

STUDIES IN BINARY SYSTEMS

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INTRODUCTION

The nature of the liquid state has always been a baffling problem to scientists. The various physical properties of pure liquids such as freezing point, boiling point, thermodynamic studies, viscosity, surface tension, X-rays, dielectric properties, spectroscopic studies in the infra red region etc., indicate that the molecules of a liquid are highly associated the degree of which usually changes with temperature and other physical conditions. On the addition of another liquid the degree of association diminishes until in very dilute solutions only single molecules exist. It is found, however, that in many cases complex formation takes place between the solvent and the solute even in the case of mixtures of non-polar liquids, which is usually indicated by the deviations of the various physical properties from the ideal laws.

In the present investigation the authors have studied the influence of complex formation in the liquid state on (1) the selective adsorption of either of the components by carbon and silica gel and on (2) the dielectric polarisation, in the entire range of concentration of mixtures of benzene and carbon tetrachloride with ethyl and amyl alcohols and acetic acid. The polarisation has been found to indicate the formation of complexes where other physical properties are not sensibly affected.

I. Adsorption from binary mixtures

A polar substance like ethyl alcohol in a liquid state at room temperature has been experimentally shown to consist of dimers which are likely to be either more or less polar than single molecules the proportion of which may be very small at room temperature. On the addition of a non-polar substance like benzene the association of alcohol is not very much affected except at very great dilutions as revealed by cryoscopic measurements.

When adsorption measurements of the system benzene ethyl

alcohol are made on a hydrophilic adsorbent like silica gel, the adsorbent will take up relatively increased amounts of alcohol with increasing concentration until the saturation point is reached, the course of the curve being given by the usual Freundlich isotherm. When the concentration is further increased the excess of the alcohol adsorbed over the solvent benzene decreases rapidly until at about 0.93 moles fraction of alcohol both the liquids are adsorbed in the same proportion as the composition of the liquid. With further increase in concentration of alcohol silica gel actually takes up more of benzene than alcohol.

When the system benzene—ethyl alcohol is treated with an

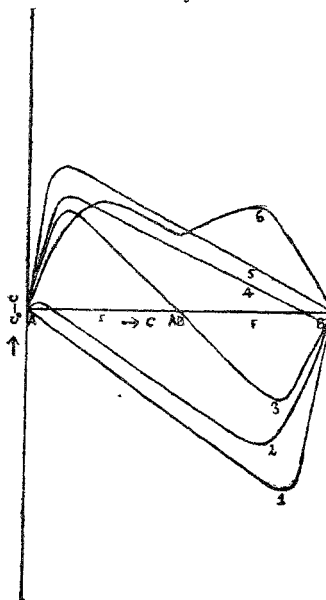


FIG. 1.

organophilic adsorbent like carbon, in dilute solutions alcohol is preferentially adsorbed up to a concentration of .04 mole fraction after which the curve passes through zero adsorption at 0.13 mole fraction. With further increase in concentration benzene is selectively adsorbed until a maximum is reached at 0.8 mole fraction of alcohol. With further increase the amount of benzene adsorbed decreases according to Freundlich law for dilute solutions.

The usual adsorption isotherm from binary liquid mixtures represents the relation between the equilibrium concentration C and $(C_0 - C)$ the change due to adsorption. Since $(C_0 - C)$ is only a relative quantity, it merely represents the selective adsorption of one of the components and does not express the true

adsorption. The shape of the apparent selective adsorption curve over the entire range of concentration, depends upon the adsorbent, the solvent and the solute and may be either (1) inverted 'U', (2) 'U' shaped or (3) 'S' shaped. Fig. I.

Curve 5 represents the selective adsorption of the solute B (positive adsorption); curve 2, 3 and 4 the selective adsorption of B up to a certain concentration, and then of A the solvent (negative adsorption), and curve I indicates the selective adsorption of the solvent (negative adsorption only). The first steep part of the curve represents true adsorption and follows Freundlich law for adsorption from dilute solutions. In more concentrated solutions the saturation point is reached after which the apparent selective adsorption decreases linearly with the composition.

The rapid fall in the selective adsorption with increasing concentration cannot be explained on the basis of saturation as in the latter case the adsorption should remain constant after having reached a maximum.

The shape of the curve may be explained on the hypothesis that in increasing concentrations the alcohol molecules are mostly associated to form dimers which are less hydrophilic than the single molecules. At a certain concentration the association would produce molecules which are as neutral as the non-polar solvent when the two components will be adsorbed in the same proportion in which they exist in the liquid state. With further increase in concentration the increase in association may produce molecules which are more "neutral" than the non-polar solvent when the latter will be adsorbed preferentially, the shape of the adsorption curve being then of 'S' type.

