Dielectric Contribution to Miscibility in the Ternary System 1-Propanol-Water-Toluene

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(Received May 13, 1958)

When a third component miscible with each of the two liquids is added, to two layers of either immiscible or partially miscible liquids, the added component distributes between the two layers. Progressive additions of the third component results in a corresponding variation of the physico-chemical properties in the two layers till at the miscibility point they tend to reach a limit at which the interphase just disappears, forming a homogeneous system. Just at the point of disappearance of the interphase we may expect a quantitative relationship between the value of dielectric constant of the solution and those of the three pure components. The ternary of system 1-propanol, water and toluene has been studied from the above point of view. Incidentally the physico-chemical properties of different percentage compositions of the two binary systems 1-propanol-water and 1-propanol-toluene were also studied.

Experimental

Preparation of Solutions.—In clean dry 100 ml. Pyrex conical flasks different ratios of the two immiscible components, water and toluene, of the ternary system under study were taken by weight in such a way that the variation was progressive in the range of 10 to 90%. The third component, 1-propanol was added at a constant temperature of 35°C from a burette as in a usual titration and shaken thoroughly after each addition till a perceptible cloudiness appeared with no distinction between the two layers. Just a little more of the component from the burette was added cautiously in drops just till the cloudiness disappeared. Now the conical flask was weighed with its contents. From this, the weight of the added 1-propanol could be easily computed. From the weights of the individual components, the mole fractions of the constituents in the ternary mixture could be computed.

Measurement of Dielectric Constant, Density and Viscosity.—For measuring the dielectric constant of the homogeneous solution "Dekameter type DKO3" of Wissenschaftlich-Technische Werkstätten was used at a fixed frequency of 1.8 Mc/sec. with Hoppler's ultra thermostat. The homogeneous solution was put into the cell, allowed to attain the temperature of 35°C and then measurement was made.

Viscosity was measured as usual with an Ostwald viscometer using Gallenkamp's glass-walled thermostat b-12210. Density was determined using the density bottle, whose volume was determined by weighing it filled with water and dividing the weight of the water by the density at 35°C, which was looked up in Lange's[1] "Hand Book of Chemistry."

Purification of the Components.—E. Merck's Purest 1-propanol[2] was dried with anhydrous potassium carbonate and distilled. The fraction boiling between 97∼98°C was collected and further dried with magnesium activated with iodine. The product was then distilled with exclusion of moisture and the distillate boiling at 97.2°C was collected and preserved in a Pyrex bottle. Baker's analysed toluene meeting the American Chemical Society specifications was dried over anhydrous calcium chloride, filtered and distilled. The distillate boiling at 110.6°C was collected and preserved in a Pyrex bottle. Conductivity water was distilled once more in a Pyrex outfit and this was preserved free from carbon dioxide and used. A dielectric constant check was made now and then. This water was used throughout the investigation.

Results obtained are detailed in the following tables.

Discussion

The equation for the molar polarization of a mixture

$$P_{1,2\cdots k}=\frac{\varepsilon_{1,2,\cdots k}-1}{\varepsilon_{1,2,\cdots k}+2}\,\frac{M_1x_1+M_2x_2+\cdots M_kx_k}{\rho_{1,2\cdots k}} \tag{1}$$

holds strictly for solutions of zero volume of mixing. Therefore, in normal practice, apart from many other factors that influence the dielectric constant of a solution the occurrence of the density factor in equation 1 limits its rigorous application.

Van Arkel and Snoek[3] adopt the equation

$$L_{1,2}=L_1v_1+L_2v_2 \tag{2}$$

where v is the volume concentration and L the volume polarization. Sugden[4] found

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[1] N. A. Lange, "Hand Book of Chemistry", Hand Book Publishers, Inc., Sandusky, Ohio (1949) p. 1385

[2] A. I. Vogel, "Practical Organic Chemistry", Longmans, London, 2nd ed., (1951), p. 168.

[3] A. E. van Arkel and J. L. Snoek, *Trans. Faraday Soc.*, **30**, 710 (1934).

