STUDIES IN BINARY SYSTEMS.

PART III. ADSORPTION AND HEATS OF ADSORPTION FROM BINARY MIXTURES OF METHYL ALCOHOL-WATER BY ACTIVE CHARCOAL AND SILICA GEL.

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INTRODUCTION.

It was shown in Parts I and II (*This Journal*, **21A**, 331, 385) that the adsorption and the heats of adsorption from binary mixtures by active charcoal and silica gel indicated the formation of complexes in the liquid systems. Sugar charcoal and silica gel showed opposite types of adsorption isotherm and the animal charcoal showed an S-type of adsorption isotherm. In the present paper we have studied the adsorption and heats of adsorption by silica gel and Norite charcoal from binary mixtures of methyl alcohol and water. It is well known that methyl alcohol-water form a complex MeOH $2H_2O$, from the measurements of fluidity, density and refractive index. It was, therefore, interesting to find out if the adsorption or the heats of adsorption also indicated the formation of this complex.

B. Il'in and B. Rosanow (*Z. Physik.*, 1929, **55**, 285) have measured the heats of wetting of wood charcoal and glass powder by aqueous methyl alcohol solutions. The following results were obtained for the heat of wetting of 1 gram of the adsorbent.

% MeOH	0	8·1	20·8	44·1	100
Carbon	5·8	10·6	13·0	16·0	17·0
Glass powder ..	0·11	..	0·07	..	0·04

The above results for the heats of wetting by carbon are of the same order as found in the present investigation.

EXPERIMENTAL.

The experimental procedure was the same as described in Parts I and II.

Measurement of Concentration Changes.—Changes of concentration of methyl alcohol-water mixtures were followed by measurement of the density of the solution before and after adsorption. As no data are available for the specific gravities of aqueous methyl alcohol at 30° at which our experiments were conducted, an accurate determination of the specific gravity was carried out. The results corrected for vacuum are given below.

TABLE I.

Sp. Gravities of Aqueous Methyl Alcohol Solutions.

% MeOH	Specific gravity	
	30° C./30° C.	30° C./4° C.
0·00	1·00000	0·99568
4·73	0·99156	0·98726
10·26	0·98225	0·97799
10·85	0·98113	0·97689
23·81	0·96075	0·95656
49·29	0·91357	0·90962
74·52	0·85562	0·85192
99·30	0·78735	0·78374
100·00	*0·78570*	*0·78230*

The value of the density for pure methyl alcohol at 30° extrapolated from the graph is 0.78230, as compared with the value 0.78250 given in Landolt Bornstein.

The curve showing the relationship of specific gravities to the composition is not linear, but is convex to the composition axis. The values for the density at 15° given in the literature show similar variations with composition. (This is due to the formation of the complex $CH_3OH\ 2H_2O$.) The changes in concentration due to adsorption were measured by interpolating the values.

Adsorption by Silica Gel.—Adsorption measurements were first done with silica gel prepared from sodium silicate and hydrochloric acid. The changes in concentration due to adsorption were too small to be measured by the density method.

Experiments were then carried out with silica gel prepared by the method of Holmes and Anderson (*cf.* Part I). The values of adsorption (C_0-C) even for this sample were also too small to be accurately measured by the density method.

Adsorption by Norite Charcoal.—The results of adsorption measurements by Norite charcoal are given in the following table (II).

TABLE II.

C_0	$C_0 - C$	C
10·26	0·60	9·66
23·81	0·69	23·12
49·29	0·83	48·46
74·52	0·45	74·07

The values are plotted in Fig. 1 (II). Methyl alcohol is selectively adsorbed throughout, its maximum adsorption being at about 49% concentration. A study of the physical properties such as density,

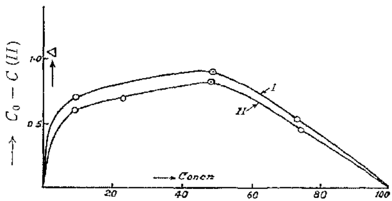

FIG. 1.

viscosity, refractive index, etc., of the binary system methyl alcohol-water shows maximum deviations from the values calculated from the additive law at about the same composition which shows maximum adsorption found above, indicating the formation of the complex $CH_3OH\ 2H_2O$. The explanation for the adsorption maxima at the composition corresponding to the formation of the complexes, will be apparent on the basis of the existence of equilibria between the components and the complex, the relative proportions of the three varying with composition, and on the basis of the fact that only one of the components is selectively adsorbed. The characteristic adsorption isotherm in such cases will not show the sharp rise required by the Freundlich isotherm in low concentrations, and the maxima showed by such isotherm will be necessarily flat as was found in the adsorption from the system toluene-acetic acid (*cf.* Parts I and II of this series).

