STUDIES IN SORPTION - DESORPTION HYSTERESIS

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C E R T I F I C A T E

This is to certify that the entire work embodied in this thesis has been carried out by the candidate under my guidance and supervision from August 1965 to January 1969 in the Department of Chemistry, Birla Institute of Technology and Science, Pilani, Rajasthan.

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CHAPTER I: INTRODUCTION

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INTRODUCTION

Sorption

When a gas or the vapour of a liquid is allowed to come into contact with a solid or liquid surface, there will usually be increased concentration of the gas or vapour molecules at the surface, regardless of the nature of the gas or surface. This process of surface concentration is known as adsorption. In particular cases adsorption may be followed by absorption as the adsorbed molecules penetrate into the interior of the adsorbent. Surfaces are generally nonuniform and contain cracks and capillaries. These are most predominent in porous adsorbents. In such cases there will be capillary condensation of the adsorbate. In addition there may be chemisorption in particular cases. In actual practice, all these phenomena invariably follow surface adsorption. True adsorption is a rarity in nature. 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 a liquid is called adsorbent, the gas or vapour adsorbed on the surface of the solid is termed adsorbate.

Physical and chemisorption

Adsorption processes are classified as physical and chemical depending upon the nature of the forces involved. In physical adsorption it is weak interaction between adsorbent and adsorbate, similar to condensation, whereas chemisorption on the other hand is due to strong interaction between the adsorbent and adsorbate, similar to chemical reactions. The term "Van der Waals adsorption" is used as a synonym for the former and the term "Activated adsorption" as a synonym for the latter. In physical adsorption, the gas molecules are bound to the surface of the adsorbent by dispersion forces[3] which are attractive in nature, and short range repulsive forces[4]. In addition there may also be forces due to quadrupole, permanent dipole and induced dipole attractions. In chemisorption, the molecules are bound to the surface by a transfer or sharing of electrons.

Adsorption of a gas on the solid surface is subjected to unbalanced forces, the inward pull being more than the outward forces. This results in a decrease in surface tension or a decrease in free energy of the system. There is also loss of degrees of freedom of the gas when it is adsorbed. It is either rigidly held to the surface or can move over the surface freely in two

directions whereas prior to adsorption the gas molecules moved freely in three dimensions. Hence there is also a decrease in entropy. The equation $\triangle F = \triangle H - T \cdot \triangle S$ shows that $\triangle H$ will decrease when the sum of $\triangle F$ and $\triangle S$ decreased. Therefore adsorption processes are always exothermic regardless of the nature of the forces involved. The decrease in the heat content of the system is termed as heat of adsorption.

Distinction between physical and chemisorption

For the distinction between physical and chemical adsorption, a number of experimental criteria are available and the decision can be easily made. However, no single criterion can differentiate between the two types satisfactorily but by taking them together it is possible to decide

(1) One of the best known of these criteria is the magnitude of the heat of adsorption. In physical adsorption, it is of the same order as the heat of liquefaction of the adsorbate and in chemisorption as the heat of chemical reaction. The heat of physical adsorption rarely exceeds twice the latent heat of condensation whereas the heat of chemisorption is in general several times more than the latent heat. Heats of chemisorption of carbon monoxide and hydrogen seemed always to exceed

some 20 and 15 K cal/mole respectively[5,6] whereas the heats of physical adsorption were always less than about 6 and 2 K cal/mole[7,8].

Although this distinction is in general valid, there are cases in which the heat of chemisorption is low. For example, with hydrogen values as low as 3 K cal/mole have been observed[9,10]. Since heats of Van der Waals adsorption do not exceed a certain limit, high heats always indicate chemisorption.

(2) Another important criterion is the rate of adsorption. Chemisorption, being a chemical process, frequently requires activation energy and so proceeds at a limited rate which increases rapidly with rise in temperature. Physical adsorption, requires no activation energy, the rate of adsorption being very high.

However, later work has shown that chemisorption is not invariably an activated process. Studies with clean metal wires and evaporated films have shown that chemisorption is sometimes rapid even at low temperatures. Roberts[11] found that hydrogen was taken up rapidly by a tungsten filament both at room temperature and at liquid air temperature to give a saturated layer even at low pressures (10^{-4} mm of Hg.). In some cases chemisorption is slow even at room temperature, e.g., hydrogen

on manganese or carbon monoxide on aluminium, whilst in others, e.g., carbon monoxide or ethylene on zinc, no chemisorption at room temperature has so far been recorded[12].

(3) Physical adsorption usually takes place at temperatures at which liquefaction would occur and the temperature will be near or below the boiling point of the adsorbate. Chemisorption on the other hand can usually take place at temperatures far above the boiling point of the adsorbate. But at certain temperatures, the two types of adsorption can occur simultaneously.

(4) Chemisorption is specific while physical adsorption is not. Chemisorption takes place on clean surfaces and only when there is chemical affinity between the adsorbent and the adsorbate.

(5) Chemisorption is always a monomolecular process but in physical adsorption multimolecular layers of physically adsorbed gas can be obtained under suitable conditions of temperature and pressure. Therefore, if the extent of adsorption is known to exceed a monolayer, it can be assumed with certainty that second and higher layers are physically adsorbed.

From the above differences it can be said that physical adsorption is a surface condensation and chemisorption a surface reaction.

FIG. 1 TYPES OF ISOTHERMS

Classification of the isotherms

When equilibrium is attained in adsorption, the amount of gas adsorbed will be a function of temperature and pressure. Adsorption equilibrium can be expressed either as isotherms, isobars or isosteres. When the pressure of the gas or vapour is varied and the temperature is kept constant, the plot of the amount adsorbed against the pressure is called the adsorption isotherm, when the temperature is varied and the pressure is kept constant, the adsorption isobar is obtained and adsorption isostere is obtained by plotting the variation of the equilibrium pressure with temperature for a definite amount of gas adsorbed. But the most convenient method is the adsorption isotherm. The adsorption isotherms obtained with numerous adsorbates and adsorbents have large variety of shapes. Brunauer, Emmett and Teller[13] classified these different isotherms into five typical categories (Figure 1), type first representing monomolecular adsorption whereas others multimolecular adsorption.

Theories of adsorption

A number of theoretical isotherms have been derived by many workers in the past. Of these the derivation of classical Freundlich equation[14] and the

isotherms derived by Langmuir[15], Brunauer and his coworkers[13,16] are important.

In deriving theoretical isotherms, three approaches are possible. First, 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. Second, in statistical terms, the equilibrium constant is given by a ratio of partition functions of vacant sites, adsorbed molecules and gas phase molecules, and isotherms may be obtained by equating this ratio to the corresponding ratio of concentrations. Third, in thermodynamic terms, the isotherm can 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 Gibbs adsorption equation.

Monomolecular adsorption

Until the year 1914 there existed no satisfactory theoretical treatment of the surface adsorption of gases and vapours. Then Langmuir proposed his theory that the adsorbed layer is monomolecular.

According to Langmuir[17], when the molecules of a gas or vapour collide with the surface of a solid, the

collision may be either elastic or inelastic. Ordinarily the collision is inelastic, and the molecule stays in contact with the surface for a certain length of time. This timelag is responsible for the phenomenon of adsorption. It is short in physical adsorption and long in chemisorption.

Langmuir derived the equation by assuming that (1) the forces of interaction between the adsorbed molecules themselves are negligible, (2) every molecule coming from the gas phase that strikes a molecule already adsorbed on the surface is elastically reflected and only those molecules that strike the bare surface condense and (3) because of the rapid falling off the intermolecular forces with distance, it is probable that adsorption is only monomolecular and

$$V = \frac{V_m . b . p}{1 + b . p}$$

where V is the volume adsorbed at pressure p, V_m the volume adsorbed when the surface is covered with a complete monomolecular layer and b is a constant. The above equation is of restricted application and is obeyed only in ideal cases.

Volmer[18] has derived the Langmuir equation thermodynamically whereas Fowler[19] has derived by employing

the principles of statistical mechanics. Others[20,21] have also made the statistical derivation of the Langmuir equation. The statistical derivation is based on three assumptions which are similar to that of Langmuir (1) adsorption is localized and takes place only through collision of gas molecules with vacant sites (2) each site can accommodate one and only one adsorbed particle (3) the energy of an adsorbed particle is the same at any site on the surface, and is independent of the presence or absence of nearby adsorbed molecules.

Analogues of Langmuir's isotherm

The isotherm derived thermodynamically by Williams[22] and kinetically by Henry[23] is based on the Langmuir model, modified by the stipulation that each adsorbed molecule occupies "n" adjacent sites. The equation after simplification reduces to

$$\ln V/p = \ln V_m.b - n\, V/V_m$$

and is also known as Williams-Henry isotherm equation. The above equation with a second power term was also derived by Wilkins[24]. No one has attempted to test the validity of these equations.

Magnus[25] also proposed a theoretical treatment of monomolecular adsorption but was only tested by himself

and his coworkers. The drawback of Magnus' theory is its very limited applicability. He himself[26] found that not even all of the charcoal data obeyed his equation.

Freundlich equation

The classical Freundlich's equation[14] is represented as

$$V = c.\ p^{1/n}$$

where V is the volume adsorbed, p the pressure of adsorbate and c and n are constants. Rideal[27] has shown that the Freundlich isotherm can be derived from the Gibbs adsorption equation, if it is assumed 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.

Theoretical considerations of Zeldowitsch[28], Halsey and Taylor[29,30] have shown that if the Langmuir adsorption is applied to a series of sites, the relative energies of which follow an exponential relationship, the Freundlich equation is obtained.

Temkin isotherm[31] is in fact derived[32] by inserting in the Langmuir isotherm the condition that the heat of adsorption decreases linearly with coverage. Such a heat fall can arise either on a uniform surface from repulsive forces or from surface heterogeneity.

Summarizing, we may state that when adsorption takes place in a monomolecular layer, the data can often be fitted satisfactorily by means of the simple Langmuir equation.

Capillary condensation

The capillary condensation theory attributes adsorption to condensation of the vapour in the capillaries of the adsorbent. Zsigmondy[33] was the first to formulate the capillary condensation theory which is governed by the well known Kelvin equation[34]

$$\ln p/p_s = \frac{-2\sigma V \cos\theta}{r R t}$$

where p is the equilibrium pressure, p_s is the normal vapour pressure, σ is the surface tension, V is the molar 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. He assumed that in small capillaries condensation takes place at pressures considerably lower than the normal vapour pressure. The capillaries of the smallest radii fill at lowest pressures and as the pressure is increased, larger capillaries start getting filled and at saturation pressure all the pores are filled with liquid.

McGavack and Patrick[35] 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_s should be used instead of the volume of the gas adsorbed at pressure p. Capillary condensation plays an important role at higher pressures.

Multimolecular adsorption

It is known that adsorbed molecules can also hold other molecules by their Van der Waal's forces giving multimolecular adsorption. To explain the multimolecular adsorption, Polanyi[36] gave his potential theory. He assumed that adsorption was due to long range attractive forces emanating from the solid surface, giving films of many molecules thick. Later on de Boer and Zwikker[37] put forward polarization theory. According to this theory, the surface is assumed to induce dipoles in the first layer of adsorbed molecules and these dipoles in turn to induce dipoles in the second adsorbed layer and so on. But no theory in itself explains all the adsorption processes and the most satisfactory theory which accounts for all the cases of adsorption is the multimolecular adsorption theory[13,16] of Brunauer, Emmett and Teller.

It is based on the same kinetic picture as the Langmuir equation and the assumption that the condensation forces are the principal forces in physical adsorption. Like Langmuir's theory the rate of evaporation from each succeeding layer is equal to the rate of condensation on the preceeding layer. It is further assumed that the heat of adsorption in each layer except first, is equal to the heat of liquefaction of the bulk liquid, thus suggesting that Van der Waals' forces of the adsorbent are transmitted to the first layer only. The adsorption on first layer is also assumed to be localized.

The BET equation is derived on the above mentioned assumptions and is written as

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

where V is the total volume of gas adsorbed at pressure p, V_m is the monolayer volume, p_s is the saturation pressure of the adsorbate and c is a constant related to the heat of adsorption and heat of liquefaction of the adsorbate. The above equation is applicable for a large number of cases of physical adsorption in the range of 0.05 to 0.30 relative vapour pressure. A simpler derivation has been given by Foster[38] and a more rigorous kinetic derivation by Hill[39].

If owing to lack of space, adsorption at saturation is restricted to n layers, the BET treatment leads to the equation[13,16]

$$V = \frac{V_m \cdot c \cdot x}{(1 - x)} \cdot \frac{1 - (n + 1)\, x^n + n \cdot x^{n+1}}{1 + (c - 1)\, x - c \cdot x^{n+1}} \qquad (B)$$

where x is the relative vapour pressure (p/p_s). This more general equation(B) can be reduced to Langmuir equation when $n = 1$ and to equation (A) when $n = \infty$.

Several defects in the multilayer theory of BET have been pointed out by the authors themselves and by others. One defect is the assumption in the theory that the heat of vaporization is the same for all layers and equal to that of the bulk liquid. Most of the workers criticized the theory stating that the authors did not consider the lateral interaction effects but actually they considered it. However, they assumed that these effects were negligible at low pressures. Various modifications and criticisms of the BET theory has been reviewed by Ries[40], Cook[41], Keenan[42], and Young and Crowell[43].

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CHAPTER II: EARLIER WORK

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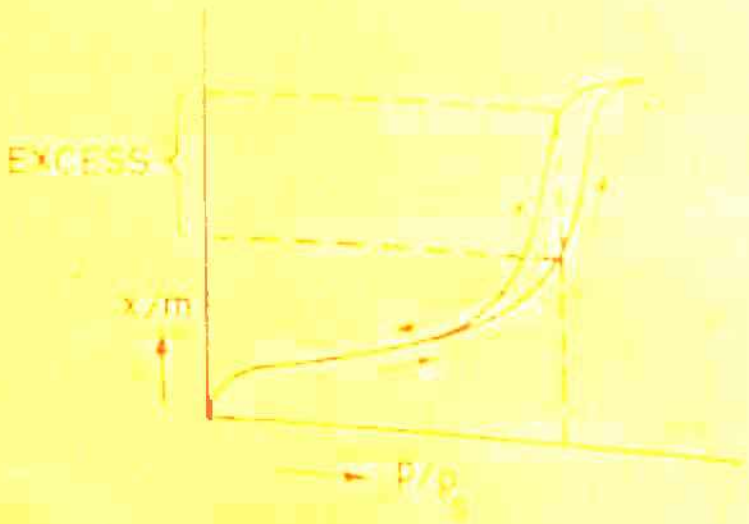

FIG. 1 HYSTERESIS IN SORPTION

SORPTION - DESORPTION HYSTERESIS

Starting from zero pressure, the extent of sorption at different vapour pressures is determined until the saturation pressure is reached. Such measurements give sorption isotherm. On the other hand, starting from the saturation pressure, the sorbent is subjected to decreasing vapour pressures and the amount of sorbate retained measured at different vapour pressures until zero pressure is reached. These measurements give desorption isotherm. These opposite processes of sorption and desorption do not coincide in a large number of systems and this phenomenon of the non-coincidence of sorption and desorption isotherms is known as "Hysteresis". The loop formed by the sorption and desorption curves is known as the hysteresis loop. It follows from a study of the hysteresis loop that the sorbent retains for the same. Vapour pressure, more of the adsorbate during desorption than during sorption, Figure 1. Hysteresis can be reversible and also irreversible but in physical adsorption it is generally reversible.

For a long time, the phenomenon of hysteresis in sorption was an unsolved problem. Van Bemmelen[44], Zsigmondy[33] and Anderson[45] revealed the existence of the

hysteresis effect in sorption. Gustaver[46] and Coolidge[47] showed the presence of hysteresis with charcoal. Winning and Williams[48] have shown that glyptal resins exhibit hysteresis in the sorption of organic vapours. Shiels[49-51] has reported the complete absence of the 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 is important in considering hysteresis effect.

McGavack and Patrick[35] obtained the hysteresis effect in the sorption of sulphur dioxide on silica gel, whereas, on keeping the gel overnight in contact with sulphur dioxide, subsequent sorptions and desorptions showed no hysteresis. Urquhart[52] reported the hysteresis effect on the sorption of water on cellulose. Sheppard and Newsome[53] on the other hand observed, that the hysteresis loop becomes smaller in three successive sorptions and desorptions in the studies of water sorption on cellulose and its derivatives. They stated that yet there is no complete explanation of the hysteresis

effect. King and Lawson[54] obtained hysteresis effect in the sorption of heavy water vapour on charcoal. They attributed this effect to rise in pressure of evacuation during studies. McBain and Ferguson[55] also noticed hysteresis in the sorption of water vapour on Gatton stone (a building material).

Burrage[56] studied the sorption of carbon tetrachloride, methyl alcohol, ethyl alcohol, propyl alcohol and formic acid on charcoal and obtained hysteresis effect in all cases. Foster[57] obtained the reproducible hysteresis loops on the sorption of methyl alcohol and ethyl alcohol on silica gel whereas Pidgeon[58] obtained hysteresis effect only in case of water while studying the sorption of water, benzene and ethyl alcohol on silica gel.

Allmand and coworkers[59] have established that hysteresis is real on the sorption of water vapour on various samples of charcoal. By the study of the sorption of vapours of water, ethyl alcohol and benzene on gels of silica and ferric oxide, Lambert and Foster[60] have shown that hysteresis effect is real and it persists even after drastic degassing of the gel surface. Though sorption - desorption hysteresis effect was observed by many early workers, whether it is a permanent and

reproducible effect and if so what is the satisfactory explanation of it, are problems which remained unsolved for some time.

By the extensive work of Rao and his school[61-74] on a large number of variety of systems, the hysteresis effect has been established to be real and the only satisfactory explanation for the hysteresis effect and all its allied phenomena such as permanence and reproducibility[61,66,69], scanning[61,63,68,69], drift[61,64] and disappearance[61,65,71,73,74] of the hysteresis loop, is the cavity concept[75,76]. All other explanations of earlier workers based on false equilibrium, false measurements of pressure, ash content of charcoal, presence of air have been disproved by the work of Rao and his collaborators.

Permanence and reproducibility of the hysteresis loop

In majority of the systems investigated, the permanence and reproducibility of the hysteresis loop has been established experimentally. In titania gel - water system, the hysteresis loop remains permanent and reproducible even after 32 sorptions and desorptions[61]. Similarly the hysteresis loop has been reproduced at the 19th cycle in silica gel - water[61], 8th cycle in silica gel - carbon tetrachloride[61], 9th cycle in rice -

carbon tetrachloride[61], 10th cycle in alumina gel - water[66] and 12th cycle in titania gel - carbon tetrachloride[69]. 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 persists. There is absolutely no doubt about the permanence and reality of the hysteresis effect.

Scanning of the hysteresis loop

A new method of study of the hysteresis loop was developed by Rao and this was called the "scanning of the hysteresis loop". The permanent and reproducible hysteresis loops in titania gel - water[61,63], silica gel - water[61], silica gel - carbon tetrachloride[61], ferric oxide - carbon tetrachloride[61], alumina gel - water[68] and titania gel - carbon tetrachloride[69] have been scanned by traversing the loops from various intermediate points on the main sorption and desorption curves. If desorption is effected starting from any intermediate point on the main sorption curve, the loop is crossed and the main desorption curve is reached. If sorption is effected from any intermediate point on the main desorption curve, the main sorption curve, however, is not reached, but a separate curve is traced till the

peak of the hysteresis loop is reached. These characteristics, which are independent of the nature of the adsorbent and the adsorbate, but are dependent solely on the size and shape of the cavities of the porous adsorbent, are explainable on the basis of the cavity theory.

Drift of the hysteresis loop

Ferric oxide gel - water system[61,64] has shown a unique behaviour. With progressive sorptions and desorptions, the gel suffers continuous decrease in sorptive capacity, the hysteresis loop suffers drift away from the axis other than that of pressure. The hysteresis loop becomes smaller and the tail end of the hysteresis loop which extends up to zero pressure in the second cycle of sorption and desorption tapers away from zero pressure in the subsequent cycles. These results indicate the decrease in the total pore volume of the gel and the widening of the cavities and their necks. This interesting effect of continuous drift of the hysteresis loop in successive sorptions and desorptions, is attributed to the irreversible change in ferric oxide gel of the aggregation of smaller particles into bigger ones.

Disappearance of the hysteresis loop

A series of sorptions and desorptions of water vapour on cereals[61], gum arabic[65] and proteins[71,74] have shown the tendency of the hysteresis loop, obtained in the first cycle of sorption and desorption, to decrease in size and disappear in subsequent cycles. Similar behaviour has also been shown by leaves of certain plants[73] when subjected to successive dehydrations and rehydrations. The disappearance of the hysteresis loop has revealed the role, in hysteresis in sorption of the elasticity of organo gels which swell on the imbibition of water and other solvating liquids. With non-solvating liquid, as in rice - carbon tetrachloride system, the gel retains its initial rigidity even after a series of sorptions and desorptions and show a permanent and reproducible hysteresis loop. The cavities entrap solvating liquid and thus exhibit hysteresis. On progressive sorptions and desorptions, they swell, become elastic and the cavities lose their power of entrapping water, the cavities collapse and thus the hysteresis loop initially exhibited, disappears.

Theories of sorption - desorption hysteresis

Though sorption - desorption hysteresis effect has been established to be real and reproducible, the

exact cause of this phenomenon has remained a puzzling problem. Any satisfactory theory of hysteresis should account for the excess (Figure 1) of the sorbate retained by the sorbent during desorption over what is taken during sorption. There have been a number of attempts to explain the difference which obviously exists between the states of adsorbate along the two sides of the hysteresis loop. Zsigmondy[33] was the first to account for hysteresis in terms of capillary condensation theory. He assumed that during adsorption, the vapour does not wet the wall of the adsorbent completely and hence wetting angle θ is not zero. The equilibrium pressure will be given by the Kelvin equation[34]

$$p_a = p_s \cdot e^{-2\sigma V \cos\theta / r R T} \qquad (1)$$

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

$$p_d = p_s \cdot e^{-2\sigma V / r R T} \qquad (2)$$

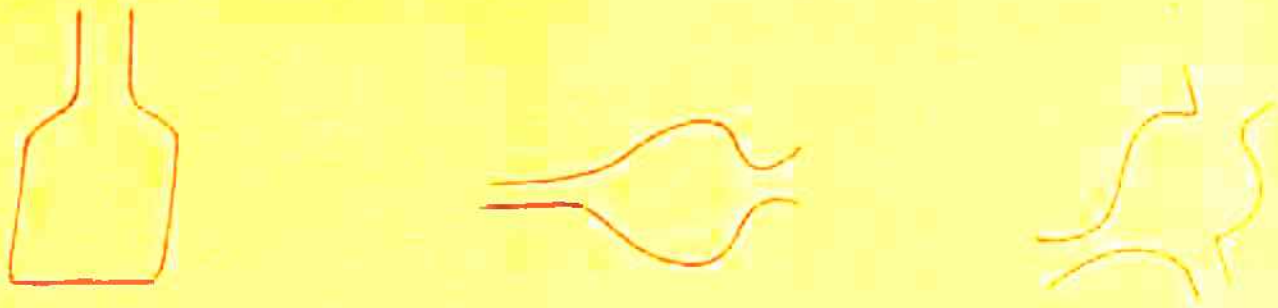

FIG. 2. INK-BOTTLE OR CAVITY.

Hence on comparing equations (1) and (2)

$$P_a > P_d$$

But Zsigmondy's explanation that hysteresis is due to the presence of impurities was discredited by the work of Rao.

Ink bottle or Cavity theory

The "ink bottle" or the cavity theory was suggested by Kraemer[75] and developed by McBain[76], Katz[77] and Rao[61]. A cavity or ink bottle is a capillary with a narrow neck like an ink bottle (Figure 2). A cavity may have two or more necks. During sorption the 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 lower than the value corresponding to the neck radius, when the cavity is suddenly emptied. Thus the process of filling is progressive and emptying is abrupt. The two processes are not identical. Certain amount of sorbate is entrapped in the cavity during desorption, thus accounting for hysteresis.

In addition to the cavities which are present mainly in the interior of the porous sorbent, Rao assumed,

that there are also the V shaped pores, present mostly on the surface. The filling and emptying of these pores are reversible and don't contribute to hysteresis. Barrer and his coworkers[78] associated hysteresis with re-entrant angles within the pores and not with V shape pores. They have also emphasized that hysteresis can arise from causes other than capillary condensation, for example the structural changes in the adsorbent.

Cohan's theory

Cohan[79] formulated his theory with Foster's idea[80] that a delay in the formation of the meniscus during adsorption is responsible for the phenomenon of hysteresis. In other words the difference in shapes of the meniscus during sorption and desorption - hemispherical in desorption and cylindrical in the initial stages of sorption. In desorption Kelvin equation of evaporation of liquid from the 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 higher 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 adsorbent.

Everett et al[81-84] and Enderby[85,86] attributed hysteresis in general to the existence of a very large number of independent domains in a system and at least some of which can exist in metastable states.

In summarizing, the ink bottle theory has been successful in explaining the hysteresis effect and all its allied phenomena such as permanence and reproducibility, scanning, drift and disappearance of the hysteresis loop. This theory accounts for all the phenomena in a qualitative way. A quantitative formulation of the theory would probably be difficult, because it involves information about the number, shape, size, the neck and body diameters of the cavities in any particular system.

Classification of hysteresis loops

Barrer et al[78] discussed various shapes of capillaries and their influence on the form of the

sorption and desorption isotherms. But de Boer[87,88] has adopted just the reverse procedure and classified hysteresis loops into five typical categories as follows and then giving the type of capillaries present.

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.

CHAPTER III: EXPERIMENTAL

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EXPERIMENTAL

In all adsorption measurements the preparation of the adsorbent surface is considered as most important. The adsorbent should be in the highest possible state of purity. In other words it should be free as far as possible from gases already adsorbed on the surface of the adsorbent.

If the surface of the adsorbent holds only gas adsorbed in the Van der Waals form, theoretically it should be possible to desorb all the adsorbed gas merely by outgassing with a vacuum pump giving a high vacuum. But in practice sometimes, with adsorbents containing fine pores, the process 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. There is no hard and fast rule for choosing the temperature of outgassing and the conditions have to be choosen by trial and error.

In addition to the impurities incidental while preparing the adsorbent, one has to be careful with

impurities that may get to the surface from the other parts of the apparatus. The most troublesome among these is stopcock grease vapour. Hence only those greases are used which have very low vapour pressure. Most of the investigators often use mercury cut-off valves in place of stopcocks. The rate of pumping is carefully controlled in order to avoid the spurting of the adsorbent during outgassing.

There are two distinct methods for the determination of adsorption isotherms, viz., volumetric and gravimetric methods.

Volumetric method

The adsorption of a gas or vapour is measured by admitting it to an evacuated space containing the adsorbent, the amount taken up by the adsorbent is determined by volume. The charge of gas or vapour before admission is measured in a gas burette, and after admission the amount remaining unadsorbed in the dead space is calculated from its pressure, temperature and known volume of the dead space. Hence the amount adsorbed is calculated. 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 isotherm. All the points are taken after ensuring that the equilibrium has been attained.

Various types of apparatus used for different adsorbates have been illustrated by Gregg and Sing[89], Young and Crowell[90] and Brunauer[91].

Gravimetric Methods

Gravimetric method consists of determining the increase in the weight of the adsorbent by adsorption of gas or vapour. There are two methods to record the increase in weight of the adsorbent. The first one involves the use of an adsorbent bulb fitted with a stopcock and attached to the apparatus via a standard joint. At each point on the isotherm after equilibrium has been established, the stopcock is closed, the bulb is removed, grease removed from the joint and the bulb is weighed on an analytical balance. But this method is very laborious. The other method involves the use of quartz fibre spring balance which was first introduced by McBain and Bakr[92] into studies in sorption.

Photograph Figure

The quartz fibre spring balance

In all the investigations presented in this thesis, the quartz fibre spring technique was employed. The sorption balance is shown in the photograph Figure 1. The essential part of it is a helical spring made out of quartz fibre. The spring 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.

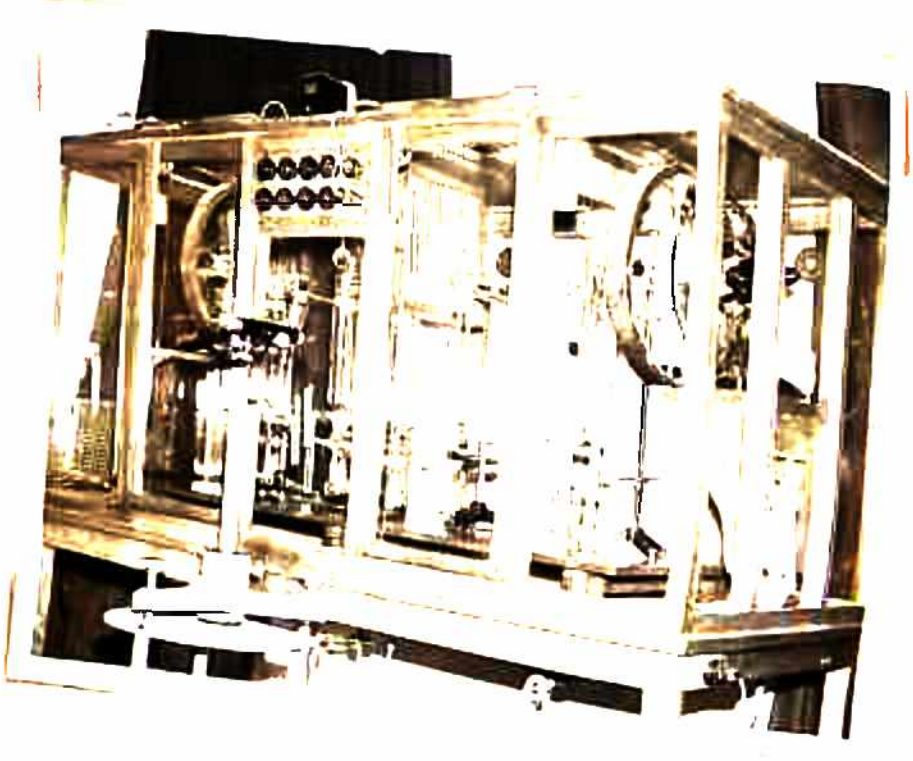
A number of techniques for fabricating quartz spirals have been given in the literature[93-96]. These springs are now available commercially. Such springs are difficult to manipulate being extremely delicate and brittle but still have gained wide acceptance owing to greater accuracy, simplicity of measurements and advantage of continuous study without disturbing the system. Some workers recommend springs of pyrex glass[97,98], beryllium - copper alloy[99-101] and molybdenum[102] because of easy fabrication and more robust but have not been used probably on account of lack of dimensional stability.

The spring technique lends itself to automatic recording of an adsorption isotherm and the apparatus have been devised by Lemcke and Hofmann[103], Van Nordstrand[104], Hooley[105] and Klevens et al[106].

Merits and demerits 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. Once the adsorbent is enclosed in the sorption tube, the observations can be extended over long intervals of time - months and even years[107] without disturbing the system. Measurement with the spring balance is quick and extraordinary simple. The quartz fibre springs can be used at moderately high temperatures as its elastic coefficient is not affected. It is noncorrodible by most of the organic liquids and its sorptive capacity for the same is negligibly small.

The spring balance is very handy for determining the adsorption of vapours at high pressures. McBain and Britton[108] have worked up to 60 atmospheric pressure with this technique whereas Morris and Maass[109] up to 46 atmospheres. It is very useful in comparative studies



Photograph Figure 2

because a number of balance tubes can be connected to the same manometer and the adsorptive properties of several solids measured under identical conditions[110-115].

The main drawback of the technique is buoyancy correction at high pressures[108,109]. But at low pressures the correction is very small. Some workers have used other types of balances such as beam type vacuum balances and torsion microbalances to avoid the buoyancy correction.

Air thermostat for constant temperature

In the study of sorption - desorption hysteresis it is necessary to maintain a constant temperature by keeping the sorption apparatus in a thermostat. In the present studies an air thermostat was constructed similar to one built by Vernon[116] and is shown in the photograph Figure 2. The thermostat chamber was built of wooden frame and glass panels. It was fitted on a wooden table. The external dimensions of the chamber are 96" long, 39" wide and 43" high. The four doors (two in the front and two on 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". There are also two square holes, 9" apart and 4" edge, in the middle of the platform. These gaps and square holes facilitate free and continuous circulation of air inside the chamber by the electric fans.

Two four bladed fans are kept on brackets, one at each end of the thermostat and the two facing each other. These brackets are 27" above the level of the working floor. 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, which is suspended from the roof in front of the fan. The diameter of the frame is 15" and the centre is in line with the centres of the fans. In each set of lamps only two horizontal lamps are controlled by the relays; the other two are auxiliary lamps operated by switches outside. The four control lamps normally work in unison, their heating capacity is arranged according to the outside temperature. In cold weather the mild heat bulbs are replaced by strong nichrome wire heaters.

The two opposing 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 downwards. 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. Thus each stream of air is kept in continuous circulatory motion coming in contact with the heating element and the thermoregulator in each cycle. The air in each half of the thermostat is thus effectively stirred.

The thermoregulator consists of a network of pyrex glass tube, 1.2 cm bore. It is filled with toluene. The open end 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[61] 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. In order to ensure the constancy of temperature in different positions inside the thermostat, readings were taken by placing a sensitive thermometer at different positions and the temperature recorded was always 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. During hot weather, 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 sparking 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 it is connected to a bulb for the adsorbate with a B-10 ground glass joint and a B-19 high vacuum stopcock. A U-tube mercury manometer is connected to the sorption apparatus with B-10 ground glass joint. Just on the opposite side of the manometer another B-19 stopcock connects the apparatus to vacuum line. To the upper end of the tube a B-50 ground glass joint is joined. Just below the joint, 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.

An Edwards high vacuum pump which produced a pressure of 10^{-2} mm was used. For sealing the ground glass joints Dow Corning silicone high vacuum grease was used. Pressure readings and elongation of the quartz helix were determined with a cathetometer reading correct to 10^{-2} mm. Quartz fibre springs used in these studies had sensitivity ranging from 20 to 45 cms 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[93]. McBain and his coworkers used gold and platinum buckets.

Sorption - desorption procedure

First the spring balance was calibrated by adding and removing known weights and measuring the corresponding extension of the helix. 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	0.3 gm
Extension	17.4 cm
Sensitivity	45.3 cm/gm

The observed and calculated stretch from the dimensions are shown as under:

Weight of the bucket = 0.0786 gm

Initial length of the spring with bucket = 1.734 cm

	Weight in gm	Observed length in cm	Observed stretch in cm for 0.05 gm	Calculated stretch in cm for 0.05 gm
While adding weights	0.05	4.002	2.268	2.265
	0.10	6.271	2.269	2.265
	0.15	8.536	2.265	2.265
While removing weights	0.10	6.272	2.264	2.265
	0.05	4.003	2.269	2.265

The above results show that spring obeys Hooke's law.

The tube was throughly 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. Next 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 measureable adsorption of water vapour on the spring and bucket. No variation in the length of the spring was noticed even after the vapours were in contact with spring for about a month, thus showing the absence of measurable adsorption of water vapour on the quartz fibre spring. McBain and Sessions[107] have also exposed these springs to various vapours for twenty years and noticed no appreciable stretch, showing the absence of adsorption by these springs.

The spring with bucket was placed inside the tube. The length of the spring was measured using a reference rod suggested by Lawson[110]. It is a glass fibre suspended within the spring coils from the same hook from which the spring is suspended. The reference rod 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, spring was taken out, the bucket was filled with the adsorbent and spring was placed again inside the tube. The upper end of the tube was covered with the ground glass cap and the system was throughly evacuated. After evacuation the pump was disconnected from the sorption

apparatus by closing the stopcock. The spring reading and the zero pressure reading of the manometer were taken with the cathetometer. Next the lower stopcock 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. These readings give sorption curve. After the saturation pressure was reached, the lower stopcock 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 equilibrium was attained. This process is continued until sufficient number of points on the desorption curve is obtained and zero pressure is reached.

From the spring reading at each equilibrium point during sorption as well as desorption, the stretch of the spring for the amount of adsorbate taken or retained respectively is obtained. Knowing the stretch of the spring for the evacuated sorbent at zero pressure, the percentage of sorbate taken or retained can be calculated. By plotting percentage sorption and desorption, against the corresponding vapour pressure of the sorbate, the sorption and desorption isotherms are obtained. From

these, the existence or nonexistence of the hysteresis effect is known.

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CHAPTER IV: STUDIES IN SORPTION - DESORPTION HYSTERESIS WITH PROTEINS

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A. VARIETAL DIFFERENCES IN GELATIN, EGG ALBUMIN AND CASEIN, IN RELATION TO SORPTION - DESORPTION HYSTERESIS WITH WATER*

Introduction

Earlier investigations on the sorption and desorption of water vapour on different varieties of organo gels such as rice grain[61], dhal[61], gum arabic[65], gum ghatti[117], gelatin[71], casein[71], egg albumin[71], and sericin[74] have revealed certain common characteristics. Either the sorption and desorption curves are coincident showing no hysteresis effect in the first cycle of sorption and desorption, or the hysteresis effect initially exhibited becomes smaller and disappears in the subsequent cycles. These characteristics are also shown by the leaves of several plants[73] when subjected to successive dehydrations and rehydrations. On the basis of the cavity theory of hysteresis, these observations have been explained by the following: the organo colloid swells on the imbibition of water - the solvating liquid, the cavities collapse, the entrapping effect is lost and the hysteresis disappears. This generalisation is further confirmed by showing in a few cases that with

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* K.Subba Rao and Bhagwan Das, J. Phys. Chem. 72, 1223, 1968.

nonsolvating liquids like carbon tetrachloride there is permanent and reproducible hysteresis loop[61].

Benson and Richardson[118] have worked with egg albumin, gelatin and bovine plasma albumin and have reported a reproducible hysteresis loop in three successive cycles in the sorption of water on egg albumin. This result of Benson prompted the author to think that varietal differences in the proteins may be responsible for the difference in the behaviour in sorption and desorption hysteresis. A systematic study with different grades of gelatin, egg albumin and casein was undertaken.

Gelatin

Two different varieties of gelatin - Difco gelatin made by Difco laboratories, Michigan, U.S.A. and Oxoid gelatin made by Oxo Ltd., London, were used. In the earlier investigation[71] gelatin of Merck Gold label quality was used.

Egg albumin

Egg albumin (Merck's albumin ovi) was used. A sample was activated by heating at 60°C in vacuum for 6 hours. Another sample was denatured by heating a 10% solution on a boiling water bath for 1 hour. The precipitated albumin was filtered, washed with water and

dried at 40°C for two hours in vacuum. Samples of (1) native, (2) activated and (3) denatured egg albumins were employed. In the earlier paper[71] Merck's soluble egg albumin was used.

Casein

Merck's alkali soluble casein and Oxoid casein hydrolysate were used. A sample of Merck's alkali soluble casein was activated by heating at 60°C for 6 hours. Another sample was denatured by heating in boiling absolute alcohol for one hour and drying in an oven at 75°C for one and half hours. Samples of (1) native, (2) activated and (3) denatured casein were employed in the studies. In the earlier work[71], Kahlbaum's casein nach Hammersten was used.

The samples were used in the form of powder. The grain size was between those of 30 and 50 mesh BSS sieves.

Results

Gelatin

Hysteresis is exhibited by both Difco and Oxoid gelatins. In the case of Difco gelatin, the sorption and desorption studies were continued up to 12th cycle.

The loops obtained in the 1st, 3rd, 5th, 7th, 9th, 11th and 12th cycles are shown in Figures 1 and 2. The percentages of water taken at saturation pressure in each of these cycles are 116.4, 119.0, 119.6, 125.3, 113.00, 103.9 and 104.3 respectively. It took about 12 days for completion of each cycle. In each cycle the gelatin was kept in contact with water vapour at saturation pressure for 2 days except in cycle 7th, in which it was 10 days. The total period required for completing the 12 cycles of sorption and desorption is more than 8 months.

With Oxoid gelatin the sorption - desorption studies were continued upto 10th cycle. The loops of the 1st, 4th, 9th and 10th cycles are shown in Figure 3. The values at saturation pressure of water are 69.8%, 67.8%, 69.2% and 68.6% respectively. The total period required for completing the 10 cycles is 3 months. At the end of each cycle the gelatin was kept in contact with water vapour at saturation pressure for 2 days.

Egg albumin:

The hysteresis loops obtained with native, activated and denatured egg albumins are shown in Figures 4-6 respectively. With native egg albumin,

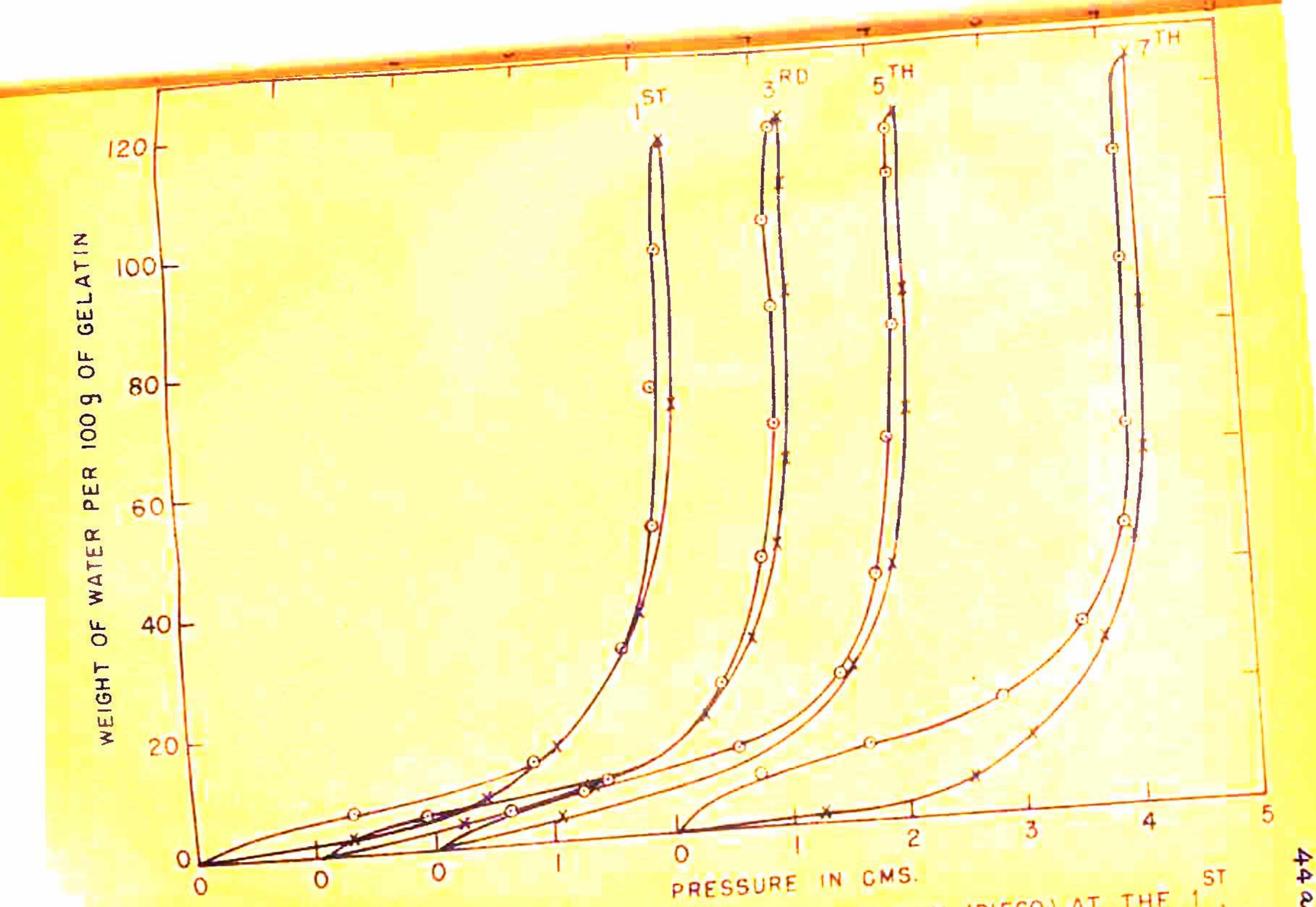


FIG. 1. SORPTION AND DESORPTION OF WATER ON GELATIN (DIFCO) AT THE 1ST, 3RD, 5TH AND 7TH CYCLES.

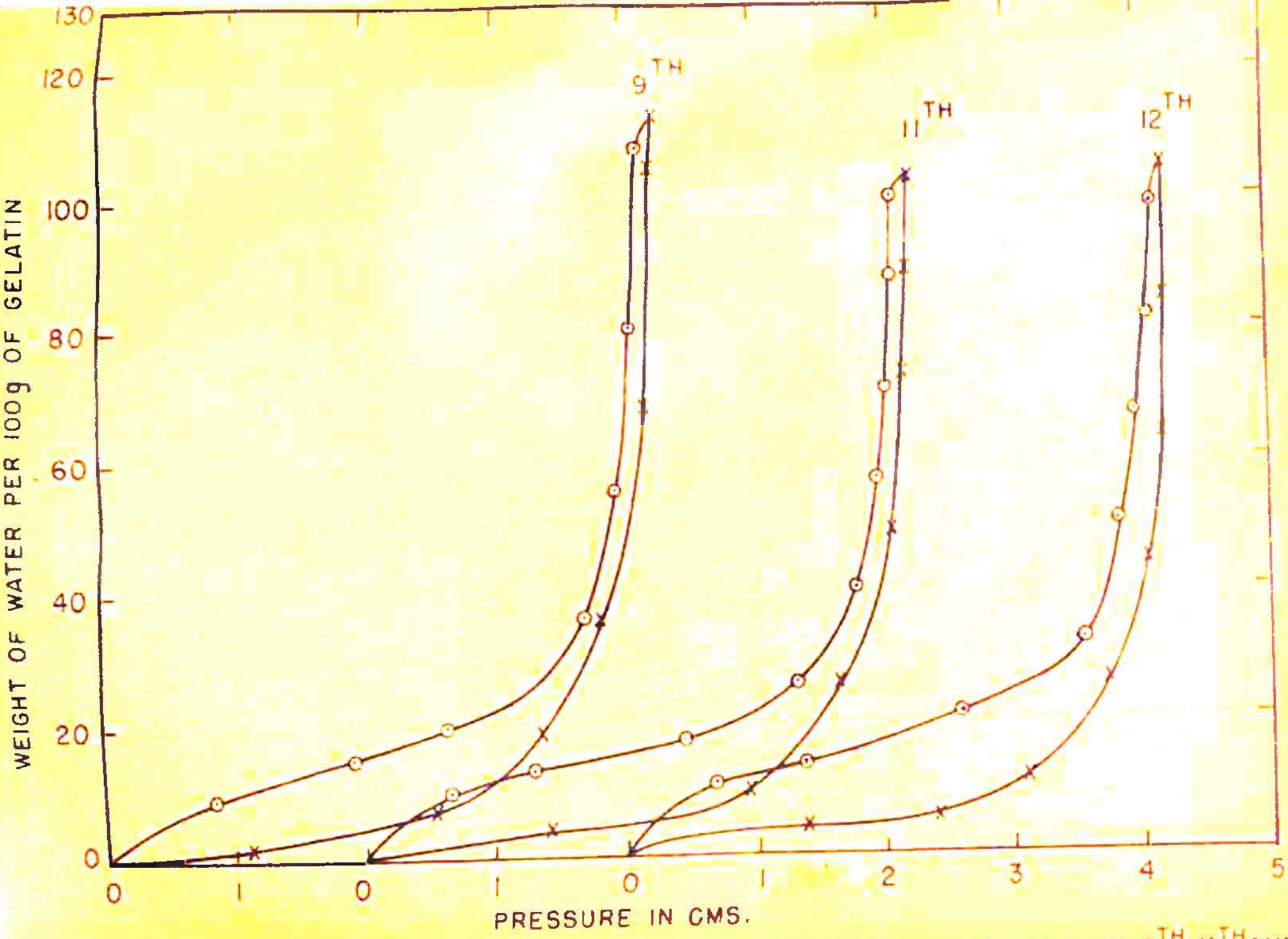


FIG. 2. SORPTION AND DESORPTION OF WATER ON GELATIN (DIFCO) AT THE 9TH, 11TH AND 12TH CYCLES.

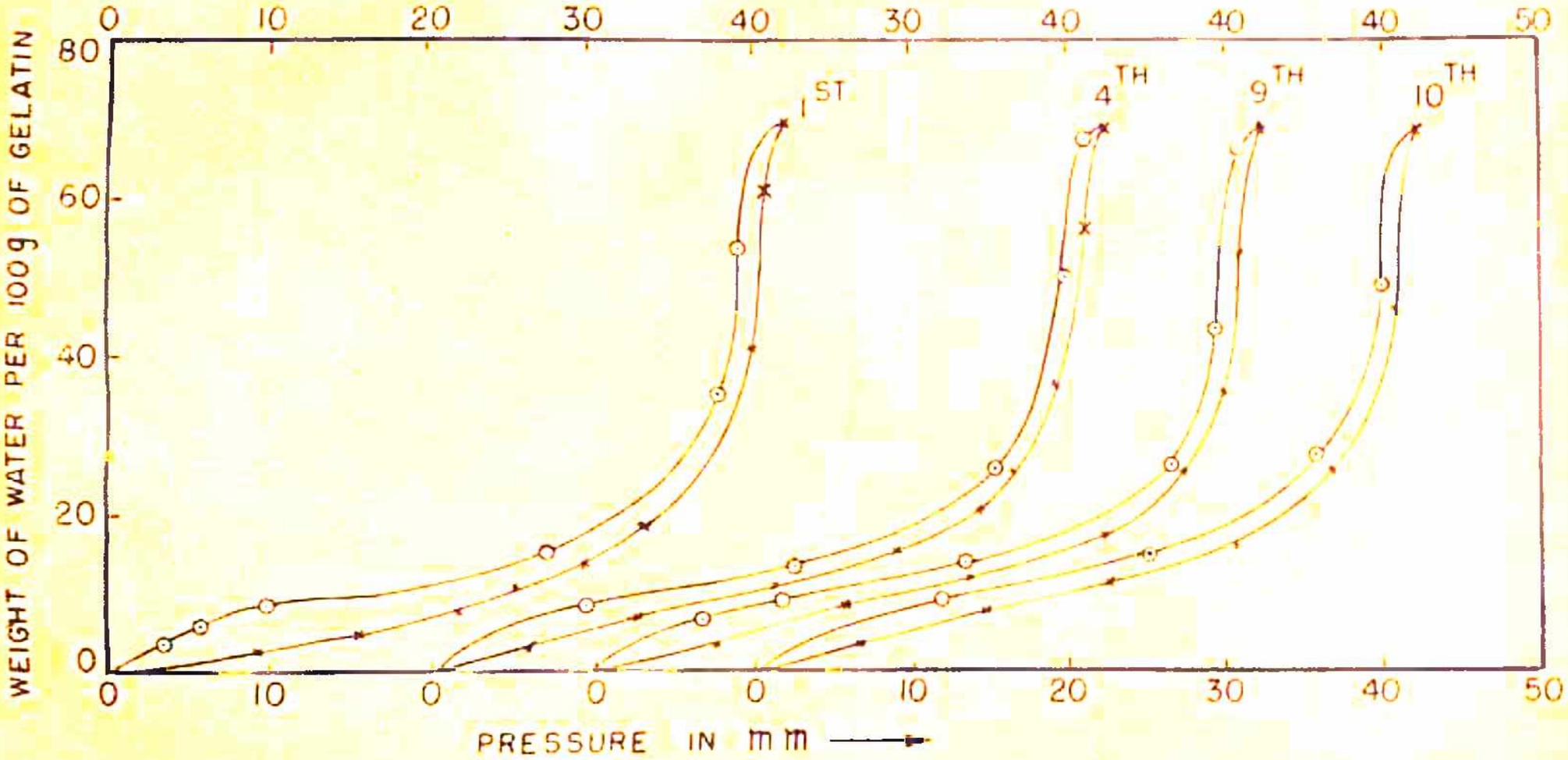


FIG. 3. SORPTION-DESORPTION HYSTERESIS OF WATER ON NATIVE GELATIN IN THE 1^{ST}, 4^{TH}, 9^{TH} AND 10^{TH} CYCLES.

