STUDIES IN BINARY SYSTEMS.

PART I. ADSORPTION FROM BINARY MIXTURES OF TOLUENE AND ACETIC ACID BY CHARCOAL AND SILICA GEL.

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INTRODUCTION.

Frau Schmidt-Walter (*Kolloid-Z.*, 1914, **41**, 242) made a study of the adsorption isotherms of the systems (1) benzene-acetic acid and (2) toluene-acetic acid on *animal charcoal.* Gustofson (*Z. Phys. Chem.*, 1916. **16**, 385) investigated the system ethyl alcohol-phenol on *animal charcoal.* Patrick and Jones (*J. Phys. Chem.*, 1925, **29**, 1) investigated the system carbon disulphide-acetic acid on *silica.* P. Rehbinder and Fr. L. Krajuschkina (*Z. Phys. Chem.*, 1929, **142A**, 282) have made simultaneous measurements of adsorption and heats of adsorption of *silica* and *charcoal* in solutions of surface active substances such as *n*-butyric acid and *i*-amyl alcohol in hexane and water. The systems ethyl carbonate-benzene, -dimethyl-aniline, -methyl benzoate, and ethyl alcohol-benzene have been studied by Bartell (*Jour. Amer. Chem. Soc.*, 1931, **53**, 2501) with *silica* and *carbon* as adsorbents. Rao (*Jour. Phys. Chem.*, 1932, **36**, 616) studied the adsorption of mixtures of ethyl alcohol—benzene, and benzene and carbon tetrachloride, and ethyl alcohol, acetone and water by *silica gel.* E. Heymann and E. Boye (*Kolloid-Z.*, 1933, **63**, 154–65) investigated the apparent adsorption curves of binary solutions of liquids over the complete range of concentrations, and obtained the three types of curves, (1) showing positive adsorption of one component over the complete range with a maximum in the curve, (2) an S-shaped curve passing through a point of equal adsorption of the two constituents, and (3) showing an apparent negative adsorption of one component over a range of concentrations in the adsorption of the systems, ethyl alcohol-benzene, -hexane, -cyclohexane, -carbon tetrachloride, nitrobenzene-hexane, acetic acid-carbon disulphide, carbon tetrachloride-methyl alcohol, -ethyl alcohol, -butyl alcohol and -amyl alcohol, on *wood charcoal* degassed at 300° and 900°. Doss and Rao (*Jour. Mysore University*, 1935, **8**, 49) investigated the adsorption of pyridine-water mixture by *silica gel.* K. S. Rao and B. S. Rao (*Proc. Indian Acad. Sci.*, 1936, **4A**, 562) studied selective adsorption of *alumina, ferric oxide* and *silica gel* from alcohol-water, alcohol-benzene, alcohol-carbon tetrachloride and benzene-carbon tetrachloride mixtures. Venkatanarasimhachar and Doss (*Ind. Acad. Sci.*, 1937, **6**, 33) studied the selective adsorption from pyridine-alcohol mixture by *silica gel.*

The usual adsorption isotherms represent the relation between C, the equilibrium concentration and ($C_0 - C$) the change due to adsorption. Since ($C_0 - C$) is only a relative quantity, it merely represents the apparent adsorption. The shape of the isotherms will depend upon the adsorbent, the solvent and the solute, and may be either U-shaped or S-shaped. The system water-acetic acid on charcoal studied by Frau Schmidt-Walter (*loc. cit.*) and the system carbon tetrachloride-acetic acid on silica, studied by Patrick and Jones (*loc. cit.*) gave an inverted U-type curve showing positive adsorption. On the other hand, the two systems, benzene-acetic acid and toluene-acetic acid, studied by Frau Schmidt-Walter (*loc. cit.*) gave isotherms which were of the form of an S, twisted round the abscissa. Both forms of curves have been obtained by numerous workers. The question arose whether this peculiar shape of the isotherm was the characteristic of the toluene-acetic acid solution or of the animal charcoal used as an adsorbent.