Heats of Adsorption.

(*a*) *Heats of Adsorption by Norite Charcoal* of the system methyl alcohol-water were determined by the method of twin calorimeters described in Part II. The results are given in the following table.

Table III.

Liquid	Heats of adsorption Heat cal /gm.	H′	Δ
Water	7·4	7·4	0
9·5% MeOH ..	9·4	8·7	0·7
48·6 ,, ..	14·9	14·1	0·8
73·0 ,, ..	18·0	17·47	0·53
99·3 ,, ..	21·0	..	..
MeOH	21·2	21·2	0

The curve showing the relation between the heats of adsorption and concentration is convex to the axis of concentration, the maximum deviation being at about 48%, corresponding to the maximum on the adsorption isotherm.

(*b*) *Heats of Adsorption by Silica.*—The adsorption measurements were first done with silica prepared from sodium silicate and hydrochloric acid. The heats of wetting of this silica were 7.0 cal./gm. with water and 13.8 cal./gm. with methyl alcohol.

Experiments were then carried out with activated silica precipitated from sodium silicate by ferric chloride. The heats of adsorption by this silica are given below:

Liquid	Water	9% MeOH	48·3% MeOH	MeOH
Heat cal./gm. ..	21·9	25·5	26·1	30·8

In the adsorption from binary mixtures, each component may be exclusively adsorbed or both may be simultaneously adsorbed. The heats of adsorption may differentiate between these two cases (*cf.* Bartell and Ying Fu, *J. Phys. Chem.*, 1929, **33**, 1758). The heat of adsorption will be nearer to the heat of wetting of the component which is selectively adsorbed, and will change with composition, when the quantity of the component adsorbed is insufficient. When there is no selective adsorption, the heat of adsorption will be the sum of the two heats of adsorption of each one of the components. If the components A and B are adsorbed in the same ratio as the composition of the solution, the heats of adsorption will be a straight line joining the heats of wetting of the two components. The preferential adsorption, therefore, will be indicated by the deviations of the observed values of the heats of adsorption from those calculated from the linear relationship. The curve showing the deviation (Δ) of the heats of adsorption from the additive law is shown in Fig. 1 (I), which is similar to the adsorption isotherm given in (II). Considering the moderate accuracy of the calorimetric arrangement, the agreement is quite satisfactory.

The deviations of heats of wetting of charcoal by aqueous methyl alcohol observed by B. Il'in (*loc. cit.*) are similar to those found in the present investigation. As the values for the selective adsorption isotherm of the same system have not been given by Il'in, it is not possible to correlate the adsorption and heats of adsorption in his experiments.

On account of the absence of any data on adsorption by silica gel, no comparison between the adsorption and heat of adsorption is possible.

SUMMARY.

Adsorption of methyl alcohol from water by Norite charcoal and silica was measured. The charcoal adsorbs methyl alcohol throughout the range of concentration, while silica shows very little preferential adsorption.

Heats of adsorption of the above system by Norite charcoal were measured by the method of twin calorimeters. The heat-concentration curve resembled the adsorption isotherm indicating that the heats of adsorption were proportional to the adsorbed amounts.

Both adsorption isotherm and the heats of adsorption, particularly the deviation of the heats of adsorption from the additive relationship, of the binary mixture methyl alcohol-water, confirmed the previous conclusions of the authors concerning the effect of complex formation on adsorption, and indicated the existence of the complex CH_3OH $2H_2O$, which has been established by other physico-chemical methods such as density, fluidity, etc.

Further work on the adsorption and heats of adsorption by silica gel and carbon activated by different methods, with the system ethyl alcohol-water, is in progress.

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