectively.

The number of water molecules contained in the monolayer over 1 gram of cellophane were also calculated and found to be 17.4×10^{20}.

There has been wide discussion in the literature (9/)

regarding the applicability of the BET equation to the sorption of water vapour by swelling polymer network. It has also been pointed out (96) that the significance of a BET monolayer in such systems is questionable. The present water sorption data, when plotted according to the isotherm equation of Frenkel (97), Halsey (98) and Hill (99) yielded wide deviations from linearity (Figure 50). The linear portion of F-H-H isotherm can correspond to multilayer adsorption at high relative pressures. Table summarizes F-H-H plots. (Table XVI).

Table XVI

F-H-H- plots for the water vapour sorption of cellophane.

p	p_o	$\log \log \frac{p_o}{p}$	x	$\log x$
4.10	4.15	-2.28	0.40	-0.398
4.05	4.15	-1.98	0.35	-0.456
4.0	4.15	-1.80	0.31	-0.509
3.9	4.15	-1.57	0.26	-0.585
3.8	4.15	-1.42	0.24	-0.620
3.7	4.15	-1.30	0.22	-0.658
3.6	4.15	-1.21	0.20	-0.699
3.5	4.15	-1.13	0.18	-0.745
3.4	4.15	-1.06	0.16	-0.796
3.3	4.15	-1.00	0.15	-0.824
3.2	4.15	-0.95	0.14	-0.854
3.1	4.15	-0.898	0.14	-0.854
3.0	4.15	-0.85	0.13	-0.886
2.5	4.15	-0.66	0.095	-1.155
2.0	4.15	-0.50	0.070	-1.260
1.5	4.15	-0.30	0.055	-1.400
1.0	4.15	-0.21	0.044	-1.602

The curved nature of the major portion of the F-H-H isotherms indicates that either capillary condensation is occurring in very fine pores or that the adsorbent is undergoing swelling or physical changes as a result of the sorption process. Brandt and Budrys (100) have published similar curves for the sorption of various vapours by polypeptides.

*****

References

1. Howsmon, J.A., "Cellulose and cellulose derivatives" Pt.1, Ed. E. Ott., H.M. Spurlin, Interscience Publishers, 1954, 393.
2. Bender, M., and Foster Jr., W.H., Trans. Faraday Soc. 1968, 64, 549.
3. Newns, A.C., Trans. Faraday Soc., 1968, 64, 551, 3147.
4. Fainberg, F.Z., and Mikhailov, N.V., Khim Volokna, 1967, 3, 43.
5. Polcin, J., Papir Celul, 1966, 21, (2), 355.
6. Daruwala, E.H., and Shet, R.T., Proc. Technol. Conf. 5th SITRA, Coimbtore, India, 1963, 177.
7. Daruwala, E.H., and Shet, R.T., J. Polymer Sci., 1964, 2(2), 943.
8. Morrison, J.L., and Dzieciuch, M.A., Can. J. Chem., 1959, 37, 1379.
9. Urquhart, A.R., J. Text. Inst., 1929, 20, T125.
10. Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 1938, 60, 309.
11. Dubinin, M.M., Quart. Rev. Chem. Soc., 1959, 9, 101, Chem. Rev. 1960, 60, 235.
12. McBain, J.W., J. Am. Chem. Soc., 1935, 57, 699.
13. Rao, K.S., J. Phys. Chem., 1941, 45, 500.
14. Bhatia, R.K.S., Chem. Age India, 1969, 2, 20, 119.
15. de Bruyne, N.A., Nature, 1938, 142, 570.
16. Kress, O., and Bialkowsky, Paper Trade J., 1931, 35, 20, 93.
17. Stamm, A.J., and Tarkow, H., J. Phys. Chem., 1950, 54, 745.
18. Kumar, U.B., Norsk Skogsind, 1957, 11, 259; 1958,12,337.
19. White Jr., H.J., and Eyring, Text. Res. J., 1947,17,523.

20. Newsome, P.T., and Sheppard, S.E., Ind. Eng. Chem., 1934, 26, 285.

21. Barkas, W.W., Trans. Faraday Soc., 1942, 38, 194.

22. Compbell, W.B., Ind. Eng. Chem., 1934, 26, 218.

23. Welo, L.A., Hilda M Ziifle, and Loeb, L., Text. Res. J., 1952, 22, 4, 254.

24. Conard, C.M., Ind. Eng. Chem. Anal. Ed. 1944, 16, 745.

25. Kettering, J., Ind. Eng. Chem. Anal. Ed., 1946,18,275.

26. Suchecki, S.M., Text. Indi. 1961, 126, 125, 23, 25.

27. Stead, G., Can. Text. J., 1964, 81 (4), 47.

28. Sisson, W.A., in E. Ott, ed, Cellulose and cellulose Derivatives (High Polymers, Vol.V), Interscience, New York, London, 1943, 203-285.

29. Hermans, P.H., Physics and Chemistry of cellulose fibres, Elsevier, New York, 1949.

30. Polanyi, M., Naturwissenschaften, 1921, 9, 288.

31. Sponsler, O.L., J. Gen. Physiol, 1926, 9, 677.

32. Meyer, K.H., and Mark, H., Z. Physik. Chem., 1929, 132, 115.

33. Meyer, K.H., and Misch, L., Ber., 1937, 70B, 266.

34. Gross, S.T., and Clark, G.L., Z. Krist. 1938, A99, 357.

35. Lamport, D.A., in "Advances in Botanical Research" Vol.II, New York, Academic Press, 1965.

36. Katz, J.R., Trans. Faraday Soc., 1933, 29, 279.

37. Preston, J.M., and Nimkar, M.V., J. Text. Inst., 1949, 40, 674.

38. Morton, W.E., and Hearle, J.W.S., "Physical properties of fibres", Butterworth Publications, London, 1962, 218.

39. Hartely, G.S., Trans. Faraday Soc., 1946, 6, 4213.

40. Horiike, K., and Kato, S., J. Japan Wood. Res. Soc., 1959, 5, 181.

41. Mckenzie, A.W., Aus. J. Appl. Sci., 1957, 8, 35.

42. Honeyman, J. Recent Adv. in Chem. of cellulose and Starch, Heywood and Co., London (1959).

43. Fox, H.W., and Zisman, W.A., J. Colloid. Sci., 1950, 5, 514; 1952, 7, 109.

44. .Kanamaru, K., and Chao, J., Kolloid-Z., 1938, 84, 85.

45. Lauer, K., Kolloid-Z., 1944, 107, 86.

46. McBain, J.W., and Fergusion, R., J. Phys. Chem., 1927, 31, 564.

47. Wahba, M., and Nashed, S., J. Text. Inst. 1957, 48,T1.

48. Benson, S.W., and Richardson, R.L., J. Am. Chem. Soc., 1955, 77, 2585.

49. Arnell, J.C., and McDermot, Proc. Intern. Congr. Surface Activity, 2nd, Lond., 1957, 113.

50. Rao, K.S., Curr. Sci., 1940, 9, 68.

51. Seborg, C.O., Ind. Eng. Chem., 1937, 29, 169.

52. Mann, J., and Marrinan, H.J., Trans. Faraday Soc., 1956, 52, 481.

53. Beever, D.K., and Valentine, L., J. Appl. Chem., 1958, 8, 103.

54. Beever, D.K., and Valentine, L., J. Text. Inst., 1958, 49, T95.

55. Majury, T.G., J. Soc. Dyers Col., 1954, 70, 442, 445; 1956, 72, 41.

56. Marsden, R.J.B., and Urquhart, A.R., J. Text. Inst., 1942, 33, T105.

57. Bagley, E., and Long, F.A., J. Am. Chem. Soc., 1955, 77, 2172.

58. Jeffries, R., J. Text. Inst. 1960, 51, T399.

59. Ray, B.R., and Bartell, F.E., J. Phys. Chem., 1963, 57, 259.

60. Jeffries, R., Trans. Faraday Soc., 1957, 53, 12, 1592.

61. Park, G.S., J. Poly. Sci., 1953, 11, 97.

62. Kokes, R.J., and Long, F.A., J. Am. Chem. Soc., 1953, 75, 2232.

63. Kokes, R.J., Long, F.A., and Hoard, J.L., J. Chem. Phys., 1952, 26, 1711.

64. Crank, J., J. Poly. Sci., 1953, 11, 151.

65. Wiegerink, J.G., Text. Res. J., 1940, 10, 357.

66. Urquhart, A.R., and Williams, A.M., Text. Inst. J. 1924, 15, T559.

67. Wahba, M., and Nashed, S., J. Text. Inst., 1958, 49, T519.

68. Kataocka, Kogyo Gijutsuin Seni Kogya Schikenshi Kenkyu Hokoku, 1958, No.45, 7.

69. Moncrieff, R.W., 'Artificial fibres' National Trade Press, Ltd., 1954, p.162.

70. Barrer, R.M., and Barrie, J.A., J. Poly. Sci., 1958, 28, 377.

71. Beever, D.K., and Valentine, L., J. Poly. Sci., 1958, 32, 5210.

72. Chabert, J., Bull. Inst. Fr. Text. Fr., 1966, 20 (125), 553.

73. Fugassi, P., and Ostapchenko, G., Fuel, 1959, 38, 259.

74. Newns, A.C., J. Poly. Sci., 1959, 41, 425.

75. Urquhart, A.R., J. Text. Inst. 1930, 21, T499.

76. Gregg, S.J., and Sing, K.S.W., "Adsorption, Surface area and Porosity", Academic Press, London, and New York, 1967, p.154.

77. Timmermans, J., Physico-chemical constants of pure organic compounds, Elsevier Publishing Co., Inc., 1950.

78. Hand-book of chemistry and physics, 44th Edition, Chemical Rubber Publishing Company, Cleveland Ohio, 1963.

79. Gregg, S.J. and Sing, K.S.W., "Adsorption, surface area and Porosity", Academic press, London and New York, 1967, p.54.

80. Moelwyn-Hughes, E.A., "Kinetics of Reactions in Solutions", Clarendon press, Oxford, 1947, p.7.

81. de Boer, J.H., "The structure and properties of porous materials", Butterworth London, 1958, p.68.

82. Rao, K.S., J. Maysore Univ., 4, Pt.1 (1943), p.1-15.

83. Peirce, F.T., J. Text. Inst., 1924, 15, T501.

84. Walker, A.C., Text. Res. J., 1937, 7, 229.

85. Argue, G.H., and Maass, O., Can. J. Res., 1935, 1313, 156.

86. Brown, K.C., Mann, J.C., and Peirce, F.T., J. Text., Inst., 1930, 21, T186.

87. Smith, S., J. Am. Chem. Soc., 1947, 69, 646.

88. Hauser, P.M., and McLaren, A.D., Indus. Eng. Chem., 1948, 40, 112.

89. Pauling, L., J. Am. Chem. Soc., 1945, 67, 555.

90. Simril, V.L., and Smith, S., Indus. Eng. Chem., 1942, 34, 226.

91. Stamm, A.J., Aus. Pulp and Paper, Ind. Tech. Assoc., Proc. 1955, 10, 244.

92. Stamm, A.J., J. Phys. Chem., 1956, 60, 76.

93. Kh.Usmanov and Ya V Park, Doklady Akad. Nauk. Uzbek. S.S.R., 1953, No. 12, 25.

94. Dean, R.B., "Modern Colloids", D.Van Nostrand Com.Inc.N.Y.1948, p.27.

95. Dean, R.B., "Modern Colloids". D. Van Nostrand Com.Inc.N.Y. 1948.

96. Bettelheim, F.A., J. Colloid. Interface Sc., 1967, 23, 301.

97. Frenkel, J., "Kinetic Theory of Liquids", Oxford Univ. Press, London, 1946.

98. Halsey, G.D., J. Chem. Phys., 1948, 16, 931.

99. Hill, T.L., Adv. Catal., 1952, 4, 212.

100. Brandt, W.W., and Budrys, R.S., J. Phys. Chem., 1965, 69, 600.

******

CHAPTER VI

SORPTION-DESORPTION HYSTERESIS IN NATURAL GUMS

SORPTION-DESORPTION HYSTERESIS IN NATURAL GUMS

Abstract

The natural gums - Karaya, Sudan, Guar and Sandarac have been used in sorption-desorption studies with water and ethyl alcohol. All the gums show decrease in size and disappearance of the hysteresis loop on successive cycles of sorptions and desorptions of the sorbate. Gum Karaya and Sandarac show greater tendency of the hysteresis loop to decrease in size and disappearance than gum Guar and Sudan. This difference in the tendencies is related to the structure of gums.

Introduction

Natural gums are highly swelling, high polymers with enough dissociable groups to make them colloidal electrolyte. The gums exhibit such a wide spectrum of physical and chemical properties that it is difficult to devise a means of classification without considering a large number of exceptions. Until quite recently gums were classified, as recommended by the early investigators, according to their behaviour when treated with water (1). They are generally divided into two main groups (2,3): 1) soluble gums - typified by gum arabic and similar gums, which dissolve in water forming more or less transparent, viscous and adhesive solutions and 2) insoluble gums - which when placed in water absorb it and swell into a thick jelly or with sufficient water present finally breakdown into a very thick translucent solution. The best known gums belong to this group are gum tragacanth and the tragacanth substitute gums such as Karaya and Kutira gums.

There are also gums with properties intermediate between the above two groups and these have been termed "semi-insoluble gums". Example of this class of gum is Persian insoluble gum.

Natural gums, proteins and synthetic ion exchange resins, all of which possess the common properties of hydration and swelling in water have shown a common behaviour in sorption-desorption hysteresis, i.e., the disappearance of the hysteresis loop initially exhibited or the gradual decrease in size of the hysteresis loop in successive sorptions and desorptions and the final disappearance. Elworthy and George (4) have studied sorption and desorption of water on sodium ghattate. Calcium arabate has been studied by Rao (5) earlier. In the present chapter the behaviour of some more natural gums 1) Gum Karaya 2) Gum Guar 3) Gum Sudan and 4) Gum Sandarac has been presented.

Gum Guar was obtained from the Department of Pharmacy, B.I.T.S., and imported samples of other gums were obtained from M/s Prachi Gobeson Limited, Calcutta.

All the samples used were in the form of powder and the grain size between those of 100 and 200 mesh B.S.S. was chosen.

Structure and composition of Gums

The molecular structures of the plant gums ranks amongst the most complicated ones known to organic chemists. All the gums possess highly complicated branched structures involving several different sugar residues. The gums have been placed into different groups according to the main structural features of the carbohydrates. Gum guar has a D-galactopyranose branch on every other D- mannopyranose unit (6,7). It is derived from the seed of the guar plant, cyamopsis tetragonolobus, family Leguminosa. Guaran, a D-galacto-D-mannoglycan (1,2), is a straight chain mannan with single membered galactose branches. The D-mannopyranose units are joined by β-(1→4) linkages, and single D-galactopyranose units are joined to this chain by α-(1→6) linkages (7). Gum Karaya is the name given to the dried exudation of the Sterculia urens tree. It is an acetylated polysaccharide which is characterized by an acidic nature and relative insolubility. The acid number has been found to vary from 13.4 to 22.7 (8,9) and molecular weight 9,500,000 as determined by Kubal (10) using svedberg ultra centrifuge method. Quantitative determinations revealed the following hydrolytic components: D-galacturonic acid (43)parts, D-galactose (14)parts, L-rhamnose (15 parts) (11). Gum Sudan belongs to galactan group in which (1→3) linkages are located largely in the main chains and (1→6) linkages in the side chains. The principal sugar residues present in the molecule are D-galactose, L-arabinose, D-glucuronic acid and L-rhamnose in some cases. Gum Sandarac is obtained from Tetraclinus articulata which belongs to a monotypic genus family. Sandarac contains about 1% of volatile oil but consists mainly of crystalline inactive pimaric acid (Sandara copimaric acid, 85%) and small amounts of sandaracinic and callitrolic acid (12).

The plant gums are amorphous (13) substances containing C, H and O and they are members of carbohydrate group. However, in some cases evidence of crystallinity has been obtained (14). The plant gums are hydrophilic substances and are neutral salts of complex polysaccharide acids, composed of hexose residues, uronic acid residues, pentose residues and methyl pentose residues, which are joined together in the most diverse manner within the same molecule.

