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Dielectric constants and refractive indices of 1-propanol or 2-propanol + cyclohexane, benzene, toluene, *o*-, *m*- and *p*-xylene at 308.15 K

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Dielectric constants and refractive indices data at 308.15 K for 1-propanol or 2-propanol with cyclohexane, benzene, toluene, *o*-, *m*- and *p*-xylene have been reported. The analysis of data shows the presence of strong specific interactions between propanol and aromatic hydrocarbon. Frohlich equation is used to calculate the apparent dipole moment of these binary mixtures.

Binary mixtures of alkanol with hydrocarbons or aromatic hydrocarbons are of great interest due to their extremely non-ideal behaviour and practical importance to chemical industry. A lot of work has been reported in the literature[1-6] on the dielectric behaviour of alkanol in hydrocarbon (inert solvent). In our earlier work[7] on propanol + cyclohexane or an aromatic hydrocarbon like benzene, toluene, *o*-, *m*- and *p*-xylene, it has been shown that the excess thermodynamic properties (V^E, H^E, G^E) can be described in terms of Mecke-Kempter association model[8], which indirectly shows the existence of strong electron donor-acceptor interaction between the hydroxyl hydrogen and π-electrons of benzene ring. In the present paper, the dielectric constant and refractive indices of these binary mixtures have been studied at 308.15 K to get further insight into the behaviour of propanol in inert and polar solvents.

Materials and Methods

1-Propanol, 2-propanol, cyclohexane, benzene, toluene, *o*-, *m*- and *p*-xylene (E. Merck) are purified by standard procedures. The purities of final samples were checked by measuring their densities at 298.15 ± 0.01 K; these agreed to within $\pm 5 \times 10^{-5}$ gm cm^{-3} with the corresponding literature values[9-12].

Dielectric constant (±0.0001) of propanol + cyclohexane or aromatic hydrocarbon (2) mixtures at 308.15 K were determined from capacity measurement using a dipolemeter (Type RL 09, Toshniwal, India). The samples were placed in a cell containing a co-axial brass cylinder and the cell was immersed in a water thermostat maintained at 308.15 ± 0.1 K. The instrument was calibrated before hand with several samples of pure liquids.

The refractive indices (±0.0001) of the binary mixtures were measured using an Abbe refractometer. The water maintained at 308.15 ± 0.01 K was circulated around the prism of refractometer to keep the temperature constant.

Results and Discussion

Dielectric constants and refractive indices of pure components and binary 1-propanol or 2-propanol + cyclohexane or benzene or toluene or *o*-, *m*- or *p*-xylene (2) mixtures at 308.15 K in the mole fraction range $0 < x_1 < 0.25$ have been recorded in Tables 1 and 2.

Deviation in dielectric constant of mixtures, Δε, from the ideal mixture have been calculated from the relation

$$\Delta\varepsilon = \varepsilon_S - x_1\varepsilon_1 - x_2\varepsilon_2$$

Table 1—Values of molar volume (V) refractive indices (η) permittivity (ε) and dipole moment (μ) of pure compounds at 308.15 K

Compound	V ($cm^3 mol^{-1}$)	(n)	ε	μ (Debye)
1-Propanol	75.910	1.3722	18.79	3.09
2-Propanol	77.968	1.3681	17.04	1.66
Cyclohexane	110.061	1.4105	2.02	0.28
Benzene	90.468	1.4844	2.2525	0.00
Toluene	108.031	1.4811	2.3536	0.31
o-Xylene	122.402	1.4895	2.4150	0.45
m-Xylene	124.725	1.4812	2.3442	0.30
p-Xylene	125.203	1.4786	2.2447	0.02

Table 2—Values of refractive indices (n), dielectric constant (ε), molar volume (V_m), deviation in dielectric constant ($\Delta\varepsilon$), and apparent dipole moment (μ_{12}) at different mole fractions of alkanol x_1 at 308.15 K

