Dielectric Dispersion and Intermolecular Association for 28 Pure Liquid Alcohols. The Position Dependence of Hydroxyl Group in the Hydrocarbon Chain

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(Received September 10, 1988)

The dielectric constants and losses of 28 linear alcohols, 1-alkanol (n=3—10), 2-alkanol (n=3—10), 3-alkanol (n=5—10), 4-alkanol (n=7—10), and 5-alkanol (n=9 and 10), have been measured at the frequencies from 1.35 to 4500 MHz at 15, 25, and 35 °C. The Kirkwood–Fröhlich equation was modified so that it could be applied to each dispersion region calculated. The concentration C_1 of linear hydrogen-bonded chain polymers, which primary dispersion originates, was evaluated by means of this modified equation. The C_1 decreases as the hydroxyl group approaches the center of a molecule, except for propanols and butanols, and also decreases with increasing temperature. For isomeric decanols, for example, the percentages of C_1 ($C_1 \times 100/C_0$) against alcohol gross stoichiometric concentration C_0 at 15, 25, and 35 °C are about 71, 63, and 53% for 1-decanol, 52,40,and 29% for 2-decanol, 22, 17, and 12% for 3-decanol, 11, 7, and 6% for 4-decanol, and 8, 6, and 5% for 5-decanol, respectively. The thermodynamic parameters, ΔF^*, ΔH^*, and ΔS^*, were obtained for dipole relaxation and viscous flow . The $\Delta F\tau^*$ decreases, although the $\Delta H\tau^*$ and $\Delta S\tau^*$ increase, as the hydroxyl group approaches the center of a molecule. The $\Delta F\eta^*$ increases linealy with the molecular volume, irrespective of the position of the hydroxyl group.

The liquid structure of alcohols has been the subject of many investigations because of its having a possible hydrogen bonding between adjacent molecules. Studies of the dielectric relaxation processes[1–3] have estimated the existence of monomers and hydrogen-bonded molecular species in pure liquid alcohols. The magnitude of the primary dispersion is usually much greater than that of the higher dispersion. Its relaxation time is long and strongly temperature dependent. Therefore, this process is considered to be attributed to the characteristic of linear hydrogen-bonded chain polymers.[2–4] A clear detailed molecular model has, however, still not been realized. It is interesting to investigate relationship between the magnitude of primary dispersion and molecular geometry. In isomeric alcohols, the magnitude of dispersion may depend on the positions of the hydroxyl and methyl groups in a chain. It is considered that any difference in their dielectric behaviors must be due entirely to a difference in the extent of intermolecular association, since these isomers have approximately the same dipole moment and the same molecular volume. The formation of a linear hydrogen-bonded chain polymer changes according to the amount of shielding of the hydroxyl group and/or to the steric hindrance of the alkyl group. In the present study, therefore, 28 pure alcohols were selected to investigate the influences due to the position of the hydroxyl group in a chain.

Wide-range measurements indicated two or three different dispersion regions at low temperature and room temperature.[2–6] No theory can satisfactorily interpret the co-existence of the two or three dispersion regions observed. Experimental data concerning the dielectric dispersion for water and liquid alcohols have usually been analyzed by means of Kirkwood–Fröhlich theory,[7–9] which was developed on the basis of a single relaxation process. This theory can not interpret the large value of the Kirkwood correlation factor. Although this equation is still used to obtain information concerning the configuration for neighboring dipole moments, there are doubtful problems in the application of this equation to data of the dielectric dispersion for liquid alcohols. Their equation was, therefore, modified; then the concentration of the primary dispersion region was calculated.

Experimental

Purification of Materials. The commercial alcohols were fractionally distilled under reduced pressure at a very high reflux ratio. About 80% of the middle fraction was distilled again by the same method. Two distillation systems were used, one consisting of a 1 m adiabatic column packed with glass-helix packings and the other consisting of a 60 cm adiabatic column with a Teflon spinning band with a rotation speed variable from 1000 to 6000 rpm. Both systems have 200—300 theoretical plates. A Molecular Sieve of 3A or 5A was used as a drying agent. The middle portion was finally distilled in a grease-free apparatus under reduced pressure before use.

Apparatus. The dielectric constants and losses were measured by making use of the following three types of apparatus over the frequency range from 1.35 to 4500 MHz.

