3636 © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 3636—3642 (1989) [Vol. 62, No. 11

Dielectric Relaxation and Intermolecular Association for Various Secondary and Tertiary Alcohols

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(Received May 24, 1989)

The dielectric constants and losses of 2-alkanol (n=4—8), 2-methyl-2-alkanol (n=3—7), six isomeric methylheptanols, and five isomeric nonanols have been measured at the frequencies from 1.35 to 4500 MHz at 15, 25, and 35 °C. The absorption has been resolved into two or three different Debye-like dispersion regions. The first, low-frequency, dispersion region could not be observed for more sterically hindered alcohols, such as several tertiary alcohols. For each alcohol, four concentrations of a linear hydrogen-bonded chain polymer (C_1), a chain dimer and trimer (C_2), a free monomer (C_3), and a nonpolar cyclic polymer (C_R) were evaluated by applying a modified Kirkwood–Fröhlich equation to each dispersion region. The equilibrium between C_1 and C_3 can be considered for more polar alcohols and that between C_R and C_3 for more sterically hindered alcohols. The mechanism of the relaxation process is discussed in terms of observations of the magnitude and relaxation time for the first region. The free energy of activation increases with increasing alkyl chain length, being about 20—23 for the first region, 16—18 for the second region, and 9—12 kJ mol^{-1} for the third region.

The coexistence of two or three dielectric dispersion regions has been found through wide-range measurements of complex dielectric constants for liquid alcohols.[1–4] In a previous paper,[5] we also reported three dispersion regions for pure 1-decanol at 15—40 °C and for cyclohexane and heptane solutions of 1-decanol at 25 °C. We assigned the three dispersion regions to a linear hydrogen-bonded chain polymer, a chain dimer and trimer, and a free monomer. However, no theory can satisfactorily interpret the coexistence of the two or three dispersion regions. The Kirkwood–Fröhlich equation,[6,7] developed on the basis of a single relaxation process, cannot explain a correlation factor that is large or the existence of a nonpolar cyclic polymer which does not contribute to the dispersion. Therefore, we have proposed a modified Kirkwood–Fröhlich equation[8] which could be applied to each dispersion region. These four concentrations, inclusive of a nonpolar cyclic polymer, were evaluated by means of the modified equation and were shown for 1-decanol as a function of temperature and dilution, respectively.[5]

In secondary and tertiary alcohols, dielectric studies have indicated a complex and interesting nature corresponding to a geometric variety of molecules. Dannhauser[4] measured the temperature dependence of the dielectric dispersions for eight isomeric $C_8H_{17}OH$ at low temperatures. A Cole–Cole plot for 3-methyl-3-heptanol shows a small, broad dispersion at 208—189 K. Moriamez et al.[9] also obtained a Cole–Cole plot for 3-ethyl-3-pentanol at room temperature. The small, broad dispersions for tertiary alcohols have been explained by the existence of a ring dimer. The measurement and analysis of the absorption become more difficult at room temperature. There have been almost no reports on detailed analyses of the two or three dispersion regions.

We have presently extended the investigation by measuring the dielectric dispersion of various secondary and tertiary alcohols. For these alcohols at room temperature it is interesting to investigate the fact that the dielectric absorption is dependent on the steric interrelation between the hydroxyl group and the terminal methyl and alkyl groups. It was also the purpose of the present work to confirm whether each of the four concentrations, obtained by means of a modified equation, indicates a reasonable behavior or not. The mechanism of the relaxation process is discussed.

Experimental

Purification of Materials. 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, as described in a previous paper.[8] The middle portion was dried and 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 of 1.35—4500 MHz.

In the 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 placed between a cell and a terminal of the RX meter's bridge. In the middle-frequency range, measurements at frequencies 60, 80, 100, 150, 200, 250, 300, 400, and 480 MHz were made with a Hewlett-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. In the 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. 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).

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In the low- and high-frequency ranges, 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 the circulation of water from a thermostat through a jacket around the cell. The frequencies of the RX meter and VHF Bridge were controlled to be within ±0.01% of the specified values.

The refractive indices were measured by making use of a Pulflich refractometer. The densities and viscosities were measured with a density meter of about 10 cm^3 in volume and with an Ostwald viscometer, respectively.