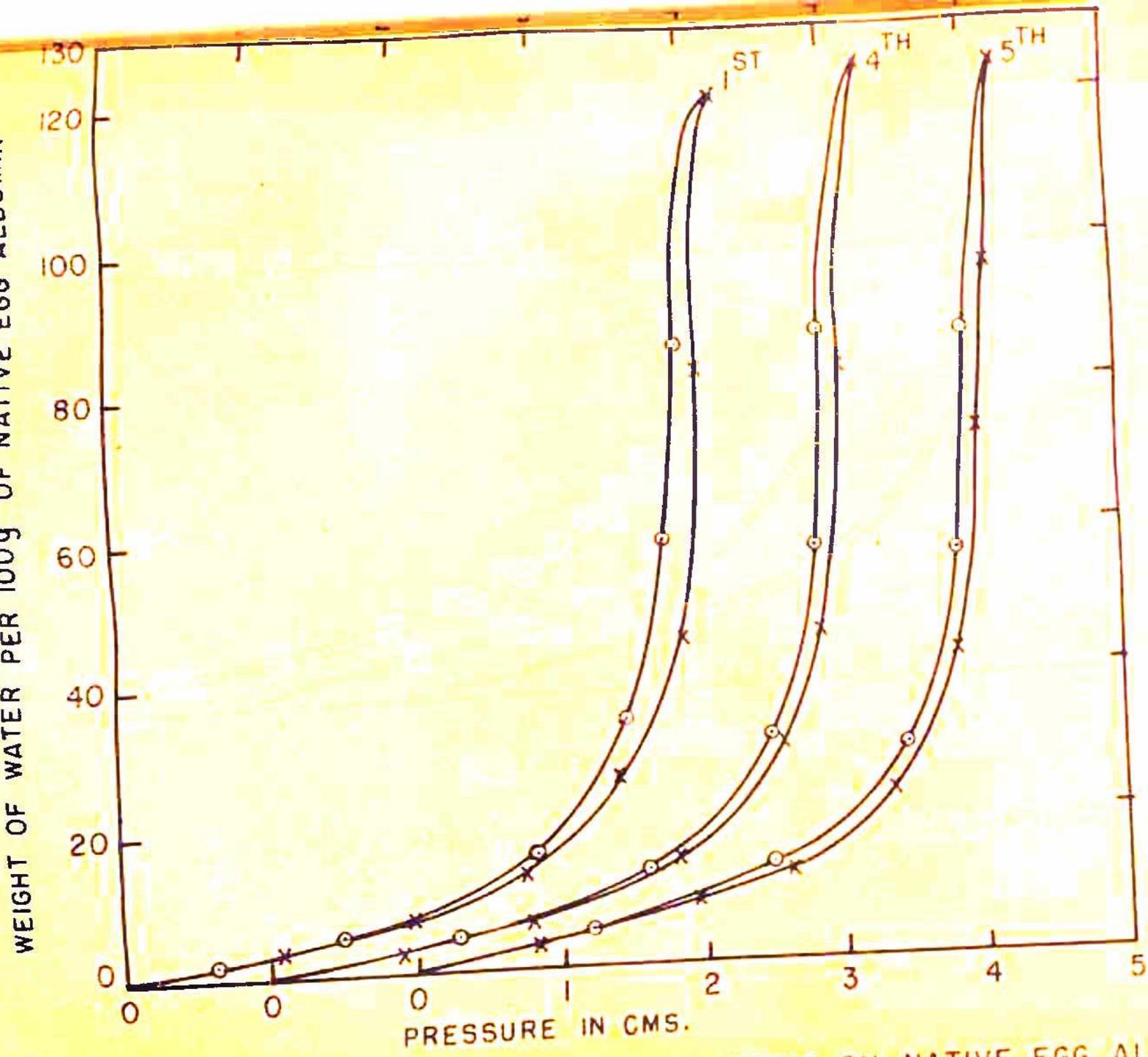


FIG. 4. SORPTION AND DESORPTION OF WATER ON NATIVE EGG ALBUMIN IN THE 1ST , 4TH AND 5TH CYCLES.

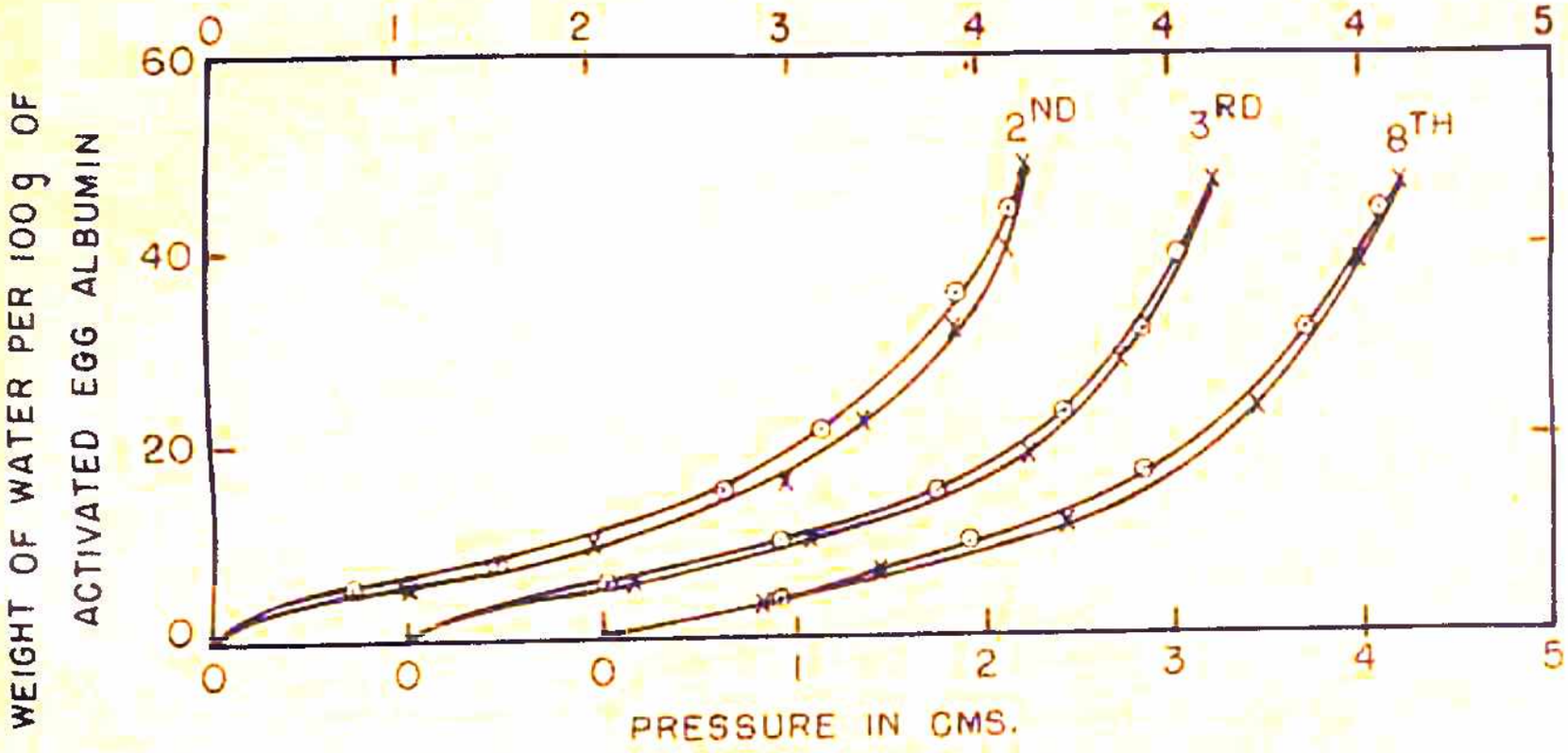


FIG. 5. SORPTION AND DESORPTION OF WATER ON EGG ALBUMIN ACTIVATED AT 60° IN 2ND, 3RD AND 8TH CYCLES.

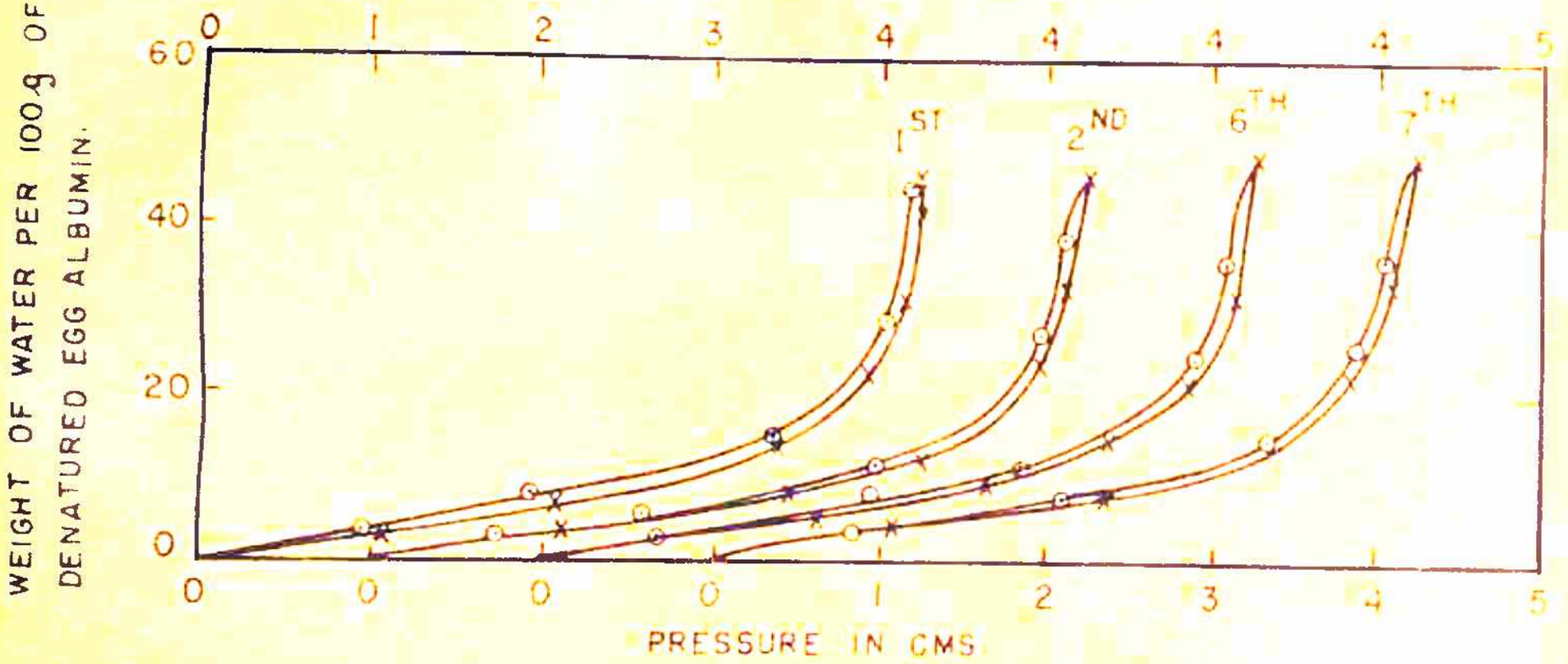


FIG. 6. SORPTION AND DESORPTION OF WATER ON DENATURED EGG ALBUMIN AT THE 1ST , 2ND , 6TH AND 7TH CYCLES.

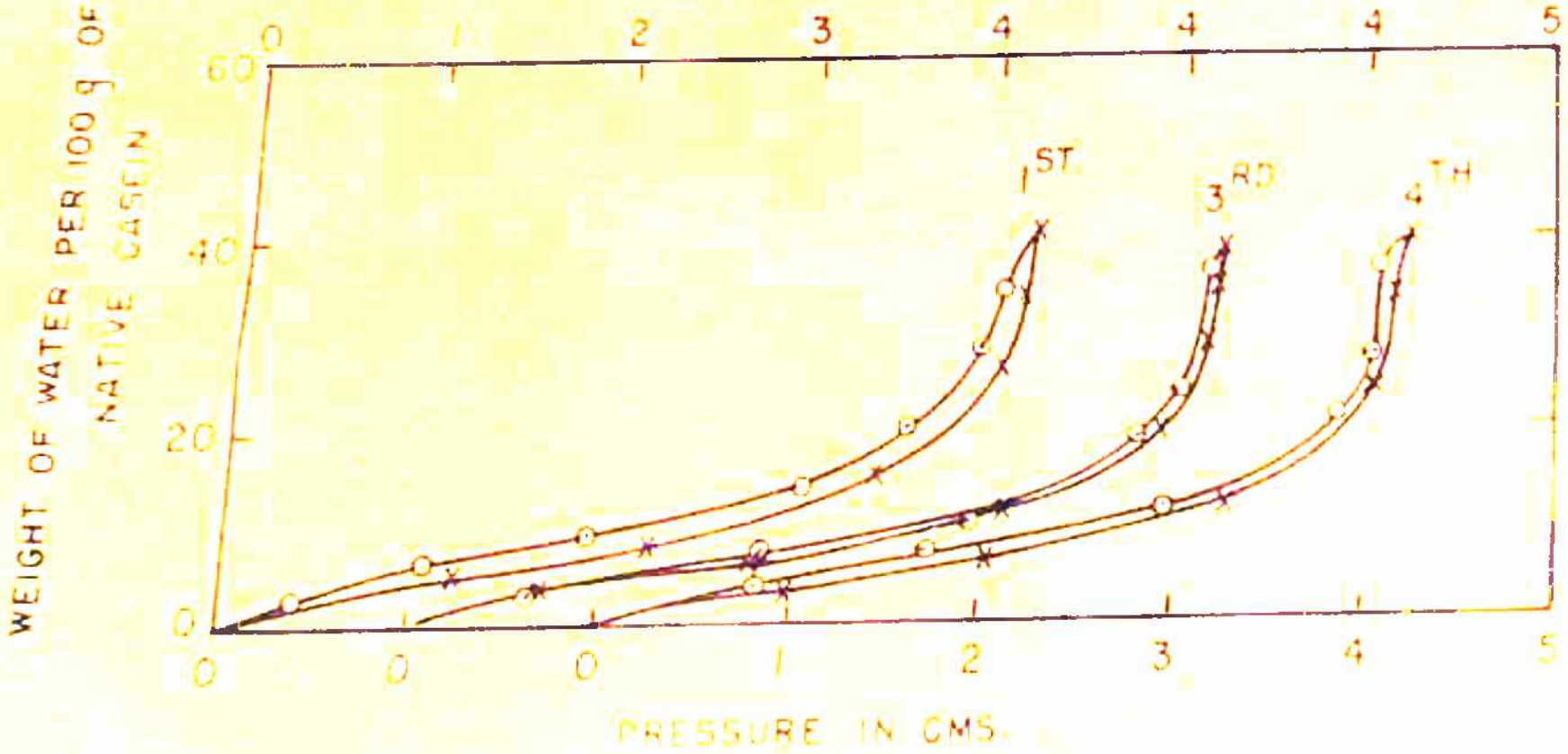


FIG. 7. SORPTION AND DESORPTION OF WATER ON NATIVE CASEIN AT THE 1ST, 3RD AND 4TH CYCLE

the amount of water taken at saturation pressure of water in the 1st, 4th and 5th cycles are 120.3%, 125.4% and 124% respectively. With activated egg albumin, the amounts of water taken in 2nd, 3rd and 8th cycles are 48.1%, 46.6% and 46.6% respectively and with denatured egg albumin the amounts of water are 45.8%, 46%, 47.4% and 48.3% respectively. The total periods of study with native, activated and denatured egg albumins were nearly 2 months, 4 months and 4 months respectively. In all these cases the albumin was kept in contact with water vapour at saturation pressure for 2 days.

Casein

With Merck's native casein, Figure 7, sorption - desorption studies have been continued upto 4th cycle. The amounts of water taken up at saturation pressure in the 1st, 3rd and 4th cycles are 40.8%, 39.0% and 40.0% respectively. The sorbent was kept in contact with water vapour at saturation pressure for 2, 5 and 5 days in the 1st, 3rd and 4th cycles respectively. The total period for completing the study was one and a half months.

With Merck's activated casein Figure 8 sorption - desorption studies were continued upto 14th cycle. The sorption capacities in the 1st, 4th, 5th, 6th, 8th and

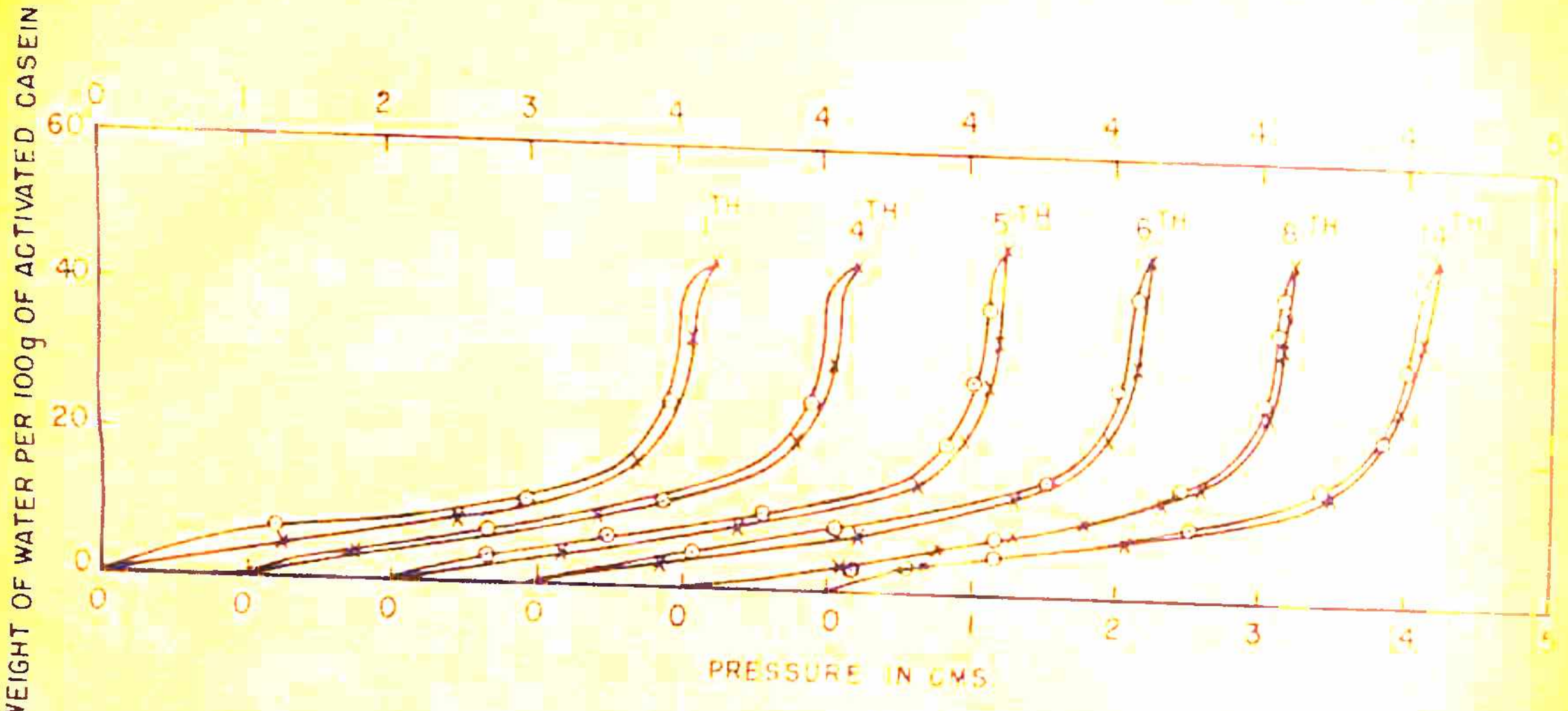


FIG. 8 SORPTION AND DESORPTION OF WATER ON ACTIVATED CASEIN AT THE 1ST, 4TH, 5TH, 6TH, 8TH AND 14TH CYCLES.

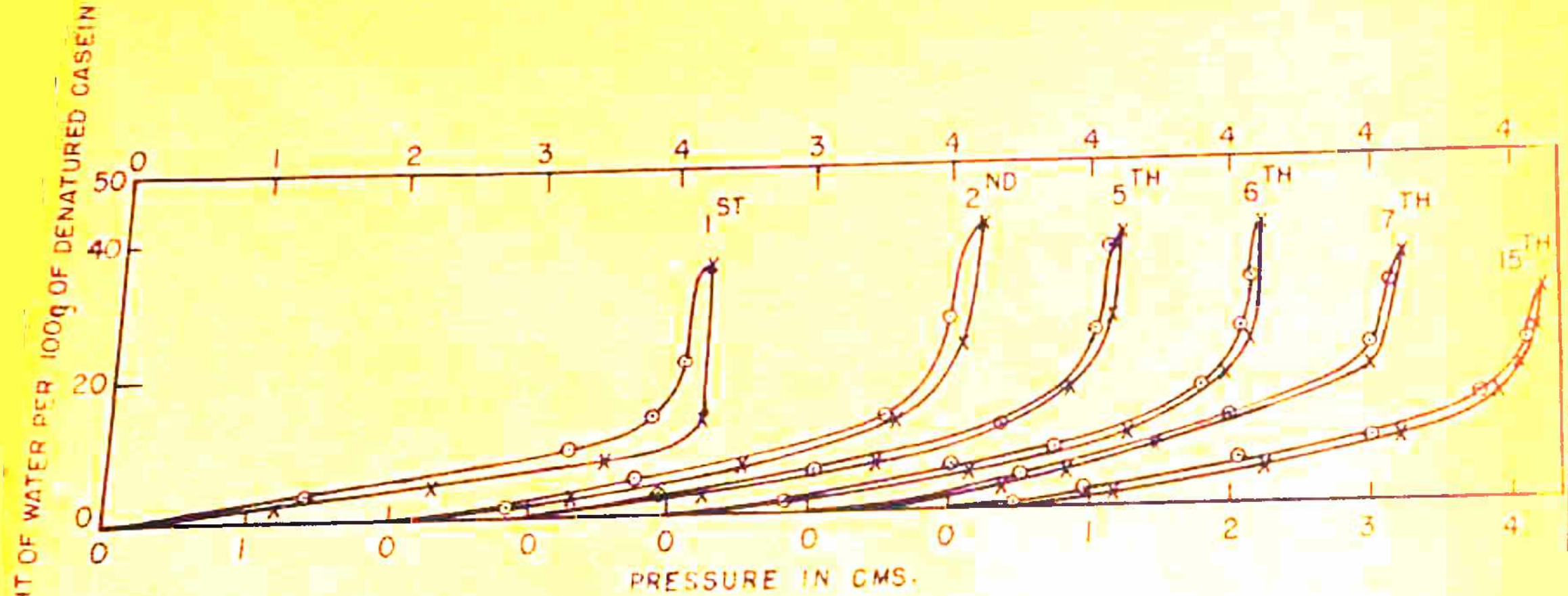


FIG. 9 SORPTION AND DESORPTION OF WATER ON DENATURED CASEIN AT THE 1ST 2ND, 5TH, 6TH, 7TH AND 15TH CYCLES.

14th cycles are 44.0%, 44.0%, 47.0%, 46.5%, 45.6% and 47.0% respectively. At the end of sorption the sorbent was kept in contact with water vapour at saturation pressure for two days in all cycles excepting the 8th in which it was kept for 20 days. The total period required to complete this study was 6 months.

In the case of denatured casein Figure 9 the sorption - desorption studies were continued upto 15th cycle. The sorptive capacities of the casein for water at saturation pressure in the 1st, 2nd, 5th, 6th, 7th and 15th cycles are 35.7%, 41.0%, 39.7%, 40.3%, 35.8% and 29.5% respectively. The time allowed at saturation was 2 days in all cycles excepting 6th and 7th in which the times were 10 days and 20 days respectively. The study lasted over 6 months.

Sorption - desorption studies were continued upto 6th cycle in the case of casein hydrolysate Figure 10. The sorptive capacities in the 1st, 2nd, 4th, 5th and 6th cycles are 581.1%, 855.1%, 857.0%, 857.0% and 857.0% respectively. The sorbent was kept in contact with water vapour at saturation pressure for 14 days in the 4th cycle and 2 days in all others. The total period required for completing the study was 3 months.

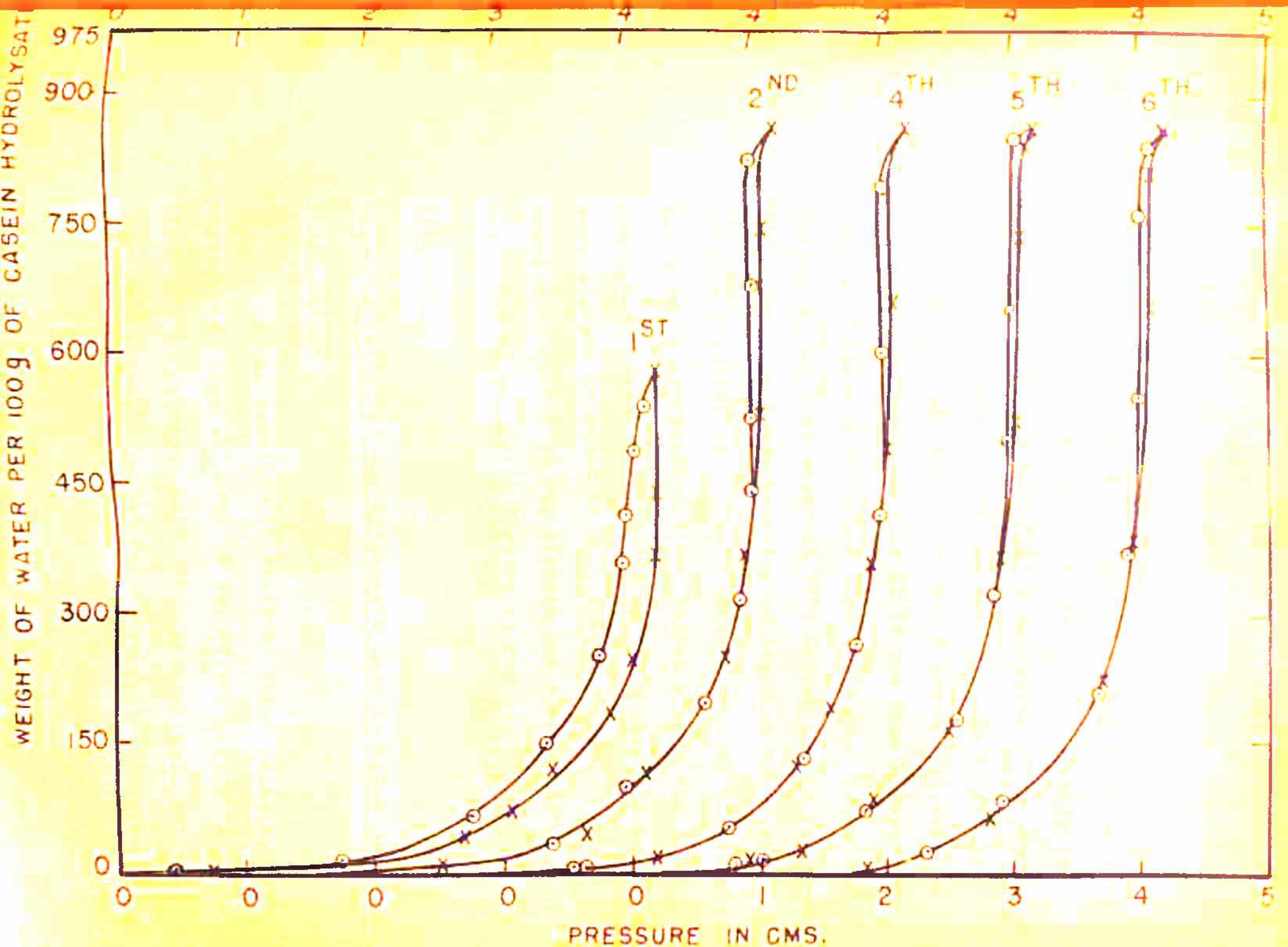


FIG. 10. SORPTION AND DESORPTION OF WATER ON OXOID CASEIN HYDROLYSATE AT THE 1ST, 2ND, 4TH, 5TH AND 6TH CYCLES.

Rate studies

Proteins like other organogels swell when they sorb water. In all swelling systems water sorption is a slow process. Incomplete equilibrium during sorption and desorption can cause hysteresis. To eliminate this effect, sufficient time was allowed till equilibrium is attained. Figure 11 is the Time - sorption curves of Difco gelatin and Oxoid gelatin. At saturation pressure of water at 35°C Difco gelatin requires about 48 hours for completion of sorption and Oxoid gelatin requires 24 hours. However at each intermediate point on the sorption and desorption curves the time required is about 6 hours and actually about 10 hours were allowed in order to ensure equilibrium. Time - adsorption curves of egg albumin are shown in Figure 12 and those of casein in Figures 13 and 14.

Discussion

Characteristics of the hysteresis loop in Difco gelatin - water system

In the sorption of water on Difco gelatin, the hysteresis loops obtained in successive cycles of sorptions and desorptions have shown several interesting characteristics. In the first cycle, the sorption and

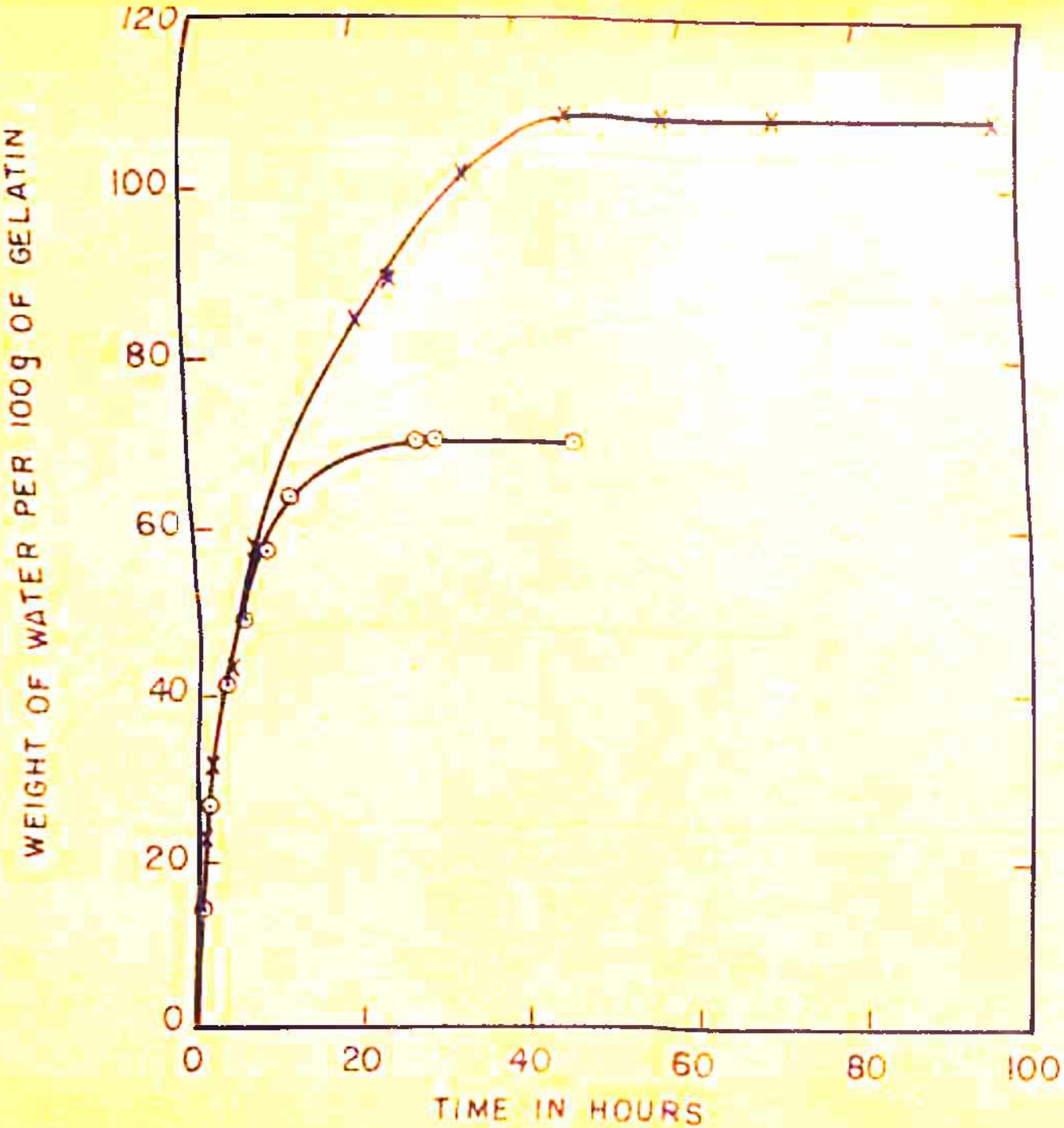


FIG. 11. TIME — SORPTION CURVE OF WATER AT SATURATION PRESSURE AT 35° ON GELATIN DIFCO x, AND GELATIN OXOID ⊙

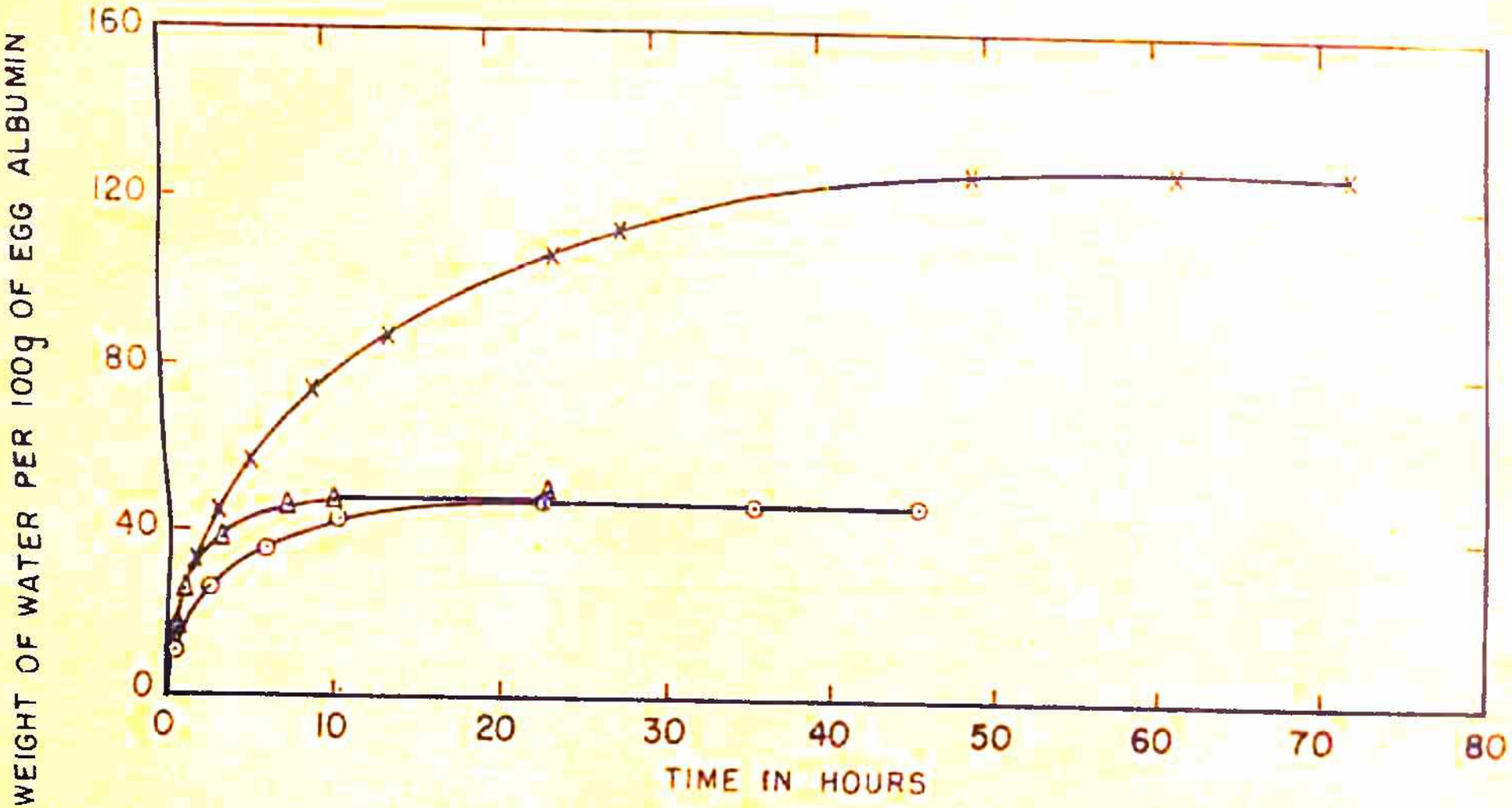


FIG. 12. TIME-SORPTION CURVE OF WATER AT SATURATION PRESSURE AT 35° ON NATIVE EGG ALBUMIN x, ACTIVATED EGG ALBUMIN Δ, AND DENATURED EGG ALBUMIN ⊙.

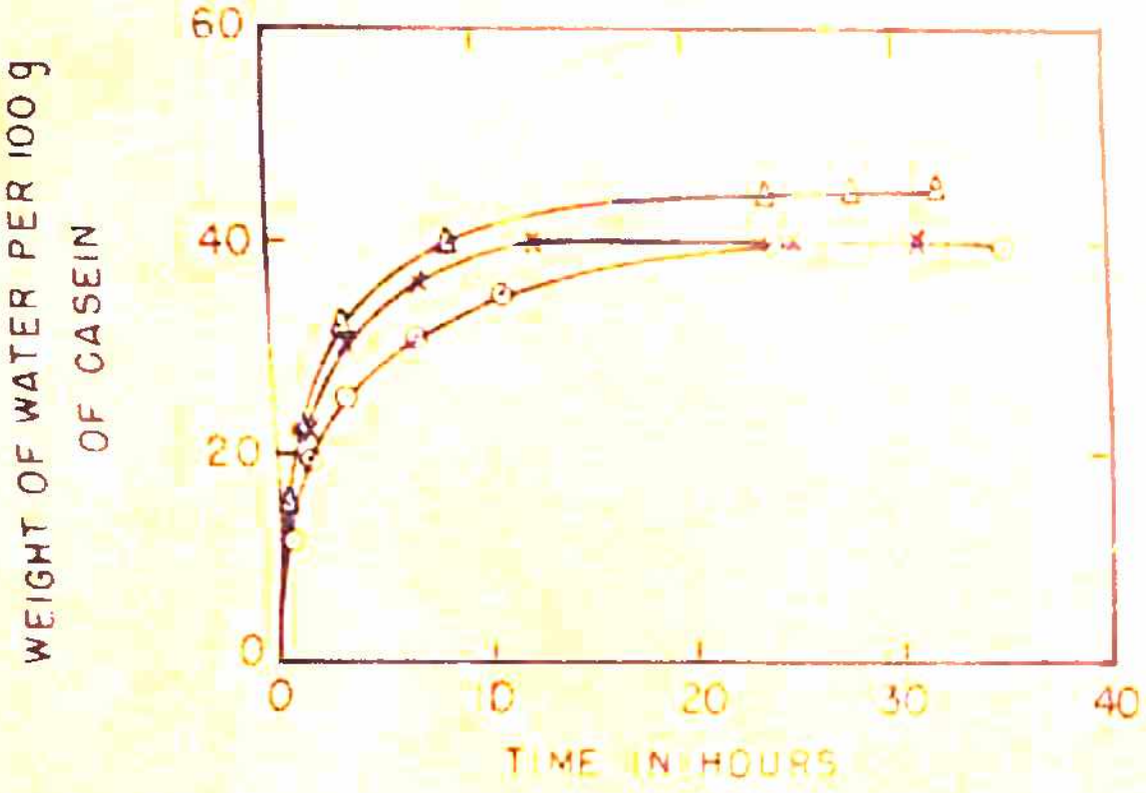


FIG 13. TIME-SORPTION CURVE OF WATER AT SATURATION PRESSURE AT 35° ON NATIVE CASEIN ×, ACTIVATED CASEIN Δ AND DENATURED CASEIN ⊙.

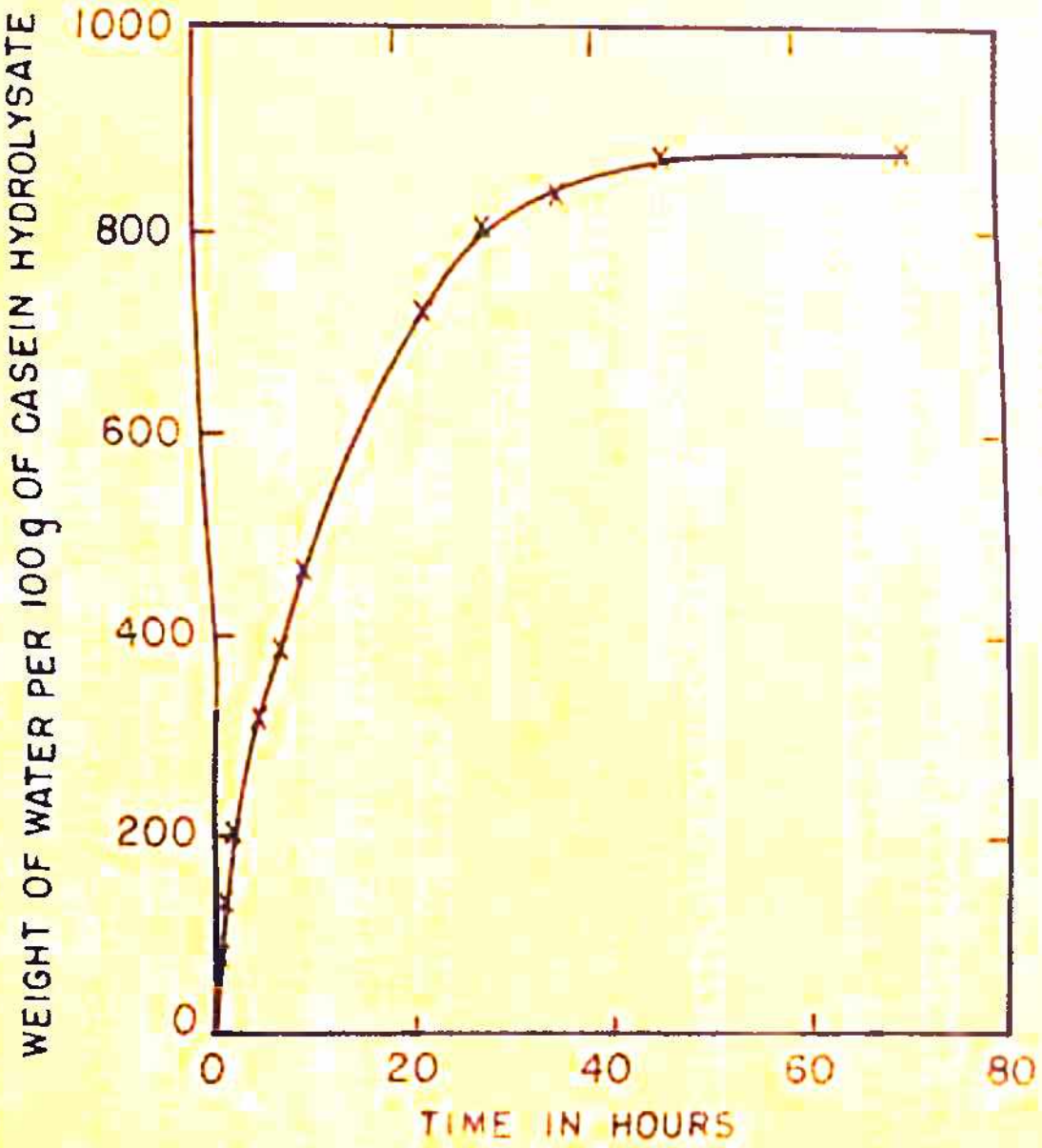


FIG. 14. TIME - SORPTION CURVE OF WATER AT SATURATION PRESSURE AT 35° ON CASEIN HYDROLYSATE.

desorption curves are separated in the low and high pressure regions showing hysteresis loops whereas in the middle the two are almost coincident. In subsequent cycles there is a tendency for the sorption and desorption curves at the centre to separate from each other. In 7th cycle the two are completely separated. The hysteresis loop in the low pressure region has become wider and this further increases slightly upto the 12th cycle. The amount of water sorbed at saturation pressure has also decreased from 7th cycle upto 12th cycle.

Explanation of the characteristics in the light of the cavity concept

Difco gelatin - water system

Benson[118] does not accept the existence of fine pore structure in proteins. He explains the hysteresis effect which he has obtained in the sorption of water and other liquids on egg albumin as a case of deformation of the polypeptide chains within the protein molecule as the polar sorbate settles into suitable positions.

Arnell and McDermot[119] attributes hysteresis to Steric effects in swelling systems and this is due to interaction between, sorbent and sorbate molecules.

Deformation and Steric effect cannot explain a permanent and reproducible hysteresis loop as in silica gel - water 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 continuous decrease in size of the hysteresis loop and its disappearance in successive sorptions and desorptions have been established by K.Subba Rao in a large number of systems such as rice, dhal, gum arabic, egg albumin, gelatin, casein, sericin which swell with water. With a nonsolvating liquid like carbon tetrachloride, the rice grain has shown a permanent hysteresis loop which has been reproduced upto 9th cycle of sorption and desorption and these results cannot be accounted for, by the deformation theory and steric effect. The cavity concept alone has been found to explain adequately both the disappearance of the hysteresis effect in rice - water system[61] and its permanence and reproducibility in rice - carbon tetrachloride system[61].

The cavity concept

An ideal plane surface adsorption is a rarity. Even non-porous sorbents have cracks and fissures on

surface. In such cases capillary condensation gets in and the entrapping effect of cavity follows. The cavity concept has been elaborated in chapter 2 and is found to be a general explanation of the hysteresis effect and all its different aspects - such as drift, scanning and disappearance.

A Cavity is a pore with constricted neck and it can also have two or more necks. Filling of cavities during sorption is progressive whereas emptying during the desorption is sudden and abrupt. Every point on the desorption curve denotes the neck radius of the cavity which is emptied. In Difco gelatin - water system the tendency for separation of the desorption curve from the sorption curve is noticeable from the 1st cycle to 5th cycle and this has become prominent in the 7th cycle in which the position of the sorption curve remains practically the same but the desorption curve shifts away from the pressure axis. This indicates that the entrapping effect of the cavities has increased. This is possible if the difference between the cavity radius and neck radius increases.

Swelling and shrinkage in relation to sorption - desorption hysteresis

The tendency of the hysteresis loop to decrease

in size and finally disappear is found to be a general phenomenon in all nonrigid materials which swell on the imbibition of solvating liquids. Explanation of this interesting phenomenon has been presented earlier in the light of the cavity concept in conjunction with the property of hydration and swelling of the sorbent material in solvating liquid. Dehydrated protein is comparatively rigid in structure. The cavities which are present entrap water and cause hysteresis. At the saturation pressure, protein will be 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 disappears.

Gelatin in contact with water is essentially a changing system. In successive sorptions and desorptions it is subjected to successive swelling and shrinkage. In these changes the cavities suffer contraction. The necks are probably more constricted than the cavities accounting for increased entrapping effect. Owing to this increased entrapping effect, the gelatin retains at lower vapour pressures more and more of the sorbate in successive sorptions and desorptions. The various changes mentioned above are quite prominent in the 7th

cycle probably because the gelatin was kept in contact with water vapour at saturation pressure for 10 days and gelatin had the facility to swell to a greater extent.

From 7th cycle to 12th cycle, there is a noticeable reduction from 125.3% to 104.3% in the sorptive capacity of gelatin. This indicates that the total cavity volume has decreased owing to shrinkage of the swollen gelatin. The total pore volume including the cavity volume is probably a small fraction of the total sorptive capacity of gelatin. Major portion of water is held by gelatin in association with the protein molecules.

The change which has been noticed in gelatin - water system is just a particular stage in the continuous process which has taken place over a period of about 8 months. The final stage is the complete collapse of the cavities and the disappearance of the hysteresis effect. If the experiments were continued further, probably this would have been observed. Several cases of the decrease in size of the hysteresis loop and their disappearance after a large number of cycles of sorption and desorption have already been reported. In sericin - water system[74] the hysteresis loop has disappeared after 11 cycles. In the hydration and dehydration of grass blades[73] the hysteresis loop disappeared in the 15th cycle.

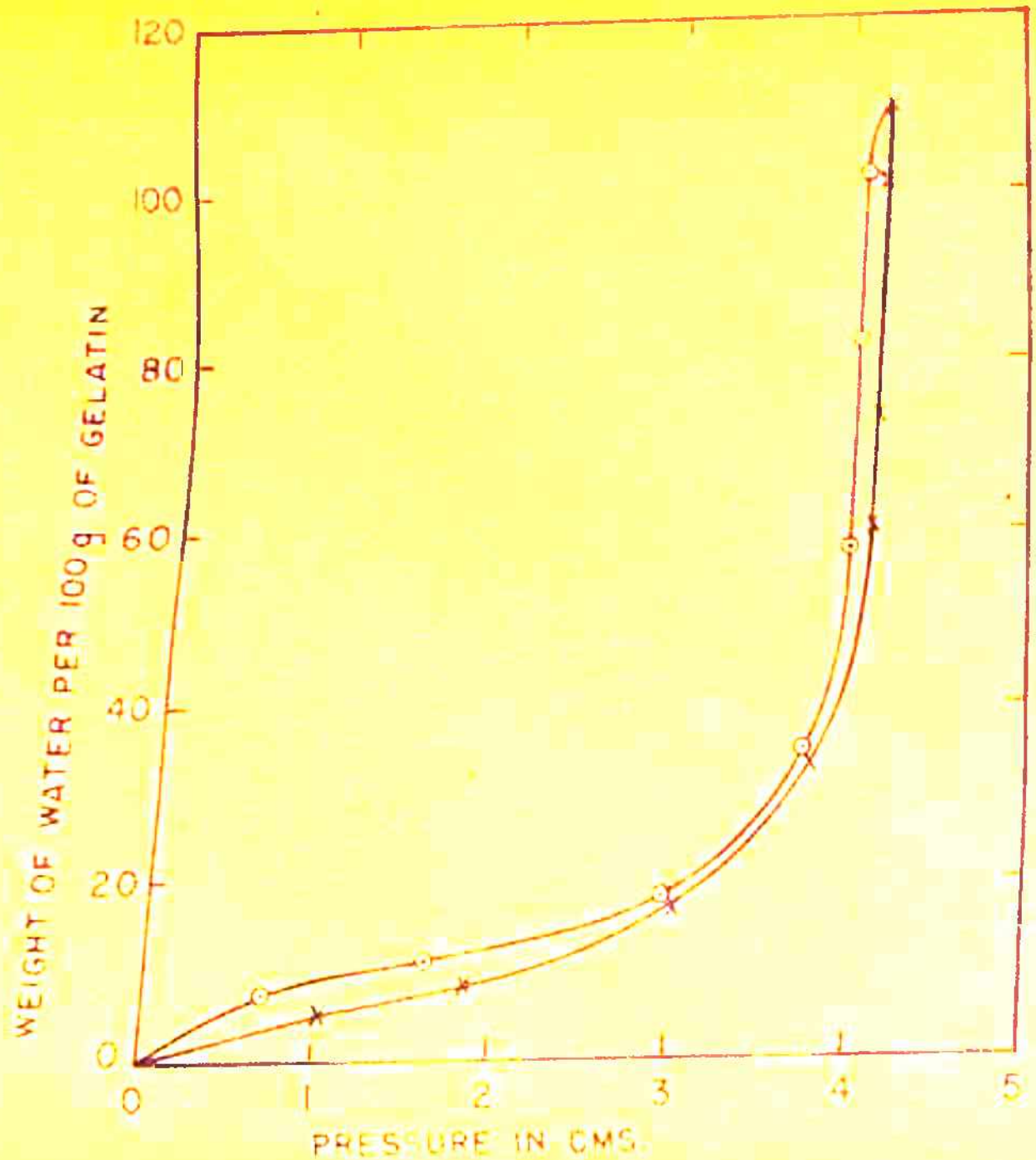


FIG. 15. SORPTION AND DESORPTION HYSTERESIS OF WATER

The behaviour of Difco gelatin in the sorption of water is unique and interesting. After the completion of the experiments over a period of 8 months another sample of the same Difco gelatin was studied. The first cycle of sorption and desorption with water was obtained and is shown in Figure 15. This hysteresis loop is identical with the first loop of the first experiment thereby confirming the reproducibility of the observations. The unique behaviour of Difco gelatin cast a doubt on the behaviour of the the quartz fibre springs. At the end of the sorption-desorption studies, the spring was taken out, its sensitiveness was determined and it was found to be the same.

Oxoid gelatin - water system

The hysteresis loops obtained with Oxoid gelatin upto 10th cycle of sorption and desorption have been shown in Figure 3. There has been a slight decrease in the size of the hysteresis loop in the low vapour pressure region. But there is no marked variation in the size and shape of the loop. These results indicate that the tendency of Oxoid gelatin to change is low and cavities tend to decrease in size and collapse slowly.

Merck Gold label gelatin

The results of sorption and desorption of water vapour on Merck Gold label gelatin have been reported by Rao[71]. The system shows no hysteresis effect. The sorption and desorption curves remain coincident in the first two cycles. The experiments were conducted at 30°C. In the light of the cavity concept the cavities that were present in the gelatin must have collapsed at the end of the first sorption. Consequently there is no hysteresis.

