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ORIENTED ADSORPTION OF ALIPHATIC NORMAL ALCOHOLS IN THE MONOLAYER ON FIBROUS SILICA GEL

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THE subject of adsorption is one of the oldest and yet it has remained new in view of the voluminous amount of researches which are being published. The adsorbent and adsorbate materials used by different workers are numerous and varied in composition and the adsorption isotherms obtained have large variety of shapes. The BET classification[1] of the different isotherms into 5 typical categories has been a distinct advance and simplification. On the theoretical interpretation of adsorption, at the time when Langmuir looked upon adsorption as purely monomolecular and Zsigmondy, McGavack and Patrick as purely capillary condensation, neither of them being completely successful in explaining all the diverse facts of adsorption, the multimolecular adsorption theory proposed by Brunauar, Emmett and Teller has been a furthed advance in the subject. The sorption-desorption hysteresis has still remained a vexed and unsolved problem.

Monsanto Company, U.S.A., has produced a new form of silica ærogel of trade name Santocel C. This is a fine loose dusty powder, white in colour. Its air volume is 94%.[2] The particles are composed of submicroscopic fibres of 25 to 35 Å diameter and approximately 330 Å apart with a specific surface of 600 sq. m. per gm. This product is essentially meant for use as a flatting agent in protective and decorative coatings.[3] It has been used by Puddington[4] in making stopcock lubricant in glycerine for organic vapours. This new form of silica-fibrous silica gel (Santocel C) has been used as the adsorbent and methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols as adsorbates in the present study of the nature of adsorption in the monolayer and sorption-desorption hysteresis.

Quartz fibre spring technique[5] has been employed in the present investigations. Fibrous silica gel was heated to 250° C. for 2 hrs. in order to remove any organic vapour and the activated gel was used in studying a series of sorptions and desorptions of the aliphatic alcohols at 35° C. The study was continued upto 3rd or 4th cycle. In each system there has been permanent and reproducible hysteresis loop and the loops have been presented in Fig. 1 in which the volume of alcohol adsorbed per 100 gm. of gel is plotted against the relative vapour pressure of the alcohol.

The isotherms of all the five alcohols have clearly defined "Knees". According to BET theory, the "Knee" signifies the transition from monomolecular to multimolecular adsorption. By the application of BET equation to the isotherms, the monolayer capacity for each alcohol is determined. From the monolayer capacity and knowing the cross-section area of the alcohol molecule, the specific surface of the fibrous silica gel has been calculated. There are three possible values for the cross-section depending upon the shape of the molecule and mode of adsorption. The molecule may be assumed to be spherical and the diameter D spherical[6] and the cross-section are obtained from molecular weight and density. The alcohol molecule being linear, there are two modes of oriented adsorption perpendicular and parallel to surface. The cross-section of the linear molecule is $(4{\cdot}55)^2$ Å^2. Knowing

the total volume of the molecule D^3 spherical, the length of the molecule and also the area along the length of the molecule are calculated. The values of the three different cross-sections are shown in Table I. The values of the specific surface calculated for these 3 cross-sections are also shown.

