Dielectric Relaxation and Intermolecular Association for 1-Decanol. Temperature and Dilution Dependences of Monomer and Three Hydrogen-Bonded Species

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The dielectric constants and losses have been measured at frequencies from 1.35 to 4500 MHz for pure 1-decanol at 15—40 °C and for cyclohexane and heptane solutions of 1-decanol at 25°C. The absorption has been resolved into three different Debye-like dispersion regions. The assignments of the three regions were made as follows: the first region being due to a linear hydrogen-bonded chain polymer (C_1), the second one to a chain dimer and trimer (C_2), and the third one to a free monomer (C_3). Four concentrations of these species (C_{1-3}) and a nonpolar cyclic polymer (C_R) were evaluated by applying a modified Kirkwood–Fröhlich equation to each dispersion region. Each of the four concentrations indicates a reasonable behavior regarding the temperature and dilution dependences. The C_1 decreases and, mainly, the C_3 increases as the temperature increases. For cyclohexane and heptane solutions, the C_1 decreases rapidly and the C_R increases correspondingly with decreasing alcohol concentration. The free energies of activation are 23.2 for the first region, 17.3 for the second region, and 11.9 kJ mol^{-1} for the third region.

Many studies[1—3] have reported the co-existence of the alcohol monomer and various hydrogen-bonded species. There is now a general agreement that the alcohol molecule has a tendency to form aggregates in a dilute solution and in the pure liquid state. Wide-range measurements of complex dielectric constants also indicated two or three different dispersion regions. At low temperatures, Cole and Davidson[4] obtained three dispersion regions for 1-propanol. Dannhauser[5] also obtained three dispersion regions for 5-methyl-3-heptanol and 6-methyl-3-heptanol. He assigned the three dispersion regions to a free monomer, OR group in the linear chain structure, and the linear hydrogen-bonded chain species. At room temperatures, Lebrun[6] measured the dielectric constants and losses for higher normal alcohols at a frequency range of 1—9.5×10^3 MHz, obtaining two relaxation times. Garg and Smyth[7] obtained three relaxation times for the ten normal alcohols from propyl through undecyl at 16 wavelengths. They attributed the long relaxation time to the breaking of hydrogen bonds in molecular aggregates followed by ROH rotation, the intermediate relaxation time to a reorientation of a free monomer, and the short relaxation time to a relaxation of the hydroxyl group by rotation around its C–O bond. Glasser et al.[8] obtained two or three relaxation times for heptane solutions of some normal alcohols. In addition to the results of Garg and Smyth, they reported that the intermediate process is related to the reorientation of a free monomer and, possibly, a small multimer or a polymer chain segment.

We are studying hydrogen bonding and intermolecular structures in liquid alcohols. In a previous paper,[9] we proposed a modified Kirkwood–Fröhlich equation for obtaining the concentration of the first dispersion region for 28 linear alcohols. Now we have extended the investigations by performing the assignment of the three dispersion regions and by obtaining the four concentrations of monomer and three hydrogen-bonded species. The concentrations are discussed in terms of changes in the temperature and dilution.

Experimental

Purification of Materials. Commercial heptane was washed with mixed acid, concentrated sulfuric acid, water, 10% potassium hydroxide solution, 1 M potassium permanganate solution (1 M=1 mol dm^{-3}), and again with water. After standing over calcium chloride for 24 hours, it was fractionally distilled. The distillate was dried over calcium hydride and distilled before use. Cyclohexane was purified by the same method as heptane. 1-Decanol was fractionally distilled twice as described before[9] and finally distilled in a grease-free apparatus before use.