Varietal differences in gelatin, egg albumin and casein in relation to the tendency of the hysteresis loop to disappear

If all the cavities collapse in the very first cycle of sorption and desorption, there will be no hysteresis loop in the first cycle itself and the sorption and desorption curves will be coincident. If on the other hand the cavities collapse in stages, the disappearance of the hysteresis loop will not be sudden. The loop decreases gradually in size and finally disappears.

Sorption - desorption hysteresis has been studied in a large number of swelling systems and these have been presented in the earlier investigations. There

have been instances in which there is no hysteresis loop at all even in the first cycle of sorption and desorption and the isotherms remain coincident in the subsequent cycles. There have also been instances in which the hysteresis loop is exhibited in the first cycle and it continuously decreases in size in the subsequent cycles tending to disappear ultimately. In some systems the loop disappears after 2 or 3 cycles and in others the disappearance is slow, as the loop persists even after 10 or 15 cycles and yet it diminishes in size in each successive cycle. Similar observations are noticeable in the present systems also - gelatin, egg albumin and casein. Interpretation of these results should obviously be based on the structure of proteins and the processes of swelling and shrinking.

Structure of proteins

The problem of structure of proteins has been extensively studied by numerous workers. The study of protein denaturation in particular has led to a better understanding of the subject. There have been exhaustive reviews on this interesting subject[120-123]. The basic elements of protein structure are essentially polypeptide chains. The structure of proteins consists of four different types - the primary, secondary, tertiary

and quaternary[124, 125]. The primary structure is the sequence of the amino acid residues in the polypeptide chains as determined by chemical analysis. The secondary structure refers to the way in which each polypeptide chain is coiled into a helix or spiral as a consequence of the links and bonds between relatively close elements of the chain. The tertiary structure describes how the more or less coiled polypeptide chains are arranged in space, folded or packed into the protein molecule by side chain interactions and the crosslinked disulphide bridges. The quaternary structure has been introduced in order to account for the level of organisation in which complex molecules are formed by association of macromolecular units.

The forces that are responsible for maintaining the above mentioned structural configurations of native proteins[121] are

(1) Hydrogen bonds between peptide linkages. The hydrogen bonds between the oxygen atoms of the carbonyl groups and the hydrogen atoms of the amide groups of peptide linkages play a basic role in determining the pattern of folding of polypeptide chains.

(2) Hydrophobic bonds - The tendency of the nonpolar groups of proteins to adhere to one another in

aqueous environments is hydrophobic bonding and this is very important in stabilizing the folded configuration in native protein.

(3) Salt linkages (Ion Pair Bonds) and other electrostatic forces - This is the attraction between positively charged amino and guanidino groups and the negatively charged carboxyl groups, which are abundant in proteins.

(4) Hydrogen bonds other than those between peptide links,

(5) Electron delocalisation,

(6) Dispersion forces and

(7) Effect of sulphide groups and other cross-linkages.

These seven different types of intermolecular bonds influence the polypeptide chain configuration of proteins. Because of the large number of peptide groups and hydrophobic groups in nearly all proteins, it is likely that these two types of the bonds are the most important in determining the overall configuration of the protein molecule. The covalent linkages of the peptide chain represents the primary structure. The

primary bonds do not determine the configuration of the chains. The secondary structure is the formation of spiral or helix from the polypeptide chain and its stabilisation by hydrogen bonding between the carbonyl and imino groups of the chain which come close to each other on the twisting of the chain. The tertiary structure depends upon the disulphide linkages.

Chemically reactive groups as centres of hydration

Proteins contain chemically reactive groups such as disulphide, phenolic, indolyl, carboxyl and basic groups and these probably act as centres of hydration. The extent to which each reactive group gets hydrated depends upon its nature. The maximum sorptive capacity of a protein is determined by the total number and nature of these polar groups.

Degree of crosslinking and accessibility of the polar groups to water molecules

The positions of these polar groups may be within or outside the spirals of the protein molecules. During sorption the accessibility of these groups to water molecules may become restricted as the degree of intramolecular crosslinking of the coils of the spiral by hydrogen and hydrophobic bonds increases. This in turn

restricts the extent of swelling and shrinkage of the protein. Consequently, the disappearance of the cavities which are responsible for entrapping the liquid becomes partial and takes places in stages. The hysteresis loop therefore gradually diminishes in size in successive sorptions and desorptions showing a tendency to disappear ultimately. In other words, the restricted accessibility of the centres of hydration for water molecules during sorption, is responsible for the slowness of the disappearance of the cavities and consequently the slowness of the disappearance of the hysteresis effect.

Varietal factor

Different samples of a particular protein may vary in the total number of polar groups and the degree of intramolecular crossshrinking. Their behaviour with regard to hydration capacity and sorption - desorption hysteresis will be different. Thus in this general phenomenon of the disappearance of the hysteresis effect, the varietal factor of the sorbent material plays an important role.

In the light of the above explanation of the gradual disappearance of the hysteresis effect based on the degree of crossshrinking and restricted accessibility of the centres of hydration to water molecules, the

results on the different varities of gelatin, egg albumin and casein may be examined.

Gelatin

The three different varities of gelatin have shown marked differences in behaviour in the sorption and desorption of water. Merck's Gold Label gelatin has shown no hysteresis effect at all even in the first cycle. Difco gelatin has shown the hysteresis effect. There is continuous decrease in total sorptive capacity at saturation pressure and enlargement of the hysteresis loop in the low vapour pressure region upto the 12th cycle of sorption and desorption. Oxoid gelatin has also shown the hysteresis effect. The hysteresis loop persists even upto the 10th cycle of sorption and desorption. The tendency to decrease is low.

Why the three different varieties of gelatin behave differently in the sorption and desorption of water is a puzzling problem. The hydration capacities at saturation pressure of water of Difco gelatin, Oxoid gelatin and Merck's Gold Label gelatin are approximately 120.0, 70.0 and 50.0% respectively. In the light of the theory based on the polar groups in the protein and their accessibility to water discussed above, this difference in hydration capacities must be attributed

to the difference in the number of polar groups present in the different varieties of gelatin. Difco gelatin has the highest and Merck's Gold Label gelatin, the lowest. The facts that in Merck Gold Label gelatin, there is no hysteresis effect at all even in the first cycle of sorption and desorption, whereas in Difco and Oxoid gelatins the hysteresis loop though continuously diminishing in size, persists upto 12th and 10th cycles respectively indicate that intramolecular crosslinking is low in the former and high in the latter.

The time of contact of the gelatin with water vapour at saturation pressure is probably an important factor. Though equilibrium is attained in about 10 hours ordinarily 2 days were allowed. In the seventh cycle in Difco gelatin - water system, the gelatin was kept in contact with water vapour for 10 days and this has resulted in a marked change in the size and shape of the loop.

Egg albumin

In the sorption and desorption of water vapour on native egg albumin (Merck's albumin ovi) there is a tendency for the decrease in size of the hysteresis loop from the first to the fifth loop. The activated egg albumin also has shown similar tendency from the second

to the eighth loop and the tendency is more marked. The denatured egg albumin also has shown the hysteresis loop upto the seventh cycle and there is a tendency for the decrease in size though less prominent, particularly in the low pressure region upto relative vapour pressure of about 0.50, part of the hysteresis loop of the first cycle has disappeared in the seventh cycle.

In the earlier study[71], Merck's soluble egg albumin has shown the hysteresis loop in the first cycle of sorption and desorption and the loop has disappeared in the second and third cycles. The same albumin after denaturation has shown no hysteresis effect at all even in the first cycle and the sorption and desorption curves are coincident in the first three cycles. As in the case of gelatin, this difference in sorption - desorption hysteresis between the two varieties of egg albumin, is due to the difference in the intramolecular bonding. The bonding is low in Merck's soluble egg albumin and high in Merck's albumin ovi.

The effect of activation and denaturation of the egg albumin is probably to reduce the intramolecular bonding because the tendency of the hysteresis to decrease in size and disappear is greater.

With native egg albumin of Armour and Company, Benson[118] has obtained hysteresis loops in three successive cycles of sorptions and desorptions and these are practically identical. With bovine plasma albumin and denatured egg albumin employing water, ethyl alcohol, diethyl ether and ethyl chloride, hysteresis loops have been obtained in the first cycle of sorption and desorption. If the study was continued in the second and subsequent cycles and with those liquids which are solvating, probably the loops would have shown a tendency to decrease in size and finally disappear. In their study of sorption - desorption hysteresis of water on native and denatured egg albumin at different increasing temperatures upto 100°C, Altman and Benson[126] have noticed that the hysteresis loop decreases in size as the temperature increases and at 100°C, the decrease in size is prominent.

Casein

Merck's alkali soluble casein - native, activated and denatured and Oxoid casein hydrolysate have all shown a common characteristic in successive sorptions and desorptions of water vapour. They all exhibit the hysteresis effect and the hysteresis loop decreases in size in successive cycles and tends to

disappear. The tendency to disappear is predominent in the case of activated casein, denatured casein and casein hydrolysate.

Kahlbaum's casein nach Hammersten in the earlier investigation[71] has shown a loop in the first cycle and it has disappeared in the second and third cycles. The above results with the different grades of casein just as in the case of gelatin and egg albumin bring out clearly the effect of varietal difference on the tendency of the hysteresis loop to decrease in size and disappear on successive sorptions and desorptions of water vapour. In Kahlbaum's casein the intramolecular bonding is less whereas in Mercks alkali soluble casein it is more. The effect of activation and denaturation of casein is to decrease the bonding.

The case of Oxoid casein hydrolysate is particularly interesting. Its sorptive capacity is 857.0%, whereas that of Merck's native casein is 40.0%. The very high value of casein hydrolysate is due to the presence of large number of reactive groups. As a result of hydrolysis of casein, the protein molecules are split up into simpler ones containing large number of amino and carboxy acid groups. When hydrolysis is stretched to the limit, the protein is converted into large number

of amino acid molecules, consequently the hydration capacity will be high. As the degree of intramolecular bonding is very low, the centres of hydration are easily accessible to water molecules during sorption. Consequently the swelling and shrinking are quick processes and the disappearance of the cavities is also quick. Therefore, either there should be no hysteresis loop at all or hysteresis loop produced in the first cycle must disappear in the subsequent cycles. These conclusions are actually borne out by the results obtained with casein hydrolysate.

Thus in the foregoing the general phenomenon of the gradual decrease in size and final disappearance of the hysteresis loop in successive sorptions and desorptions in proteins with water has been adequately explained on the basis of the cavity theory of hysteresis in conjunction with the structure of proteins. The intramolecular crosslinking by hydrogen and hydrophobic bonds in protein molecules determines the accessibility to water molecules of the reactive groups which are the centres of hydration. The restricted accessibility affects the extent of swelling and in turn the collapse of the cavities and the disappearance of the hysteresis effect.

Success of cavity concept as an explanation of the sorption - desorption hysteresis

Many cases of the gradual decrease in size of the hysteresis loop and its final disappearance on successive sorptions and desorptions are already on record. There is need for a satisfactory explanation of this general phenomenon.

To completely rule out the idea of the existance of pores in proteins and other swelling sorbents is not justifiable in view of the fact that ideally plane surface sorption is a rarity in nature. If the existence of pore is permitted, the cavity entrapping effect inevitably follows. The magnitude of this pore volume may be very small compared with the total sorptive capacity of the material which is mostly a case of hydration. This argument is borne out by the fact that in many of the systems studied, the total sorptive capacity has remained practically the same though the hysteresis loop has disappeared.

Activated rice[61] has taken 25 grams of water per 100 gms of rice whereas the volume of carbon tetrachloride taken is only 1 cc per 100 gms. Volume of carbon tetrachloride taken is a measure of the pore space and this is very small compared with the hydration capacity

of rice grains. What portion of the total pore volume, the cavities occupy is a problem difficult to tackle. A quantitative formulation of the entrapping effect of the cavity is needed. So far no mathematical formulation of the cavity effect has been made and probably any such attempt would be difficult because it involves information about the number, shape, size, the neck and body diameters of the cavities in any particular porous system. Nevertheless the cavity theory of hysteresis has been successful so far in explaining in a qualitative way, all cases of hysteresis and the associated phenomena.

Another significant point emerges from the cavity concept. Hysteresis is due to entrapping of liquid. The entrapping effect is determined by the difference between the body radius and neck radius of the cavity. In two cavities of same body radii, one having smaller neck entraps more liquid and consequently produces a bigger hysteresis loop. The one having wider neck produces a smaller hysteresis loop. This is probably the explanation of the difference between the 1st and 12th loops in Difco gelatin - water system. Thus the cavity theory of hysteresis coupled with the swelling and shrinkage of the sorbent in a solvating liquid has been able to explain satisfactorily

all the variations in size and shape of the hysteresis loop observed in successive sorptions and desorptions.

Proteins, gums, rice grain have no similarity in chemical composition. But they all behave in the same way with regard to sorption - desorption hysteresis. The properties that are common to them are hydration and swelling.

B. EFFECT OF HYDROLYSIS OF GELATIN ON SORPTION - DESORPTION HYSTERESIS WITH WATER

Sorption - desorption hysteresis has been studied with different varieties of gelatin and reported in the previous section. The differences in the tendency of the hysteresis loop to decrease in size and disappear indicate the differences in the degree of intramolecular crosslinking in the molecules of the different varieties of gelatin. Hydrolysis breaks up the gelatin molecules into smaller ones. In this process not only the degree of crosslinking is reduced but also the total number of reactive groups is increased. These in turn should increase the hydration capacity of gelatin and the tendency of the hysteresis loop to decrease in size. Therefore, a systematic study of sorption - desorption hysteresis with hydrolysed gelatin was undertaken.

Three different samples of hydrolysed gelatins are prepared from the native gelatin made by Oxo Ltd., London. 5 gm of gelatin powder was mixed with 10 cc of water in a glass stoppered bottle and was suspended in boiling water at 100°C for 12 hours. The resulting mass was dried for 2 days in air at room temperature and then for one day in a vacuum dessicator.

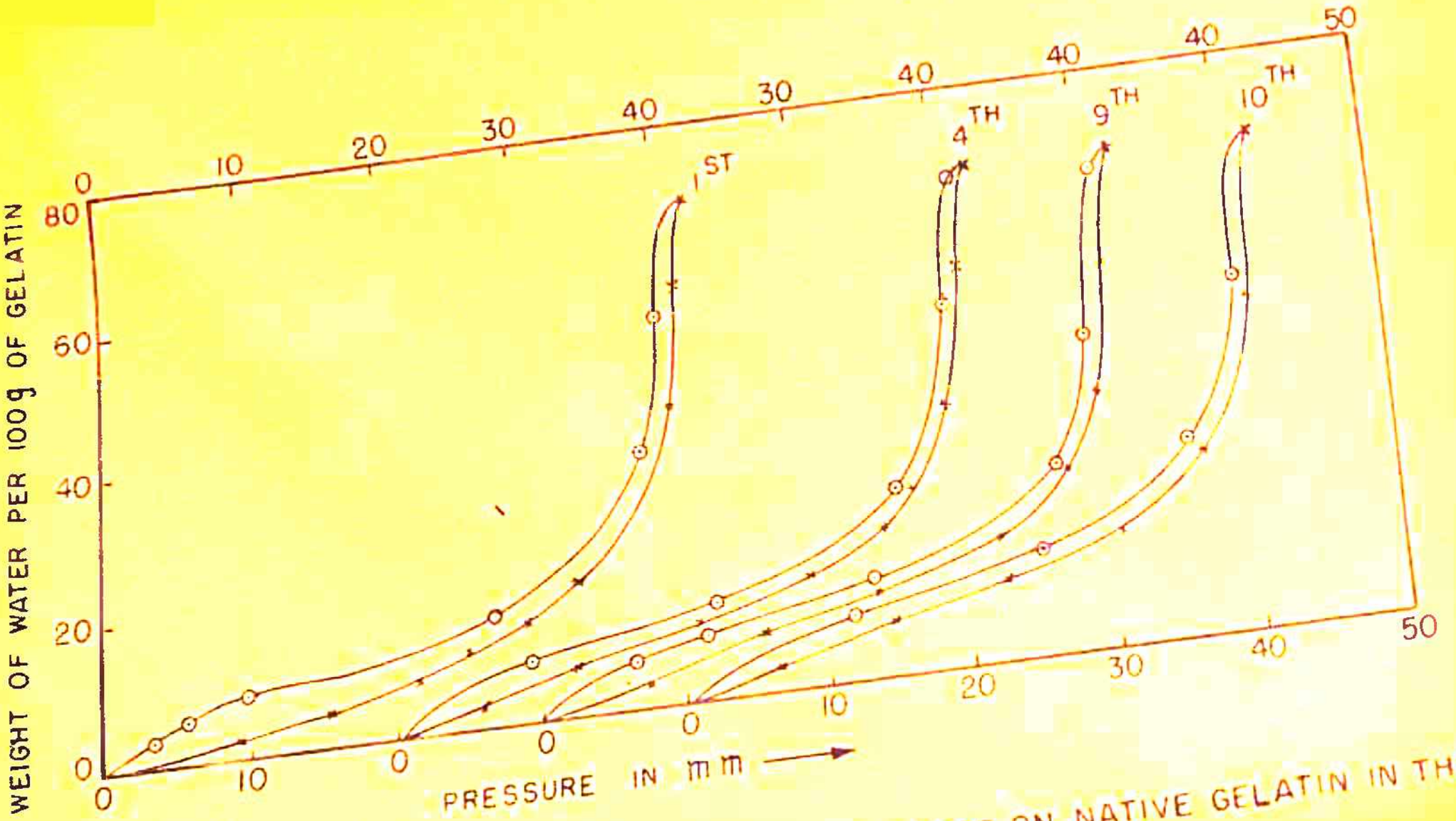


FIG. 1. SORPTION-DESORPTION HYSTERESIS OF WATER ON NATIVE GELATIN IN THE 1ST, 4TH, 9TH AND 10TH CYCLES.

Similarly other two samples were prepared by hydrolysing native gelatin at 119°C and 133°C for 2 hours in an autoclave and drying in the same way.

Results

Native gelatin

With native gelatin the sorption and desorption studies were continued upto 10th cycle. The loops of the first, fourth, ninth and tenth cycles are shown in Figure 1. The values at saturation pressure of water are 69.8, 67.8, 69.2 and 68.6% respectively. At the end of each cycle the gelatin was kept in contact with water vapour at saturation pressure of water for 2 days. The total period of study was 3 months.

Gelatin hydrolysed at 100°C

The hysteresis loops obtained with gelatin hydrolysed at 100°C are shown in Figure 2. The amount of water taken at saturation pressure of water in the first and second cycles are 72.1 and 71.8% respectively. The sample was kept in contact with water vapour at saturation pressure for 2 and 5 days respectively. The total period was about a month.

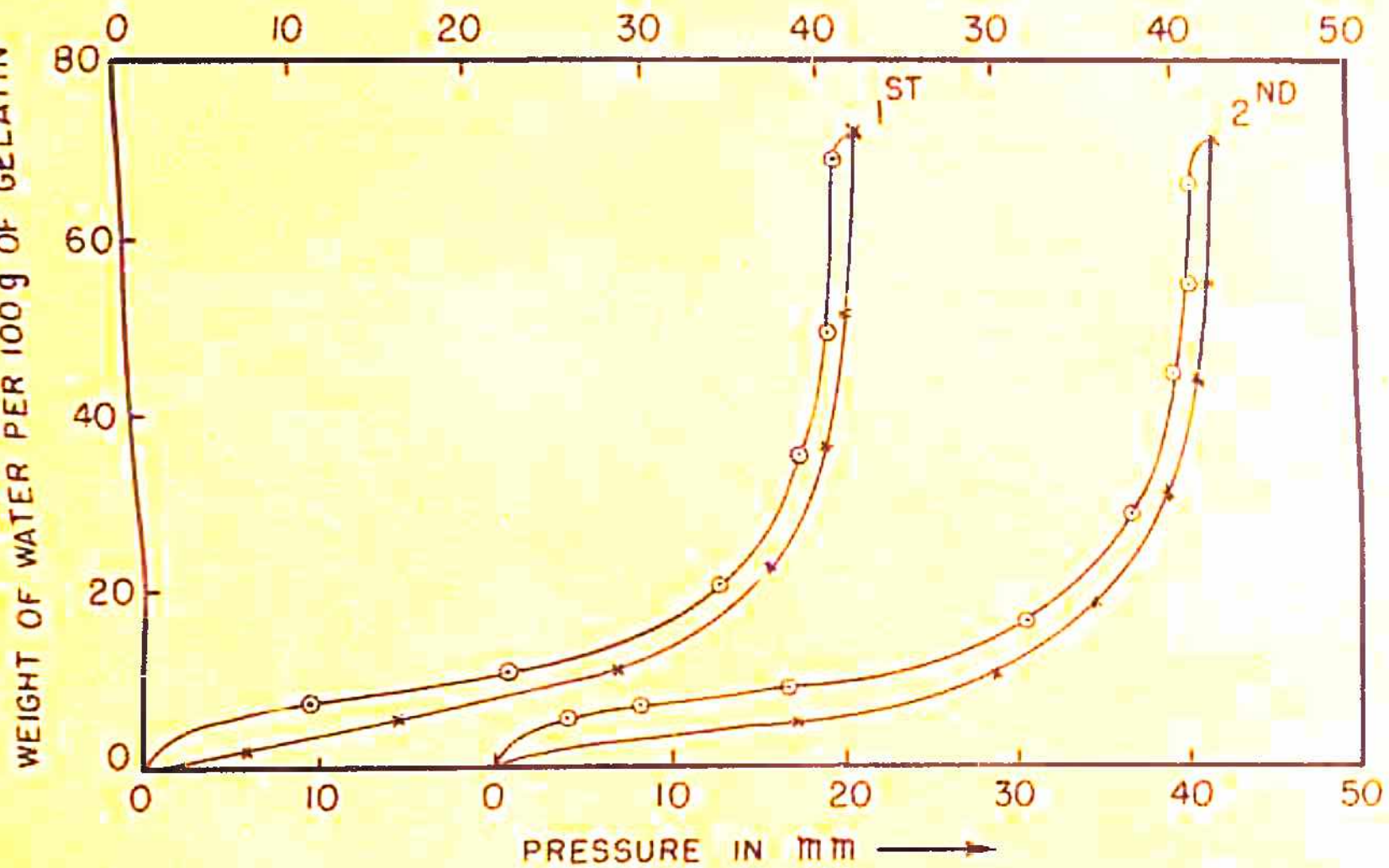


FIG. 2. SORPTION–DESORPTION HYSTERESIS OF WATER ON GELATIN HYDROLYSED AT 100°C IN THE 1ST AND 2ND CYCLES.

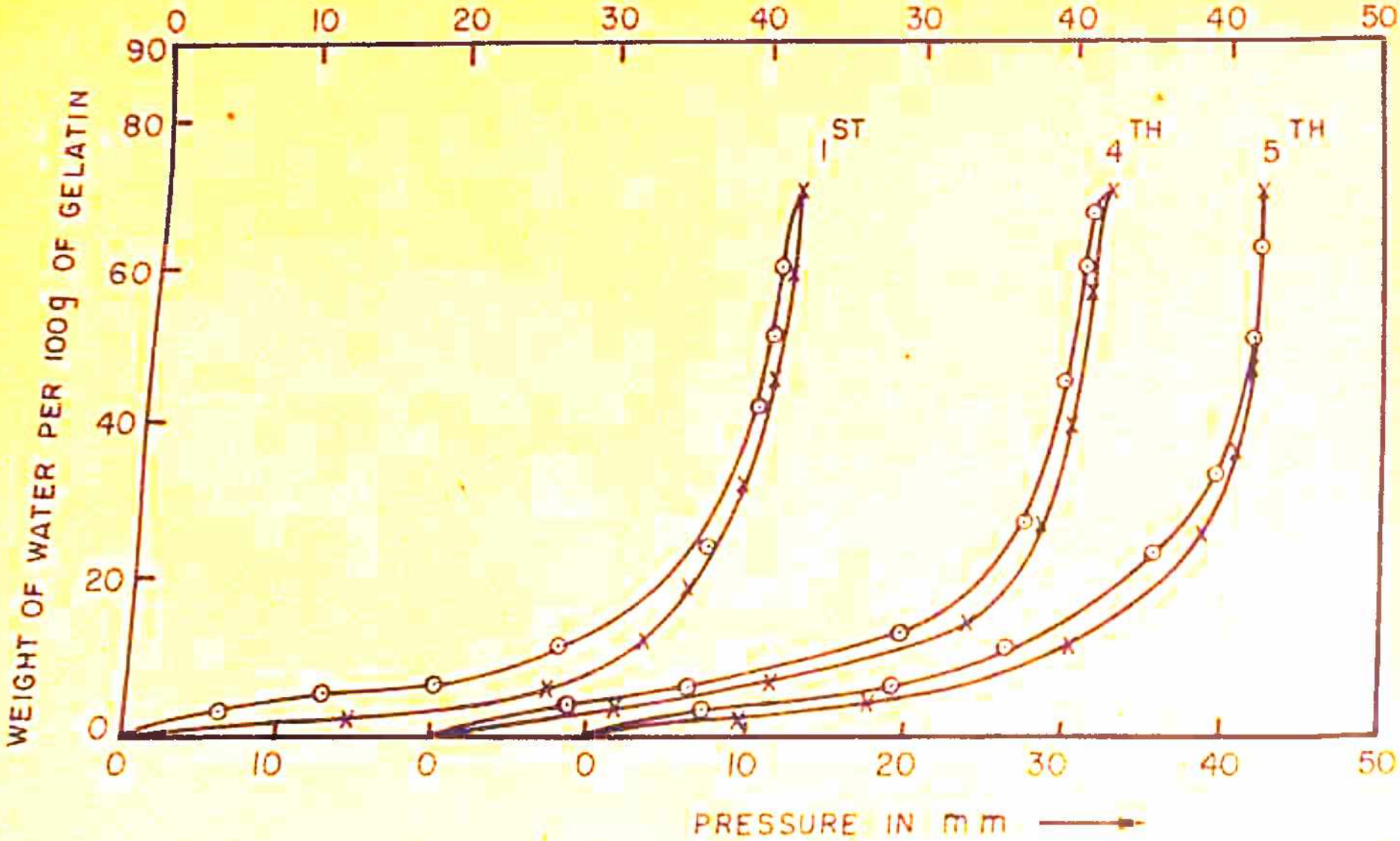


FIG. 3. SORPTION-DESORPTION HYSTERESIS OF WATER ON GELATIN HYDROLYSED AT 119° C IN THE 1ST, 4TH AND 5TH CYCLES.

Gelatin hydrolysed at 119°C

Sorption - desorption studies have been continued upto 5th cycle. The loops of the first, fourth and fifth cycles are shown in Figure 3 and the amount of water taken at saturation pressure of water are 70.4, 70.3 and 70.8% respectively. At the end of each cycle the gelatin was kept in contact with water vapour at saturation pressure of water for two days. The total period for completing the study was about one and a half month.

Gelatin hydrolysed at 133°C

With gelatin hydrolysed at 133°C, Figure 4, the sorption - desorption studies were continued upto 7th cycle. The sorptive capacities in the first, second and seventh cycles are 92.1, 93.0 and 95.1% respectively. At the end of sorption the gelatin was kept in contact with water vapour at saturation pressure for 2 days in all the cycles. The total period required to complete the study was about 2 months.

Changes in gelatin on hydrolysis[127]

Proteins are macromolecular substances yielding amino acids as major products of complete hydrolysis. Protein is broken down step by step into simpler bodies -

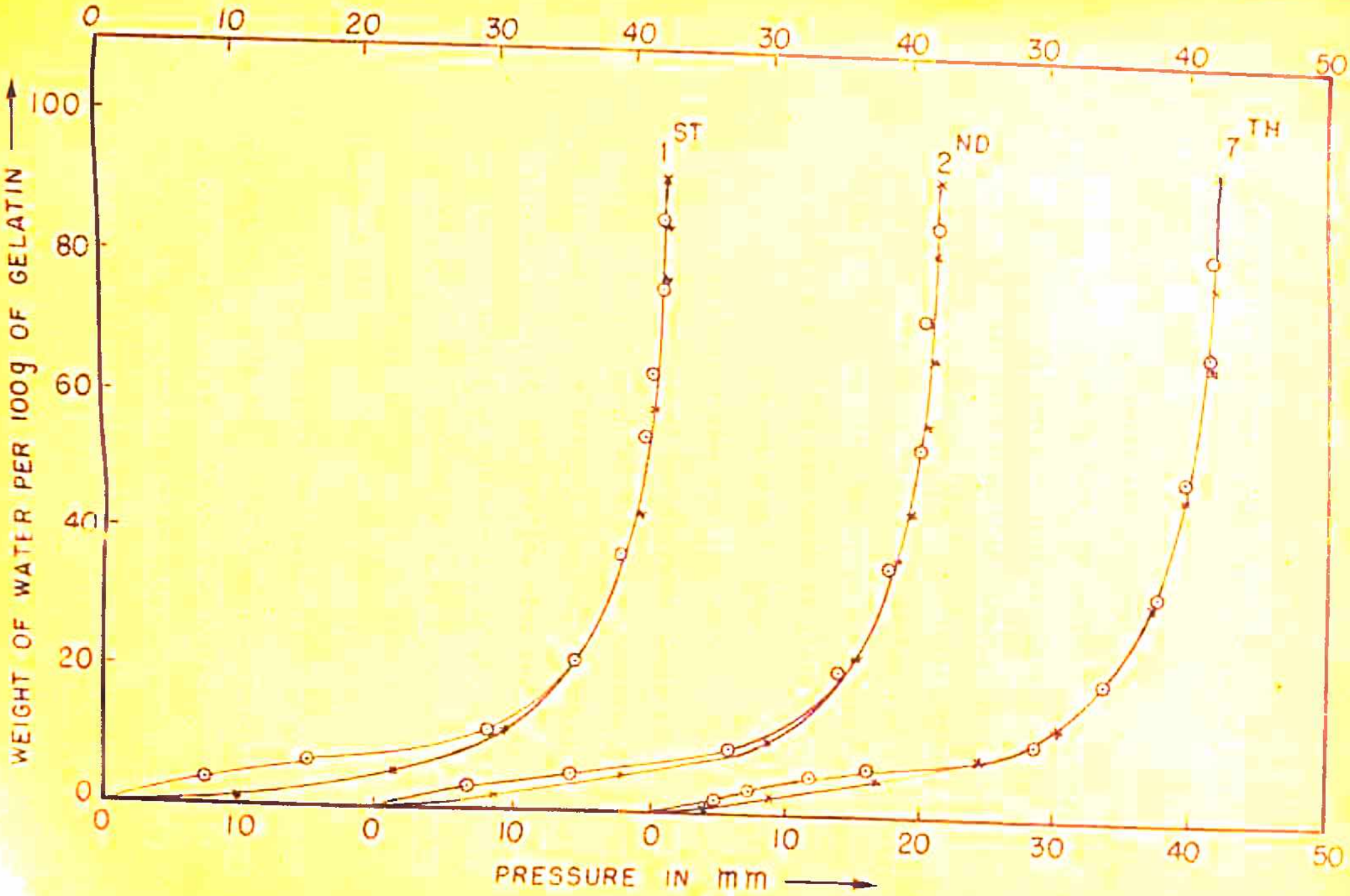


FIG. 4. SORPTION-DESORPTION HYSTERESIS OF WATER ON GELATIN HYDROLYSED AT 133°C IN THE 1ST, 2ND AND 7TH CYCLES.

proteoses, peptones, polypeptides, amino acids and finally ammonia.

The proteins in the presence of water can be hydrolysed to amino acids by prolonged heating, e.g., by superheated steam without the addition to the system of any acid, alkali or ferment, indicates that the process of hydrolysis is occuring, although slowly, at all temperatures and in the absence of catalysors other than, possibly, the hydrogen or hydroxyl ions of water itself. The influence of rising temperature is to accelerate the reaction of breaking of more and more protein molecules into simpler units. Fairly complete hydrolysis occurs at temperatures above 100°C and it sets in more rapidly at higher temperatures[128]. Hydrolysis can also be brought about by heating in acid or alkaline solutions or treating with enzymes. Whatever may be the method of hydrolysis, if the hydrolysis is complete, the end product will be a mixture of amino acids.

Discussions

In the sorption and desorption of water vapour on native gelatin the tendency of the hysteresis loop to decrease in size is slight from first cycle to tenth cycle. The hysteresis loops obtained with gelatin hydrolysed at 100°C are almost the same as those with

the native gelatin. With gelatin hydrolysed at 119°C there is a tendency of the hysteresis loop to decrease in size in the low and high pressure regions from first to fifth cycle. Gelatin hydrolysed at 133°C also shows similar changes more markedly. The sorptive capacity remains practically the same in all the cycles but is more than that of native gelatin. The hysteresis loop decreases in the lower region whereas there is no hysteresis loop above relative vapour pressure of 0.5 even in the first cycle. These results indicate that hydrolysis of gelatin plays an important role in the sorption - desorption hysteresis with water.

As shown earlier, the disappearance of the hysteresis effect is explained on the basis of the cavity theory in conjunction with the structure of proteins. The number of polar groups determines the hydration capacity and the degree of intramolecular crosslinking determines the accessibility of the polar groups to water. Restricted accessibility restricts the swelling of the protein. This decreases the tendency of the cavities to disappear and consequently the tendency of the hysteresis loop to disappear. As a result of hydrolysis of gelatin there is decrease in the degree of intramolecular crosslinking, more polar groups are

produced and these are more easily accessible towater. On account of greater ease of swelling by the hydration of water, the cavities decrease in size more easily and disappear. Consequently the tendency of the hysteresis loop to decrease in size and finally disappear is also greater in the case of hydrolysed gelatins.

The native and hydrolysed gelatin at 100°C do not show any marked variation in the size and shape of the loop. These results indicate that the tendency of native and hydrolysed gelatin at 100°C to change is low and cavities tend to decrease in size and collapse slowly. The curves obtained by native gelatin and gelatin hydrolysed at 100°C are almost the same thereby showing that practically no hydrolysis of gelatin has taken place at 100°C. Actually it has also been pointed out[127] that hydrolysis normally takes place above 100°C.

It is known that hydrolysis sets in more rapidly at higher temperatures. Hence at 119°C the hydrolysis of gelatin results in more polar groups and lesser crosslinking. Owing to lesser crosslinking there is greater accessibility of the polar groups to water, the cavities disappear more easily than in the native gelatin and hence greater ease of the disappearance of the hysteresis loop.

In the case of gelatin hydrolysed at 133°C the sorption and desorption curves coincide above relative vapour pressure of 0.5. Below this, there is a small hysteresis loop which decreases in size from the first cycle to the seventh. These results indicate that at 133°C gelatin undergoes hydrolysis to a still greater extent producing more polar groups thereby increasing sorptive value greater than native gelatin and lesser crosslinking. Polar groups are more easily accessible to water and consequently the swelling of gelatin is quicker. Owing to greater ease of swelling, the cavities decrease in size and disappear more quickly.

The above discussion brings out clearly the effect of hydrolysis of gelatin on its hydration capacity and the tendency of the hysteresis loop to disappear.

C. EFFECT OF HARDENING BY FORMALDEHYDE OF EGG ALBUMIN AND CASEIN ON SORPTION - DESORPTION HYSTERESIS WITH WATER

The effect of varietal differences in gelatin, egg albumin and casein and hydrolysis of gelatin on sorption - desorption hysteresis with water has been presented in the previous sections. Varietal differences have been attributed to differences in the degree of intramolecular crosslinking and the number of polar groups in the proteins. Hydrolysis also produces similar differences in proteins. Hardening of egg albumin and casein is a well known phenomenon. Its effect is to increase the intramolecular cross-linking in the proteins and this in turn should affect their behaviour in sorption - desorption hysteresis with water. Therefore systematic study of sorption - desorption hysteresis with hardened egg albumin and casein was undertaken.

Egg albumin (Merck's albumin ovi) was used. Two hardened samples of egg albumin were prepared according to the method given by Houwink[129] by immersing 5 gm each of egg albumin in 5% and 10% formaldehyde respectively and keeping the mixture for 20 days in both the cases at room temperature. After 20 days the samples

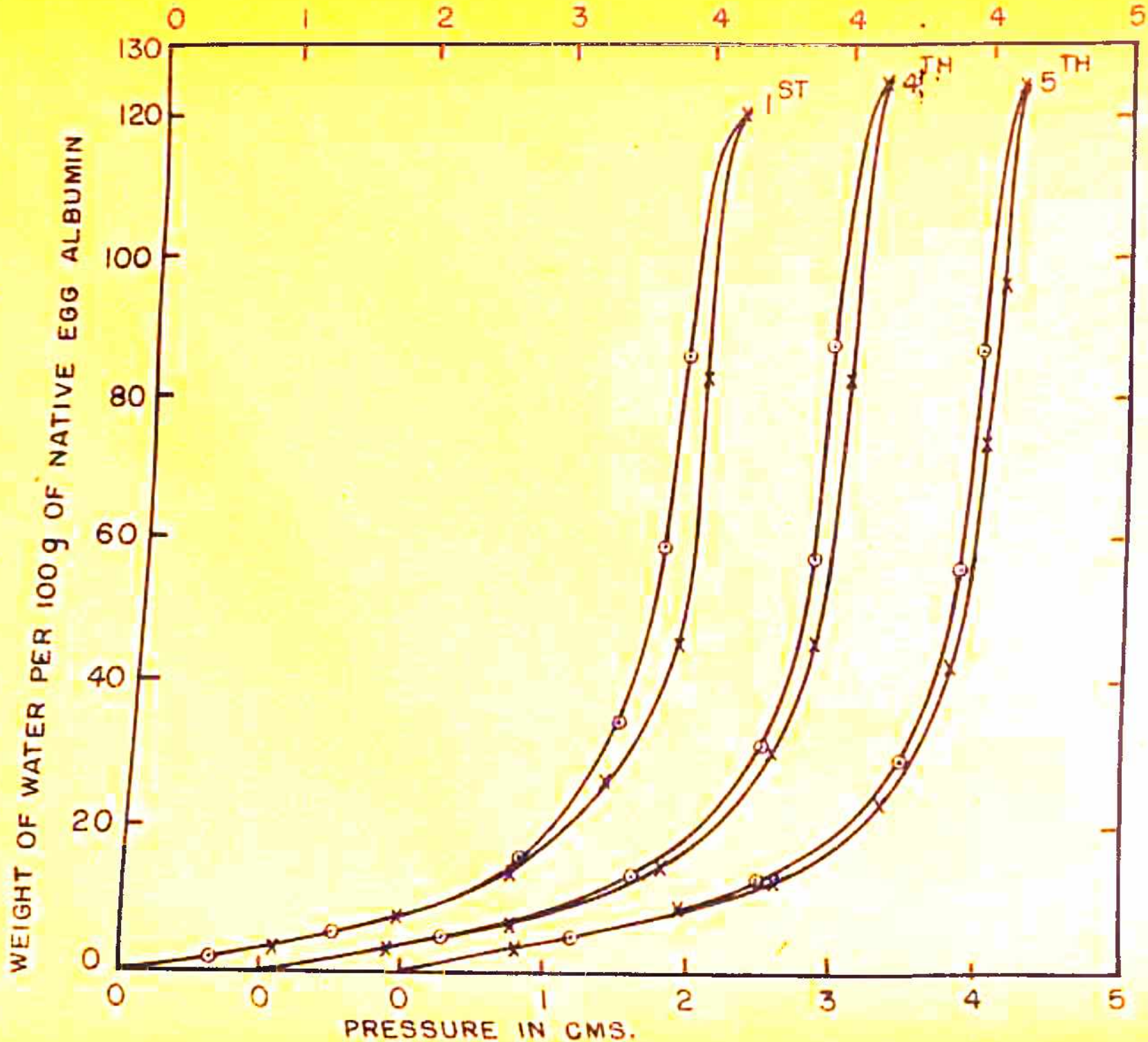


FIG. 1. SORPTION AND DESORPTION OF WATER ON NATIVE EGG ALBUMIN

were separated, washed several times with distilled water and finally dried over calcium chloride dessicator for 2 days.

Similarly two hardened samples of casein (Merck's alkali soluble) were prepared. Grain size between 30 and 50 British Standard Sieve was chosen in all the cases.

Results

Egg albumin

The hysteresis loops obtained with native egg albumin are shown in Figure 1. The amounts of water taken at saturation pressure of water in the first, fourth and fifth cycles are 120.3, 125.4 and 124.0% respectively. The total period of study was nearly 2 months. The albumin was kept in contact with water vapour at saturation pressure for 2 days in all the cycles.

The sorption and desorption studies were continued upto the 10th cycle with egg albumin hardened with 10% formaldehyde for 20 days. The loops of the first, third, fourth and tenth cycles are shown in Figure 2. The values at saturation pressure of water

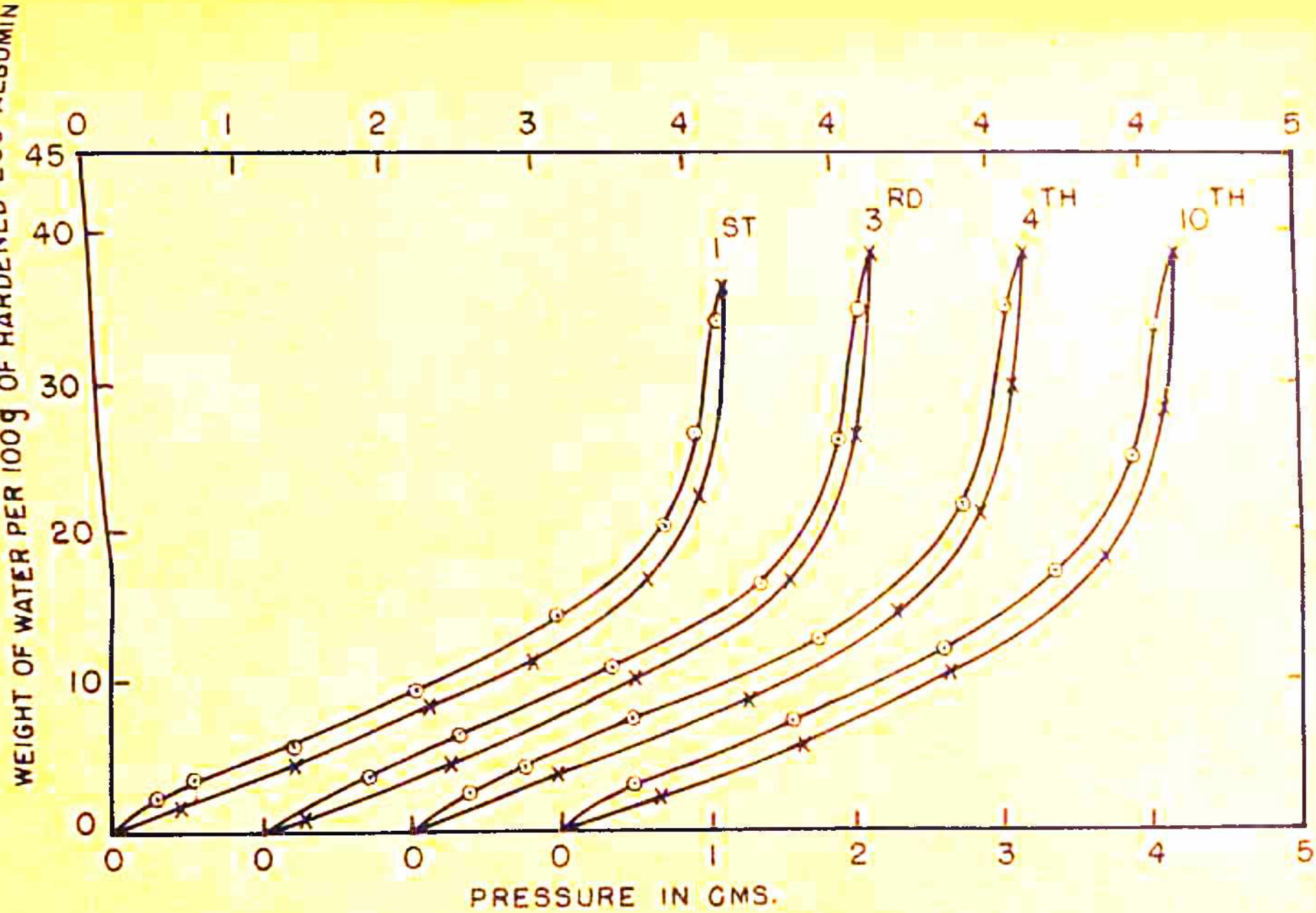


FIG. 2. SORPTION AND DESORPTION OF WATER ON EGG ALBUMIN HARDENED WITH 10% FORMALDEHYDE FOR 20 DAYS IN 1^{ST}, 3^{RD}, 4^{TH} AND 10^{TH} CYCLES.

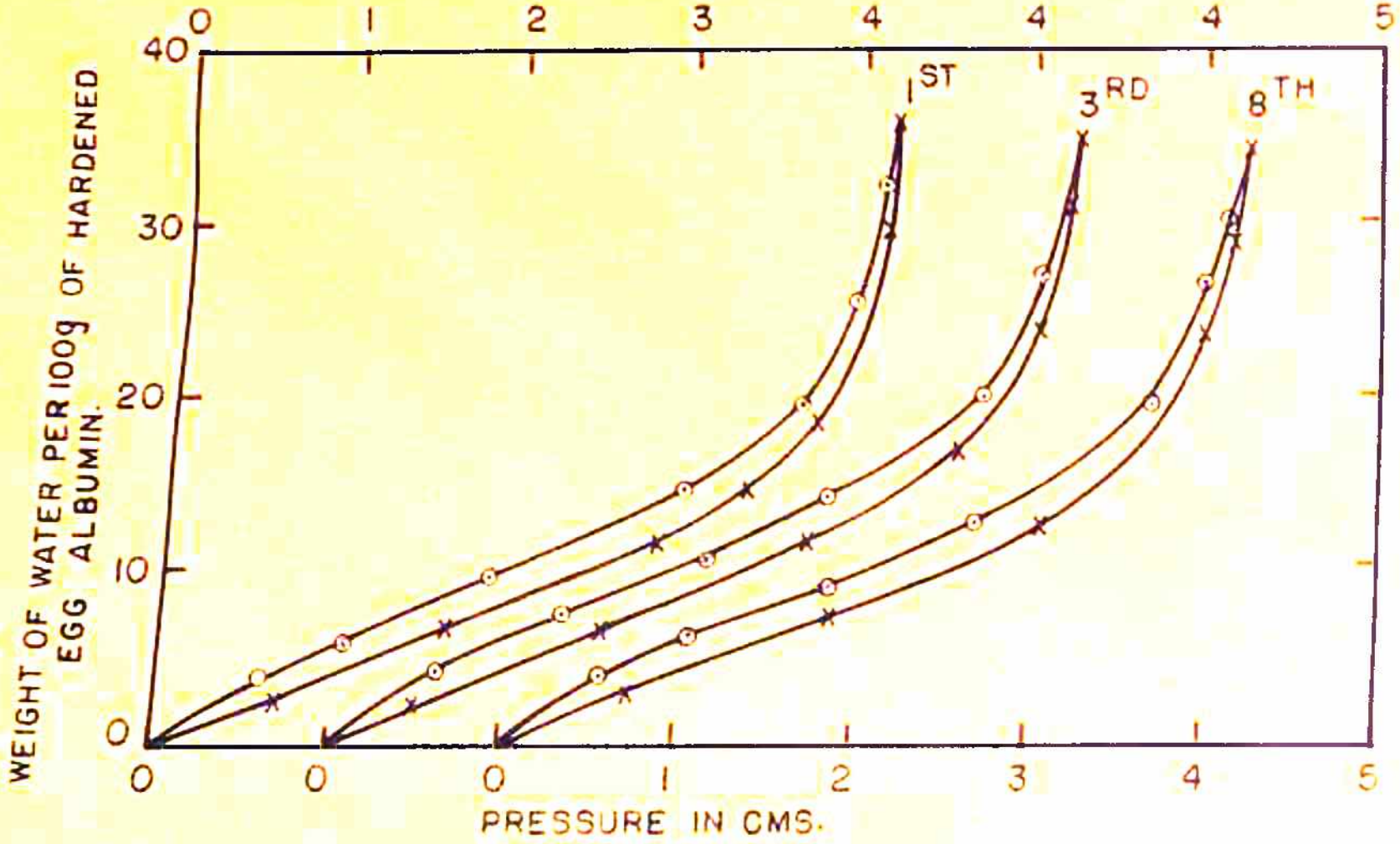


FIG. 3. SORPTION AND DESORPTION OF WATER ON EGG ALBUMIN HARDENED WITH 5 % FORMALDEHYDE FOR 20 DAYS IN 1ST, 3RD AND 8TH CYCLES.

are 36.2, 38.4, 38.4 and 38.4% respectively. The total period of study was nearly 2 months. The albumin was kept in contact with water vapour at saturation pressure for 2, 1, 1 and 1 day respectively.

In case of egg albumin hardened with 5% HCHO for 20 days, the sorption and desorption studies were continued upto the eight cycle. The loops obtained in the first, third and eight cycles are shown in Figure 3. The percentages of water taken at saturation pressure in each of these cycles are 35.4, 34.6 and 34.7, respectively. The total period required for completing the 8 cycles of sorption and desorption is nearly 2 months. In each cycle the albumin was kept in contact with water vapour at saturation pressure for one day.

Casein

With native casein, Figure 4, the sorption - desorption studies have been continued upto the fourth cycle. The amounts of water taken up at saturation pressure in the first, third and fourth cycles are 40.8, 39,0 and 40.0% respectively. The sorbent was kept in contact with water vapour at saturation pressure for 2, 5 and 5 days, respectively. The total period for completing the study was 1.5 months.

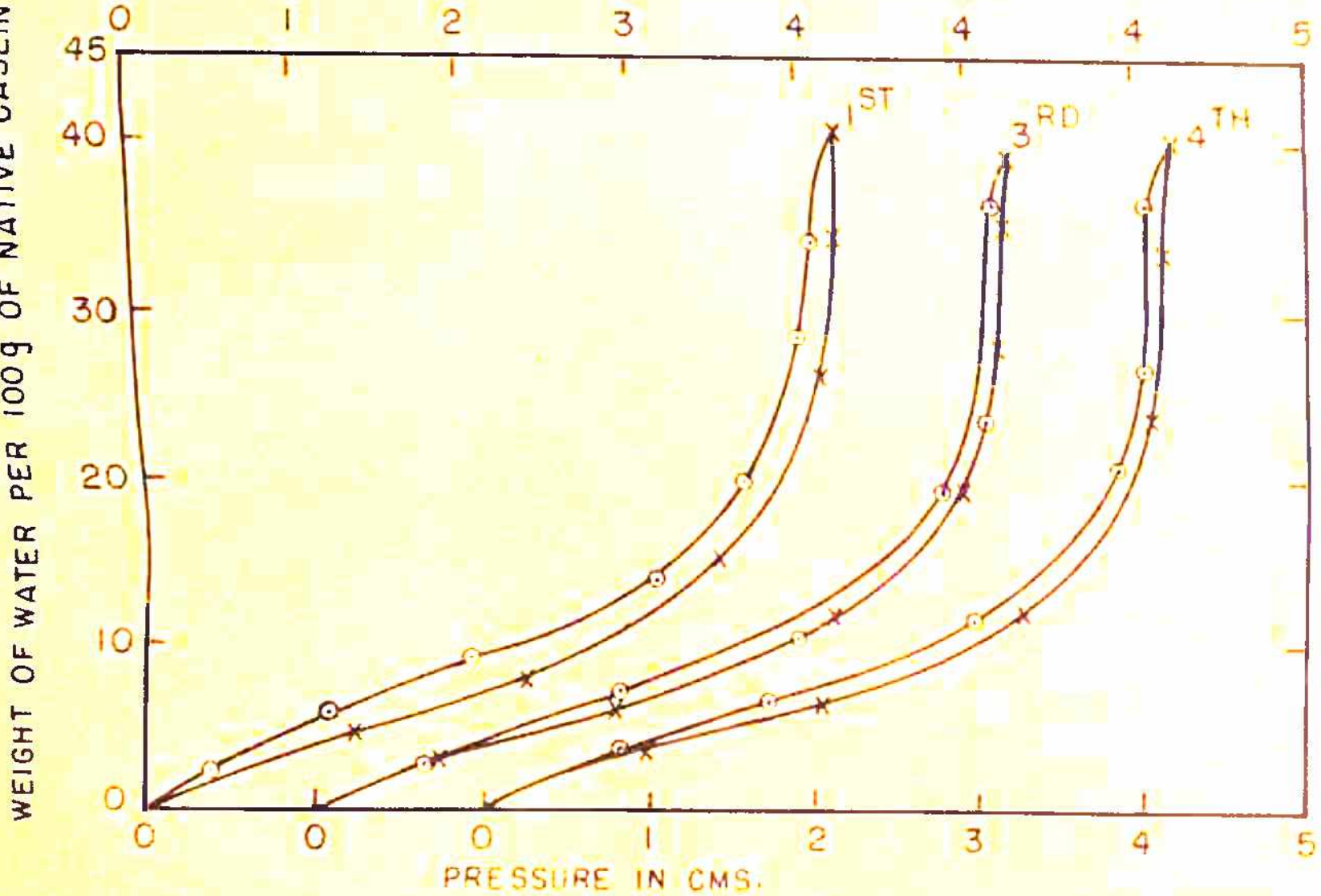


FIG. 4. SORPTION AND DESORPTION OF WATER ON NATIVE CASEIN IN 1ST, 3RD AND 4TH CYCLES.

