Dielectric Dispersion at Meter Waves of 1-Hexanol and 1-Octanol in Cyclohexane Solutions

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The dielectric constants and losses of 1-hexanol and 1-octanol in cyclohexane solutions were measured in the frequency range 60—480 MHz at various temperatures. The values $\varepsilon_0-\varepsilon_\infty$ deviate widely from the linear dependence on concentration. The curve of $(\varepsilon_0-\varepsilon_\infty)/c$ plotted against concentration c falls rapidly as c decreases. Its value seems to be zero at the concentration of 1 mol/l. A comparison with the values of higher alcohols given in literature shows that the curve is almost uniquely determined for each temperature as a function of the concentration of hydroxyl group alone, irrespective of the length of C–C chain in alkyl group of alcohols. As shown by Ibbitson and Moore, there exist considerable amounts of dimers, trimers and cyclic polymers in the dilute solutions of 1% by weight. The cause for the large values of dielectric constant cannot be merely attributed to the formation of hydrogen-bonded aggregates of molecules. A possible structure of the aggregates is discussed.

Since Mizushima[1] investigated the dielectric dispersion of alcohols in 1927, studies in this field have been made by several authors with various methods. Lebrun[2] measured the dielectric constants and losses of 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol at 20°C in the frequency range 1—9.5×10^3 MHz, obtaining two relaxation times. Garg and Smyth[3] measured those of ten normal alcohols from propyl through dodecyl in the wavelength range 30,000—0.22 cm. They analyzed the dispersion into three separate regions. The dispersion process with the longest relaxation time was attributed to the breaking of the hydrogen bonds in molecular aggregates followed by the rotation of alcohol molecules.

Measurements on dilute solutions of alcohols were carried out by Johari and Smyth.[4] It was shown that normal alcohols in dilute benzene solutions have two relaxation processes instead of three, lacking the one attributable to the associated molecules.

Theoretical studies on the dielectric constant of liquid were made by Onsager, Kirkwood[5] and others. Kirkwood succeeded at least qualitatively in explaining the large values for alcohol. His theory is by no means satisfactory. It does not take into account the existence of three relaxation processes in liquid alcohols. The lowest frequency relaxation process dominates in the dispersion region. A study on the process would help elucidate complicated problems with regard to liquid structure.

The dielectric constants and losses of alcohols have been determined. Cyclohexane was selected as a solvent among others, because the value $\varepsilon_0-\varepsilon_\infty$ for the solution of an alcohol is nearly equal to that of the other, if the concentrations of hydroxyl group are equal to each other, although the relaxation frequencies are quite different.

Experimental

Purification of Materials. 1-Hexanol was washed with a 10% solution of sodium hydroxide and distilled through a 50 cm column under reduced pressure. The middle portion was distilled fractionally through a 1 m column packed with Dixon packings at 30 Torr. About 20% of the distillates was separated off at a reflux ratio of 180: 1, in which at least four impurities were found to be present by gas chromatography with a column containing Silicone Oil SE-30 as a fixed phase liquid. Removal of one of them was difficult,[6] and seemed almost impossible by distillation at 50 Torr. In the middle fraction, there was no perceptible peak originating from impurity in its chromatogram. Molecular Sieve 5A was used as a drying agent.

1-Octanol was purified by the same method as described above except that it was distilled fractionally at 15 Torr. The gas chromatograms resembled those of 1-hexanol when the temperature of the column was elevated.

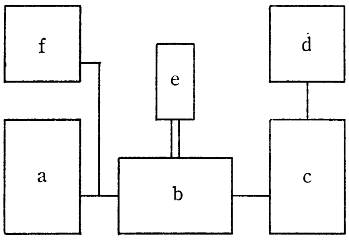

Fig. 1. Block diagram of the apparatus. a: signal generator hp 608C, b: VHF bridge hp 803A, c: VHF detector hp 417A, d: null detector hp 415E, e: sample holder, f: frequency counter.

Cyclohexane was washed with concentrated sulfuric acid, with mixed acid and again with sulfuric acid. It was distilled fractionally through a 1 m column packed with Helipack packings and dried with calcium hydride. Density 0.7738, n_D 1.4235, ε_0 2.016 at 25°C.