With the exception of gum tragacanth, which contains

D-galacturonic acid units, the plant gums are distinguished by the fact that D-glucuronic acid is the acid component present in them all. The D-glucuronic acid component is present in the pyranose form. The hexose encountered in plant gums are D-galactose and D-mannose and they too have the pyranose form. The pentose arabinose is always found in the furanose form and is a member of the L-series of sugars while xylose which occurs in the pyranose modification, belongs to the D-series. The methyl pentose found in plant gums are L-rhamnose and L-fucose and these assume the pyranose structure.

The chemical behaviour and water solubility of the gums (15,16) depend on the presence of hydroxyl groups which can form intramolecular hydrogen bonding and hydrogen bonding with water molecule. Structures containing immense arrays of -OH group can hold, by hydrogen bonding, large proportions of water molecules. These water molecules are removable with greater and greater difficulty as the process of drying goes on and hydrogen bonding between -OH groups of macromolecule itself gradually replaces bonding with the solvent. At this stage a highly viscous syrup is produced which becomes hard and glass like on further drying. The hard glass like dehydrated gum resists solution in water owing to intramolecular hydrogen bonding and dissolves only after a prolong period of digestion during which the gum swells markedly before dispersing.

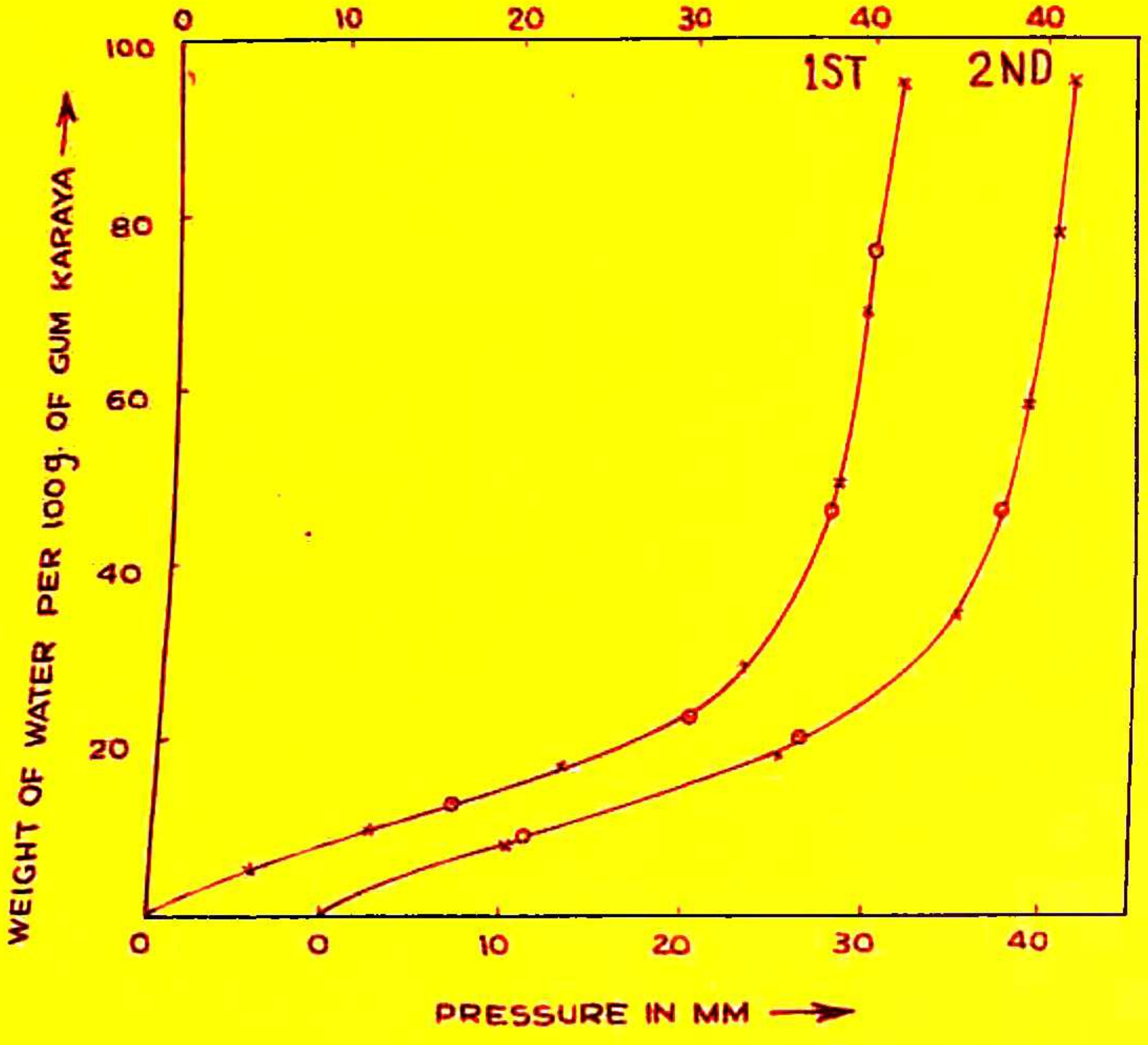


FIG. I SORPTION-DESORPTION HYSTERESIS OF WATER ON GUM KARAYA AT THE 1ST AND 2ND CYCLES.

The details of these processes are still in large measure obscure but physico chemical studies of viscosity relationships, gel formation, etc., have shown that they are highly complicated and markedly dependent on the presence of ionizable groups (15) such as -COOH, in the molecular structure. The difference in H bond formation is probably responsible for the variation in properties of the gums.

In the present studies, the differences in the behaviour of different gums towards sorption is attributed to the difference in degree of intra and intermolecular hydrogen bonding and also hydrogen bonding with sorbate.

Results

Sorption and desorption studies with Karaya Gum with water vapour have been continued up to 2nd cycles, Figure 1. The amounts of water taken up at saturation pressure of water in the 1st and 2nd cycles are 94.6% and 95.0% respectively.

With Guar gum, Figure 2, the sorption-desorption studies have been continued up to 9th cycles. The sorptive capacities in the 1st, 3rd, 5th and 9th cycles are 66.1%, 64.8%, 62.1% and 62.3%, respectively. The study took about 3 months.

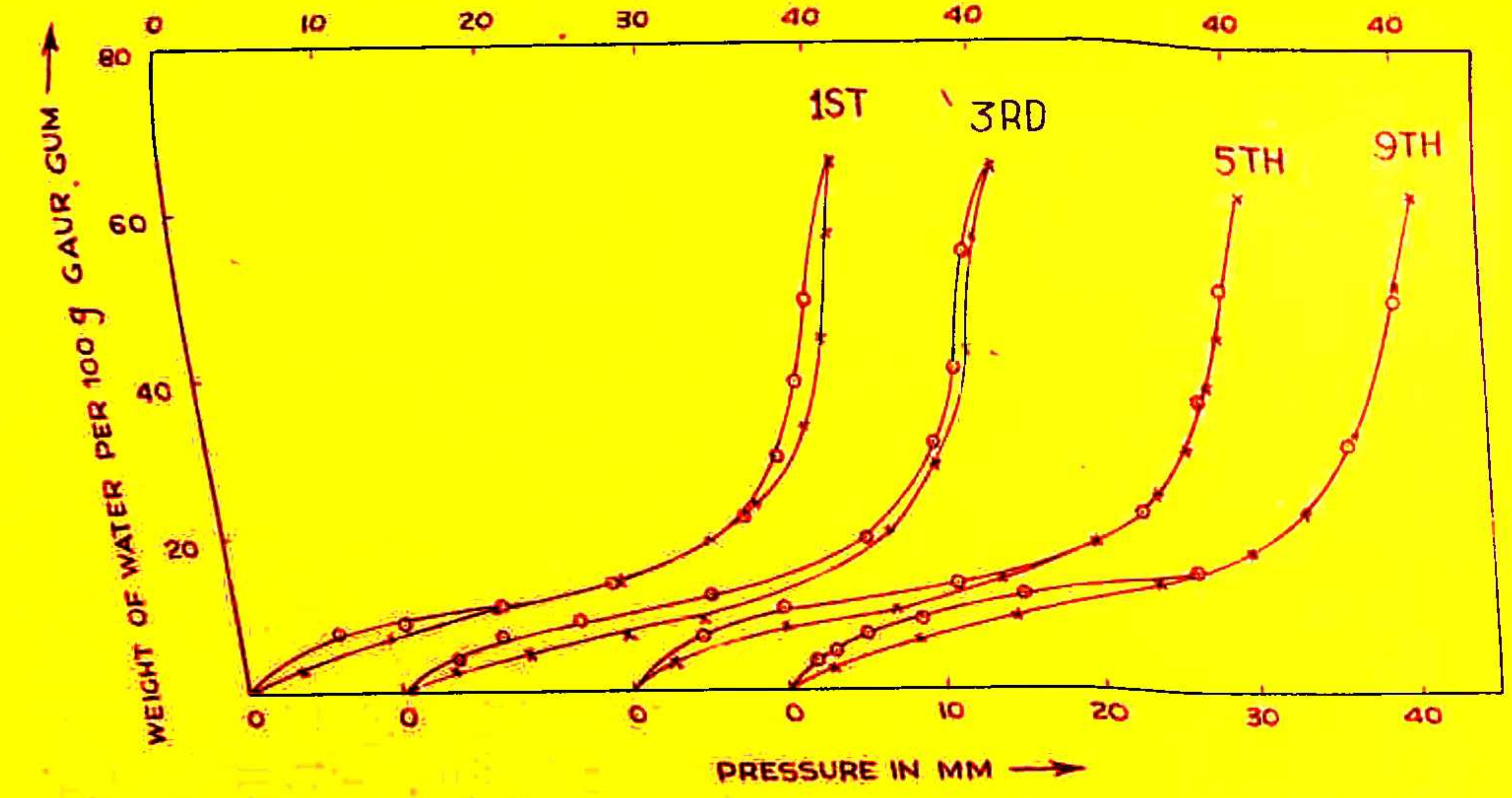


FIG.2 SORPTION-DESORPTION HYSTERESIS OF WATER ON GUAR GUM AT THE 1ST, 3RD, 5TH, AND 9TH CYCLES.

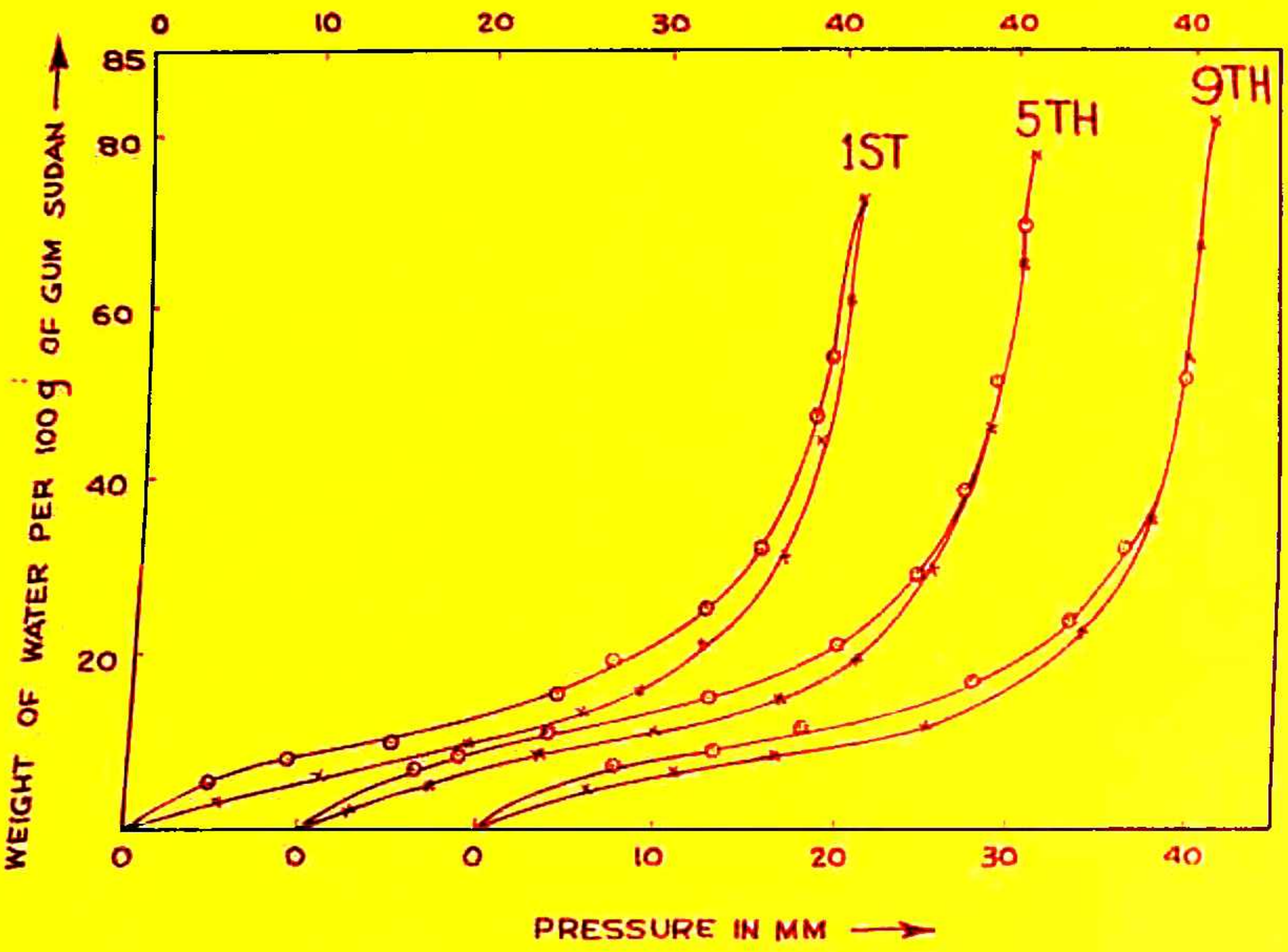


FIG 3 SORPTION - DESORPTION HYSTERESIS OF WATER ON GUM SUDAN AT THE 1ST, 5TH, AND 9TH CYCLES.

In the case of Gum Sudan, the sorption-desorption studies were continued up to 9th cycles. The sorption values at saturation pressure of water in 1st, 5th and 9th cycles are 72.5%, 78.0% and 82.0%, respectively. Figure 3.

Figure 4 presents the sorptions and desorptions of ethyl alcohol on Gum Sandarac. The study was continued up to 3rd cycle. The volumes of ethyl alcohol taken at the saturation pressure in 1st, 2nd and 3rd cycles are 290, 220, and 225 c.c. per 100 grams of gum, respectively. At the end of the 1st cycle, the gum retained 11.8 c.c. of alcohol per 100 grams of gum which could not be removed even by drastic evacuation for 12 hours. This 'bound' alcohol was not replaced even by water sorption on the same sample.

The equilibrium water sorption values for Gum Karaya, Gum Sudan and Gum Guar are presented in Table I.