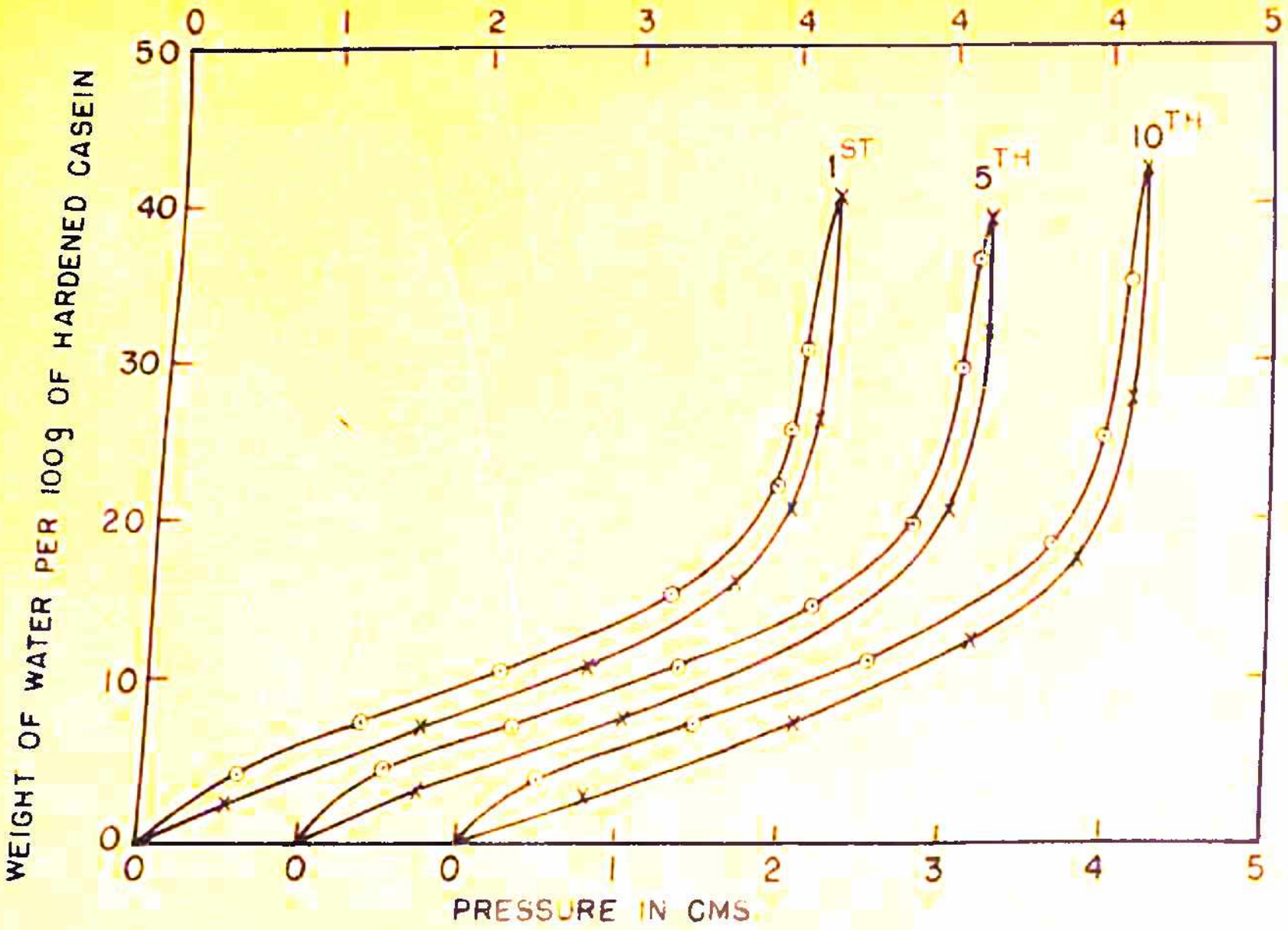


FIG. 5. SORPTION AND DESORPTION OF WATER ON CASEIN HARDENED WITH 10% FORMALDEHYDE FOR 20 DAYS IN 1ST, 5TH AND 10TH CYCLES.

The hysteresis loops obtained with casein hardened with 10% formaldehyde for 20 days are shown in Figure 5. The values at saturation pressure of water in the first, fifth and tenth cycles are 40.6, 39.0 and 42.4% respectively. The total period of the study was 1.5 months. The casein was kept in contact with water vapour at saturation pressure for one day in all the cycles.

Sorption - desorption studies were continued upto the eleventh cycle in the case of casein hardened with 5% formaldehyde for 20 days, Figure 6. The sorptive capacities in the first, seventh and eleventh cycles are 45.5, 45.6 and 45.6% respectively. The sorbent was kept in contact with water vapour at saturation pressure for two days in all the cycles. The total period required for the study was nearly 1.5 months. In hardened samples 4 hours were sufficient for the attainment of equilibrium.

Theory of hardening of egg albumin and casein

The hardening or tanning of collagen with different tanning agents is known since long. Tanning modifies the properties of the material. The product obtained by tanning is resistant to the action of water and heat. The swelling in water is either reduced or

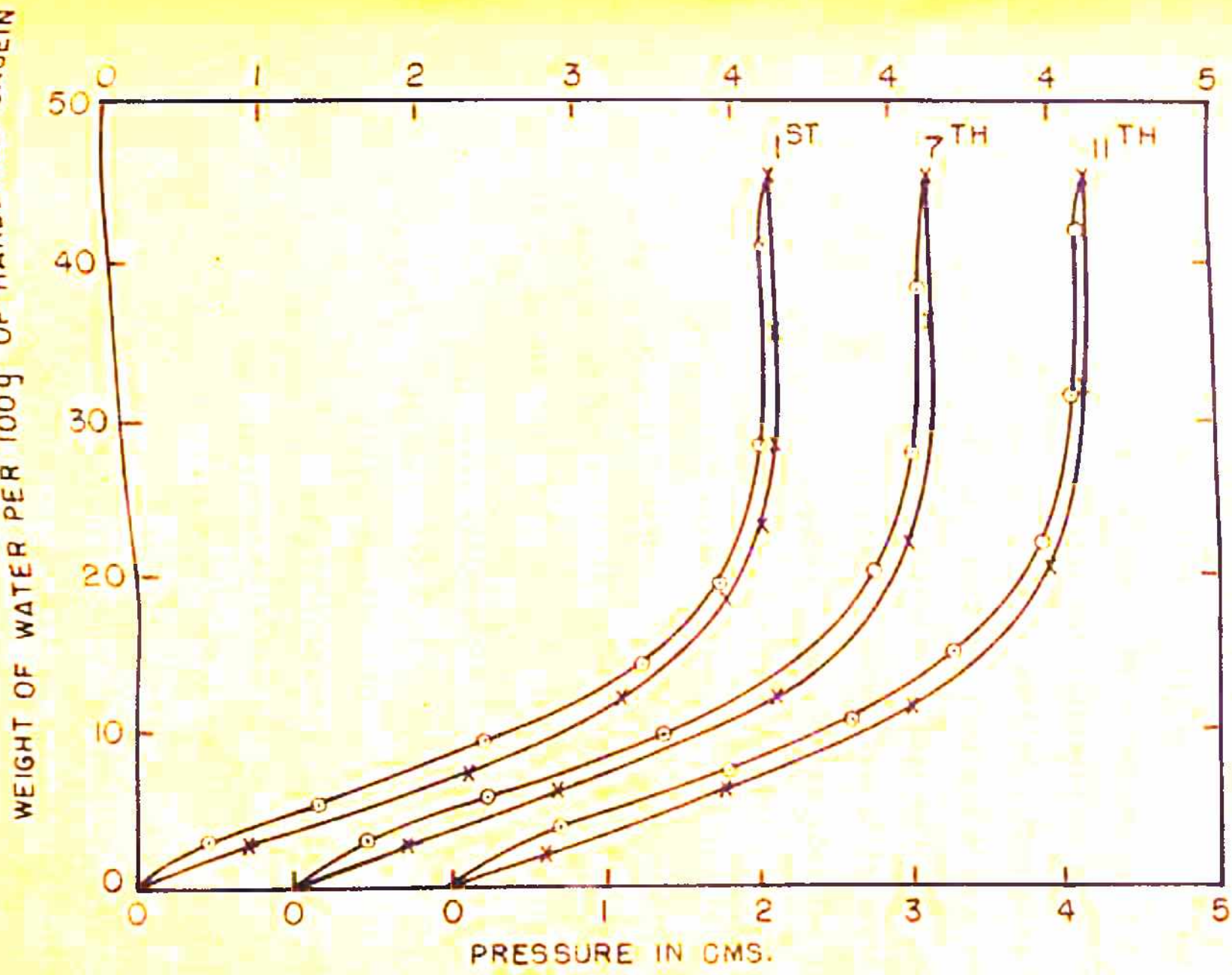


FIG. 6. SORPTION AND DESORPTION OF WATER ON CASEIN HARDENED WITH 5 % FORMALDEHYDE FOR 20 DAYS IN 1ST, 7TH AND 11TH CYCLES.

completely eliminated. Certain reactive groups are inactivated. Proteins are also hardened with different hardening agents. Formaldehyde is commonly used for hardening. That hardening by formaldehide is a case of crosslinking of proteins was suggested by Meyer[130]. Formaldehyde has been widely used as a hardening agent probably due to its high reactivity and with a vast range of possible reactions with any one of a number of different kinds of fundamental groups in proteins. These groups are capable of undergoing addition and condensation reactions with formaldehyde to form methylene crosslinks[131-136] which increase the degree of intramolecular crosslinking. There is still considerable doubt as to the position of the methylene crosslinks in the protein molecule.

Nitschmann and coworkers[137,138] showed experimentally that there was loss of water during the reaction of casein with gaseous formaldehyde indicating the condensation type of crosslinking. They concluded that in the hardening of casein, the reaction is methylene bridge formation between E-amino groups of lycine and the nitrogen of adjacent peptide linkages. This view was further confirmed by Fraenkal-Conrat and his coworkers[132,133] while working with other proteins.

Results of experiments of Fraenkal-Conrat and Olcott[134] with proteins and macromolecular model compounds, showed that methylene bridges are formed in the interaction of formaldehyde with a primary amide or guanidyl group and an amine or amino acid but not between an amide and guanidyl groups. However, they were unable to prove Nitschmann and Hadorn's conclusion[137] about the crosslinking between amino and peptide groups.

Consden et al[139] and Middlebrook et al[140] showed that the crosslinking occured between sulphhydryl groups when reduced keratins are treated with formaldehyde at elevated temperature.

The above results reveal that different groups are available for condensation reaction with formaldehyde. The primary reaction of formaldehyde with proteins, probably is the formation of methylol group which then gives crosslinking methylene bridge. These crosslinks may be intramolecular and promote the formation of cyclic structures or they may be intermolecular and promote the formation of molecular aggregates.

Hardening of casein is of major technological importance. Treatment with formaldehyde makes casein tougher, more resistant to swelling and enzymatic action. The amount of formaldehyde bound in casein is a function

of time and concentration of formaldehyde. Upto 1.5% bound formaldehyde, the mechanical properties depend upon the amount bound. More than this limiting value can be bound but does not contribute to hardening.

Regarding the hardening of egg albumin, no information is available in the literature. This is probably because it has no technological application. However the mechanism of hardening and the structure of hardened egg albumin may be considered to be the same as in the case of casein.

Discussions

Native egg albumin and casein exhibit the hysteresis effect on the sorption and desorption of water vapour. The loops decrease in size on successive sorptions and desorptions of water vapour. These results of gradual disappearance of the hysteresis loops have been explained in the previous sections on the basis of the cavity theory in conjunction with the structure of proteins. The intramolecular crosslinking determines the accessibility of the reactive polar groups to water. Restricted accessibility restricts the swelling of the protein and this decreases the tendency of the cavities to disappear and consequently the tendency of the hysteresis loop to disappear.

As a result of hardening of egg albumin and casein with formaldehyde, there is increase in the degree of intramolecular crosslinking. The number of polar groups are also reduced. The accessibility of polar groups to water is restricted due to the formation of crosslinks and hence the swelling of hardened egg albumin and casein is restricted. With egg albumin hardened by 10% formaldehyde, the 1st and 10th hysteresis loops are almost identical and with egg albumin hardened by 5% formaldehyde, the 1st and 8th loops are also identical. Similarly in the case of casein hardened with 10% formaldehyde, the 1st and 10th loops are identical and in casein hardened with 5% formaldehyde, the 1st and 11th loops are identical. There is no tendency for the hysteresis loop to decrease in size in successive sorptions and desorptions. These results indicate that the crosslinking by methylene bridges is so high that the accessibility of polar groups of the hardened egg albumin and casein to water is restricted and the swelling of the hardened samples is completely lost. Therefore the tendency of the cavities to disappear is also lost. The hardened egg albumin and casein behave like a rigid gel. The cavities which are made up of rigid walls in hardened egg albumin and casein entrap water and have no tendency

to collapse in contact with water, consequently the hysteresis effect persists even after a large number of cycles of sorptions and desorptions. The concentrations of formaldehyde of 10% and 5% bring about complete hardening.

In the case of hardened egg albumins the sorptive capacity is reduced to about 40.0% whereas native egg albumin takes about 120.0%. In casein all the samples, both hardened and unhardened have practically the same sorptive capacity about 40.0%. The number of polar groups determines the hydration capacity and the degree of intramolecular crosslinking determines the accessibility of the polar groups to water. Native egg albumin probably contains more polar groups and less of intramolecular crosslinking by hydrogen and hydrophobic bonds than in native casein. On hardening by formaldehyde the degree of intramolecular crosslinking by methylene bridges has gone to such an extent in both egg albumin and casein that they have become nonswellable and the sorptive capacity is almost the same.

The present results are in conformity with those of Rao and coworkers[74]. They have shown the effect of hardening of sericin by formaldehyde and basic chromium sulphate on the sorption - desorption hysteresis. The

hysteresis effect persisted in hardened sericin even after a number of cycles whereas native sericin showed the tendency of disappearance of the hysteresis effect in successive cycles.

CHAPTER V: SORPTION - DESORPTION HYSTERESIS IN SILICA GEL

A. SORPTION - DESORPTION HYSTERESIS IN GLASSY SILICA GEL AND FIBROUS SILICA GEL (SANTOCEL C) WITH WATER, CARBON TETRACHLORIDE AND ALIPHATIC ALCOHOLS

Introduction

In spite of the voluminous work that has already accumulated, sorption - desorption hysteresis is still a vexed and unsolved problem. Amongst the sorbents which have been extensively worked out are the charcoals and gels of oxides. Silica gel is one such sorbent. Silica has been used in various forms - nonporous silica, silica powder loose and compacted, glassy silica gel, chalky silica gel, silica gel prepared by mixing the reactant solutions at high temperatures[70,141], silica gel activated by igniting to different temperatures[142].

Monsanto Company, U.S.A. have produced a new form of silica of trade name Santocel C. This new form of silica and also the transparent glassy silica gel have been employed in the present investigations for studying sorption - desorption hysteresis with water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols.

Preparation of glassy silica gel

Glassy silica gel was prepared according to the

procedure of Rao and Doss[143] and used by Rao[61] in the earlier work. To a solution of pure sodium silicate of density 1.118, equal volume of 3N hydrochloric acid was added and the gel was allowed to set at room temperature. The gel was washed free from sodium chloride and dried at 100°C. The dried gel of size between 30 and 50 mesh, British Standard Sieve was activated by heating to 450°C for 4 hours.

Preparation and properties of fibrous silica gel (Santocel C)[144]

Santocel is technically known as "silica aerogel". It is often confused with silica gel because of the similarity of their names. Their appearance and properties are different. Silica gel commonly used as drying agent, is a heavy, glass like material with very small pore size. It is transparent and hygroscopic. Santocel is light and porous. It is not hygroscopic nor, in itself transparent.

The method of manufacture of Santocel C is a trade secret of Monsanto Co. The principle of the method is briefly given in a publication[144]. Santocel is a gel from which the liquid phase has been removed without altering its structure. The liquid removed is

replaced by air. Drying a gel by ordinary drying process would result in great shrinkage and formation of a hard, glossy silica gel. This shrinkage is prevented in the manufacture of Santocel. The result is a dry, light material having the same volume and solid structure as the original gel.

A particle of Santocel is composed of an intertangled "brush heap" of sub ultra microscopic sized fibers. Theoretical measurements show these fibers to have a diameter of from 25 to 35 A, while the space between them is of the order of 330 A. A highly magnified particle of Santocel under an electron micrograph shows these fibers to be interwoven in the same manner as cotton fibers in a ball of cotton battings. The surface presented by this structure is tremendous, giving a specific surface of the order of 600 sq m/g. Santocel is 90% silica in the dry state. 94% of the volume of the mass of Santocel is air.

At the finish of the manufacturing process, Santocel has density 7.5 lb/cu ft. The Santocel is then air - ground to an average particle size of 3-5 microns in diameter to produce a grade of Santocel designated as Santocel C R. The air grinding bulks this material, because of occluded air, to a density of 3 lb/cu ft.

Santocel C R being bulky and dusty is inconvenient to handle. Therefore it is vacuum compressed to a density of 6 lb/cu ft. This product is called Santocel C. On account of its fibrous structure, it is called fibrous silica gel in this chapter.

The Santocel C obtained as a gift sample from the Monsanto Company, U.S.A., was heated to 450°C for 4 hours in order to remove any organic vapours and the activated gel was used in sorption - desorption studies.

Sorbates

The following sorbates were employed.

Water	Double distilled
Carbon tetrachloride	German (L.P.) redistilled B.P.76°
Methyl alcohol	B.D.H. (British Drug House) (A.R.) redistilled B.P. 64°
Ethyl alcohol	Distilled over calcium B.P.78°
n-Propyl alcohol	B.D.H.(L.R.) redistilled B.P.97°
n-Butyl alcohol	B.D.H.(L.R.) redistilled B.P.116°
n-Amyl alcohol	E.Merck(G.R.) redistilled B.P.137°

Results and discussions

A series of sorptions and desorptions were carried out with water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols on glassy

and fibrous silica gels. Duplicate experiments were conducted in all the systems. The results of one experiment have been presented. Equilibrium was established within an hour but actually 2 hours were allowed to ensure complete equilibrium. In every case there is permanent and reproducible hysteresis loop and the loop has been reproduced upto 3rd or 4th cycle of sorption and desorption. The results have been given in Figures 1 to 14. The permanent and reproducible hysteresis loops obtained with the different sorbates with glassy silica and fibrous silica gels have been shown together in Figures 15 and 16, respectively to facilitate a comparative study. In Figures 15 and 16 the sorption and desorption curves are presented by plotting the volume of sorbate taken or retained per 100 g of gel against the relative vapour pressure.

Bound sorbates and micropores

At the end of the first cycle of sorption and desorption, certain amount of sorbate is retained by the gel irreversibly in particular cases inspite of several hours of evacuation. The amounts of these bound sorbates are shown in Table 1 and Figures 15 and 16.

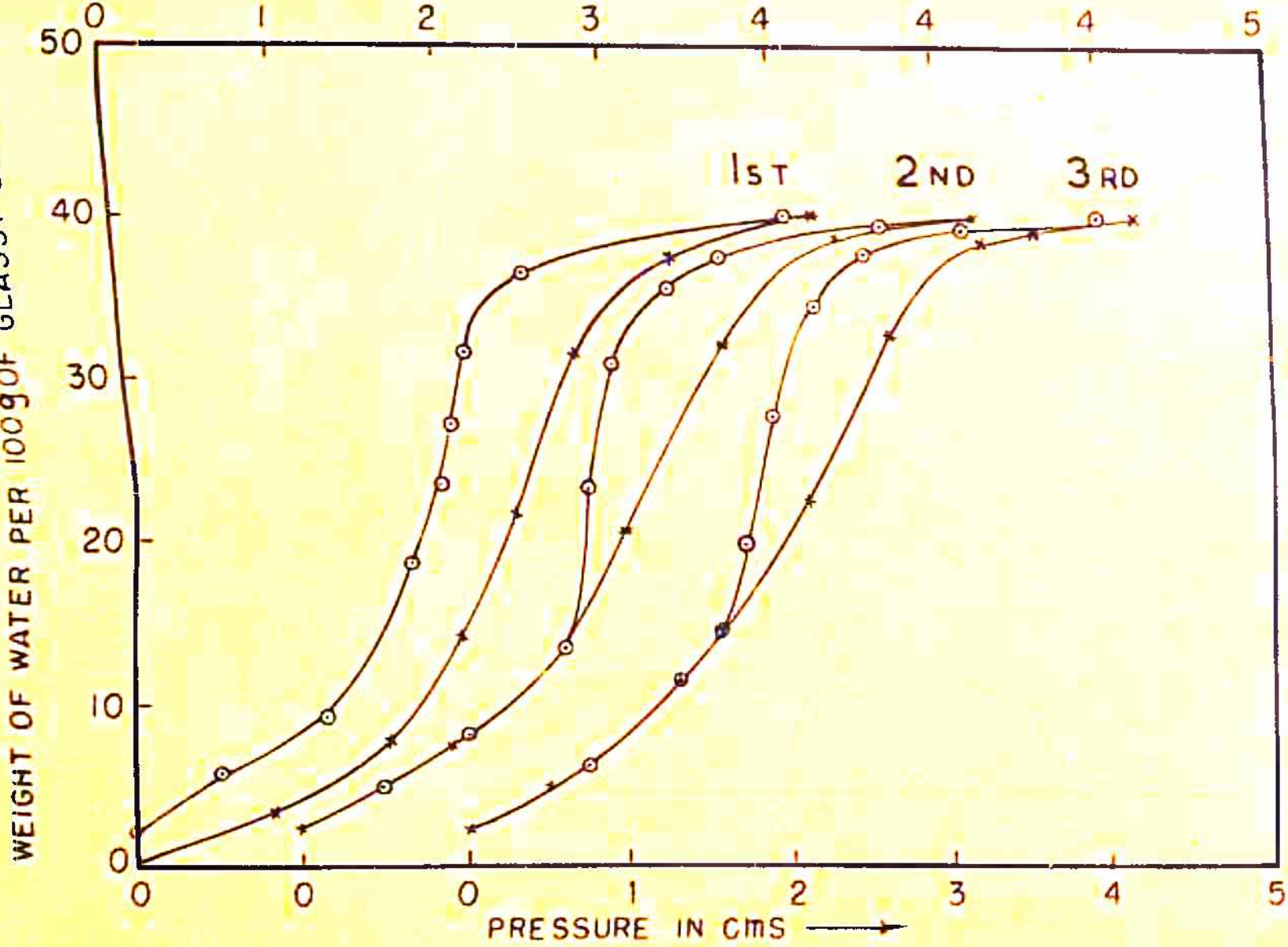


FIG. 1. SORPTION AND DESORPTION OF WATER ON GLASSY SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

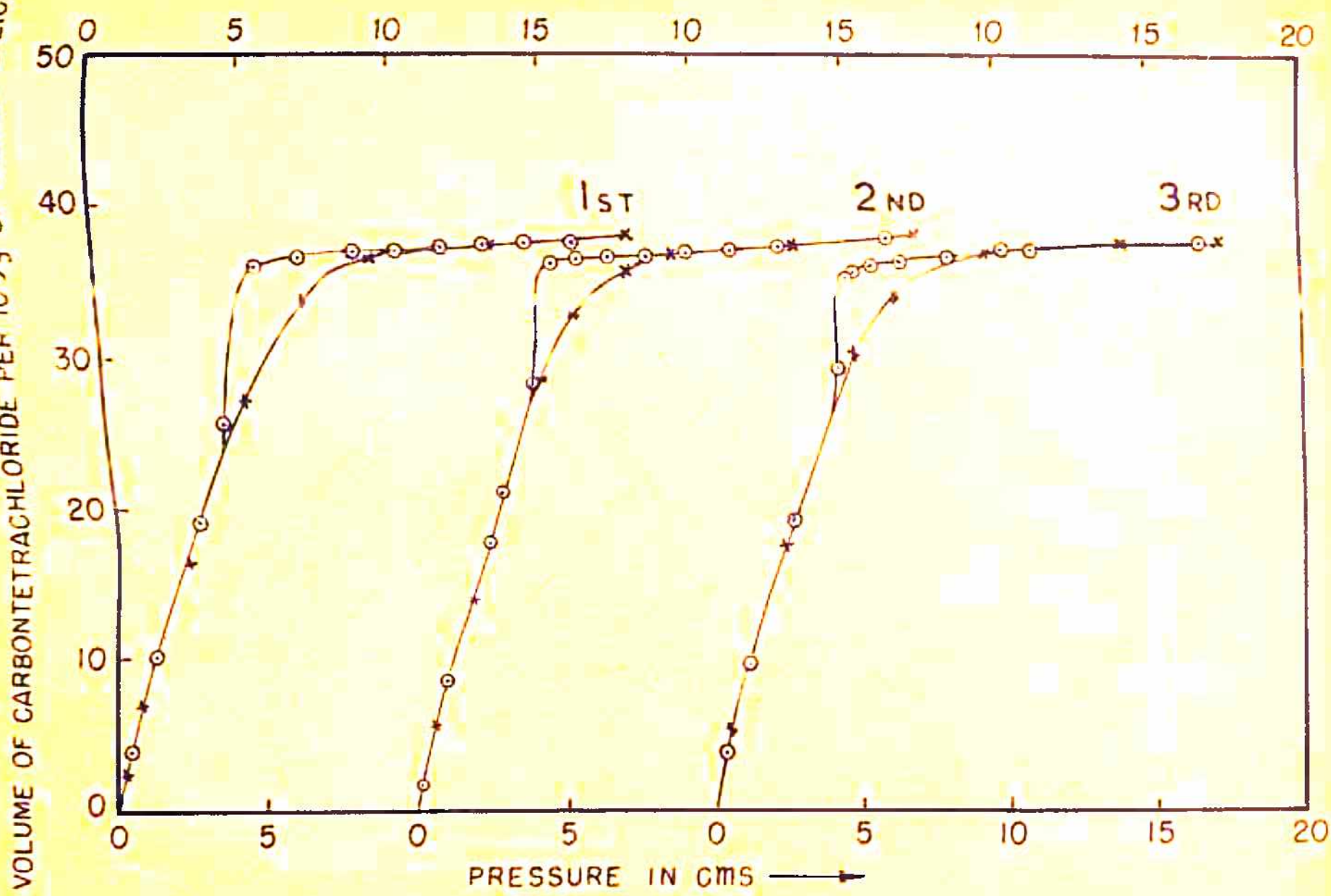


FIG. 2. SORPTION AND DESORPTION OF CARBON TETRACHLORIDE ON GLASSY SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

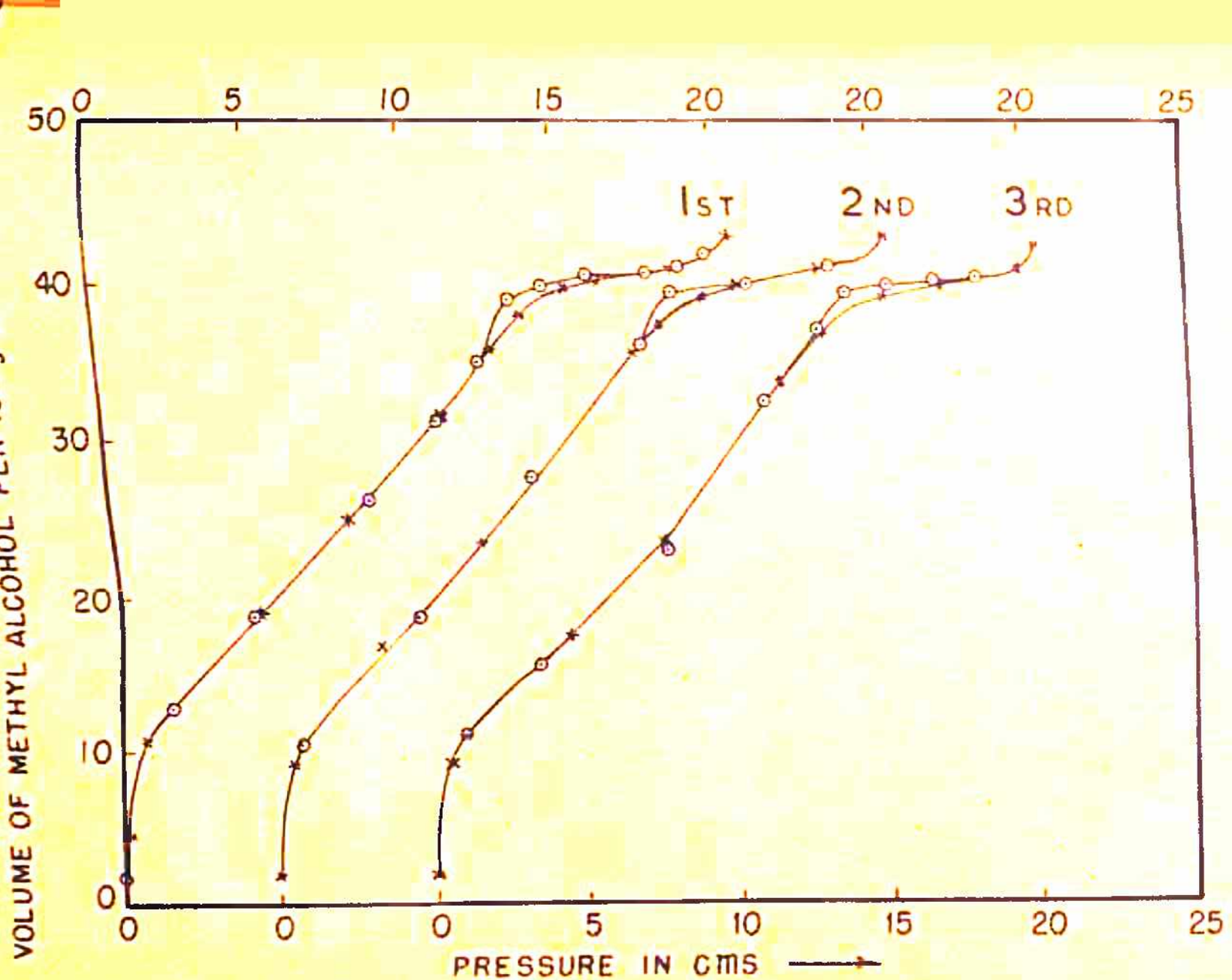


FIG. 3. SORPTION AND DESORPTION OF METHYL ALCOHOL ON GLASSY SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

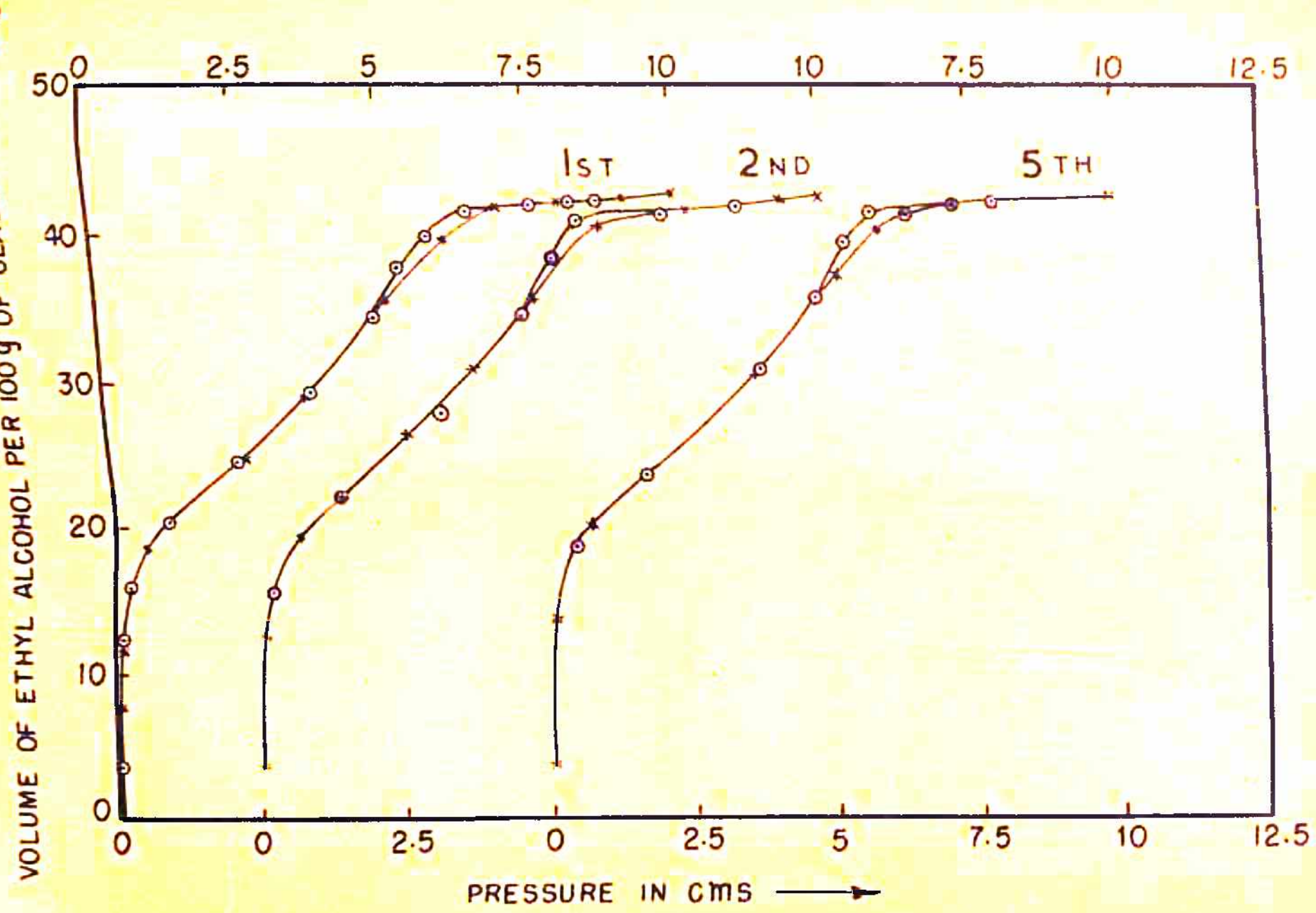


FIG. 4. SORPTION AND DESORPTION OF ETHYL ALCOHOL ON GLASSY SILICA GEL IN 1ST, 2ND AND 5TH CYCLES.

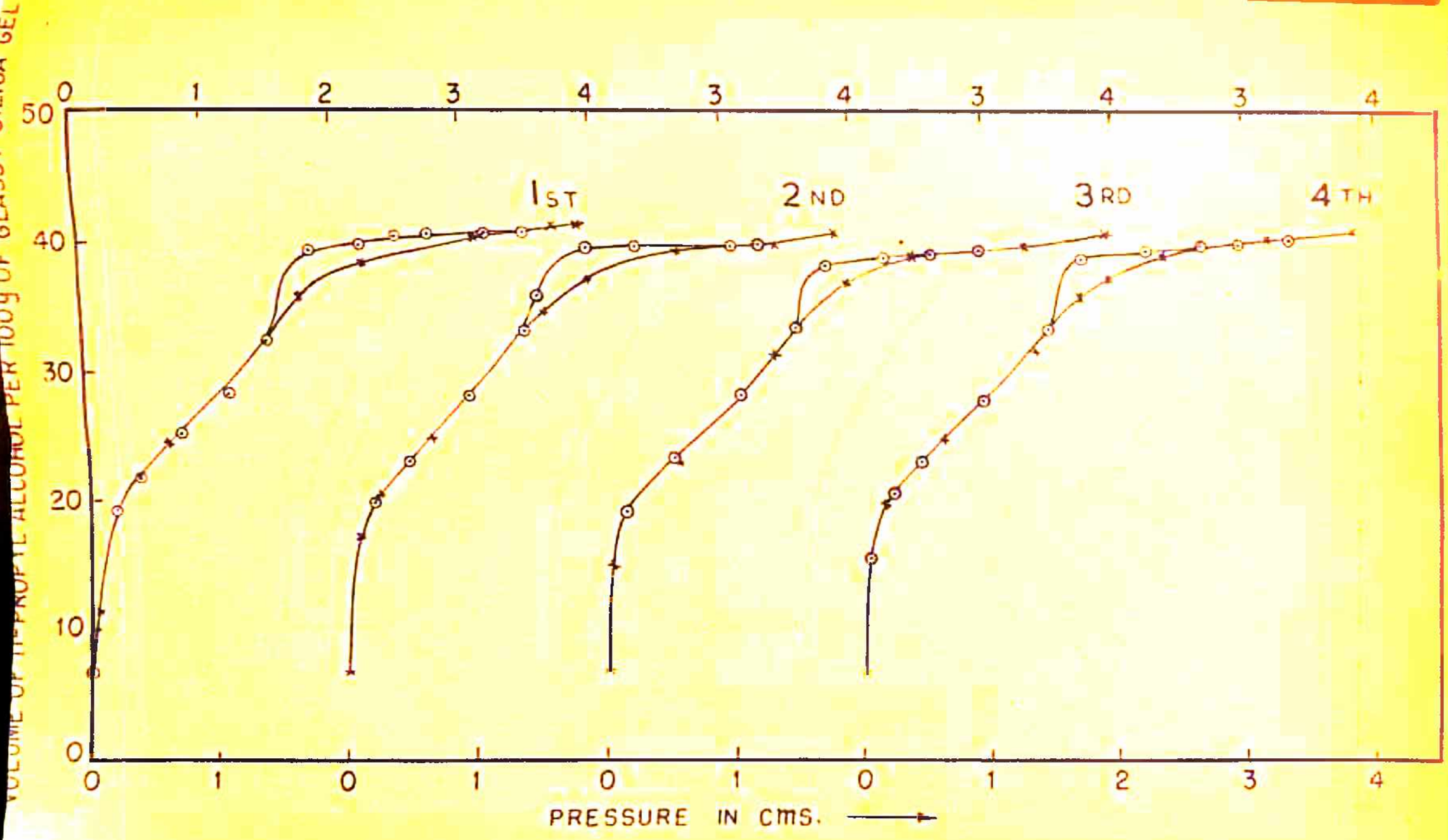


FIG. 5. SORPTION AND DESORPTION OF n-PROPYL ALCOHOL ON GLASSY SILICA GEL IN 1ST, 2ND, 3RD AND 4TH CYCLES.

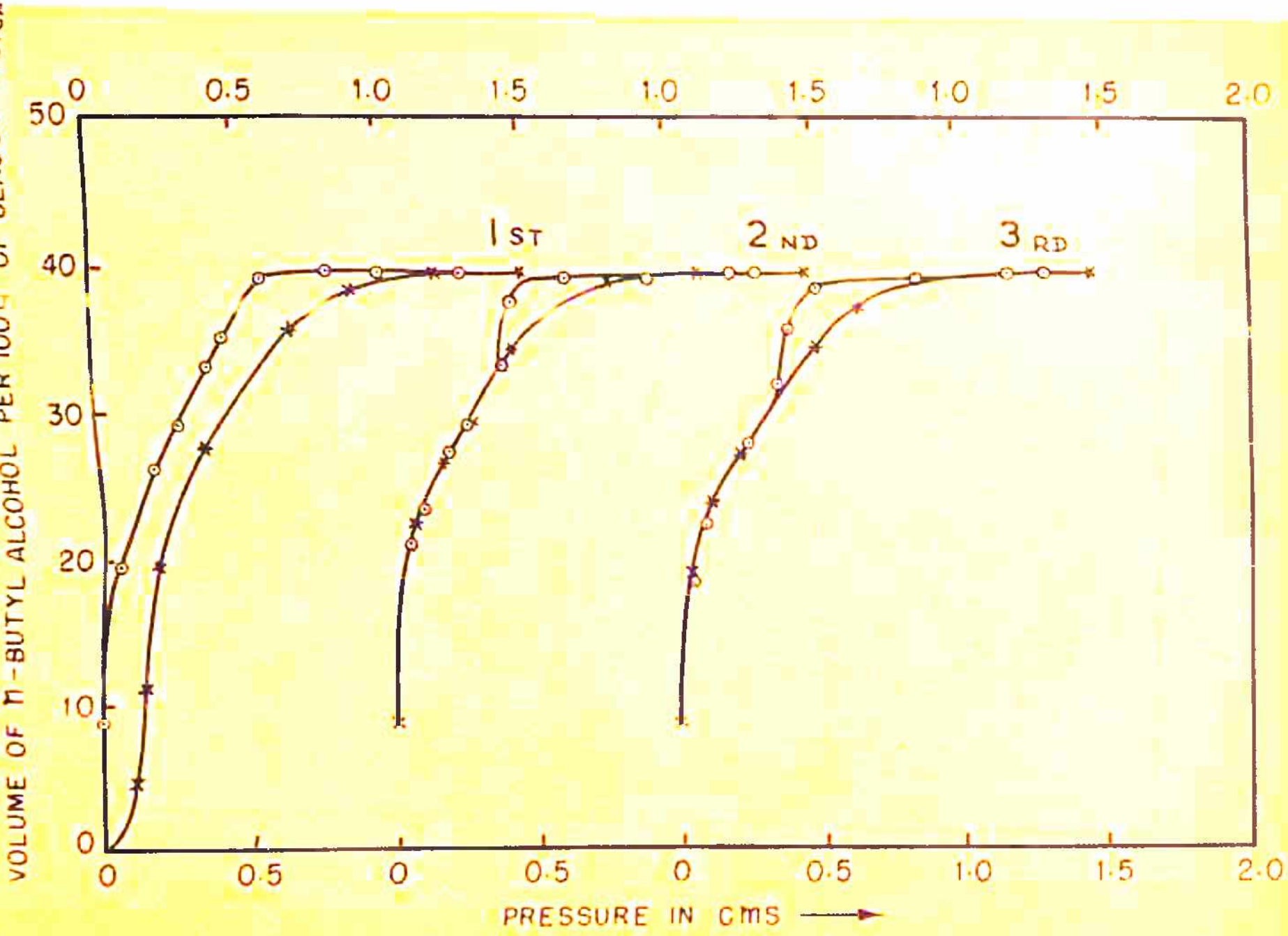


FIG. 6. SORPTION AND DESORPTION OF N-BUTYL ALCOHOL ON GLASSY SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

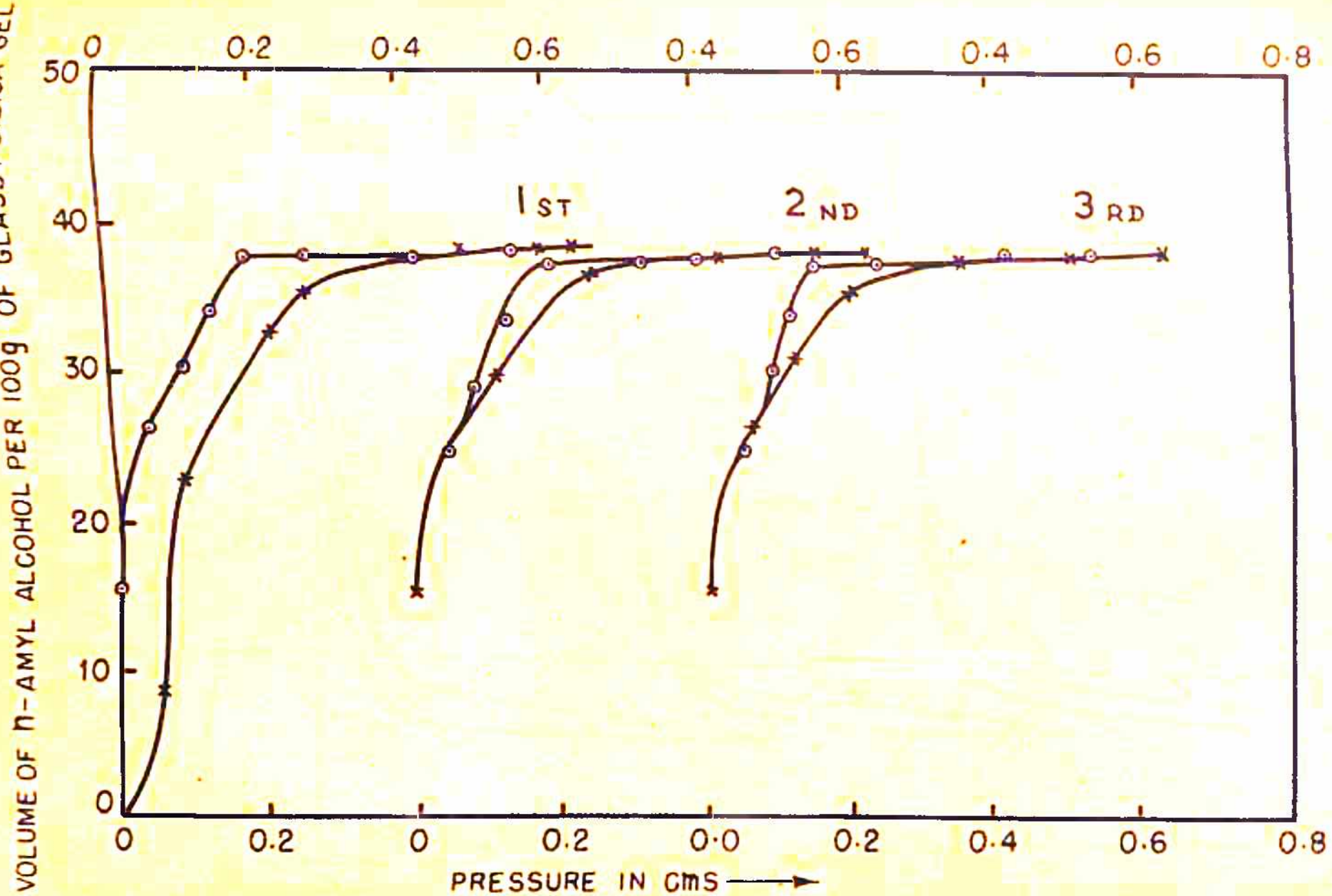
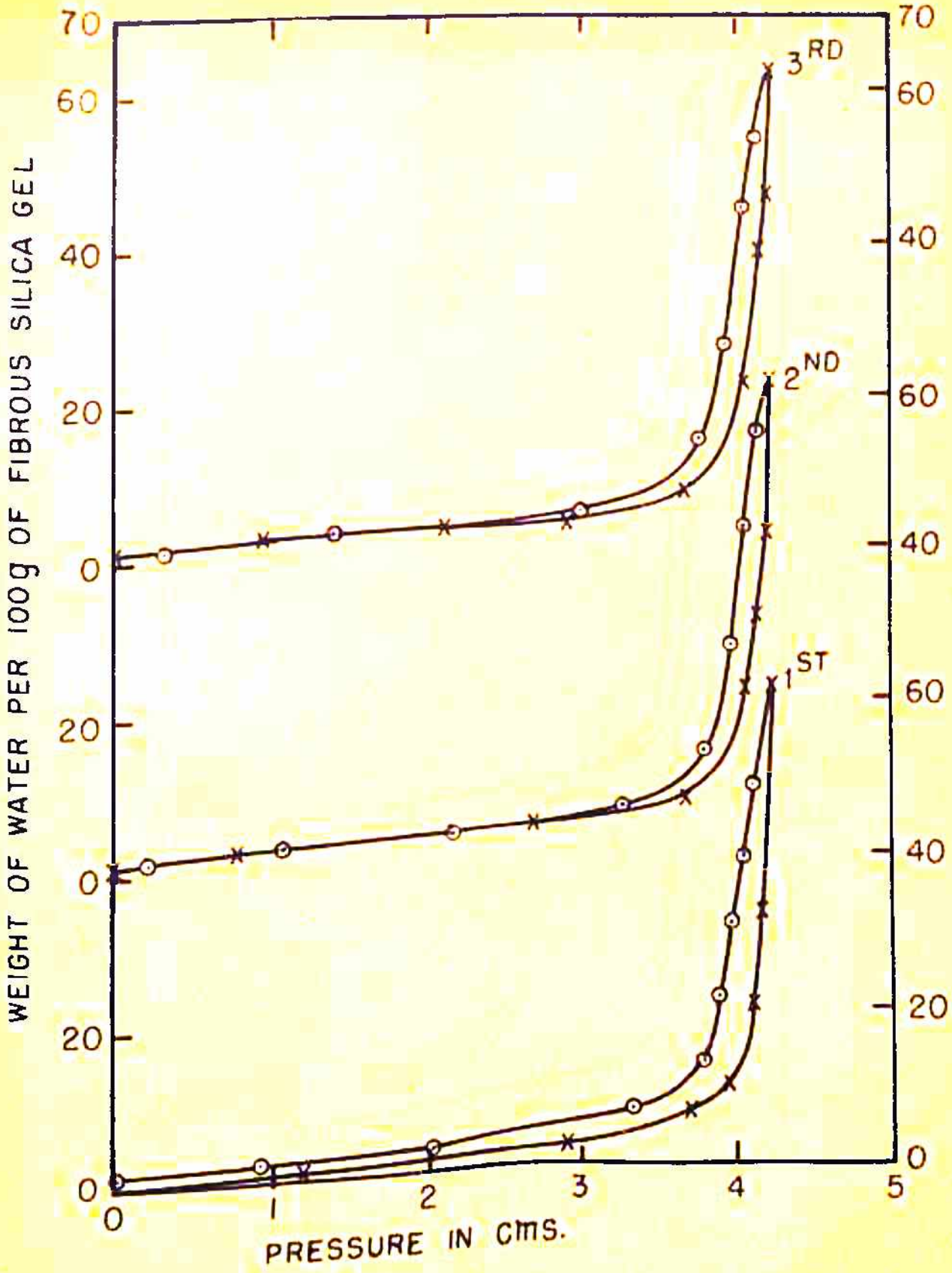


FIG. 7. SORPTION AND DESORPTION OF n-AMYL ALCOHOL ON GLASSY SILICA GEL IN 1^{ST}, 2^{ND} AND 3^{RD} CYCLES.



