Dielectric Study of the Intermolecular Association of Alcohols in Solutions of Benzene

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(Received September 2, 1975)

The relative permittivity at 1 MHz, the refractive index at the wavelength of sodium D-line and density of the nine alcohols, 1-propanol (A), 2-propanol (B), 1-butanol (C), 2-methyl-1-propanol (D), 1-pentanol (E), 1-hexanol (F), 1-heptanol (G), 3-methyl-2-hexanol (H), 3-methyl-3-hexanol (I), have been measured at 25 °C in benzene in the entire concentration range. The measurements for 1-dodecanol (J) have been made in dilute solutions only. The dipole moments of these molecules in dilute solutions, using Higasi's equation, and the apparent dipole moment for various solute concentrations, using Kirkwood-Fröhlich equation, have been calculated. The results suggest that at low concentrations the alcohols associate to form weakly polar multimers. At high concentrations and in pure liquids, the isomers in which the hydroxyl group is relatively free, favour the formation of highly polar multimers, whereas the isomers in which the hydroxyl group is sterically blocked by the methyl group, favour the formation of closed or ring dimers having low dipole moment.

The low frequency relative permittivity, the electric dipole moment, the Kirkwood correlation factor and dielectric relaxation measurements are useful for studying liquid structure.[1,2] Alcohols have probably been studied more extensively than any other group of compounds and their dielectric absorption is well established. Nevertheless a complete molecular model of the liquid structure capable of explaining the experimental results in alcohols is as yet incomplete. The position of the hydroxyl and the methyl groups on the hydrocarbon chain in alcohols greatly influence the relative permittivity and the correlation factor and consequently the degree and type of hydrogen bonding in these liquids.[3-5] In 1929, Smyth and Stoops[3] reported on the temperature dependence of the relative permittivity of twenty-two isomeric alcohols and also the dilute solution studies of two of these compounds in benzene. They concluded that there is a possibility of both parallel and antiparallel alignments of near-neighbour dipoles. The particular type depends on the molecular geometry, temperature and dilution in nonpolar solvents. Dannhauser made systematic studies on the temperature dependence of the relative permittivity of eight lower alcohols[6] and eight isomeric octanols.[4] He explained the results in terms of the alcohol association into highly polar linear chain *n*-mers ($n=1,2,3,4....$) and ring dimers having small or zero dipole moment.

Hydrogen bonding in aliphatic alcohols in dilute solution has also received considerable attention. However, most of the data available to date is limited to low concentrations only.[7-9] Rajala and Crossley[10] studied the association of butanols and 1-decanol in the concentration range from 0.2 to 1.0 mol fraction in different solvents and concluded that alcohol association is initially dominated by the formation of small, weakly polar multimers, and eventually large highly polar multimers predominate.

The present work reports the data of the relative permittivity for several alcohols in benzene as a nonpolar solvent in the entire concentration range. In these alcohols the alcohol molecular size and the steric environment of the hydroxyl group are the variables. The data is analysed in terms of the Kirkwood correlation factor, the liquid structure of these alcohols being discussed.

Experimental

Materials. The name and the specifications of the alcohols as given by the manufacturer are given in parentheses after each sample.

(A) 1-propanol (E. Merck A. G., pure grade),
(B) 2-propanol (B. D. H., A. R.),
(C) 1-butanol (B. D. H., A. R.),
(D) 2-methyl-1-propanol (B. D. H., A. R.),
(E) 1-pentanol (Riedel A. G.),
(F) 1-hexanol (Eastman, for chemical purposes),
(G) 1-heptanol (Fluka A. G., practical grade),
(H) 3-methyl-2-hexanol (Fluka A. G., purum),
(I) 3-methyl-3-hexanol (Fluka A. G., purum),
(J) 1-dodecanol (Eastman, for chemical purposes).

Alcohols A—E and G were all dried and distilled and the middle fraction for each sample was collected for use. Alcohols F and H—J were used as such. Benzene (B. D. H., A. R.) which was previously dried by passing sodium wire was subsequently distilled and the middle fraction thus obtained was used. The refractive indices of all the alcohols (except for 1-dodecanol) and of benzene were measured. The values were found to compare well with those given in literature. The melting point of 1-dodecanol was found to be distinct, its value of 23 °C coinciding closely with the literature value of 22.6 °C.