Table I

Sorption capacities of different natural gums for water vapour

Gum	Sorption capacity g/100 g of gum
Karaya	95.0
Sudan	82.0
Guar	62.3

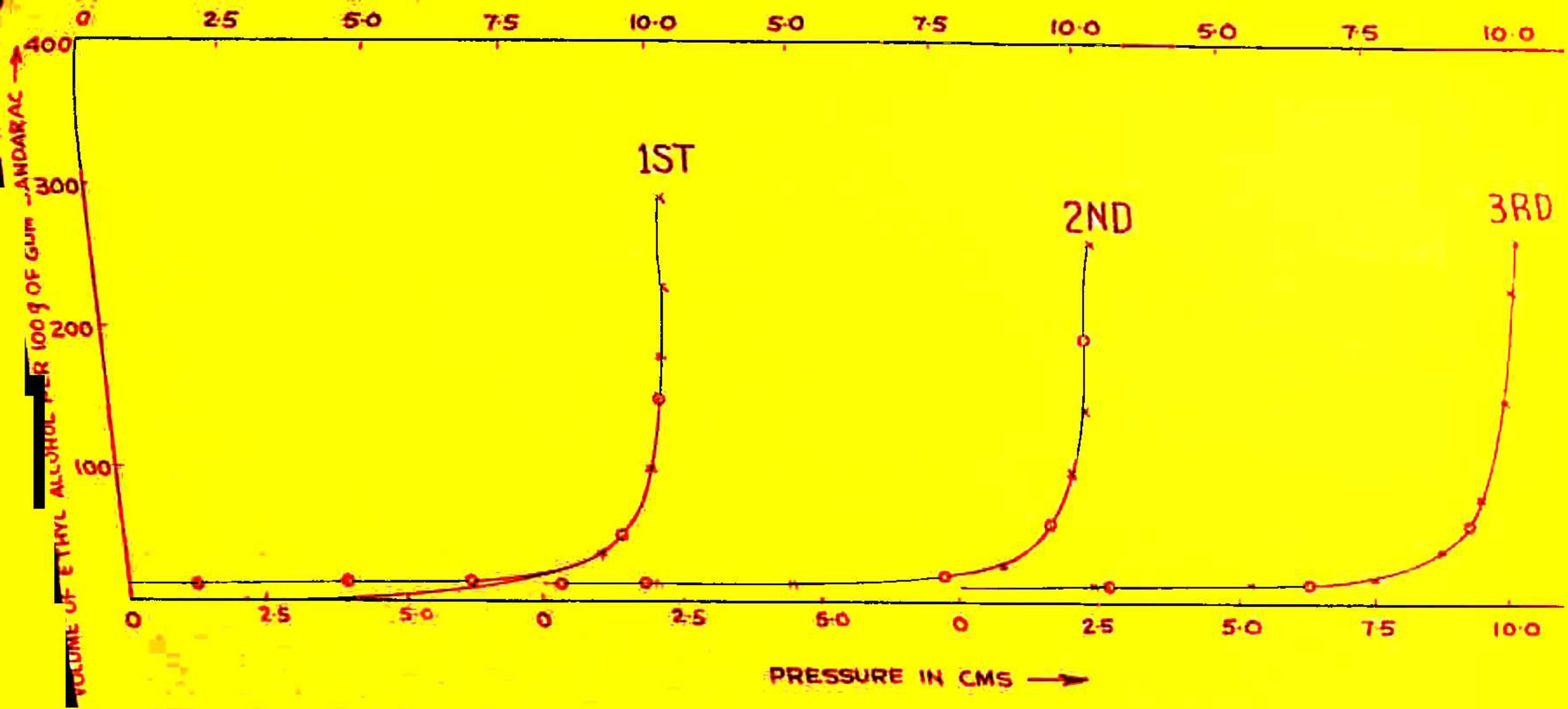


FIG. 4 SORPTION - DESORPTION HYSTERESIS OF ETHYL ALCOHOL ON GUM SANDARAC AT THE 1ST, 2ND, AND 3RD CYCLES.

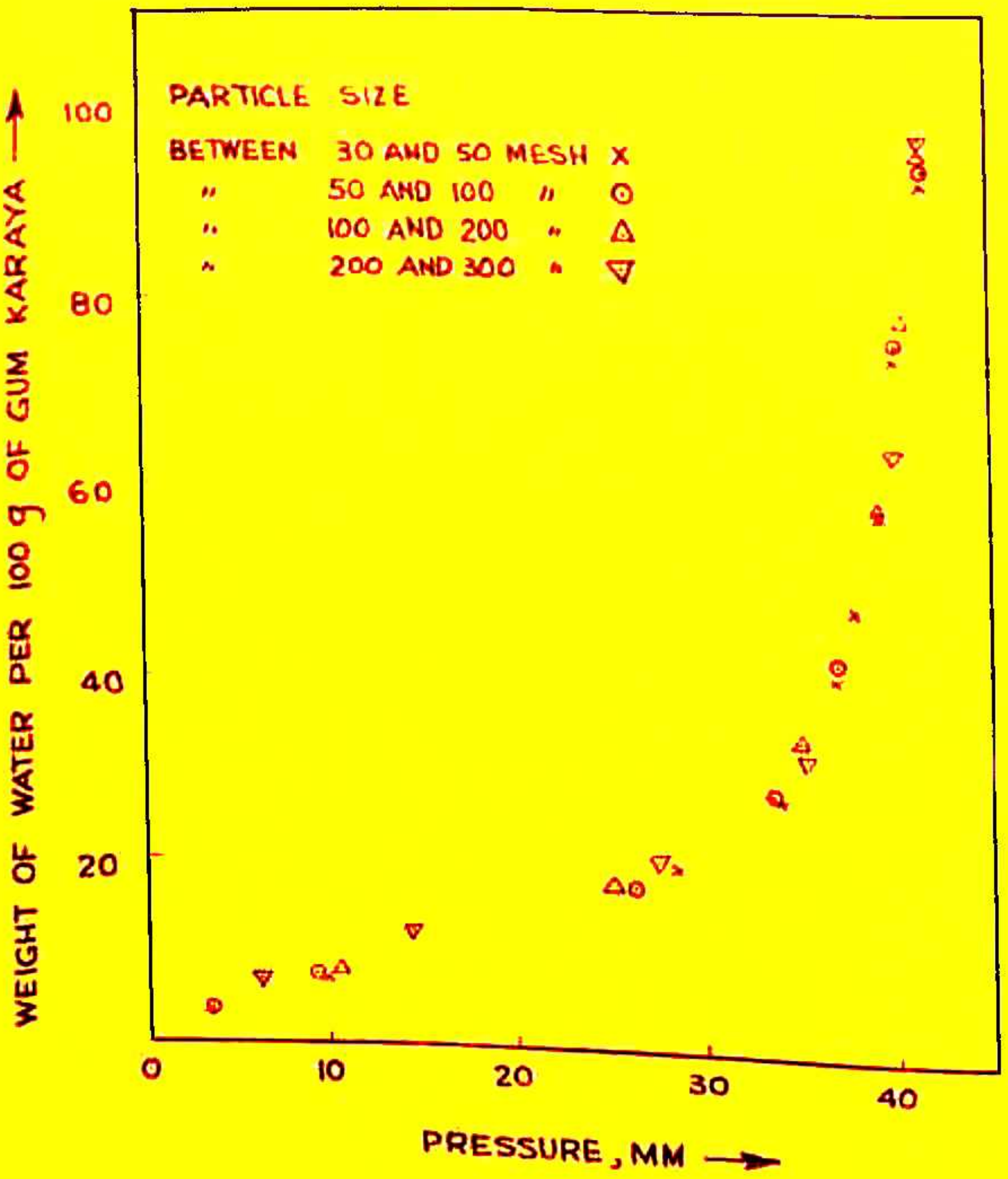


FIG.5 EFFECT OF PARTICLE SIZE ON SORPTION WATER BY GUM KARAYA.

Effect of particle size

A study of the effect of particle size on the extent of adsorption is desirable since this provides a means of varying the external surface area. If the adsorption is of Van der Waals type, then it would be expected that the extent of adsorption would vary directly with the specific surface area. Sorption isotherm data were accordingly obtained for four different particle size fractions - particle size between 30 and 50 mesh, 50 and 100 mesh, 100 and 200 mesh and 200 and 300 mesh were obtained from Gum Karaya. The data are plotted in Figure 5. Figure 5 reveals that the extent of adsorption is almost the same for all the different particle size fractions.

Discussion

Sorption-desorption hysteresis

In Gum Sudan, the hysteresis loop decreases in low pressure region and disappears in higher pressure region from 1st to 9th cycle although the decrease being small. In Gum Guar, the hysteresis loop changes in shape and size on successive sorptions and desorptions. In the low and high vapour pressure regions of the first cycle there are loops and in the middle the sorption-desorption curves are coincident. It is a case of 'split hysteresis loop'. With progressive sorptions and desorptions, the hysteresis loop in the high vapour pressure region completely disappears but the desorption curve shifts away from the sorption curve. This shift is quite predominant in the low vapour pressure region of the hysteresis loop in the 9th cycle. In Gum Sandarac, the hysteresis loop exhibited in the 1st cycle completely disappears in the 2nd and 3rd cycles. Gum Karaya does not show a hysteresis loop at all in the first two cycles.

All these results show either the disappearance of the hysteresis loop initially exhibited or the gradual and continuous decrease, in successive sorptions and desorptions and the final disappearance. These results are in conformity with those already reported with many other organo gels. These results are explained on the basis of the cavity theory, in conjunction with the properties of hydration and swelling of the gum. All the gums swell with solvating liquid but vary in degree of solvation and swelling. Solvation and swelling are determined by the number of polar groups (-OH and -COOH groups) which are the centres of hydration and the degree of intra and intermolecular crosslinking by hydrogen bonds. The polar groups of the macro molecules of the gums are accessible to water (or other solvating liquid) and this results in hydration (or solvation) and swelling of the gum. The accessibility of polar groups to water molecules vary in each gum and hence hydration capacity and swelling vary. Greater the accessibility of the polar groups, quicker is the swelling and consequently, the cavities disappear more easily and the hysteresis loop disappears in a fewer number of cycles.

In Gum Sudan, the sorptive values continuously increase from 1st to 9th cycles and there is a small decrease in the size of the hysteresis loop in the lower and disappearance in the higher vapour pressure region. These results show that the polar groups are partially accessible to water and more and more groups are being accessible to water as the sorption and desorption are tried. Due to partial accessibility of the polar groups to water, swelling is restricted, there by the cavities decrease and disappear in size slowly and hence the slow decrease in size and the disappearance of the hysteresis loop.

In case of Gum Karaya, the sorptive value remains practically the same in first two cycles. In other words, all the polar groups are accessible to water, consequently greater ease of swelling, the cavities decrease in size and disappear more quickly and no hysteresis is exhibited even in the first cycle.

In Gum Guar, the slight decrease in the total sorptive capacity and slight increase in the entrapping effect in the low vapour pressure region suggests that probably swelling and shrinkage are not uniform. Swelling and shrinkage, which are accompanied by sorption and desorption respectively, if non uniform, result in localised stresses and strains and may affect the extent of collapse of cavities. It is expected that if further sorptions and desorptions were continued on the same sample of gum, the constricted necks of the cavities would further shrink and finally collapse and the hysteresis loop would disappear.

The results presented in this chapter on the behaviour of the different natural gums in sorption-desorption hysteresis confirm the earlier generalization that all organo gels, on the imbibition of water, either show no hysteresis loop or the hysteresis loop initially exhibited decreases in size on successive sorptions and desorptions and finally disappears.

The explanation of this general phenomena is the cavity concept in conjunction with the properties of hydration and swelling. Hydration and swelling are determined by the number of polar groups which are the centres of hydration and the degree of inter and intra molecular cross linking. The accessibility of the polar group to sorbate molecules determines the ease of disappearance of the cavities and thereby the ease of disappearance of the hysteresis loop.

Effect of particle size

An estimate of the particle size of the various fractions, determined from sieve sizes, showed that the total variation in particle size was about ten fold; however, Figure 5, shows that the extent of adsorption is about the same for all the fractions. It appears then, that sorption of water vapour by Gum Karaya is a bulk property of the adsorbent and apparently independent of particle size. This suggests that adsorption of water vapour on Gum Karaya is more specific than Vander Waals adsorption.

*****

References

1. Jacobs, M.B., "The Chemistry and Technology of Food and Food Products", Interscience, New York, Vol. 1 (1944), p.819.
2. Mantell, C.L., "The water soluble gums, Reinhold Publishing Corporation, New York, 1947.
3. Howes, F.N., "Vegetable gums and resins", Chronica Botanica Company, Waltham Mass., 1949.
4. Elworthy, P.H., and George, T.M., J. Pharmacy and Pharmacology, 1964, 16, 258.
5. Rao, K.S., Curr. Sci., 1940, 9, 19.
6. Ahmed, Z.F., and Whistler, R.L., J. Am. Chem. Soc., 1950, 72, 2524.
7. Whistler, R.L., and Smart, C.L., "Polysaccharide Chemistry", Academic Press Inc., New York, N.Y., 1953, 296.
8. Peyer, W., Suddent. Aportheker-Ztg. 1925, 65, 569.
9. Thrun, W.E., Ind. Eng. Chem., 1935, 27, 1218.
10. Kubal, J.V., J. Colloid. Sci., 1948, 3, 457; Collection Czechoslov. Chem. Communs. 1948, 13, 378; Chem. Abstr. 1949, 43, 1626.
11. Beauquesne, L., Compt. rend. 1948, 222, 1056.
12. Howes, F.N., "Vegetable gums and resins", Chronica Botanica Company, Waltham, Mass., 1949, 136.
13. Jones,J.K.N., and Smith, F., Advances in carbohydrate Chemistry, Academic Press, N.Y., 1949, 243.
14. Aspinall, G.O., "Recent advances in Food Science, Butterworth, London, 1963, 3, 282.
15. Hirst, E.L., Proceedings of the 4th International Congress of Biochemistry, 1958, 1, 31.
16. Hirst, E.L., Soc. Chem. Ind. (London) Monogr. No. 24, 3, 1966, Chem. Abst. 1967, 66, 66974q.

******

CHAPTER VII

SORPTION-DESORPTION HYSTERESIS IN SYNTHETIC ION EXCHANGE RESINS AND SOME SWELLING SYSTEMS

PART I

SORPTION-DESORPTION HYSTERESIS IN CELLEX
RESINS WITH WATER
VAPOUR

SORPTION-DESORPTION HYSTERESIS IN CELLEX RESINS WITH WATER VAPOUR

Abstract

The four cellulose resins - Cellex P, cellex E, Cellex T and Cellex D have been used in sorption-desorption studies with water vapour. All the resins show decrease in size and disappearance of the hysteresis loop on successive cycles of sorption and desorption of water. These results have been explained on the basis of the cavity theory in conjunction with the swelling and shrinkage of the resins. The tendency of the hysteresis loop to disappear in the sorption of water on resins has been attributed to the degree of cross-linking of molecules in the resin.

Introduction

Ion exchange resins are essentially cross-linked polymer networks to which are attached ionized or unionized groups. In cation exchange resins there are, of course, acidic groups, i.e., SO_2H, $-CO_2H$, $-PO_3H_2$ and in anionexchange resins the groups are basic, i.e., quarternary ammonium, aliphatic and aromatic amine groups. Of many different natural and synthetic products which show ion exchange properties, two different types of ion exchangers are widely used: 1) monofunctional synthetic polymers with polymethacrylate or polystyrene matrices and 2) chemically substituted exchangers derived from natural polymers such as cellulose and dextran. In both, the ion exchange properties are determined principally by the kind of functional ionic group introduced into the molecules. The matrix of the synthetic polymer is wholly hydrophobic while that of the natural polymer is essentially hydrophilic.

The development of cellulose ion exchangers (1,2) introduced an indispensable tool for the fractionation of complex biochemical mixtures. These excellent adsorbents owe their ionic and adsorbent properties to the basic or acidic groups introduced into the bio-polymer by synthetic procedures involving the formation of ester or ether linkages with constituent hydroxyl groups of the molecules and to the hydrophilic nature of the gel like matrix. In the polysaccharide molecule the equivalent of low cross-linkage is produced by hydrogen bonding between poly-glucose chains. The charged groups are spaced approximately 50 A^{o} apart compared to the closer spacing of 10 A^{o} for synthetic polymers (3). A limited substitution is essential in order to preserve an insoluble macromolecular structure. However, the matrix is elastic and can be expanded. Therefore, the ion exchange resins swell by taking up the solvent. The extent of swelling depends upon the degree of cross-linking of the molecules. The degree of cross-linking is varied by varying the amounts of cross-linking agent.

Ion exchange resins used

The following commercially available synthetic ion exchange resins with cellulose matrix have been used. These resins were supplied by Bio-Rad Laboratories, New York.

Cellex E

It is a highly purified cellulose powder containing tertiary amine exchange group (ECTEOLA).

Cellex T

It is a highly purified cellulose powder containing quaternary amine exchange groups (TEAE).

Cellex P

It is a highly purified cellulose powder containing phosphonic acid exchange groups (P) in the sodium form.

Cellex D

It is a highly purified cellulose powder containing diethyl-aminoethyl exchange groups (DEAE).