The 'S' type of the curve can also be explained on the basis of the existence of complexes of molecular composition in the binary mixtures.

When a complex is present a binary system will behave as a ternary one. Suppose a complex is formed at AB, then the curve might take the form as represented by curves 3 or 5.

The system can be supposed to behave like a binary one

between A and AB, and also between AB and B. The curve will take either 'S' or 'M' shape as represented by the figure depending on the selective nature of the adsorbent. If the point where the curve passes the axis should correspond to the composition of the complex and also if the adsorbent adsorbs only one of the components in preference to the other, supposing at E the composition is 75% B and 25% A, all the free A will go to make AB then, at E 50% B and 25% AB will be present so that the curve between A and AB will be in the positive direction. Between AB and B only A will be left free and naturally the curve will be in the negative direction such that the curve will take an 'S' form. The curve can also show a flat maximum at AB. As the concentration of B is increased more of B will go to form the complex AB so that the variation in the adsorption of B will not change with concentration.

If the adsorbent has a special affinity for the complex formed, it will adsorb the complex formed and naturally at the point where the formation of the complex will be a maximum the apparent adsorption will be a minimum (Curve 6).

If there is more than one complex present in the system, the selective adsorption curve can have a complicated shape.

The 'S' type of curve has been usually attributed to the existence of two types of adsorption centres on one and the same adsorbent which may be suitably activated to different relative degrees by changing the conditions as found in the case of *charcoal*. The fact that even an entirely hydrophilic adsorbent like silica gel gives an 'S' type of curve and the fact that even the most active organophilic adsorbent prepared also gives an 'S' type of curve with the system benzene-ethanol, would seem to favour an entirely novel treatment of the subject based upon the nature of primary and secondary adsorption phenomena. According to this idea a *hydrophilic* adsorbent like silica gel may, by primary adsorption of single molecules of ROH group, become *organophilic* owing to the oriented adsorption of the polar group OH, which would leave a surface saturated with the organic radical CH_3CH_2- . In the same way an oriented adsorption of alcohol with the hydro-carbon radical attached

to the adsorbent would leave the OH groups free on the surface which will then function as a hydrophilic adsorbent. The preferential adsorption of alcohol from benzene by either carbon or silica gel should on the above hypothesis give a 'S' shaped curve over a very small range of concentration over which the curves are twisted on the positive or negative side of the abscissa as found by Bartell and others.

The nature of the selective adsorption is thus a very complicated phenomena which is dependent on (1) the nature of the solution which may consist of single and associated molecules of the polar solute, the latter behaving as non-polar molecule at high concentrations; (2) the existence of the complex between the solvent and the solute in molecular proportion, the percentage of which would depend on the equilibrium between the reacting molecules; (3) the existence of two kinds of adsorption centres on one and the same adsorbent and (4) the conversion of an organophilic into hydrophilic adsorbent by primary adsorption of the oriented polar molecule.

II. Polarization and Complex formation

The dielectric constants of binary liquid mixtures have been determined for a large number of polar substances in non-polar solvents with a view to calculate the dipole moments of the molecules. It is assumed that the solvent does not combine with the solute and any disturbing factor usually called the 'solvent effect' is eliminated by extrapolation to infinite dilution on the assumption that in dilute solutions of the non-polar solvents like benzene and carbon tetrachloride the solute polar molecules are free to respond to the applied electrical field. There is increasing evidence, however, to show that alcohols dissolved in inert solvents like benzene and carbon tetrachloride form addition compounds with the solvent and that in dilute solutions most of the polar molecules are linked to the molecules of the solvent on account of the mass effect of the latter.

The polarisation of a binary mixture is given by the expression

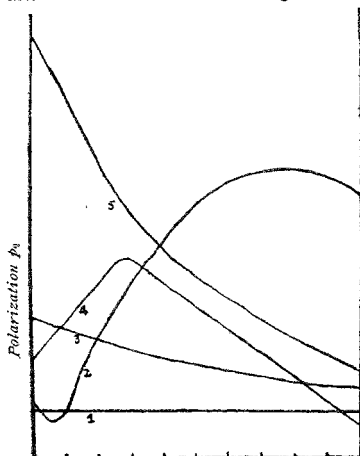
$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{f_1 M_1 + f_2 M_2}{d}$$

where ϵ is the dielectric constant, f_1 and f_2 are mole fractions of the

solute and the solvent, of molecular weights M_1 and M_2 , and d is the density of the mixture.

Debye ("Polar Molecules") has shown that three types of polarization—concentration curves are possible for dilute solutions of polar substances in non-polar solvents. They are illustrated by the curves of (I) ethyl alcohol—benzene, (II) ethyl ether—benzene and (III) nitrobenzene—benzene, where benzene is to be considered as a non-polar substance.

