CCIII.—*Adsorption by Silicic Acid Gel in the System* n-*Butyl Alcohol–Benzene.*

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IN a subsequent paper the adsorption by silicic acid gel of the aliphatic alcohols in a number of solvents will be described. The system *n*-butyl alcohol–benzene was chosen for a more detailed study throughout the whole concentration range because one of us had already developed a good method of analysis, the absence of which has hitherto constituted the chief difficulty in work, such as this, involving both very dilute and very concentrated solutions.

The results obtained are discussed in the light of Williams's equation (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 23), and a method has been devised of obtaining what he regards as the true adsorption, in the case of silicic acid gel, without further experimentation. This method has been confirmed by vapour-adsorption experiments. The results are in agreement with the view of Ostwald and Izaguirre (*Kolloid Z.*, 1922, **30**, 279), *viz.*, that the apparent adsorption can be satisfactorily interpreted if the true adsorption of each component is expressed by a Freundlich isotherm. The difference between the value of the true adsorption according to the equation of Williams and that of Ostwald and Izaguirre, is attributed to capillary adsorption. The concentration of the solution thus adsorbed is now shown to be equal to that of the equilibrium solution, in agreement with theory.

EXPERIMENTAL.

Preparation of Silicic Acid Gel.—The gel used in these experiments was prepared by a method similar to that of McGavack and Patrick (*J. Amer. Chem. Soc.*, 1920, **42**, 951). Water glass of good quality was diluted with distilled water to a specific gravity of 1·185, and added to an equal volume of hydrochloric acid solution (10% by weight of hydrochloric acid). These were thoroughly stirred during mixing, and for 5 minutes afterwards, by a high-speed electric stirrer. The solution, protected from atmospheric impurities, was left to set. After 24 hours it was a thin jelly, and after 48 hours it had become firm and slightly opalescent. The gel, broken up into fairly big pieces, was placed in a large Büchner funnel attached to a filtering flask, and a stream of water was passed upwards through it. Initial washings were done with tap water, which had previously passed through tubes containing silica gel, and the final washings with distilled water. (No alkali must be allowed to come into contact with the gel.) Washing was continued until, on boiling a sample of gel with distilled water, a negative test for chloride was given with silver nitrate. The gel was drained on a cloth filter and allowed to dry slowly in the air for a week or so, being carefully protected from dust. At the end of this time, it was further dehydrated by heating in a porcelain container in an electric oven at 100° for 24 hours. The material now had the same semi-opaque appearance as the activated gel, and was broken up in a mortar, and sieved to pass all particles between 18 and 30 to the inch.

Activation of the Gel.—The gel was placed in a wide tube in an air-oven, heated to 150°, and dried by a slow stream of dry, carbon dioxide-free air. After 3 hours' activation, it was allowed to cool in the air current, and then stored in bottles having well-ground stoppers and kept over anhydrous calcium chloride.

Determination of Water Content.—The water content of the activated gel was determined by heating a weighed quantity in a platinum crucible in a bench muffle furnace over a Mèker burner : over 50 hours' heating at bright red heat was required for the expulsion of all the water, the final loss of weight corresponding to a water content of 5·20%. At the end of the adsorption experiments, a further determination gave a value of 5·27%. This small change would not affect the adsorption, since it has been shown that the adsorptive capacity of silica gel remains constant over a considerably wider range of water content than the above (Jones, *J. Physical Chem.*, 1925, **29**, 326).

n-*Butyl Alcohol.*—This was fractionally distilled. The material used gave, with aqueous hydrochloric acid, the critical solution temperature of the pure material (Jones, J., 1929, 799).

Benzene.—Kahlbaum's benzene "for analysis" was shaken with concentrated sulphuric acid until the latter gave no coloration. The product was washed with water, then with dilute caustic soda solution, and again with water, dried over calcium chloride, and fractionated through a column of the type used by Clarke and Rahrs (*J. Ind. Eng. Chem.*, 1923, **15**, 349). The product had m. p. 5·45°.

