

## STUDIES IN BINARY SYSTEMS

### PART IX.—SYSTEM BENZENE—ACETIC ACID

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In Parts V to VIII it was shown that a critical study of the cryoscopic and polarization data of binary mixtures of alcohol in inert solvent and of binary mixtures of two inert solvents like benzene and carbon tetrachloride, indicated the presence of additive complexes in the liquid mixtures. The complex nature of the apparent selective adsorption of the components from several systems was explained on the basis of complex formation. In the present paper the authors have extended this study to the system benzene—acetic acid.

The freezing point determinations by Baud (*Z. physik. Chem.*, 1888, **2**, 715) and others (Roloff *Z. physik. Chem.*, 1895, **17**, 325) of this system does not seem to indicate the presence of any additive compound between benzene and acetic acid and the freezing points vary directly with composition. The calculation of the molecular weight by Beckmann (*Z. physik. Chem.*, 1897, **22**, 610) Trautz and Moschel (*Z. anorg. allgem. Chem.*, 1926, **155**, 13) indicates that acetic acid exists as double molecules, a conclusion also drawn from other physical properties of this system.

The dielectric constant values of this system have been determined by Smyth and Rogers (*Jour. Amer. Chem. Soc.*, 1930, **52**, 1824). The polarization curve deviates from the straight line relationship and increases to a maximum at 0.8 moles acetic acid. Smyth and Rogers explain the results as due to dissociation of the complex molecules of acetic acid into single molecules, which would however increase the polarization. The view that acetic acid molecules remain in their polymerised form in dilute solutions and dissociate in concentrated solution is however untenable.

A study of the physical properties of this system would indicate that complex compounds are formed between the single benzene molecules and double molecules of acetic acid even though no indication of the presence of such complexes are shown by the freezing point determinations. This may be because the complexes formed

might be very unstable in the liquid mixtures but may be stable on the surface of the adsorbent where conditions may be more favourable.

Frau Schmidt Walter (*Kolloid Z.*, 1914, **41**, 242) studied the adsorption of the systems benzene acetic acid and toluene acetic acid on *animal charcoal* and obtained an 'S' type of curve in both the cases.

Kane and Jatkar (*This Journal*, 1938, **21A**, 331-344, 385-394 and 410-413) studied the selective adsorption from toluene and acetic acid by carbon and silica gel and found that the concentration at which selective adsorption and heats of adsorption from binary mixtures of toluene acetic acid by *active carbon* and *silica gel* is a maximum, minimum or zero is due to the formation of complexes  $C_6H_5CH_3 \cdot (CH_3COOH)_2$ ,  $C_6H_5CH_3 \cdot 2 (CH_3COOH)_2$  and  $C_6H_5CH_3 \cdot 3(CH_3COOH)_3$ . It was therefore interesting to find out if the selective adsorption from the system benzene acetic acid on *silica gel* and *carbon* would give similar results.

#### EXPERIMENTAL

The blood charcoal, sugar charcoal and silica gel were taken from the stock prepared previously and the adsorption experiments were carried out in the manner already described. The results are given in the following table and represented in fig. I.