x_1	n	ε	V_m (cm^3mol^{-1})	μ_{12} (Debye)
	1-Propanol (1) + Cyclohexane (2)			
0.0387	1.4051	2.6322	108.872	3.129
0.0812	1.4042	2.6713	107.543	2.107
0.1258	1.4031	2.9901	106.125	1.966
0.1649	1.4012	3.0724	104.864	1.719
0.2015	1.4002	3.3225	103.672	1.676
	1-Propanol (1) + Benzene (2)			
0.0362	1.4771	3.7245	90.011	4.175
0.0998	1.4722	3.9823	89.177	2.593
0.1452	1.4674	4.4514	88.560	2.332
0.1933	1.4641	4.5002	87.891	1.990
0.2379	1.4562	4.9212	87.260	1.899
	1-Propanol (1) + Toluene (2)			
0.0573	1.4722	4.3014	106.239	3.989
0.0967	1.4694	4.4332	104.699	3.086
0.1693	1.4658	4.7017	102.699	2.377
0.2086	1.4610	4.7525	101.447	2.119
0.2591	1.4400	5.0336	99.831	1.949
	1-Propanol (1) + *o*-Xylene (2)			
0.0536	1.4860	3.9019	119.977	3.903
0.0785	1.4825	4.0414	118.842	3.305
0.1180	1.4800	4.2122	117.032	2.754
0.1526	1.4786	4.2873	115.439	2.419
0.2145	1.4721	4.7017	112.575	2.158
	1-Propanol (1) + *m*-Xylene (2)			
0.01501	1.4703	4.1019	124.022	8.211
0.0480	1.4744	3.5545	122.463	3.852
0.0743	1.4740	3.6716	121.212	3.169
0.1356	1.4581	3.9018	118.269	2.422
0.1388	1.4725	3.9213	118.115	2.403
0.2040	1.4351	4.4714	114.955	2.183
	1-Propanol (1) + *p*-Xylene (2)			
0.0493	1.4758	3.7515	122.844	4.223
0.0892	1.4729	3.6724	120.915	2.993
0.1361	1.4710	3.8526	118.632	2.477
0.1628	1.4676	3.9419	117.326	2.281
0.1958	1.4648	4.3013	115.706	2.223
	2-Propanol(1) + Cyclohexane (2)			
0.0333	1.4061	2.3014	109.194	2.318
0.0792	1.4044	2.3542	107.946	1.479
0.1215	1.4023	2.4014	106.750	1.166
0.1576	1.4001	2.3017	105.750	0.653
0.1660	1.4016	2.3845	105.452	0.826
0.1977	1.3982	2.5764	104.506	1.005
	2-Propanol (1) + Benzene (2)			
0.0397	1.4772	3.4215	90.115	3.619
0.0948	1.4722	3.6623	89.578	2.450
0.0971	1.4720	3.5724	89.554	2.345
0.1820	1.4607	4.4414	88.641	2.055
0.2069	1.4581	4.5714	88.357	1.954
	2-Propanol (1) + Toluene (2)			
0.0389	1.4751	4.1324	106.960	4.727
0.0728	1.4719	4.4562	106.007	3.645
0.1074	1.4682	4.5517	105.017	3.008
0.1552	1.4653	4.7525	103.628	2.541
0.1959	1.4600	4.8018	102.429	2.2376
	2-Propanol (1) + *o*-Xylene (2)			
0.0538	1.4832	2.9017	120.130	2.325
0.0987	1.4782	2.8533	118.210	1.518
0.1294	1.4762	2.9212	116.886	1.376
0.1523	1.4721	3.0714	115.894	1.434
0.2170	1.4670	3.2012	113.064	1.235
	2-Propanol (1) + *m*-Xylene (2)			
0.0551	1.4780	3.5717	122.284	3.615
0.0790	1.4716	3.7820	121.212	3.187
0.1182	1.4674	3.8113	119.440	2.566
0.1502	1.4650	4.0313	117.982	2.378
0.1840	1.4640	4.0725	116.432	2.128
	2-Propanol (1) + *p*-Xylene (2)			
0.0532	1.4740	2.5818	122.832	1.999
0.0981	1.4708	2.5213	120.793	1.168
0.1297	1.4680	2.5422	119.340	0.977
0.1646	1.4651	2.7526	117.723	1.182
0.1912	1.4622	2.9220	116.483	1.269

where x_1, x_2 and ε_1, ε_2 are the mole fractions and dielectric constants of alkanol (1) and of component 2, respectively and ε_S is the dielectric constant of binary (1 + 2) mixtures. Values of $\Delta\varepsilon$ for the binary mixtures at 308.15 K have been recorded in Table 2 and plotted against mole fraction x_1, of alkanol in Figs 1 and 2. The plots are linear. For 1-propanol (1) + aromatic hydrocarbon (2), $\Delta\varepsilon$ changes sign from positive to negative with increase in mole fraction of alkanol (x_1) but for 1- or 2-propanol (1) + cyclohexanone (2), $\Delta\varepsilon$ is negative for the composition range studied. Positive value of $\Delta\varepsilon$ shows[13] the strong specific interaction between the components of binary mixture

$$[(n_1^*)^2 - 1]/[(n_1^*)^2 + 2] = 1.1\,[n_1^2 - 1)/n_1]$$

V_m, V_1 and V_2 are the molar volume of solution, alkanol and cyclohexane or aromatic hydrocarbon respectively. V_m was calculated by the equation

$$V_m = x_1 V_1 + x_2 V_2 + V^E$$

where V^E is the molar excess volume of binary (1 + 2) mixture of mole fraction x_1. The V^E values were calculated from the $V_n(n = O - 3)$ parameters reported earlier[15]. In Frohlich equation L is the Avogadro number, k is the Boltzmann constant, P_1^* is the dipole moment of the isolated polar molecules, g is the Kirkwood factor and ε_0 is the permittivity of a vacuum. The apparent dipole moment $\mu_{app} = [g(p_1^*)^2]^{1/2}$ calculated from Frohlich equation for the present binary (1 + 2) systems at different mole fractions have been recorded in Table 2 and shown graphically in Figs 3 and 4. The apparent dipole moment decreases sharply at very low mole fraction $x_1 < 0.06$ then start decreasing gradually for 1-propanol + cyclohexane or aromatic hydrocarbons (2). While in the case of 2-propanol (1) + cyclohexane or aromatic hydrocarbon (2), μ_{app} decreases slowly with increasing mole fraction of 2-propanol.