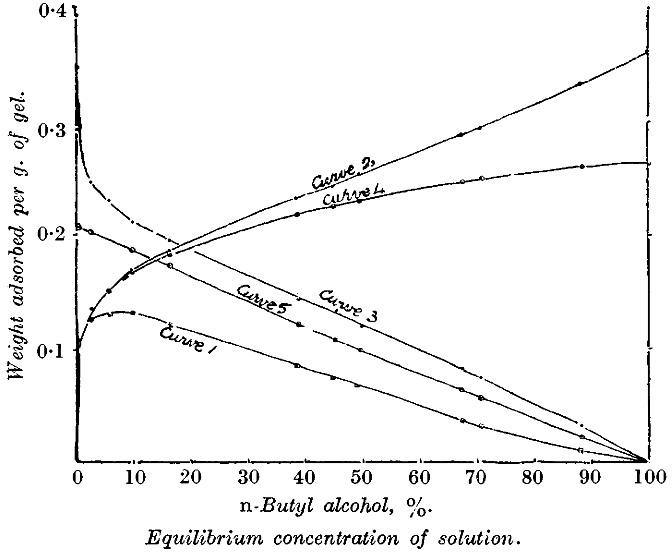
Adsorption Determination.—The adsorption was carried out in tubes of an inverted T shape, having a volume of about 40 c.c. A known weight of the gel was introduced from a weighing bottle into the weighed tube, and 25 c.c. of a previously analysed solution were added. The tube was quickly drawn off and sealed at a constriction. By reweighing the tube, the weight of solution could be calculated. The tubes were shaken for 24 hours, in the direction of their length, in an electrically heated and controlled air thermostat, kept at 27° ± 0·01°. They were then opened, and samples of the equilibrium solution were removed by a pipette and analysed by the critical-solution-temperature method especially devised (Jones, J., 1923, **123**, 1392).

Calculation of the Adsorption.—The apparent adsorption per g. of the adsorbent (x/m) at various values of the equilibrium concentration is given in Table II, col. 2, and shown graphically in Curve 1, Fig. 1. These values are obtained from the relation

$$x/m = M(C_0 - C)/100\,G \quad . \quad . \quad . \quad . \quad (1)$$

where M is the initial mass of the solution, G the weight of gel used, and C_0 the initial and C the equilibrium concentration of n-butyl alcohol per 100 g. of solution, all weights being in grams. It is evident from the results that (a) the alcohol is always positively selectively adsorbed throughout the concentrations examined, *i.e.*, the adsorbed solution is always richer in alcohol than the equilibrium solution, and (b) the curve passes through a maximum at $C = ca.\ 12$, reaching zero values for x/m at $C = 0$ and 100. No region occurs, in the high equilibrium concentrations of alcohol, where there is a negative selective adsorption of the alcohol, as there is of the acid in the case of charcoal–benzene–acetic acid investigated by Schmidt-Walter (*Kolloid Z.*, 1914, **14**, 242).

FIG. 1



Curve 1. *Apparent adsorption of* n-*butyl alcohol* (x/m).
,, 2. *Adsorption of* n-*butyl alcohol*, U_W } *Calculated according to Williams's*
,, 3. ,, ,, *benzene*, W_W } *equations* (*modified*).
,, 4. *Values of* $U = KC^{1/n}$. } *True adsorptions.*
,, 5. ,, ,, $W = L(100 - C)^a$. }

Williams (*loc. cit.*) pointed out that the value of the adsorption as calculated from equation (1) represented the truly adsorbed quantity of solute only on the assumption that the mass of the unadsorbed solution remained unchanged before and after adsorption. If no solvent (second component) were adsorbed, the correct expression for the adsorption of the solute per g. of adsorbent would be

$$U_0 = M(C_0 - C)/G(100 - C) \quad . \quad . \quad . \quad . \quad (2)$$

If adsorption of the solvent occurs, then the true adsorption of the first component (U) and of the second component (W) per g. of adsorbent is given by the equation

$$U = U_0 + WC/(100 - C) \quad . \quad . \quad . \quad . \quad (3)$$

In order, therefore, to determine the values of U and W, the two unknowns in this equation, it is necessary to have a second relation between them. One such relation, which was suggested by Williams (*loc. cit.*), could be obtained by allowing the adsorbent to remain in contact with the vapour above a solution which would have a value C at equilibrium, and weighing the total adsorbate. If this total weight be designated by I, then

$$U + W = I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and equations (3) and (4) can be solved for U and W, U_0 being calculable from (2).

It is interesting to apply these results to the system under investigation. Col. 3, Table II, shows the values of U_0 calculated according to (2), *i.e.*, as if no benzene had been adsorbed as well. These values begin to differ markedly from the corresponding values of x/m (obs.) at an equilibrium concentration of between 1% and 2%, the difference increasing rapidly with concentration. The values of U_0 when plotted against C, however, also reach a maximum, but this appears to be very flat over the range 9—40% equilibrium concentration. At higher concentrations the U_0–C curve falls, and probably would reach zero again at 100% equilibrium concentration.