The difficulties in the interpretation of the selectivity-concentration curves in the adsorption from binary mixtures, particularly, the significance of the maxima, minima and zero selectivity have been pointed out by Ostwald (*Kolloid-Z.*, 1922, **30**, 279), by Bartell (*Jour. Amer. Chem. Soc.*, 1929, **51**, 1643) and by Doss and Rao (*loc. cit.*). Most of the researches on the adsorption from binary systems have been directed to understand the nature, specificity and the active area of the adsorbents. Very little attention has been paid to the nature of the liquid mixture, which may modify the adsorption isotherm. Most of the liquid mixtures that have been studied for adsorption, are known to form compounds or complexes as revealed by other methods of investigation, such as fluidity, freezing point, vapour pressures, etc., the actual nature and amount of the complexes depending upon the equilibrium conditions in the liquid. We are, thus, not dealing with a binary mixture but really with a ternary and sometimes quarternary mixtures. The adsorbent can have a preferential affinity for one or more of the complexes, which may profoundly modify the adsorption isotherm.

In the present paper we have presented the data on the adsorption isotherm of silica gel, sugar charcoal and animal charcoal from binary mixture of toluene and acetic acid. We have shown that the concentrations at which maxima, minima and zero selectivity occur for the different adsorbents, correspond to the preferential adsorption of the complexes $C_6H_5CH_3(CH_3COOH)_2$, $C_6H_5CH_3$ $2(CH_3COOH)_2$ and $C_6H_5CH_3\,3(CH_3COOH)_2$. The multiple of two molecules of the acetic acid in the complexes is due to acetic acid existing on the surface of the adsorbent, as double molecules.

EXPERIMENTAL.

PREPARATIONS OF THE ADSORBENTS.

(1) *Norite charcoal* used was a commercial sample.

(2) *Silica gel* was prepared according to the method of Holmes and Anderson (*Ind. Eng. Chem.*, 1925, **17**, 280). The product obtained was quite white and granular. It was powdered and the portion between 80 and 200-mesh was activated by passing dry air at 150°.

(3) *Animal charcoal* was prepared by following the procedure adopted by Frau Schmidt-Walter (*Kolloid-Z.*, 1914, **14**, 242). The charcoal as obtained, was digested with nitric and hydrochloric acids and aqua regia, washed by boiling with distilled water, and activated by heating to 800° in a silica tube in vacuum for five hours. The original charcoal contained 15%, acid-treated charcoal 6%, and the activated sample 13% of ash. Frau Schmidt-Walter (*loc. cit.*) does not mention the ash-content of the animal charcoal used in her work.

(4) *Sugar charcoal*:—Pure crystalline sugar was charred in a silica dish and the black mass obtained was powdered in an agate mortar and activated by a modification of the method of Bartell and Miller (*Jour. Amer. Chem. Soc.*, 1922, **44**, 1866), which consisted of heating the charcoal at 900° C. in a slow current of dry air. 25 grams of charcoal could adsorb 45% of acid from 100 c.c. of a solution of 0.02N benzoic acid (*cf.* Miller, *J. Phys. Chem.*, 1926, **30**, 1164). Successive lots of the adsorbent could be prepared which possessed the same activity. The progress of activation was measured in relation to the period of heating. The activity reached, as indicated by the benzoic acid test, was 10%, 15%, 25%, 35% and 45%, when the period of heating was 0, 2, 5, 7½ and 10½ hours respectively.

The yield of charcoal showing 45% adsorption and containing 1% of ash was about 6–7% on the weight of sugar.

Adsorption Measurements.—The general procedure adopted in carrying out the adsorption experiments was as follows: The dry adsorbent was weighed into small conical stoppered flasks and a fixed volume of the solution added. The proportion between the weight of the adsorbent and the volume of the solution for each system was arrived at by a few trials so as to get a measurable change in concentration after adsorption. In the experiments with sugar charcoal, the quantity of the solution added each time, was also weighed. The flasks were well stoppered and shaken in a mechanical shaker for half-an-hour at the room temperature which varied between 25° to 27°. For the separation of the suspended adsorbent, the solutions were centrifuged in glass stoppered test-tubes tapering at the bottom.

The changes in concentration were followed by measuring the refractive index n_D of the solutions before and after adsorption on a Pulfrich refractometer. The cell was cemented on to the prism by Secotine which was not attacked by acetic acid or toluene. Similarly the silvered thermometer case which dips into the cell was not attacked by acetic acid. The cover over the cell was tight fitting so that evaporation was prevented as far as possible. A solution of toluene in acetic acid did not show any change in the reading when left in the cell for 15 minutes. Each determination did not take more than 5 minutes.

The readings on the divided circle of the refractometer were correlated with the respective concentrations of acetic acid in toluene, so that by a reference to these values, the strength of an unknown solution could be determined directly. The results are given below, 'i' being the refractometer reading at 25°, for the various concentrations of the acid.

TABLE I.

Values of 'i' for various acetic acid-toluene solutions.