G. 8. SORPTION AND DESORPTION OF WATER ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

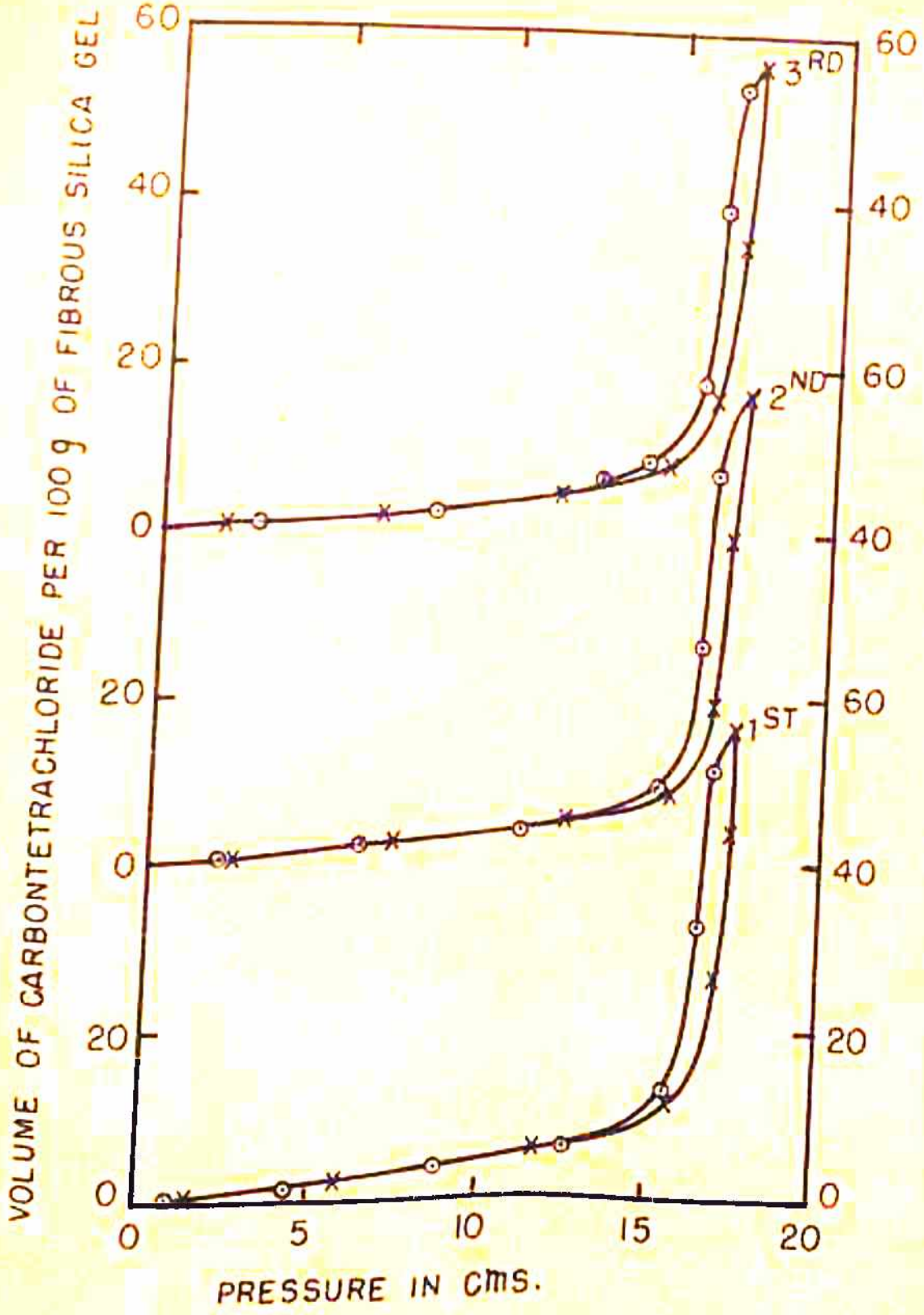


FIG. 9. SORPTION AND DESORPTION OF CARBONTETRACHLORIDE ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

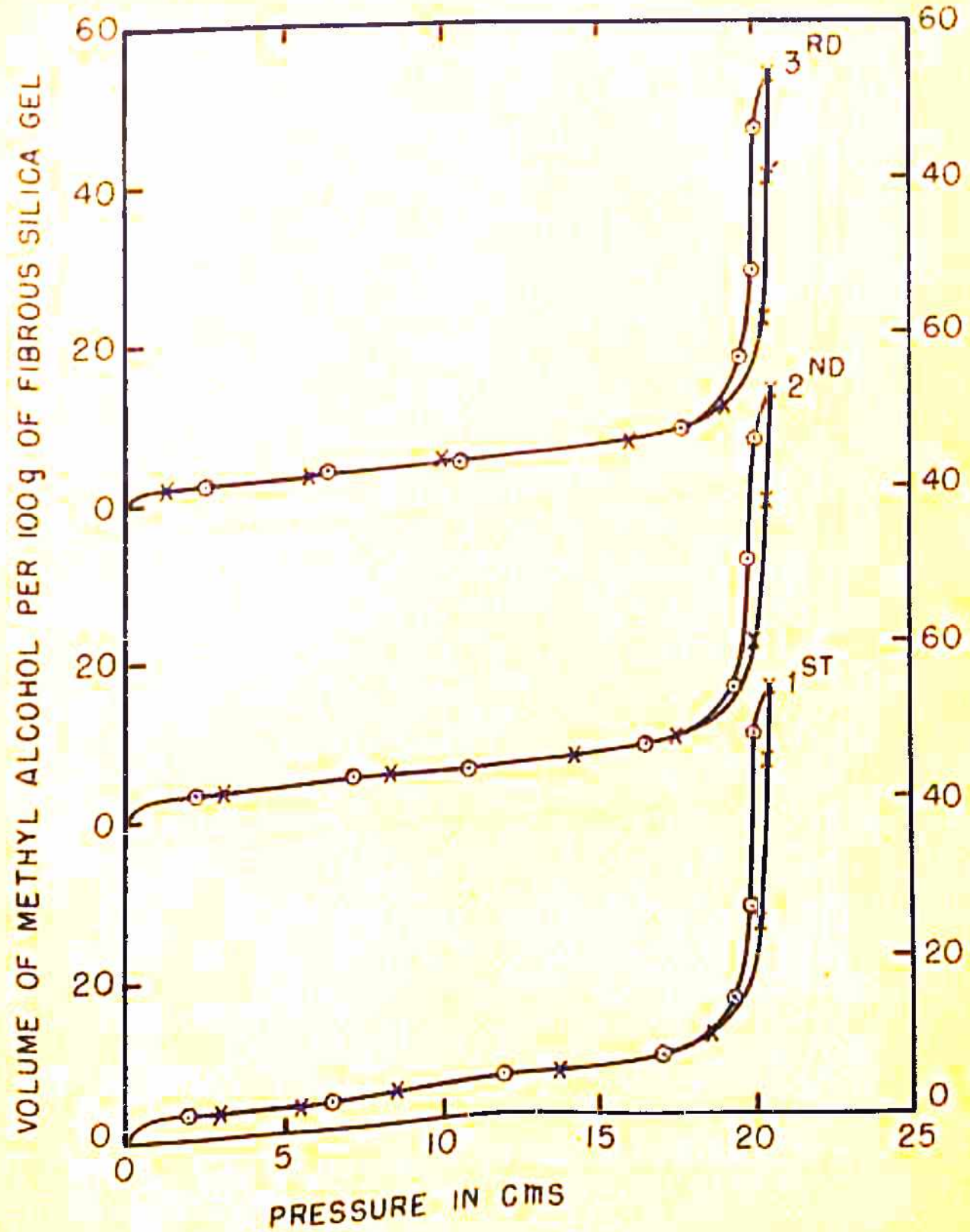


FIG. 10. SORPTION AND DESORPTION OF METHYL ALCOHOL ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

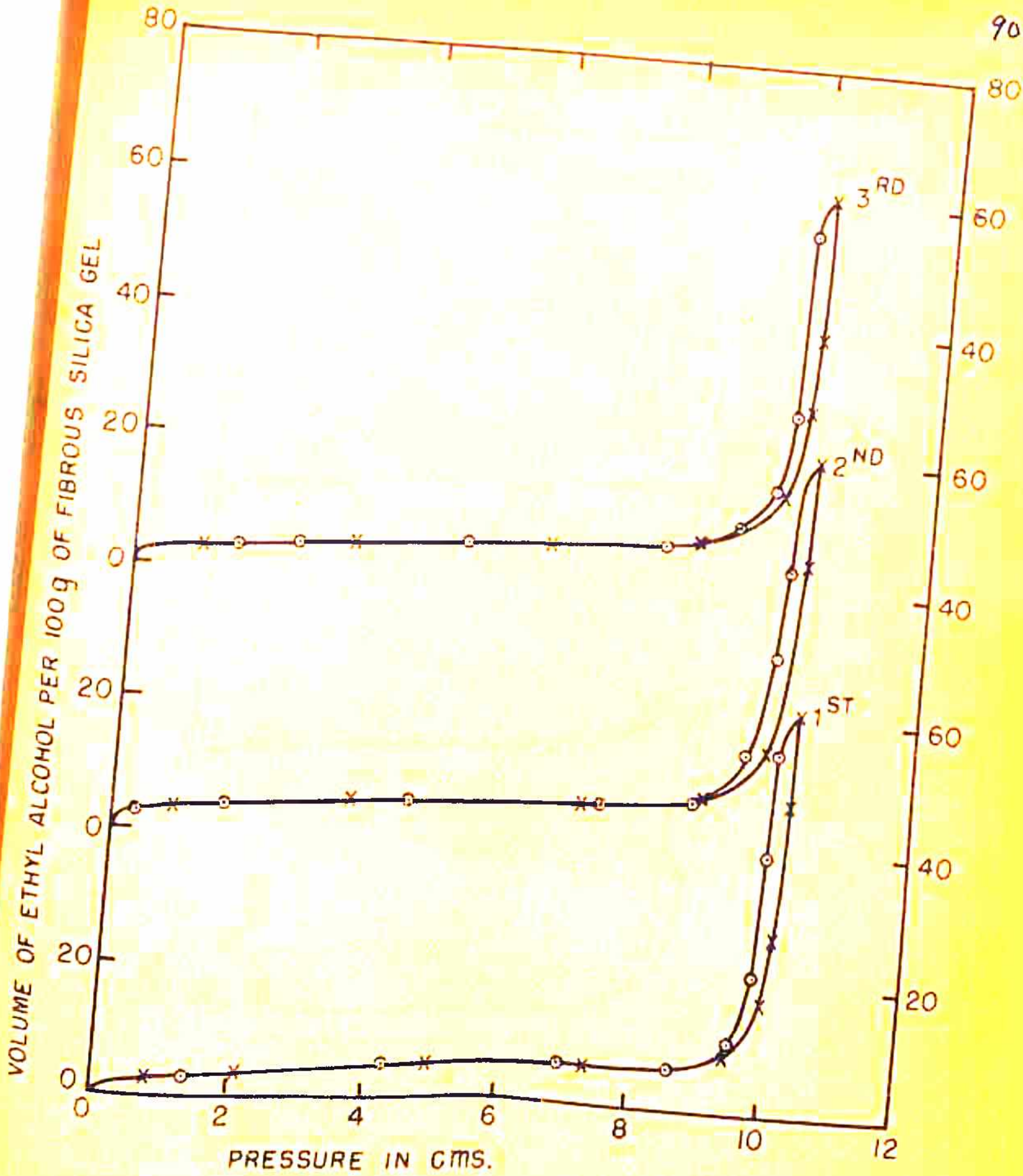


FIG. 11. SORPTION AND DESORPTION OF ETHYL ALCOHOL ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

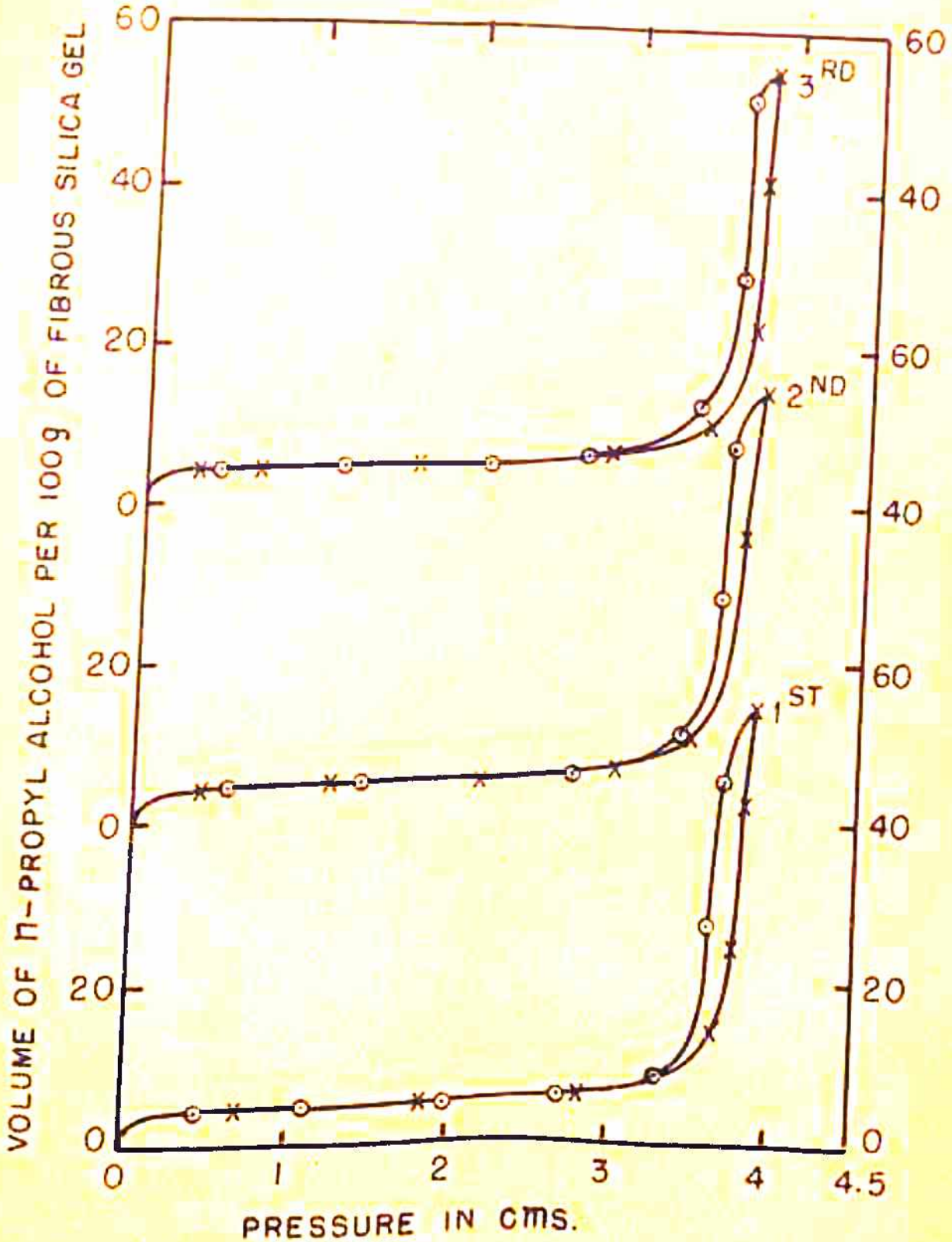


FIG. 12. SORPTION AND DESORPTION OF n-PROPYL ALCOHOL ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

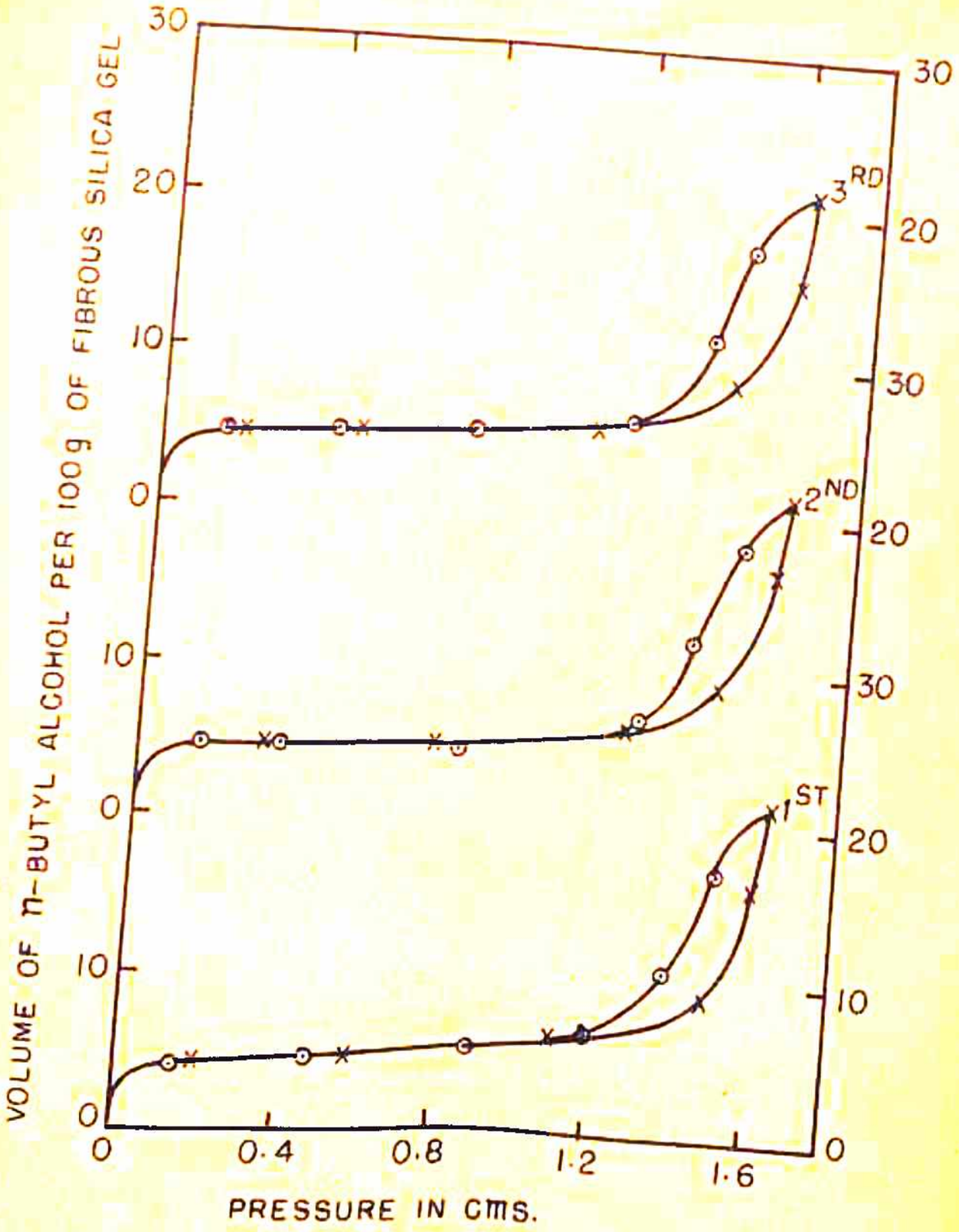


FIG. 13. SORPTION AND DESORPTION OF n-BUTYL ALCOHOL ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

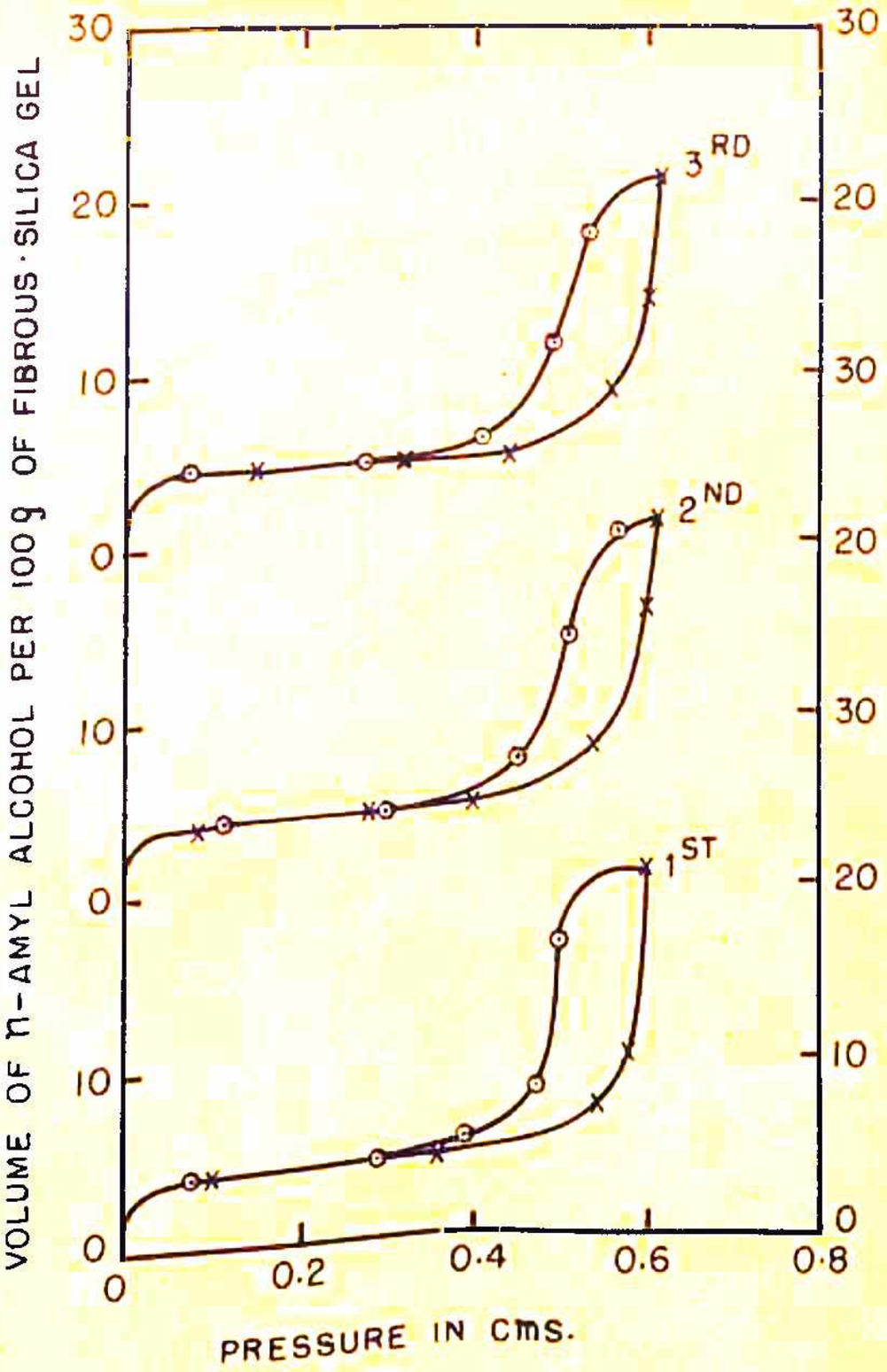


FIG. 14. SORPTION AND DESORPTION OF n-AMYL ALCOHOL ON FIBROUS SILICA GEL IN THE 1ST, 2ND AND 3RD CYCLES.

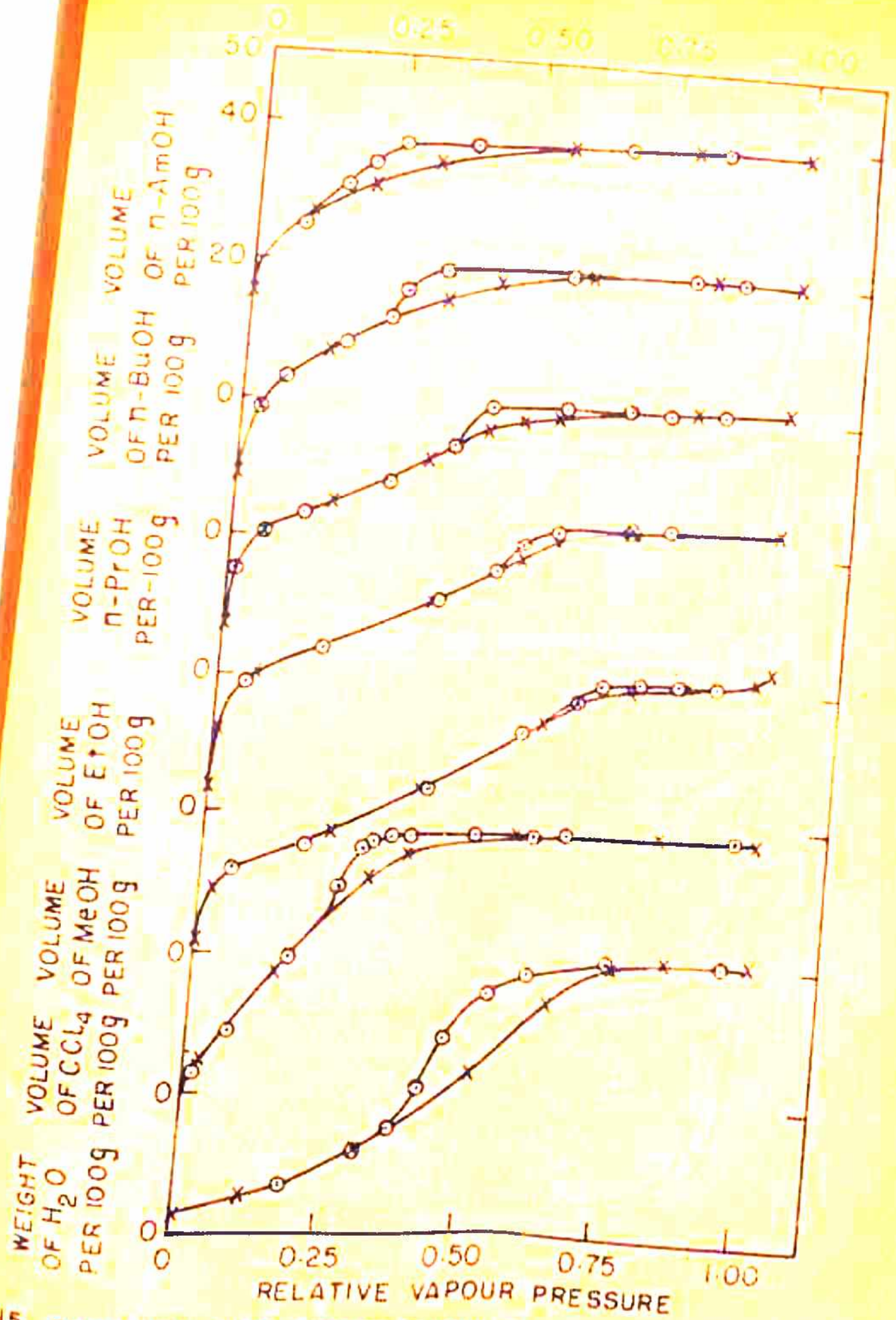


FIG. 15. SORPTION AND DESORPTION ON GLASSY SILICA GEL OF WATER, CARBON TETRACHLORIDE, METHYL, ETHYL n-PROPYL, n-BUTYL AND n-AMYL ALCOHOLS.

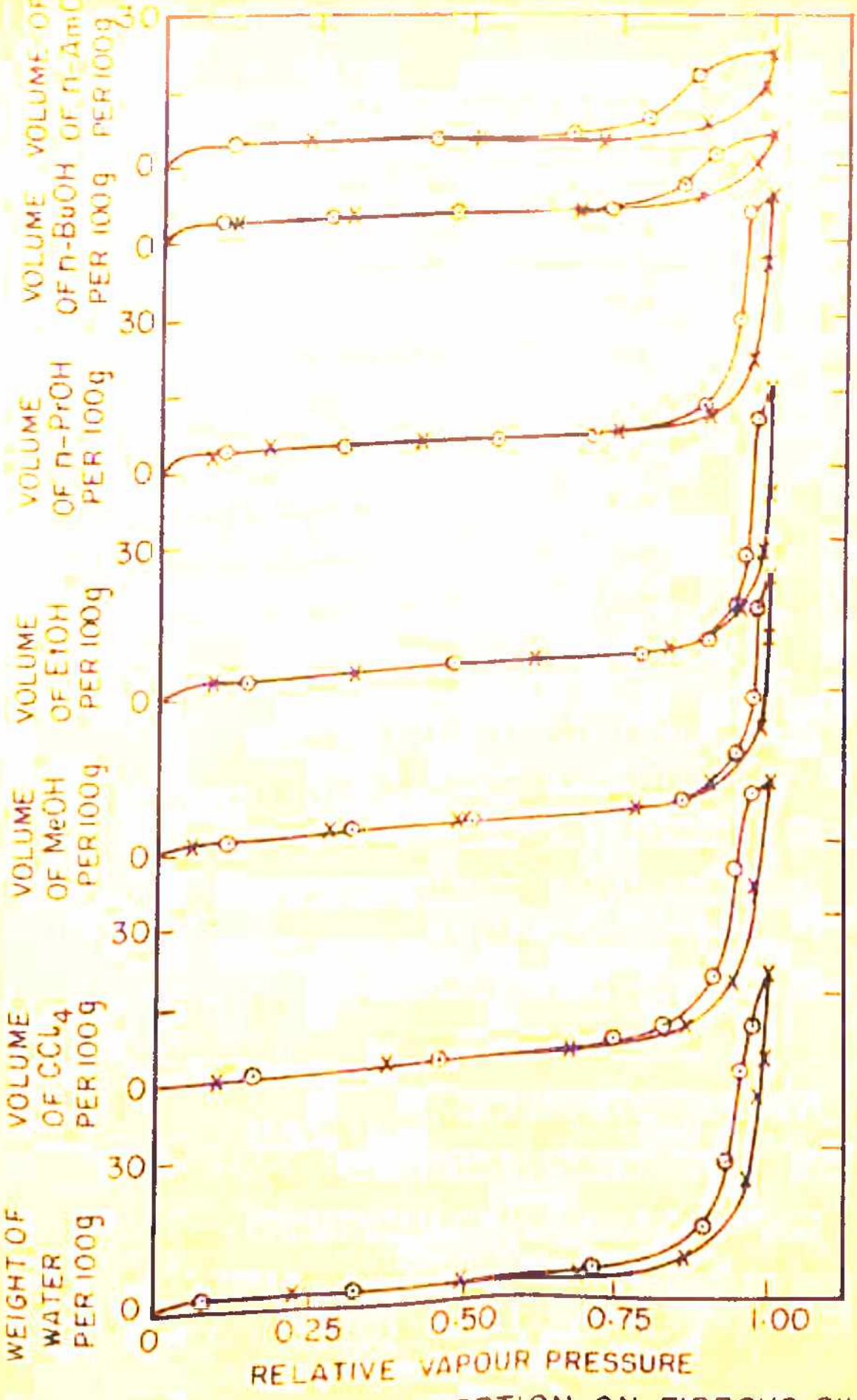


FIG. 16. SORPTION AND DESORPTION ON FIBROUS SILICA GEL OF WATER, CARBON TETRACHLORIDE, METHYL, ETHYL, n-PROPYL, n-BUTYL AND n-AMYL ALCOHOLS.

Table I: Volumes of bound sorbates in cm^3/100 g of gel

	Glassy silica gel	Fibrous silica gel
Water	2.3	1.4
Carbon tetrachloride	0.0	0.0
Methyl alcohol	1.8	0.0
Ethyl alcohol	3.5	0.0
n-Propyl alcohol	6.8	0.0
n-Butyl alcohol	8.9	0.0
n-Amyl alcohol	15.3	0.0

Glassy silica gel retains irreversibly different amounts of all the sorbates excepting carbon tetrachloride and the volume of bound alcohol increases from Methyl alcohol to n-Amyl alcohol. Ordinarily removal of the alcohols and water in this region is slow and requires about 8 to 12 hour of evacuation and later it becomes constant.

In the case of fibrous silica gel, the desorption of the last portion of the sorbate is complete within about 15 minutes and there is no bound sorbate excepting in the case of water, 1.4 cm^3% of which is bound irrevercibly inspite of 8 hours of evacuation.

Based on the capillary condensation theory of sorption, the reason for the existence of bound alcohols and water in glassy silica gel is that it has micropores as indicated by the steepness of the sorption isotherms commencing from zero relative vapour pressure. When once the molecules are sorbed in these micropores it is difficult to dislodge them. Carbon tetrachloride is completely removed within 3 hours of evacuation and this exceptional behaviour is attributed to its non-polar character.

Fibrous silica gel however is a contrast to glassy silica gel. Excepting for a small initial sorption due to monolayer formation, the isotherm is practically horizontal and shows no appreciable increase in sorption upto relative vapour pressure of 0.7. This indicates the absence of micropores and even the transitional pores as per Dubinin's Classification[145]. The small volume of water irreversibly held may be chemisorbed. Chemisorption as a general explanation of all cases of bound sorbates is inadmissible in view of the fact that chemisorption is a surface phenomenon and fibrous silica gel retains no bound alcohols at all.

Application of BET equation and monolayer capacities

The sorption isotherms of the five aliphatic

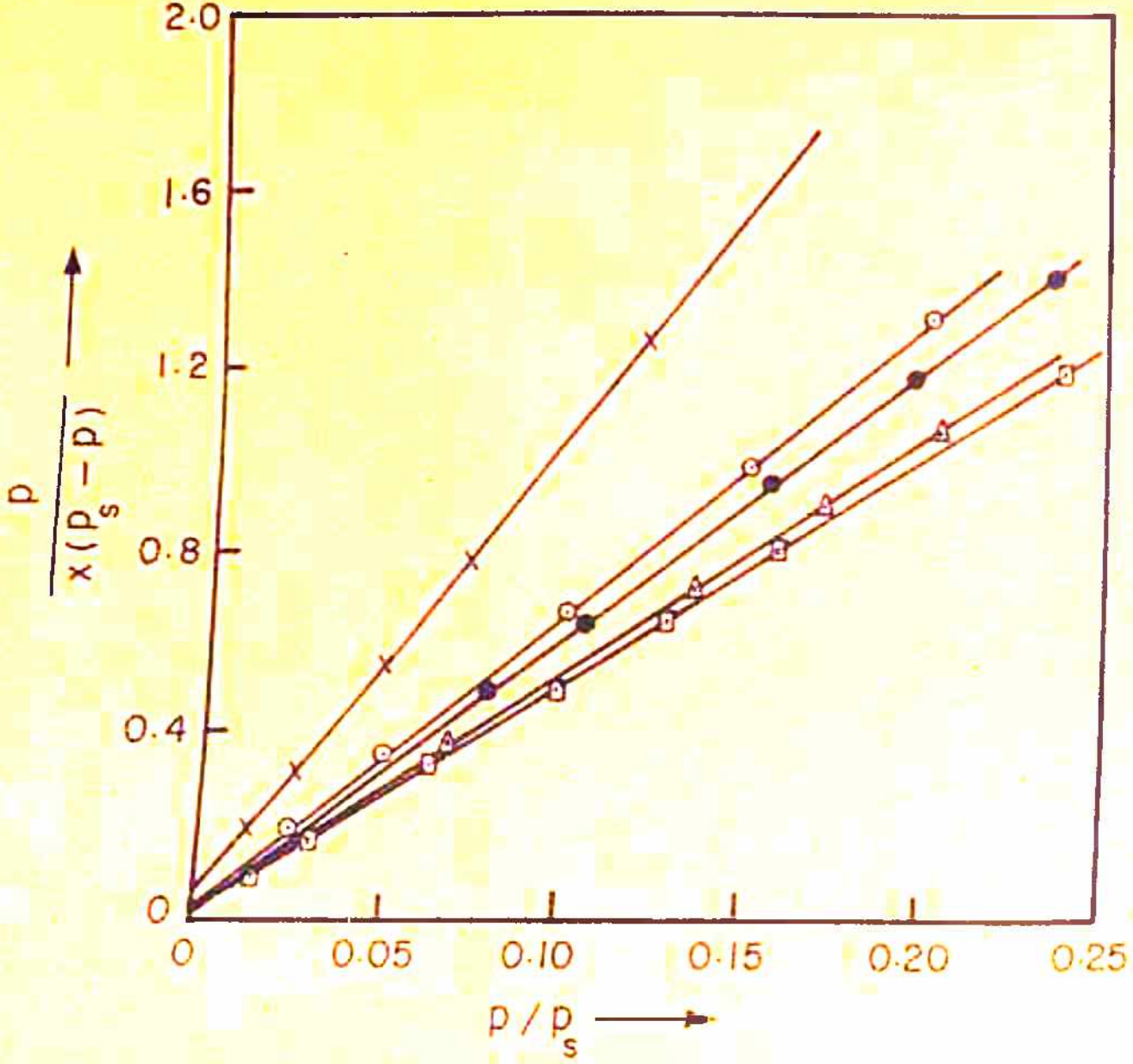


FIG. 17. BET PLOT FOR METHYL x, ETHYL ⊙, n-PROPYL ●, n-BUTYL △ AND n-AMYL ⊡ ALCOHOLS ON GLASSY SILICA GEL

alcohols on both glassy silica gel and fibrous silica gel have clearly defined "Knees" followed by linear portion. According to BET theory[13] the "Knee" signifies the transition from monomolecular to multimolecular sorption.

The BET equation has been applied to the isotherms of the five alcohols by plotting $\frac{p}{x(p_s - p)}$ against p/p_s and the BET plots shown in Figures 17 and 18 are straight lines. From the slope and intercept of the straight lines the monolayer capacity, x_m in each case has been calculated by employing the relation $x_m = \frac{1}{s + i}$ where s = slope, i = intercept.

Alternatively the value of monolayer capacity can also be read out directly from the isotherms with reasonable accuracy[146,147]. The isotherms of all alcohols with the two gels display a long straight portion after the "Knee". This feature is not strictly compatible with the BET equation which yields an inflection point in an S type isotherm. The point at which the linear portion begins is termed point B and indicates the completion of the monolayer. The sorption at point B is the monolayer capacity x_B. The value of x_B for each system has been taken directly from the isotherm.

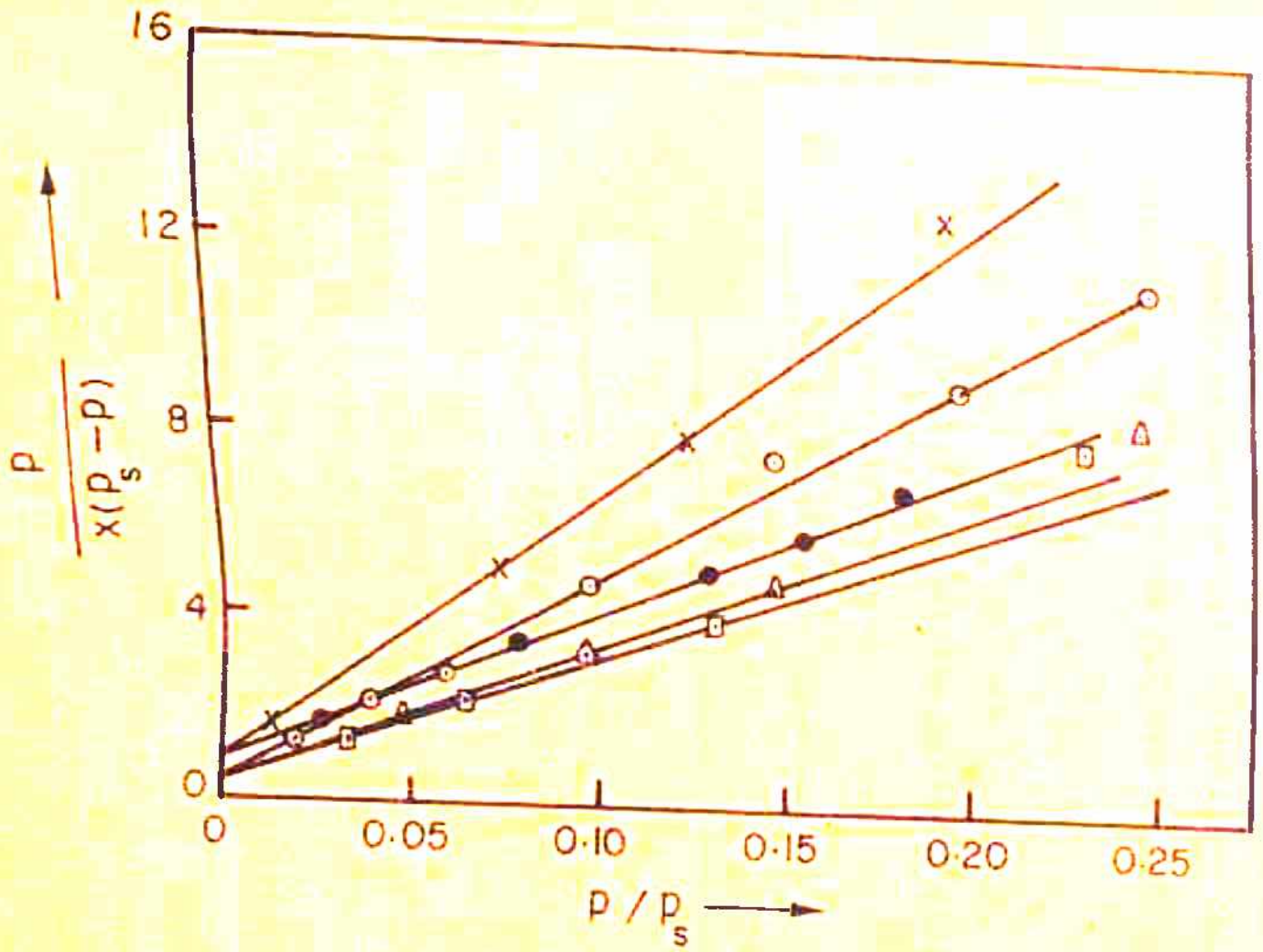


FIG. 18 BET PLOT FOR METHYL x, ETHYL o, n-PROPYL •, n-BUTYL Δ, AND n-AMYL □ ALCOHOLS ON FIBROUS SILICA GEL.

The values of monolayer capacities x_m and x_B for the five alcohols and the relative vapour pressures at which the monolayers are fully formed have been given in Table 2 for both glassy and fibrous silica gels.

The sorption isotherm of water and carbon tetrachloride with the two gels do not show well defined "Knees". Therefore the BET equation is not applied in these cases.

Table 2: Monolayer capacities x_m and x_B in g per g of sorption and the corresponding relative vapour pressure.

	Glassy silica gel			Fibrous silica gel		
	x_m	x_B	p/p_o	x_m	x_B	p/p_o
Methyl alcohol	0.106	0.093	0.049	0.017	0.016	0.05
Ethyl alcohol	0.154	0.155	0.062	0.022	0.023	0.06
n-Propyl alcohol	0.168	0.162	0.065	0.028	0.028	0.10
n-Butyl alcohol	0.194	0.192	0.068	0.034	0.036	0.10
n-Amyl alcohol	0.196	0.195	0.064	0.037	0.037	0.16

Table 2 reveals that the coincidence between the values of x_m and x_B for each alcohol is remarkably good.

This coincidence is true for both the gels. There is however slight variation in the relative vapour pressures of the different alcohols at which the monolayer is complete.

The two gels used in these experiments are entirely different from one another in their porous structures and the 5 alcohols differ in their molecular shapes and sizes. But still the values of x_m and x_B in each case are almost coincident. This illustrates clearly the success of the BET theory of sorption.

Monolayer capacity and specific surface

From the monolayer capacity, the specific area of the surface of the sorbent can be calculated by the equation[148]

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

where S = Specific surface in m^2/g of sorbent

x_m = Monolayer capacity in g of sorbate per g of sorbent

M = Molecular weight of sorbate

N = Avogadro's constant

A_m = Molecular cross-section of sorbate

The molecular diameter D spherical is given by the equation[149]

$$D = 1.33 \times 10^{-8} \times V_m^{1/3}$$

where V_m = molecular volume.

Nitrogen is the most widely used of all the sorbates for the determination of specific surface. Majority of sorbents studied yield with nitrogen type II isotherm with sharp "Knee". With such sharp knee, the values of x_m , x_B and x_y (point of inflection) tend to coincide, consequently nitrogen is particularly suited for the determination of specific surface.

In the present experiments with the 5 aliphatic alcohols the isotherms show sharp "Knees". Calculation of the surface area from the monolayer capacity should yield values of reasonable accuracy. Apart from the absolute value of the specific surface of silica gel, a comparative study of the values of the specific surface obtained with the 5 alcohols is worth considering.

In calculating the specific surface, the value of molecular cross-section should be known. The molecular cross-section for spherical packing is obtained from the molecular diameter D given in the above equation. From these values and the values of x_m shown in Table 2 the specific surface of the gels is calculated. The results of these calculations are shown in Table 3.

Table 3: Specific surface of silica gels considering alcohol molecules as spheres.

	Molecular cross-section in A^2	Specific surface in m^2/g of gel	
		Glassy silica gel	Fibrous silica gel
Methyl alcohol	21.2	421.8	68.4
Ethyl alcohol	27.0	542.5	76.3
n-Propyl alcohol	31.4	529.1	86.7
n-Butyl alcohol	36.0	566.5	99.6
n-Amyl alcohol	40.2	537.1	101.7

Excepting the case of methyl alcohol, the values of specific surface of glassy silica gel calculated from the monolayer capacities for the 4 alcohols bear good coincidence. The values of specific surface of fibrous silica gel however do not coincide. This lack of coincidence cast a doubt on the correctness of the procedure in taking the value of the diameter assuming the alcohol molecule to be spherical. Therefore the possibility of the oriented sorption of the alcohol molecules on the surface of the silica gel has been examined.

Monolayer and oriented adsorption

The aliphatic alcohols are linear in shape increasing in length from methyl alcohol to n-amyl alcohol. It is not strictly correct to assume the cubical or spherical shape for the molecules. The linear adsorbed molecule can be held on the surface of the adsorbent either at its end, i.e., perpendicular to surface or it may be lying flat on, i.e., parallel to the surface. In these two possible modes of adsorption the areas occupied by the adsorbed molecules on the sorbent surface are different. Assuming that the alcohol molecule is a rectangular rod, it is necessary to calculate the cross-section area of the rod and also the area of one of the four sides along the length of the rod.

The thickness of the hydrocarbon chain is 4.55 A[149]. Therefore the thickness of all the 5 alcohols is the same. From the volume of the molecule, i.e., D^3 (Table 4) and its thickness 4.55 A, the length of the linear molecule can be calculated. The area of the end and the side along the length of the linear molecule are also calculated and are shown in Table 4. Assuming the two modes of oriented adsorption namely perpendicular to surface and parallel to surfaces, the specific areas are calculated and are shown in Table 4.

Table 4: Specific surface of silica gels considering alcohol molecules as linear

	Diameter D spherical in A	Length of the molecule in A	Cross section in A^2	Area of side in A^2	Specific surface in m^2/g of gel			
					Glassy silica gel		Fibrous silica gel	
					Molecules perpendicular to surface	Molecules parallel to surface	Molecules perpendicular to surface	Molecules parallel to surface
Methyl alcohol	4.6	4.7	20.7	21.4	412.6	426.6	66.9	69.2
Ethyl alcohol	5.2	6.8	20.7	30.9	415.4	620.0	58.4	87.2
n-Propyl alcohol	5.6	8.5	20.7	38.5	349.3	651.3	57.2	106.8
n-Butyl alcohol	6.0	10.4	20.7	47.5	325.7	746.6	57.2	131.2
n-Amyl alcohol	6.3	12.1	20.7	55.0	276.7	734.3	52.4	139.0

Assuming sorption of molecules of alcohol to be either completely perpendicular to surface or parallel to surface, the values obtained for surface area in glassy silica gel are not coincident. For all molecules held perpendicular to surface the values of specific surface for the 5 alcohols decrease from methyl to n-amyl alcohol. For all molecules held parallel to surface the values increase. It follows that in the monolayer on glassy silica the molecules of sorbed alcohols are neither entirely perpendicular nor entirely parallel to the surface. It is a combination of both the modes of sorption.

On fibrous silica gel however, the results are significant. Assuming oriented sorption of the alcohol molecules perpendicular to the surface, the values of surface area for the different alcohols are almost the same. But for sorption of alcohol molecules parallel to surface, the values are not coincident. These results indicate that on fibrous silica gel surface, the sorbed molecules in the monolayer are all oriented and are held perpendicular to surface. The question arises why on the surface of fibrous silica there is oriented adsorption and on the surface of glassy silica gel there is not. Based on the capillary condensation theory of sorption, the steepness of the sorption isotherms of alcohols on

glassy silica gel and the flatness in fibrous silica gel indicate that glassy silica gel consists of micropores and in fibrous silica gel the surface is mostly open and is comparatively less in magnitude. Oriented sorption is easily possible on open surface whereas it is obstructed in micropores whose diameters are comparable to those of alcohol molecules. It is interesting that the existence of oriented sorption on the surface of the sorbent is revealed by the present investigations.

As sorption of the 5 alcohols on the surface of glassy silica gel consists of both types, i.e., molecules oriented perpendicular and parallel to the surface, an attempt was made to find out the percentage of the total number of molecules held perpendicular and percentage held parallel to the surface. The total number of molecules of alcohol contained in the monolayer on the surface of 1 g of gel is given by

$$\frac{x_m N}{M}$$ where x_m = Monolayer capacity

M = Molecular weight of alcohol

N = Avogadro's constant

and these are, for methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols 19.90, 20.04, 16.88, 15.73 and 13.37 x 10^{20} respectively. From these, the number of molecules held perpendicular to surface is calculated from the following

equation by assuming that the specific surface of the gel is equal to what is calculated for methyl alcohol and this is equal to 412 $m^2 g^{-1}$. This assumption is justifiable in view of the fact that methyl alcohol molecule is almost cubical in shape and its thickness and height are 4.55 A and 4.7 A respectively.

$$x C_a + (n - x) S_a = 412$$

where x = number of molecules held perpendicular to surface

C_a = cross-section area of linear molecule in m^2

S_a = side area of linear molecule in m^2

n = total number of molecules held in the monolayer on surface of 1 g of gel.

From the values of x and n, the percentages of molecules held perpendicular to the surface are calculated for ethyl, n-propyl, n-butyl and n-amyl alcohols and these are 100, 79.2, 79.5 and 70.5 respectively. The values are significant. In the case of methyl and ethyl alcohols, adsorption is completely oriented and all the molecules are held perpendicular to surface. As the length of the linear alcohol molecules increases, some of the molecules are held parallel to surface and this is about 20% of the total number of molecules in the case of n-propyl and n-butyl alcohols and about 30%

with n-amyl alcohol. The decrease in the percentage of alcohol molecules held perpendicular to surface as the molecular length increases is due to the microporous structure of glassy silica gel. The micropores whose diameter is comparable to the diameter of alcohol molecules probably inhibit the perfect geometrical alignment of the linear molecules perpendicular to the surface.

The above percentages of the two types of oriented adsorption are obtained by assuming that some molecules are held completely perpendicular to surface and some completely parallel. This is an ideal assumption and may not be strictly true. There is still an alternative possibility. All the molecules in the monolayer may be held vertical with the polar OH group anchored on gel surface. Owing to crowding of the molecules in the narrow pores of the gel, the hydrocarbon chains of the molecule may be subjected to compression and distortion and thus each molecule occupies more space than 20.7 A which is the normal cross-section of the alcohol molecule. The probability of this mechanism is borne out by the figures that percentages of n-propyl and n-butyl alcohol molecules adsorbed perpendicular to surface are as high as about 80%. Considering the facts that on fibrous silica gel, whose surface is mostly open and pores macro, sorption is

completely oriented perpendicular to surface, and that in glassy silica gel, pores are all micro, adsorption in the monolayer in glassy gel also seems to be essentially of the oriented type, i.e., perpendicular to surface with polar OH group anchored on the surface and the compressed or distorted hydrocarbon chain occupying greater area. These are indeed very striking and interesting conclusions. Evidence of oriented adsorption of molecules on solid surfaces are not many though oriented adsorption of molecules in films on liquid surfaces is well known and well established.

Sorption - desorption hysteresis and application of Cohan's and Cavity theories

All the seven sorbates - water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols have produced permanent and reproducible hysteresis loops with both glassy and fibrous silica gels, Figures 1-14. The loops of all the sorbates with glassy silica gel have been shown in Figure 15 and those with fibrous silica gel in Figure 16. Cohan's theory of sorption - desorption hysteresis has been described in chapter II.

The theories that have been advanced so far to explain sorption - desorption hysteresis are given in

chapter II. Cohan[79] has shown that pressure p_h at which hysteresis loop begins corresponds to the equilibrium pressure for $r_c = 2$ D where r_c is the radius of the capillary and D is the diameter of sorbate molecule. On the basis of Cohan's theory the value of D is given by the equation

$$D = \frac{-\sigma M}{dRT \ln p_h/p_o}$$

where M = Molecular weight of sorbate

d = Density of sorbate

σ = Surface tension of sorbate

According to Cohan's theory if the pressure at which hysteresis loop begins is known, it is possible to calculate the molecular diameter of the sorbate. By employing the above equation Cohan has calculated in his paper[150], the values of D for a large number of sorbates from the experimental results of different workers. The values agree in some cases, are higher in others and lower still in others than the molecular diameter D_{cubic} or $D_{spherical}$ obtained from molecular weight and density.

Cohan's theory has been applied to the results, the values of D calculated from the equation for both

glassy and fibrous silica gels are shown in Table 5. The values of D_{cubic} and $D_{spherical}$ are also shown to facilitate comparison.

Table 5: Molecular diameter D_{cubic}, $D_{spherical}$ and $D_{from\ Cohan's\ theory}$ in A

	D_{cubic}	$D_{spherical}$	Glassy silica gel $D_{Cohan's\ theory}$	Fibrous silica gel $D_{Cohan's\ theory}$
Water	3.1	3.5	5.1	14.6
Carbon tetrachloride	5.4	6.1	6.8	33.6
Methyl alcohol	4.1	4.6	7.6	52.2
Ethyl alcohol	4.6	5.2	7.0	47.2
n-Propyl alcohol	5.0	5.6	7.0	41.2
n-Butyl alcohol	5.3	6.0	5.9	29.5
n-Amyl alcohol	5.6	6.3	5.0	35.7

With glassy gel as the sorbent, the molecular D calculated from Cohan's theory agrees with D spherical only in the case of n-butyl alcohol, is less in the case of n-amyl alcohol and higher in all other alcohols. With fibrous silica gel as sorbent the value is very much higher and varies from 3 to 6 times the value of

D spherical. These indicate the limitations of Cohan's theory of hysteresis.

Ink bottle or Cavity Theory

The "Ink bottle" or the Cavity theory of hysteresis has also been described in the previous chapter. A cavity is a capillary with a narrow neck like an ink bottle. A cavity may have two or more necks. During sorption the 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 lower than the value corresponding to the neck radius when the cavity is suddenly emptied. Thus the process of filling is progressive and emptying is abrupt. The two processes are not coincident. Certain amount of sorbate is entrapped in the cavity during desorption, thus accounting for hysteresis. In the light of the cavity theory, permanent and reproducible hysteresis loops obtained in a large number of systems have been explained.

