STUDIES IN BINARY SYSTEMS

PART V.—SYSTEM BENZENE–ETHYL ALCOHOL

By (Miss) Nagamani Shama Rao and S. K. K. Jatkar

In the present paper the authors have studied the selective adsorption from the binary mixtures of benzene with ethyl alcohol by activated charcoal and silica gel.

The freezing points of this system have been investigated by several authors [Baud (*Z. Physik Chem.*, 1888, **2,** 715), Pickering (*J. Chem., Soc.*, 1893, **63,** 998–1027), Peterson and Rodebush (*J. Phys. Chem.*, 1928, **32,** 709,) Washburn, Hovizda and Vold (*J. Amer. Chem. Soc.*, 1931 **53,** 3237)] who showed that the freezing point lowering in higher concentrations of the mixture is much less than that would be expected from the freezing point data (Timmermann, 'Les solution concentrees' P. 385) the results are in agreement with the idea that the molecules of alcohols are associated more than 3·5 times at the freezing point temperatures, which finding is in agreement with the results of the author on the system benzene-*iso*amyl alcohol as will be shown in part VI.

The value of the molecular weight calculated from the data of Washburn, Hovizda and Vold (*Loc. Cit.*) is about 156, as compared with the theoretical value 124 assuming the complex C_6H_6 C_2H_5OH to be present.

(*a*) *Dielectric Constant and Polarization.*—Graffunder and Erich Heymann (*Z. Physik*, 1931, **72,** 744), found that the P_2 curve (see Fig. 1) showed a maximum which Debye interpreted to mean that in concentrated solutions an association of the dipole takes place in such a way that they are added one on to one another in the direction of their axes.

It should however be pointed out that the P_2 composition curve is more in agreement with the view that the complex C_6H_6 C_2H_5OH is formed, which is supported by all other physical properties of the mixtures.

(*b*) *Adsorption.*—In spite of voluminous work on the activation of *carbon* by different methods there is no data in the literature on the

comparative activity of *carbons prepared from different sources* for adsorption of a polar substance from its mixture with a non-polar solvent over a complete range of concentration.

Investigations of this type have been carried out mostly with *silica gel.* B. II'in and Simananov (*Z. Physik*, 1930, **66,** 613–8) have published experimental data on the inversion of adsorption from aqueous fatty acid solutions by two modifications of active carbon prepared from sugars. The Debye figures (X-ray) for these carbons were found to be identical. Although numerous instances are known no satisfactory explanation for this inversion of adsorption has been given.

Bartell, Schaffler and Sloan (*Jour. Amer. Chem. Soc.*, 1931, **53,** 2501) obtained an 'S' shaped curve both when *silica gel* and *carbon* were used as adsorbents. In the case of silica gel the curve passes through zero selectivity at about 0·2 moles alcohol and through a maximum at about 0·85 moles alcohol.

Heymann and Boye (*Kolloid Z.*, 1933, **63,** 154–65) also show that the adsorption curve for benzene—ethyl alcohol by *carbon* is of an 'S' type. For *charcoal* degassed between 900–1000°C the curve passes through a negative maximum at about 0·75 moles alcohol and crosses the concentration axis at about 0·1 mole alcohol. For charcoal degassed at 300°C the curve follows closely the former curve and crosses the concentration axis at about 0·2 moles fraction alcohol.

K. S. Rao and B. S. Rao (*Proc. Ind. Acad. Sci.*, 1937, **4A,** 562–70) have shown that alcohol is selectively adsorbed on alumina gel and ferric oxide gels over the entire range of concentration.

Bartell and Lloyd have published a paper on "Alteration of Adsorption Properties of *Charcoal*" (*Jour. Amer. Chem. Soc.*, 1938, **60,** 2120) in which they report that *sugar charcoal* could be changed from extremely organophilic charcoal to charcoal approaching the hydrophilic adsorbent *silica* in adsorption properties by controlling the temperature and nature of the oxidising atmosphere.