Apparatus. The dielectric constants and losses were measured using the following three apparatus over frequencies from 1.35 to 4500 MHz. A Boonton Radio RX meter (Type 250A) was used for measurements at frequencies of 1.35, 6.3, 17, 30, and 45 MHz. Measurements at frequencies 60, 80, 100, 150, 200, 250, 300, 400, and 480 MHz were made with a Hewlett-Packard VHF Bridge (Model 803A). A General Radio Precision Slotted Line (Type 900-LB) was used for measurements at frequencies of 600, 750, 1000, 1400, 2000, 3000, and 4500 MHz. In the measurements of low and high frequency regions, two cells were carefully made of a GR Precision Inner-Conductor Rod, an Outer-Conductor Tube, and a GR 900-BT connector. This equipment was described in detail in a previous paper.[9]

Results and Discussion

Dielectric Relaxation. The Cole–Cole plots are

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shown for pure 1-decanol at 15, 20, 25, 35, and 40 °C in Fig. 1 and for cyclohexane solutions of 1-decanol at 25 °C in Fig. 2. The first dispersion region can be described by a Debye-like semicircular arc, though it is evident that the experimental data can not be satisfactorily fitted by the arc in the high-frequency region of the dispersion. At first glance it looks as if the Cole–Cole plots can be grouped into three dispersion types as pointed out for isomeric decanols in a previous paper.[9] The first type is best described by several overlapping Debye-like semicircular arcs, such as pure 1-decanol at 15 °C in Fig. 1. The second one by a Davidson–Cole skewed arc, such as pure 1-decanol at 40 °C in Fig. 1 and 60 mol% in Fig. 2. The third one by a Cole–Cole depressed-center semicircular arc, such as 30 mol% in Fig. 2. It has usually been considered that the dispersion type was determined by a difference in the measured compounds. However, the shape of the locus of the dispersion is dependent of the temperature and dilution. The shape of the locus for one compound changes from a Debye type to a Davidson–Cole type, as shown in Fig. 1 and from a Davidson–Cole type to a Cole–Cole type, as shown in Fig. 2. This fact indicates that the difference in these dispersion types is determined by a ratio of the magnitudes between the first and other regions calculated. It was, therefore, assumed that dielectric absorption was the sum of several overlapping Debye-like dispersion regions. In this study, the experimental data were analyzed by separation into three different dispersion regions. The dielectric parameters of the three regions were calculated using a least-squares method, as described in a previous paper.[9] The limiting high-frequency dielectric constant, ε_3, of the third region contains experimental errors because of lack of the higher frequencies of the region. Therefore, the ε_3 was assumed to be an average value in all measurements, whose value was calculated using $(\varepsilon_3-1)/(\varepsilon_3+2)=(n_D^2-1)(1+0.19)/(n_D^2+2)$. The calculated dielectric parameters are given in Table 1, together with the refractive indices n_D (measured by the use of a Pulfrich refractometer), densities d, and with viscosities η. The calculated results of the three dispersion regions are also shown by the solid lines in Figs. 1 and 2.

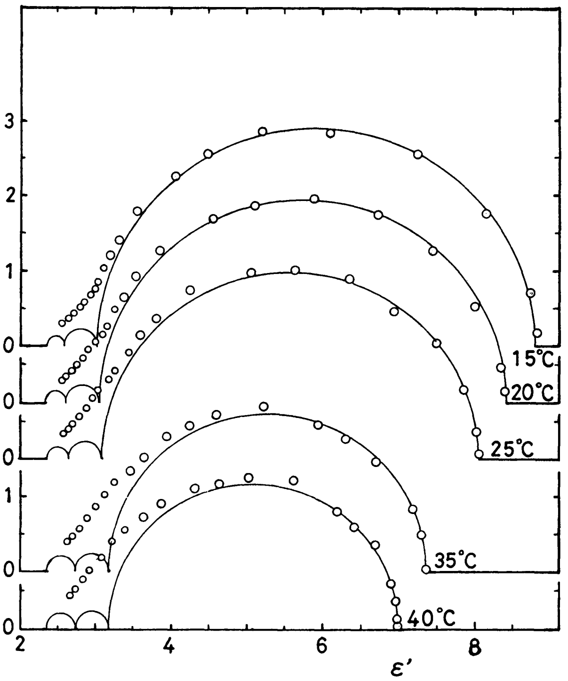

Fig. 1. Cole–Cole plots for pure 1-decanol at 15—40 °C. For clarity, curves have been displaced along the ordinate. Three dispersion regions calculated are shown by solid lines.