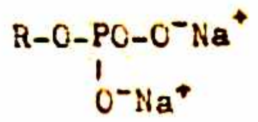
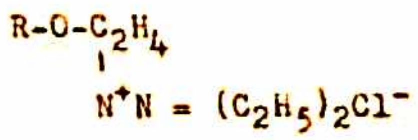
Table I summarizes the type, functional groups, exchange capacity and chemical designation of these ion exchange resins.

Results

In the case of cellex P, the 1st, 2nd and 4th hysteresis loops obtained in the sorption and desorption of water are shown in Figure 1. The amount of water taken at the saturation pressure is 23.7%. The sorption-desorption studies were continued up to 3rd cycle in case of cellex E. The curves obtained at the 1st, 2nd and 3rd cycles are shown in Figure 2. The resin takes 26.3% water at the saturation pressure. There is hysteresis loop in the first cycle and it disappears in the subsequent cycles. With cellex T, Figure 3, the amount of water taken at saturation pressure in the 1st, 2nd and 3rd cycles is 30.0%. There is hysteresis loop in the low pressure region of 1st cycle which disappears in the 2nd and 3rd cycles. In case of cellex D, Figure 4, sorption-desorption studies were continued up to 2nd cycle. The amounts of water taken in the 1st and 2nd cycles are 48.0% and 47.5% respectively. There is no hysteresis loop at all.

Table I

Cellulose Ion Exchange Resins

Chemical designation	Type	Functional group	Manufacturer's designation	Ion exchange capacity meq/g
Epichlorhydrin triethanolamine (ECTEOLA)	Intermediate base	$R\text{-}(NH_2)x$	Cellex E	0.38
Triethylamine	Strong base	$R\text{-}O\text{-}C_2H_4\text{-}N^+ \equiv (C_2H_5)_3Cl^-$	Cellex T	0.50
Phosphonic acid phosphyonyl	Intermediate acid	 $R\text{-}O\text{-}\underset{\overset{\mid}{O^-Na^+}}{PO}\text{-}O^-Na^+$	Cellex P	0.765
Diethyl amino ethyl	Strong base	 $R\text{-}O\text{-}\underset{\overset{\mid}{N^+N = (C_2H_5)_2Cl^-}}{C_2H_4}$	Cellex D	0.780

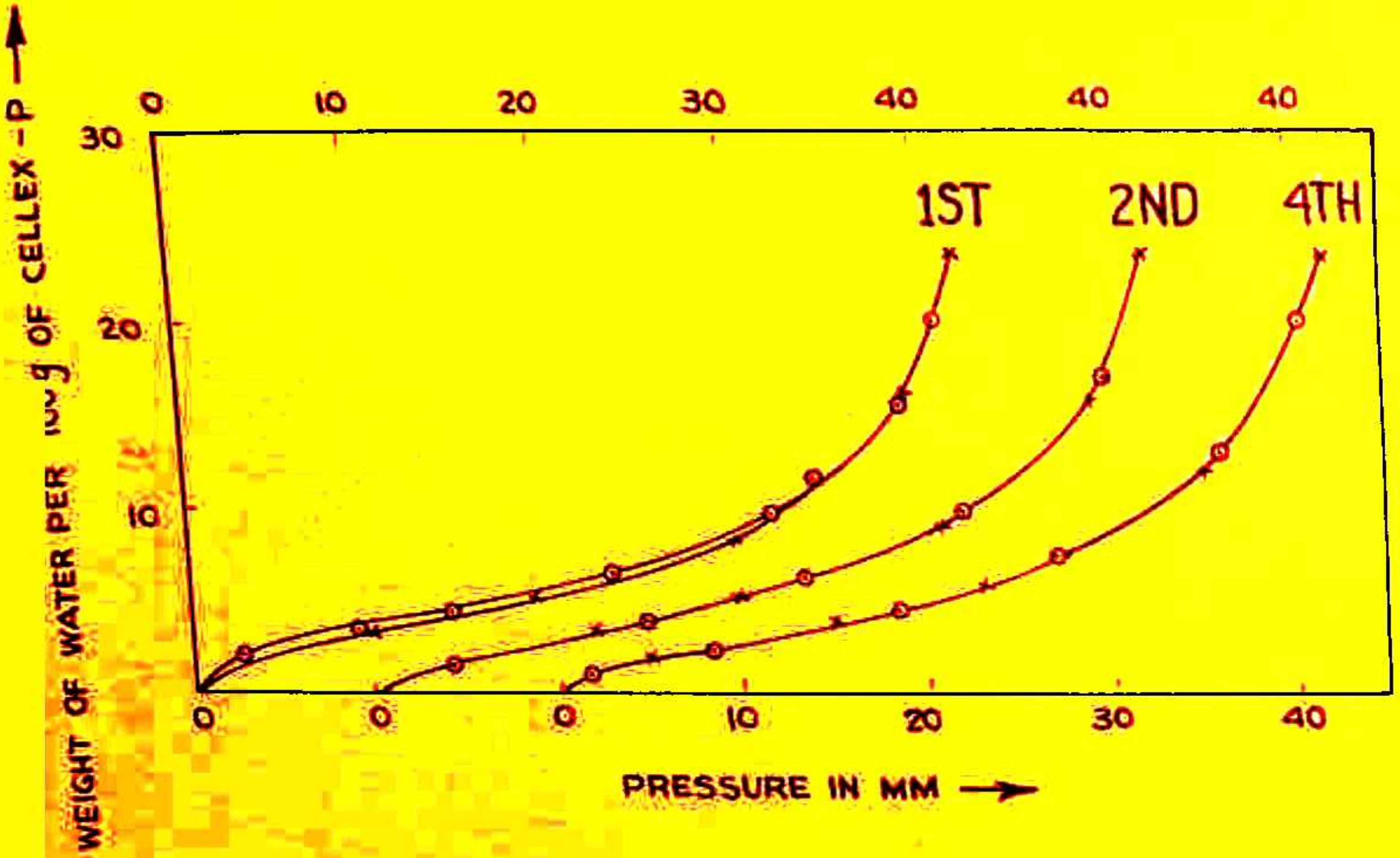


FIG. I SORPTION - DESORPTION OF WATER ON CELLEX - P AT THE IST, 2ND AND 4TH CYCLES.

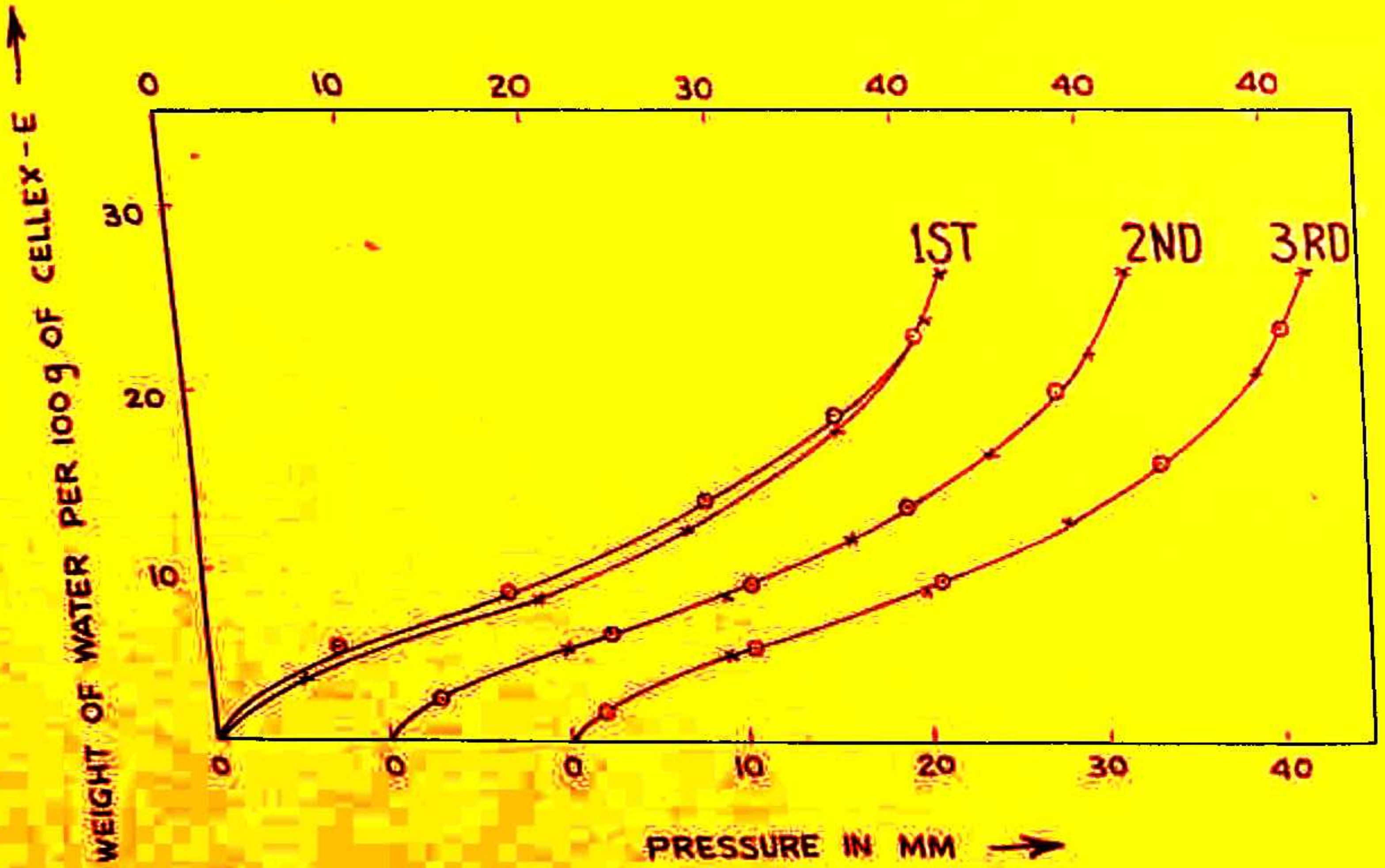


FIG.2 SORPTION - DESORPTION OF WATER ON CELLEX-E AT THE 1ST, 2ND, AND 3RD CYCLES.

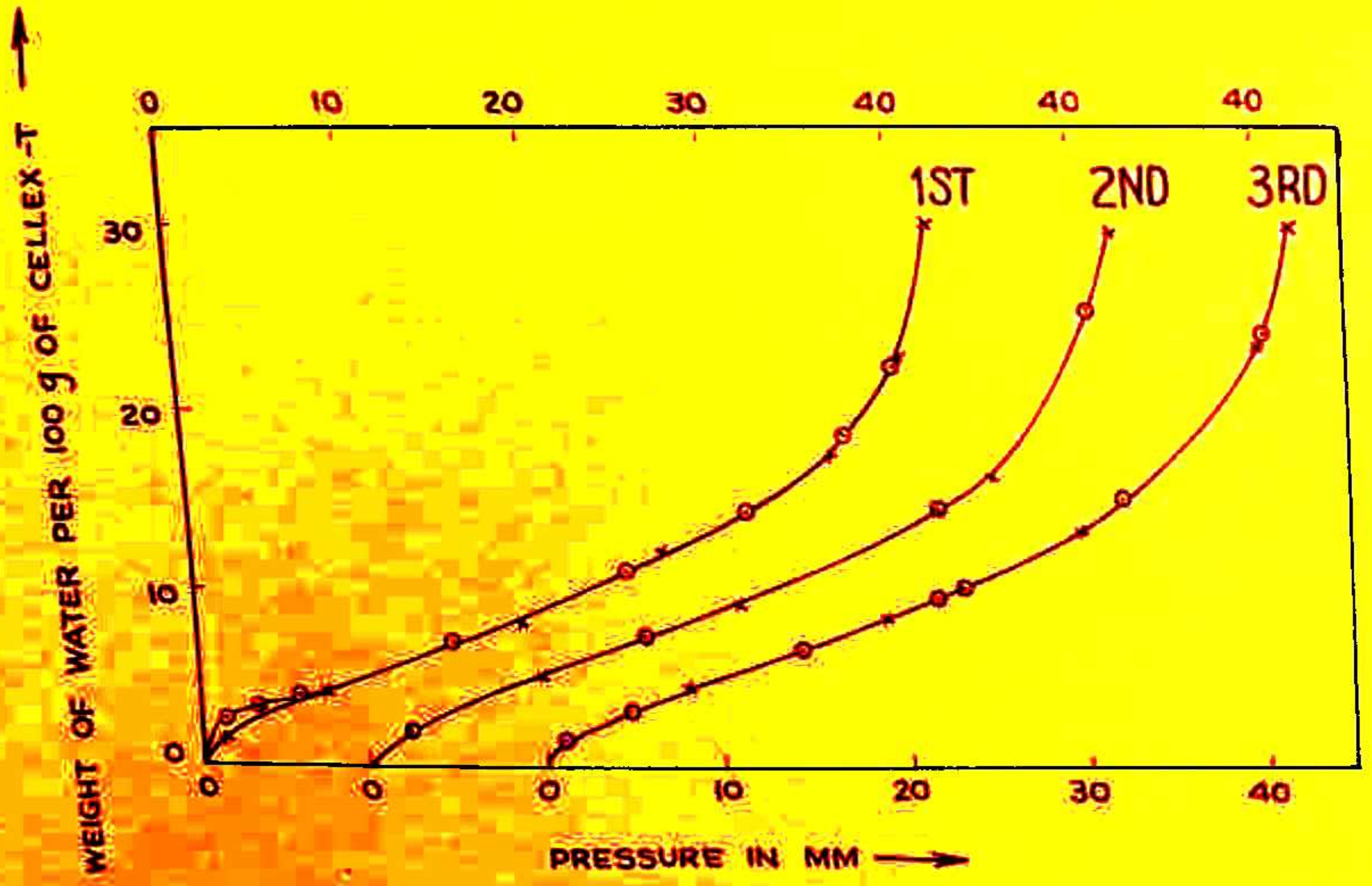


FIG. 3 SORPTION - DESORPTION OF WATER ON CELLEX-T AT THE 1ST, 2ND, AND 3RD CYCLES.

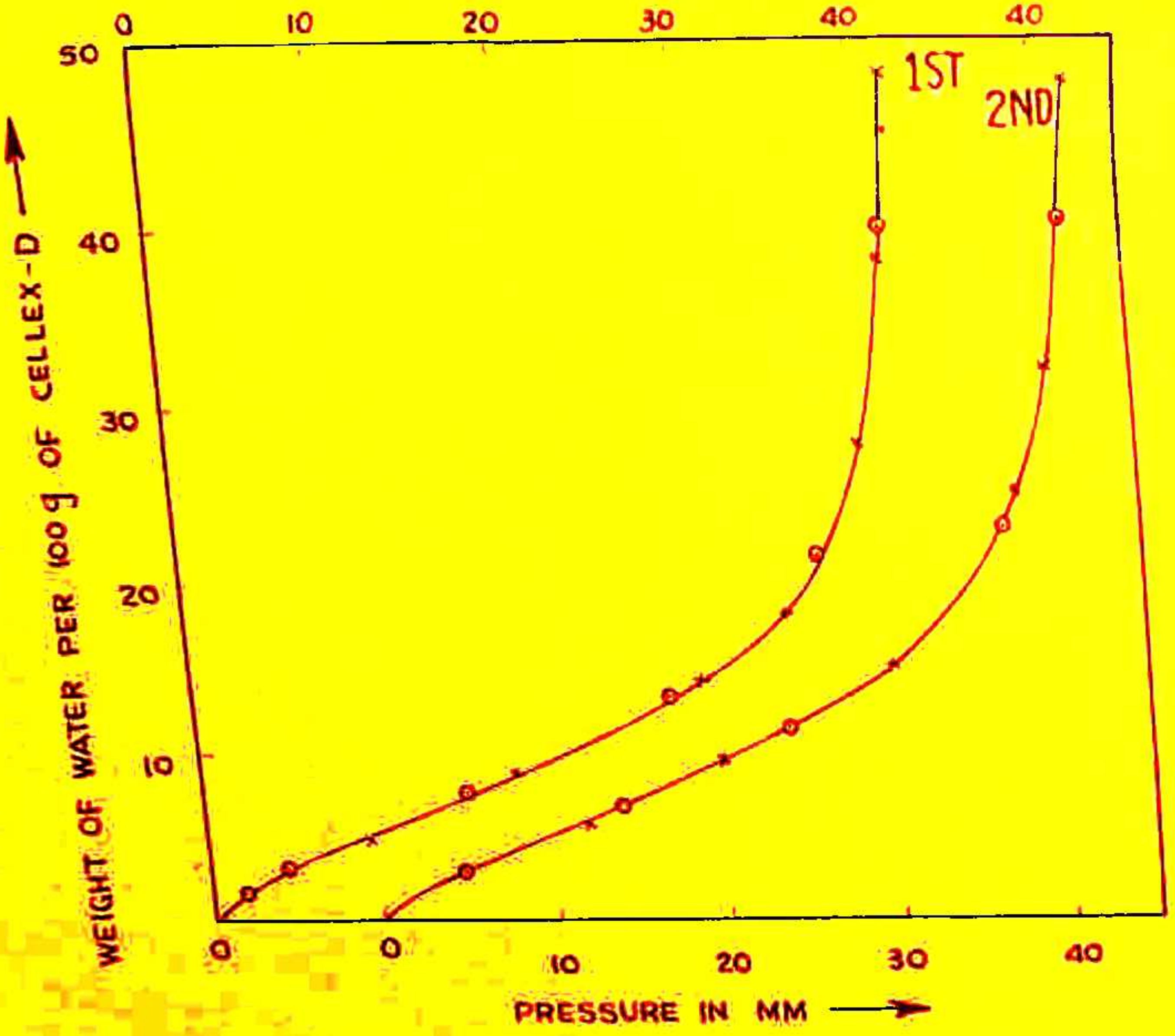


FIG. 4 SORPTION - DESORPTION OF WATER ON CELLEX-D AT THE 1ST AND 2ND CYCLES.