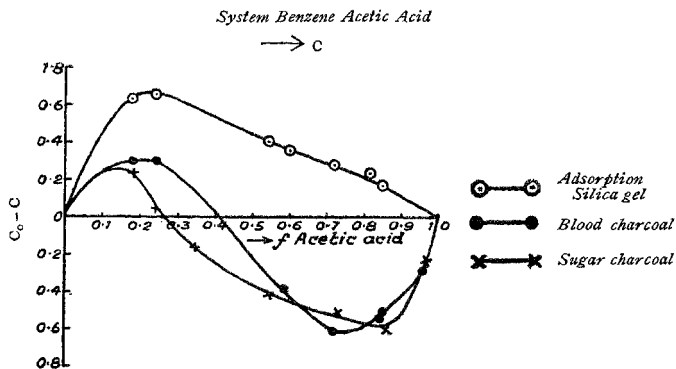


FIG I

TABLE I

<i>Silica gel</i>		<i>Sugar Charcoal</i>		<i>Blood Charcoal</i>	
C (f)	$C_c - C$ %	C (f)	$C_c - C$ %	C (f)	$C_c - C$ %
0.18	0.65	0.18	+0.26	0.18	0.3
0.24	0.67	0.24	+0.05	0.24	0.03
0.54	0.42	0.34	-0.15	0.60	-0.39
0.60	0.36	0.54	-0.4	0.72	-0.61
0.72	0.29	0.72	-0.5	0.84	-0.54
0.81	0.24	0.85	-0.6	0.85	-0.51
0.84	0.17	0.96	-0.23	0.96	-0.28

## DISCUSSION

'S' type of curves are given both by blood charcoal and sugar charcoal and inverted 'U' type by silica gel. For sugar charcoal the curve passes through zero selectivity at 0.25 moles acetic acid and through a negative maximum at about 0.8 moles acetic acid. For blood charcoal the curve crosses the concentration curve at 0.4 moles acetic acid and through a maximum at about 0.8 moles acetic acid. In the case of silica gel the curve passes through a maximum at 0.2 moles acetic acid.

Kane and Jatkar (*loc. cit.*) have shown that in the adsorption of acetic acid from toluene, silica gel and carbon give opposite type of adsorption curves. In the case of animal charcoal, the curve was of 'S' type, which they ascribed to the action of ash in the charcoal which was in the nature of silica. The results in the present investigation show that the system benzene acetic acid-carbon gives an 'S' type of adsorption curve even for pure charcoal in complete agree-

ment with the results of Frau Schmidt Walter (*loc. cit.*). The flat negative maxima obtained in the case of blood charcoal, sugar charcoal and animal charcoal also occur in the region corresponding to the formation of the complex  $C_6H_6 \cdot 2(CH_3COOH)_2$  and  $C_6H_6 \cdot (CH_3COOH)_2$ , in agreement with the results of Kane and Jatkar for the system toluene-acetic acid, the multiple molecules of acetic acid being due to the association of acetic acid molecules.

The shape of the curve of the system silica gel-benzene acetic acid can be explained by the existence of double molecules of acetic acid in concentrated solutions. As shown in the Introduction, the apparent adsorption reaches a maximum in dilute solutions of acetic acid which is obviously due to the single molecules. As the per cent. of the acid is increased the apparent adsorption decreases due to the fact that acetic acid exists mainly as a dimer which is non-polar. It is significant to point out that in this system the apparent adsorption reaches a maximum for all the adsorbents used in the same region of about 0.2 mole fraction acetic acid.

In the case of carbon, the positive adsorption is again due to the existence of single molecules of acetic acid and the reversal in the adsorption in concentrated solutions is due to the organophilic nature of the charcoals. It is obvious that the acetic acid dimer possesses a residual polarity and behaves as a polar substance compared to benzene.

Comparing the adsorption of acetic acid from benzene with that from toluene, the negative adsorption in the case of the latter is due to the existence of almost entirely double molecules of acetic acid even in dilute solutions.

#### SUMMARY

The selective adsorption curves of acetic acid from benzene solutions in the entire range of concentration on (i) sugar charcoal and (ii) blood charcoal, were of 'S' type passing through a negative maximum to composition corresponding to  $C_6H_6 \cdot 2(CH_3COOH)_2$  and

a positive maximum at  $C_6H_6 (CH_3 COOH)_2$ . It is interesting to note that the polarization curve for this system passes through a maximum at the former composition.

Silica gel gives an inverted 'U' type of curve acetic acid being preferentially adsorbed. The curve passes through a maximum when the composition is  $C_6H_6 (CH_3 COOH)_2$ . It appears from these results that the dimers of acetic acid molecules can form loose co-ordinate compounds with benzene.

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