Measurements. Relative permittivity measurements at the frequency of 1 MHz were made with a dielectrometer based on the heterodyne beat method.[11] A two-terminal dielectric cell (type DFL 2, made in Germany), with air capacitance of 17.9 pF, was used. The refractive indices at the wavelength of the sodium D-line were measured with Abbey's refractometer (Andhra Scientific Company Ltd., Machilipatnam, India). The desity measurements were, made with a pycnometer having a volume of 11.563 ml. Temperature was maintained at 25 °C within 0.1 °C. The accuracy in the relative permittivity measurements was estimated to be ±0.5%. The accuracy in the refractive indices measurements was estimated upto the fourth decimal place and that for the density measurements 0.03%.

Results of the Measurements. The values of the low frequency relative permittivity ε_0, the relative permittivity at infinite frequency ε_∞, and the square of refractive index n_D^2, at each concentration (mole fraction) for the alcohols C, G, H,

TABLE 1. VALUES OF ε_0, ε_∞, n_D^2, μ_{eff} AND g AT DIFFERENT CONCENTRATIONS (mole fractions f_2) IN BENZENE AT 25 °C

$f_2\times10^2$	ε_0	ε_∞	n_D^2	μ_{eff} (D)	g	$f_2\times10^2$	ε_0	ε_∞	n_D^2	μ_{eff} (D)	g
		1-Butanol						3-Methyl-2-hexanol			
1.96	2.347	2.269	2.238	1.68	1.00	0.44	2.289	2.273	2.242	1.62	0.93
3.45	2.408	2.265	2.234	1.71	1.04	1.69	2.333	2.269	2.236	1.65	0.96
6.54	2.542	2.256	2.222	1.75	1.08	2.69	2.372	2.233	2.265	1.69	1.01
13.45	2.895	2.237	2.200	1.82	1.17	5.13	2.450	2.258	2.224	1.64	0.96
21.12	3.438	2.216	2.175	2.07	1.52	11.19	2.640	2.240	2.201	1.62	0.93
40.55	5.799	2.162	2.115	2.33	1.92	31.69	3.010	2.188	2.139	1.44	0.74
60.06	9.434	2.106	2.059	2.67	2.52	59.90	3.569	2.125	2.075	1.47	0.76
82.22	13.901	2.042	1.999	2.82	2.98	80.56	3.989	2.088	2.044	1.51	0.81
100.00	17.203	1.989	1.953	3.00	3.19	100.00	4.476	2.058	2.022	1.58	0.88
		1-Heptanol						3-Methyl-3-hexanol			
0.54	2.290	2.272	2.242	1.54	0.84	0.37	2.285	2.273	2.243	1.52	0.82
1.29	2.314	2.270	2.237	1.71	1.04	0.99	2.313	2.270	2.240	1.76	1.10
3.17	2.398	2.265	2.232	1.74	1.07	1.81	2.324	2.268	2.236	1.57	0.87
7.68	2.571	2.252	2.215	1.73	1.07	3.27	2.381	2.263	2.230	1.61	0.92
24.37	3.304	2.209	2.158	1.83	1.19	6.57	2.487	2.251	2.216	1.62	0.92
39.41	4.414	2.176	2.123	2.08	1.54	11.98	2.627	2.234	2.197	1.56	0.86
60.51	6.801	2.135	2.085	2.48	2.18	30.85	2.996	2.178	2.139	1.46	0.75
79.00	8.820	2.104	2.054	2.68	2.54	57.17	3.225	2.114	2.082	1.33	0.63
100.00	11.013	2.074	2.023	2.84	2.88	81.79	3.242	2.065	2.040	1.21	0.52
						100.00	3.248	2.034	2.019	1.16	0.48

and I, are given in Table 1. For the rest of the alcohols the data are not given here.

ε_∞ has been calculated by first calculating a_∞ by the method reported elsewhere[12,13] and then using the relation:

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \tag{1}$$

Here $\varepsilon_{1\infty}$ is the relative permittivity of benzene and w_2 is the weight fraction of the solute. The effective dipole moment at each concentration was calculated using the Kirkwood-Fröhlich equation:[14]

$$\mu_{eff}^2 = g\mu_0^2 = \frac{9kT(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{4\pi N\varepsilon_0(\varepsilon_\infty+2)^2} \tag{2}$$

where kT is the thermal energy and N is the number of solute molecules per ml. The Kirkwood correlation factor g was estimated by taking the dipole moment of the alcohol molecules in vacuum μ_0 to be 1.68 D.[5] The values of μ_{eff} and g for the alcohols C, G, H, and I are given in Table 1.