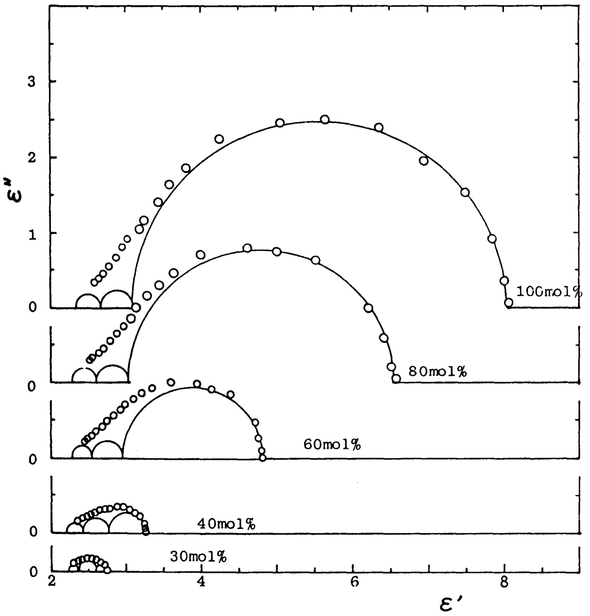

Fig. 2. Cole–Cole plots for cyclohexane solutions of 1-decanol at 25 °C. For clarity, curves have been displaced along the ordinate. Three dispersion regions calculated are shown by solid lines.

The thermodynamic parameters, the free energy of activation ΔF^*, the heat of activation ΔH^*, and the entropy of activation ΔS^*, were obtained by applying the Eyring's equation[9,10] to the three dispersion regions in Table 2.

Assignment of the Three Dispersion Regions. For very dilute cyclohexane solutions (less than 1 mol%) of ethanol, Ibbitson and Moore[11] reported that the near-infrared spectra contained a broad absorption band at 3350 cm^{-1} in addition to two bands at 3520—3540 and 3644—3650 cm^{-1}. From measurements of the dielectric constant and the solute polarization, they attributed the three bands to the presences of a nonpolar cyclic polymer, a linear dimer and trimer, and a free monomer. Meantime, the first dispersion region vanished in the vicinity of 15 mol% of 1-decanol, as shown in Table 1. This observation was in agreement with the results for cyclohexane solutions of 1-hexanol

Table 1. Dielectric Parameters, Refractive Indices, Densities, and Viscosities

	Dielectric constants				Relaxation times					
	ε_0	ε_1	ε_2	ε_3	τ_1 / ps	τ_2 / ps	τ_3 / ps	n_D	d / g cm^{-3}	$\eta\times10^3$ / N s m^{-2}
t/°C						1-Decanol				
15	8.78	3.03	2.60	2.37	3302	178	20	1.4392	0.8328	17.84
20	8.38	3.07	2.63	2.36	2490	179	21	1.4374	0.8295	—
25	8.03	3.10	2.66	2.35	1888	176	20	1.4354	0.8261	11.74
35	7.33	3.20	2.75	2.33	1103	168	19	1.4317	0.8195	8.11
40	6.97	3.18	2.77	2.33	800	160	18	1.4299	0.8160	—
mol%						1-Decanol in cyclohexane at 25 °C				
80.01	6.54	3.04	2.62	2.30	1696	206	23	1.4336	0.8186	8.13
59.93	4.82	2.97	2.55	2.28	1438	246	28	1.4313	0.8096	5.15
39.92	3.28	2.78	2.43	2.22	1210	235	25	1.4287	0.7991	3.06
29.89	2.76	2.61	2.37	2.18	1115	266	27	1.4273	0.7934	2.26
mol%						1-Decanol in heptane at 25 °C				
79.93	6.11	3.02	2.61	2.31	1494	218	27	1.4285	0.8038	5.96
60.08	4.27	2.95	2.52	2.26	1207	282	32	1.4202	0.7781	2.97
39.98	2.90	2.64	2.36	2.17	878	265	31	1.4102	0.7491	1.47
30.02	2.51	2.45	2.26	2.11	901	243	34	1.4048	0.7333	1.05