Low Frequency Range: A Boonton Radio RX meter (Type 250A) was used for measurements at frequencies of 1.35, 6.3, 17, 30, and 45 MHz. An adaptor (GR 900-QNP) and a T-type adaptor (which is joined to an inductor) were put between a cell and a terminal of RX meter's bridge. The necessary corrections of coaxial transmission line were made

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according to the transmission line formulas by the use of the terminations (Type GR 900-W50, GR 900-W200, and GR 900-WO4) and the reference air lines (Type GR 900-LZ) as standard equipments. Two dielectric cells were carefully made of a GR Precision Inner-Conductor Rod, an Outer-Conductor Tube, and a GR 900-BT connector. The temperature of the cell was kept constant within ±0.1 °C of the specified values by circulation of water from a thermostat through a jacket around the cell.

Middle Frequency Range: Measurements at frequencies 60, 80, 100, 150, 200, 250, 300, 400, and 480 MHz were made with a Hewlet-Packard VHF Bridge which comprised a VHF Signal Generator (Model 608C), a VHF Detector (Model 417A), a VHF Bridge (Model 803A), an SWR meter (415E), and a frequency counter. This apparatus was described in detail by Komooka.[10] The frequencies of the RX meter and VHF Bridge were controlled to be within ±0.01% of the specified values.

High Frequency Range: 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. This equipment has a slotted section of 9/16-inch and is a precision coaxial transmission line with a characteristic impedance of 50.0 ohm±0.1%. The signal sources were a Modulating Power Supply (Type 1264-B) and a VHF Oscillator (Type 1362), a Modulating Power Supply (Type 1264-B) and a Lockable Oscillator (Type 1218-BV), and a HP Signal Generator (Type 8616A). The line was fitted with a movable carriage which provides a mount for a detector diode, a tuning stub, an adjustable probe, and a Type 874 output connector which was connected with an SWR meter (415E). Two cells were identical to those used in the measurement of the low-frequency range described above.

Calculation of Dielectric Parameters. In general, the dielectric constant ε' and loss ε'' are described by

$$\varepsilon_j' = \varepsilon_\infty + \sum_{i=1}^{n} \left(\frac{\varepsilon_{i-1} - \varepsilon_i}{2} \left(1 - \frac{\sinh \theta_i}{\cosh \theta_i + \sin(\frac{\pi}{2} h_i)}\right) \right)$$

and

$$\varepsilon_j'' = \sum_{i=1}^{n} \left(\frac{\varepsilon_{i-1} - \varepsilon_i}{2} \left(\frac{\cos(\frac{\pi}{2} h_i)}{\cosh \theta_i + \sin(\frac{\pi}{2} h_i)} \right) \right),$$

where ε_∞ is the limiting high-frequency dielectric constant. $\theta_i = (1-h_i)\ln(f_j/fr_i)$. h_i is constant, $0 \leqq h_i < 1$. When $0 < h_i < 1$, the dispersion is a Cole–Cole like, depressed-center semicircular arc. In the limit $h_i = 0$, it reduces to a Debye-like, semicircular arc. $\varepsilon_{i-1} - \varepsilon_i$ is a magnitude and fr_i is a relaxation frequency of the i-th dispersion. ε_j' and ε_j'' are experimental values at frequency f_j. The dielectric parameters were calculated by the equations with the least-squares method.

Results and Discussion

Dielectric Relaxation. The Cole–Cole plots are shown in Fig. 1 for isomeric pentanols and in Fig. 2 for isomeric decanols, respectively. Primary dispersion is quantitatively described by a Debye-like semicircular arc, though it is also evident that the data can not be satisfactorily fitted 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. The first one is best described by several overlapping Debye-like semicircular arcs, $\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + i\omega\tau)$, such as isomeric pentanols in Fig. 1 and 1-decanol in Fig. 2. The second one by Davidson–Cole skewed arc, $\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty)/(1 + (i\omega\tau))^\beta$,