These authors do not mention the extensive work of B.II'in on a similar subject (Cf. *Z. Physik. Chem.*, 1931, **A155,** 403). The binary system benzene-ethanol was used for the study of preferential

adsorption, all the curves obtained being of the 'S' type, which indicated zero adsorption for the various charcoals at 0·1, 0·2, 0·25, 0·3, 0·6 and 0·7 mol. fraction of ethyl alcohol, and showed a flat negative maxima at 0·8 mol. fraction of ethyl alcohol in all cases. Kane and Jatkar suggested that the complexes formed in the system benzene-ethyl alcohol, will have molar proportions of 1:4, 1:3, 1:2, 1:1 and 4:1, as the zero selective adsorption by the adsorbent has been shown to be due to the preferential adsorption of the complex of the composition of the liquid mixtures giving zero selectivity.

The object of this investigation is to study the adsorption isotherm of the system benzene-ethyl alcohol with carbon prepared by different methods and compare the results with corresponding system with silica gel prepared from nickel silicate and by Norit charcoal.

Experimental

Materials used.—(1) *Norit,* (2) *Blood Charcoal.*—The commercial samples dried at 110°C were used for the experiments.

(3) *Sugar Charcoal.*–Sample I, got by charring pure crystalline sugar was activated in steam at about 1000°C in an electric furnace and cooled in an atmosphere of carbon dioxide.

Sample II, was activated in an atmosphere of hydrogen and cooled in carbon dioxide.

(4) *Silica Gel.*–Nickel silicate was precipitated from a solution of nickel nitrate by sodium silicate. The silica gel was prepared from nickel silicate by digesting with hydrochloric acid and thorough washing. The white granular gel was powdered and the portion below 80-mesh was dried at 110°C.

The adsorption measurements were carried out in the following manner. Definite amounts of the mixtures were taken and 3% of the adsorbents were added to the different mixtures. The mixtures were shaken thoroughly and kept for over four hours to attain equilibrium. Then the mixtures were centrifuged and the adsorption was calculated by measuring the change in the refractive angle on a Pulfrich Refractometer at a constant temperature taking the usual precautions. To measure the change more accurately

readings on the drum were noted. The slope of the curve of the refractive angle and composition was calculated between two adjacent points and this was multiplied by the change in the reading between the original and the adsorbed mixtures. This gave the excess of the amount of one of the constituents adsorbed by the adsorbent. The substance that was adsorbed was recognised by the sign of the calculated C_o–C. C*f* represents mol fraction of ethyl alcohol and C_o–C the weight percent of alcohol retained by the absorbent which was 3% by weight of the liquid mixture. The final results are given in table I, and represented in Fig. 1.

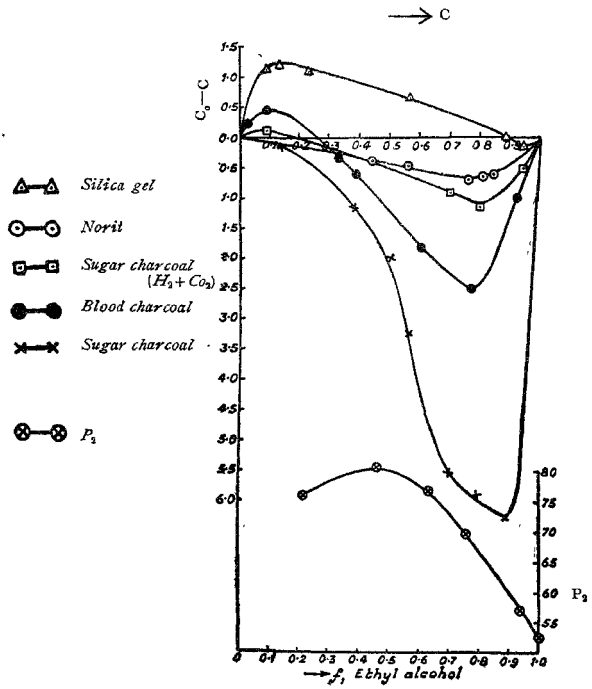

FIG. I

TABLE I

1. *Norit*		2. *Sugar Charcoal* ($H_2 : CO_2$)	
Cf	C_o–C	Cf	C_o–C
0·84	−0·64	0·94	−0·5
0·8	−0·66	0·80	−0·15
0·76	−0·71	0·70	−0·87
0·56	−0·47	0·09	+0·13
0·44	−0·39		