Apparatus. Dielectric constants and losses were measured with a Hewlet-Packard Type 803A VHF bridge which operates as a Byrne bridge. The setup for measurement is shown by a block diagram in Fig. 1. The error in the measurement of impedance, according to the specifications, may be within 2% in magnitude and within 1.2° in phase angle when the necessary corrections are made to the bridge readings.

The sample holder or cell is shown diagrammatically

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[1] S. Mizushima, *Physik. Z.*, **28**, 418 (1927).

[2] A. Lebrun, *Ann. Phys.* (Paris), **10**, 16 (1955).

[3] S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, **69**, 1294 (1965).

[4] G. P. Johari and C. P. Smyth, *J. Amer. Chem. Soc.*, **91**, 6215 (1969).

[5] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

[6] A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents", second ed., Interscience Publishers, New York, N. Y. 1955, p. 354.

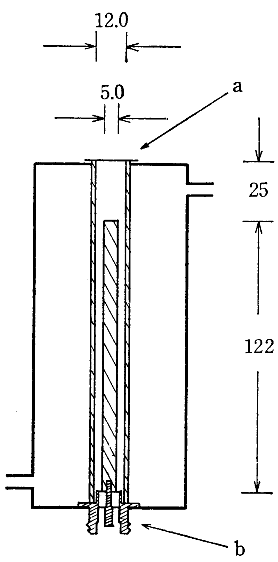

Fig. 2. Sample holder. a: thin glass plate, b: type-N jack. All dimensions in mm.

with dimensions in Fig. 2. Made of brass, it is an open-circuited coaxial line equipped with a N-female type connector at one end. As the outer conductor is 2.5 cm longer than the inner one, leakage of high frequency signals is effectively prevented. The electrical length and characteristic impedance of the cell were so determined that the measured values of the dielectric constant of cyclohexane, benzene and chlorobenzene agree with the values at low frequencies reported in various papers. The electrical length thus obtained is 12.5 cm, which is 0.3 cm longer than the physical length of the inner conductor. The characteristic impedance is 52.5Ω, which agrees with the value calculated from the dimensions of the cell.

The electrical length of the transmission line which connects the cell to bridge was about 9.2 cm. This showed slight variations with frequency within 0.1 cm.

Method of Calculations. The imput admittance Y of an open-circuited cell of coaxial type is given by

$$Y = i\frac{\sqrt{\varepsilon}}{Z_0}\tan\frac{2\pi\sqrt{\varepsilon}fl}{c} \tag{1}$$

if wall losses are neglected, where $\varepsilon(=\varepsilon'-i\varepsilon'')$ is the complex dielectric constant of a substance filled in the cell, c light velocity; Z_0 and l the characteristic impedance and electrical length of the cell, respectively. If we put

$$a = \frac{2\pi i f l Z_0}{c}Y \text{ and } z = \frac{2\pi i\sqrt{\varepsilon}fl}{c}, \tag{2}$$

a and z are complex numbers and fulfill the following equations:

$$a = z\tanh z \tag{3}$$

or

$$z = a\coth z. \tag{3'}$$

Equation (3′) can be solved easily by means of successive approximations. If z_i is the i-th approximate value of z, the $(i+1)$-th approximation is given by

$$z_{i+1} = a\frac{2z_i+\sinh 2z_i}{2a-1+\cosh 2z_i}. \tag{4}$$

Static value ε_0 and high frequency limit ε_∞ of dielectric constant and relaxation frequency f_r are calculated in the following way. By Debye's theory the following equations hold at each frequency f:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0-\varepsilon_\infty)\frac{1}{1+(f/f_r)^2} \tag{5}$$

$$\varepsilon'' = (\varepsilon_0-\varepsilon_\infty)\frac{f/f_r}{1+(f/f_r)^2}. \tag{6}$$