Table 2. Thermodynamic Parameters, ΔF^*, ΔH^*, and ΔS^*, for Three Dispersion Regions of 1-Decanol

	$\Delta F^{*a)}$ / kJ mol^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}
First region	23.2	39.6	55.1
Second region	17.3	0.72	−55
Third region	11.9	2.2	−33

a) The values of ΔF^* was calculated at 298 K.

measured by Komooka[12] and of ethanol measured by Sagal.[13] From the above consideration, therefore, there are at least a free monomer, a linear dimer and trimer, and a nonpolar cyclic polymer in addition to a higher polar polymer which the first dispersion region originates. These species should correspond to the dielectric dispersion regions observed.

The relaxation times of unassociated liquids were collected from the literature for room-temperature values. Chlorobenzene[14,15] has a relaxation time of 11—14 ps, bromobenzene[14,15] 17—18 ps, 1-bromo-3-methylbutane[15,17] 13—22 ps, 1-chlorooctane[16] 17 ps, 1-bromooctane[15,16] 22—43 ps, 1-iodooctane[16,18] 39—45 ps. In view of these relaxation times, it is considered that the third relaxation time shown in Table 1 is attributed to the reorientation of a free monomer. The free energy of activation ΔF^* is 10.4 kJ mol^{-1} for chlorobenzene and 10.9 kJ mol^{-1} for 1-bromo-3-methylbutane, also corresponding to that of the third region, as shown in Table 2.

The first dispersion region is large, strongly dependent on the temperature (in comparison with the other), and decreases rapidly with dilution. This process is apparently associated with a linear hydrogen-bonded species. It has been reported that this process could be ascribed to the breaking of the hydrogen bonds in molecular aggregates followed by ROH rotation,[7] to a single highly polymer,[1] and to the switching mechanism of the OH moment as one hydrogen bond is broken and another formed.[13] In addition to these models, it may be considered to be due to the existence of an alcohol molecule which forms two hydrogen bonds between an oxygen atom in the molecule and two hydrogen atoms of neighboring molecules, since the magnitude of this region is much greater than the other. Such an alcohol molecule has three hydrogen bonds instead of the four hydrogen bonds of a water molecule in the "flickering cluster model"[19] proposed by Frank and Wen. If such a molecule exists, a more complex polymer can be formed disorderly by joining two linear and cyclic polymers in a three-dimensional spread. The existence of such a molecule, however, has still not been confirmed by experiments. Studies of the X-ray diffraction[20] interpreted this aggregate as a linear hydrogen-bonded chain polymer. It is, therefore, considered that the first dispersion region is attributed to the linear hydrogen-bonded chain polymer. This polymer has various chain lengths which may be dependent on the temperature, dilution, and amount of shielding of the hydroxyl group.

Since the second dispersion region is always small in magnitude, it may be considered to be formed as an intermediate. It becomes difficult to separate the first and second regions as the temperature increases. When the magnitude of the first region decreases, there are some cases in which there is no distinction between the first and second regions. From the above consideration, the second process is due to a short linear chain polymer, such as a chain dimer and trimer.

It is concluded that the first region can be attributed to a linear hydrogen-bonded chain polymer (probably $n \geqq 4$), the second region to a chain dimer and trimer ($n=2$ and 3), and the third region to a free monomer ($n=1$).