[4] S. Sugden, *Nature*, **133**, 415 (1934).

that when P_2 is plotted against volume polarization for solutions of benzo nitrile, nitrobenzene and chlorobenzene in a number of non-polar solvents, all the points for each substance lie near a straight line through the entire range of solutions to the pure liquid. For the change in polarization of the solute in concentrated solution Sugden⁵⁾ found a very simple relation ship

$$ {}_cP_2=A-B\,\frac{\varepsilon_c-1}{\varepsilon_c+2} \tag{3}$$

where A and B are constants. From these considerations it is clear that volume polarization seems to be more fundamental than molar polarization.

Böttcher⁶⁾ derives the equation

$$\frac{\varepsilon-1}{\varepsilon+2}=\sum_k\varphi_k\cdot\frac{\varepsilon_k-1}{\varepsilon_k+2} \tag{4}$$

which is the same as

$$L_{1,2\cdots k}=L_1V_1+L_2V_2\cdots L_kV_k \tag{5}$$

where $\frac{\varepsilon-1}{\varepsilon+2}=L_{1,2\cdots k}=$volume polarization of the mixture, $\varphi_k=V_k=$volume fraction of the component k, and $\frac{\varepsilon_k-1}{\varepsilon_k+2}=L_k=$volume polarization of the component k.

In equation 5 V_k is the ratio of the volume v_k of component k to the total volume $v_1+v_2\cdots v_k$ in the mixture. Let $n_1,n_2\cdots n_k$ be the actual number of molecules contained in $v_1,v_2\cdots v_k$ cc. respectively. Therefore the volume fraction V_k equals effectually $n_k/\sum n_k$ which is the same as the mole fraction x_k. The total volume polarization $L_{1,2\cdots k}$ of the mixture as measured will be due to the sum of total contribution of $\sum n_k$ molecules. Hence we may write,

$$\sum_k L_kx_k=L_{1,2\cdots k} \tag{6}$$

Equation 6 is clearly independent of the volume of mixing. Volume polarization L is a dimensionless function and depends only on the number of molecules present in unit volume and their polarisabilities.

Data obtained in the above investigations have been used to compare equation 6 with the well known equation

$$\sum_k P_kx_k=P_{1,2\cdots k} \tag{7}$$

Table I records the data obtained for the ternary system. Table II brings out a comparison of the equations 6 and 7. It is quite clear that percentage deviation from the mean value is almost negligible with equation 6, whereas deviations are considerable with equation 7.

Akerlöf⁷⁾ determined the dielectric constant of mixtures of 1-propanol and water at 25°C. Table III gives the data on density, viscosity and dielectric constant of mixtures of 1-propanol and water at 35°C as determined in this laboratory.

Plots of molar polarization and volume polarization against mole percent of 1-propanol (not given) show a linear variation. The plot of dielectric constant against mole percent of alcohol (not given) falls off rapidly with increasing mole percent of alcohol. The viscosity curve (not given) shows a maximum at about 28 mole percent of 1-propanol. The last column of Table III shows that at about 26 mole percent of 1-propanol, the volume contraction is maximum. If from viscosity and volume contraction data we have to conclude any molecular combination involving solute-solvent interaction we must expect with Hassel and Uhl⁸⁾ anomalously high molecular polarization about 28 mole percent of 1-propanol which is obviously not true here. It is also known⁹,¹⁰⁾ that the effect of association on the dielectric constant depends on the sizes and shapes of the participating dipoles. As a result of a greater electrostatic moment of a polymerized molecule than the simple one the dielectric constant of the solvent will be greater in its associated state. Deassociation in some solutions is indicated by the lowering of the dielectric constant of that component in solution. Conversely when dipole-dipole interaction occurs, the forces holding the electric charge will be weakened as a result of probable increase of the electrostatic moment of the molecule and the dielectric constant of a component becomes greater in solutions than in its pure state. In this context merely from the viscosity peak, it is rather unsafe particularly in the absence of absorption and Raman spectra, to conclude the existence of a compound of whatever composition between 1-propanol-water. Further investigations are required to solve this

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5) S. Sugden, *Trans. Faraday Soc.*, **30**, 720 (1934).