The dipole moments of these molecules in dilute solutions were calculated using the modified Higasi equation[15] given below:

$$\mu = B\sqrt{(a_0-a_\infty)}, \tag{3}$$

where a_0 is given by the relation:

$$\varepsilon_0 = \varepsilon_1 + a_0 w_2 \tag{4}$$

TABLE 2. VALUES OF ε_0 (PURE LIQUID), a_0, a_∞, THE DIPOLE MOMENT μ CALCULATED BY HIGASI'S METHOD[15] IN BENZENE AND THE VALUES OF μ_{eff} IN THE PURE LIQUID CALCULATED USING THE KIRKWOOD-FRÖHLICH EQUATION AT 25 °C

Material	ε_0 (pure liquid)		a_0	a_∞	μ (dilute solution)		μ_{eff} (pure liquid)	
	Expt. values	Lit. values			Expt. values (D)	Lit. values (D)	Expt. values (D)	Lit. values (D)
1-Propanol (A)	20.317	20.10[16] 20.33[8] 21.1[17] (20 °C)	5.440	−0.330	1.78	1.54—1.76	3.01	3.09[18] 2.97[6]
2-Propanol (B)	19.348	18.3[16] 19.41[6]	5.200	−0.391	1.75	1.64—1.80	3.00	2.94[6]
1-Butanol (C)	17.203	17.10[10,16] 17.51[6] 17.68[17] (20 °C)	4.047	−0.285	1.71	1.53—1.76	3.00	2.84[10] 2.85[8] 2.89[6]
2-Methyl-1-propanol (D)	17.224	17.12[10] 17.7[16] 17.936[6]	4.000	−0.305	1.71	1.59—1.81	3.03	2.85[10] 2.88[6] 2.96[18]
1-Pentanol (E)	14.883	13.9[16] 15.15[17] (20 °C)	3.400	−0.245	1.71	1.59—1.71	2.98	—
1-Hexanol (F)	12.829	13.3[16] 13.2[17] (20 °C)	3.000	−0.223	1.73	1.55—1.73	2.95	2.86[8]
1-Heptanol (G)	11.013	11.55[17] (20 °C)	2.674	−0.200	1.74	1.67—1.73	2.84	2.83[8]
3-Methyl-2-hexanol (H)	4.476	—	2.370	−0.216	1.65	—	1.58	—
3-Methyl-3-hexanol (I)	3.248	—	2.125	−0.240	1.58	—	1.16	—
1-Dodecanol (J)	—	—	1.515	−0.157	1.69	1.52	—	—

Values of μ_{eff} in the pure liquid form are calculated by taking the values of g at 27 °C and using the relation $\mu_{eff}^2 = g\mu_0^2$; $\mu_0 = 1.68$ D.

ε_0 and ε_1 are the relative permittivity of the solution and the solvent respectively, and w_2 is the weight fraction of the solute. a_∞ is the same as defined by Eq. 1. The constant B is given by:

$$B = \frac{1}{2(\varepsilon_1+2)}\sqrt{\frac{27kTM_2}{\pi N_A d_1}} \tag{5}$$

where the different symbols have their usual meaning. Values of the dipole moment are given in Table 2.

Discussion

The values of the relative permittivity of alcohols in the pure liquid form are given in Table 2. There is a close agreement between the experimental and literature values. There is also an agreement between our values of the dipole moments calculated using Higasi's equation[15] in dilute solutions of benzene and the literature values (Table 2) except for the case of 1-dodecanol. For this alcohol our value of the dipole moment is 1.69 D whereas the literature value is 1.52 D. However, our value is quite close to the value of 1.68 D of the alcohol molecule in a vacuum. The values of the dipole moments for 3-methyl-2-hexanol and 3-methyl-3-hexanol are not found in literature. The dipole moments in the pure liquid for all the alcohols except 1-dodecanol are given in Table 2. These values compare within 3% to the literature value of the dipole moment for the alcohols where available.

The concentration dependence of the relative permittivity for the first nine alcohols is shown in Fig. 1. The curves for 1-butanol and 2-methyl-1-propanol almost overlap each other. The plots of the correlation factor *g versus* the alcohol mole fraction are shown in Figs. 2 and 3.