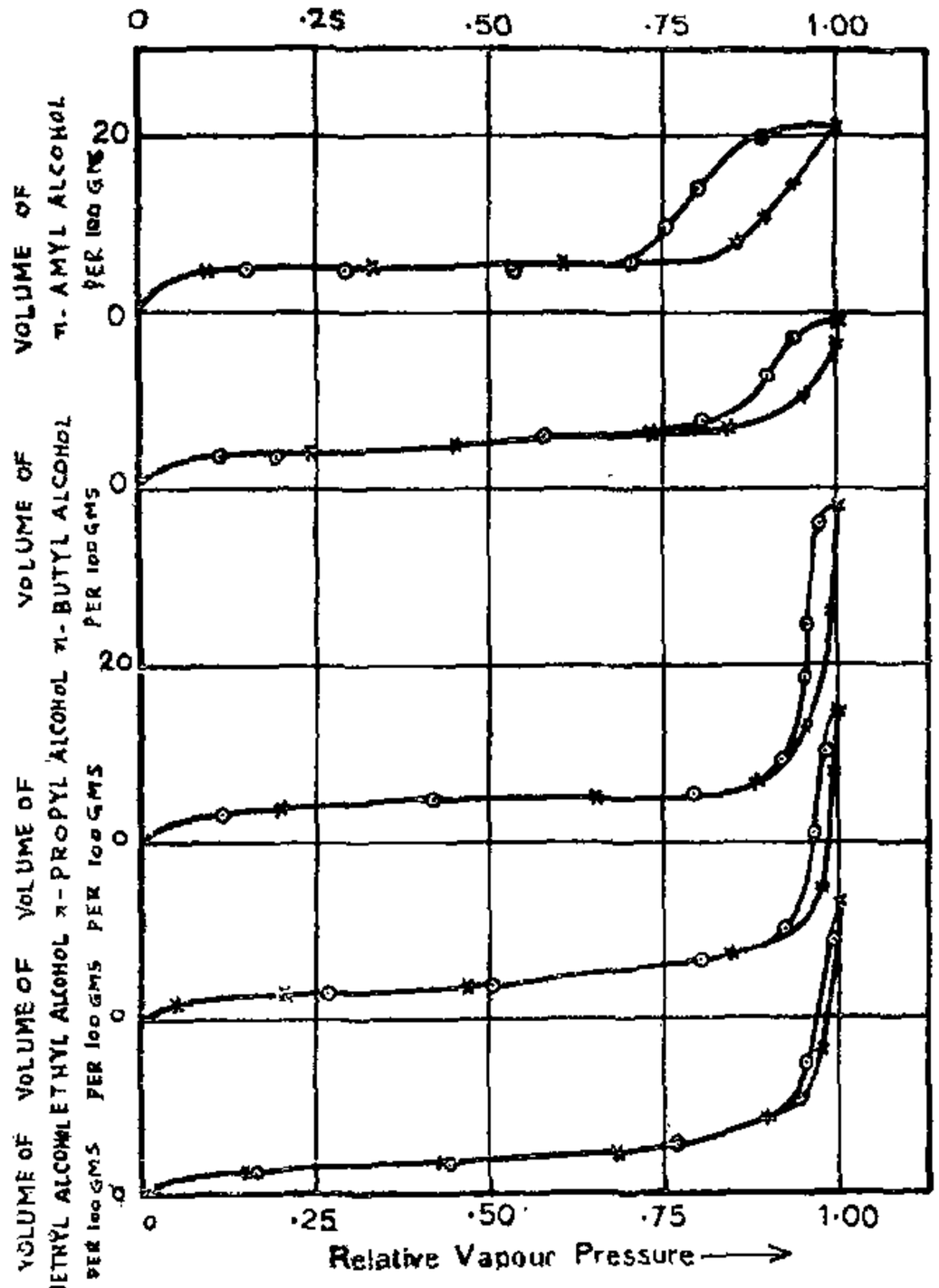

FIG. 1. Sorption and desorption on fibrous silica gel (Santocel C) of methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol and *n*-amyl alcohol.

Assuming the alcohol molecules to be spherical, the specific surface areas are calculated for the 5 alcohols and these are not the same. The value increases from methyl to *n*-amyl alcohol. Assuming the molecules as linear and oriented adsorption perpendicular to surface, the specific surface areas calculated are all nearly the same. Assuming oriented adsorption parallel to surface, the specific surface areas obtained are not the same. The value increases from methyl to *n*-amyl alcohol. It follows from these results that adsorption of the five linear aliphatic normal alcohol molecules is completely of oriented type and the molecules are held perpendicular to the gel surface.

