STUDIES IN BINARY SYSTEMS

PART X—SYSTEM ETHYL ALCOHOL–WATER

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The freezing point determinations of alcohol water mixtures have been done by Pickering (*J. Chem. Soc.*, 1893, **63**, 998) and others. A kink is observed from about 40% alcohol corresponding to the region where $C_2H_5OH\ 3H_2O$ and $C_2H_5OH\ 2H_2O$ exist.

The fluidity deviations and the density deviations from Dunstan's values of this system were found to be a maximum at about 45 per cent. alcohol corresponding to $EtOH\ 3H_2O$.

The conductivity measurements from this laboratory (unpublished) show a maximum in the region 50 to 70 per cent. alcohol where $C_2H_5OH\ 2H_2O$ and $C_2H_5OH\ H_2O$ exist.

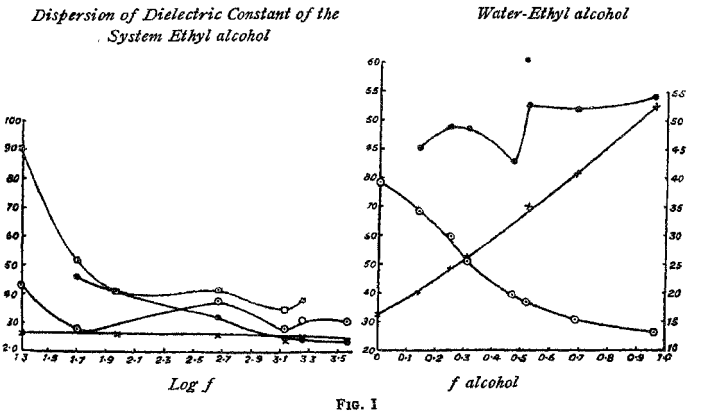

FIG. I

The adsorption of alcohol from water-ethyl alcohol mixtures by carbon degassed at 300° and 900° has been studied by Heymann and Boye (*Kolloid Z.*, 1933, **63**, 154). The selective adsorption curve shows a sudden change when the composition of the mixture is 0·5 moles alcohol and reaches a maximum at about 0·2 moles alcohol.

Experimental

Dielectric Constant and Polarisation :— The dielectric constants of the mixtures of ethyl alcohol and water were measured at 96 Kc. according to the method described in part VI. The results are given in the following table with the calculated values of P_{12} and P_2 and shown graphically in Fig I.

Table

f_2	Density	ϵ_{25}	P_{12}	P_2
0·0	1·000	78·5	16·2	...
0·14	0·9524	68·5	20·3	45·4
0·25	0·9198	59·9	24·4	49·2
0·31	0·9014	51·1	26·1	48·2
0·47	0·8661	39·8	28·8	43·0
0·51	0·8580	40·0	38·9	60·6
0·52	0·8555	36·7	35·2	52·7
0·69	0·8280	30·4	40·8	51·8
0·96	0·7903	25·8	52·6	54·1

The measurement of the authors clearly indicates an abrupt change in the P_2 curve at 0·5 moles alcohol and a maxima at 0·25 mole alcohol corresponding to the formation of 1:1 and 1:3 compounds of alcohol and water respectively.

Graffunder and Erick Heymann (*Z. Phys.*, 1931, **72**, 744) got a concave curve for the dielectric constant-concentration variation of this system. J. Wymann (*J. Amer. Chem. Soc.*, 1931, **53**, 3292) and Gosta Akerloff (*J. Amer. Chem. Soc.*, 1932, **54**, 4130) obtained a straight line relationship between dielectric constant and composition. The

probable reason for the variation may be found in the fact that Wymann and Akerloff conducted their measurements at 10 meters and 150 meters respectively and Graffunder at 100 meters, while the present author carried out the experiments at 3000 meters. These results would indicate that the ethyl alcohol-water mixtures show a dispersion of dielectric constant with frequency.

Attempt was therefore made to measure this dispersion for various percentages of alcohol. The apparatus used and the method followed was the same as described in Part VI. The results are given in the following table. No results could be obtained with lower concentration of alcohol owing to high conductivity in our apparatus. The results are shown graphically in (fig I).

Kc./Sec.	100%	98% alcohol	87·8% alcohol	74% alcohol
23·6	...	26·1	42·4	91·1
49·5	45·9	26·4	27·2	51·8
94·5	40·8	26·2	...	41·6
473	31·8	25·6	37·5	41·7
1350	24·3	23·7	28·0	34·4
1842	25·6	25·1	30·6	38·2
3750	24·5	24·3	30·3	...

While pure alcohol shows highly anomalous dispersion, 98 per cent. alcohol shows very little dispersion, the dielectric constant being the same at high frequencies. With further dilution the dispersion increases with the frequency. The high dispersion observed is due to the formation of the complex $C_2H_5OH\ H_2O$.

Summary

The dielectric constants of alcohol water mixtures were determined in the entire range of concentration at 3000 meters. The polarization P_2 showed a maximum at the composition $C_2H_5OH\ 3H_2O$ and a minimum followed by a sharp rise at the composition $C_2H_3OH\ H_2O$.

The dispersion of dielectric constant of alcohol water mixtures up to 74 per cent. alcohol was measured from 23 to 3750 Kc. and was found to be highly anomalous for pure alcohol and when the composition was C_2H_5OH H_2O and negligible for 98 per cent. by weight of alcohol.

The results of the various physical properties of the system and of the selective adsorption by carbon are in confirmation of the above findings.

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