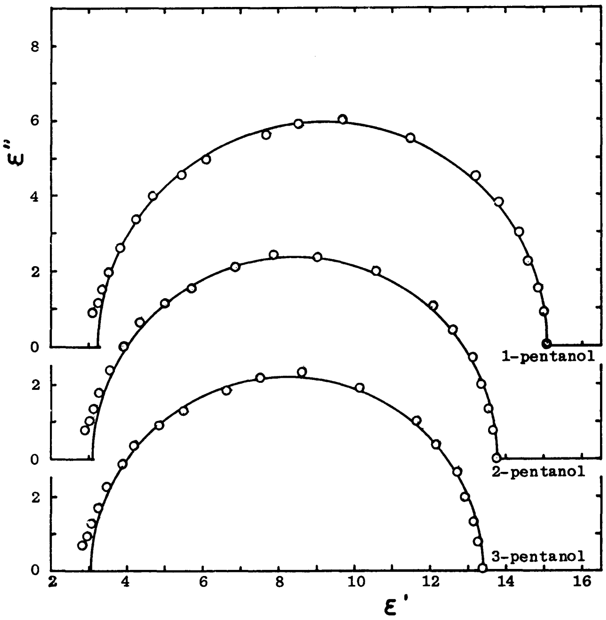

Fig. 1. Cole–Cole plots for isomeric pentanols at 25 °C.

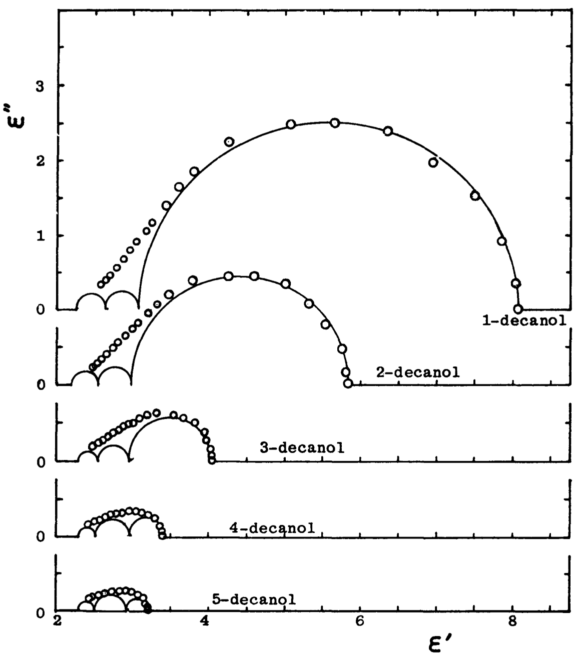

Fig. 2. Cole–Cole plots for isomeric decanols at 25 °C, together with calculated behavior for the three dispersion regions.