The total period for completing this study was about 2 months. In each case and in all the cycles, the resin was kept in contact with water vapour at saturation pressure for 2 days and in few cases for more than 2 days.

Discussion

The results obtained with different cellex resins show either decrease in size or disappearance of the hysteresis loop on successive sorptions and desorptions of water. These results can be explained on the basis of cavity theory (4,5) in conjunction with the property of swelling of the resins as described in the earlier chapter. All resins swell with water. The dehydrated resins are comparatively rigid in structure. The cavities which are present entrap water and cause hysteresis. At the saturation pressure of water all the resins are in swollen condition and the cavity walls become elastic. During desorption, the cavity walls yield, the cavities collapse, the entrapping effect is lost and thus the hysteresis loop decreases in size and disappears. In other words, the decrease in size and disappearance of hysteresis depend upon the extent of swelling of the resin which in turn depends upon the degree of cross-linking. Helfferich (6) has reported that the resins swell more when their fixed inorganic groups are completely ionized and according to Osborn (7), strongly acidic or basic resins are taken as more or less fully ionized under all conditions.

It has also been reported (8-11) that highly cross-linked, resins have a lesser degree of swelling, because of greater number of cross-links in the network. In other words, the degree of cross-linking of the resin depends upon the amount of the cross-linking agent used. Hence, the sorptive values should be in the reverse order, i.e., higher the degree of cross-linking, lesser the sorptive value. A survey of the literature on the amount of the cross-linking agent used in these cellex resins was made but the degree of cross-linking could not be obtained. However, present investigations reveal that the degree of cross-linking follows the trend:

Cellex P > Cellex E > Cellex T > Cellex D

It is expected that in a resin of lesser cross-linking, there is greater swelling. The cavities collapse more easily and consequently, the hysteresis loop disappears in a fewer number of cycles of sorption and desorption, i.e., the tendency of hysteresis loop to decrease in size and finally disappearance depends upon the ease of collapse of the cavities present, which in turn depends upon the degree of swelling of the resin or on the degree of cross-linking. Conversely, in a resin of higher degree of cross-linking, the swelling is less, the cavities collapse less readily and so the hysteresis loop persists over a larger number of cycles, although the loop decreases in size in successive cycles. These results are borne out by the present studies.

Tager and coworkers (12,13) have reported while working with ion exchange resins that although total sorptive capacities of different resins remained the same in all the cycles, the hysteresis loop decreased in size and finally disappeared. This indicated that the total cavity volume was a very small fraction of the sorptive capacity of the resin.Tager et al pointed out that high sorptive value was associated with the ability of ion exchanger to swell. These conclusions have been borne out by the present results, i.e., the total sorptive capacity in each case has remained the same in all the cycles though the hysteresis loop has decreased and disappeared.

A small hysteresis effect in the water vapour sorption studies with ion exchange resins has been obtained by Gregor et al (9,14,15) and Dickel and Hartmann (16). Gregor et al (15) have attributed the small hysteresis(below 0.1 p/p_o) to short range order among the polymer chains. It is expected that, if the studies were further continued by these authors in the second and subsequent cycles, probably the hysteresis would have disappeared.

In these studies, the progressive decrease in size of the hysteresis loop and its ultimate disappearance on successive sorptions and desorptions have been established to be general phenomena. All these systems have a common molecular structural characteristic. The properties common to all these sorbents are hydration and swelling. The common structural feature is intra-molecular cross linking. The degree of cross-linking determines the extent of swelling and accessibility of polar groups to water molecules. These in turn determine disappearance of the cavities and the disappearance of the sorption-desorption hysteresis effect.

*****

PART II

SORPTIVE PROPERTIES OF AGAR AND ISPAGHULA

SORPTIVE PROPERTIES OF AGAR AND ISPAGHULA

Abstract

By employing quartz fibre spring technique, a series of sorptions and desorptions of water vapour at 35°C have been obtained on Agar and Ispaghula. These adsorbents have shown a common characteristic in the sorption and desorption of water vapour, i.e., the hysteresis loop initially exhibited showed a tendency to decrease in size and disappearance in the subsequent cycles. This gradual decrease and final disappearance of hysteresis loop has been attributed to the gradual collapse of the cavities in seccessive cycles of sorptions and desorptions. A reasonably good fit for BET and F-H-H equations, in the low and high relative pressure regions, respectively, has been obtained. The BET surface areas for the two adsorbents have also been calculated.

Introduction

In common with most, if not all, swelling systems, on the imbibition of solvating liquids exhibit a general phenomenon, i.e., either there is no hysteresis effect in the very first cycle of sorption and desorption, or the hysteresis loop initially exhibited decreases in size in successive cycles of sorptions and desorptions and finally disappears. Explanation of this interesting phenomenon has been presented in the earlier chapters on the basis of cavity theory (4,5) in conjunction with the properties of hydration and swelling of the adsorbent in solvating liquid. The generality of this phenomenon has been established by work on a number of swelling systems (17-19).

Agar is a seaweed colloid (physico-colloid) extracted from Gelidium, belonging to the red algae (Rhodophyta). It is amorphous, porous, translucent, membranous, faintly yellowish, brittle when dry and tough when damp and available in the market as powder, flakes, rectangular blocks and in bundles of slender strips. Agar is the sulfuric ester of a linear galactan. It consists of a long chain of D-galactopyranose residues, attached by 1,3,-glycosidic linkages. This chain is terminated at the reducing end by one residue of L-galactopyranose. Attached to the rest of the chain through carbon atom 4, this L-galactose residue is esterified at carbon atom 6 with sulphuric acid. There are probably as many as 53 galactose units to each SO_4H group, and at least 140 such units to each non-reducing end group (20).

Ispaghula (Plantago ovata seed) is the cleaned, dried, ripe seed of plantago-Psyllium Linn'e or of Plantago indica

Linn'e (21). De jussieu (21) recognised two distinct groups of true plantains, the stemless plantago and those with stems-Psyllium. The plantain group or the genus Plantago comprises about 200 species. The leaves are simple, either radical or cauline, usually ribbed. The fruit is a 2 celled pyxis containing two or many seeds (22). The seed of Plantago-ovata is broadly elliptical to ovate boat shaped, from 2 to 3.5 mm. in length and from 1 to 1.5 mm. in width. The colour is white with a pinkish tinge.

No data are available on the sorption-desorption hysteresis of water vapour on these two adsorbents. This paper presents a series of sorptions and desorptions at 35°C on these two swelling adsorbents.

Experimental

The adsorbents had following specifications: Agar (Harleco, U.S.A.), particle size between 100 and 200 mesh, B.S.S., moisture content 13.2%, ash content 3.2%, acid insoluble ash 0.48%.

Ispaghula (B.G. Telephone brand, marketed by the Sidhpur Sat Isabgol factory, Sidhpur, Gujarat), seed length 1.0 - 3.0 mm, seed width 1.0 - 1.75 mm, boat shaped, white with a pinkish tinge, particle size between 100 and 200 mesh, moisture content 10.5%, ash content 2.96%.

Results

Complete sorptions and desorptions of water vapour on Agar and Ispaghula are presented in Figures 5 and 6, respectively. The weight of water adsorbed per 100 grams of the adsorbent has been plotted against the vapour pressure of water. In case of Ispaghula, hysteresis loop initially exhibited disappears in the 2nd cycle while in case of Agar, the disappearance is gradual and sorption-desorption isotherms become coincident in the 3rd cycle. The percentages of water, at its saturation pressure for the two adsorbents are presented in Table II.

Table II:

Sorption capacities of Agar and Ispaghula for water vapour at 35°C .

	Sorption capacities, %			
	Sorption-desorption cycles			
Adsorbent	1st	2nd	3rd	4th
Agar	60.0	69.8	69.5	69.5
Ispaghula	72.5	80.5	82.0	-

Discussion

There are two theories of sorption-desorption hysteresis - Cohan's theory (23) and cavity theory (4,5). The

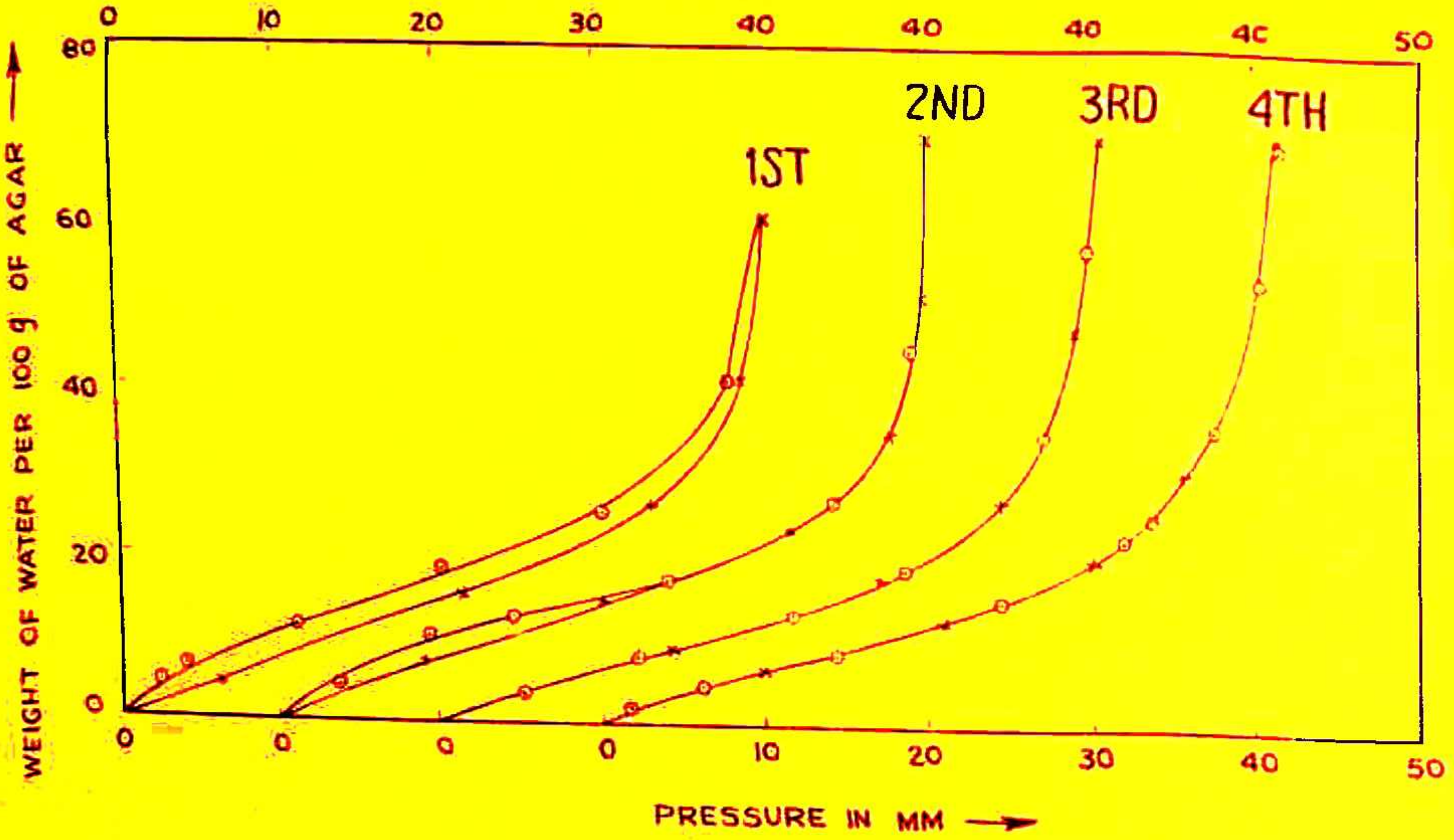


FIG. 5 SORPTION - DESORPTION HYSTERESIS OF WATER VAPOUR ON AGAR AT 1ST, 2ND, 3RD, AND 4TH CYCLES.

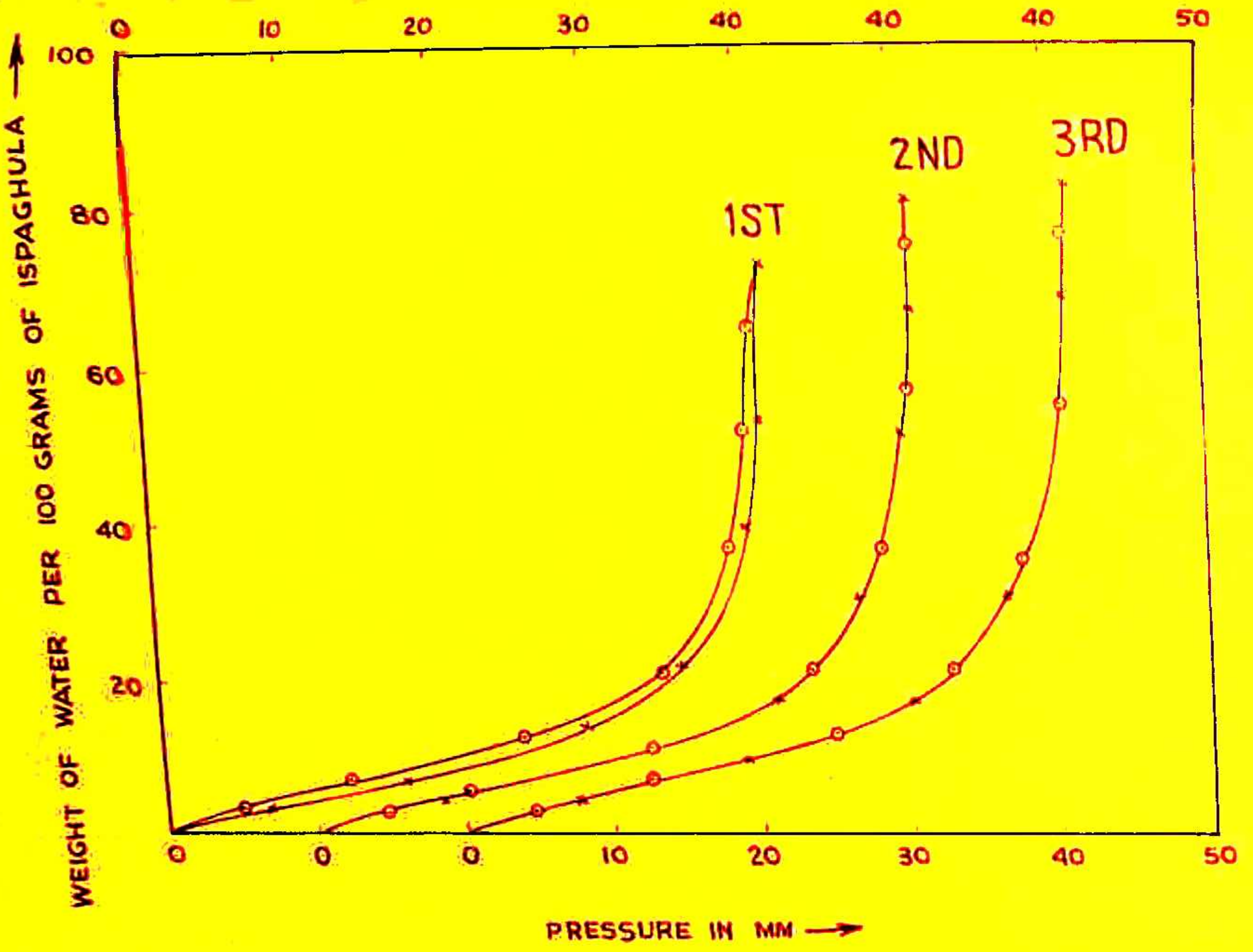


FIG. 6 SORPTION-DESORPTION HYSTERESIS OF WATER VAPOUR ON ISPAGHULA AT 1ST, 2ND, AND 3RD CYCLES.

cavity theory postulates that hysteresis effect is due to the entrapping of the liquid sorbate by cavities during desorption. The shape and position of the loop depends upon the shape and size of the cavities.