The permanent and reproducible hysteresis loops presented in this paper are further confirmation of

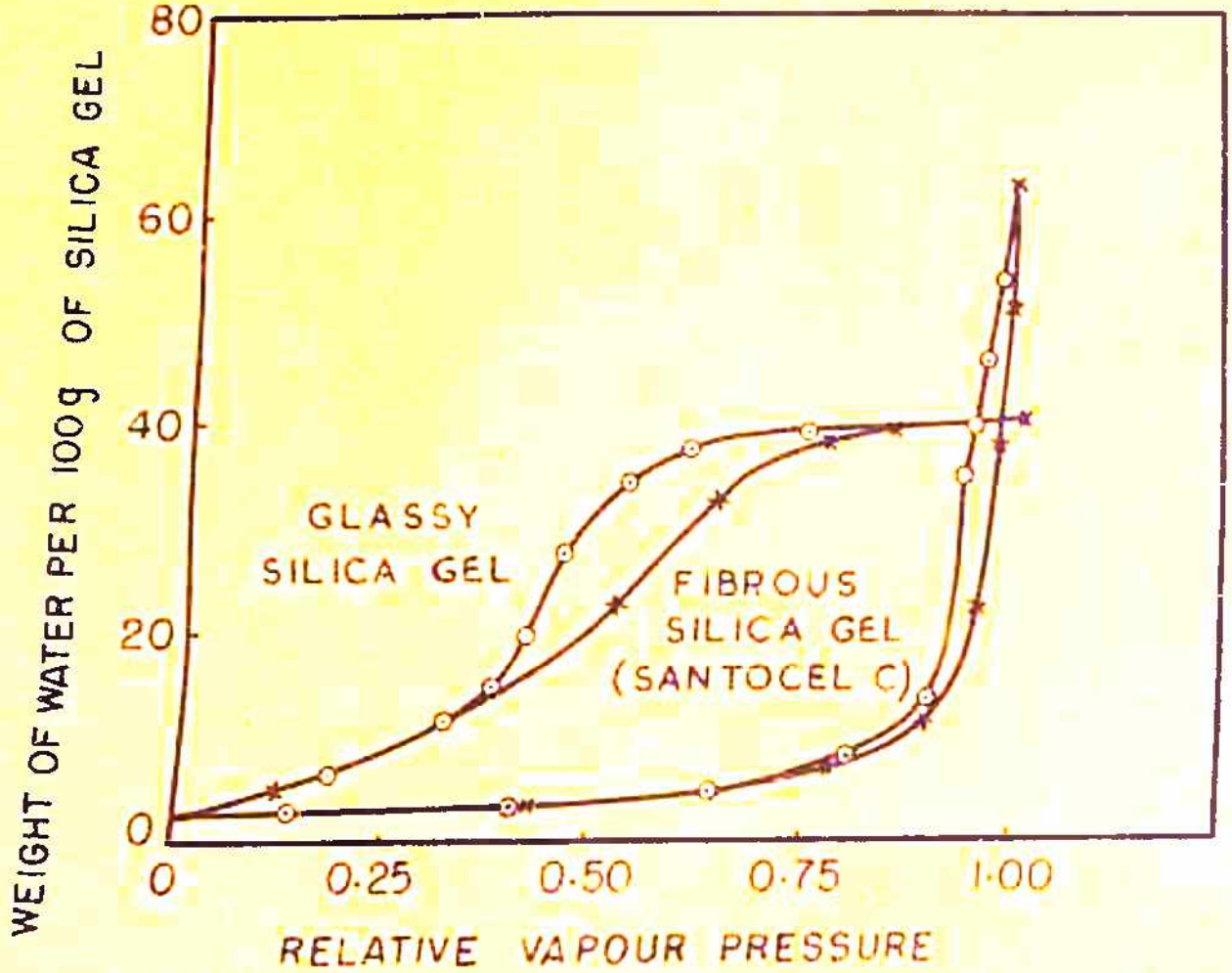


FIG. 19. SORPTION-DESORPTION HYSTERESIS OF WATER ON GLASSY SILICA GEL AND FIBROUS SILICA GEL (SANTOCEL C)

the cavity theory. One noteworthy feature of the cavity theory is its generality and it can explain all cases of hysteresis in a qualitative way.

Pore size distribution in glassy and fibrous silica gels

Following the procedure of Foster[151,152], the pore size distribution has been determined from the isotherms. In these determinations no allowance is made for changing thickness of the adsorbed layer on the walls of pores. The isotherms of water have been chosen for these calculations and these are shown separately in Figure 19. Foster's procedure has been applied only to the isotherm with glassy silica gel and the pore size distribution curve obtained has been shown in Figure 20. The procedure could not be applied to fibrous silica gel as the isotherm is asymptotic to the saturation pressure ordinate. The predominent pore size however was obtained approximately by direct estimation from the isotherm itself.

According to the cavity theory of hysteresis the desorption curve of hysteresis loop indicates the neck radius and sorption curve the body radius of the cavity. The predominent neck and body radii of cavities obtained for both the gels are shown in Table 6.

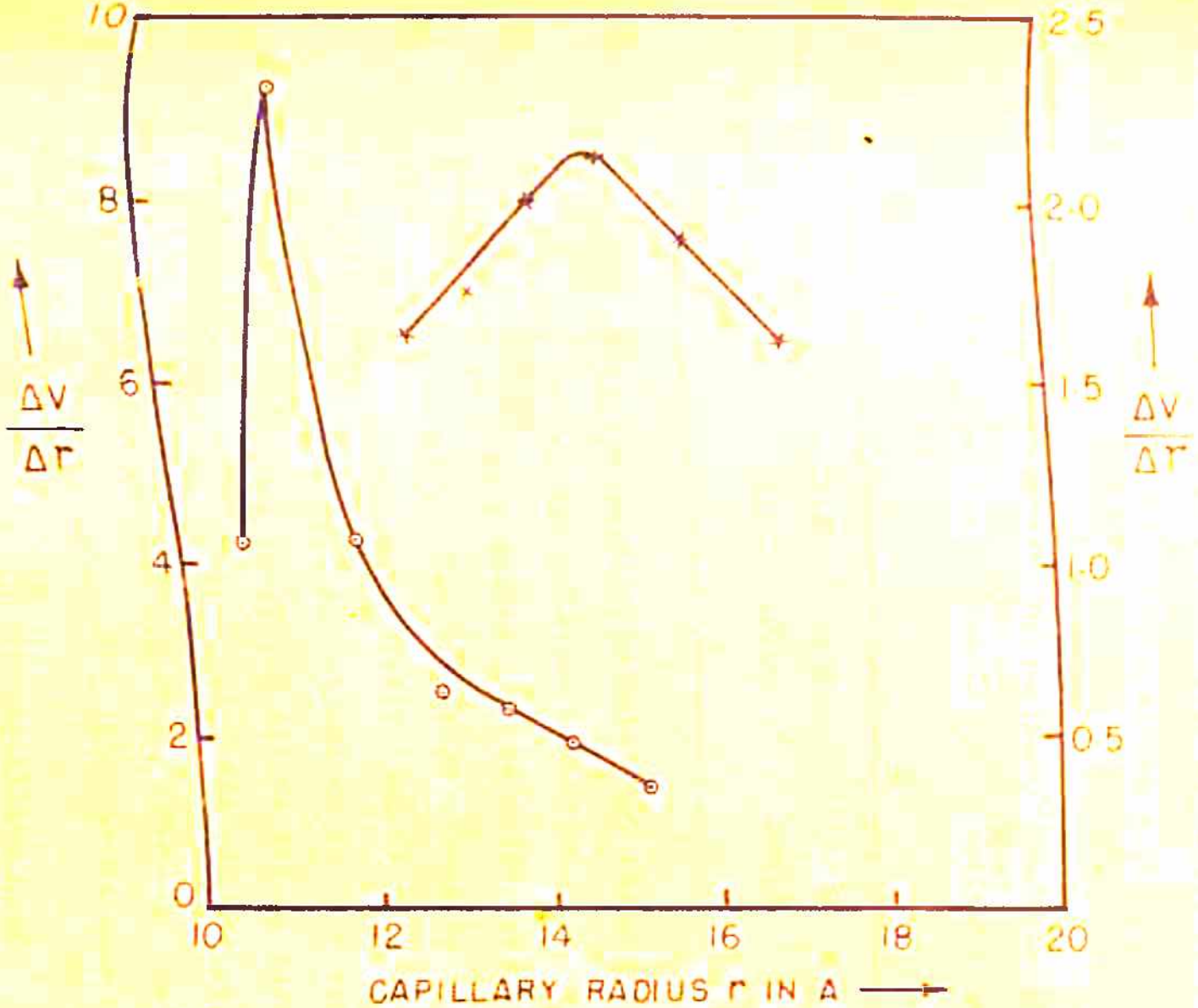


FIG 20. PORE SIZE DISTRIBUTION IN GLASSY SILICA GEL FOR SORPTION ISOTHERM X, DESORPTION ISOTHERM ⊙

The smallest neck radius corresponding to the point of inception of the hysteresis loop is also shown.

Table 6: Pore size distribution expressed in A in glassy and fibrous silica gels

	Smallest neck radius	Predominent neck radius	Predominent body radius	Minimum cavity neck radii and maximum cavity radii
Glassy silica gel	10.2	11.5	15.0	10 - 45
Fibrous silica gel	29.2	137.4	393.4	29 - ∞

It is interesting to note that the predominent pore sizes in the two gels are far apart. It is mostly micropores in glassy silica gel and macropores in fibrous silica gel. The predominent pore radii in the two gels are separated so widely that at relative vapour pressure of 0.75 corresponding to pore radius of 35 A the pore volume in glassy silica gel is just complete and the pore volume in fibrous silica gel begins. The former sorbs its maximum capacity of 40% and the later only about 4% which is about 1/15th the maximum capacity.

Pore shapes in glassy and fibrous silica gels

In glassy silica gel the surface is mostly

internal. After all the capillaries are filled, the sorption isotherm of water touches the saturation vapour pressure ordinate almost at right angles. Whereas the isotherm with fibrous silica gel is asymtotic indicating that the surface is largely external and is favourable for almost indefinite sorption. It is interesting to note that in glassy silica gel, sorptive capacities at saturation pressure for water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols are practically the same and are 40.0, 38.2, 43.3, 42.7, 41.0, 39.8 and 38.3 cm^3 per 100 g respectively, whereas with fibrous silica gel the sorptive capacities for the sorbates are different and they are 62.2, 56.8, 52.0, 61.2, 54.6, 21.4 and 21.6 cm^3 per 100 g respectively.

According to de Boer's[87,88] classification of hysteresis loops, the hysteresis loop of fibrous silica gel is of type A and the capillaries in this gel are cylindrical in shape open at both ends. The hysteresis loop of glassy silica gel is of type E which is very common type and the pores are of ink bottle shape. Glassy silica gel and fibrous silica gel are indeed two typical cases. Though made up of the same material, they are entirely different in their pore size distribution and pore shapes owing to difference in the modes of preparation of the gel.

Relation between contact angle of sorbate and sorption - desorption hysteresis

In the case of glassy silica gel, the overall shape of the hysteresis loops and form of the sorption and desorption isotherms of the 5 alcohols are approximately the same. But in the case of fibrous silica gel they differ markedly. The isotherm of methyl alcohol rises asymtotically to the saturation pressure ordinate. But from ethyl alcohol upto n-amyl alcohol there is gradual deviation. The isotherm of amyl alcohol cuts the saturation pressure ordinate at an angle. In addition, the sorptive capacities at saturation pressure for n-butyl and n-amyl alcohols are much less - 21.4% and 21.6% respectively, nearly one-third of the sorptive capacities for methyl, ethyl and n-propyl alcohols. These significant deviations in contrast with glassy silica gel require an explanation. Gregg[153] has discussed the effect of contact angle of the sorbate on the shape of the isotherm. Ordinarily, in the application of Kelvin equation to the study of the isotherm, the contact angle is assumed to be zero when the surface is pure and free from impurities. This is true of liquids like water which wets the surface of the sorbent and whose isotherm is asymptotic to the saturation

pressure ordinate. But with liquids which have definite contact angles, the isotherms intersect the ordinate at an angle.

In the present experiments, the asymptotic nature of methyl alcohol isotherm indicates almost indefinite large uptake of sorbate at saturation vapour pressure. One may infer from this that the contact angle is zero[153]. The interception of the amyl alcohol isotherm at an angle with the saturation pressure ordinate indicates the existence of definite contact angle. Considering the gradual changes in the shapes of sorption and desorption isotherms, the hysteresis loops, the total sorptive capacities at saturation pressure of the five aliphatic alcohols - methyl, ethyl, n-propyl, n-butyl, n-amyl on fibrous silica gel, it follows that there is steady increase in contact angle from methyl to amyl alcohol. A search of the literature on contact angle was made and the values of contact angles of the five alcohols could not be obtained. Fox and Zisman[154] 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[155,156] of methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols are 21.1, 21.45, 22.55, 23.35 and 24.3 dynes per cm at 35^{o} respectively. In the light of Fox and Zisman's conclusion, these values indicate that the contact angle increases from that of methyl alcohol to n-amyl alcohol.

3. SORPTION - DESORPTION HYSTERESIS IN FIBROUS SILICA GEL (SANTOCEL C) WITH ISOMERIC MONOHYDRIC ALIPHATIC ALCOHOLS*

Introduction

Fibrous silica gel (Santocel C) has been used in earlier studies[157] on the sorption and desorption hysteresis of normal aliphatic alcohols. In all the systems studied permanent and reproducible hysteresis loops are obtained. The surface area calculated from monolayer capacity for each alcohol reveals oriented type of sorption in the monolayer.

The present studies have been made with isomeric monohydric aliphatic alcohols with fibrous silica gel. The specific surface of fibrous silica gel activated at 250° for 2 hours has been determined and reported[157] by measuring monolayer capacity for the normal aliphatic alcohols and assuming oriented sorption of alcohol molecules perpendicular to surface. Assuming this value of specific surface and oriented sorption of isomeric alcohols on the surface of fibrous silica gel, the cross-sections of the alcohol molecules are calculated and are presented in this section.

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Experimental:

The Santocel C obtained from the Monsanto Company, U.S.A., was heated to 250° for 2 hours in order to remove any organic vapours and the activated gel was used in sorption and desorption studies.

The following sorbates were employed:

Iso-propyl alcohol, B.D.H.(British Drug House), A.R., redistilled, B.P. 82.0°.

Iso-butyl alcohol, B.D.H., A.R., redistilled, B.P. 107.0°.

Sec-butyl alcohol, Basic and Synthetic Chemicals (India), A.R. grade, redistilled, B.P. 97.0°.

Tert-butyl alcohol, B.D.H., L.R., redistilled, B.P. 82.5°.

Active amyl alcohol, E.Merck, E.P., redistilled, B.P. 129.0°.

Iso-amyl alcohol, B.D.H., L.R., redistilled, B.P. 131.0°.

Permanent and reproducible hysteresis loops

A series of sorptions and desorptions were carried out with Iso-propyl, Iso-butyl, Sec-butyl, Tert-butyl, Active amyl and Iso-amyl alcohols on fibrous silica gel. Duplicate experiments were done but the

results of one experiment have been given. In all the cases, permanent and reproducible hysteresis loops have been obtained and the loops have been reproduced upto 3rd or 4th cycle of sorption and desorption. The results are shown in Figures 1 to 6. The permanent and reproducible hysteresis loops of the different alcohols obtained in the 3rd or 4th cycle have been given together in Figure 7 for purpose of comparison by plotting the sorption values against the relative vapour pressure.

Monolayer capacities

In all the systems, except for a small initial sorption due to monolayer formation, the isotherms are practically horizontal and show no appreciable increase in sorption upto relative vapour pressure of about 0.75. 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[145].

The sorption isotherms have clearly defined "knees" followed by linear portion. According to BET[13] theory the "knee" signifies the transition from monomolecular to multimolecular sorption. Therefore the BET equation has been applied to obtain the monolayer capacity x_m in each case. The BET plots were straight lines.

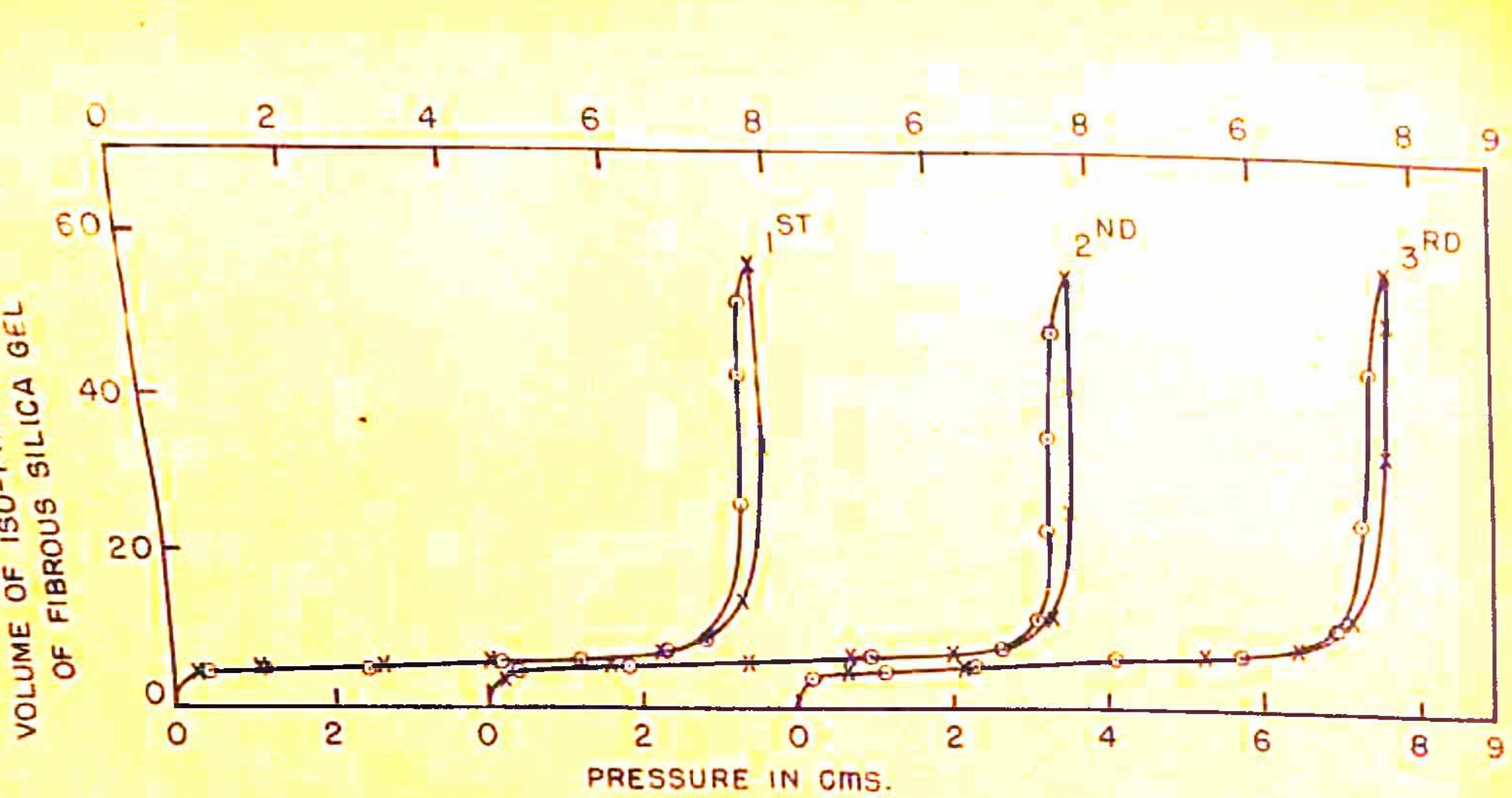

FIG. 1. SORPTION AND DESORPTION OF ISO-PROPYL ALCOHOL ON FIBROUS SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

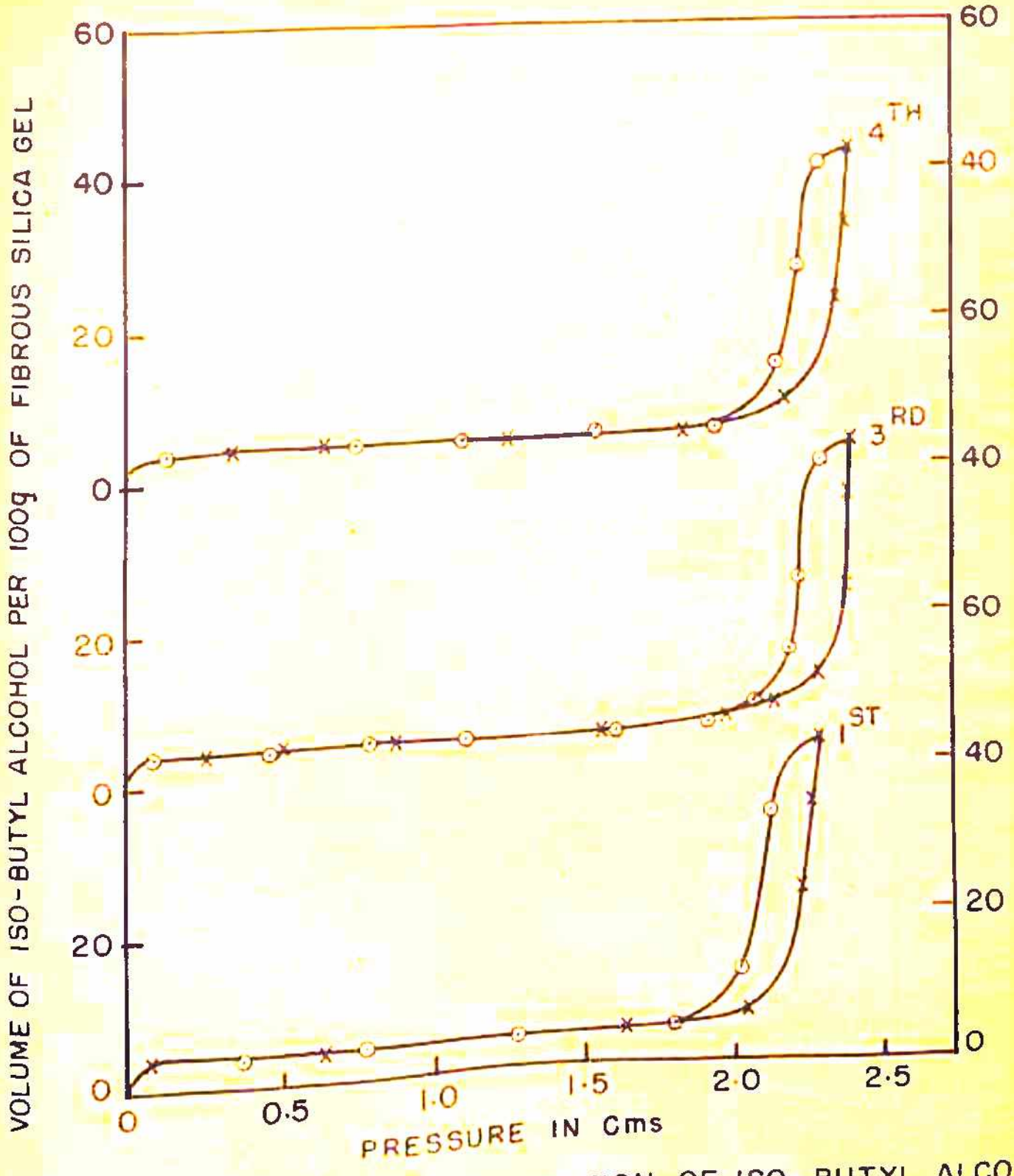

FIG. 2 SORPTION AND DESORPTION OF ISO-BUTYL ALCOHOL ON FIBROUS SILICA GEL IN 1ST, 3RD AND 4TH CYCLES.

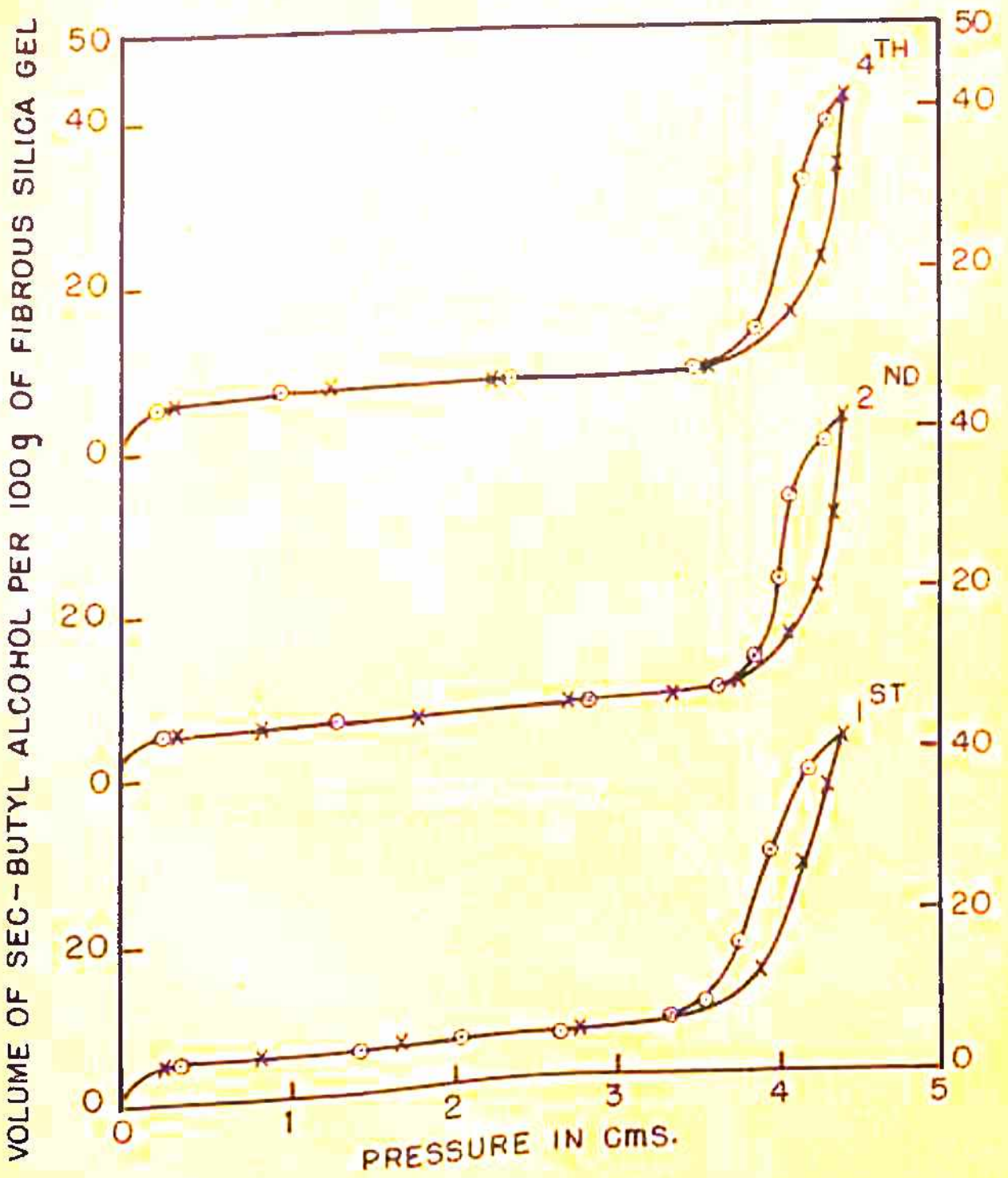

FIG. 3. SORPTION AND DESORPTION OF SEC-BUTYL ALCOHOL ON FIBROUS SILICA GEL IN 1^{ST}, 2^{ND} AND 4^{TH} CYCLES.

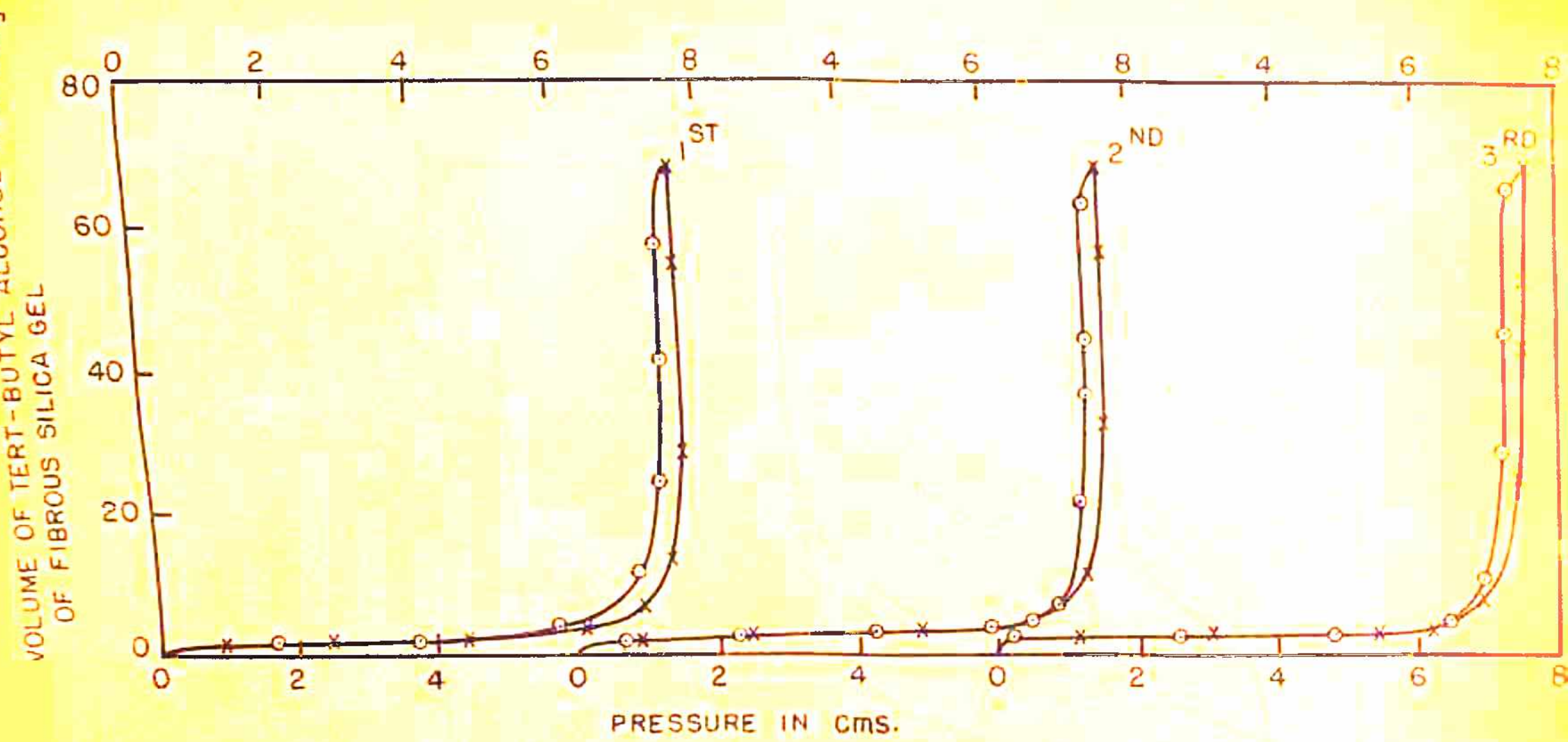

FIG 4. SORPTION AND DESORPTION OF TERT-BUTYL ALCOHOL ON FIBROUS SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

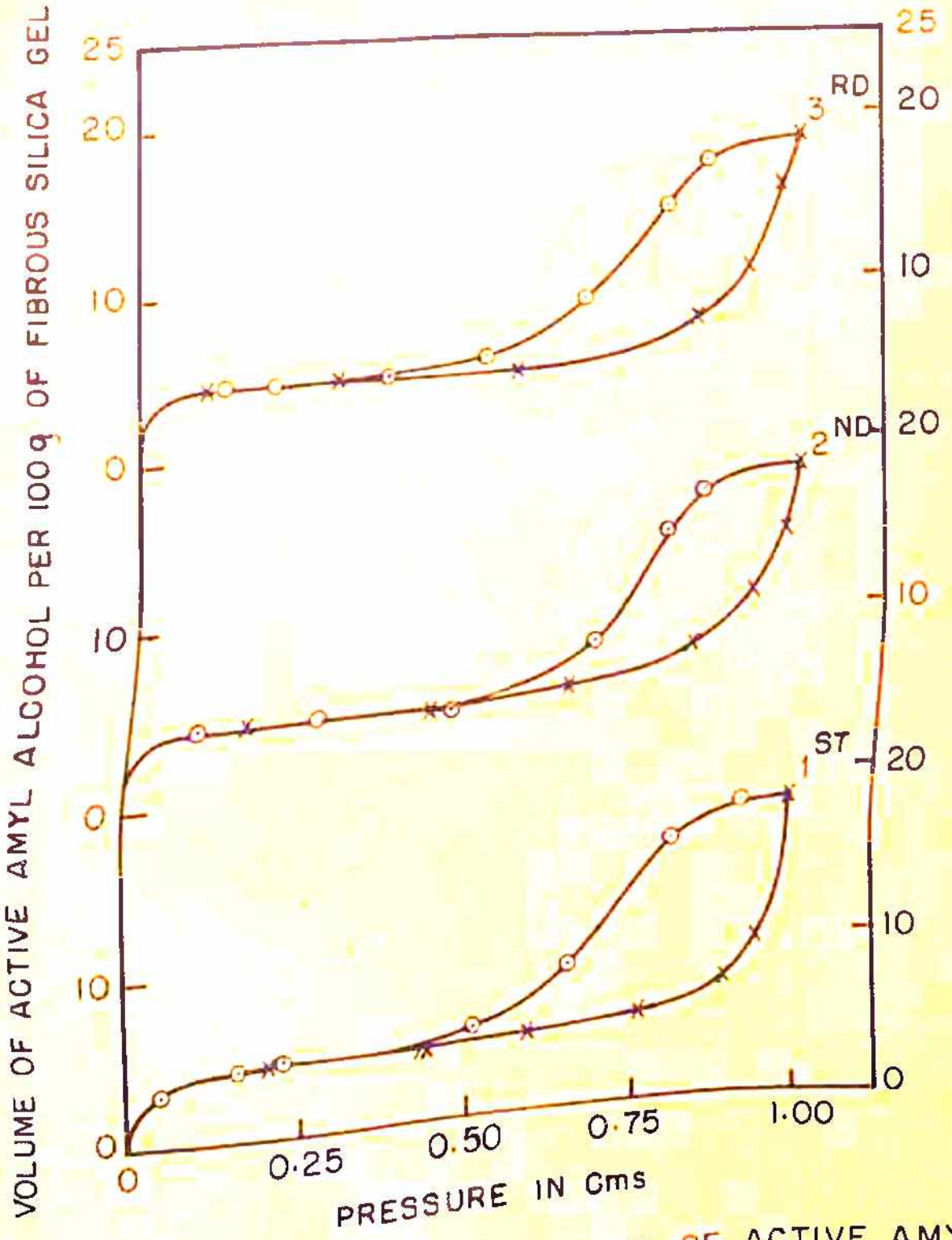

FIG. 5. SORPTION AND DESORPTION OF ACTIVE AMYL ALCOHOL ON FIBROUS SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

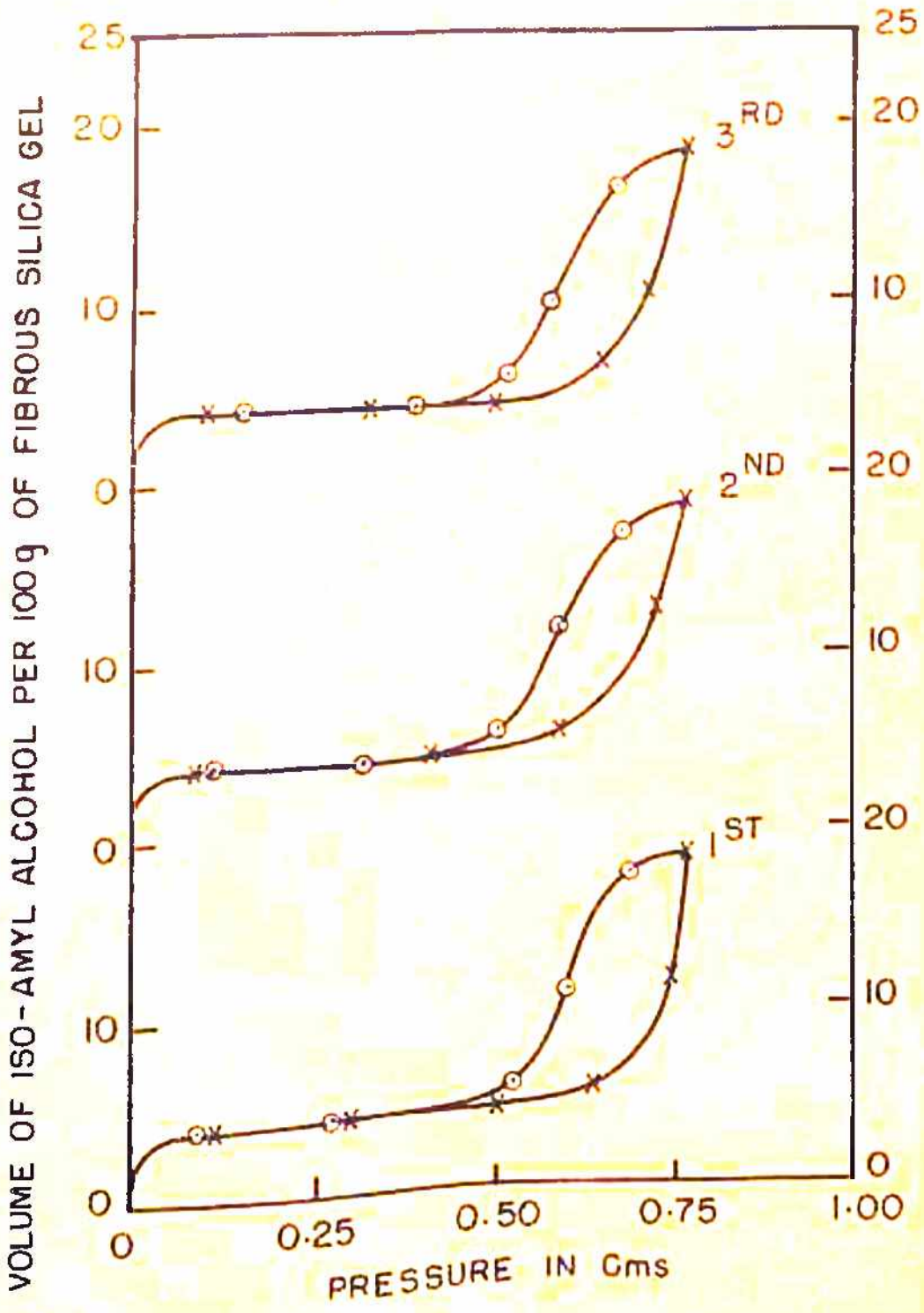

FIG. 6 SORPTION AND DESORPTION OF ISO-AMYL ALCOHOL ON FIBROUS SILICA GEL IN 1ST, 2ND AND 3RD CYCLES.

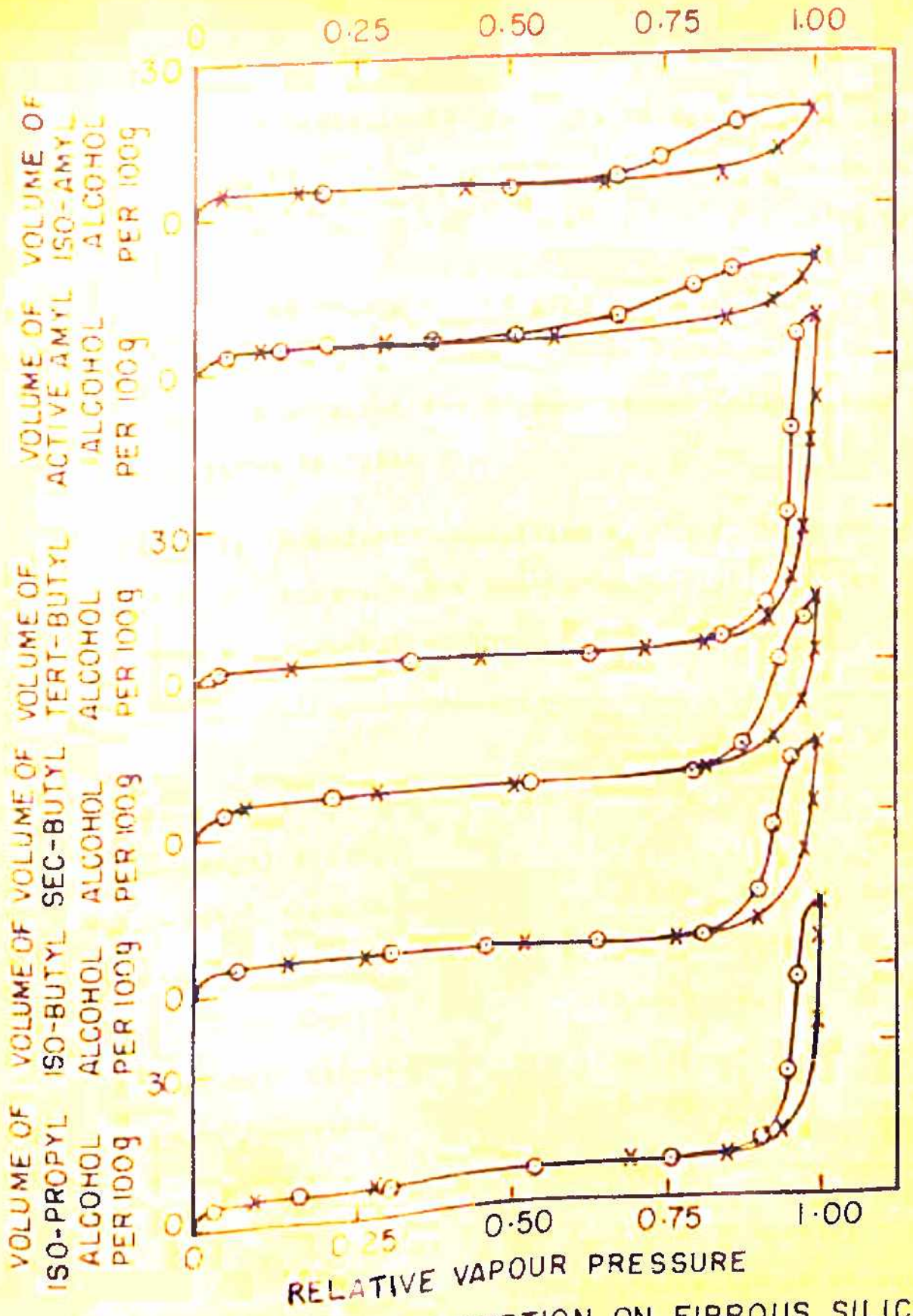

FIG. 7 SORPTION AND DESORPTION ON FIBROUS SILICA GEL OF ISO-PROPYL, ISO-BUTYL, SEC-BUTYL, TERT-BUTYL, ACTIVE AMYL AND ISO-AMYL ALCOHOLS.

Alternatively the value of monolayer capacity can also be read out directly from the isotherms as described in the previous section and is denoted by x_B.

The values of monolayer capacities x_m and x_B for the isomeric alcohols and the relative vapour pressures at which the monolayers are fully formed have been given in Table 1.

Table 1: Monolayer capacities x_m and x_B in g per g of sorption and the corresponding relative vapour pressure

	x_m	x_B	p/p_o
Iso-propyl alcohol	0.040	0.039	0.10
Iso-butyl alcohol	0.029	0.031	0.13
Sec-butyl alcohol	0.041	0.040	0.09
Tert-butyl alcohol	0.013	0.015	0.05
Active-amyl alcohol	0.039	0.037	0.20
Iso-amyl alcohol	0.029	0.032	0.15

The values of x_m and x_B for each alcohol are almost same. However, there is variation in relative vapour pressures of the different alcohols at which the monolayer is complete.

Calculation of molecular diameters, assuming oriented adsorption and knowing specific surface

From the monolayer capacity, the specific area of the surface of the sorbent has been calculated as described in the preceding section. In the sorption and desorption of normal monohydric aliphatic alcohols on fibrous silica gel the specific surface area of the gel has been calculated[157] by assuming oriented sorption of the linear alcohol molecules perpendicular to surface in the monolayer and is found to be 58 m^2/g. Assuming this value of the specific surface and also oriented sorption of the isomeric aliphatic alcohol molecules with OH group on the surface of fibrous silica gel, the molecular cross-sections of the isomeric aliphatic alcohols have been calculated and are shown in Table 2. The cross-section of the normal aliphatic alcohol molecules is also given in the table to facilitate comparison.

The cross-section of the hydrocarbon chain in normal aliphatic alcohols is 20.7 A^2. Excepting Iso-propyl and Sec-butyl alcohols the molecular cross-sections of the isomeric alcohols are higher than 20.7 A^2. This is to be expected in view of the presence of side CH_3 groups and that isomeric alcohols are not linear in

Table 2: Molecular cross-sections in A^2 of isomeric alcohol molecules taking the specific surface area of fibrous silica gel as 58 m^2/g.

Alcohol	Molecular cross-section in A^2
Iso-propyl alcohol	14.5
Iso-butyl alcohol	25.0
Sec-butyl alcohol	17.4
Tert-butyl alcohol	55.5
Active-amyl alcohol	22.0
Iso-amyl alcohol	28.8
Normal aliphatic alcohols (Taken from earlier work[157])	20.7

structure unlike normal aliphatic alcohols. That tertiary butyl alcohol has the biggest cross-section, i.e., 55.5 A^2 is a significant finding. This is to be expected as its molecule has 3 side CH_3 groups and is non-linear in structure. The cause of the low values of molecular cross-sections of Iso-propyl and Sec-butyl alcohols is not clear.

A search of the literature was made for data on molecular cross-sections of the isomeric alcohols and these could not be obtained.

Sorption - desorption hysteresis and applicability of Cohan's theory

All the isomeric alcohols have given permanent and reproducible hysteresis loops. Equilibrium was established within an hour but actually 2 hours were allowed to ensure complete equilibrium. The amounts taken at saturation pressure of Iso-propyl, Iso-butyl, Sec-butyl, Tert-butyl, Active amyl and Iso-amyl alcohols are 56.5, 42.8, 41.5, 68.1, 18.8 and 18.5 cm^3 per 100 g of fibrous silica gel respectively. The amounts taken of n-propyl, n-butyl and n-amyl alcohols are 38.7, 19.0 and 21.0 cm^3 per 100 g of gel reported earlier[157]. Excepting the isomers of amy alcohol, the sorption values of which at saturation pressure are slightly less than that of n-amyl alcohol, the saturation values of propyl and butyl isomers are 1.5 to 3 times higher than the normal alcohols.

By applying Cohan's theory as described in preceding section, the values of D obtained are shown in Table 3. The values of D_{cubic} and $D_{spherical}$ are also shown to facilitate comparison.

The Table reveals that the molecular diameter D calculated from Cohan's theory are very much higher and varies from 3 to 10 times the value of $D_{spherical}$.

Table 3: Molecular diameters D_{cubic}, $D_{spherical}$ and D from Cohan's theory in A

	D_{cubic}	$D_{spherical}$	$D_{Cohan's\ theory}$
Iso-propyl alcohol	4.3	5.7	60.4
Iso-butyl alcohol	4.5	6.0	38.6
Sec-butyl alcohol	4.5	6.0	40.6
Tert-butyl alcohol	4.6	6.1	50.5
Iso-amyl alcohol	4.8	6.4	15.1

These indicate the limitations of Cohan's theory of hysteresis. Cavity theory however can explain the permanent and reproducible hysteresis loops obtained with all the isomeric alcohols by postulating the entrapping of the sorbate liquid in the cavity.

Contact angle of the sorbate in relation to sorption - desorption hysteresis

As in the case of normal aliphatic alcohols, there is marked variation in the size and shape of the isotherms and the hysteresis loops of the isomeric alcohols. The isotherms of Tert-butyl, Iso-propyl and Iso-butyl alcohols rise practically asymptotic to the saturation pressure ordinate whereas Sec-butyl,

Iso-amyl and Active amyl alcohols cut the saturation pressure ordinate at an angle.

Gregg[153] has discussed the effect of contact angle of the sorbate on the shape of the isotherm. Ordinarily, in the application of Kelvin equation to the study of the isotherm, the contact angle is assumed to be zero when the surface is pure and free from impurities. This is true of liquids like water which wets the surface but with liquids which have definite contact angles, the isotherms intersect the ordinate at an angle.

A search of the literature on contact angle was made but the values could not be obtained for isomeric monohydric alcohols. Fox and Zisman[154] 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[155,158] of the Ter-butyl, Iso-propyl, Iso-butyl, Sec-butyl and Iso-amyl alcohols are 18.8, 20.5, 21.8, 22.2 and 22.7 dynes per cm at 35° respectively. In the light of Fox and Zisman's conclusion, the contact angles of these alcohols should be in the order Tert-butyl < Iso-propyl < Iso-butyl < Sec-butyl and < Iso-amyl alcohol. It is interesting to note that the sorption values at saturation pressure

of these alcohols vary in the reverse order Tert-butyl 68.1% > Iso-propyl 56.5% > Iso-butyl 42.8% > Sec-butyl 41.5% > Iso-amyl 18.5%. In other words sorbates of low contact angles have the isotherms, rising asymptotically to the saturation pressure ordinate, and high sorption values at saturation pressure. Whereas sorbates of high contact angles have isotherms cutting the saturation pressure at an angle, and low sorption values.

The value of the surface tension of Active amyl alcohol could not be obtained. But from the shape of the isotherm it follows that the contact angle of Active amyl alcohol is nearly equal to that of Iso-amyl alcohol.

C. SORPTIVE PROPERTIES OF FIBROUS SILICA GEL (SANTOCEL C) ACTIVATED AT DIFFERENT TEMPERATURES*

The mode of preparation and treatment of sorbents have been reported by earlier workers to influence the nature and extent of sorption. Precipitated silica gel obtained by mixing, sodium silicate and ammonium chloride solutions has been found to differ markedly in shape of the isotherms and the size and position of the hysteresis loops from glassy silica gel obtained from set silicic acid jelly of a mixture of sodium silicate and hydrochloric acid solutions[159]. Weiser and collaborators[141,160] have reported that if hydrous oxide gels are prepared by mixing boiling solutions of the reactants, the hysteresis effect obtained in the sorption and desorption of water, is eliminated. Such elimination has been reported with silica gel in particular. Krishnappa and others[161] have studied that when silica gel is activated at different temperatures varying from 35° to 1000°, its sorptive capacity for water first decreases upto 140°, remains practically constant from 140° to 500° and suffers a marked decrease at 1000°.

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* K.Subba Rao and Bhagwan Das, Current Science, 37, 599, 1968.

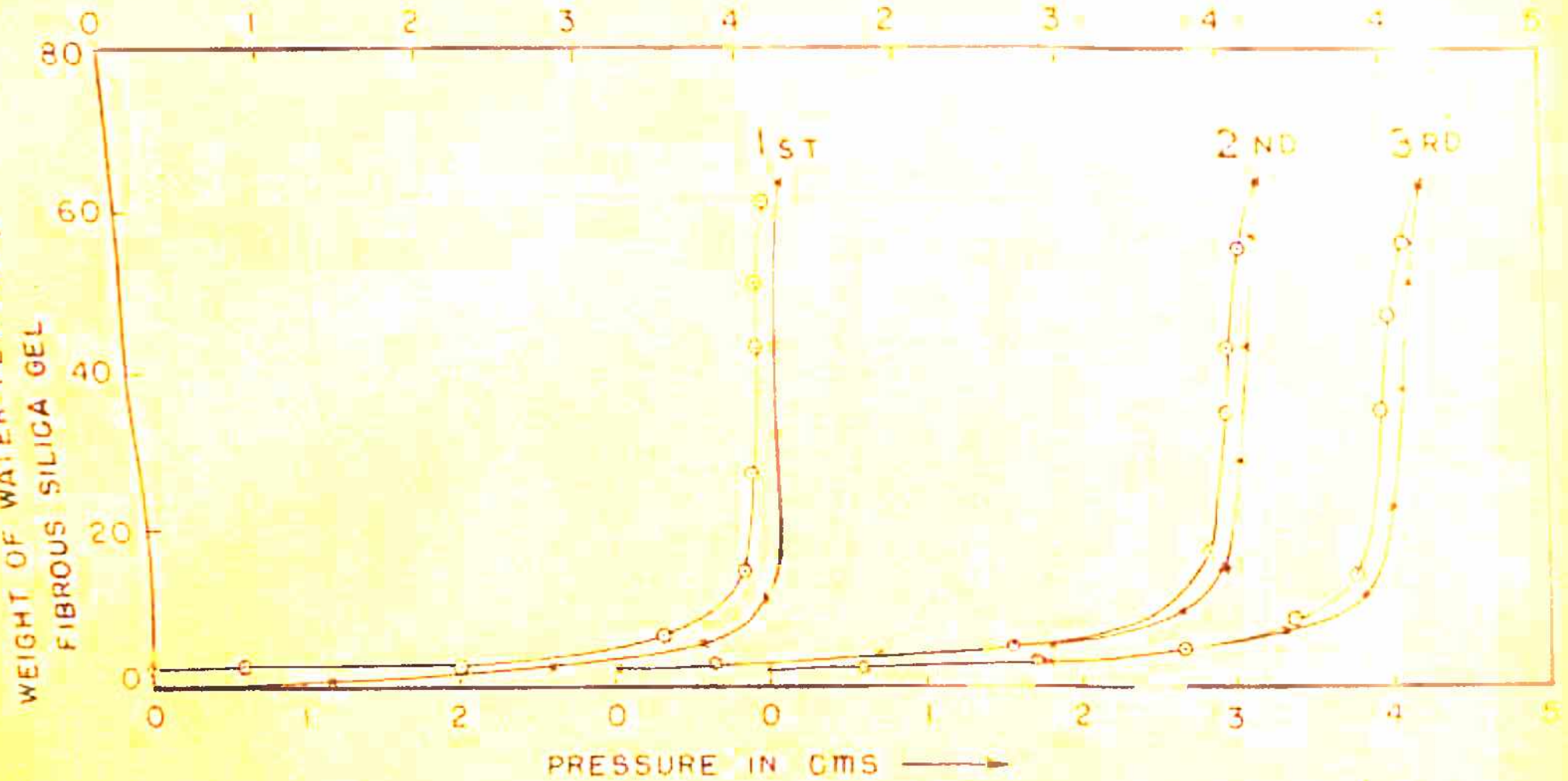

FIG. 1 SORPTION AND DESORPTION OF WATER ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND AND 3RD CYCLES.