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

Compound	ε_0	ε_1	fr	n_D	d	$\eta \times 10^3$
			MHz		g cm^{-3}	N s m^{-2}
15 °C						
1-Propanol	21.77	3.78	322	1.3878	0.8075	2.52
1-Butanol	18.81	3.56	204	1.4015	0.8132	3.40
1-Pentanol	16.24	3.39	142	1.4120	0.8185	4.71
1-Hexanol	14.18	3.28	104	1.4201	0.8219	6.31
1-Heptanol	12.48	3.20	80.0	1.4262	0.8252	8.48
1-Octanol	10.98	3.12	65.8	1.4314	0.8282	11.04
1-Nonanol	9.80	3.08	55.0	1.4357	0.8306	14.17
1-Decanol	8.78	3.03	48.2	1.4392	0.8328	17.84
2-Propanol	20.99	3.53	273	1.3807	0.7890	2.85
2-Butanol	18.42	3.29	169	1.3994	0.8105	4.65
2-Pentanol	15.46	3.16	120	1.4087	0.8131	5.27
2-Hexanol	12.51	3.06	94.5	1.4171	0.8173	6.61
2-Heptanol	10.48	3.00	74.5	1.4233	0.8195	8.41
2-Octanol	8.84	2.98	62.0	1.4284	0.8233	10.84
2-Nonanol	7.53	2.90	53.1	1.4329	0.8261	13.80
2-Decanol	6.59	2.86	46.7	1.4366	0.8285	17.26
3-Pentanol	15.38	3.02	105	1.4128	0.8240	8.35
3-Hexanol	11.35	2.99	84.6	1.4186	0.8227	8.80
3-Heptanol	7.72	2.95	80.7	1.4243	0.8243	9.17
3-Octanol	5.92	2.93	73.2	1.4289	0.8264	10.82
3-Nonanol	4.75	2.87	67.1	1.4332	0.8287	13.27
3-Decanol	4.22	2.79	58.4	1.4366	0.8302	16.46
4-Heptanol	6.58	2.98	86.4	1.4223	0.8209	9.23
4-Octanol	4.35	2.88	93.8	1.4271	0.8226	11.10
4-Nonanol	3.66	2.76	88.3	1.4314	0.8250	13.48
4-Decanol	3.36	2.71	76.7	1.4352	0.8272	16.27
5-Nonanol	3.48	2.78	94.1	1.4315	0.8252	14.98
5-Decanol	3.16	2.68	86.3	1.4350	0.8272	18.13
25 °C						
1-Propanol	20.44	3.64	474	1.3833	0.7991	1.95
1-Butanol	17.54	3.44	314	1.3973	0.8057	2.59
1-Pentanol	15.10	3.37	223	1.4082	0.8115	3.51
1-Hexanol	13.12	3.27	169	1.4162	0.8148	4.57
1-Heptanol	11.53	3.23	133	1.4225	0.8186	5.97
1-Octanol	10.11	3.19	112	1.4276	0.8214	7.63
1-Nonanol	9.00	3.17	94.5	1.4319	0.8241	9.59
1-Decanol	8.03	3.10	84.3	1.4352	0.8260	11.74
2-Propanol	19.41	3.43	438	1.3753	0.7808	2.08
2-Butanol	16.72	3.28	301	1.3950	0.8025	3.10
2-Pentanol	13.78	3.23	226	1.4044	0.8053	3.46
2-Hexanol	11.06	3.16	179	1.4129	0.8096	4.22
2-Heptanol	9.25	3.11	144	1.4191	0.8131	5.33
2-Octanol	7.80	3.11	116	1.4245	0.8160	6.75
2-Nonanol	6.66	3.06	104	1.4290	0.8190	8.43
2-Decanol	5.82	2.99	94.1	1.4326	0.8212	10.42
3-Pentanol	13.38	3.20	218	1.4081	0.8155	4.69
3-Hexanol	9.66	3.17	180	1.4143	0.8144	4.90
3-Heptanol	6.71	3.15	169	1.4202	0.8160	5.38
3-Octanol	5.35	3.13	146	1.4250	0.8188	6.47
3-Nonanol	4.49	3.06	127	1.4293	0.8213	8.00
3-Decanol	4.05	2.96	113	1.4329	0.8229	9.80
4-Heptanol	5.85	3.16	172	1.4182	0.8120	5.47
4-Octanol	4.24	3.13	204	1.4232	0.8153	6.74

Table 1. (Continued)

Compound	ε_0	ε_1	fr	n_D	d	$\eta \times 10^3$
			MHz		g cm^{-3}	N s m^{-2}
4-Nonanol	3.69	3.09	175	1.4275	0.8179	8.16
4-Decanol	3.42	3.00	141	1.4314	0.8202	9.82
5-Nonanol	3.54	2.99	200	1.4277	0.8181	8.95
5-Decanol	3.24	2.91	161	1.4312	0.8201	10.84
			35 °C			
1-Propanol	19.17	3.46	699	1.3792	0.7914	1.54
1-Butanol	16.38	3.40	470	1.3934	0.7979	2.00
1-Pentanol	14.04	3.36	351	1.4042	0.8039	2.63
1-Hexanol	12.11	3.35	276	1.4124	0.8080	3.40
1-Heptanol	10.57	3.33	217	1.4186	0.8117	4.34
1-Octanol	9.27	3.37	186	1.4239	0.8149	5.46
1-Nonanol	8.22	3.23	162	1.4282	0.8171	6.69
1-Decanol	7.33	3.25	144	1.4317	0.8195	8.11
2-Propanol	17.91	3.35	682	1.3708	0.7722	1.54
2-Butanol	15.09	3.28	507	1.3909	0.7938	2.15
2-Pentanol	12.28	3.28	400	1.4002	0.7969	2.35
2-Hexanol	9.76	3.25	340	1.4088	0.8018	2.89
2-Heptanol	8.20	3.27	283	1.4157	0.8054	3.57
2-Octanol	7.03	3.25	248	1.4205	0.8084	4.46
2-Nonanol	5.95	3.27	218	1.4249	0.8115	5.57
2-Decanol	5.30	3.23	193	1.4286	0.8143	6.78
3-Pentanol	11.61	3.27	429	1.4037	0.8067	2.82
3-Hexanol	8.24	3.25	389	1.4098	0.8061	3.05
3-Heptanol	6.03	3.24	392	1.4158	0.8085	3.49
3-Octanol	5.01	3.22	362	1.4208	0.8112	4.20
3-Nonanol	4.33	3.17	323	1.4252	0.8138	5.20
3-Decanol	3.98	3.17	295	1.4286	0.8157	6.30
4-Heptanol	5.41	3.25	412	1.4139	0.8050	3.50
4-Octanol	4.20	3.25	463	1.4191	0.8078	4.37
4-Nonanol	3.72	3.15	439	1.4235	0.8104	5.27
4-Decanol	3.45	3.10	404	1.4274	0.8130	6.33
5-Nonanol	3.59	3.08	513	1.4235	0.8106	5.71
5-Decanol	3.31	3.01	543	1.4272	0.8129	6.88