From these equations, the relation

$$\varepsilon'' = \frac{1}{f_r}\varepsilon' f - \frac{\varepsilon_\infty}{f_r}f \tag{7}$$

can be derived. According to the method of least squares, we can choose $1/f_r$ and ε_∞/f_r so that the following expression is minimum:

$$\sum_i\left(\varepsilon_i''-\frac{1}{f_r}\varepsilon_i' f_i+\frac{\varepsilon_\infty}{f_r}f_i\right)^2 = \text{min.} \tag{8}$$

where ε_i' and ε_i'' are experimental values at frequency f_i. Then, ε_0 is calculated from

$$\sum_i(\varepsilon_i'-\varepsilon_\infty) = (\varepsilon_0-\varepsilon_\infty)\sum_i\frac{1}{1+(f_i/f_r)^2}. \tag{9}$$

Measurements. Dielectric constants and losses were measured at the frequencies 60, 80, 100, 150, 200, 250, 300, 400, and 480 MHz. Frequencies were controlled to be within ±0.1% of the specified values. Temperatures were kept constant by circulation of water from a thermostat through a jacket around the cell. No measurements were made for dilute solutions with relaxation frequency out of the frequency range.

Results

Some typical plots of complex dielectric constant $\varepsilon=\varepsilon'-i\varepsilon''$ for 1-hexanol and solutions are shown in Fig. 3. The plots for each liquid are on a semicircle within experimental error. It is sufficient if we consider a single dispersion process in each liquid in the frequency range where measurements are made. The observed dielectric constant and loss of 1-hexanol at 25°C are given in Table 1 with the calculated values from Eqs. (5) and (6).

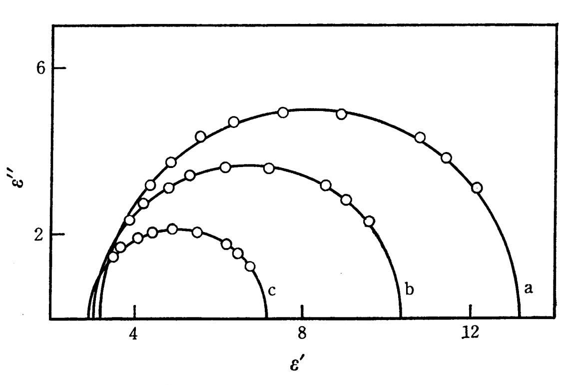

Fig. 3. Complex dielectric constants of 1-hexanol in cyclohexane soltuions at 25°C. a: 100%, b: 80.12%, c: 60.44%.

The dielectric parameters calculated from Eqs. (8) and (9) of pure 1-hexanol and 1-octanol and cyclohexane solutions are given in Tables 2 and 3, together with the refractive indices measured by use of a Pulfrich refractometer and with densities.

TABLE 1. OBSERVED AND CALCULATED DIELECTRIC CONSTANT AND LOSS OF 1-HEXANOL AT 25°C

(MHz) f	(obsd) ε'	ε''	(calcd)$^{a)}$ ε'	ε''
60	12.12	3.11	12.10	3.10
80	11.39	3.84	11.41	3.82
100	10.75	4.31	10.67	4.34
150	8.86	4.88	8.88	4.96
200	7.49	4.92	7.45	4.96
250	6.31	4.70	6.40	4.69
300	5.52	4.35	5.66	4.33
400	4.82	3.74	4.74	3.65
480	4.33	3.19	4.31	3.19

a) From Eqs. (5) and (6) with $\varepsilon_0=13.179$, $\varepsilon_\infty=3.160$, $f_r=172.9$ MHz.