Dehydrated Agar and Ispaghula have comparatively rigid structure. During sorption, the filling of the cavities by liquid sorbate is progressive and proceeds from the neck to the body of the cavity. Whereas, during desorption emptying of the cavities is sudden and abrupt. The cavity gets emptied when the neck gets emptied. Thus, cavities entrap water and cause hysteresis.

Adsorbents capable of swelling in contact with water are essentially changing systems. During sorption, the adsorbent swells and cavity walls become elastic whereas, during desorption, it shrinks and cavities collapse in stages. If all the cavities collapse in the very first cycle, there will be no hysteresis in the first cycle itself. If, on the other hand, the cavities collapse in stages, the disappearance will be gradual. Present results indicate that the tendency of Agar to change is low and cavities tend to decrease in size and shape and collapse slowly as compared to Ispaghula.

Applicability of BET equation

Swelling systems yield isotherms which are characterized by their being convex to pressure axis. The isotherms

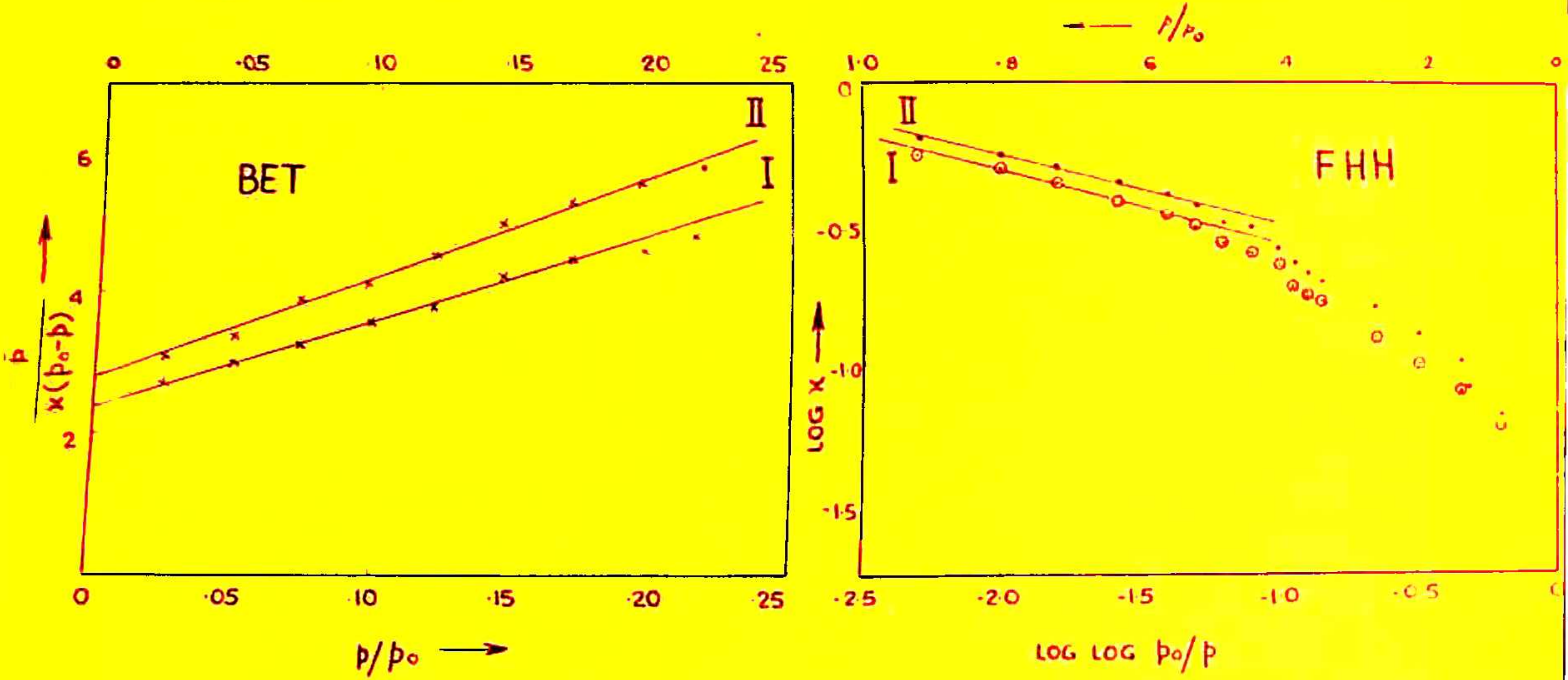


FIG. 7 BET AND FHH PLOTS FOR WATER SORPTION ON AGAR (I) AND ISPAGHULA (II).

yield no clearly defined "knees". The experimental test of the validity of the BET procedure for calculation of the monolayer capacity from type III isotherms of BET classification (23) are too few and too unrepresentative to permit a clear decision on its merits to be reached. BET equation has been applied to calculate the monolayer capacity (x_m) from the isotherms, in a manner analogous to that applied to type II - isotherms (24). The BET plots (Table III) yield straight lines, Figure 7.

Table III

BET plots for the sorption of water on Agar and Ispaghula

Relative vapour pressure p	Sorption, x g/g		$\frac{p}{x(p_0-p)}$	
	Agar	Ispaghula	Agar	Ispaghula
0.024	0.009	0.008	2.70	3.08
0.048	0.017	0.015	3.00	3.37
0.072	0.024	0.020	3.24	3.89
0.096	0.030	0.026	3.56	4.10
0.120	0.036	0.030	3.80	4.56
0.145	0.040	0.034	4.22	5.00
0.169	0.045	0.038	4.51	5.33
0.193	0.052	0.043	4.60	5.56
0.217	0.058	0.048	4.80	5.78

From the slope and intercept of the lines the specific surface (S) in m^2/g of the sorbent has been calculated as usual (24). From the monolayer capacity, the number of molecules (N_o) in the monolayer have also been calculated using the expression:

$$N_o = \frac{x_m . N}{M}$$

where N amd M are Avogadro's number and molecular weight of the sorbate, respectively.

The monolayer capacity (x_m), specific surface (S) and number of molecules (N_o) have been presented in the Table IV.

Table IV

Monolayer capacity (x_m), specific surface (S) and number of molecules in the monolayer (N_o) of water on Agar and Ispaghula.

Adsorbent	x_m	S	N_o
Agar	0.069	246.6	23.2×10^{20}
Ispaghula	0.058	205.6	19.4×10^{20}

Applicability of F-H-H- equation

Several workers (25,26) have criticised the application of BET equation to the sorption of water vapour by swelling polymer network. When the present water sorption data were plotted (Table V) according to the isotherm equation of

Frenkel (27), Halsey (28), and Hill (29), wide deviations from linearity were observed, Figure 7.

Table V

F-H-H- plots for the water sorption by Agar and Ispaghula

log log p_o/p	Agar		Ispaghula	
	x	log x	x	log x
-2.28	0.61	-0.215	0.56	-0.252
-1.98	0.57	-0.244	0.51	-0.292
-1.80	0.49	-0.310	0.45	-0.347
-1.57	0.43	-0.366	0.39	-0.409
-1.42	0.39	-0.409	0.35	-0.459
-1.30	0.35	-0.456	0.31	-0.509
-1.21	0.31	-0.509	0.27	-0.569
-1.13	0.29	-0.538	0.25	-0.602
-1.06	0.26	-0.585	0.23	-0.638
-1.00	0.24	-0.620	0.21	-0.678
-0.95	0.22	-0.658	0.19	-0.721
-0.89	0.21	-0.678	0.18	-0.745
-0.85	0.20	-0.699	0.17	-0.770
-0.66	0.15	-0.824	0.13	-0.886
-0.50	0.12	-0.921	0.10	-1.000
-0.36	0.09	-1.050	0.08	-1.100
-0.21	0.06	-1.222	0.06	-1.220

The linear portion of F-H-H- isotherm shown in the present paper can correspond to multilayer adsorption at high relative pressures. However, the curved nature of these F-H-H isotherms indicates that either capillary condensation is occurring in very fine pores or that the adsorbent is undergoing swelling and physical changes as a result of the sorption process. Similar results have been published by Brandt and Budry (30) while studying the sorption of various vapours by polypeptides.

****

References

1. Sober, H.A., Hartley, R.W., Jr., Carrole, W.R., and Peterson, E.A., Fractionation of proteins, in "The Proteins", Vol. 3, Second edition, Ed.H. Neurath, N.Y., Academic Press, 1965.
2. Peterson, E.A., and Sober, H.A., "The plasma proteins", Vol.1, Ed. F.W. Putnam, N.Y., Academic Press, 1960.
3. The Encyclopedia of Biochemistry, Ed. R.J. Williams and E.M. Lansford, Jr., Reinhold Publishing Corporation, N.Y., 1967.
4. McBain, J.W., J. Am. Chem. Soc., 1935, 57, 699.
5. Rao, K.S., J. Phys. Chem., 1941, 45, 500.
6. Helfferich, F., Ion exchange, McGraw-Hill Book Company, Inc., 1962, p.102.
7. Osborn, G.H., Synthetic ion exchangers, Chapman and Hall, Ltd., London, 2nd Ed., 1961, p.4.
8. Davies, C.W. and Yeoman, G.D., Trans. Faraday Soc., 1953, 49, 968.
9. Greger, H.P., Gutoff, P., and Bergman, J.I., J. Colloid Sci., 1951, 6, 245.
10. Pepper, K.W., Reichenberg, D., and Hale, D.K., J. Chem. Soc., 1953, 3129.
11. Sundheim, B.R., Waxman, M.H., and Greger H.P., J. Phys. Chem., 1953, 57, 974.
12. Tager, A.A., Vysokomolekulyarnye Soedineniya, 1960, 2, 994, C.A. 1961, 55, 10746d.
13. Tager, A.A., Pashkov, A.B., Tsilipotkina, M.V., and Bykova, N.I., Vysokomolekulyarnye Soedineniya, 1960, 2, 997; CA. 1961, 55, 10746e.
14. Greger, H.P., Sundheim, B.R., Held, K.M., and Waxman, M.H., J. Colloid. Sci., 1952, 7, 511.
15. Waxman, M.H., Sundheim, B.R., and Greger, H.P., J. Phys. Chem., 1953, 57, 969.

16. Dickel, G., and Hartmann, J.W., Z. Physik. Chem. (Frankfurt) 1960, 23,1.

17. Rao, K.S., Curr. Sci., 1940, 9, 19.

18. Elworty, P.H., and George, T.M., J. Pharm. Pharmacol., 1964, 16, 258.

19. Rao, G.N.S., Rao, K.S., and Rao, B.S., Proc. Ind. Aca. Sci., 1947, A25, 221.

20. Encyclopedia of Chemical Technology, Ed. Kirk et al, I., Interscience Publishers, 1947, p. 232.

21. United States Dispensatry, Osol-Farrar, 24th Ed. J.B. Lippincott Co., London, 1947, p.900.

22. Cohan, L.H., J. Am. Chem. Soc., 1938, 60, 433.

23. Brunauer, S., Emmett, P.H., and Teller, E. , J. Am. Chem. Soc., 1938, 60, 309.

24. Gregg, S.J., and Sing, K.S.W., "Adsorption Surface area and Porosity", Academic Press, London, and New York, 1967.

25. Pauling, L., J. Am. Chem. Soc., 1945, 67, 555.

26. Bettelheim, F.A., J. Colloid. Interface Sci., 1967,23, 301.

27. Frenkel, J., "Kinetic theory of liquids",Oxford Univ. Press, London, 1946.

28. Halsey, G.D., J. Chem. Phys. 1948, 16, 931.

29. Hill, T.L., Adv. Catal., 1952, 4, 212.

30. Brandt, W.W., and Budrys, R.S., J. Phys. Chem., 1965, 69, 600.

*****

CHAPTER VIII

PUBLISHED PAPERS

LIST OF PAPERS PUBLISHED/ACCEPTED

1. Sorption of water and organic vapours on starch at 35°C.

   S.L. Gupta and R.K.S. Bhatia, Ind. J. Chem. 1969,7,1231.

2. Influence of certain modifications of starch on its sorptive properties with water vapour.

   S.L. Gupta and R.K.S. Bhatia, Ind. J. Chem. (in press).

3. Sorption-desorption hysteresis of n-aliphatic alcohols on cellulose acetate.

   R.K.S. Bhatia, J. Inst. Chem., 1969, XLI, IV, 125.

4. Sorptive properties of cellobiose.

   S.L. Gupta and R.K.S. Bhatia, Ind. J. Appl. Chem. (in press).

5. Sorption-desorption hysteresis of water, methyl alcohol and ethyl alcohol on raw cotton.

   R.K.S. Bhatia, Chem. Age India, 1969, 20, 2, 119.

6. Effect of activation temperature of cellulose acetate on sorption-desorption hysteresis with water.

   R.K.S. Bhatia, Chem. Age India (in press).

7. Hysteresis in water vapour sorption and desorption on guar gum.

   S.L.Gupta and R.K.S.Bhatia,Ind. J. Appl. Chem.(in press).

8. Sorption-desorption hysteresis of water vapour on cellophane.
R.K.S. Bhatia, Chem. Era (in press).

9. Calculation of physico-chemical data from sorption measurements system: Cellulose acetate-n-aliphatic alcohols.
S.L. Gupta and R.K.S Bhatia, J. Inst. Chem. (in press).

10. Adsorption hysteresis in some swelling systems.
S.L. Gupta and R.K.S. Bhatia, Kolloid Zeist & Zeist fur polymere (accepted).

******

Sorption-Desorption Hysteresis of Water, Methyl Alcohol and Ethyl Alcohol on Raw Cotton

R. K. S. Bhatia
Chemistry Department
Birla Institute of Technology & Science
Pilani (Rajasthan)

By employing the Quartz Fibre spring technique, a series of sorption and desorption Isotherms of water, methyl alcohol and ethyl alcohol, at 35°C, on raw cotton, have been obtained. A permanent hysteresis loop is exhibited in each system. The size of the hysteresis loop decreases as the molecular weight of the sorbate increases.

The sorptive capacities of raw cotton for various sorbates decreases in the order water > methyl alcohol > ethyl alcohol > n-propyl alcohol > n-butyl alcohol. The sorption becomes practically negligible with n-butyl alcohol. Raw cotton-alcohol systems exhibit the phenomena of "Bound Alcohol". These interesting results have been explained in the light of "Cavity theory of hysteresis."

Introduction

Very many major studies of synthetic polymers, cellulose, starch and proteins with adsorbates, particularly water, have been reported,[1] but a few data are available on the sorption of non-aqueous liquids by cellulose fibres and, in many cases, the data are inconsistent. These inconsistencies are due to the variation in sample history and drying methods.