such as 3-decanol in Fig. 2. The third one by Cole–Cole depressed-center semicircular arc, $\varepsilon^*-\varepsilon_0=(\varepsilon_0-\varepsilon_\infty)/(1+(i\omega\tau)^\alpha)$, such as 5-decanol in Fig. 2. ε^* is the complex dielectric constant, ε_0 and ε_∞ are the limiting low- and high-frequency dielectric constants, ω is the angular frequency, τ the relaxation time, and α and β are parameters, $0<\alpha$ or $\beta<1$. However, the loci of these compounds are temperature dependent and will change probably from a Debye type to a Davidson–Cole type or a Cole–Cole type by a decrease in the magnitude of the primary dispersion region in comparison with those of other dispersion regions. We assumed, therefore, that the dielectric absorption for each compound was the sum of several overlapping Debye-like dispersion regions. The dielectric parameters of the primary dispersion calculated are listed in Table 1, together with refractive indices, densities, and with viscosities.

The magnitude, $(\varepsilon_0-\varepsilon_1)T/C_0$, of primary dispersion region is plotted in Fig. 3 against the alcohol gross concentration C_0. T is the absolute temperature. Figure 3 shows that the curves from 1-propanol to 1-decanol and from 2-propanol to 2-decanol indicate a maximum at about 11 mol dm^{-3}, in the vicinity of butanols, respectively. The dielectric properties of higher alcohols (at lower alcohol concentration than the maximum) are often different with those of lower alcohols (such as propanols and butanols). For higher alcohols, the value of the magnitude decreases with decreasing alcohol concentration and becomes extremely small as the hydroxyl group approaches the center of a molecule. The magnitude of 5-decanol is 13 K mol^{-1} dm^3, being about 5% of that of 1-decanol. These isomers differ remarkably from each other in the average value of magnitude per one hydroxyl group. The difference leads us to anticipate that the magni-

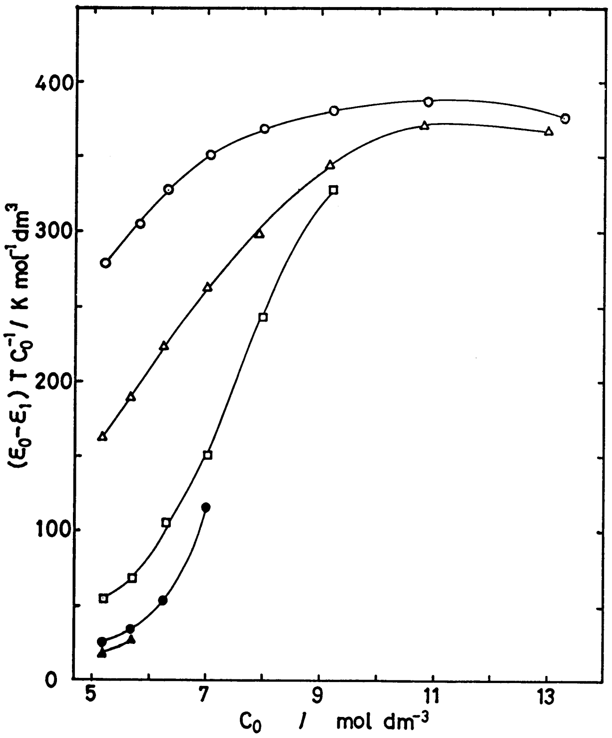

Fig. 3. The magnitude of primary dispersion region as a function of alcohol gross concentration C_0 at 25 °C.
○: 1-propanol-1-decanol, △: 2-propanol-2-decanol, □: 3-pentanol-3-decanol, ●: 4-heptanol-4-decanol, ▲: 5-nonanol and 5-decanol.

tude is intimately related to the extent of hydrogen bonding and to the existence of a nonpolar cyclic polymer. It is desired to examine the equilibrium between linear chain polymers and nonpolar cyclic polymers.

