STUDIES IN BINARY SYSTEMS

PART VI.—SYSTEM *Iso*AMYL ALCOHOL—BENZENE

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

INTRODUCTION

In Part V it was shown that the complex nature of the selective adsorption curve of the system ethyl alcohol-benzene on carbon and silica gel, could be explained on the basis of the formation of complexes in the binary mixtures. It was interesting to find out if the system benzene *iso*amyl alcohol behaved in the same way.

EXPERIMENTAL

(*a*) *Freezing point*:— The freezing points of this system were determined over a range of concentration of 0 to 26% *iso*amyl alcohol by using the Beckmann method. Results are given in the following table:—

TABLE I

f_1 *iso*amyl alcohol	Fall in the freezing point	Apparent molecular weight
0·004	0·235	93 (338)
0·015	0·800	107
0·02	1·11	126
0·04	1·451	148
0·06	2·029	179
0·11	2·914	224
0·15	3·405	305
0·18	4·251	299
0·18	4·274	303
0·18	4·257	307
0·24	4·379	306

The molecular weight calculated assuming that all the *iso*amyl alcohol goes to form the complex $C_6H_6 3AmOH$ in very dilute solutions, was 338, as compared with the theoretical value 342. It was also found that the molecular weight of *iso*amyl alcohol calcutated from the fall in the freezing point reached a constant value of about 306 which seems to indicate that *iso*amyl alcohol is associated about 3·5 times at 0° C as in the case of ethyl alcohol.

POLARIZATION

(*b*) *I. Dielectric Constant.*— The dielectric constant measurements of the mixtures were carried out on a very simple apparatus (see fig. I) C_1 and C_2 are two standard condensers, one measuring up to 100 micro-micro farads and the other up to 1000 micro-micro-farads. The valve used was Marconi LP_2 with 40 volts in the anode. A quartz oscillator of 96 K c.s. was used. If the capacity of the anode circuit is increased the plate-current will fall at first slowly and then more rapidly until it reaches a minimum, after which a very small rise of capacity will cause the plate current to increase considerably. As the circuit stops the oscillation at final setting of the condensers and it can start again only with a considerably lower setting, a switching arrangement was devised as shown in the figure. It was also found that quartz crystals which could oscillate very easily with as low a capacity in the anode circuit as possible, are absolutely essential for the success of the method. Similarly the method also fails when the conductivity of the liquid is very high when it interferes with sharpness of the setting.

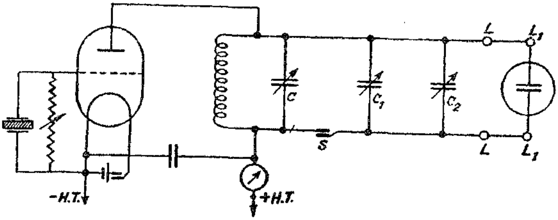

FIG. I

The measuring cell after washing well with alcohol and drying is introduced in the circuit and the reading of the condenser when the current is minimum in the anode is noted. Then the cell is completely filled with the mixture, the components of which are previously purified and dried and the reading on the condenser is noted again. To measure the capacity of the cell at different temperatures, an oil bath with a stirrer and a heater with a variable resistance is used.

To insert the cell X each time in the circuit lead wires were provided at L and L and a switch was inserted for reasons already mentioned. Considering that the leads have some capacity, for calculating the dielectric constant of the mixtures the formula $E=(X_M-a)/(X-a)$ where a is the correction for the capacity of the leads of the condenser was used and the value of a was determined by taking the standard dielectric constants of the components used for preparing the mixtures from Landölt's tables.

RESULTS

The values of the various physical properties of this system are given in the following table and represented in Fig. 2

TABLE II

f_1 *iso*amyl alcohol	Density	Dielectric constant	P_{12}	P_2 *iso* AmOH
0·0	0·8699	2·29	26·70	0
0·12	0·8611	2·66	32·76	77·2
0·14	0·8590	2·95	36·43	94·7
·19	0·8567	3·03	37·64	84·3
·22	0·8549	3·36	41·32	92·3
·25	0·8528	3·53	43·56	95·2
·32	0·8482	3·60	44·43	82·6
·42	0·8415	4·55	52·95	89·2
·53	0·8349	5·70	60·86	91·8
·60	0·8291	7·17	68·19	95·5
·72	0·8230	9·35	76·44	95·8
·81	....	11·16	82·14	94·8
1·0	0·8068	16·47	91·48	91·5

DISCUSSION

The refractive indices (not given here) show a slight variation from the straight line relationship at about 0·75 moles fraction benzene corresponding to AmOH $3C_6H_6$.

The fluidity deviation composition curve (Bhide and Watson This *Journal* 1927, **10A,** 72) of this system was of an 'S' type crossing the composition axis at about 0·5 moles corresponding to AmOH C_6H_6 and through positive and negative maximum points at 0·25 and 0·75 moles the first one corresponding to C_6H_6 3AmOH.

Bhide and Watson (*loc. cit.*) get a minimum in the velocity co-efficient at about the same concentration at which the complex C_6H_6 3 AmOH is formed. It is interesting to point out that the polarization curve obtained in the present investigation is exactly the inverse of the velocity co-efficient curve given by Bhide and Watson. This would indicate that the decrease in the velocity co-efficient and also the minimum in the conductivity curve observed by these authors are due to the formation of the complex between benzene and *iso*amyl alcohol molecules.