TABLE 2. DIELECTRIC PARAMETERS, REFRACTIVE INDICES AND DENSITIES OF 1-HEXANOL IN CYCLOHEXANE SOLUTIONS

x (mol%)	ε_0	ε_∞	f_r (MHz)	n_D	d (g/cm^3)
			15°C		
100.00	14.22	3.17	106	1.4198	0.8222
89.88	12.78	3.08	104	1.4201	0.8181
79.53	11.25	3.01	102	1.4206	0.8138
69.74	9.61	2.93	105	1.4211	0.8097
60.19	7.84	2.83	111	1.4217	0.8056
49.98	5.97	2.74	125	1.4224	0.8014
40.20	4.39	2.63	151	1.4231	0.7975
30.58	3.24	2.47	205	1.4241	0.7936
			20°C		
100.00	13.66	3.16	135	1.4180	0.8187
88.93	12.18	3.08	132	1.4182	0.8141
79.76	10.81	3.00	132	1.4187	0.8101
70.10	9.21	2.93	135	1.4190	0.8059
59.92	7.40	2.83	145	1.4196	0.8016
50.68	5.80	2.77	161	1.4201	0.7977
40.15	4.21	2.64	194	1.4209	0.7930
30.14	3.15	2.48	253	1.4230	0.7891
			25°C		
100.00	13.18	3.16	173	1.4161	0.8151
89.73	11.75	3.03	171	1.4163	0.8107
80.12	10.35	2.99	172	1.4166	0.8064
70.38	8.82	2.94	175	1.4170	0.8021
60.44	7.15	2.88	186	1.4174	0.7977
50.26	5.47	2.77	209	1.4179	0.7932
40.08	4.07	2.67	246	1.4185	0.7888
32.58	3.29	2.51	308	1.4192	0.7856
			30°C		
100.00	12.70	3.17	221	1.4140	0.8113
90.20	11.37	3.08	219	1.4141	0.8070
80.59	10.04	3.06	216	1.4144	0.8026
70.28	8.41	2.96	227	1.4146	0.7982
59.62	6.69	2.88	244	1.4150	0.7934
49.45	5.13	2.78	275	1.4154	0.7889
			35°C		
100.00	12.18	3.22	277	1.4122	0.8077
89.55	10.84	3.12	275	1.4121	0.8031
80.25	9.50	3.07	280	1.4121	0.7993
70.37	8.01	3.00	287	1.4124	0.7943
59.87	6.40	2.89	313	1.4127	0.7893
49.70	4.94	2.81	349	1.4132	0.7847

TABLE 3. DIELECTRIC PARAMETERS, REFRACTIVE INDICES AND DENSITIES OF 1-OCTANOL IN CYCLOHEXANE SOLUTIONS

x	ε_0	ε_∞	f_r	n_D	d
		20°C			
100.00	10.55	3.03	89	1.4294	0.8250
90.91	9.69	2.98	90	1.4290	0.8215
80.93	8.61	2.92	94	1.4284	0.8176
70.07	7.23	2.85	102	1.4276	0.8126
60.32	6.02	2.78	112	1.4271	0.8083
50.69	4.78	2.70	134	1.4267	0.8038
40.41	3.68	2.58	172	1.4263	0.7988
30.08	2.93	2.44	235	1.4258	0.7936
		25°C			
100.00	10.14	3.04	116	1.4275	0.8215
90.77	9.26	2.99	119	1.4270	0.8178
79.96	8.12	2.94	124	1.4262	0.8132
70.07	6.95	2.88	133	1.4256	0.8090
60.70	5.79	2.81	149	1.4251	0.8047
50.66	4.59	2.71	175	1.4244	0.7999
40.49	3.60	2.60	218	1.4239	0.7948
		30°C			
100.00	9.70	3.04	153	1.4196	0.8179
91.45	8.93	3.01	155	1.4190	0.8145
80.22	7.76	2.94	164	1.4183	0.8097
69.69	6.57	2.90	178	1.4175	0.8050
59.75	5.42	2.82	197	1.4168	0.8002
49.57	4.32	2.73	233	1.4162	0.7952
		35°C			
100.00	9.32	3.06	192	1.4237	0.8144
89.71	8.36	3.03	202	1.4228	0.8101
80.09	7.36	2.93	216	1.4221	0.8059
70.54	6.35	2.88	230	1.4216	0.8016
59.83	5.20	2.83	254	1.4208	0.7966

Discussion

The value $\varepsilon_0-\varepsilon_\infty$ decreases rapidly with the decrease in the concentration of alcohol, as seen from Table 2 or 3. The ratio $(\varepsilon_0-\varepsilon_\infty)/c$ at 25°C is plotted against concentration c for both alcohols in Fig. 4. We see a large dependence of $\varepsilon_0-\varepsilon_\infty$ on concentration. The two curves are situated closely to each other; especially at low concentration below 4 mol/l they coincide within experimental error. This indicates that the magnitude of $\varepsilon_0-\varepsilon_\infty$ is mainly determined by the concentration of