6) C. J. F. Böttcher, "Theory of Electric Polarisation", Elsevier, Amsterdam, (1952), p. 203.

7) G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

8) O. Hassel and A. H. Uhl, *Naturwissenschaften*, **18**, 247 (1930).

9) R. N. Kerr, *J. Chem. Soc.*, **1926**, 2796.

10) J. W. Williams and I. J. Krchma, *J. Am. Chem. Soc.*, **48**, 1886 (1926).

TABLE I

(1-Propanol-water-toluene).

Mole fraction			Density	Viscosity in centipoises	Dielectric constant	Volume contraction in ml. per 1000 ml. of solution
1-Propanol x_1	Water x_2	Toluene x_3				
0.5042	0.2793	0.2166	0.8326	0.8804	12.70	4.861
0.4888	0.3351	0.1761	0.8355	0.9553	14.49	8.557
0.4645	0.3996	0.1359	0.8399	1.0360	16.50	8.971
0.4138	0.4976	0.0886	0.8487	1.1840	20.35	10.720
0.3657	0.5778	0.0565	0.8588	1.3160	25.00	12.650
0.3191	0.6400	0.0409	0.8694	1.3910	28.48	14.700
0.2754	0.6928	0.0318	0.8794	1.4740	32.00	15.770
0.2197	0.7603	0.0200	0.8936	1.5620	37.53	10.840
0.1389	0.8501	0.0110	0.9169	1.7000	46.80	7.316

TABLE II

$\sum_{k=1,2,3} P_k x_k$	$P_{1,2,3}$	% deviation from the mean value	$\sum_{k=1,2,3} L_k x_k$	$L_{1,2,3}$	% deviation from the mean value
44.885	52.85	8.149	0.7672	0.7960	1.843
43.500	50.56	7.506	0.7952	0.8181	1.419
41.702	47.51	6.510	0.8239	0.8377	0.831
38.529	42.83	5.286	0.8600	0.8658	0.336
35.738	38.91	4.251	0.8857	0.8888	0.175
33.257	35.76	3.659	0.9011	0.9018	0.042
31.033	33.15	3.301	0.9115	0.9118	0.014
28.198	29.73	2.644	0.9251	0.9243	0.043
24.111	25.27	2.347	0.9395	0.9387	0.043

TABLE III

(1-Propanol-water)

Mole fraction		Density	Viscosity in centipoises	Dielectric constant	Volume contraction in ml. per 1000 ml. of solution
1-Propanol x_1	Water x_2				
—	1.0000	0.9941	0.723	74.94	—
0.0243	0.9757	0.9815	0.849	69.75	6.69
0.0599	0.9400	0.9661	1.038	64.37	14.91
0.1044	0.8956	0.9454	1.232	58.50	17.46
0.1392	0.8608	0.9305	1.348	51.38	19.75
0.2072	0.7928	0.9063	1.472	43.30	19.36
0.2629	0.7371	0.8902	1.519	38.75	20.16
0.3383	0.6617	0.8722	1.523	34.00	18.68
0.4273	0.5727	0.8553	1.494	29.71	17.44
0.5839	0.4161	0.8326	1.406	25.00	13.08
0.8250	0.1750	0.8085	1.290	20.95	8.40
1.0000	—	0.7918	1.614	18.90	—

question.

Data of dielectric constant, density and viscosity of mixtures of 1-propanol and toluene, are given in table V. Table VI shows that both the equations 6 and 7 fail with the system.

Plots of molar polarization and volume polarization (not given) against percentage composition of 1-propanol show a continuous increase with a tendency for a maximum in the former about 75 mole percent of the alcohol. The dielectric constant and viscosity (curves not given) vary with mole percent of 1-propanol in a similar way, increasing rapidly and continuously with increase of alcohol.