The most comprehensive studies on the sorption of various non-aqueous sorbates on cotton cellulose have been reported by Chao[2] and Lauer.[3] Recently,[4] Usmonov et al have reported that swelling capacity of cotton decreases as the molecular weight of the alcohol sorbate increases.

In the present paper a series of sorption and desorption isotherms of water, methyl alcohol and ethyl alcohol on raw cotton, at 35°C, are reported. A permanent hysteresis loop is exhibited. Sorption—Desorption hysteresis has been explained in the light of the cavity theory of hysteresis.[5]

Experimental

Quartz fibre spring technique[6, 7] has been employed in the present investigations. Raw cotton was taken directly from cotton boll and evacuated for two hours in adsorption apparatus. The evacuated cotton was used in studying a series of sorptions and desorptions of various sorbates. Re-distilled water and alcohols, made air-free by slow evaporation for one hour, were used as sorbates. The temperature of the thermostat was maintained at 35 ± 1°C.

Results

Complete sorption and desorption isotherms (at 35°C) of water, methyl alcohol and ethyl alcohol are presented in figures 1, 2 and 3 respectively.

Fig. 1 represents the sorption and desorption of water vapour on raw cotton. The study was continued up to 24 cycles of sorptions and desorptions. The sorption capacities of raw coton at the saturation pressure of water vapour are 39.1, 32.5, 32.3% at the 1st, 18th and 24th cycles respectively.

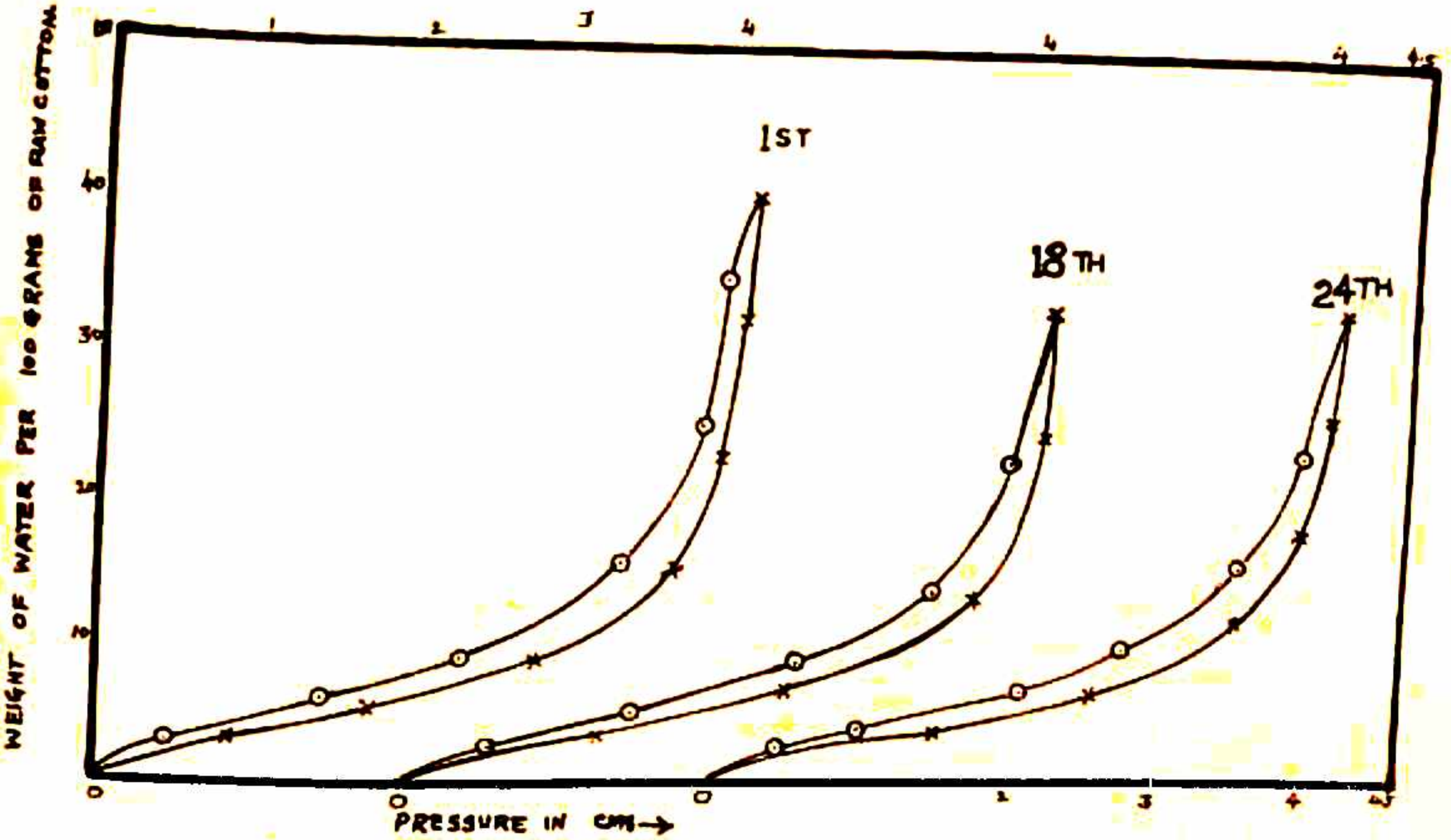


FIG. 1

Sorption—Desorption Hysteresis of Water on Raw Cotton at *the 1st, 18th* and *24th* cycles

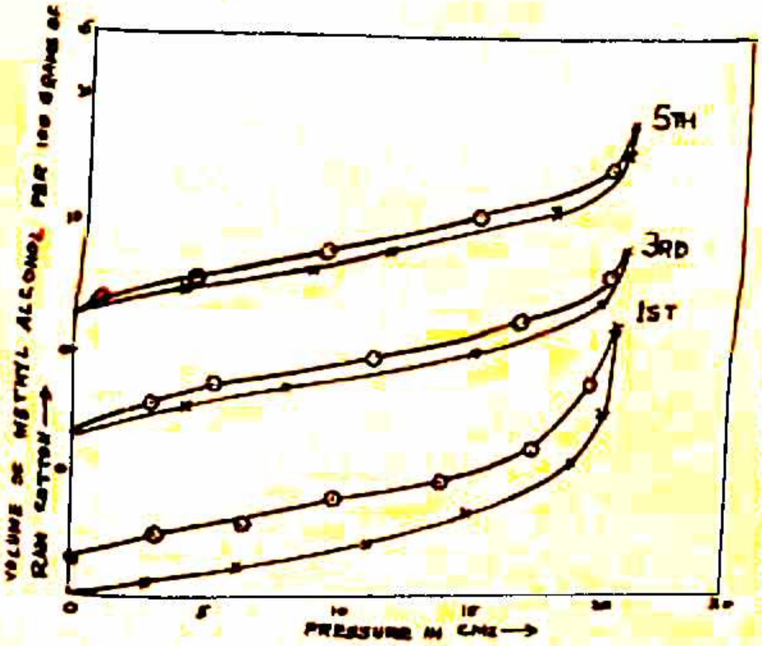


FIG. 2.

Sorption—Desorption Hysteresis of Methyl Alcohol on Raw Cotton at the 1st, 3rd and 5th cycles.

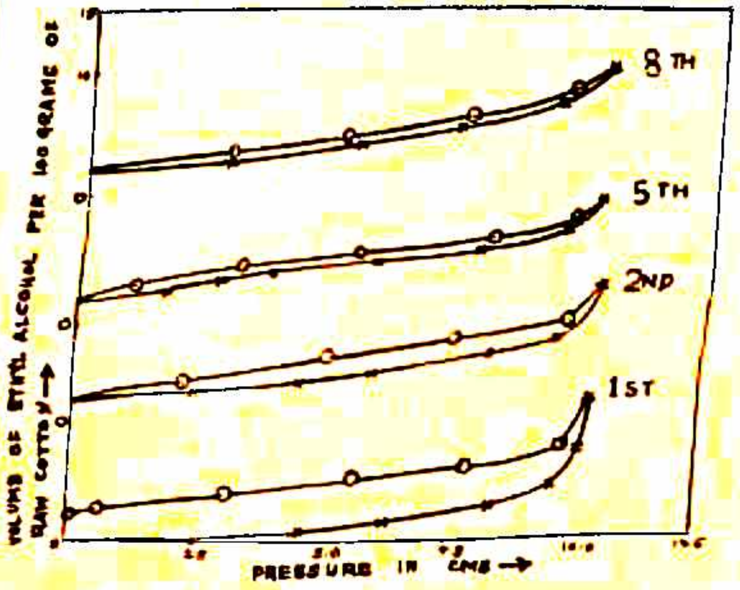


FIG. 3.

Sorption—Desorption Hysteresis of Ethyl Alcohol on Raw Cotton at the 1st, 2nd, 5th and 8th cycles

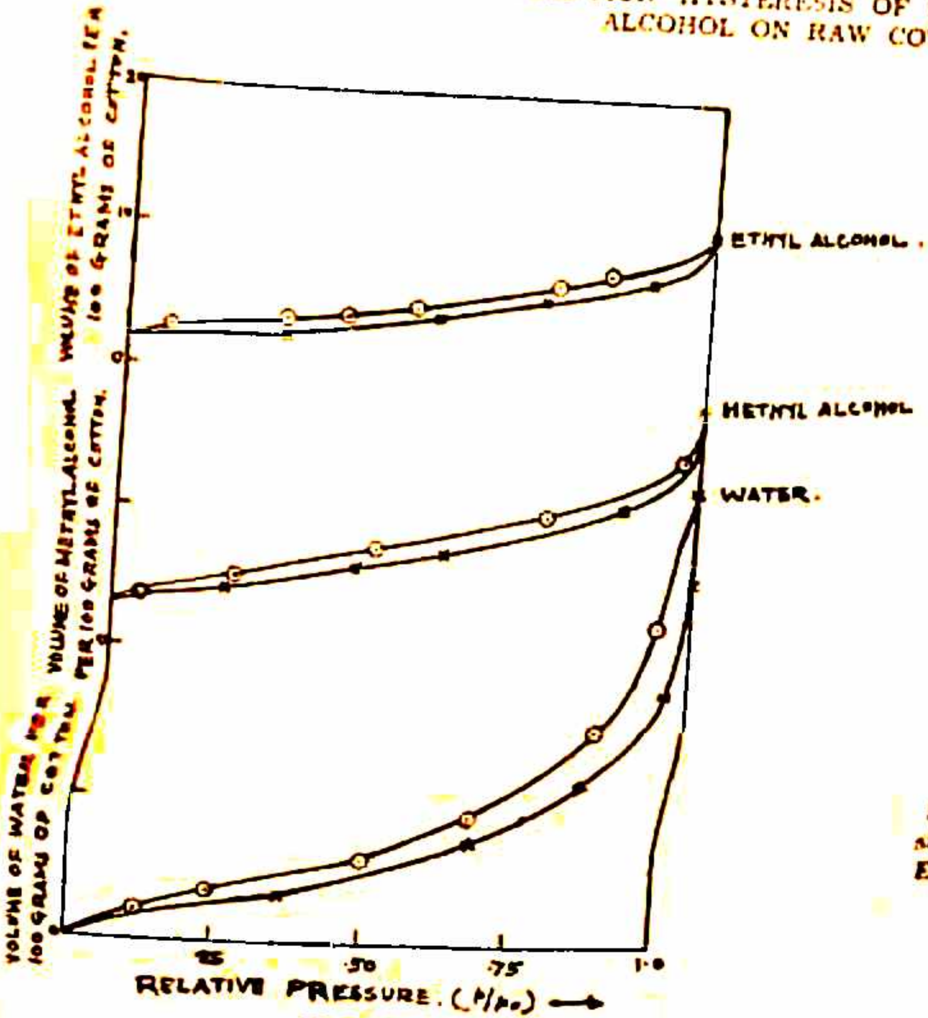


FIG.4.

Sorption — Desorption Hysteresis of Water, Methyl Alcohol and Ethyl Alcohol at the 24th, 5th and 8th cycles.

The sorption and desorption of methyl and ethyl alcohols on raw cotton are presented in figures 2 and 3 respectively. The experiments were continued up to the 5th and 8th cycles respectively. The maximum uptake of methyl alcohol, at the saturation pressure, is 22.2, 17.8, 18.1 ccs at the 1st, 3rd and 5th cycles, while the sorption capacities of ethyl alcohol are 10.4, 9.50, 9.55, 8.0 ccs per 100 gms of cotton, at the 1st, 2nd, 5th, and 8th cycles respectively.

In raw cotton-alcohol systems, at the end of the 1st cycle, cotton irreversibly retains certain amounts of alcohols, which is termed as "Bound Alcohol". The amounts of bound methyl and ethyl alcohols are 2.92 and 2.2 ccs per 100 gms of cotton.

Discussion

To facilitate a comparative study of the hysteresis loops, the sorption capacities of cotton are plotted against the relative pressure instead of actual pressures of water, methyl alcohol, and ethyl alcohol (fig. 4).

The shapes of the adsorption isotherms are significant. The isotherms are of type III of BET classification.[*] The isotherm of water rises asymptotically to the saturation pressure ordinate, whereas the isotherms of methyl and ethyl alcohols cut the saturation pressure ordinate at an angle. It follows that there is a gradual increase in contact angle from water to ethyl alcohol.

A satisfactory explanation for hysteresis effects for rigid non-swelling gels may be made on the basis of the capillary condensation theory. This explanation, however, is not applicable to substances capable of swelling, such as cellulose fibres.

The permanent hysteresis obtained with water and alcohols on cotton can best be explained in the light of the cavity theory of hysteresis. According to the cavity concept, sorption-desorption hysteresis is due to entrapping of liquid sorbate by cavities with constricted necks.

There has been a gradual variation in the shapes and shift in the positions of the hysteresis loops. According to the de Boer classification.[1] type c hysteresis loops are obtained in every case. The loops extend over the whole pressure range.

Raw cotton-water vapour system is a fairly rigid system. A permanent but slightly decreased hysteresis loop is exbited even after 24 cycles of sorptions and desorptions. Raw cotton in contact with water is a changing system. At the end of each sorption, cotton swells with the water taken up at the saturation pressure. During desorption cotton shrinks and the cavities collapse in stages. The decrease in sorptive capacity from 39.1% to 32.3% and slight decrease in the area of the loop may be attributed to this gradual disappearance of the cavities. Raw cotton-alcohol systems show the phenomenon of "Bound Alcohol". After the end of the first sorption-desorption cycle, cotton irreversibly retains small amounts of alcohols. The bound methyl and ethyl alcohols are 2.92 and 2.2 ccs per 100 gms of cotton. Probably, this alcohol is held up in fine pores of the cotton structure and causes the cavities to decrease in size. As the size of the cavities decreases, the difference between the neck radius and body radius also decreases, and so the entrapping effect also decreases. Thus, gradual decrease in the size of the hysteresis loops with methyl alcohol and ethyl alcohol may be attributed to this "Bound Alcohol" in conjunction with increasing molecular size of the alcohol molecules.

Acknowledgement

The author's thanks are due to Professor S. L. Gupta, Head of the Chemistry Department, B.I.T.S., for his interest and instructive suggestions in the present work; and to the Director, B.I.T.S., for the award of an Institute fellowship.

References

1. Everett, "The Solid-Gas Interface", Ed. Flood, Vol. 2 pp. 710-12, 1967.
2. Chao Kolloid-Z-84, 85 (1938).
3. Lauer Kolloid-Z, 107, 86 (1944).
4. Usmonov et al, Dokl. Akad. UZ. SS. R 20 (2) (1963).
5. McBain, *J. Am. Chem. Soc.*, 57, 699, (1935).
6. K. S. Rao, *J. Phy. Chem.* 45, 500, (1941).
7. K. S. Rao, Bhagwan Das, *J. Phy. Chem.* 72, 1223 (1968).
8. Brunauer, Emmett and Teller, *J. Am. Chem. Soc.*, 60, 309, (1938).
9. de Boer, "The Structure and Properties of Porous Materials", Butterworth, London, p. 68, *(1958)*.