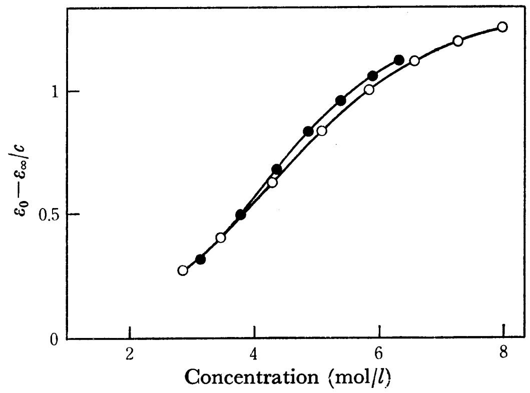

Fig. 4. Comparison of 1-hexanol and 1-octanol at 25°C. ○: 1-hexanol, ●: 1-octanol.

hydroxyl group irrespective of the length of C–C chain in alkyl group of alcohols. If it is proportional to the number of alcohol molecules per unit volume, these curves can be interpreted as representing the concentration dependence of the contribution 'of a molecule to dielectric dispersion. We see from Tables 2 and 3 that the variation of refractive indices of the solutions is so small that its influence can be ignored. It is suggested that a large change in the properties of alcohol molecules takes place in the concentration range 2—7 mol/*l*.

The situation stated above remains unchanged if we examine the concentration dependecne of

$$\frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)\,T}{\varepsilon_0(\varepsilon_\infty+2)^2c}$$

according to Onsager's equation in which ε_∞ is used in place of n^2. The two curves plotted in Fig. 5 represent the relation. We cannot consider these curves to represent the concentration dependence of Kirkwood's *g*-factor. The value 31.6 for pure 1-octanol becomes 8.4 at the concentration of 2.4 mol/*l*; the ratio 31.6/8.4= 3.76 is much greater than the value 2.57 of *g*-factor calculated for normal alcohols.[7] Other equations for the dielectric constant of liquid will give the same conclusion.

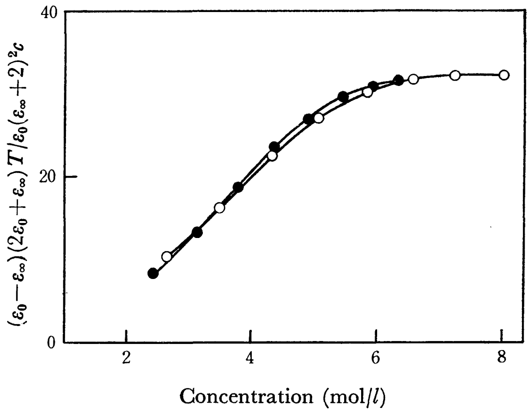

Fig. 5. Plots of $(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)T/\varepsilon_0(\varepsilon_\infty+2)^2c$ for 1-hexanol and 1-octanol at 20°C.

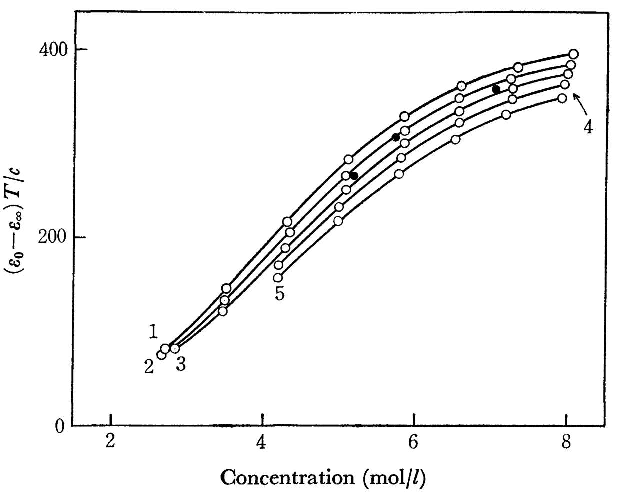

Fig. 6. Plots of $(\varepsilon_0-\varepsilon_\infty)T/c$ for 1-hexanol against concentration. 1: 15°C, 2: 20°C, 3: 25°C, 4: 30°C, 5: 35°C. ●: calculated from Lebrun's data at 20°C for 1-heptanol, 1-nonanol and 1-decanol (from right to left).