The shapes of the adsorption isotherms of the alcohols are significant. After the initial adsorption due to the formation of monolayer there is no appreciable increase in adsorption with increase in relative vapour pressure upto about 0·75. Above this, there is steep rise. These indicate that pores in fibrous silica gel are mainly macro and surface open. On such a surface completely oriented adsorption is easily possible whereas in micropores it is likely to be obstructed. The existence of completely oriented adsorption of the alcohol molecules on the surface of fibrous silica gel is indeed a very interesting and striking conclusion. Evidences of oriented adsorption of molecules on solid surfaces are not many, though oriented adsorption of molecules in films on liquid surface is well known and well established.

The permanent and reproducible hysteresis loops obtained with the five alcohols are explained in the light of the ink bottle or cavity theory[5,7] of hysteresis. Sorption-desorption hysteresis is due to entrapping of liquid sorbate by cavities with constricted necks. According to cavity theory of hysteresis, every point on the sorption curve enclosing the hysteresis loop denoted the cavity radius and every point on the desorption curve cavity neck radius. The point of inception of

TABLE I

Specific surface of fibrous silica gel considering alcohol molecules as spherical and linear

	Molecule as spherical		Molecules as linear		Specific surface in m^2 per gm. of gel		
	Diameter D spherical in Å	Cross-section in $Å^2$	Cross-section in $Å^2$	Area of side in $Å^2$	Molecules as spherical	Linear molecules perpendicular to surface	Linear molecules parallel to surface
Methyl alcohol ..	4·6	21·2	20·7	21·4	65·5	64·1	66·3
Ethyl alcohol ..	5·2	27·0	20·7	30·9	63·4	48·5	72·4
n-Propyl alcohol ..	5·6	31·4	20·7	38·5	86·7	57·2	106·8
n-Butyl alcohol ..	6·0	36·0	20·7	47·5	103·4	59·4	136·2
n-Amyl alcohol ..	6·3	40·2	20·7	55·0	175·4	57·3	152·0

the hysteresis loop indicates the smallest neck radius. In fibrous silica gel, the smallest neck radius and the predominant body and neck radii of cavity are 31·0, 380·0 and 150·0 Å respectively. According to de Boer's classification[8,0] of hysteresis loops, the hysteresis loop of fibrous silica gel is of type A and the capillaries in the gel are cylindrical in shape.

There has been a gradual variation in the shape and shift in the position of the hysteresis loop and decrease in total sorptive capacity at saturation pressure from methyl alcohol to *n*-amyl alcohol. The isotherm of methyl alcohol rises asymptotically to the saturation pressure ordinate whereas the isotherm of *n*-amyl alcohol cuts the saturation pressure ordinate at an angle. The volumes of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl alcohols taken are 33·0, 33·3, 38·7, 19·0 and 21·0 c.c. per 100 gm. of gel respectively.

Gregg[9] has discussed the effect of contact angle of the sorbate on the shape of the sorption isotherm. In the application of Kelvin equation to sorption isotherm, the contact angle is ordinarily assumed to be zero, if the surface is free from impurities. This is true of liquids like water whose contact angle is zero and whose isotherm is asymptotic to the saturation pressure ordinate. But with liquids which have definite contact angle, the isotherm intersects the ordinate at an angle. The asymptotic nature of methyl alcohol isotherm indicates almost indefinite large uptake of sorbate at saturation pressure. From this the contact angle of methyl alcohol on the gel surface may be assumed to be zero. The interception of the *n*-amyl alcohol isotherm at an angle with the saturation pressure ordinate indicates the existence of a definite contact angle. Considering the gradual changes in the shapes of sorption and desorption isotherms, the hysteresis loops, the total sorption value at saturation pressure of the five alcohols—methyl, ethyl, *n*-propyl, *n*-butyl and *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 values of contact angles of the five alcohols could not be obtained. Fox and Zisman[10] 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[11,12] of the 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° C. 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.

The foregoing studies reveal the existence of oriented adsorption of alcohol molecules in the monolayer on the surface of fibrous silica gel and the effect of contact angle of the alcohols on the shapes of the isotherms and the hysteresis loops.

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