Acid %	i	Acid %	i
0·00	38°, 29′	50·05	48°, 51′
2·574	39°, 4′	59·32	50°, 42·5′
4·996	39°, 35′	69·81	52°, 52′
5·096	39°, 36·5′	78·36	54°, 37′
7·70	40°, 10′	90·18	57°, 5·5′
10·17	40°, 41′	92·53	57°, 35′
20·90	42°, 55′	95·10	58°, 8·5′
30·00	44°, 49′	97·38	58°, 38′
39·78	46°, 47′	100·00	59°, 13′

The concentration determinations of unknown solutions were made by linear interpolation of the above results.

The following precautions had to be observed in order to obtain concordant results. All the solutions containing the initial solutions and their corresponding equilibrium solutions were kept in a water-bath maintained at 25°. When the thermometer of the refractometer indicated a steady temperature, the initial solution was poured into the cell and covered by the thermometer case. The divided circle was then rotated until the sharp edge of the refracted ray as seen in the telescope, nearly crossed the intersection point of the cross-webs. The circle was clamped and finer adjustment made by means of the micrometer screw until the successive readings on the slow-motion drum were nearly concordant. The readings on the circle as well as on the slow-motion drum were noted. The former gave the concentration of the initial solution. This solution was then taken out, the cell was dried *in situ*, and the equilibrium solution corresponding to the initial solution measured before, was put into the cell. The position of the circle was not disturbed and only the micrometer screw was rotated in order to bring the intersection of the cross wires on the edge of the refracted ray, and readings were taken as before. The difference between the two readings on the drum, one for the initial solution and one for the equilibrium solution, gave the change in concentration due to adsorption, in minutes. The difference in the value of '*i*' for acetic acid and toluene amounts to 20°, 44′, *i.e.*, 1244′. Thus 1 minute corresponds to 0.08% change in concentration, so that the concentrations of the initial solutions could be read with accuracy upto about 0.1%, while the change in concentration could be measured upto 0.01%.

The refractive index of toluene and acetic acid remained unaltered when treated with the adsorbent.

The following results indicate the experimental procedure adopted and the method of calculating the adsorption data:

TABLE II.

Adsorption of acetic acid from toluene by sugar charcoal.

Charcoal 0·5 gm. : 5 c.c. of the solution.

No.	Wt. of the flask gm.	+ charcoal gm.	+ solution gm.	Wt. of charcoal gm.	Wt. of solution gm.
I	11·508	12·012	16·560	0·504	4·548
II	13·137	13·639	18·266	0·502	4·627
III	11·527	12·027	16·887	0·500	4·860

TABLE II—*Contd*

Readings with the refractometer (25° C)

No.	Reading on the disc (i)	Reading on the slow-motion drum		Reading on the disc ('i')
		Before Adsorption	After Adsorption	
I ..	45°, 36′	2, 25·20	2, 32·80	45°, 44′
	Change $C_0 - C = 25·20 - 32·80 = - 7'·60$			
II ..	48°, 21·5′	2, 22·55	2, 33·20	48°, 32′
	Change $C_0 - C = 22·55 - 33·20 = - 10'·65$			
III ..	53°, 33′	2, 23·10	2, 38·05	53°, 47′·5
	Change $C_0 - C = 23·10 - 38·00 = - 14·90$			

From the preceding measurements, the following results are obtained:—

No	C_0 % acetic acid	$(C_0 - C)$ min.	$(C_0 - C)/0·5$ gm.	C
I ..	34·40	− 7·60	− 0·607	35·007
II ..	47·50	− 10·65	− 0·849	48·349
III ..	73·25	− 14·90	− 1·192	74·442

(1) *Silica gel.*—The following tables give the adsorption values for two samples of silica, each being prepared in the same manner.

TABLE III.

(First sample) 1 gm. silica : 10 c.c. solution.

% Acetic acid			% Acetic acid		
C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
5·13	3·11	2·02	50·00	48·20	1·80
11·20	8·71	2·49	60·50	59·11	1·39
13·30	10·69	2·61	69·90	68·83	1·07
20·20	17·73	2·47	78·00	77·12	0·88
29·80	27·51	2·29	90·00	89·57	0·43
40·50	38·46	2·04	95·74	95·48	0·26

TABLE IV.

(Second sample) 1 gm of silica : 10 c.c. of solution.