Concentration of Primary Dispersion Region. Experimental data concerning the dielectric dispersion have usually been analyzed by means of the Kirkwood–Fröhlich equation:[8,9]

$$\varepsilon_0 - n_D^2 = \frac{3\,\varepsilon_0}{2\varepsilon_0 + n_D^2} = \left(\frac{n_D^2+2}{3}\right)^2 \frac{4\pi N_0\mu_0^2}{3\,kT}\, g, \qquad (1)$$

where n_D is the refractive index, N_0 the number of molecule per unit volume, and μ_0 the dipole moment of the molecule in vacuum. From Eq. 1, in which 1.05 n_D^2 was used in place of n_D^2,[11] the Kirkwood correlation factors g were calculated to be 3.14, 3.19, 3.15, 3.07, 2.97, 2.83, 2.70, and 2.56 at 25 °C for pure normal alcohols from propyl through decyl, respectively. These g factors are much greater than 2.39 obtained by Oster and Kirkwood[8,12] for a model of an infinite hydrogen-bonded chain of alcohol molecules with free rotation about the hydrogen bonds. For isomeric decanols at 25 °C, the respective g factors are 2.56 for 1-decanol, 1.77 for 2-decanol, 1.00 for 3-decanol, 0.70 for 4-decanol, and 0.62 for 5-decanol. The observation that the g factor is less than unity has been interpreted as being due to an antiparallel alignment of near-neighbor dipole moments. The g factor increases with decreasing temperature and becomes 4.7 for an infinitely long chain of 6-methyl-3-heptanol at a very low temperature.[11] The large values of the g factor can not be interpreted satisfactorily for liquid alcohols. Dannhauser[13] proposed a partial hindrance of the rotation in place of the free rotation about the hydrogen bonds described in the Kirkwood model.[8] We believe that the large value of the g factor is attributed to the value of 1.05 n_D^2 which is usually less than the limiting high-frequency dielectric constant and that a concentration factor should be introduced instead of the molecular volume into the Kirkwood–Fröhlich equation[8,9] in the same manner that the existence of a nonpolar cyclic polymer is considered when the g factor is less than unity. If their equation is applied to the data of liquid alcohols, we must take care concerning the following four points: 1) The dispersion of liquid alcohols can be resolved into some overlapping relaxation processes; 2) therefore, the choice of n_D^2 must be corrected for each dispersion region calculated; 3) alcohol molecules must be assigned to each dispersion region; and 4) if nonpolar cyclic polymers exist, their concentrations must be neglected in order to not contribute to the dispersion. According to the Kirkwood–Fröhlich theory, therefore, we propose that the cavity field G inside a spherical cavity with dielectric constant ε_i instead of the n_D^2 must be replaced by $G=3\varepsilon_0\,E/(2\varepsilon_0+\varepsilon_i)$. E is the macroscopic field. The dipole moment μ in the Kirkwood equation can be expressed by making use of the vacuum moment μ_0 for a spherical molecule as follows: $\mu=(\varepsilon_i+2)\mu_0/3$. In order to apply the Kirkwood–Fröhlich equation to the some overlapping dispersion regions, this equation was modified as follows:

$$\varepsilon_{i-1} - \varepsilon_i = \frac{3\,\varepsilon_{i-1}}{2\varepsilon_{i-1}+\varepsilon_i}\left(\frac{\varepsilon_i+2}{3}\right)^2 \frac{4\pi N_A\mu_0^2}{3\times10^3\,kT}\, C_i\, g_i. \qquad (2)$$

Where

$$C_0 = \sum_{i=1}^{k} C_i + C_{\mathrm{ring}}, \qquad (3)$$

$$g = 1, \text{ if } n = 1 \text{ and } g = 1 + Z\sum_{m=2}^{n} f(\cos^2\frac{\theta}{2})^{m-1}, \text{ if } n \geqq 2, \qquad (4)$$

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

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 Avogadro's number, C_0 the gross stoichiometric concentration in mol dm^{-3} of all alcohol molecules, C_i the alcohol concentration which the i-th