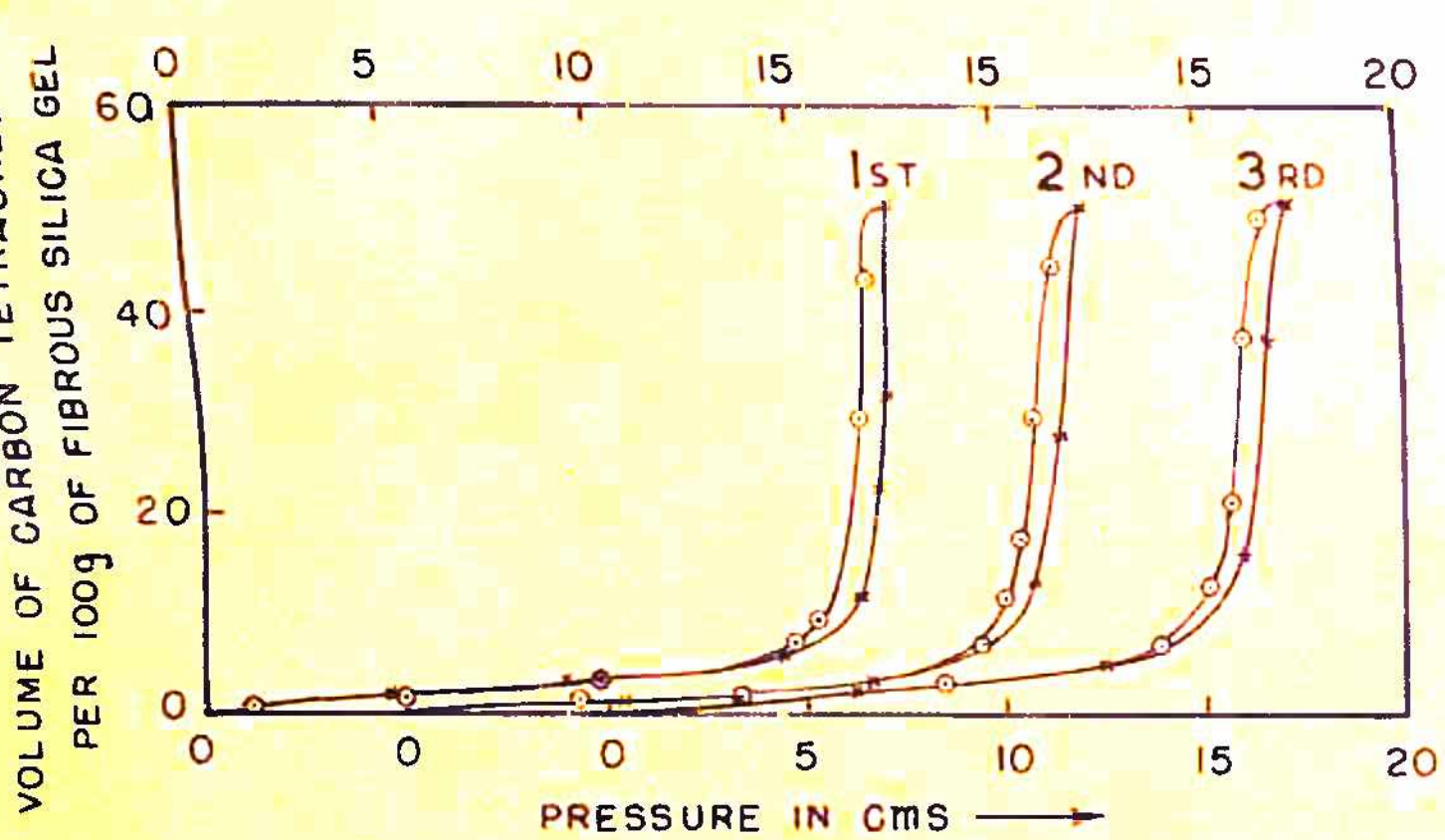

FIG. 2. SORPTION AND DESORPTION OF CARBON TETRACHLORIDE ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND AND 3RD CYCLES.

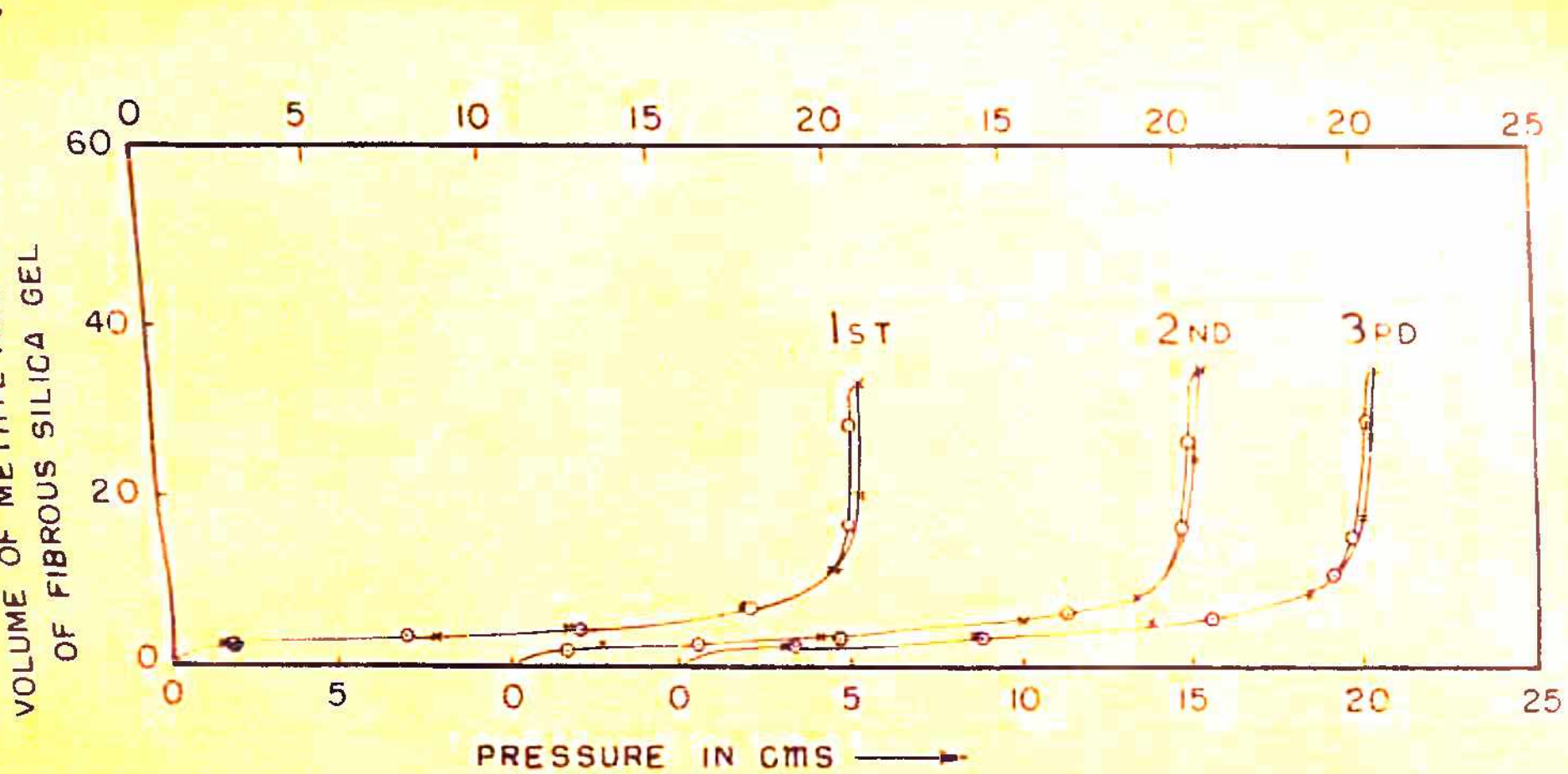

FIG. 3. SORPTION AND DESORPTION OF METHYL ALCOHOL ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND, AND 3RD CYCLES.

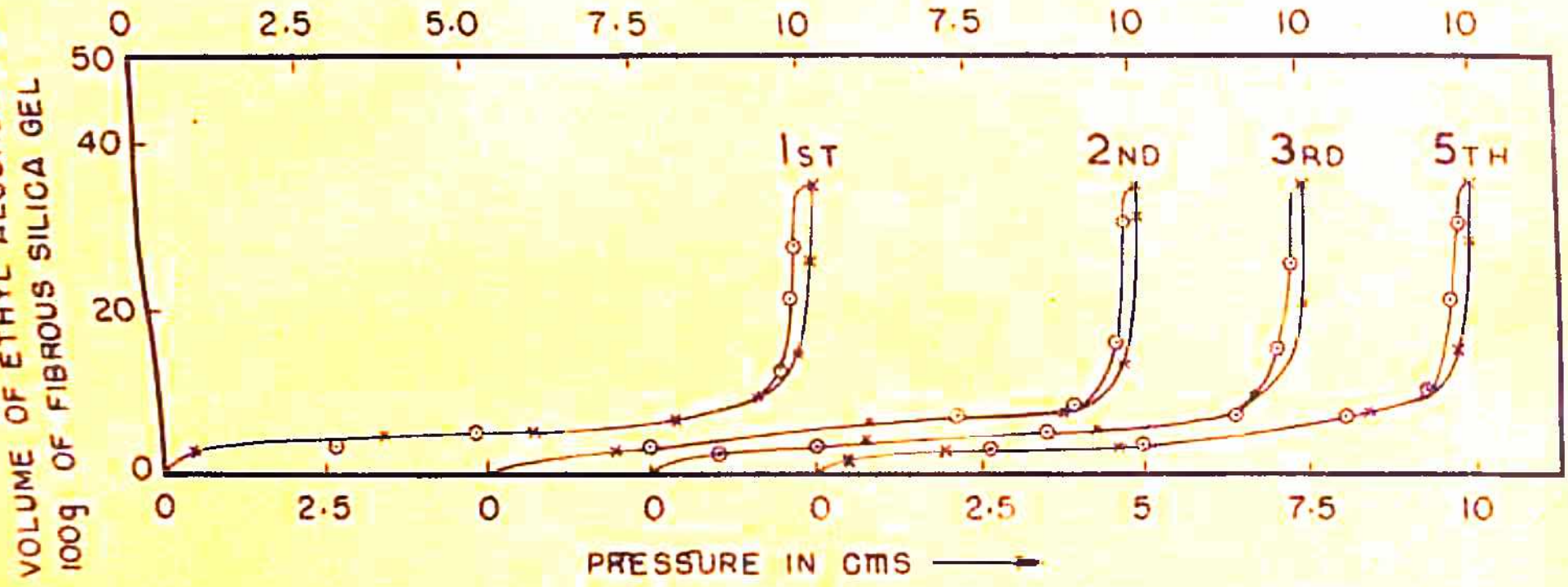

FIG. 4. SORPTION AND DESORPTION OF ETHYL ALCOHOL ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1^{ST}, 2^{ND}, 3^{RD} AND 5^{TH} CYCLES.

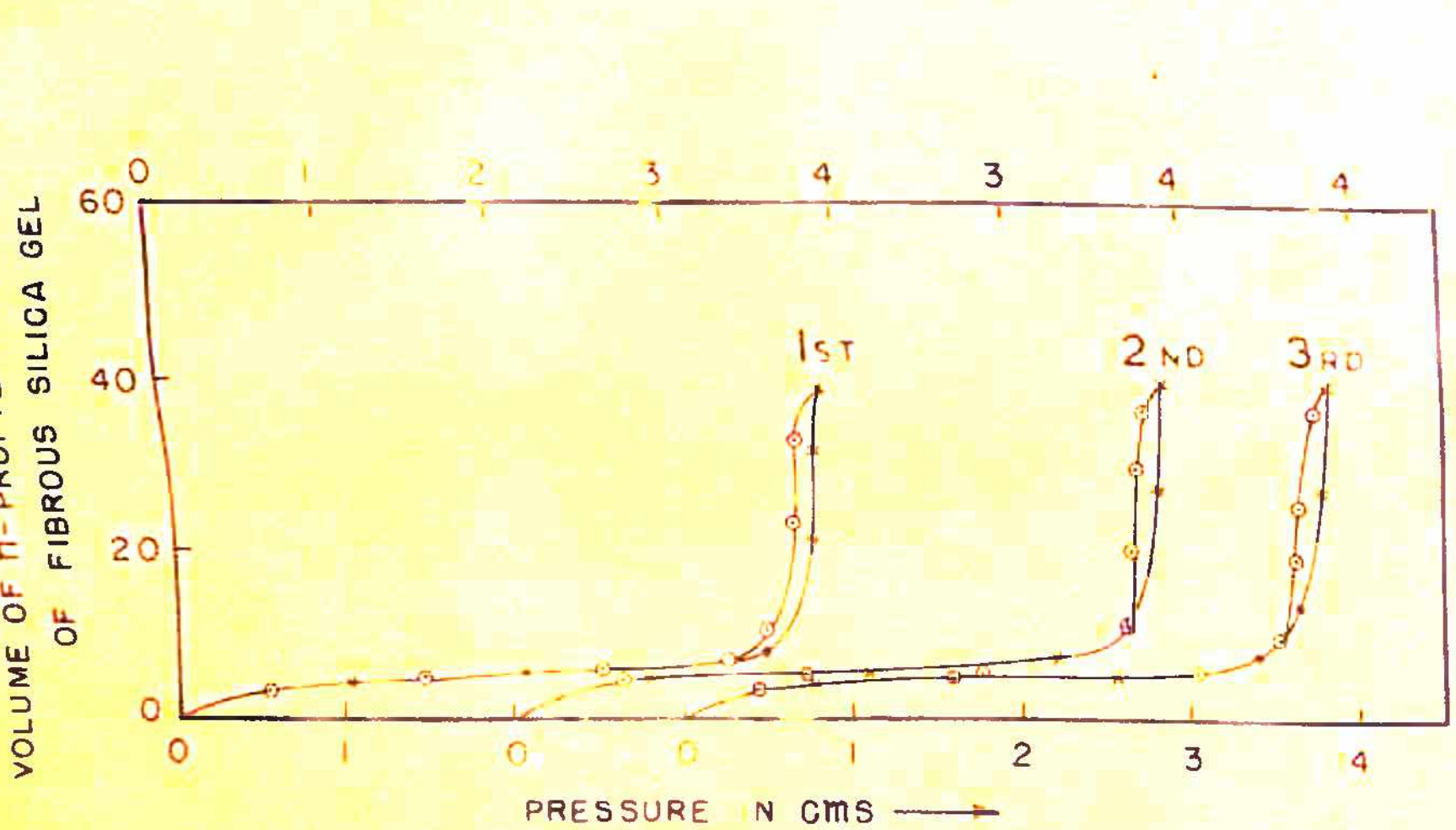

FIG. 5. SORPTION AND DESORPTION OF n-PROPYL ALCOHOL ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND AND 3RD CYCLES.

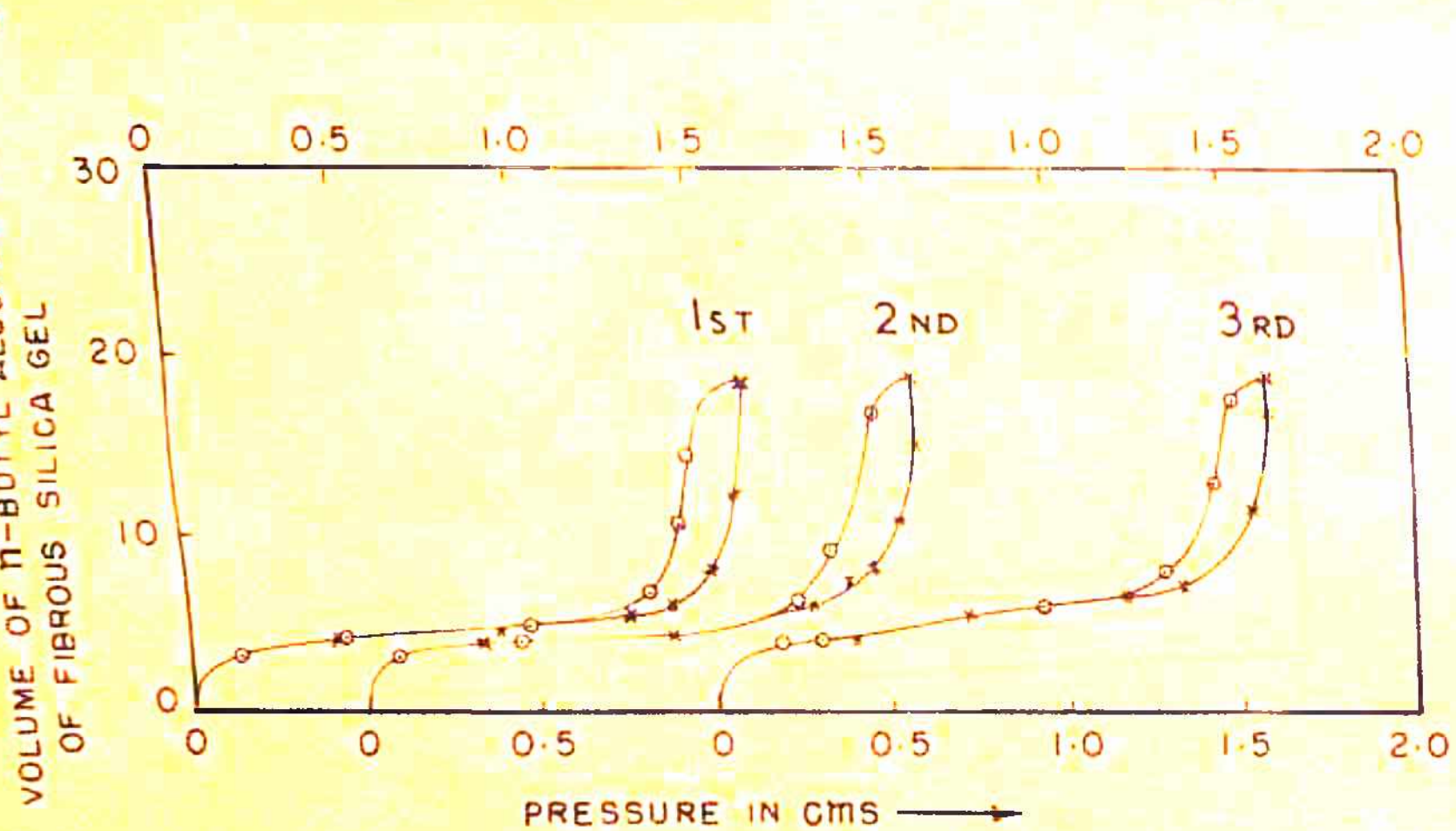

FIG. 6. SORPTION AND DESORPTION OF n-BUTYL ALCOHOL ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND AND 3RD CYCLES.

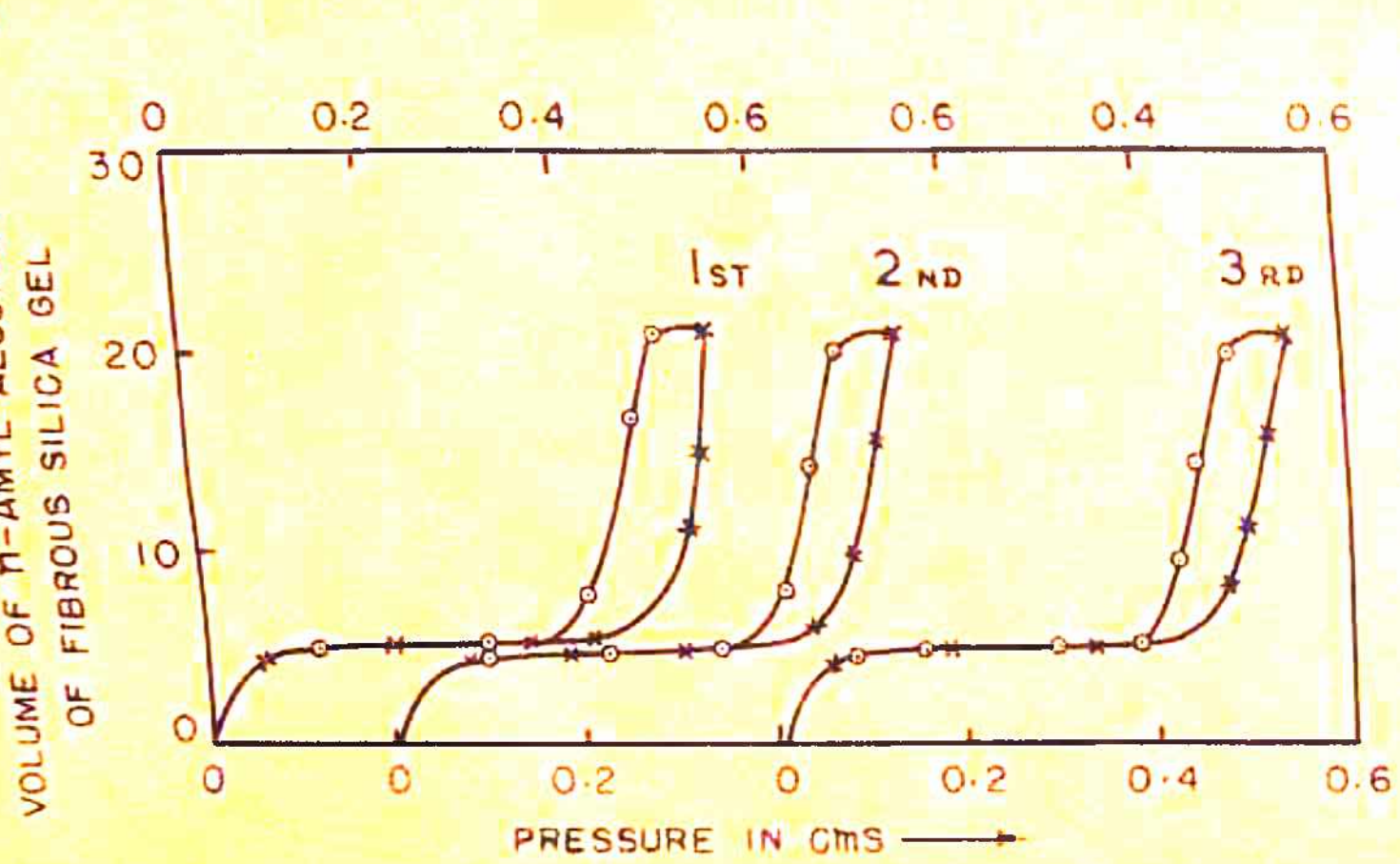

FIG. 7. SORPTION AND DESORPTION OF n-AMYL ALCOHOL ON FIBROUS SILICA GEL ACTIVATED AT 250° IN 1ST, 2ND AND 3RD CYCLES.

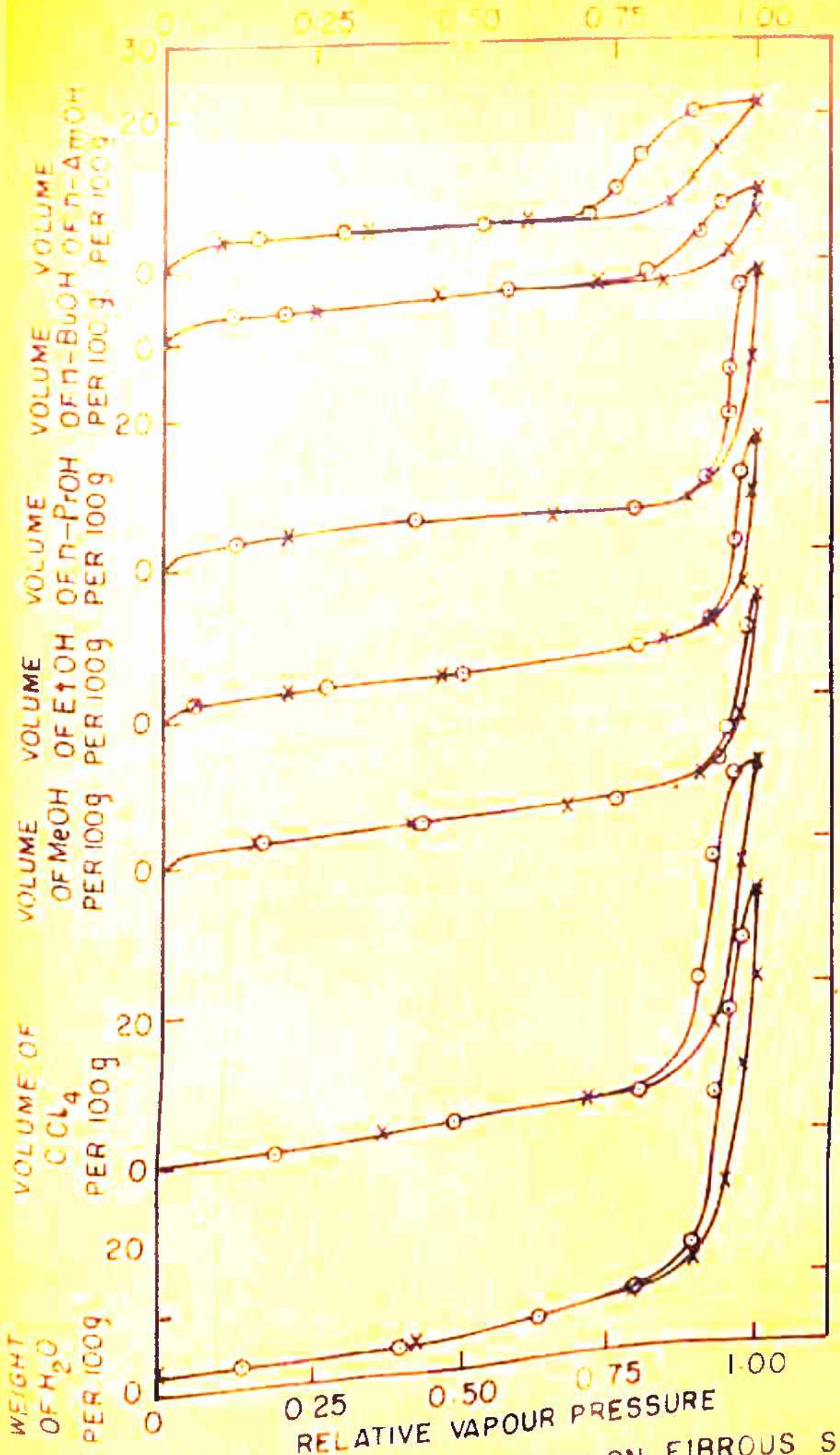

FIG 8. SORPTION AND DESORPTION ON FIBROUS SILICA GEL ACTIVATED AT 250° OF WATER, CARBON TETRACHLORIDE, METHYL, ETHYL, n-PROPYL, n BUTYL AND n-AMYL ALCOHOLS.

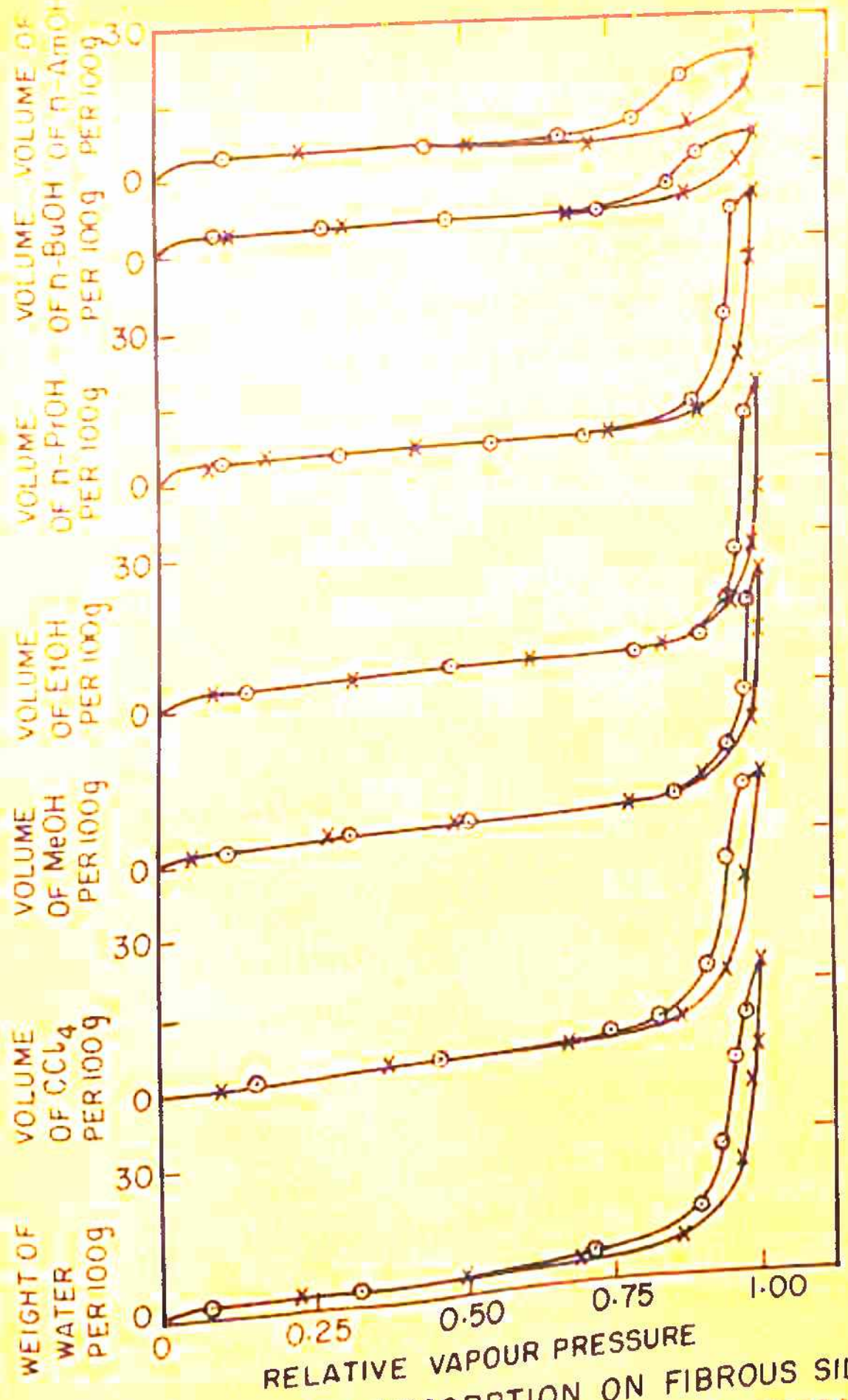

FIG. 9. SORPTION AND DESORPTION ON FIBROUS SILICA GEL ACTIVATED AT 450 OF WATER, CARBON TETRACHLORIDE, METHYL, ETHYL, n-PROPYL, n-BUTYL AND n-AMYL ALCOHOLS.

inspite of several hours of evacuation. The amounts of bound water held by the two samples of silica gel activated at 250° and 450° are 2.5 cm^3 and 1.4 cm^3/ 100 g of gel respectively. The small volume of water irreversible held may be chemisorbed. The sorptive capacities of the two samples at saturation pressure for the different sorbates are given in Table 1.

Table 1: Sorptive capacities of fibrous silica gel in cm^3/100 g.

	Activated at 250°	Activated at 450°
Water	64.0	62.2
Carbon tetrachloride	50.0	56.8
Methyl alcohol	33.0	52.0
Ethyl alcohol	33.3	61.2
n-Propyl alcohol	38.7	54.6
n-Butyl alcohol	19.0	21.4
n-Amyl alcohol	21.0	21.6

When the temperature of activation of the silica gel is raised from 250° to 450°, the sorption values at saturation pressure of methyl, ethyl and n-propyl alcohols have appreciably increased, that of

carbon tetrachloride has increased slightly, whereas the values of other sorbates remain practically the same.

Application of BET equation and monolayer capacities

Excepting water and carbon tetrachloride, the sorption isotherms of the five aliphatic alcohols have clearly defined "knees". The BET equation has been applied to the isotherms according to procedure described in previous sections. The monolayer capacities x_m have been calculated. The value of monolayer capacity was also read out directly from the isotherms and denoted by x_B. The values of monolayer capacities x_m and x_B for the five alcohols and the relative vapour pressures at which the monolayers are fully formed are calculated as given in the preceding sections and have been given in Table 2.

The agreement is good between the values of x_m and x_B for each alcohol with the two samples of gel activated at 250° and 450°.

Monolayer capacity and specific surface

From the monolayer capacity, the specific area of the sorbent is calculated as described in section A of the present chapter. The molecular diameter

Table 2: Monolayer capacities x_m and x_B in g per g of sorption and the corresponding relative vapour pressures.

	Silica gel activated at 250°			Silica gel activated at 450°		
	x_m	x_B	p/p_o	x_m	x_B	p/p_o
Methyl alcohol	0.016	0.016	0.05	0.017	0.016	0.05
Ethyl alcohol	0.018	0.017	0.05	0.022	0.023	0.06
n-Propyl alcohol	0.028	0.028	0.10	0.028	0.028	0.10
n-Butyl alcohol	0.035	0.032	0.13	0.034	0.036	0.10
n-Amyl alcohol	0.041	0.041	0.22	0.037	0.037	0.16

$D_{spherical}$ is assumed for calculating the molecular cross-section. Knowing the molecular cross-sections of the five aliphatic alcohols and their monolayer capacities x_m, the specific surface areas of the two gels are obtained. The results are shown in Table 3.

Table 3: Specific surface of fibrous silica gel considering alcohol molecules as spheres.

	Molecular cross-section in A^2	Specific surface in m^2/g of fibrous silica gel	
		Activated at 250°	Activated at 450°
Methyl alcohol	21.2	65.5	68.4
Ethyl alcohol	27.0	63.4	76.3
n-Propyl alcohol	31.4	86.7	86.7
n-Butyl alcohol	36.0	103.4	99.6
n-Amyl alcohol	40.2	175.4	101.7

In both the gels the value of the specific surface goes on increasing from methyl to n-amyl alcohol. This shows the incorrectness of assuming the five aliphatic alcohol molecules as spheres. By assuming alcohol molecule as a rectangular rod and its two mode of sorptions, as described in the earlier sections, the specific areas are calculated and presented in Table 4.

Table 4: Specific surface of fibrous silica gel considering alcohol molecules as linear

	Diameter in A	Length of the molecule in A	Cross-section in A^2	Area of side in A^2	Specific surface in m^2/g of gel			
					Activated at 250°		Activated at 450°	
					Molecules perpendicular to surface	Molecules parallel to surface	Molecules perpendicular to surface	Molecules parallel to surface
Methyl alcohol	4.6	4.7	20.7	21.4	64.1	66.3	66.9	69.2
Ethyl alcohol	5.2	6.8	20.7	30.9	48.5	72.4	58.4	87.2
n-Propyl alcohol	5.6	8.5	20.7	38.5	57.2	106.8	57.2	106.8
n-Butyl alcohol	6.0	10.4	20.7	47.5	59.4	136.2	57.2	131.2
n-Amyl alcohol	6.3	12.1	20.7	55.0	57.3	152.0	52.4	139.0

The following interesting conclusions emerge from the results of Table 4. In both the gels, the values of specific surface obtained for the five alcohols are practically the same if oriented sorption perpendicular to the surface of the linear alcohol molecules is assumed. If oriented sorption parallel to surface is assumed, the value of the specific surface goes on increasing from methyl to n-amyl alcohol. Therefore it follows that sorption of the five aliphatic normal alcohols in the monolayers on the surface of fibrous silica gels activated at 250° and 450° are of the oriented type perpendicular to surface.

Secondly, for this oriented type of sorption perpendicular to surface, the specific surface values obtained of the gel activated at 250° are almost the same as those of gel activated at 450°. Variation in the temperature of activation has not made any difference in specific surface area of the gel.

Sorption - desorption hysteresis

Figures 8 and 9 reveal that the hysteresis loops of the two gels activated at 250° and 450° for any particular alcohol are almost identical in shape and point of commencement of the loop. The applicability of Cohan's theory to the hysteresis loops of the five

alcohols with silica gel activated at 250° and 450° has been studied. The values of molecular diameters $D_{Cohan's\ theory}$ have been calculated and are shown along with $D_{spherical}$ in Table 5.

Table 5: Molecular diameters D in A of fibrous silica gel

	$D_{spherical}$	$D_{Cohan's\ theory}$	
		With gel activated at 250°	With gel activated at 450°
Water	3.5	15.5	14.6
Carbon tetrachloride	6.1	43.3	33.6
Methyl alcohol	4.6	52.2	52.2
Ethyl alcohol	5.2	47.2	47.2
n-Propyl alcohol	5.6	41.2	41.2
n-Butyl alcohol	6.0	33.2	29.5
n-Amyl alcohol	6.3	28.8	35.7

In all the cases the values of D obtained by the application of Cohan's theory are higher than $D_{spherical}$ indicating the inapplicability of Cohan's theory to the results.

Pore size distribution

According to the cavity theory of hysteresis,

the desorption curve of hysteresis loop indicates the neck radius and sorption curve the body radius of the cavity. The predominent neck and body radii of cavities are obtained from the midpoints of the steep parts of desorption and sorption curves respectively. The isotherms of water have been employed. Body and neck radii have been calculated by the application of Kelvin equation. The values of both the samples are shown in Table 6. The smallest neck radius corresponding to the point of inception of the hysteresis loop is also shown.

Table 6: Pore size distribution in A of fibrous silica gel

	Smallest neck radius	Predominent neck radius	Predominent body radius
Gel activated at 250°	31.0	150.0	380.0
Gel activated at 450°	29.2	137.4	393.4

The results show that the values of smallest neck radius, the predominent cavity body and neck radii remain almost the same on heating fibrous silica gel from 250° to 450°. Higher temperature has not changed markedly the porous structure of fibrous silica gel. Similar results have been reported by Milligan and

Rachford[162]. In their silica gel, hysteresis loop is not destroyed by moderate or even excessive heat treatment. However heat of 400° to 600° actually increased the area of the loop.

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CHAPTER VI: SORPTION - DESORPTION HYSTERESIS IN SYNTHETIC ION-EXCHANGE RESINS WITH WATER

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SORPTION - DESORPTION HYSTERESIS IN SYNTHETIC ION-EXCHANGE RESINS WITH WATER

Organic ion-exchange resins are typical gels. Their framework, the so called matrix, consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains along with ionic groups. These resins are cross-linked polyelectrolytes. The matrix of the resins is hydrophobic. Hydrophilic components such as sulphonic, carboxylic and amino groups etc., are introduced into the matrix and linear hydrocarbon macromolecules containing such groups are soluble in water. But the resins are made insoluble by introduction of cross-links which interconnect the hydrocarbon chains.

An ion exchange resin particle is practically one single macromolecule. Its dissolution would require rupture of carbon - carbon bonds. Thus the resins are insoluble in all solvents by which they are not destroyed. However matrix is elastic and can be expanded. Therefore the resins swell by taking up the solvent. The extent of swelling of resins depends upon the degree of crosslinking of the molecules. The degree of crosslinking is varied by varying the amounts of crosslinking agent. Divinyl benzene is commonly used as crosslinking agent.

Most of the commercial resins available in the market are stable in all common solvents, except in the presence of strong oxidizing or reducing agents, and withstand temperatures upto about 100°C. Strong base anion-exchange resins begin to deteriorate above 60°C.

As shown in the previous chapters, the disappearance of the hysteresis loop depends upon the extent of swelling which in turn depends upon the degree of crosslinking. Hence this aspect has been studied by sorption - desorption hysteresis with synthetic ion exchange resins of different degree of crosslinking.

Ion exchange resins used

The following commercially available synthetic ion exchange resins with polystyrene matrix are used. These are products of Rohm and Haas Company, U.S.A., and marketed by British Drug House (India). All the resins are of laboratory reagent grade and the cross-linking agent is divinyl benzene.

Amberlite IRC-50

It is weakly carboxylic cation exchanger with 10% divinyl benzene[163].

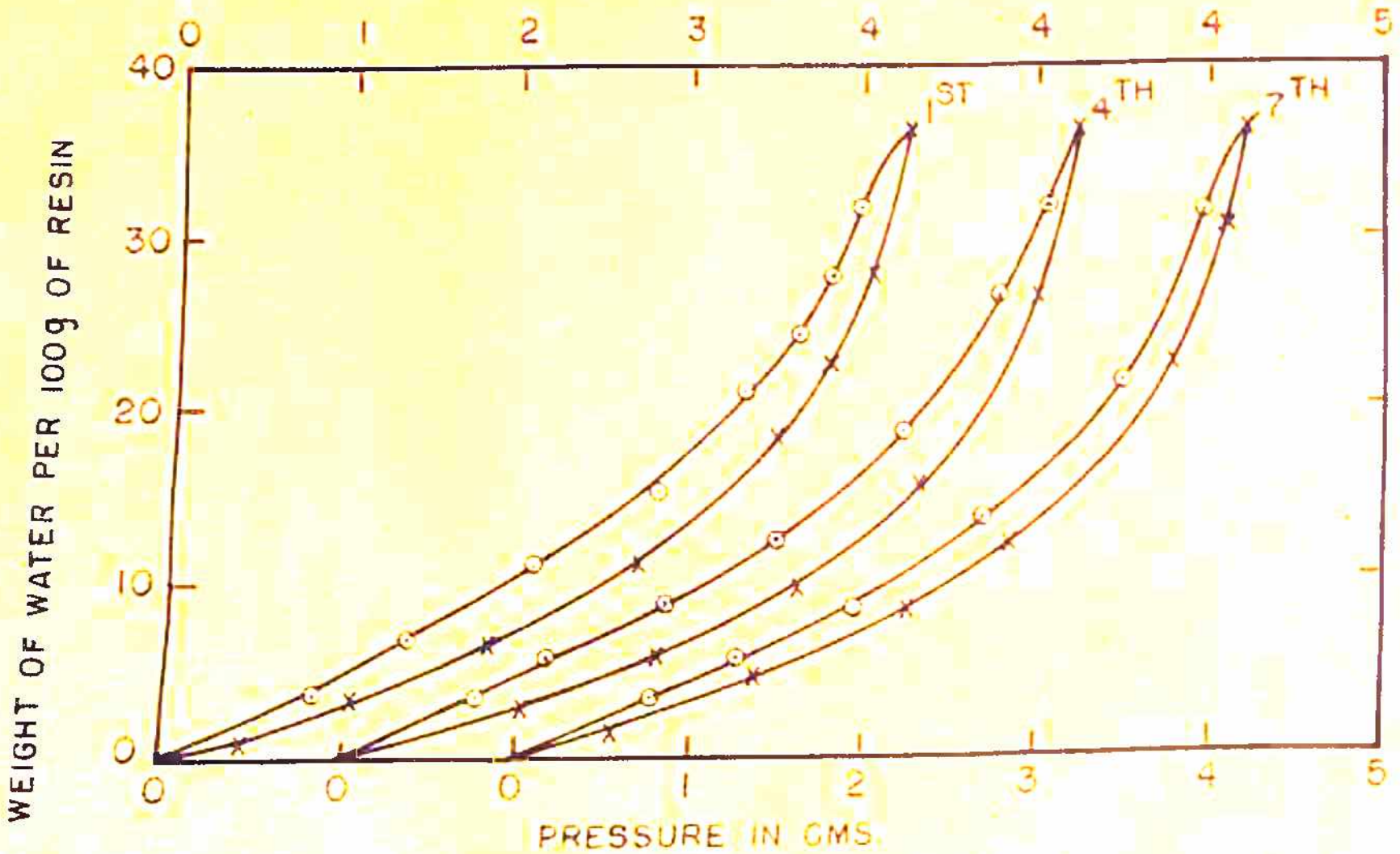

FIG. 1. SORPTION AND DESORPTION OF WATER ON AMBERLITE I RC-50 RESIN IN 1ST, 4TH AND 7TH CYCLES.

Amberlite IR-120 (Na^+ form)

It is strongly acidic cation exchanger having 8% divinyl benzene and sulphonic as ionogenic group[164].

Amberlite IRA-400

It is strongly basic anion exchange resin with 8% divinyl benzene[164]. Its ionogenic group is $- N(alkyl)_3^+$.

Amberlite IRA-410

It is also strongly basic anion exchanger with 6% divinyl benzene[164]. Its ionogenic group is $- N(alkylol)(alkyl)_2^+$.

The samples were used in the original spherical bead form and size was between those of 18 and 30 mesh British Standard Sieve. A series of sorptions and desorptions of water vapour on the samples was carried out.

Results

In the case of Amberlite IRC-50, the first fourth and seventh hysteresis loops obtained in the sorption and desorption of water are shown in Figure 1. The amount of water taken at saturation pressure is

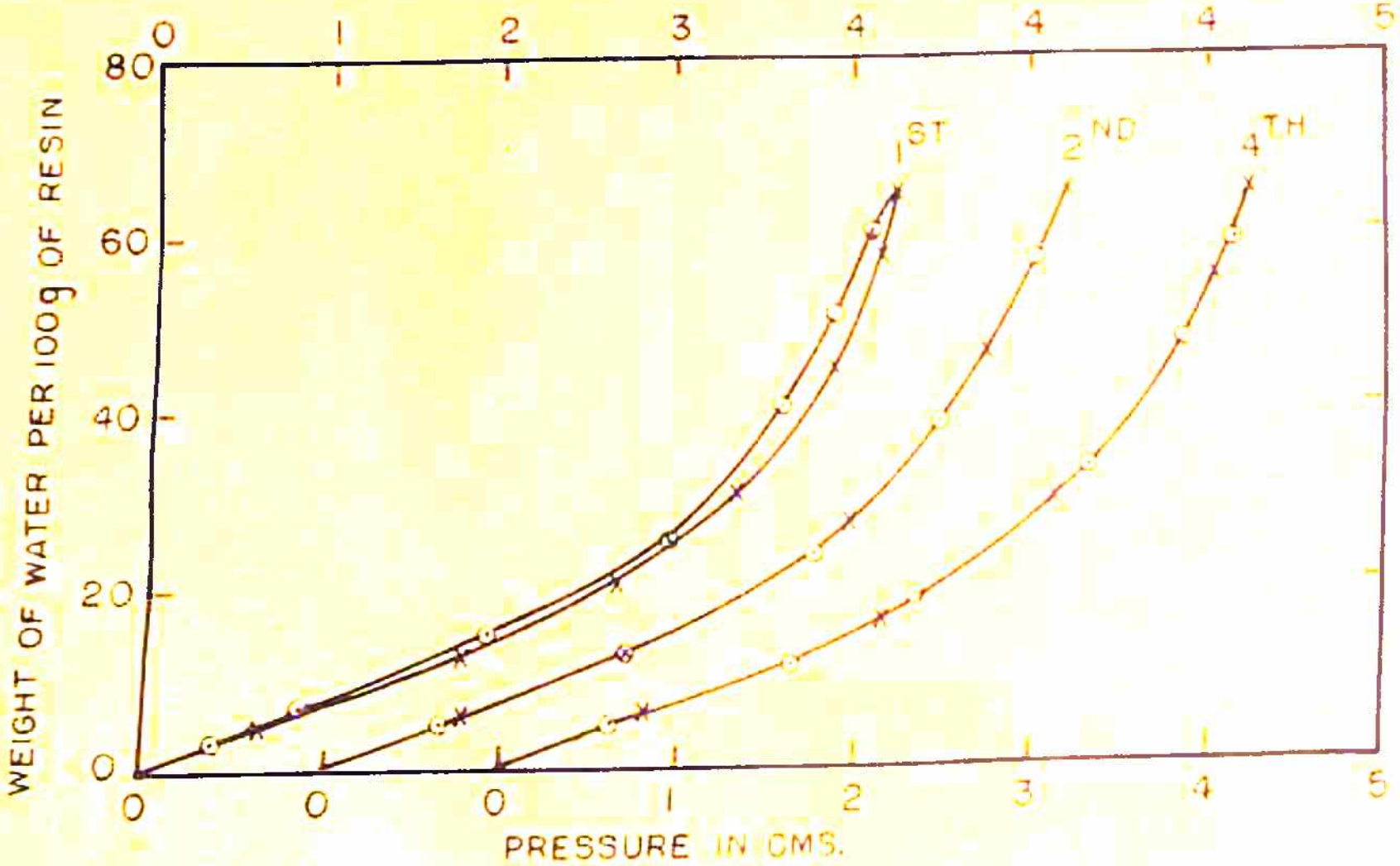

FIG. 2. SORPTION AND DESORPTION OF WATER ON AMBERLITE IR-120 (Na^+ FORM) RESIN IN 1ST, 2ND AND 4TH CYCLES.

36.2%. The sorption and desorption studies were continued upto the fourth cycle in case of Amberlite IR-120. The curves obtained in the first, second and fourth cycles are shown in Figure 2. The resin takes 64.5% of water at saturation pressure. With Amberlite IRA-400, Figure 3, the amount of water taken at saturation pressure in the first, second and third cycle is 64.5%. In the case of Amberlite IRA-410, Figure 4, the sorptive capacity in the first, second and third cycle at saturation pressure is 51.3%.

In all the systems, the resins were kept in contact with water vapour at saturation pressure for 2 days. In order to ensure complete equilibrium 10 hours were allowed between two consecutive readings, whereas actually 6 hours were sufficient for the attainment of equilibrium. The total period required for completing sorption - desorption studies in each case is about 25 days.