% Acetic acid			% Acetic acid		
C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
5·90	3·72	2·18	14·57	12·21	2·36
8·42	6·05	2·37	16·33	13·95	3·38
12·05	9·68	2·37	44·66	42·85	1·81
			73·00	72·17	0·83

Fig. 1 represents the above two isotherms which are nearly identical, the maximum being quite pronounced between 8 and 16%. The acetic acid is preferentially adsorbed throughout. The first sharp rise represents the Freundlich isotherm in dilute solutions representing true adsorption. The isotherm falls when saturation of the surface takes place and the remaining part of the curve showing apparent adsorption is practically a straight line.

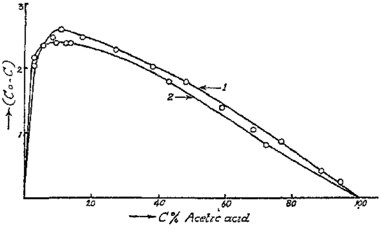

FIG. 1.

Toluene—Acetic acid—Silica.

1. First sample
2. Second sample

(2) *Sugar charcoal.*—The adsorption was measured with two samples having 45% and 46.5% activity respectively and the results are shown in the following tables:—

TABLE V.

Adsorption by Sugar Charcoal (45% activity).

0·5 gm. of charcoal : 5 c.c. of solution

Acetic acid			Acetic acid		
C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
2·20	2·20	0·00	34·40	35·01	— 0·61
5·40	5·40	0·00	47·50	48·35	— 0·85
10·60	10·65	— 0·05	73·25	74·44	— *1·19*
15·45	15·60	— 0·15	90·25	91·24	— 0·99
20·14	20·42	— 0·28	96·25	96·81	— 0·56

TABLE VI.

Adsorption by Sugar Charcoal (46.5% activity).

0·5 gm. of charcoal : 5 c.c. of solution.

Acetic acid			Acetic acid		
C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
28·47	28·94	— 0·47	55·42	56·43	— 1·01
37·77	38·44	— 0·67	65·20	66·39	— 1·19
46·59	47·45	— 0·86	83·67	74·87	— 1·20

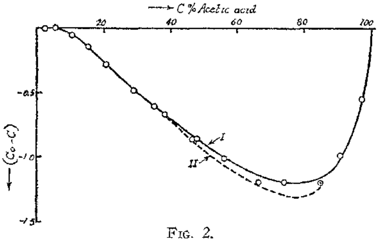

FIG. 2.

Toluene—Acetic acid—Sugar Charcoal

1. First sample.
2. Second sample.

The figures in both the above tables are plotted in Fig. 2. Owing to a slightly greater activity of the second sample, the adsorption changes are somewhat higher than those with the first sample. Toluene is adsorbed selectively and the isotherm therefore lies completely in the negative region. Thus, while silica adsorbs more of acetic acid, pure carbon (sugar charcoal) adsorbs more of toluene.

That silica and carbon behave quite opposite to each other has been illustrated in many cases. Thus Hofmann (*Z. Phys. Chem.*, 1913, **83**, 385) observed that when powders of various solids were allowed to distribute between organic liquids and water, silica always passed into water while carbon either went into the organic liquid or remained at the interface, but never entered the water. Measurement of adhesion tension for certain liquids against silica and carbon have shown that those liquids that possess a high adhesion tension against silica, have invariably a smaller one against carbon (Bartell and Osterhof. "Colloid Symposium Monograph", V, 1927, p. 124). Holmes and McKelvevy (*J. Phys. Chem.*, 1928, **32**, 1523) have shown that Traube's rule applied by Freundlich ("Colloid and Capillary Chemistry", translated from 3rd German Edition, p. 195) to the adsorption of fatty acids from water by charcoal is reversed in the case of silica. Freundlich (*Ibid.*, p. 192) also mentions that adsorption is low in organic liquids such as benzene, alcohol, etc., in which case, a low interfacial tension against solids is assumed. But Patrick and Jones (*J. Phys. Chem.*, 1925, **29**, 1) observed notable absorption from benzene, toluene, etc., on silica. In the present work also, it was observed that the benzoic acid test for the activity of charcoal is not applicable in the case of silica, for it does not adsorb any acid at all. A consideration of the heats of wetting also points to the same fact, as will be shown in Part II of this series.

(3) *Animal charcoal.*—Experiments were first done with unactivated animal charcoal. This was expected to give the S-type isotherm, but the value showed that the isotherm was all along positive. By shaking unactivated animal charcoal with acetic acid alone, the value of '*i*' (the reading on the divided circle) for acetic acid decreased by 6 units. On the other hand, there was no change in the value of '*i*' when the charcoal was treated with toluene. The results are given in Table VII; the values in the third column have been corrected for the change due to the effect of acetic acid on charcoal.