Application of Williams's Equations.—Equations (3) and (4) can be applied to adsorption by silicic acid gel without any further experimentation save the determination of the apparent adsorption curve, since we have shown that within the limits of experimental error the same volume is adsorbed at saturation whether the adsorbate is a pure liquid or a solution. Bachmann (*Z. anorg. Chem.*, 1913, **79**, 202) pointed out that if silicic acid gel is immersed in various liquids and then rapidly dried, externally, by filter paper, the weight of liquid taken up, divided by its ordinary density at that temperature, gives a constant value for the volume of liquid adsorbed.

We have shown for our gel that, by this method, almost constant volumes are adsorbed (see Table I, a), in spite of wide differences in such properties of the liquids as compressibility, viscosity, and molecular weight. If adsorption is accomplished through the vapour phase, with air completely removed from the system or not, the volume adsorbed, either of the pure liquid or of a solution where a considerable selective adsorption has occurred from the saturated vapour, is constant within the errors of experiment (see Table I, b). Moreover, this value is in agreement with that observed by the immersion method.

TABLE I.

(a) *Direct immersion.*

	Wt. per g.	Vol. per g.		Wt. per g.	Vol. per g.
Water	0·450	0·450	Chloroform	0·638	0·430
Ethyl alcohol	0·360	0·455	Ethyl ether	0·320	0·446
Toluene	0·383	0·442	α-Bromonaphthalene	0·633	0·435
Hexane	0·286	0·433	Decane	0·335	0·442

(b) *Vapour experiments.*

	Wt. per g.	Vol. per g.
Water	0·448	0·448
Hexane	0·294	0·445
Methyl alcohol	0·345	0·446
Toluene	0·382	0·442
Benzene-*n*-butyl alcohol :		
Conc. in the gel phase = 37·98%*	0·382	0·451
,, ,, ,, = 44·83%	0·379	0·450
,, ,, ,, = 67·39%	0·371	0·450

* These concentrations were obtained by adsorption through the vapour (see below).

It appears therefore that the adsorbates are not subjected to any considerable compression in the adsorption space, and no error of any moment is introduced if we put $I = VD$, where V is the constant gel volume, and D is the density of the solution within the gel, which is given the same value as the density of a solution of the same concentration outside the gel. Then, by putting the value of U_0 from (2) and of W from (4) into (3), it can be shown that

$$U_W = M(C_0 - C)/100\,G + VDC/100 \qquad (5)$$

i.e.,

$$U_W = x/m(\text{obs.}) + VDC/100 \qquad (6)$$

where U_W and W_W refer to the adsorption of the solute and solvent respectively, when calculated from Williams's equation as modified by us in this work. The only quantity which must be determined is D, and this, and hence U_W, can be evaluated in the following way by a method of successive approximation. It is immaterial which value of U_W is chosen, but a fairly close first approximation is obtained by taking U_W equal to U (see Table II, col. 7). The density–concentration curve of n-butyl alcohol–benzene has been found to depart only slightly from a straight line; it is sufficient, then, to use the specific volumes of the pure components instead of the partial specific volumes, and an approximate value for the concentration of the solution present in the gel phase can be calculated from the expression

$$U_W V_A + W_W V_B = I V_s \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V_s is the specific volume of the adsorbate, $I V_s = 0{\cdot}450$ c.c. (see Table I), V_A is the specific volume of the alcohol, and V_B that of the benzene. By reference to the density–concentration curve, we get an approximate value for D, and substituting this in (6), we get a value for U_W. This new value when put in (7) will give us a better value for the concentration and a closer value for D, and so on. It is found that after two or three successive approximations of this kind, D approaches a limiting value which can be used for the calculation of U_W. Thus, *e.g.*, when $C = 45{\cdot}00$, U (col. 7) is 0·227 g.; from (7) the concentration in the gel phase is calculated to be 60·85%, which corresponds to $D_{4^\circ}^{25^\circ} = 0{\cdot}8313$; from (6) $U_W = 0{\cdot}2403$ g.; this value of U_W substituted in (7) gives a concentration of 64·59%, which corresponds to $D_{4^\circ}^{25^\circ} = 0{\cdot}8286$; from (6), $U_W = 0{\cdot}2398$ g. A further approximation gives a value for the concentration of 64·43% and U_W is but slightly altered: U_W can then be put equal to 0·240 g.