Results and Discussion

The Cole–Cole plots show that the first dispersion region can be best described by a Debye-like semicircular arc, though it is evident that the experimental data cannot be satisfactorily fitted in the high-frequency region of the absorption. By assuming that the absorption was the sum of several overlapping Debye-like dispersion regions, the data were resolved into two or three different dispersion regions. The limiting high-frequency dielectric constant, ε_3, of the third region contains experimental errors because of a lack of the higher-frequency data of the third region. ε_3, therefore, was assumed to be an average value in all measurements, evaluated using $(\varepsilon_3-1)/(\varepsilon_3+2)=(n_D^2-1)(1+0.19)/(n_D^2+2)$. n_D is the refractive index. The dielectric parameters of two or three dispersion regions were calculated using a least-squares method, as described in a previous paper,[8] and were given for 2-methyl-2-alkanols and isomeric methylheptanols in Table 1, together with the refractive indices, densities, and viscosities. The dielectric parameters were abbreviated for 2-alkanols and isomeric nonanols, since those for the first region were described in a previous paper.[8] We believe that the first dispersion region can be attributed to a linear hydrogen-bonded chain polymer ($n\geqq 4$), the second region to a chain dimer and trimer (n=2 and 3), and the third region to a free

Table 1. Dielectric Parameters, Refractive Indices, Densities, and Viscosities of Methyl-Substituted Alkanols

Compound	ε_0	ε_1	ε_2	ε_3	τ_1	τ_2	τ_3	n_D	d	$\eta\times10^3$
					ps	ps	ps		g cm^{-3}	N s m^{-2}
						15 °C				
2-me-2-buta	6.26	3.54	2.97	2.25	481	145	9	1.4075	0.8134	5.55
2-me-2-pent	3.76	3.59	2.79	2.27	1044	191	11	1.4129	0.8112	4.17
2-me-2-hexa	3.32	3.22	2.69	2.29	1438	195	12	1.4204	0.8164	6.00
2-me-2-hept	3.13	3.00	2.58	2.32	1675	191	13	1.4257	0.8196	8.55
7-me-3-hept	5.93	2.95	2.59	2.32	2214	216	15	1.4289	0.8264	10.82
6-me-3-hept	4.74	2.94	2.58	2.33	1448	223	15	1.4291	0.8220	11.87
5-me-3-hept	3.53	2.92	2.56	2.33	1253	235	15	1.4292	0.8285	12.41
4-me-3-hept	—	3.16	2.74	2.34	—	384	15	1.4328	0.8360	11.86
3-me-3-hept	—	2.90	2.65	2.33	—	162	13	1.4306	0.8320	11.10
4-me-4-hept	—	2.78	2.57	2.33	—	138	10	1.4284	0.8276	11.44
						25 °C				
2-me-2-prop	12.53	—	3.14	2.16	518	—	12	1.3849	0.7804	4.52
2-me-2-buta	5.72	3.49	3.00	2.23	239	72	7	1.4026	0.8043	3.48
2-me-2-pent	—	3.83	2.90	2.25	—	149	10	1.4089	0.8033	2.88
2-me-2-hexa	—	3.41	2.77	2.28	—	146	11	1.4162	0.8089	3.97
2-me-2-hept	—	3.20	2.66	2.30	—	151	11	1.4217	0.8120	5.39
7-me-3-hept	5.35	3.21	2.68	2.31	1099	232	15	1.4250	0.8188	6.47
6-me-3-hept	4.60	3.14	2.65	2.30	872	219	14	1.4229	0.8146	6.83
5-me-3-hept	—	3.60	2.80	2.31	—	485	16	1.4254	0.8212	7.29
4-me-3-hept	—	3.28	2.75	2.33	—	196	12	1.4286	0.8283	6.70
3-me-3-hept	—	3.00	2.73	2.32	—	110	11	1.4264	0.8240	6.28
4-me-4-hept	—	2.87	2.64	2.31	—	97	7	1.4243	0.8197	6.27
						35 °C				
2-me-2-prop	10.64	—	3.21	2.14	267	—	10	1.3800	0.7701	2.63
2-me-2-buta	5.41	—	3.32	2.21	—	123	11	1.3979	0.7949	2.32
2-me-2-pent	—	3.89	3.06	2.23	—	106	9	1.4045	0.7947	2.06
2-me-2-hexa	—	3.47	3.04	2.26	—	109	11	1.4118	0.8005	2.76
2-me-2-hept	—	3.29	2.91	2.28	—	121	13	1.4175	0.8040	3.60
7-me-3-hept	—	4.91	2.94	2.30	—	444	15	1.4208	0.8112	4.20
6-me-3-hept	—	4.40	2.89	2.29	—	377	31	1.4188	0.8068	4.37
5-me-3-hept	—	3.69	2.78	2.30	—	243	25	1.4214	0.8137	4.56
4-me-3-hept	—	3.42	2.84	2.31	—	130	13	1.4242	0.8204	4.11
3-me-3-hept	—	3.14	2.89	2.30	—	117	12	1.4218	0.8159	3.89
4-me-4-hept	—	2.98	2.75	2.29	—	74	7	1.4199	0.8117	3.82