Discussion

In case of Amberlite IRC-50, hysteresis loop obtained in the first cycle of sorption and desorption of water persists. There is tendency for the decrease in size of the hysteresis loop from the first to seventh

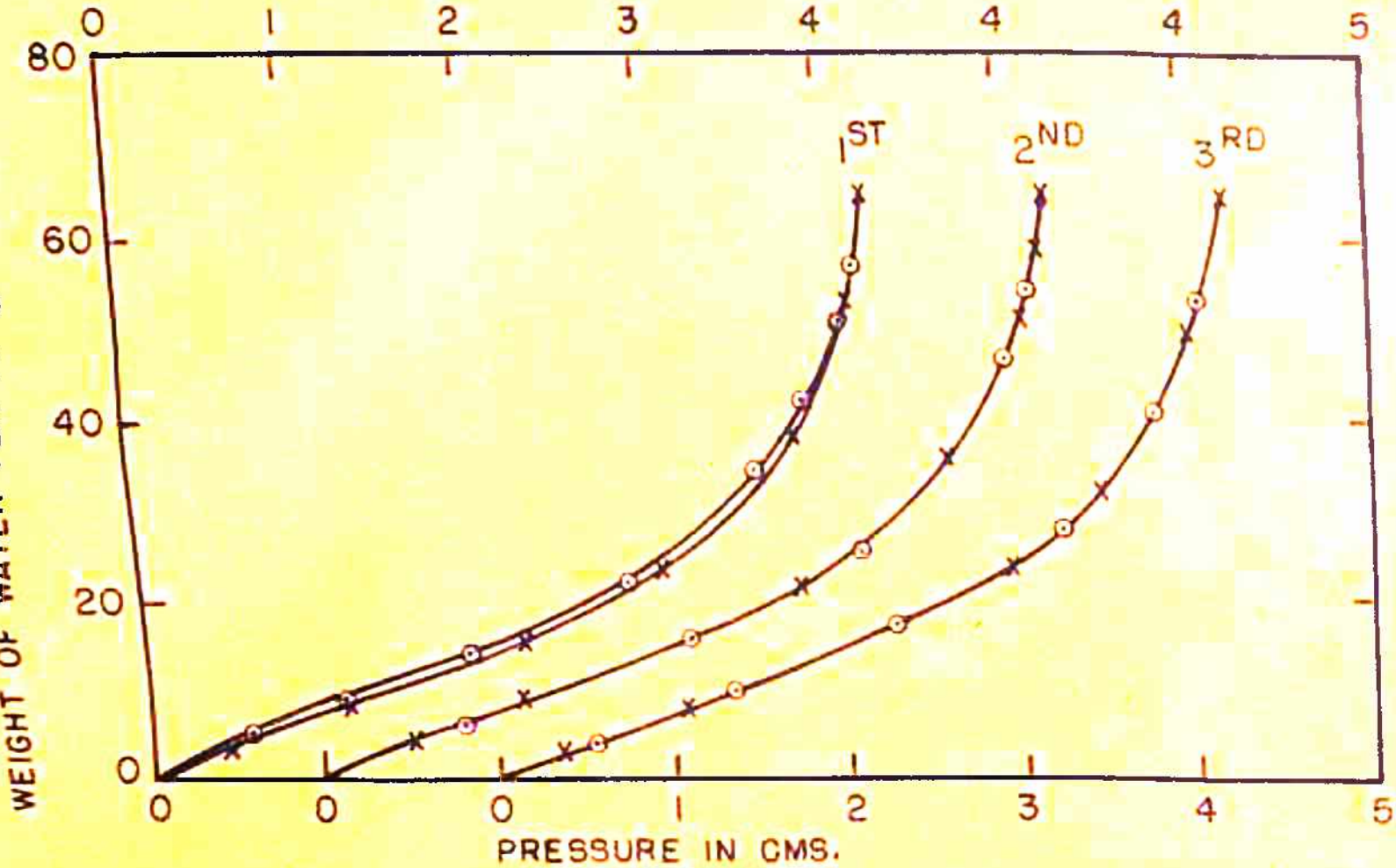

FIG. 3. SORPTION AND DESORPTION OF WATER ON AMBERLITE IRA-400 RESIN IN THE 1ST, 2ND AND 3RD CYCLES.

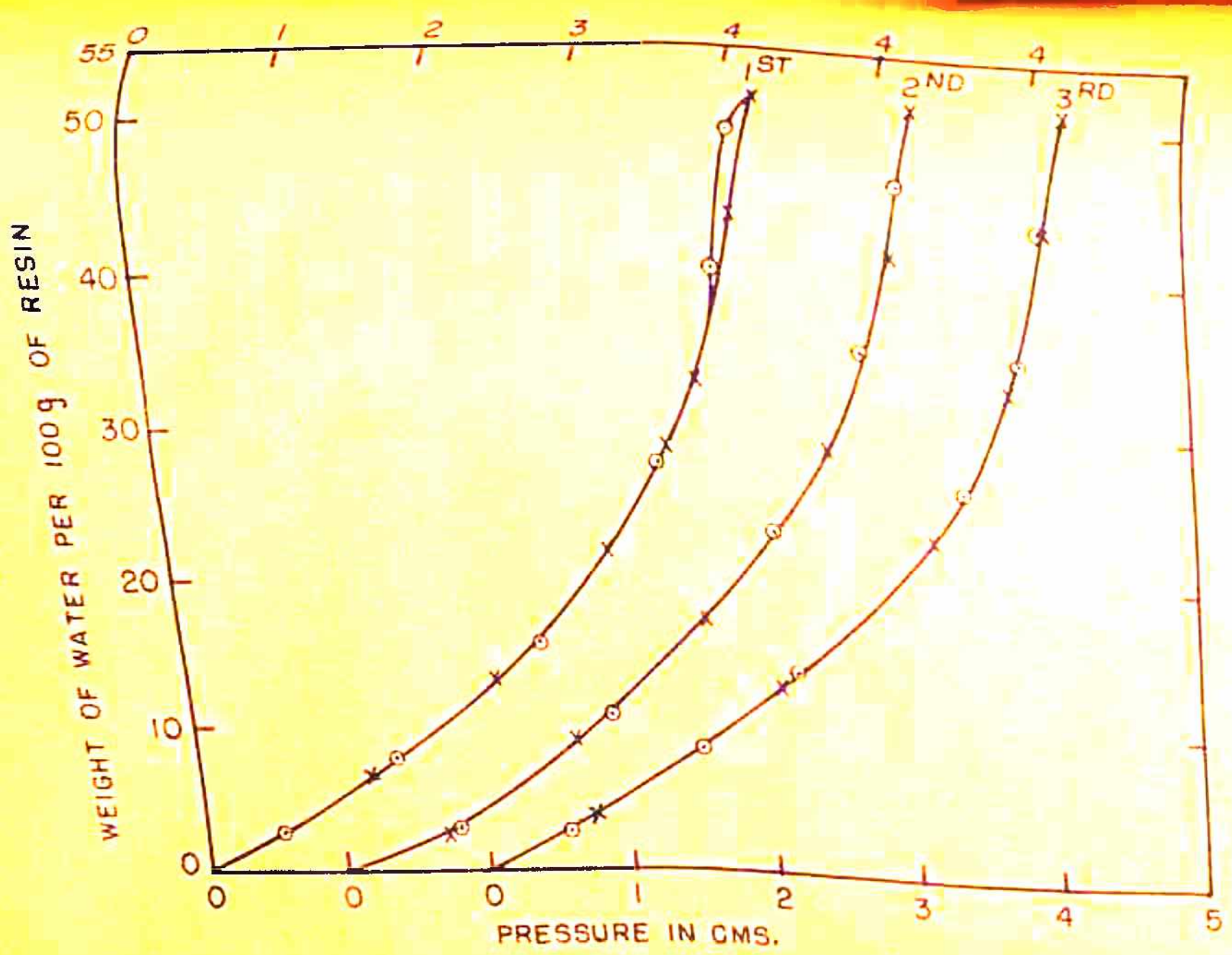

FIG. 4 SORPTION AND DESORPTION OF WATER ON AMBERLITE IRA-410 RESIN IN THE 1ST, 2ND AND 3RD CYCLES.

cycle. With Amberlite IR-120, hysteresis loop is obtained in the first cycle and this disappears in the second and fourth cycles. In the case of Amberlite IRA-400, there is hysteresis loop in the first cycle and the loop disappears in the second and third cycles. Similarly with Amberlite IRA-410, a small hysteresis loop is obtained in the high pressure region in the first cycle and it disappears in the second and third cycles.

All these results show either decrease in size or disappearance of the hysteresis loop on successive cycles of sorptions and desorptions of water and the results can be explained on the basis of the cavity theory in conjunction with the property of swelling of the sorbent 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 the hysteresis loop depend upon the extent of swelling

of the resin which in turn depends upon the degree of crosslinking. Resins swell more when their fixed ionogenic groups are completely ionized[165] and strongly acidic and basic resins are taken as more or less fully ionized under all conditions[166].

Degree of crosslinking of synthetic resin and its effect on sorption - desorption hysteresis

The sorptive capacities for water at saturation pressure of the four resins and the corresponding amounts of crosslinking agent - divinyl benzene used in the preparation of the resins are given in Table 1.

Table 1

Resin	Weight of water taken in gm per 100 gm of resin	Percentage of crosslinking agent (DVB)
Amberlite IRC-50	36.2	10
Amberlite IR-120	64.5	8
Amberlite IRA-400	64.5	8
Amberlite IRA-410	51.3	6

The degree of crosslinking of the resin depends upon the amount of the divinyl benzene used. Table 1

reveals that degree of crosslinking is in the order - Amberlite IRC-50 > Amberlite IR-120 = Amberlite IRA-400 > Amberlite IRA-410. It is also known that highly crosslinked resins have a lesser degree of swelling[167-170] because of greater number of crosslinks in the network. Hence the sorptive values should be in the reverse order, i.e., higher the degree of crosslinking, lesser the sorptive value and this has been found to be true excepting in the case of Amberlite IRA-410. These results are in conformity with the results of Gregor et al[163,168] who showed that the volume of swollen resin decreases with increasing crosslinking.

The tendency of the hysteresis loop to decrease in size and finally disappear depends upon the ease of collapse of the cavities present, which in turn depends upon the degree of swelling of the resin or in other words on the degree of crosslinking. In a resin of lesser crosslinking 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. Whereas in a resin of higher degree of crosslinking, the swelling is less, the cavities collapse less readily and hence the hysteresis loop persists over a larger number of cycles.

the resin is the highest 10%. Therefore the cavities collapse slowly and the hysteresis loop decreases in size continuously tending to completely disappear after a large number of cycles of sorptions and desorptions. Complete disappearance would have been observed if the studies were continued beyond the 7th cycle. However the above studies reveal that higher the degree of crosslinking, greater is the number of sorption and desorption cycles required for the complete disappearance of the loop.

The above results bring out clearly the relation between the tendency of the hysteresis loop to disappear in the sorption of water on resins and the degree of crosslinking of molecules in the resin.

The total sorptive capacity in each case has remained the same in all the cycles though the hysteresis loop has decreased and disappeared. This indicates that the total cavity volume is a very small fraction of the total sorptive capacity of the resin, which is mostly a case of hydration as in the case of egg albumin, casein and gelatin. Tager and his coworkers[171,172] have also obtained similar results while working with ion exchange resins. They have

pointed out that high sorptive value cannot be explained by its porosity but is associated with the ability of ion exchange resin to swell. However, Kanamaru et al[173] have inferred from their study on Amberlite IR-120 (- SO_3H type) that the pores in the resin have a mean radius of 50 - 100 A.

Gregor et al[163,170,174] and Dickel and Hartmann[175] have also noticed a small hysteresis effect in their studies with water vapour sorption with ion exchange resins. Gregor et al[174] have attributed the small hysteresis effect obtained below 0.1 relative humidity in the case of polystyrene sulphonic acid at 25° in the water vapour sorption, as due to short range order among the polymer chains. If the studies were continued by these authors in the second and subsequent cycles, probably the loops would have disappeared.

In the foregoing 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. Different varieties of gelatin, egg albumin and casein have shown this behaviour. Hydrolysed gelatin and hardened egg albumin and casein have behaved in the same way. Even synthetic ion exchange resins

have shown the same behaviour. These are all systems which swell in water. They all have a common molecular structural characteristic, i.e., intramolecular crosslinking. The crosslinks are mainly hydrogen and hydrophobic bonds in native proteins, methylene bridges in addition to the above in hardened proteins, and the crosslinking agent in synthetic ion exchange resins. The properties common to all these sorbents are hydration and swelling. The common structural feature is intramolecular crosslinking. The degree of crosslinking determines the extent of swelling and accessibility of polar groups to water molecules. These in turn determine the disappearance of the cavities and the disappearance of the hysteresis effect.

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CHAPTER VII: SORPTION - DESORPTION HYSTERESIS IN NATURAL GUMS

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SORPTION - DESORPTION HYSTERESIS IN NATURAL GUMS WITH WATER

Different classes of substances such as starch, protein, synthetic ion exchange resin and natural gum, all of which have 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 sorption - desorption cycles and the final disappearance. Calcium arabate has been studied by Rao[65] earlier. Elworthy and George[117] have studied sorption and desorption of water on sodium ghattate. In the present chapter the behaviour of some more natural gums (1) Gum Arabic or Acacia, (2) Prosopis Spicigera, (3) Ghatti and (4) Tragacanth gum has been presented.

Natural gums and their properties:

The true gums are generally divided into two main groups[176,177] (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 break down into a very thick translucent solution. The best known gums belonging to this group are gum tragacanth and the tragacanth substitute gums such as karaya, carob seed 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.

The following natural gums have been used in the present studies:

(1) Gum Arabic or Acacia, (2) Prosopis Spicigera, (3) Ghatti and (4) Tragacanth gum.

Gum Arabic

It is an exudate from the bark of acacia trees. It is a polyelectrolyte and its solutions are highly viscous and mainly a mixture of calcium, magnesium and potassium salts of arabic acid. The gum arabic molecule in structural complexity, is considered to stand between hemicellulose and the simple sugars. The molecular weight has been found to be of the order of 240,000.

Prosopis Spicigera gum

It is dark in colour, brittle and soft. It is not always entirely soluble in water but the gum swells and form jelly from the portion which is not easily soluble.

Gum Ghatti

It is an amorphous, translucent exudate of the Anogeissus latifolia tree of the Combretaceae family. The gum exudate occurs in rounded tears and has a glassy fracture. The colour of the exudate varies from very light brown to dark brown. The exact chemical structure of ghatti is not known but it is basically the calcium salt of ghattic acid. About 90% of it is soluble in water.

Gum Tragacanth

It is an exudate of the shrubs belonging to the genus Astragalus trees. It is a light coloured material which swells and partially dissolves in water. The soluble part is called tragacanthin and the insoluble portion is termed bassorin, the latter constituting 60 to 70% of the total. Gum tragacanth absorbs a large amount of water and swells greatly to form a soft adhesive paste but does not dissolve.

In the present work acacia gum (Pulvis acaciae)

of Stafford Allen and Sons Limited, London was used. Prosopis spicigera was collected by local persons of Thirpali near Pilani, Rajasthan. Gum ghatti (product of India) was of Johnson Limited, London. Tragacanth gum, imported stuff was 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 30 and 50 mesh BSS was chosen.

Composition and structure of the gums[178-180]

The plant gums are amorphous[178] substances containing carbon, hydrogen and oxygen and they are members of the carbohydrate group. However, in some cases evidence of crystallinity has been obtained[181]. The plant polysaccharide gums are hydrophilic substances and are neutral salts of complex polysaccharide acids, composed of hexose residues, uronic acid residues, pentose residues and methylpentose 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 uronic acid component (D-glucuronic acid) is present in the pyranose form. The hexoses 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 methylpentoses found in plant gums are L-rhamnose and L-fucose and these assume the pyranose structure.

The molecular structures of the plant gums rank amongst the most complicated 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 acacia belongs to galactan group in which 1 $\rightarrow$3 linkages are located largely in the main chains and 1$\longrightarrow$ 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 ghatti is also from the galactan group, which is built up of residues of D-glucuronic acid, D-galactose, D-mannose, L-arabinose and D-xylose with traces of L-rhamnose. In this gum inner chains of D-galactopyranose residues are joined by 1 $\rightarrow$ 6 linkages. Elworthy and George[182] have

shown by light scattering methods that ghatti gum molecules appear to be rod shaped. Gum tragacanth is a mixture of a neutral polysaccharide, an acidic polysaccharide and a glycosidic portion which appears to be a steriod. The acidic component, tragacanthic acid is an example of galacturonan group and is composed of D-galacturonic acid, L-fucose and D-xylose. Neutral polysaccharide contains mainly L-arabinose together with some D-galactose. The main chain is probably composed of 1 $\longrightarrow$ 4 linkages of D-galacturonic acid residues with other sugar residues attached to side chains.

The chemical behaviour and water solubility of the gums[179,183] depend on the presence of hydroxyl groups which can form intramolecular hydrogen bonding and hydrogen bonding with water molecules. Structures containing immense arrays of hydroxyl group, hold by hydrogen bonding large proportions of water molecules. These are removable with greater and greater difficulty as the process of drying goes on and hydrogen bonding between hydroxyl groups of macromolecules itself gradually replaces bonding with the solvent. At this stage a highly viscous syrup is produced which becomes hard and glasslike on further drying. The many possibilities

Figure 1. The amounts of water taken up at saturation pressure of water in the first, third, fourth and fifth cycles are 69.3, 74.2, 81.0 and 96.4% respectively. The total period required for the study was about two and a half months. With Prosopis spicigera, Figure 2, the sorption - desorption studies have been continued upto sixth cycle. The sorptive capacities in the first, second, fourth and sixth cycles are 101.8, 105.6, 115.5 and 120.5% respectively. The study took nearly two months. In the case of gum Ghatti, Figure 3, the sorption - desorption studies were continued upto seventh cycle. The sorption values at saturation pressure of water in first, second and seventh cycle are 61.0, 61.2 and 60.0% respectively. The total period required to complete this study is two months. In the case of Tragacanth gum, the sorption and desorption studies were continued upto the fourth cycle and the loops obtained are shown in Figure 4. The sorptive capacities in the first, third and fourth cycles are 127.5, 137.4 and 135.9% respectively. The total period for completing this study was two months. In each case and in all the cycles the gum was kept in contact with water vapour at saturation pressure for two days and in few cases for more than two days.

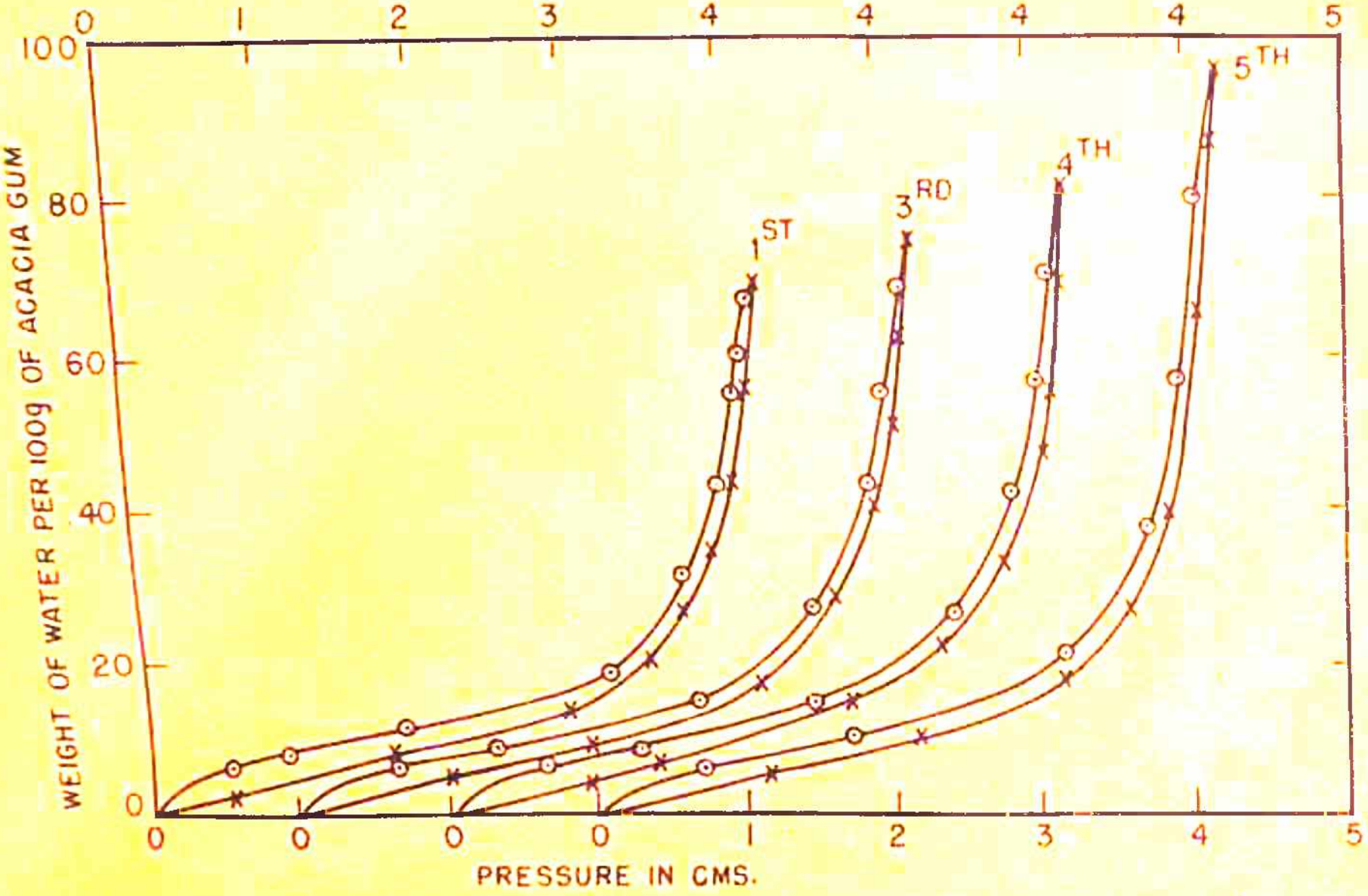

FIG. 1. SORPTION AND DESORPTION OF WATER ON ACACIA GUM IN 1ST, 3RD, 4TH AND 5TH CYCLES.

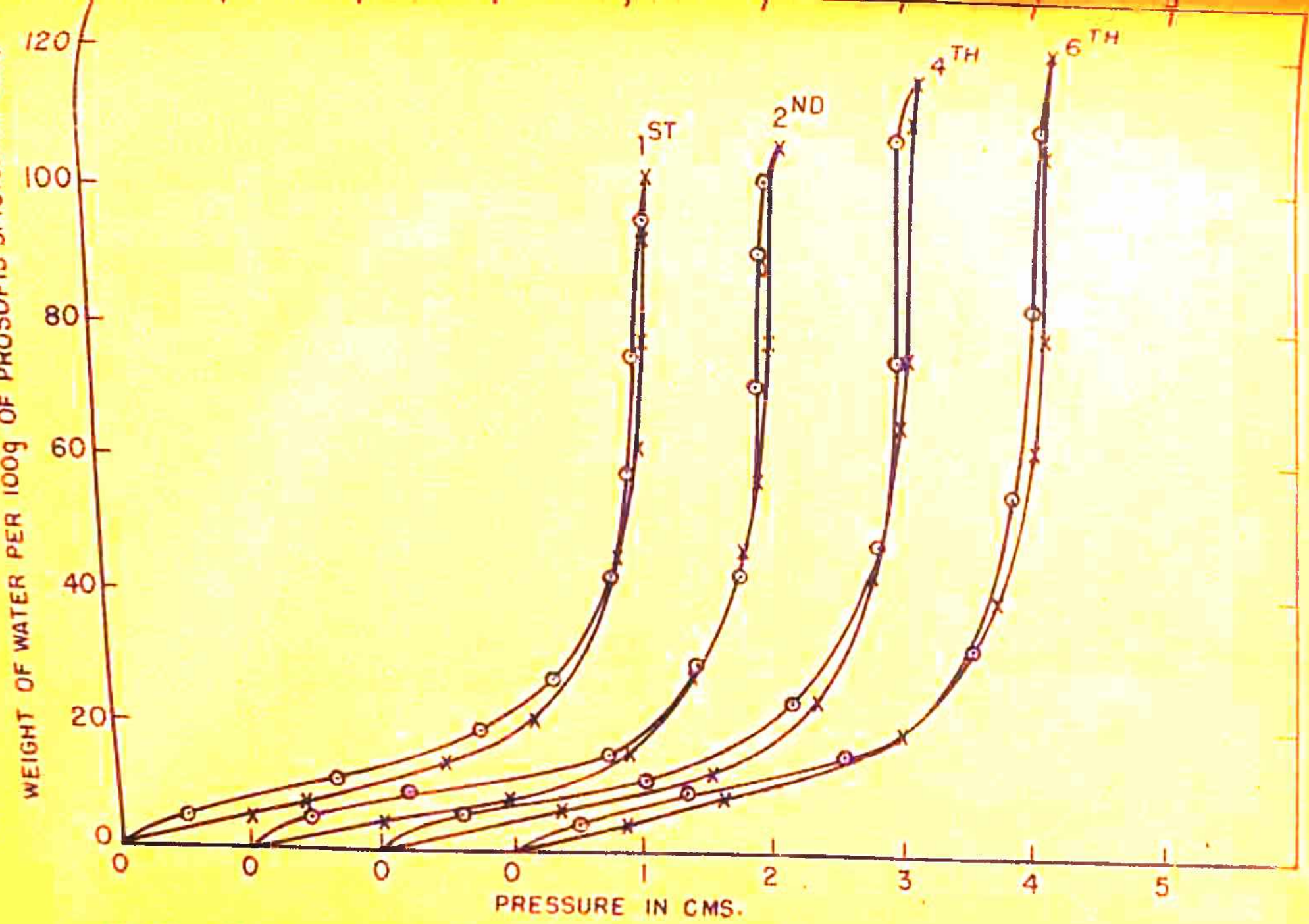

FIG. 2 · SORPTION AND DESORPTION OF WATER ON PROSOPIS SPICIGERA GUM IN 1ST , 2ND , 4TH AND 6TH CYCLES.

1526

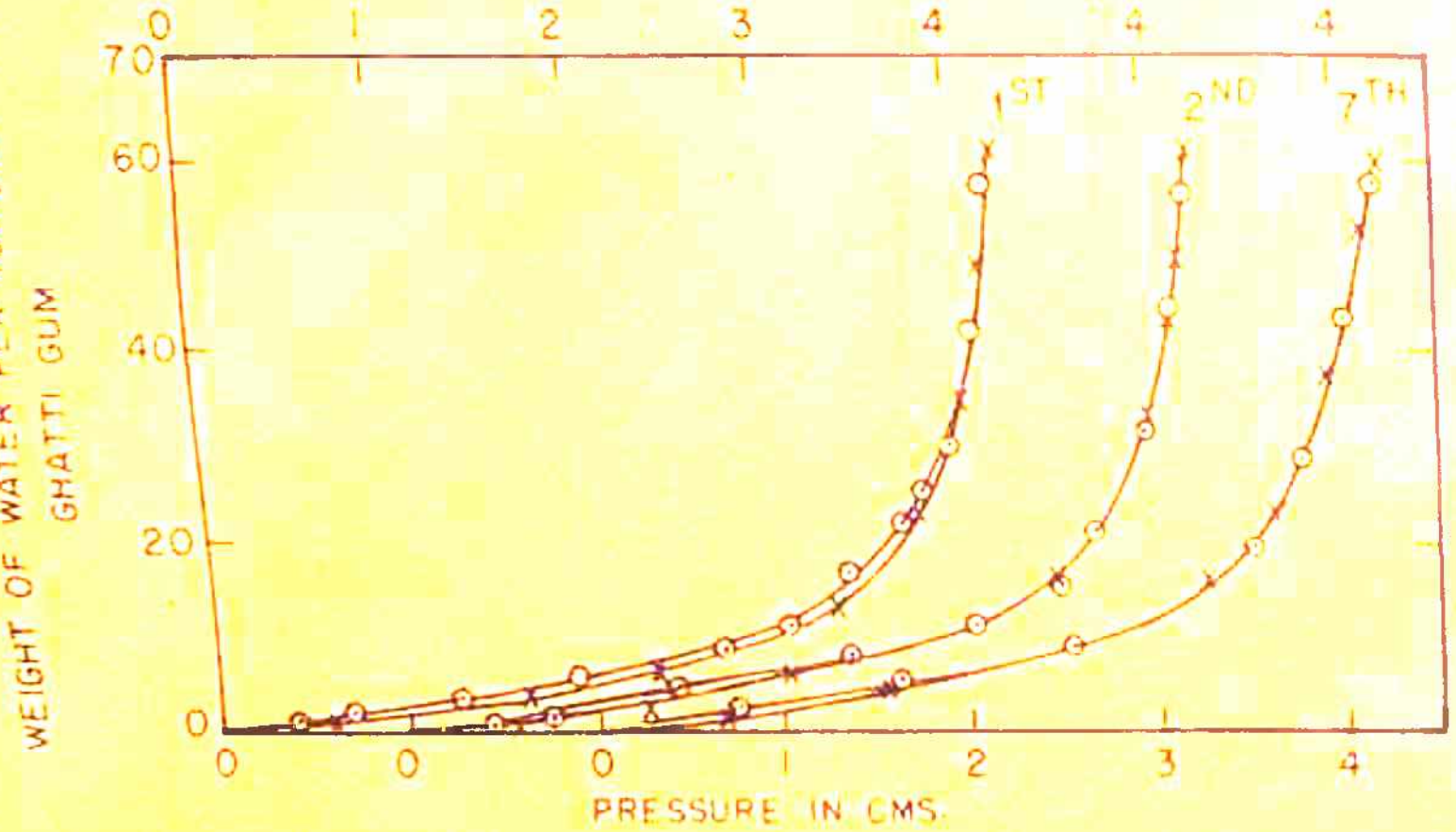

FIG. 3. SORPTION AND DESORPTION OF WATER ON GHATTI GUM IN 1^{ST}, 2^{ND} AND 7^{TH} CYCLES.

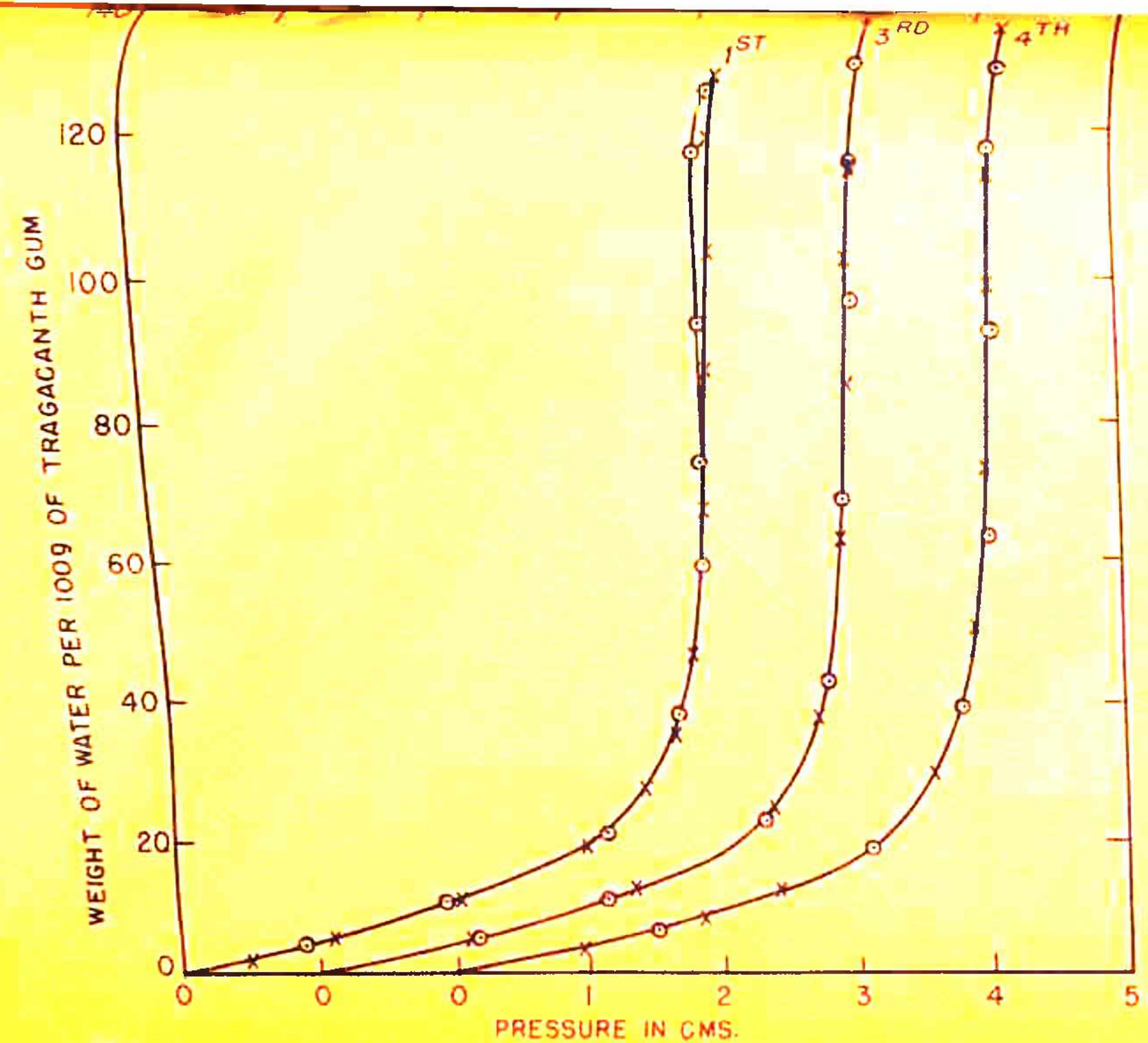

FIG. 2. SORPTION AND DESORPTION OF WATER ON TRAGACANTH GUM IN 1ST 3RD AND 4TH CYCLES.

152a

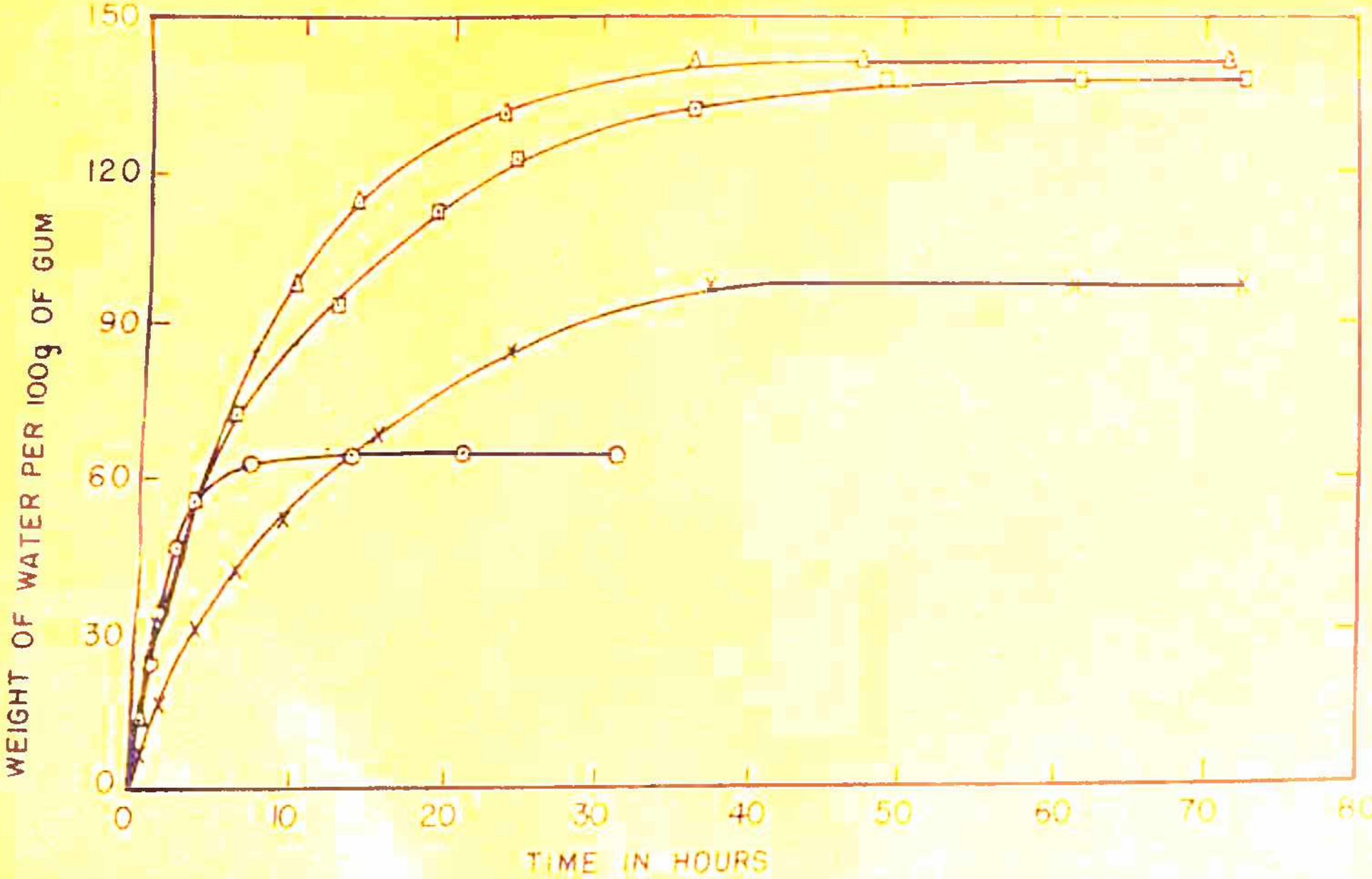

FIG. 5. TIME-SORPTION CURVE OF WATER AT SATURATION PRESSURE ON ACACIA X, PROSOPIS SPICIGERA Δ, GHATTI ⊙ AND TRAGACANTH GUM □.

Rate studies

Gums like other organo gels swell when they sorb water. In all swelling systems water sorption is a slow process. Incomplete equilibrium during sorption and desorption can cause hysteresis. To eliminate this effect, sufficient time was allowed till equilibrium is attained. Time - sorption curves of different gums are shown in Figure 5. At saturation pressure of water Acacia, Prosopis Spicigera, Ghatti and Tragacanth gums require 40, 40, 10 and 50 hours for completion of sorption of water respectively. At each intermediate point on the sorption and desorption curves the time required for equilibrium is about 8 hours except Ghatti gum (4 to 5 hours). But in all the cases about 10 hours were allowed in order to ensure complete equilibrium.

Discussions

In Acacia gum, the hysteresis loop decreases in the low pressure region from first to fifth cycle but the tendency to decrease is small. In the case of Prosopis Spicigera the hysteresis loop obtained in the first cycle of sorption and desorption also decreases in the lower pressure region from first to sixth cycle.

The hysteresis loop obtained in the first cycle of sorption and desorption of water on Ghatti gum decreases in second and seventh cycles and the sorption and desorption curves are coincident above relative vapour pressure of 0.5. With Tragacanth gum, the hysteresis loop obtained in the first cycle in the high pressure region, disappears in the third and fourth cycles.

All these results show either the disappearance of the hysteresis loop initially exhibited or the gradual and continuous decrease in size in successive sorptions and desorptions and the final disappearance. These results are in conformity with those already reported with many other organo gels. The 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 water but vary in degree of hydration and swelling. Hydration and swelling are determined by the number of polar groups (hydroxyl and carboxyl groups) which are the centres of hydration and the degree of intra and intermolecular crosslinking by hydrogen bonds. The polar groups of the macromolecules of the gums are accessible to water and this results in hydration 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 to water, quicker is the swelling and consequently the cavities disappear more easily and the hysteresis loop disappears in a fewer number of cycles or sorption and desorption.

In Acacia and Prosopis Spicigera gums the sorptive values increase continuously from first cycle onwards and there is small decrease in the size of the hysteresis loop in the lower 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 sorptions and desorptions are tried. Due to partial accessibility of the polar groups to water, swelling is restricted, thereby the cavities decrease in size slowly and hence the slow decrease in size and the disappearance of the hysteresis loop.

In the case of Ghatti gum the sorptive value remains practically the same from first to seventh cycle. 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. Therefore greater ease of disappearance of the hysteresis loop.

In gum Tragacanth, the small hysteresis loop in the high pressure region in the first cycle disappears in subsequent cycles. In third cycle the sorption value increases due to accessibility of the some of the more polar groups to water, which were not accessible to water in first cycle. The ease of swelling also increases, consequently cavities disappear more easily and hence the disappearance of the hysteresis loop.

The results presented in this chapter on the behaviour of the different natural gums in sorption - desorption hysteresis confirms the earlier generalisation 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 phenomenon 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 intra and intermolecular crosslinking. The accessibility of the polar groups to water molecules determines the ease of disappearance of the cavities and thereby the ease of disappearance of the hysteresis loop.

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C O N C L U S I O N S

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CONCLUSIONS

The main aspects of the studies in sorption - desorption hysteresis presented in this thesis are summarized below.

Varietal differences in gelatin, egg albumin and casein in relation to sorption - desorption hysteresis

A survey of the literature on the sorption and desorption of water on proteins show that either there is no hysteresis at all even in the first cycle of sorption and desorption or the hysteresis loop initially exhibited decreases in size in the subsequent cycles and finally disappears. In some cases the hysteresis loop persists even after a large number of cycles of sorption and desorption still showing decrease in size in successive cycles. These results indicate the possibility of varietal differences in proteins playing an important role in sorption - desorption hysteresis. To confirm this point of view, different varieties of proteins such as Difco and Oxoid gelatins, Merck's albumin ovi, Merck's alkali soluble casein and Oxoid casein hydrolysate were studied. Activated and denatured samples of egg albumin and casein were also studied. Water vapour was the common sorbate with all these samples. The hysteresis

loop initially exhibited in all the samples showed a tendency to decrease in size and finally disappear in the subsequent cycles. However, the tendency to decrease in size varied from sample to sample. The disappearance of the hysteresis effect has been explained in the light of the cavity theory of hysteresis in conjunction with the properties of hydration and swelling of gelatins, egg albumins and caseins with water. The decrease in size of the hysteresis loop and its disappearance are attributed to the gradual collapse of the cavities in successive cycles of sorptions and desorptions.

In the case of Difco and Oxoid gelatins, the hysteresis loop persists even beyond 12th and 10th cycles of sorption and desorption respectively, whereas Merck's gold label gelatin shows no hysteresis effect at all even in the first cycle. Merck's albumin ovi shows hysteresis effect which persists beyond 5th cycle with the loop size diminishing in each successive cycle, whereas Merck's soluble egg albumin shows hysteresis effect in the first cycle and the affect disappears in the 2nd and subsequent cycles. Similarly Merck's native casein has shown hysteresis loop in the 4th cycle, whereas Kahlbaum's casein nach Hammersten has a loop in the first cycle and it disappears in the 2nd and sub-

sequent cycles. These significant differences in the tendency of the hysteresis loop to decrease in size and disappear of the different varieties of gelatin, egg albumin and casein are closely related to their structures. The protein molecules are essentially polypeptide chains coiled into helix or spiral. The helical structure is stabilised by intramolecular hydrogen and hydrophobic bonding. Besides there are also intermolecular hydrogen and hydrophobic bondings between two or more neighbouring helical chains. The polar groups are the centres of hydration. The hydration capacity of the protein is determined by the number and nature of such hydration centres. The extent of swelling is restricted by the degree of intra and intermolecular crosslinking, which in turn restricts the hydration capacity also. The accessibility of the polar groups to water varies from sample to sample and this property accounts for the fact that certain varieties of proteins lose the hysteresis loops more easily than others. Thus the varietal differences in proteins are actually related to their molecular structure.

The Difco gelatin has shown unique and interesting behaviour. From the first cycle of sorption and desorption to the 12th cycle lasting over a period of

8 months, there is decrease in total sorptive capacity and the hysteresis loop in the low pressure region widens. These indicate that the cavity necks have shrunk more than the body resulting in increased entrapping effect.

Effect of hydrolysis of gelatin on sorption - desorption hysteresis

Proteins can be hydrolysed to amino acids by superheated steam. Three samples of gelatin hydrolysed at 100°C, 119°C and 133°C have been prepared from native Oxoid gelatin and sorption - desorption hysteresis with water has been studied. Hydrolysed gelatins have greater sorptive capacity for water and show greater tendency of the hysteresis loop to decrease in size and disappear than the native gelatin and the tendency increases as the temperature of hydrolysis increases. The disappearance of the hysteresis effect has been explained on the basis of the cavity theory in conjunction with the properties of swelling and shrinking.

Proteins are macromolecular substances yielding amino acids as major products of complete hydrolysis. Higher temperature bring about increased hydrolysis. As a result of hydrolysis, the number of polar groups which are the hydration centres, is increased and the

degree of intra and intermolecular crosslinking is reduced. Consequently the hydration capacity of the protein increases and the polar groups are more easily accessible to water molecules. Therefore the tendency of the cavities to collapse and the hysteresis loop to decrease in size and disappear is increased.

Native gelatin and gelatin hydrolysed at 100°C are nearly the same with regard to their behaviour in sorption and desorption hysteresis because there is no appreciable hydrolysis at 100°C. But at 119°C and 133°C there is increased hydrolysis. The hydrolysed gelatins have higher hydration capacities and greater tendency of the hysteresis loop to decrease in size and disappear. The highest decrease in size of the hysteresis loop has been observed with gelatin hydrolysed at 133°C and this is because at this temperature the breakdown of gelatin by hydrolysis is the highest. The number of polar groups produced is high, the degree of crosslinking low. Therefore the polar groups are easily accessible to water. Swelling is easy, the cavities collapse quickly and the tendency of the hysteresis loop to disappear is the highest.

Effect of hardening of proteins on sorption - desorption hysteresis

Proteins are hardened with formaldehyde and give an insoluble product with an increase in molecular weight. Hardening is a case of crosslinking of proteins by methylene crosslinks. These crosslinks may be intramolecular and promote the formation of cyclic structures or they may be intermolecular and promote the formation of molecular aggregates. As the degree of crosslinking increases, the extent of swelling decreases and the accessibility of the polar groups to water decreases. Consequently the tendency of the cavities to collapse and the hysteresis loop to decrease in size decreases.

Egg albumin and casein have been hardened with formaldehyde. The sorption - desorption studies were made with water vapour. The hardened samples show the hysteresis effect which persists in the subsequent cycles. Whereas, the native egg albumin and casein show hysteresis loop which decreases in size in the subsequent cycles of sorption and desorption. The results indicate that the hardened samples behave like a rigid gel and according to the cavity theory, the cavities have no tendency to collapse in contact with water and thus the cavities retain the entrapping effect. So the hysteresis loop persists even after a number of

cycles of sorptions and desorptions. Thus the tendency of the hysteresis loop to decrease in size and disappear is dependent upon the degree of crosslinking.

Sorption - desorption hysteresis in glassy and fibrous silica gels with normal aliphatic alcohols

Sorption - desorption hysteresis has been studied on glassy and fibrous silica gels (Santocel C of Monsanto Co., U.S.A.) with water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols. In all the cases permanent and reproducible hysteresis loops are obtained.

Bound sorbates and micropores:- At the end of first cycle of sorption and desorption, glassy silica gel retains irreversibly certain amounts of all the sorbates excepting carbon tetrachloride. The bound alcohols and water are attributed to the polar character of the molecules and the presence of micropores in the gel. The exceptional behaviour of carbon tetrachloride is due to its nonpolar character. The small amount of water held irreversibly in case of fibrous silica gel may be chemisorbed.

Monolayer capacities and specific surface:- The isotherms of the five alcohols on the two gels show clearly defined

knees followed by linear portion. Therefore by applying BET theory, monolayer capacities have been determined in each case. From these, the specific areas have been determined by assuming alcohol molecules to be spherical. The values of specific surface of glassy silica gel calculated bear good coincidence excepting the case of methyl alcohol. The value of specific surface of fibrous silica gel however does not coincide and goes on increasing from methyl to n-amyl alcohol.

Monolayer and oriented adsorption:- Therefore by assuming alcohol molecules as linear with its two possible modes of sorption, i.e., perpendicular and parallel to surface, the specific areas are calculated. The results indicate that in the monolayer on glassy silica gel, the molecules of sorbed alcohols are neither entirely perpendicular nor parallel to the surface. The percentages of molecules held perpendicular to the surface are calculated for ethyl, n-propyl, n-butyl and n-amyl alcohols and these are 100, 79.2, 79.5 and 70.5 respectively, by assuming that the specific surface of the gel is equal to what has been calculated for methyl alcohol. This assumption is justifiable in view of the fact that methyl alcohol molecule is almost cubical in shape.

In the case of fibrous silica gel, the sorbed molecules in the monolayer are all oriented and are held perpendicular to surface because the values of surface area for the different alcohols are almost the same.

Cohan's and cavity or ink bottle theories of sorption - desorption hysteresis:- Cohan's theory of hysteresis has been applied to the permanent and reproducible hysteresis loops by calculating the molecular diameter D from the point of inception of the hysteresis loop. The values obtained are higher and in some cases 3 to 6 times higher than D spherical calculated from molecular weight and density. These indicate the limitations of Cohan's theory.

However, the cavity or ink bottle theory explains in a qualitative way the hysteresis effect observed in all the cases and also the different aspects of hysteresis.

Pore size distribution and pore shapes in the gels:- The predominent neck and body radii of the cavities in the two gels have been determined. The results show the existence mainly of micropores in glassy silica gel and macropores in fibrous silica gel. The pores in the former gel are all ink bottle shaped and in the latter cylindrical.

Contact angles of alcohols in relation to sorption - desorption hysteresis:- With fibrous silica gel, the isotherm of methyl alcohol rises asymptotically to the saturation pressure ordinate. But from ethyl alcohol to normal amyl alcohol there is gradual deviation. The isotherm of normal amyl alcohol cuts the saturation pressure ordinate at an angle. In addition the sorptive capacities for normal butyl and normal amyl alcohols are much less, nearly one-third of the sorptive capacities for methyl, ethyl and normal propyl alcohols. These results indicate that the contact angle of methyl alcohol is zero, that of normal amyl alcohol has a definite value and that there is a steady increase in contact angle from methyl to normal amyl alcohol.

Sorption - desorption hysteresis in fibrous silica gel with isomeric aliphatic alcohols

The sorption - desorption studies with monohydric isomeric alcohols - Iso-propyl, Iso-butyl, Sec-butyl, Tert-butyl, Active amyl and Iso-amyl alcohols have been made on fibrous silica gel. Permanent and

reproducible hysteresis loops have been obtained in all the cases and the isotherms of all the alcohols have clearly defined "knees". By the application of BET theory, the monolayer capacities have been determined.

Cross sections of isomeric alcohol molecules:- Assuming oriented sorption of the isomeric alcohols with the OH group attached to surface and taking the specific surface area of fibrous silica gel as 58 m^2/g as calculated by assuming oriented sorption of the linear normal alcohol molecules perpendicular to surface in the monolayer; the cross-sections of the isomeric alcohol molecules have been calculated. Excepting Iso-propyl and Sec-butyl alcohols, all others have cross-sections greater than that of normal aliphatic alcohols. These higher values are to be expected in view of the side CH_3 groups. The exceptional behaviour of Iso-propyl and Sec-butyl alcohols is not clear.

Cohan's theory of hysteresis can not explain the observations satisfactorily, whereas cavity theory can explain all the cases of hysteresis. Similar to the isotherms of normal monohydric alcohols, the shapes of the isotherms of the different isomeric alcohols show an increase in contact angle from Iso-propyl alcohol to Iso-amyl alcohol. Isomeric alcohols of low contact

angle have high sorption values at saturation pressure and alcohols of high contact angles have low sorption values.

Effect of activation temperature on sorption properties of fibrous silica gel

The effect of activation temperature of fibrous silica gel on its sorptive properties has been studied. Gels activated at 250° and 450° have been used. Water, carbon tetrachloride, methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols have been used as sorbates. At the end of first cycle of sorption and desorption, certain amount of water is irreversibly held and this is probably due to chemisorption. By the application of BET theory to the sorption isotherms of the five normal aliphatic alcohols, the monolayer capacities have been determined. The two gels have the same monolayer capacities. From the monolayer capacities, the specific surface has been calculated assuming separately the molecules to be spherical, and linear with its two modes of oriented sorption perpendicular, and parallel to surface. The results indicate oriented sorption of the aliphatic alcohol molecules perpendicular to surface in the monolayer on both the silica gels activated

at 250° and 450°. The specific surfaces of the two gels are practically the same. Increase of temperature from 250° to 450° has not produced any change in the specific surface.

The permanent and reproducible hysteresis loops are obtained with both the gels. Cohan's theory of hysteresis is not able to explain the results satisfactorily. The shapes of sorption and desorption isotherms and the position of the hysteresis loop of the different normal alcohols are the same for the two gels. Hence the pore size distribution in the two gels is the same. Increase in the temperature of activation has not brought about any appreciable change in the fibrous silica gel.

Sorption - desorption hysteresis in synthetic ion exchange resins

The four resins - Amberlite IRC-50, IR-120, IRA-400, IRA-410 having crosslinking with 10, 8, 8 and 6% divinylbenzene respectively have been used. All the resins show decrease in size and disappearance of the 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 as described in the case of proteins. The sorptive value at saturation pressure decreases as the degree of crosslinking increases. However, Amberlite IRA-410 is an exception to the series. The degree of crosslinking determines the extent of swelling and the accessibility of the polar groups of the resin to water molecules. Higher the degree of crosslinking, lower is the extent of swelling. Hence the loop persists in Amberlite IRC-50 even beyond 7th cycle whereas it disappears in all other resins. In other words the tendency of the hysteresis loop to disappear in the sorption of water on resins depends upon the degree of crosslinking of molecules in the resin.

Sorption - desorption hysteresis in natural gums

The natural gums - Arabic, Prosopis Spicigera, Ghatti and Tragacanth gums have been used in sorption - desorption studies with water. All the gums show decrease in size and disappearance of the hysteresis loop on successive cycles of sorptions and desorptions of water. Gum Ghatti and Tragacanth show greater tendency of the hysteresis loop to decrease in size and disappear than gum Acacia and Prosopis Spicigera. This difference in the tendencies is related to the structure of gums.

Gums have highly complicated branched structures involving several different sugar residues. Water solubility of the gums depends on the presence of hydroxyl groups, structures containing immense arrays of hydroxyl groups hold by hydrogen bonding large proportions of water molecules. In dry gum the bondings with water are replaced by intramolecular hydrogen bonding between the hydroxyl groups. The degree of this intramolecular bonding in the dry gum determines its tendency of the hysteresis loop to decrease in size and disappear. Greater the degree of intramolecular cross-linking, lesser is the tendency and the gum shows hysteresis loop persisting even after a large number of cycles of sorption and desorption.

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