The experimental data, inclusive of the three values measured by Garg and Smyth[7] at wavelengths of 3.22, 1.25, and 0.22 cm, have been resolved into four different Debye-like dispersion regions. The four relaxation times obtained are 2490, 179, 27.9, and 3.06 ps at 20 °C and 800, 160, 23.7, and 2.91 ps at 40 °C for pure 1-decanol. The second region could not be found in the Garg and Smyth's analysis because of experimental errors[8] in their measurements at the highest band of the RX meter. The band of the RX meter was not used in our measurements. Meantime, Glasser et al.[8] resolved the dielectric absorption into three dispersion regions at higher concentrations for heptane solutions of some normal alcohols. It is considered that the three regions measured by Glasser et al. correspond to the three higher-frequency regions, except for the lowest-frequency region. The free energies of activation for the four dispersion regions are about 23.2, 17.3, 12.7, and 7.3 kJ mol^{-1}, respectively.

In this study, the highest-frequency region could not be obtained because of the narrow range of the measuring frequencies. This region is attributed to a relaxation of the hydroxyl group by rotation around its C–O bond, as described by Garg and Smyth.[7]

Concentrations of Monomer and Three Hydrogen-Bonded Species. In a previous paper,[9] we proposed a modified Kirkwood–Fröhlich equation as follows:

$$\varepsilon_{i-1} - \varepsilon_i = \frac{3\varepsilon_{i-1}}{2\varepsilon_{i-1} + \varepsilon_i}\left(\frac{\varepsilon_i + 2}{3}\right)^2 \frac{4\pi N_A \mu_0^2}{3 \times 10^3\, kT} C_i\, g_i, \tag{1}$$

$$C_0 = \sum_{i=1}^{k} C_i + C_R, \tag{2}$$

$$g = 1, \text{ if } n = 1 \text{ and } g = 1 + Z\sum_{m=2}^{n} f\left(\cos^2\frac{\theta}{2}\right)^{m-1}, \text{ if } n \geqq 2, \tag{3}$$

$$f = \frac{(\mu_H + \mu_R)(\mu_H + \mu_R \cos\theta)}{\mu_H^2 + \mu_R^2 + 2\mu_H\mu_R \cos\theta}\,.$$

In this equations, ε_{i-1} and ε_i are the limiting low- and high-frequency dielectric constants of the i-th dispersion, N_A is Avogadro's number, μ_0 the dipole moment of the molecule in vacuum, kT the thermal energy, g_i the Kirwood correlation factor of the i-th dispersion, C_0 the gross stoichiometric concentration in mol dm^{-3} of all alcohol molecules, C_i the alcohol concentration at which the i-th dispersion originates, C_R that of nonpolar cyclic polymer, and Z the coordination number. Additionally, μ_H and μ_R are the components of the dipole moment of alcohol molecule ROH along the O–H and O–R bonds, respectively, θ is the angle between the O–H and O–R bonds, m represents m-th molecule, and n is the number of alcohol molecule in the linear hydrogen-bonded chain polymer. It was assumed in Eqs. 1—3 that $Z=2$, $\mu_H=1.53$ D, $\mu_R=1.20$ D, $\mu_0=1.68$ D, and $\theta=105°$ for linear alcohols such as 1-decanol.

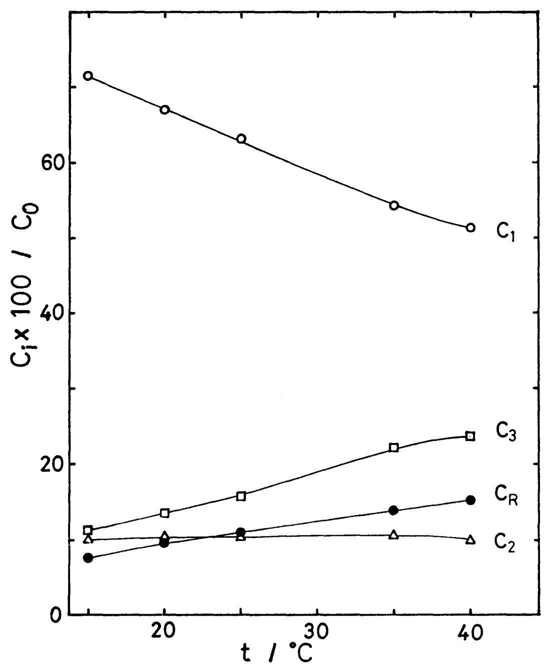

Fig. 3. Percentages of C_i for pure 1-decanol as a function of temperature.