Indian Journal of Chemistry
Vol. 7, December 1969, pp. 1231-1233

210

Sorption of Water & Organic Vapours on Starch at 35°C

S. L. GUPTA & R. K. S. BHATIA
Department of Chemistry, Birla Institute of Technology & Science, Pilani

Manuscript received 3 *April* 1969; *revised manuscript received* 2 *June* 1969

A series of sorption-desorption studies, at 35°C, of water, methyl alcohol, ethyl alcohol, and carbon tetrachloride vapours have been carried out on starch, employing the quartz fibre spring technique. The polar sorbates yield sigmoid isotherms with linear hysteresis effect. The hysteresis effect increases as the molecular weight of the sorbate increases. The sorptive capacity of starch shows the following trend in binding these vapours: water methyl alcohol > ethyl alcohol > carbon tetrachloride. Time-adsorption curves, constructed for the polar sorbates, show that the rate of adsorption follows the order: methyl alcohol > ethyl alcohol > water. Starch-alcohol systems exhibit the phenomenon of 'bound alcohol'. The results have been explained in the light of the 'cavity theory' of hysteresis. A reasonably good fit for the BET equation has been obtained for starch-water and starch-methyl alcohol systems. Specific surface area of starch for the two sorbates and the number of molecules in the monolayers have also been calculated.

THE interaction of adsorbates, particularly water, with polymers, cellulose, starch and proteins is different from that of gel and rutile systems. In the former systems very strong interaction between the adsorbate and adsorbent is normally observed, resulting in major changes in structure[1]. More information about the interaction between sorbed vapours and these systems may be obtained by the study of simpler systems.

The interaction of water with starch has already been reported[2-5]. Bushuk and Winkler[6] studied the sorption of water and organic vapours on wheat flour and reported that water sorption was a bulk property and did not depend on the particle size. It was also reported that hysteresis effect increases as the molecular volume of the sorbate increases.

The present communication summarizes the results of a comparative study of a series of sorptions and desorptions, at 35°C, of polar sorbates like water, methyl alcohol and ethyl alcohol, and non-polar sorbates like carbon tetrachloride on starch. These studies were initiated to gather more information about the interaction of water and some organic vapours with starch, from the point of view of hysteresis and time dependence.

Materials and Methods

Starch (Schmidt & Berg., Hamburg Fu. 1, Germany) was used as adsorbent in all the experiments.

Redistilled methyl alcohol (BDH, AR), carbon tetrachloride (AR, Reanal, Budapest) and double distilled water were used as sorbates while ethyl alcohol was kept in contact with calcium metal for 24 hr and then distilled.

Procedure — The quartz fibre spring technique[7] was employed in the present investigations. The adsorbent was evacuated for 2-3 hr in adsorption apparatus before starting a sorption-desorption cycle. The adsorption apparatus was kept inside an air thermostat of the type constructed by Vernon[8]. The temperature of the thermostat was kept at 35° ± 0·1°C by means of a toluene regulator in conjunction with an electronic relay. The springs of sensitivities ranging from 40 to 45 cm/g load were used. A cathetometer reading correct to 0·001 cm was used to read the stretch of the springs. By exposing the evacuated adsorbent to water, methyl alcohol and ethyl alcohol, at their saturation pressures, at 35°C, the extent of sorption with time was measured.

Results

The hysteresis loops obtained with water, methyl alcohol and ethyl alcohol are shown in Figs. 1-3.

Starch-water vapour system — Permanent and reproducible hysteresis is exhibited by starch-water vapour system. The sorption and desorption studies were continued up to 7th cycle. The loops obtained in the 1st, 3rd, 6th and 7th cycles are shown in Fig. 1. The amounts of water taken at saturation pressure in each of these cycles are 32·5, 32·0 and 31·5 cc respectively.

Starch-alcohol systems — Hysteresis loops of 1st, 2nd and 6th cycles with methyl alcohol and ethyl alcohol on starch are presented in Figs. 2 and 3 respectively. Permanent hysteresis is exhibited in both the systems. The loops are reproducible after the first cycle. At the end of 1st sorption-desorption cycle, starch retains irreversibly certain amount of alcohol which cannot be removed even by drastic evacuation for 10 to 12 hr. The amounts of bound methyl alcohol and ethyl alcohol are 3·2 and 6·6 cc per 100 g of starch respectively. The values of sorption at saturation pressure of methyl alcohol in each of the cycles are 26·8, 25·4 and 24·6 cc respectively.

The amount of ethyl alcohol taken up at saturation pressure of ethyl alcohol in the 1st, 2nd and 6th cycles are 16·5, 16·3 and 16·4 cc respectively.

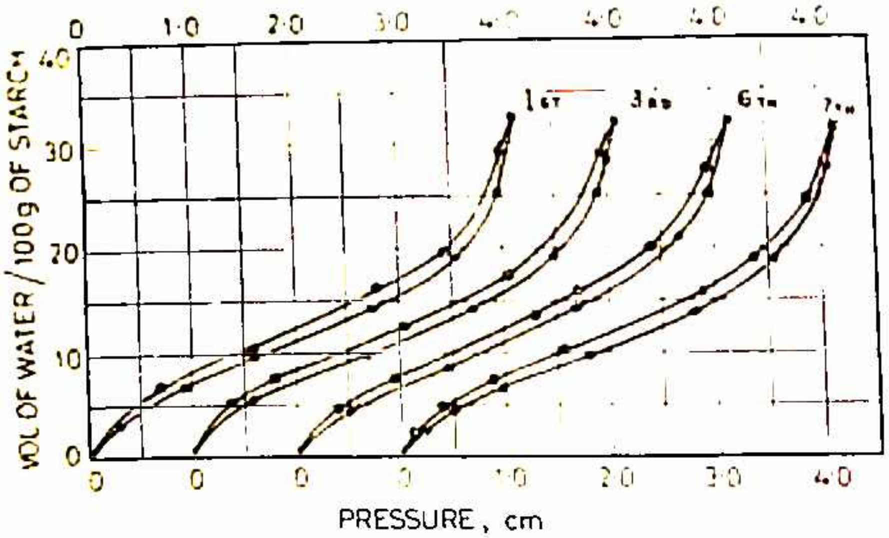


Fig. 1 — Sorption-desorption hysteresis of water vapour on starch at the 1st, 3rd, 6th and 7th cycles

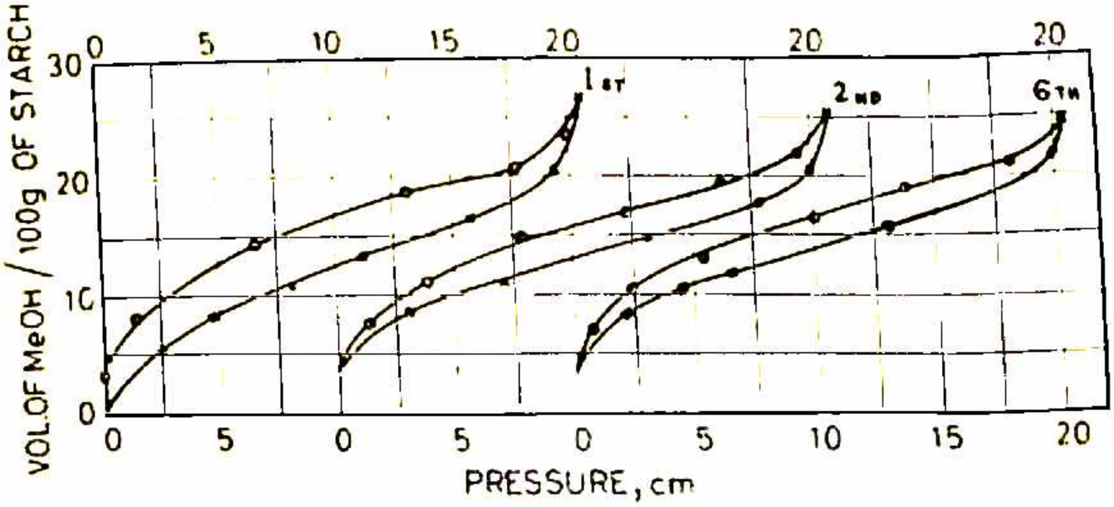


Fig. 2 — Sorption-desorption hysteresis of methyl alcohol on starch at the 1st, 2nd and 6th cycles

Starch-carbon tetrachloride system — With carbon tetrachloride, sorption-desorption studies were continued up to 3rd cycle. It was not possible to obtain accurate data for adsorption of carbon tetrachloride with this technique due to very low sorptive capacity of starch for this sorbate. The sorption capacities in the 1st, 2nd and 3rd cycles are 0·3, 0·3 and 0·2 cc per 100 g of the adsorbent.

Time-adsorption curves — The time-adsorption curves for the adsorption of water, methyl alcohol and ethyl alcohol vapours at 35° are given in Fig. 4. The rate curves show that, under similar experimental conditions, methyl alcohol is adsorbed on starch much faster than either ethyl alcohol or water.

Discussion

The isotherms of water, methyl alcohol and ethyl alcohol are essentially sigmoid in shape, although the isotherms for ethyl alcohol show only a slight concavity to the pressure axis in the low pressure range. In addition to the sigmoid shape, the polar sorbates exhibit the linear hysteresis effect, i.e. the hysteresis loop extending over the entire pressure range. The size of the hysteresis loops shows the following trend: ethyl alcohol > methyl alcohol > water.

The permanent and reproducible hysteresis obtained with polar sorbates can be explained in the light of 'ink bottle' or 'cavity theory'[9,10] of hysteresis. The 'cavity theory' postulates that sorption-desorption hysteresis is due to the entrapping of liquid sorbate by cavities with constricted necks. With the larger sorbate molecules, a greater entrapping effect results. The molecular volume increases in the order: water 18·79 cc, methyl alcohol 42·74 cc and ethyl alcohol 62·28 cc; likewise the entrapping effect also increases, giving wider hysteresis loops.

Further, for the polar sorbates, the molecular volume seems to be the main factor upon which the extent of sorption depends. The effect is exhibited, particularly by the isotherms of two alcohols. These two alcohols have essentially the same polarity (methyl alcohol 1·69 and ethyl alcohol 1·70 D), so the decrease in the extent of sorption may be due to the increase in the molecular size.

Applicability of BET equation — Excepting ethyl alcohol, the sorption isotherms of water and methyl alcohol exhibit clearly defined 'knees'. According to BET theory[11], the 'knee' signifies the transition from monomolecular to multimolecular sorption. The BET equation has been applied to the isotherm

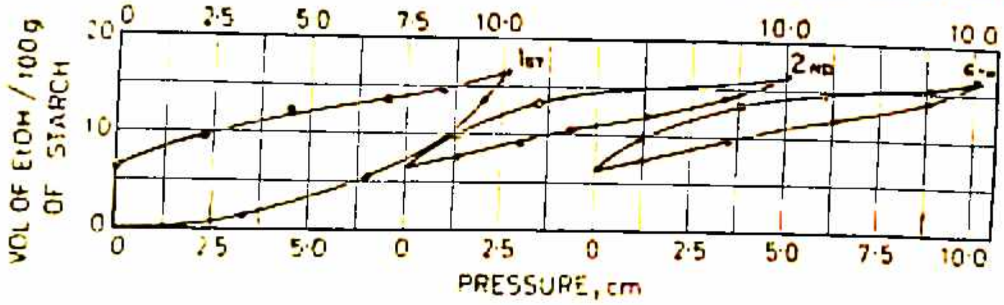


Fig. 3 — Sorption-desorption hysteresis of ethyl alcohol on starch at the 1st, 2nd and 6th cycles

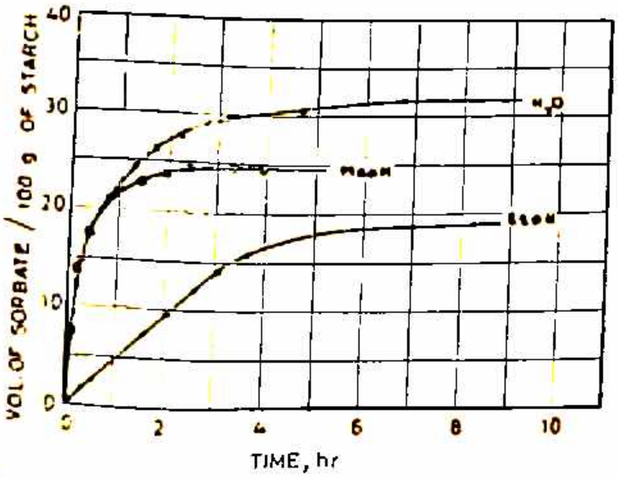


Fig. 4 — Time-adsorption curves for water, methyl alcohol and ethyl alcohol at their saturation pressures, at 35°, on starch

of water and methyl alcohol which yielded straight lines. From the slope and intercept of the lines the monolayer capacities x_m have been calculated. The value of monolayer capacity was also read out directly from the isotherms with reasonable accuracy[12,13a] and this is denoted by x_B. The values of monolayer capacities x_m and x_B for the two sorbents and the relative vapour pressures at which the monolayers are fully formed are presented in Table 1.

The agreement is good between the values of x_B and x_m.

The total number of water and methyl alcohol molecules, contained in the monolayer on the surface of 1 g of starch have also been calculated and found to be $20{\cdot}1\times10^{20}$ and $18{\cdot}3\times10^{20}$ respectively.

From the monolayer capacity and cross-section area of the sorbate, the specific surface of the adsorbent has been calculated[13b]. Assuming the water molecules to be spherical ($Am = 10{\cdot}6$ Å²), the specific surface area of starch comes out to be 210·0 m²/g. For methyl alcohol, the specific surface of starch depends upon the mode of adsorption. Assuming the alcohol molecules as spheres, the specific surface comes out to be 333·4 m²/g. If the molecules are considered linear, the adsorbed molecules can be held either perpendicular or parallel to the surface of the adsorbent. Knowing the cross-section and the area of the side[14] the specific surface is calculated and found to be 378·2 m²/g and 390·7 m²/g respectively. Each of these values is higher than that obtained from water sorption. However, if Am for water is arbitrarily adjusted to 14·8 Å², as suggested by Harkins[15], the specific surface comes out to be 303·4 m²/g which is in moderately good agreement with the value obtained for methyl alcohol, considering the molecules as spheres.

TABLE 1 — MONOLAYER CAPACITIES x_m AND x_B (g/g of sorbent) AND THE CORRESPONDING RELATIVE VAPOUR PRESSURES

Vapour	x_B	x_m	p/p_0
Water	0 062	0·060	0·197
Methyl alcohol	0 100	0·097	0·194

Acknowledgement

The authors are thankful to Dr C. R. Mitra, Director, for the award of a research fellowship to one of them (R.K.S.B.).

References

1. McIntosh, R. L., in *The solid-gas interface*, edited by E. A. Flood (Marcel Dekker Inc., New York), 1967, 540.
2. Sato, H., *J. Tokyo chem. Soc.*, **72** (1951), 790.
3. Hellman, N. N., Boesch, T. F. & Melvin, E.H., *J. Am. chem. Soc.*, **74** (1952), 348.
4. Ubertis, B., & Roversi, B., *Stärke Die*, **5** (1953), 266.
5. Khawas, F. El., Tawashi, R. & Czetschlindenwald, H. V., *J. Soc. cosmet. Chem.*, **17** (2) (1966), 103.
6. Bushuk, W. & Winkler, C. A., *Cereal Chem.*, **34** (1957), 87.
7. Rao, K. S. & Das, B., *J. phys. Chem. Ithaca*, **72** (1968), 1223.
8. Vernon, W. H. J., *Trans. Faraday Soc.*, **27** (1931), 241.
9. Rao, K. S., *J. phys. Chem. Ithaca*, **45** (1941), 500.
10. McBain, J. W., *J. Am. chem. Soc.*, **57** (1935), 699.
11. Brunauer, S., Emmett, P. H. & Teller, E., *J. Am. chem. Soc.*, **60** (1938), 309.
12. Emmett, P. H. & Brunauer, S., *J. Am. chem. Soc.*, **59** (1937), 1553.
13. Gregg, S. J. & Sing, K. S. W., *Adsorption, surface area and porosity* (Academic Press Inc., London), 1967, (a) 54, (b) 65.
14. Rao, K. S. & Das, B., *Curr. Sci.*, **21** (1968), 5, 599.
15. Harkins, W. D., *The physical chemistry of surface films* (Reinhold Publishing Co. Inc., New York), 1952, 235.