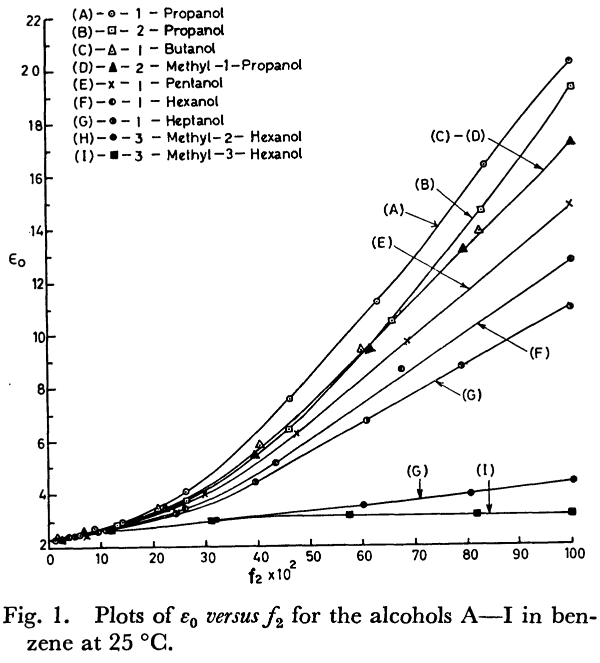

Fig. 1. Plots of ε_0 *versus* f_2 for the alcohols A—I in benzene at 25 °C.

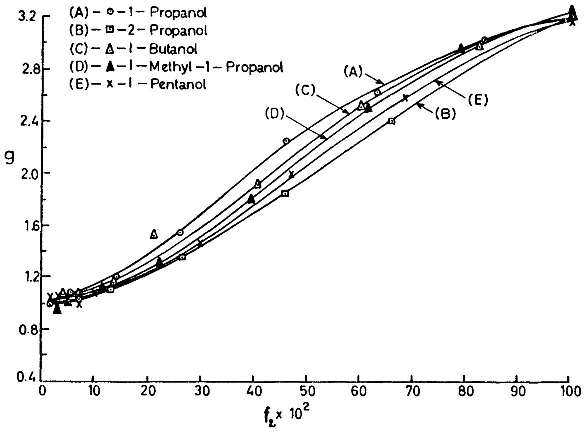

Fig. 2. Plots of *g versus* f_2 for the alcohols A—E in benzene at 25 °C.

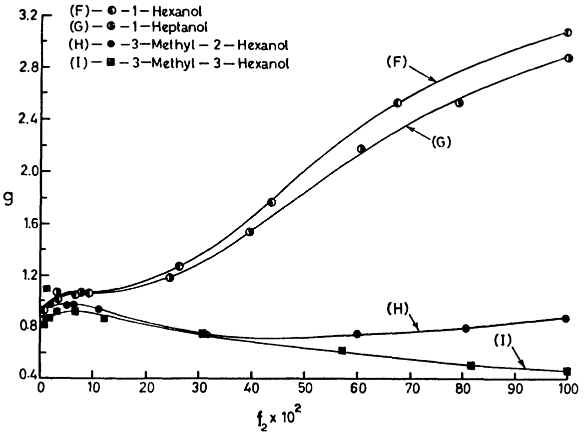

Fig. 3. Plots of *g versus* f_2 for the alcohols F—I in benzene at 25 °C.

Effect of ε_∞ on the Dipole Moment and the Correlation Factor. Our results yield dipole moments μ_{eff} calculated using the Kirkwood-Fröhlich relation.[14] The values are listed in Table 1. The dipole moments are compared with the literature values when available. Our values for 1-butanol in the concentration range 0.019—0.065 mole fraction lie within the range 1.68—1.75 D. It has been found that the discrepancy is due to different values of ε_∞ obtained by using different methods for its evaluation. Several authors[7–9] have calculated the value of ε_∞ by fitting the permittivity data to the Cole-Cole plots using a digital computer. We have calculated the values of ε_∞ using Eq. 1. On using the values of ε_∞ as given by Johari and Smyth[19] for 1-butanol in benzene in the same concentration range, we find that our values of dipole moments at about the same concentration range lie within 1.48—1.60 D and therefore, compare well with the values given by Crossley.[9] The comparison is shown in Table 3. The dipole moments calculated by using our values, are, therefore, higher by a factor of about 0.2 D at low concentrations in all the alcohols. Consequently, *g* values are also higher than those quoted in literature. For higher concentrations and in pure liquids the difference in the dipole moments is expected to be less for the alcohols A to G since the relative permittivity at infinite frequencies ε_∞ makes dipole moments less sensitive to slight changes in ε_∞. Since the relative permittivity of the alcohols H and I is of the order of magnitude as the square of refractive index, a small uncertainty in the