The g factor can be calculated from Eq. 3. The value of the g factor is 1 if $n=1$, 1.87 if $n=2$, 2.19 if $n=3$, 2.31 if $n=4$, 2.36 if $n=5$, and 2.38 if $n \geqq 6$, respectively. According to our assignments, it is assumed that the g_1 is 2.38 for the first region, the g_2 is 2.03 as an average value for the second region, and the g_3 is unity for the third region. The concentrations C_i can be calculated from Eq. 1 by making use of these g_i factors and of the experimental values of ε_{i-1} and ε_i listed in Table 1. The percentages of C_1, C_2, C_3, and C_R against the gross stoichiometric concentration C_0, $C_i \times 100/C_0$, are shown for change of temperature (Fig. 3) and for change of dilution (Fig. 4). For example, the respective percentages of C_1, C_2, C_3, and C_R are 71, 10, 11, and 8% at 15 °C and 52, 10, 24, and 16% at 40 °C for pure 1-decanol. Those for cyclohexane solutions of 1-decanol are 54, 11, 19, and 16% at 80 mol% and 16, 17, 21, and 46% at 40 mol% at 25 °C. Figure 3 shows that the C_1 decreases and both C_3 and C_R increase, as the temperature increases. C_2 does not change in the temperature range 15—40 °C. It is considered that depolymerization occurs for the linear hydrogen-bonded chain polymer. For cyclohexane and heptane solutions of 1-decanol, it is shown in Fig. 4 that the C_1 decreases rapidly and that C_R increases correspondingly, as the concentration of 1-decanol decreases. Both

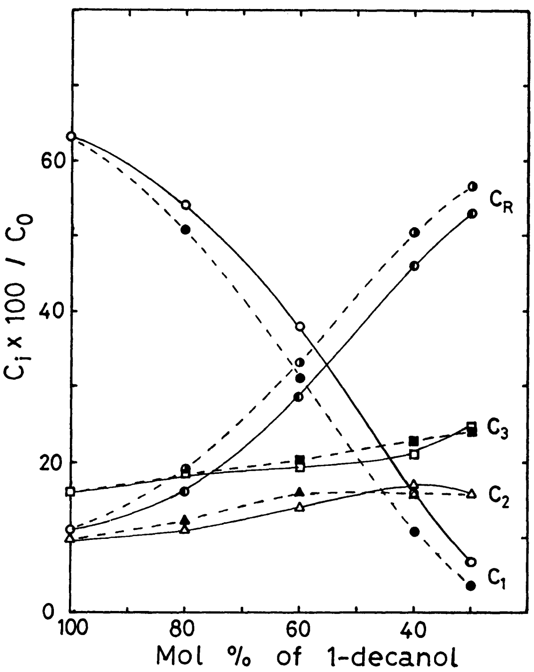

Fig. 4. Percentages of C_i for cyclohexane and heptane solutions of 1-decanol as a function of mol% of 1-decanol. Cyclohexane solutions are shown by solid lines and heptane solutions are shown by dotted lines.

C_2 and C_3 also increase slightly. The length of the linear hydrogen-bonded chain polymer probably becomes short by breaking the hydrogen bonds due to a hindrance of the nonpolar solvent. It is considered from Fig. 4 that the nonpolar cyclic polymer becomes a most stable structure in dilute solutions, although the linear hydrogen-bonded chain polymer is favorable in pure 1-decanol. We can understand the behavior of the four concentrations regarding the changes in temperature and dilution.

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