monomer (n=1), as described before.[5] The Kirkwood correlation factors were evaluated according to the Kirkwood equation:[6,8,10] g_1=2.38 for the first region, g_2=2.03 as an average value for the second region, and g_3=unity for the third region. Four concentrations, a linear chain polymer (C_1), a chain dimer and trimer (C_2), a free monomer (C_3), and a nonpolar cyclic polymer (C_R), were calculated by means of a modified Kirkwood-Fröhlich equation[8] by making use of these g_i factors and the experimental values of ε_{i-1} and ε_i for the i-th dispersion.

For five 2-alkanols at 25 °C, the Cole-Cole plots are shown in Fig. 1 and the percentages of C_1, C_2, C_3, and C_R against the gross stoichiometric concentration C_0, C_i×100/C_0, are shown in Fig. 2. The absorption could be resolved into three dispersion regions, except for 2-butanol, as shown by the solid lines in Fig. 1. The magnitude, $\varepsilon_0-\varepsilon_1$, of the first region decreases from 13.44 for 2-butanol to 4.69 for 2-octanol with increasing alkyl chain length. Figure 2 shows that the percentage of C_1 decreases from 71% for 2-butanol to 50% for 2-octanol because of a steric hindrance of the long alkyl group. C_1 decreases linearly with the magnitude. C_2 increases slightly with increasing alkyl chain length, although C_3 decreases, and the sum of C_2 and C_3 almost does not change. Therefore, C_R increases inversely as C_1. The magnitudes of the first region for these 2-alkanols are less than those of normal alcohols[8] having the same number of carbon atoms. It is considered that the formation of a linear hydrogen-bonded chain becomes difficult because of the steric hindrance of the long alkyl group and the terminal methyl group. Figure 2 shows that a linear chain polymer is mainly in equilibrium with a free monomer for 2-butanol and with a nonpolar cyclic polymer for 2-octanol.

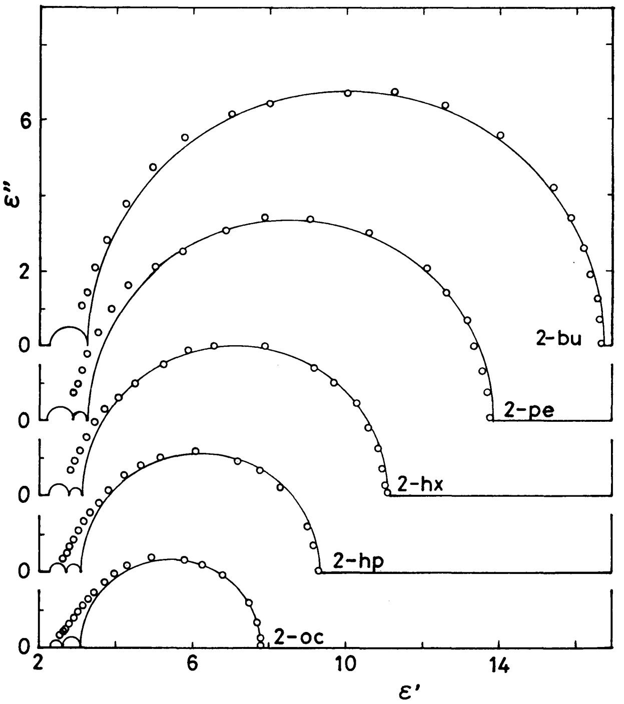

Fig. 1. Cole-Cole plots for 2-alkanol (n=4—8) at 25 °C, together with calculated behavior for the two or three dispersion regions. Butanol, pentanol, hexanol, heptanol, and octanol are abbreviated to bu, pe, hx, hp, and oc, respectively.