3. *Sugar Charcoal* ($H_2O : CO_2$)		4. *Blood Charcoal*		5. *Silica gel*	
Cf	C_o–C_{mean}	Cf	C_o–C_{mean}	Cf	C_o–C_{mean}
0·88	−6·27	0·96	−0·28	0·94	−0·12
0·80	−5·89	0·85	−0·51	0·80	+0·04
0·70	−5·5	0·84	−0·54	0·565	+0·66
0·57	−3·2	0·72	−0·61	0·238	+1·11
0·5	−1·97	0·60	−0·39	0·152	+1·2
0·38	−1·14	0·24	+0·31	0·09	+1·11
0·13	−0·13	0·18	+0·3		

DISCUSSION

For silica gel, sugar charcoal (sample II) and blood charcoal the curve is of an 'S' type. For norit and sugar charcoal activated in steam and carbon dioxide the curve is of an inverted 'U' type. For silica gel the curve crosses the concentration axis at 0·9 moles alcohol and goes through a maximum at about 0·15 to 0·2 moles alcohol. For sugar charcoal (sample II) the curve crosses the concentration axis at about 0·2 moles and goes through a negative maximum about 0·75 moles alcohol (corresponding to C_6H_6 $3C_2H_5OH$). Similarly for blood charcoal the curve has zero adsorption at 0·25 moles alcohol and passes through a negative maximum at 0·75 moles alcohol (corresponding to C_6H_6 $3C_2H_5OH$). For norit also the curve passes through a maximum at 0·75 moles alcohol. The significance

of the maxima occurring at the composition corresponding to three molecules of alcohol would appear to be in agreement with the finding from the freezing point data that alcohol molecules are associated to a maximum of about three. The adsorbing power of the sugar charcoal activated in steam and carbon dioxide is very great, 1 gm. of the charcoal selectively adsorbing nearly its equivalent weight of benzene from a solution containing 0·9 moles of alcohol to 0·1 of benzene.

In dilute solutions of alcohol the selective adsorption curves reach a maximum for both silica gel and carbons at approximately the same concentration. The adsorption in this region is not governed by the Freundlich law owing to the fact that the solution contains decreasing amounts of single molecules of alcohol which are strongly adsorbed by primary forces. The rapid decrease in selective adsorption with increasing concentration is due to the saturation of the primary adsorption centres and to the decreased dissociation of the dimers and trimers of alcohol molecules. The zero selective adsorption at about 0·25 moles of alcohol in the case of carbons is the resultant of the two adsorption factors; one that of the primary adsorption of single molecules of alcohol and the other the adsorption of benzene by the organophilic nature of carbon, the two components being adsorbed in the same relative proportion as the composition of the solution.

With further increase in concentration the selective adsorption of benzene becomes the predominant factor when carbon is used owing to its organophilic nature. The highest selective activity is shown by sugar charcoal treated with steam and carbon dioxide, which shows only a 'U' type of curve. The 'S' type of curve is shown by the carbons possessing comparatively low activity. The maximum adsorption in the case of all adsorbents including silica gel, occurs at 0·75 mole fraction of alcohol, which fact would seem to indicate that the adsorption in this region is mainly governed by the composition of the solution which, as pointed above, corresponds to the formation of the complex $C_6H_6.3C_2H_5OH$. The further drop in the curves represent the usual Freundlich adsorption.

SUMMARY

The system benzene—ethyl alcohol does not behave as a purely binary mixture, but as a complicated one perhaps containing monomers, dimers, trimers of alcohol molecules and complexes between alcohol and benzene molecules.

The polarisation P_2 curve shows a minima when the composition of the liquid mixture corresponds to the formation of the complex C_6H_6 C_2H_5OH.

The selective adsorption of the components of this system gives 'S' type of curves for sugar charcoal and for silica gel and blood charcoal. 'U' type of curves are obtained for sugar charcoal (activated by steam and CO_2) and Norit. The shapes of the adsorption isotherms were explained on the basis of complex formation and on the association of polar molecules to form non-polar ones. The maxima in the selective adsorption of this system occurs at the composition corresponding to C_6H_6 3 C_2H_5OH, indicating the complex formation between the associated alcohol molecules with benzene.

Department of Pure and Applied Chemistry,
General Chemistry Section,
Indian Institute of Science,
Bangalore.