TABLE VII.

Adsorption by unactivated animal charcoal.

1 gm. of charcoal : 15 c.c. of solution.

% Acetic acid C_0	Change in concn. in minutes		$(C_0 - C)$ corrected	C
	Observed	Corrected		
2·20	7	6·9	0·55	1·65
10·10	11	10·4	0·83	9·27
15·30	16	15·1	1·21	14·09
39·90	11·6	9·1	0·73	39·17
59·90	5	1·4	0·11	59·79
70·80	4·5	0·3	0·024	70·77
81·80	3·5	− 1·4	− 0·11	81·91
85·00	3	− 2·1	− 0·17	85·17
94·70	2	− 3·7	− 0·30	95·00

Further experiments were done with the activated animal charcoal, in different proportions. The results are given in Tables VIII, IX and X and shown graphically in Fig. 3, Curves A, B and C.

TABLE VIII.

Adsorption by activated animal charcoal.

0·5 gm. of charcoal : 10 c.c. of solution

C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
10·15	9·99	0·16	70·37	70·45	− 0·08
20·76	20·48	0·28	79·30	79·30	..
29·60	29·44	0·16	90·12	89·96	0·16
59·56	59·64	− 0·08			

The ratio 1.5 gm. of charcoal: 10 c.c. of solution was found better suited and the results obtained, are given in the following table (Table IX).

TABLE IX.

1·5 gm. of charcoal · 10 c.c. of solution.

C_0	C	$(C_0 - C)$	C_0	C	$(C_0 - C)$
2·57	2·08	0·49	59·32	59·52	– 0·20
5·10	4·30	*0·80*	69·81	70·13	– 0·32
7·70	6·91	0·79	78·36	78·72	– 0·36
10·17	9·45	0·72	90·18	90·24	– 0·02
20·90	20·34	0·56	92·53	92·56	– 0·03
30·00	29·56	0·44	95·10	94·98	0·12
39·78	39·54	0·24	97·38	97·14	0·24
50·05	49·97	0·08			

The values for adsorption of animal charcoal for a ratio of 1 : 10 are given in the following table:—

TABLE X.

1 gm. of charcoal : 10 c.c. of solution.

Adsorption		
C_0	C	$(C_0 - C)$
7·7	7·34	0·36
30·0	29·90	0·10
50·4	50·60	– 0·20
69·3	69·62	– 0·32
85·5	85·82	– 0·32

The curves as plotted in Fig. 3 (A), (B) and (C) lie in the positive as well as in the negative region. Thus, in low concentrations of acetic acid, the acetic acid is preferentially adsorbed and in higher concentrations, toluene is preferentially adsorbed.

In curve B, the end portion of the isotherms cuts the abscissa twice. According to Powlow (*Kolloid-Z.*, 1926, **40**, 116), an isotherm which proceeds twice through the zero value is quite possible.

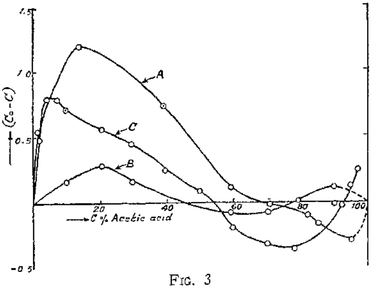

FIG. 3

Toluene—Acetic Acid—Animal Charcoal.

A Table IX
B Table VIII
C Table X

The S-type Isotherm.—The adsorption isotherm of animal charcoal occupies a position in between the isotherm of silica and sugar charcoal. The ash content in the animal charcoal used in the present work was brought down from 15% to 6% by treatment with acids, but it again rose to 13% on activation. The adsorption may therefore have been influenced by the carbon as well as by the ash. Hence for the first portion of the isotherm which is positive, the polar nature of the ash preponderates and acetic acid is adsorbed to a greater extent; in the negative part of the isotherm, the non-polar nature of the carbon preponderates and toluene is preferentially adsorbed.