The value of W_W can clearly be calculated from a similar equation, *i.e.*,

$$W_W = VD(100 - C)/100 - x/m \quad . \quad . \quad . \quad (8)$$

The values of U_W and W_W so calculated are in Cols. 5 and 6, Table II, and are shown graphically in Fig. 1, Curves 2 and 3.

Adsorption from the Saturated Mixed Vapours.—In order to supply a check on the figures, some experiments were done in which adsorption took place from the vapour, first in the presence of air, and secondly in a vacuum. For the first set, the method adopted was very similar to that used by Tryhorn and Wyatt (*Trans. Faraday Soc.*, 1925, **21**, 399). Approximately the same quantity of gel was weighed into a series of boiling-tubes, and a weighed solution of alcohol in benzene of known concentration and contained in small test-tubes was introduced. The boiling-tubes were sealed off and placed in a thermostat; after various times they were opened and the solution in the small tubes was weighed and analysed A check on the total weight of adsorbate could be obtained by weighing the gel. From these data the gradual approach of the adsorbate to equilibrium could be seen. As a mean of several experiments,

TABLE II.

1. C.	2. $\frac{x}{m}$ (obs.).	3. U_0.	4. $\frac{x}{m}$ (calc.).	5. U_W.	6. W_W.	7. U.	8. $\frac{x}{m}$ (theor.).	9. W.	10. $\Delta\frac{x}{m}$	11. $\Delta\frac{x}{m}$ (calc.)
0·00	—	—	—	—	0·393	—	—	0·209	—	—
0·05	0·056	0·056	0·056	0·056	0·333	0·056	0·056	0·209	—	—
0·096	0·062	0·062	0·062	0·062	0·326	0·064	0·064	0·209	—	—
0·19	0·070	0·070	0·074	0·074	0·316	0·074	0·074	0·208	—	—
0·50	0·086	0·086	0·087	0·088	0·298	0·090	0·090	0·207	—	—
0·97	0·104	0·105	0·100	0·108	0·285	0·103	0·102	0·207	−0·002	0·002
2·55	0·126	0·129	0·118	0·136	0·246	0·127	0·123	0·203	−0·003	0·005
5·90	0·128	0·136	0·129	0·150	0·230	0·150	0·141	0·196	0·013	0·012
7·98	0·129	0·140	0·132	0·159	0·221	0·159	0·147	0·192	0·018	0·015
9·93	0·132	0·147	0·131	0·169	0·210	0·167	0·150	0·187	0·018	0·019
16·45	0·120	0·144	0·125	0·181	0·196	0·185	0·154	0·173	0·034	0·029
38·30	0·087	0·143	0·088	0·231	0·143	0·220	0·136	0·125	0·051	0·048
45.00	0·072	0·131	0·075	0·240	0·133	0·227	0·125	0·111	0·053	0·050
48·84	0·067	0·131	0·068	0·251	0·123	0·231	0·118	0·103	0·051	0·050
67·39	0·036	0·110	0·038	0·288	0·084	0·247	0·081	0·064	0·045	0·043
70·59	0·032	0·109	0·033	0·293	0·075	0·250	0·073	0·057	0·041	0·040
88·18	0·010	0·085	0·012	0·332	0·032	0·261	0·031	0·022	0·021	0·019
100·00	—	—	—	0·362	0·000	0·262	—	—	—	—

0·145 g. of alcohol and 0·237 g. of benzene were adsorbed per g. of gel from an equilibrium solution of 4·552% alcohol; hence the *n*-butyl alcohol content of the gel phase was 37·98%. From Curves 2 and 3 (Fig. 1) it can be seen that, from a solution of the above composition, the weights of alcohol and benzene adsorbed should be 0·145 g. and 0·233 g. respectively, corresponding to an alcoholic content of 38·4%.

In the second group of experiments the gel was contained in a bulb, on the vertical stem of which a glass septum was blown. Immediately below this was a side arm through which the gel was evacuated. This was done very thoroughly during a period of over 24 hours, a two-stage mercury-vapour pump backed by an oil pump being used. The pressure was measured by a large McLeod gauge, and when the mercury in this clicked against the top of the manometer, pumping was further continued for some hours and the gel system isolated by a **U**-tube containing mercury. If, on further testing, no air was being evolved, the side arm was sealed off. One such evacuated gel-container was sealed above the septum to the side arm of a similar bulb-tube, in which was the solution. Near to this bulb another small empty bulb-tube was sealed, in such a manner that, after the liquid had been rendered air-free, a portion of it could be transferred to the empty bulb, this sealed off, and the liquid in it estimated. The apparatus then contained the evacuated gel and air-free solution separated by the septum, and was transferred to a thermostat, and allowed to attain the bath temperature; the septum was broken by a small glass rod, and adsorption began.