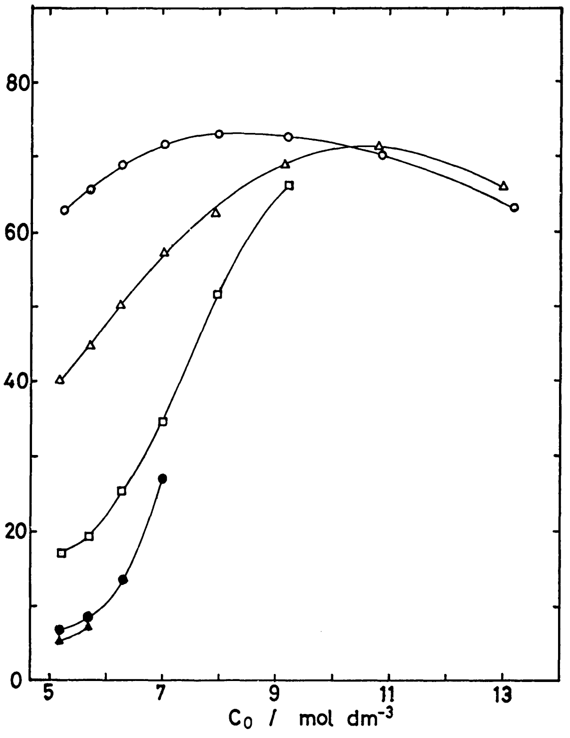

Fig. 4. The concentration (%) of primary dispersion region as a function of alcohol gross concentration C_0 at 25 °C.
○: 1-propanol-1-decanol, △: 2-propanol-2-decanol, □: 3-pentanol-3-decanol, ●: 4-heptanol-4-decanol, ▲: 5-nonanol and 5-decanol.

dispersion originates, C_{ring} that of a 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 O–H and O–R bonds, m represents m-th molecule, and n is the number of alcohol molecule in the linear chain polymer. It was assumed in Eqs. 2—4 that $Z=2$, $\mu_{\mathrm{H}}=1.53$ D, $\mu_{\mathrm{R}}=1.20$ D, $\mu_0=1.68$ D, and $\theta=105°$ for the liquid alcohols investigated. The g_1 of the primary dispersion was calculated from Eq. 4, as being 1.87 if $n=2$, 2.31 if $n=4$, and 2.38 if n is greater than 6, respectively. If g_1 is assumed to be 2.38, the concentration of C_1 which the primary dispersion region originates can be calculated from Eq. 2 by making use of the experimental values of ε_0 and ε_1. The percentage of C_1, $C_1 \times 100/C_0$, against the gross stoichiometric concentration is shown in Fig. 4 at 25 °C. Figure 4 shows, for example, that the respective percentages of C_1 for isomeric decanols are 63% for 1-decanol, 40% for 2-decanol, 17% for 3-decanol, 7% for 4-decanol, and 6% for 5-decanol at 25 °C. Six percent of the gross concentration for 5-decanol is only associated with the formation of linear hydrogen-bonded chain polymers which the primary dispersion region originates. The other 94% for 5-decanol must exist as a monomer and some hydrogen-bonded short linear chains and nonpolar cyclic species. The C_1 generally decreases with increasing temperature. The percentages of C_1 for isomeric hexanols at 15, 25, and 35 °C are 76, 73, and 66% for 1-hexanol, 73, 62, and 53% for 2-hexanol, and 67, 52, and 41% for 3-hexanol, respectively. It may be that the depolymerization of linear hydrogen-bonded chain polymers occurs as the temperature increases.

Thermodynamic Parameters. The thermodynamic parameters, the free energy of activation ΔF^*, the heat of activation ΔH^*, and the entropy of activation ΔS^*, were calculated by the Eyring's equations,[14,15] which are described for dipole relaxation and for viscous flow as follows:

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F\tau^*}{RT}\right) = \frac{h}{kT}\exp\left(-\frac{\Delta S\tau^*}{R}\right)\exp\left(\frac{\Delta H\tau^*}{RT}\right)$$

and

$$\eta = \frac{Nh}{V}\exp\left(\frac{\Delta F\eta^*}{RT}\right) = \frac{Nh}{V}\exp\left(-\frac{\Delta S\eta^*}{R}\right)\exp\left(\frac{\Delta H\eta^*}{RT}\right)$$

Here, τ is the relaxation time, h Planck's constant, RT the thermal energy, η the viscosity, and V is the molecular volume. ΔH^* and ΔS^* were calculated by the least-squares method in the temperature range 15—35 °C and ΔF^* was obtained at 25 °C. The thermodynamic parameters calculated are given in Table 2.