Sharp decrease in apparent dipole moment in the systems containing 1-propanol in the mole fraction range $x_1 < 0.06$ (Fig. 3) can be explained owing to high degree of polymerization that results in extensive chain formation. Addition of cyclohexane (inert solvent) break these chains into monomers or polymers of small molecular weight. The linear chains of 1-propanol having high dipole moment, changes into the randomly distributed monomer molecules of 1-propanol. Therefore, the apparent dipole moment decreases sharply. Further increase in the mole fraction of 1-propanol will also change linear chains into monomers or polymers of low molecular weight species but to a lower extent. Thus the change in apparent dipole moment becomes slow and ultimately it becomes almost constant at mole fraction $x_1 > 0.2$ (Fig. 3) showing that the amount of cyclohexane is not sufficient to break more hydrogen bonded 1-propanol. In 2-propanol chain formation is less extensive due to branching of alkyl group which provides steric hindrance. Therefore, addition of cyclohexane (inert solvent) results in uniform decrease in apparent dipole moment. Now replacement of cyclohexane with benzene should result in electron donor-acceptor interactions between hydroxyl hydrogen and π-electron and yield high dipole moment species. Therefore, apparent dipole moment of mixtures

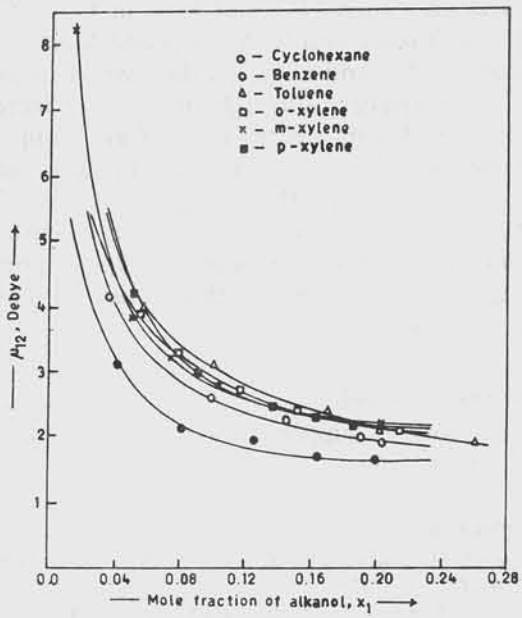

Fig. 3—Plot of apparent dipole moment versus mole fraction of 1-propanol in various (1 + 2) binary systems of 308.15 K

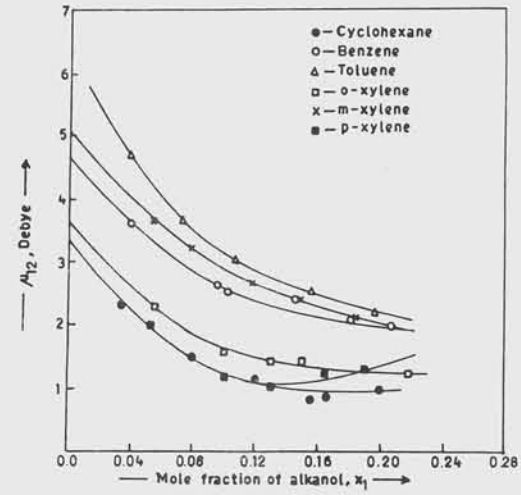

Fig. 4—Plot of apparent dipole moment versus mole fraction of 2-propanol in various (1 + 2) binary systems at 308.15 K

containing benzene should be more than those containing cyclohexane. This is indeed true in the present case (Figs 3 and 4). In the case of propanol + toluene mixtures, hydroxyl hydrogen should interact more strongly with π-electrons of toluene as electron density at benzene ring further increases due to the presence of $-CH_3$ group. This means the apparent dipole moment of systems containing toluene should be more than that of benzene. This is again in agreement with our experimental results (Figs 3 and 4). A similar type of behaviour was also observed by Weith *et al.*[16]

for self associated HCl and HBr in CCl_4, C_6H_6 and 1, 4-dioxane and by Schupp and Mecke[17] for phenol in CCl_4 and C_6H_6. In the case of mixtures containing xylenes, although there is an increase in electron density due to two $-CH_3$ groups, simultaneously there is an increase in steric hindrance which reduces the strength of interactions between hydroxyl hydrogen and π-electron of benzene ring. Therefore, apparent dipole moment of these mixtures are less than those of toluene (Figs 3 and 4).

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