The isotherm may be a resultant of two opposing influences of the two constituents in the animal charcoal. It should be possible to draw a theoretical isotherm which is the resultant of the 13% effect of ash and 87% effect of carbon using the isotherms obtained with pure silica and sugar charcoal. This is illustrated in Fig. 4. In all these cases, the ratio of the weight of the adsorbent to the volume of solution is 1: 10. Curves I, II and III represent the adsorption isotherm of silica, sugar charcoal and animal charcoal respectively, and curve IV shows the theoretical isotherm calculated as above. The departure of curve IV from curve III may be accounted for on the assumption that the surface is richer in ash than the bulk of the adsorbent. During activation, charcoal is reduced to less than half of its original quantity. This loss is due to the burning off of carbon particles on the surface which results in exposing the ash particles. Thus, previous to activation, a large number of ash particles are covered up by those of carbon but after activation, they are uncovered and thus present a larger surface than before for the same quantity of the adsorbent.

This counteracting effect of ash is also seen in the case of sugar charcoal. On account of the use of silica vessels in its preparation and activation, it contained 1% ash. Due to its influence, therefore, the isotherms with sugar charcoal is flat up to 5% concentration of acetic acid.

Referring to Fig. 3, the curve B, in which 5% adsorbent was used, passes through the *x*-axis at 43.4% and 79.6% corresponding to the complexes $C_6H_5CH_3\ (CH_3COOH)_2$ and $C_6H_5CH_3\ 3(CH_3COOH)_2$, which are preferentially adsorbed. The curve A in the same figure which was obtained by using 15% of the animal charcoal, passes through the abscissa at about 70%, which compares with the value 72.4% required for the formation of the complex $C_6H_5CH_3\ 2(CH_3COOH)_2$. The curve C in the above figure was obtained with 10% of the adsorbent and the adsorption isotherm passes through the abscissa at about 52% of acid which does not indicate any compound formation. The curve, however, shows a flat maxima between 72.4% and 79.6%, and again passes through the *x*-axis at about 83% of the acid, the last of which corresponds to the formation of $C_6H_5CH_3\ 4(CH_3COOH)_2$. The curve A shows maxima in this region. In Fig. 4, the adsorption isotherm of sugar

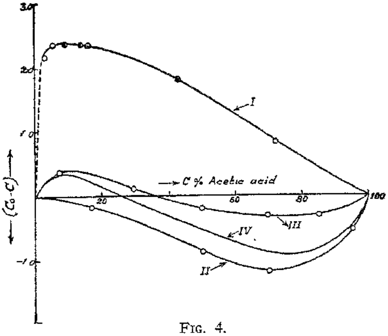

FIG. 4.

Comparison of Adsorption Isotherms.

System: Toluene—Acetic Acid on

I. Silica
II. Sugar Charcoal
III. Animal „
IV. Theoretical Isotherm

charcoal (curve II) shows maxima at 72%. The adsorption isotherm of animal charcoal (curve III) passes through the zero adsorption at about 40% and shows very flat maxima between 72% to 84%. The adsorption isotherm of silica gel shown in Fig. 1 does not reveal any striking peculiarities as in the case of adsorption of animal and sugar charcoal. The latter indicates the formation of the complexes of toluene and acetic acid having 1, 2, 3 and 4 double molecules of the acid. Work is in progress to confirm the existence of these complexes by various physico-chemical methods.

Our thanks are due to Dr. H. E. Watson for his keen interest and helpful guidance during the course of the investigation.

SUMMARY.

A study of the system toluene-acetic acid with respect to its adsorption isotherm has been made for three adsorbents, activated silica, animal charcoal and sugar charcoal. The results obtained indicate that the preferential adsorption of either of the components depends on the nature of the adsorbent and its activity. With animal charcoal, toluene is preferentially adsorbed at low toluene concentrations and acetic acid at concentrations above 60%, giving an S-type adsorption.

With sugar charcoal toluene is preferentially adsorbed at all concentrations and with silica the reverse phenomenon is observed.

The difference in the behaviours of animal and sugar charcoals has been explained as due to the ash contained in the former. It has been shown that S-type isotherm is a result of the combined influence of the polar nature of ash and the non-polar nature of carbon in the animal charcoal.

The adsorption isotherm obtained for the system with animal charcoal and sugar charcoal, particularly the one with the former in different proportions of the adsorbent and the solution, indicate that the selective adsorption is either zero or shows very flat maxima and minima at compositions approximately corresponding to the formation of the compounds $C_6H_5CH_3$ $(CH_3COOH)_2$, $C_6H_5CH_3$ $2(CH_3COOH)_2$, $C_6H_5CH_3$ 3 $(CH_3COOH)_2$ and $C_6H_5CH_3$ $4(CH_3$-$COOH)_2$.

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