Role of Dielectric Constant at the Miscibility Point in the Ternary System 2-Propanol-Water and Carbon Tetrachloride

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Two liquids are known[1] to be miscible in all proportions when both are sufficiently alike to obey Raoult's law. Only when the internal forces are quite unlike, separation of two liquid phases is known to occur. The fundamental question underlying all problems relating to solubility is the nature and the strength of intermolecular forces. The thermodynamic condition for equilibrium in any system is that the total free energy should be a minimum. If separation into two layers minimises the free energy of the system, it will happen so. Deviations from ideal behavior occur either owing to lowering the temperature or by choosing components more unlike in attractive forces. Either of these changes, when pursued far enough, can bring about a separation into two liquid phases.

A new outlook is developed in the following investigations. The work of Coomber[2] and McC. Lewis[3] shows that dielectric constant of a liquid system is related to its internal pressure. To an inhomogeneous mixture of two liquids progressive addition of a third component which happens to mix with both the liquids entails in a distribution of the added component between the two layers. With successive additions of the third component there is to be expected, as a result of the distribution between the two phases a progressive variation of the physico-chemical properties in the two layers. Just at the miscibility point these properties in the respective layers should tend to a limit at which the phase boundary just disappears forming a homogeneous system. Since internal pressure is connected with the dielectric constant (loc. cit.), at the transition when the phase boundary disappears, we may expect a quantitative relationship among the values of dielectric constant of the solution and those of the three pure components. The ternary system 2-propanol-water-carbon tetrachloride has been studied from the above point of view. We have reported[4] earlier our results on the ternary system 1-propanol-water-toluene.

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[1] E. Washburn, *Trans. Am. Electrochem. Soc.*, **22**, 330 (1912).

[2] D. I. Coomber, *Trans. Faraday Soc.*, **35**, 304 (1939).

[3] W. C. McC. Lewis, *Phil. Mag.*, **28**, 104, (1914).

[4] K. M. Somasundaram and C. V. Suryanarayana, This Bulletin, **31**, 838 (1958).

TABLE I. 2-PROPANOL–WATER–CARBON TETRACHLORIDE

Mole fraction			Density	Viscosity in centipoises	Dielectric constant
2-Propanol x_1	Water x_2	CCl_4 x_3			
0.4397	0.2385	0.3222	1.1650	1.047	8.09
0.4345	0.3362	0.2291	1.0810	1.114	10.80
0.4101	0.4149	0.1752	1.0480	1.223	13.50
0.3853	0.4788	0.1355	1.0170	1.319	16.05
0.3431	0.5584	0.0986	0.9940	1.452	20.52
0.3057	0.6323	0.0622	0.9625	1.570	24.87
0.2844	0.6591	0.0565	0.9636	1.629	28.01
0.2349	0.7283	0.0364	0.9515	1.723	33.00
0.1939	0.7872	0.0188	0.9380	1.672	40.70

TABLE II

$\sum_3 P_3x_3$	$P_{1,2,3}$	% deviation from the mean value	$\sum_3 L_3x_3$	$L_{1,2,3}$	% deviation from the mean value
42.211	48.48	6.911	0.6946	0.7030	0.6009
40.948	47.73	7.647	0.7572	0.7656	0.5516
39.190	45.45	7.396	0.7967	0.8065	0.6113
37.545	43.14	6.937	0.8259	0.8337	0.4700
35.112	39.97	6.471	0.8559	0.8666	0.6212
32.913	36.32	4.920	0.8847	0.8886	0.2200
31.811	35.26	5.142	0.8908	0.9003	0.5304
29.196	31.54	3.860	0.9097	0.9141	0.2413
27.010	28.49	2.667	0.9264	0.9298	0.1832

TABLE III. 2-PROPANOL–WATER

Mole fraction		Density	Viscosity in centipoises	Dielectric constant
2-Propanol x_1	Water x_2			
—	1.0000	0.9941	0.7225	72.94
0.0232	0.9770	0.9813	0.947	71.00
0.0514	0.9486	0.9692	1.248	66.25
0.0956	0.9044	0.9499	1.639	58.22
0.1578	0.8422	0.9226	1.954	49.72
0.1914	0.8086	0.9097	2.040	45.98
0.2619	0.7381	0.8857	2.116	38.62
0.3526	0.6474	0.8618	2.095	32.47
0.4829	0.5171	0.8354	1.938	26.51
0.6797	0.3203	0.8072	1.699	20.70
0.8819	0.1183	0.7866	1.529	18.35
1.0000	—	0.7736	1.550	17.50