For I, the molar polarization starts with a finite value (for $f_2 = 0$) and increases with increasing concentration. For type II it will be



Mole Fraction of Polar Component.

FIG. II

1. Ether in Benzene.
2. *n* Octanol in Heptane.
3. Chlorobenzene in Benzene.
4. Ethanol in Benzene.
5. Acetone in Carbon tetrachloride.

constant over the entire range and for type III the molar polarization decreases with increasing concentration. Debye cites the case of ethyl alcohol in benzene, the molar polarization of which starts with 72 c.c. attaining a maximum value of 96 c.c. and finally decreasing and reaching in pure alcohol the value of 52 c.c. But no explanation has been offered for this kind of behaviour.

Smyth ("Dielectric Constant and Molecular Structure") also shows that the P_{12} and P_2 values of dilute ethyl alcohol solutions increase with increasing temperature instead of decreasing as required by theory.

P_{12} curve given by Smyth resembles that given by Debye,

but the P_2 curve shows a marked minimum, thus differing from the figure given by Debye. Smyth attributes these changes in the P_2 curves as due to orientation effect of the molecules.

Although the P_2 curves obtained by the present authors for different systems are in general of the same type as those given by Debye and Smyth, they are characterised by a marked kink at compositions corresponding to the formation of molecular complexes.

It is well known that polar liquids like alcohols are associated, the degree of association being about two. On addition of a non-polar substance like benzene, the dimers of alcohol are split up into simpler molecules so that the polarization increases.

If in mixtures of polar and non-polar substance the non-polar substance has no effect on the polar substance then, the polarization P_2 of the polar substance should remain constant whatever be its concentration *i.e.*, the polarization P_2 concentration curve should be horizontal, the height from the concentration axis being the value of the polarization P_2 of the pure polar liquid. But the various systems studied do not show this kind of behaviour, indicating that the presence of the non-polar substance has an effect on the polar substance so that the polarization P_2 goes to a maximum or minimum. If the polar substance is associated, then on addition of the non-polar substance, it will be split up into simpler molecules and the polarization increases. Thus a maximum point in the curve is reached. The minimum point on the curve can be explained on the basis of complex formation; when a complex is formed maximum amount of the free molecules of the substances will go to form the complex, thus leaving behind only a small proportion of free components of the substances, consequently the percentage composition of the polar liquid will be less than that calculated from the apparent composition. The polarization drops and the curve will pass through a minimum. As the concentration of the polar liquid is increased further, the free polar molecules will increase with the consequent rise in the value of polarization. The results of the present investigation show that there is a dip in the P_2 curve for ethyl alcohol-benzene at about 0.5 moles ethyl alcohol, corresponding to C_2H_5OH C_6H_6 , and in benzene-carbon tetrachloride for C_6H_6 CCl_4 and in *iso*amyl alcohol-benzene for C_6H_6 3 AmOH and in *iso*amyl alcohol-carbon tetrachloride for AmOH- CCl_4 . This kind of dip is also observed in the P_2 curve for *iso*amyl

alcohol (P. 184, "Dielectric Constant and Polar Molecules," Smyth) at about 0.5 moles which suggests that there is a complex $\text{AmOH} \cdot \text{C}_6\text{H}_6$ present. This dip in the curve may, as mentioned above, be due to the formation of the complex, instead of the postulation of two isomers of the amyl alcohol as done by Smyth.

The presence of these complexes is supported by the study of the adsorption of the system by different adsorbents.

Smyth ("Dielectric Constant and Molecular Structure") has discussed in detail some of the causes for molecular association in liquids. These he attributes to the presence of stray forces and *Van der Waals* forces. He points out that molecules associate due to sharing of electrons or possibly of hydrogen bonds between their structures and also due to *Van der Waals* forces.

According to Thomson ("Chemistry and Industry" 1938, 52, 512) the organic molecular complexes in solution are held together purely by *physical forces* or by definite *co-ordinate linkages* according as the polarization is *less* than the sum of the two components for the former and *more* in the latter. He has also pointed out that 1:1 formations are most usual when both components are mono-molecular.

The systems *isoamyl alcohol-carbon tetrachloride*, ethyl alcohol, water, ethyl alcohol-benzene show high exaltation in the value of polarization P_2 of the two components thus indicating definite co-ordinate linkages to be present in the systems. This linkage can be considered to be formed by the hydrogen bond present in the alcohols. The exaltation occurs at molecular compositions. The position of the maxima is shifted on either side of the composition $\text{C}_6\text{H}_6 \cdot 2 \text{ROH}$ on account of the effect of mass law. In all the systems a dip in the P_2 -concentration curve is noticed mostly corresponding to 1:1 complex. This would mean that complexes in solution are formed as a result of both physical forces and co-ordinate linkages.