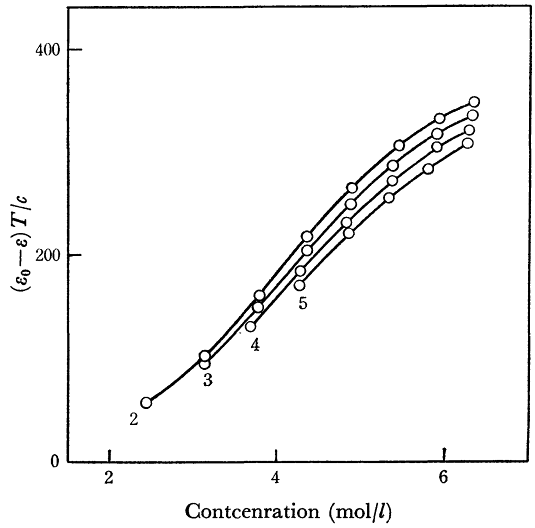

Fig. 7. Plots of $(\varepsilon_0-\varepsilon_\infty)T/c$ for 1-octanol against concentration.

In Figs. 6 and 7, the values $(\varepsilon_0-\varepsilon_\infty)T/c$ are plotted against *c* at various temperatures for 1-hexanol and 1-octanol in cyclohexane solutions, respectively. In order to facilitate comparison of the curves at different temperatures, the values in the ordinates are multiplied by the absolute temperature. The slope of these curves at middle concentration is steep at low temperature. With increasing temperature, it becomes gradual and the curve shifts toward high concentration side as a whole. If we extrapolate the curves to lower concentration, their values vanish in the vicinity of 1 mol/*l*.

The curves seem to indicate that the mechanism of association to hydrogen-bonded polymers which have an anomalously large dielectric constant is of co-operative nature. At sufficiently low concentration, the percentage of alcohol molecules which form the polymers will be zero; when the concentration reaches a certain value near 1 mol/*l*, the percentage will begin to increase; with increasing concentration, the percentage increases rapidly and finally it would attain a saturated value if the concentration increased further beyond that of pure alcohols. It is easy to explain the large temperature dependence of dielectric constant of the alcohols if we assume the mechanism of co-operative nature.

Ibbitson and Moore[8] reported that alcohols in the dilute solution of 1% by weight have two near infrared absorption bands besides the one attributable to monomers. The two bands were attributed to the presence of dimers, trimers and cyclic polymers. They also found that, with the appearance of the two bands, the solute polarization began to decrease from a constant value at lower concentrations. Therefore, we cannot expect a considerable amount of molecules to form the polymers with large dielectric constant at such concentration.

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[7] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

[8] D. A. Ibbitson and L. F. Moore, *J. Chem. Soc B*, **1967**, 76.

The saturation property can be inferred from the values $(\varepsilon_0-\varepsilon_\infty)T/c$ for pure alcohols. The calculated values from the data by Saxton *et al.*[9] are 331 and 354 at 20°C for methanol and ethanol, respectively; 382 for 1-propanol, 395 for 1-butanol and 378 for 1-pentanol from the data tabulated by Brot, Magat, and Reinisch[10] at the same temperature. Smaller values for methanol and ethanol might be due to the smallness of their refractive indices.

The points for 1-heptanol, 1-nonanol, and 1-decanol calculated from Lebrun's experiments lie approximately on our curve as seen from Fig. 6.

The polymers are supposed to have the structure of nets composed of alcohol molecules bridged by hydrogen bonds. The two dimensional spread is necessary for co-operative phenomenon. It can be easily imagined that chain multimers and cyclic polymers join together to form a net when concentration increases.

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[10] C. Brot, M. Magat, and L. Reinisch, *Kolloid-Z.*, **134**, 101 (1953).