The calculation of the adsorption of both components was not materially different from that used in the first group of vapour experiments.

In a series of such experiments, the concentration of the alcohol in the gel phase gave as an average value 37·70% when the equilibrium solution had a concentration of 4·547%. The agreement with the preceding actual and theoretical values is as close as could be expected from the nature of the experiments.

These results show that there is a competition for the silica surface by the two components of the system : benzene is quite considerably adsorbed in dilute solutions of the alcohol, and as the concentration of the latter increases, the adsorption of the benzene is decreased at first rapidly and then more slowly until it is finally replaced completely by the alcohol at 100% *n*-butyl alcohol content. That the benzene should be adsorbed by the silica surface is not surprising in view of the fact that it is selectively adsorbed by silica gel from petroleum solution (Patrick and Jones, *J. Physical Chem.*, 1925, **29**, 1). It will be noticed that the values of U_W and U are, within the experimental error, the same up to an equilibrium concentration of above 20%, *i.e.*, the true adsorption according to Williams, as calculated by us, obeys the equation of the Freundlich type up to this concentration (compare Gustafson, *Z. physikal. Chem.*, 1916, **91**, 405).

Distinction between " True " and Capillary Adsorption.—In the application of equation (3) a possibly important error is involved. The extent of this depends on the amount of capillary condensation that occurs in these porous systems, and would vary, not only with the total internal volume of the adsorbent per gram, but also with the distribution of the capillary diameters. The values U_W and W_W, calculated above, include the amounts of the two components which, if adsorption is accomplished through the vapour phase, are adsorbed by the mechanism of capillary condensation, *i.e.*, through the reductions of vapour pressure produced by curved liquid surfaces. This adsorbed amount will have the same concentration of the components at equilibrium as is present in the equilibrium liquid. If the porous adsorbent is immersed in the liquid, this adsorbate will form an extension of the equilibrium liquid into the gel phase. In other words, the use of (4) in combination with (3) will give the composition of the liquid in the gel phase, but this will not all be truly adsorbed by forces emanating from the solid. Moreover, if the temperature of adsorption be below the critical solution temperature of the two components of the solution, then there is the possibility of an actual liquid–liquid phase separation in the capillaries, of the type suggested by Patrick and Jones (*loc. cit.*).

It has not hitherto seemed possible to distinguish clearly, theoretically or experimentally, between the later stages of adsorption on the solid and capillary condensation. The recent results obtained in the Johns Hopkins laboratory show that the attractive forces at a curved liquid surface may be much greater than would be anticipated from the application of the Poynting–Thomson equation. Any attempt to prevent capillary condensation, *e.g.*, by maintaining the adsorbent at a higher temperature than the solution from which adsorption is proceeding, may only succeed in preventing a certain unknown amount of this kind of adsorption, and in this case, which is a particular case of adsorption from unsaturated mixed vapour, the solution which is condensed in the capillaries would have a different concentration from the equilibrium solution, and this would produce a certain amount of selective adsorption.

This problem can, however, be approached in a different way. For very dilute solutions, below 1%, U, U_0, and x/m have values whose differences are usually within the experimental error of determination. Therefore, if we can find an equation that will fit the x/m–C curve accurately in these low concentrations, it would seem reasonable to assume that its deviations at higher concentrations are due to the fact that the value for x/m has not been corrected. Thus Ostwald and Izaguirre (*loc. cit.*), using the experimental fact that the results of Schmidt-Walter (*loc. cit.*) in the system charcoal–acetic acid–water obey the Freundlich isotherm in the very dilute concentrations, assume that this isotherm gives the true adsorption of the solute throughout the entire range of concentrations, the constants being obtained from the values in these dilute concentrations. From equation (3), if U be put equal to $KC^{1/n}$, then $KC^{1/n} = U_0 + WC/(100–C)$, and from (2)

$$x/m \text{ (theor.)} = KC^{1/n}(100-C)/100 - WC/100 \quad . \quad . \quad (9)$$