Table 2 shows that $\Delta H\tau^*$ increases with increasing alkyl chain length for normal alcohols and is nearly equal for secondary alcohols irrespective of length of alkyl chain, except for lower alcohols. $\Delta H\tau^*$ also increases as the hydroxyl group approaches the center of a molecule for isomeric alcohols, namely being expressed as 1-<2-<3-<4-<5-ol. $\Delta S\tau^*$ indicates the same tendency as the behavior of $\Delta H\tau^*$. $\Delta S\tau^*$ becomes large as the hydroxyl group approaches the center of a molecule. Therefore, it is noticeable that $\Delta F\tau^*$ increases with increasing alkyl chain length, being the same as that described for $\Delta H\tau^*$, but varies inversely as $\Delta H\tau^*$ in order to be a large value of $\Delta S\tau^*$ for isomeric alcohols, namely being expressed as 1->2->3->4->5-ol. It seems that the reorientation of a dipole moment of an alcohol molecule requires the rupture of hydrogen bondings and the rearrangement of some surrounding dipole moments, so that both $\Delta H\tau^*$ and $\Delta S\tau^*$ have large values. It is interesting that increases in $\Delta H\tau^*$ and $\Delta S\tau^*$ are strongly associated with the amount of shielding of the hydroxyl group in the hydrocarbon chain.

Table 2 shows that the $\Delta H\eta^*$ and $\Delta S\eta^*$ of normal alcohols increase with increasing alkyl chain length, being smaller than those of secondary alcohols. The $\Delta H\eta^*$ and $\Delta S\eta^*$ of secondary alcohols are nearly

Table 2. Thermodynamic Parameters, ΔF^*, ΔH^*, and ΔS^* for Temperature Dependence of Relaxation Times and Viscosities

Compound	Relaxation time			Viscosity		
	ΔF_τ^*	ΔH_τ^*	ΔS_τ^*	ΔF_η^*	ΔH_η^*	ΔS_η^*
	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
1-Propanol	18.9	26.1	23.9	14.6	17.4	9.2
1-Butanol	20.0	28.3	28.0	15.8	18.9	10.3
1-Pentanol	20.8	30.9	33.9	17.0	20.8	12.8
1-Hexanol	21.5	33.6	40.5	18.0	22.2	14.0
1-Heptanol	22.1	34.4	41.2	19.0	24.2	17.3
1-Octanol	22.5	35.9	44.7	19.9	25.4	18.4
1-Nonanol	22.9	37.4	48.6	20.7	27.1	21.6
1-Decanol	23.2	37.9	49.3	21.4	28.5	23.7
2-Propanol	19.1	31.3	40.8	14.9	21.8	23.3
2-Butanol	20.1	38.0	60.2	16.3	27.8	38.4
2-Pentanol	20.8	41.9	70.6	17.0	29.1	40.5
2-Hexanol	21.3	44.8	78.7	17.9	29.9	40.4
2-Heptanol	21.9	46.8	83.6	18.8	31.0	41.1
2-Octanol	22.3	48.6	88.2	19.6	32.1	42.0
2-Nonanol	22.6	49.6	90.6	20.4	32.9	41.7
2-Decanol	22.9	49.8	90.4	21.2	33.9	42.7
3-Pentanol	20.9	49.5	95.9	17.7	39.3	72.3
3-Hexanol	21.3	53.8	109	18.3	38.3	67.3
3-Heptanol	21.4	55.8	115	18.8	35.0	54.2
3-Octanol	21.6	56.4	117	19.5	34.2	49.4
3-Nonanol	21.9	55.4	112	20.3	33.9	45.8
3-Decanol	22.2	57.2	117	21.0	34.8	46.2
4-Heptanol	21.3	55.1	113	18.8	35.1	54.5
4-Octanol	21.0	56.4	119	19.6	33.8	47.5
4-Nonanol	21.2	56.6	119	20.3	34.0	45.9
4-Decanol	21.5	58.7	125	21.0	34.2	44.2
5-Nonanol	20.9	60.0	131	20.6	34.9	48.2
5-Decanol	21.1	65.1	148	21.3	35.1	46.5

equal, irrespective of the length of the alkyl chain and of the position of hydroxyl group, except for lower alcohols and some 3-alkanols. However, $\Delta F\eta^*$ increases with increasing alkyl chain length and is nearly equal for isomeric alcohols.

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