TABLE IV

$\sum_2 P_2x_2$	$P_{1,2}$	% deviation from the mean value	$\sum_2 L_2x_2$	$L_{1,2}$	% deviation from the mean value
—	17.42	—	—	0.9610	—
18.551	18.57	0.0512	0.9586	0.9590	0.0209
19.908	19.90	0.0201	0.9552	0.9559	0.0366
22.051	22.05	0.0023	0.9503	0.9504	0.0053
25.070	25.17	0.1991	0.9432	0.9419	0.0690
26.690	26.86	0.3174	0.9393	0.9376	0.0906
30.130	30.38	0.4130	0.9317	0.9262	0.2960
34.510	34.77	0.3753	0.9212	0.9128	0.4580
40.825	41.05	0.2748	0.9065	0.8948	0.6204
50.368	50.12	0.2468	0.8843	0.8680	0.9303
60.274	59.73	0.4533	0.8617	0.8523	0.5484
—	65.91	—	—	0.8484	—

TABLE V. 2-PROPANOL–CARBON TETRACHLORIDE

Mole fraction		Density	Viscosity in centipoises	Dielectric constant
2-Propanol x_1	CCl_4 x_2			
—	1.0000	1.5652	0.7942	2.205
0.1721	0.8279	1.4500	0.8910	2.84
0.3180	0.6820	1.3460	0.8742	3.84
0.4248	0.5752	1.2680	0.8710	5.09
0.5556	0.4444	1.1680	0.8828	7.04
0.6238	0.3762	1.1110	0.9042	8.60
0.8251	0.1749	0.9389	1.0300	13.10
0.8748	0.1252	0.8919	1.0510	14.30
0.9326	0.0674	0.8390	1.1090	15.68
0.9623	0.0377	0.8168	1.1350	16.27
1.0000	—	0.7736	1.5500	17.80

TABLE VI

$\sum_2 P_2x_2$	$P_{1,2}$	% deviation from the mean value	$\sum_2 L_2x_2$	$L_{1,2}$	% deviation from the mean value
—	28.66	—	—	0.2865	—
34.66	36.13	2.077	0.3832	0.3802	0.393
40.19	44.79	5.413	0.4654	0.4863	2.196
44.20	51.87	7.984	0.5252	0.5769	4.690
49.13	57.66	7.989	0.5988	0.6680	5.463
51.69	61.49	8.660	0.6367	0.7169	5.926
59.29	65.24	4.779	0.7499	0.8013	3.313
61.15	65.69	3.582	0.7777	0.8160	2.403
63.36	65.73	1.836	0.8105	0.8305	1.219
64.48	65.12	0.491	0.8272	0.8358	0.517
—	65.91	—	—	0.8484	—

Experimental

Preparation of solutions, measurements of dielectric constant, density and viscosity were done as given in our previous paper (loc. cit., this bulletin).

Purification of the Components.—E. Merck's purest 2-propanol was refluxed[5,6] with an excess of freshly burnt calcium oxide and distilled. The distillate was dried over small pieces of magnesium ribbon and fractionally distilled. The fraction boiling at 82.4°C was collected and stored in a pyrex bottle. E. Merck's pro analysi carbon tetrachloride was distilled, the distillate boiling at 76.8°C was collected and stored in a Pyrex bottle. Conductivity water was distilled once more in a Pyrex outfit and this was preserved free from carbon dioxide. A dielectric constant check was made now and then. This was used throughout the investigation.

All the experiments were performed at 35°C. Results obtained are given in Tables I to VI.

Discussion

In our previous publication in this bulletin[4] on the ternary system 1-propanol–water–toluene we had derived the equation

$$\sum_k L_k x_k = L_{1,2\cdots k} \tag{1}$$

where L_k is the volume polarization of the k-th component, $L_{1,2\cdots k}$, that of the mixture of k components and x_k, the mole fraction. This derivation was made on the usual assumption of isomegethic solutions as done in some theories of solutions which means that

$$\bar{v}_1=\bar{v}_2=\cdots\cdots=\bar{v}_k \tag{2}$$

On this assumption,

$$V_k=\frac{v_k}{\sum v_k}=\frac{n_k\cdot\bar{v}_k}{\sum n_k\cdot\bar{v}_k}=\frac{n_k}{\sum n_k}=x_k$$

But the above assumption 2 is not correct with real solutions. We rarely meet with solutions wherein the molecules of the components have the same molar volume. We shall now consider the consequences of this assumption.

Turning to the experimental values, Table II shows that Eq. 1 holds excellently well at the point of disappearance of the phase boundary, whereas the well known equation.

$$\sum_k P_k\cdot x_k = P_{1,2\cdots k} \tag{3}$$

fails thoroughly.