Table 3. Values of the dipole moments of 1-butanol by taking the values of ε_∞ (at about the same concentration range)

$f_2 \times 10^2$	ε_0	ε_∞	μ_{eff} (D)
From Johari and Smyth[19]			
1.96	2.347	2.286	1.48
3.45	2.408	2.296	1.51
6.54	2.542	2.296	1.60
From the data given by Crossley[9] in benzene[a]			
2.35	—	—	1.46
3.53	—	—	1.55
5.24	—	—	1.60

a) The author[9] did not give the values of ε_0 and ε_∞.

value of ε_∞ will greatly affect the values of the dipole moment, and consequently, the value of g.

Behaviour of alcohols A—G and effect of Chain-length. The correlation factor g is a measure of those short-range intermolecular forces that lead to the specific dipole-dipole orientations. According to the Kirkwood-Fröhlich theory[14] $g\mu_0^2$ is the square of the dipole moment of the spherical cavity so that its size is macroscopically small and microscopically large. The size should be such that the surroundings can be assumed to have relative permittivity of the liquid. The value of g greater than unity is interpreted in terms of predominantly parallel alignment of the near-neighbour dipoles and g less than unity corresponds to a structure such that its dipole moment is less than that of the monomer. A more specific interpretation depends on the introduction of a molecular model of the liquid structure.

The plots of g against the alcohol mole fraction for alcohols A—G are shown in Figs. 2 and 3. In the absence of the association of the neighbouring molecules, g should be unity for all concentrations. Strong self association is evident for large alcohol concentrations in benzene and in pure liquids. As concentration of alcohols increases from 0.15 to 0.90 mole fraction, values of g increase in the order 1-heptanol$<$1-hexanol$<$1-pentanol$<$2-methyl-1-propanol$<$1-butanol$<$1-propanol. Propanols and butanols attain almost the same value in pure liquid. The trend shows that self association (with the exception of 2-propanol) decreases with increase in the length of hydrocarbon chain.

Taking into account the effect of ε_∞ as discussed above, we can say that the values of g are about 20—25% less than unity at the concentration range of *ca.* 0.2 mole fraction. With the increase of alcohol concentration the values of g increase and approach unity at the concentration of *ca* 0.20 mole fraction. This leads us to the conclusion that the initial association involves the formation of multimers having smaller dipole moments than the free monomer. These multimers may be closed or open dimers and timers.[4,20,21] Above the concentration of 0.2 mole fraction g increases rapidly with the increase of the alcohol concentration for the alcohols. (Figs. 2 and 3). Dannhauser[4] and also, Gold and Perrine[22] suggest the association into linear chains as mechanism responsible for the large values of g. Some authors support the existence of highly polar cyclic tetramers.[23,24] In 2-propanol the values of g are lower (Fig. 2) than 1-propanol, 1-butanol and 1-pentanol in the concentration range 0.15—0.90 mole fraction. This is probably due to the chain-branching close to the –OH group which presents steric factors for the formation of large multimers.

Behaviour of 3-*Methyl*-2-*hexanol and* 3-*Methyl*-3-*hexanol.* The values of g decrease with the increase of the alcohol concentration for 3-methyl-3-hexanol in the entire concentration range. Whereas in the case of 3-methyl-2-hexanol it decreases initially with the increase of concentration in the range 0.10—0.35 mole fraction above which it again starts increasing with comparatively less slope. In these alcohols the –OH group is so effectively screened due to the presence of the neighbouring $-CH_3$ group that association is restricted to small weakly polar multimers, preferably ring dimers, the values of g for pure liquids being less than unity. Association into higher open chain *n*-mers or highly polar cyclic tetramers is not possible because of steric effects. The results are in agreement with those given by Dannhauser[4] and Crossley *et al.*[25] for 2-methyl-3-heptanol, 3-methyl-3-heptanol, and 4-methyl-3-heptanol in pure liquids.

It is evident that in a liquid alcohol for a given temperature and concentration, one has to assume equilibrium between different structures. The equilibrium constants between the various structures are strongly dependent on the nature of alcohol and its concentration in an inert solvent.

The research project was financed by the Department of Atomic Energy. One of the authors (Buta Singh) is grateful to Professor B. S. Sood, Head, Department of Physics, for the encouragement during the work.

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