Ramanov and Eltsin (*Amer. Chem. Abs.* 1937, **31,** 6069; *Physik Z Sowjetunion* 1937, **II,** 526) have measured the dielectric constants of some alcohols in benzene for a wave length of 57·75 cm. They find that at very low concentrations the polarization curve goes through a maximum and according to the above mentioned authors this indicates that association *increases* the dipole moment of the alcohol.

P. C. Mahanti (*Jour. Ind. Chem. Soc.*, 1929, **8,** 743) has found the dielectric constants ot this system from 72 to 100% benzene and his values in that region agree with those obtained by the authors. The curve is convex towards the composition axis.

The polarization values vary directly with composition.

The polarization P_2 curve goes to a maximum at about 0·25 moles fraction of *iso*amyl alcohol. Corresponding to the formation of the complex which is also indicated by the freezing point data AmOH $3C_6H_6$. The curve passes through a minimum at 0·3 moles after which the polarization increases and attains a steady value from 0·5 moles.

Adsorption.—The adsorption measurements were carried out in the same manner as described in Part I. The weight of adsorbents used was 3%. The results are given in the following table and represented in fig. 2.

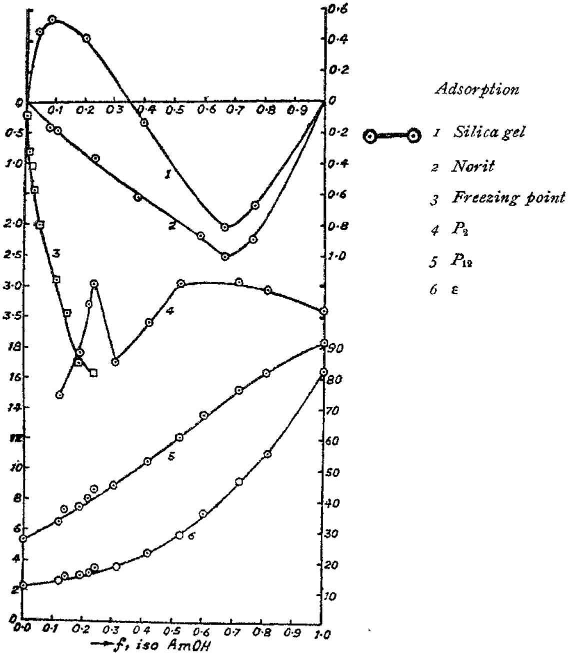

FIG. 2

TABLE III

Norit		Silica gel	
C f	C_0-C %	C f	C_0-C %
0·77	−0·88	0·77	− 0·67
0·67	−1·04	0·67	−0·81
0·59	−0·87	0·51	−0·31
0·38	−0·61	0·40	−0·13
0·24	−0·37	0·20	+0·42
0·10	−0·19	0·08	+0·54
0·08	−0·17	0·04	+0·46

DISCUSSION

The adsorption measurements of the system benzene-*iso*amyl alcohol gave an 'S' type of curve with silica gel and an inverted 'U' type for Norit. Both the curves pass through a flat negative maximum at about 0·65 to 0·75 mole fraction *iso*amyl alcohol corresponding to C_6H_6 2AmOH and C_6H_6 3 AmOH.

As in the case of the system ethyl alcohol-benzene-silica gel, *iso*amyl alcohol is selectively adsorbed in dilute solutions of benzene which reaches a maximum at 0·1 mole fraction *iso*amyl alcohol. The selective adsorption decreases with further increase in concentration owing to polymerisation until zero selectivity is reached at 0·35 moles alcohol. The curve afterwards passes through a negative maximum at about 0·75 moles fraction *iso*amyl alcohol when the selective adsorption of benzene takes place. In the case of carbon the curve shows preferential adsorption of benzene, the maximum occurring at the composition as in the case of silica gel.

In the case of adsorption of benzene by silica gel, as the amount of benzene is increased, there will be more single molecules of *iso*amyl alcohol due to dissociation which single molecules will be strongly adsorbed in increasing proportions until the selective adsorption becomes zero and then positive.

Owing to the organophilic nature of the carbon, the adsorption is always that of benzene. The marked deviation of adsorption in dilute solutions from the exponential law is due to the formation of the complex and the absence of the small positive adsorption observed in the case of the system benzene-ethyl alcohol, is due to the strong association of the *iso*amyl alcohol even in dilute solutions.

The results of spectroscopic measurements in the infra red show that there are double molecules of alcohol rather than a single molecule linked to a molecule of the solvent in concentrated solutions.

Comparing the system benzene—*iso*amyl alcohol with benzene-ethyl alcohol, the polarization values of both the systems reach a maximum value at about 0·5 moles.

SUMMARY

The freezing point determination seems to indicate that *iso*amyl alcohol is associated about 3·5 times in benzene solutions as in the case of ethyl alcohol.

The dielectric constant measurements of the binary mixtures of benzene and *iso*amyl alcohol were carried out on a simple apparatus using quartz crystal oscillator of 96 kc. The polarization P_2 concentration curve showed a minimum at 0·66 mole fraction benzene, and maxima at 0·5 mole and at 0·25 mole owing to the formation of 1:1 and 1:3 compounds.

The selective adsorption of this system on silica gel is of an 'S' type and for norit 'U' type. Both the curves pass through negative maximum in the region where the complexes may exist in appreciable proportions.

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