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5) A. I. Vogel, "Practical Organic Chemistry", Longmans, 2nd Ed., London (1951), p. 168.

6) A. A. Maryott, *J. Am. Chem. Soc.*, **63**, 3079 (1941).

Comparison of Tables IV and VI shows that in the case of 2-propanol–water system both Eq. 1 and 3 hold excellently, whereas with 2-propanol–carbon tetrachloride system both the Eq. 1 and 3 are inapplicable. Akerlöf⁽⁷⁾ determined the dielectric constants of mixtures of 2-propanol–water at 25°C. Our data in Table III were collected at 35°C.

In this laboratory⁽⁸⁾ the general observation made was that in about thirteen ternary systems investigated so far, Eq. 3 fails thoroughly while Eq. 1 succeeds just at the point of disappearance of the phase boundary. Further in polar-polar binary mixtures both Eqs. 1 and 3 are applicable, whereas in polar-nonpolar binary combinations both Eqs. 1 and 3 fail. From these observations one conclusion can be drawn, that Eq. 1 is in now way better than Eq. 3 in general but the former seems to be holding excellently at the transition of disappearance of the phase boundary.

We have pointed out above that the derivation of Eq. 1 assumes that the molar volumes of the participating species of molecules must be the same, which is not really so, as far as the three components 2-propanol, water and carbon tetrachloride are concerned. Even then, if Eq. 1 should hold good specially at the transition of disappearance of the phase boundary, one has to conclude that at the transition when the two phases should disappear, conversely one should obtain the condition that the molar volumes of the different species of molecules must be the same. That means condition 2 is satisfied at the transition. This may perhaps mean that for two phases to become homogeneous condition 2 is to be satisfied.

Let us examine the implication of condition 2 being satisfied at the transition of the disappearance of the phase boundary. Usually we obtain the molar volume of a substance by dividing the molecular weight by the macroscopic bulk density. The molar volume thus obtained is actually due to the molecules as well as the voids. Obviously such a computation is no indication of the actual size of the molecules. Molar volume thus obtained may be written as $(V_{ma}+\phi_v)$, where V_{ma} is the actual volume due to the molecules and ϕ_v that due to the voids. In this context, if Eq. 1 holds good at the transition of the disappearance of the phase boundary, by converse the condition

$$(V_{ma}+\phi_v)_1=(V_{ma}+\phi_v)_2=(V_{ma}+\phi_v)_3 \qquad (4)$$

is valid. Of course ϕ_v is a characteristic constant for a given liquid at a particular temperature. In other words satisfaction of condition 4 seems to be a precondition for liquid-liquid miscibility. Relation 4 seems to imply that just at the transition when a phase boundary disappears to form a homogeneous system, there seems to be occurring an equipartition of space by the different species of molecules, irrespective of their sizes, constituting the homogeneous system resulting from the disappearance of the phase boundary. For a successful theory of liquid–liquid miscibility the future seems to revolve on a thorough understanding of the ϕ_v factor in Eq. 4 in all its qualitative and quantitative aspects.

In the binary system 2-propanol-carbon tetrachloride the viscosity variation is anomalous. A plot of viscosity against mole per cent of 2-propanol shown in the graph exhibits a minimum at about 45 mole per cent of 2-propanol. Sugden⁽⁹⁾ explained a similar phenomenon of negative viscosity in aqueous solutions as due to the strong dipole action of one of the constituents in the solution having the effect of depolymerizing the associated molecules of the other constituent entailing in a decrease of viscosity. But in this binary system carbon tetrachloride molecule is not a dipole. Sometimes a shortening of the length of the associated polymers is given as an explanation for lowering of viscosity. But then this presupposes a length of the associated polymer of the alcohol more than that due to two molecules. Of course, we can not assume a long chain formation of a compound between 2-propanol and carbon tetrachloride. The situation, therefore, leaves us in doubt as to what is the causative factor for such a decrease in viscosity.

Summary

To understand why a heterogeneous system of two immiscible liquids so exists without mixing we have made a new approach of studying the physical properties of the system just at the transition of the disappearance of the phase

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7) G. Akerlöf, ibid., **54**, 4125 (1932).

8) K. M. Somasundaram, Ph. D. thesis, Annamalai University (1958).

9) J. N. Sugden, *J. Chem. Soc.*, **1926**, 183.

boundary after the addition of an optimum amount of a third component which is freely miscible with the two heterogeneous components thus resulting in the formation of a ternary system. At the transition of the disappearance of the phase boundary we have found that $\sum_3 L_3x_3 = L_{1,2,3}$, wherein L represents volume polarization and x the mole fraction, holds good. The implications of the validity of the above equation have been discussed.

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