If no solvent is adsorbed,

$$x/m \text{ (theor.)} = KC^{1/n}(100 - C)/100 \quad . \quad . \quad . \quad (10)$$

and the x/m (theor.)–C curves will then be identical with the x/m (obs.)–C curves; otherwise

$$\frac{x}{m}\text{ (theor.)} - \frac{x}{m}\text{ (obs.)} = \Delta\frac{x}{m} = \frac{WC}{100}, \text{ or } W = 100\Delta\frac{x}{m}/C.$$

It was found by Ostwald and Izaguirre that if log $100\Delta\frac{x}{m}/C$ is plotted against log (100–C) a straight line is obtained, *i.e.*, W can be put equal to $L(100–C)^a$ and obeys a relation of the Freundlich type, so that the assumption of such a relation for the true adsorption of the one component has led, through the experimental results, to a similar relation for the true adsorption of the solvent. The experimental results are fitted then by the expression

$$x/m\,(\text{obs.}) = KC^{1/n}(100-C)/100-L(100-C)^{\alpha}C/100 \qquad (11)$$

The constants K and $1/n$ are obtained from the $\dfrac{x}{m}$ (obs.)–C curve in dilute solutions of the alcohol, and the constants L and α from the curve connecting $\Delta\dfrac{x}{m}/C$ with $100-C$.

In the system now under investigation, we have found that our results can be interpreted satisfactorily in a similar manner, the appropriate values being $K = 0{\cdot}1039$, $L = 0{\cdot}1585 \times 10^{-2}$, $1/n = 0{\cdot}2057$, $a = 1{\cdot}060$. In Table II, Col. 7 gives the value of U from the expression $U = KC^{1/n}$ (see Fig. 1, Curve 4), Col. 9 the values of W from the expression $W = L(100-C)^{a}$ (Fig. 1, Curve 5), Col. 8 the values of x/m (theor.) calculated from equation (10), Col. 10 the differences $\Delta(x/m)$ between x/m (theor.) and x/m (obs.), and Col. 11 the calculated values of $\Delta(x/m)$ when L and α have the values given above. From the values in Cols. 11 and 8, the x/m (calc.) values in Col. 4 have been derived. The agreement between the observed and the calculated values of x/m is close and, with the exception of one point ($C = 2{\cdot}55$), within the experimental error.

We can thus get an equation that will fit the apparent adsorption curve, and it is really composed of two Freundlich isotherms, one for the solvent and one for the solute. The matter may be summed up as follows. Equation (3) is undoubtedly the correct general equation for the calculation of the true adsorptions of the two components of the solution. If (4) is the second equation used in order to obtain values for U and W, these values will give the total amounts of the two components that are present in the gel phase and will include a certain amount of capillary adsorption of both components. If, however, following Ostwald and Izaguirre, one uses $U = KC^{1/n}$ as the second equation, then, if the assumption involved in its use is correct, the values of U and W so obtained are the true adsorptions of the components and do not include the capillarily adsorbed material. Therefore, the differences between the values of U and W calculated by these two methods should enable us to calculate

TABLE III.

C, %.	Alcohol, g.	Benzene, g.	C (calc.), %.
16·45	0·004	0·023	14·8
38·30	0·011	0·018	37·9
45·00	0·013	0·022	37·1
48·84	0·020	0·020	50·0
67·39	0·041	0·020	67·2
70·59	0·043	0·018	70·5
88·18	0·070	0·010	87·6

the concentration of the solution that is capillarily adsorbed, and this should be equal to the equilibrium concentration of the solution. In Table III are given the weights of the two components present in the solution that is thus adsorbed, at the corresponding equilibrium concentrations; they are the differences between U_W and U for the alcohol, and between W_W and W for the benzene. Where the differences are small, and of the order of the experimental error in the determinations, they are omitted; but, as is seen from the table, for concentrations above 16·45% the results are in close agreement, considering the small amounts of the components that are adsorbed in this way.

It can be concluded that the curve showing the relation between $\frac{x}{m}$ (obs.) and C in this system can be interpreted satisfactorily if the true adsorption of each component follows a curve of the type of the well-known Freundlich isotherm. In addition, a certain amount of the internal gel solution, varying considerably with the equilibrium concentration, is adsorbed not by the solid but owing to the liquid capillary forces, and in experiments where the adsorbent is immersed in the solution, or where the adsorption is from saturated mixed vapours, this portion will have the same concentration as the equilibrium solution.

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