Several other binary systems worked recently in this laboratory show that both equations 6 and 7 are valid in polar-polar binary mixtures and definitely fail in the case of polar-nonpolar mixtures. It is rather difficult to explain this fact.

TABLE IV

$\sum_{k=1,2} P_k x_k$	$P_{1,2}$	% deviation from the mean value	$\sum_{k=1,2} L_k x_k$	$L_{1,2}$	% deviation from the mean value
—	17.42	—	—	0.9610	—
18.568	18.59	0.0592	0.9582	0.9583	0.0052
20.254	20.28	0.0641	0.9543	0.9548	0.0262
22.387	22.53	0.3111	0.9500	0.9504	0.0211
24.041	24.23	0.3914	0.9463	0.9441	0.1163
27.280	27.55	0.4922	0.9392	0.9337	0.2936
29.940	30.27	0.5480	0.9337	0.9264	0.3924
35.520	33.88	0.5342	0.9254	0.9166	0.4889
37.754	38.11	0.4953	0.9164	0.9055	0.5955
45.207	45.48	0.3010	0.9000	0.8890	0.6151
56.670	56.69	0.0176	0.8747	0.8694	0.3039
—	65.01	—	—	0.8566	—

TABLE V
(1-Propanol-toluene)

Mole fraction		Density	Viscosity in centipoises	Dielectric constant	Volume contraction in ml. per 1000 ml. of solution
1-Propanol x_1	Toluene x_2				
—	1.000	0.8528	0.5474	2.34	—
0.1148	0.8852	0.8459	0.5495	2.82	0.825
0.2642	0.7358	0.8393	0.5691	4.00	−2.248
0.3860	0.6140	0.8335	0.6002	5.09	−0.224
0.5022	0.4978	0.8272	0.6466	6.90	−0.223
0.6123	0.3877	0.8215	0.7062	9.25	1.045
0.7121	0.2879	0.8157	0.7902	11.50	2.396
0.8095	0.1905	0.8097	0.8888	14.05	2.840
0.9353	0.0647	0.8005	1.0880	17.43	3.186
1.0000	—	0.7918	1.6140	18.90	—

TABLE VI

$\sum_{k=1,2} P_k x_k$	$P_{1,2}$	% deviation from the mean value	$\sum_{k=1,2} L_k x_k$	$L_{1,2}$	% deviation from the mean value
—	33.42	—	—	0.3092	—
37.056	39.51	3.205	0.37217	0.3777	0.738
41.760	49.83	8.918	0.45380	0.5000	4.848
45.610	55.25	9.557	0.52060	0.5772	5.156
49.270	60.94	10.590	0.58400	0.6630	6.336
52.760	64.74	10.200	0.64450	0.7335	6.604
55.935	66.13	8.345	0.69926	0.7778	5.318
58.986	66.48	5.973	0.75231	0.8130	3.877
62.962	65.63	2.075	0.82111	0.8455	1.462
—	65.01	—	—	0.8566	—

Tables I, III and V show that in all cases there is involved some volume contraction. Equation 6 holds excellently in the ternary system. Equation 6 cannot be claimed, therefore, to have set right the error due to volume of mixing inherent in equation 1. On the other hand as observed recently with several other ternary systems in this laboratory, equation 6 may be considered to give tentatively a quantitative condition involving a dielectric contribution of the components to miscibility. In other words, just at the point wherein two phases disappear to give a homogeneous system, equation 6 seems to apply excellently.

Summary

In place of the familiar equation $\sum_k P_k x_k = P_{1,2\cdots k}$, which does not hold good in many cases, we have formulated alternatively

the equation $\sum_{k} L_k x_k = L_{1,2\cdots k}$ where L is volume polarization. This equation has been applied to the ternary system 1-propanol-water and toluene just at the point of miscibility, when to a given ratio of toluene and water addition of an optimum amount of 1-propanol results in the disappearance of the two phases. Also the new equation has been applied to two fully miscible binary systems 1-propanol-water and 1-propanol-toluene. It has been concluded that the new equation gives a condition concerning the dielectric contribution of the components to miscibility in the ternary system.

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