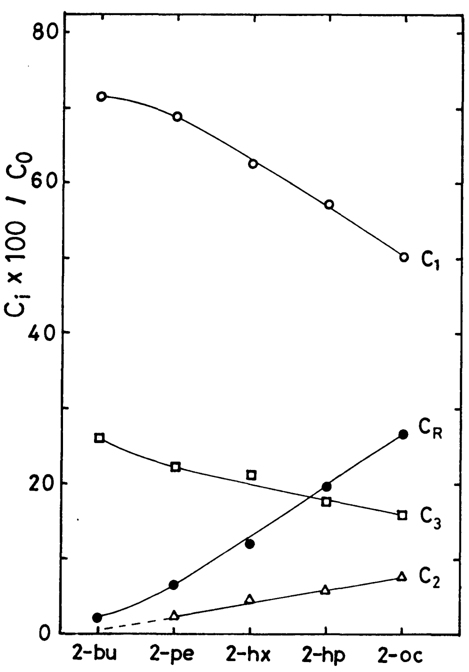

Fig. 2. Percentages of the C_{1-R} at 25 °C as a function of 2-alkanol (n=4—8). Dotted line shows an estimated value.

For five 2-methyl-2-alkanols at 25 °C, the Cole-Cole plots and the percentages of C_{1-R} are shown in Figs. 3 and 4. The absorption could not be resolved into three dispersion regions for 2-methyl-2-pentanol, 2-methyl-2-hexanol, and 2-methyl-2-heptanol. The magnitude of the first region decreases extremely from 9.39 for 2-methyl-2-propanol to 2.23 for 2-methyl-2-butanol. The percentage of C_1 also decreases from 55 to 15%, as shown in Fig. 4. It is considered for 2-methyl-2-pentanol that the first region comprises both first and second regions, although it could not be resolved into two regions. Separation between the first and second regions becomes difficult, since the magnitude of the first region approaches that of the second one. Moreover, the relaxation frequencies of the Cole-Cole plots in Fig. 3 and an extrapolation (shown as a dotted line) of the C_1 curve in Fig. 4 indicate that the first region vanishes into nothing for 2-methyl-2-hexanol and 2-methyl-2-heptanol. A comparison between Figs. 1 and 3 shows that the tertiary alcohols are more hindered species for intermolecular association. Association into a linear chain polymer becomes unfavorable because of the steric hindrance of the terminal methyl groups. The percentages of C_1, for example, are 69% for 1-octanol, 50% for 2-octanol, and

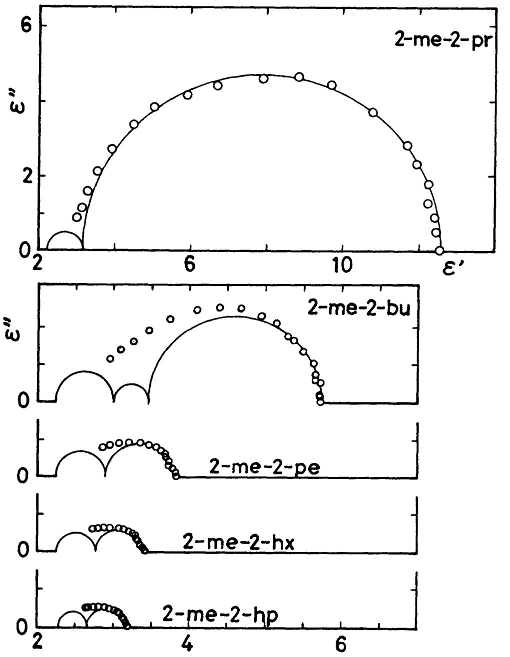

Fig. 3. Cole–Cole plots for 2-methyl-2-alkanol (n=3—7) at 25 °C, together with calculated behavior. Methyl and propanol are abbreviated to me and pr, respectively.

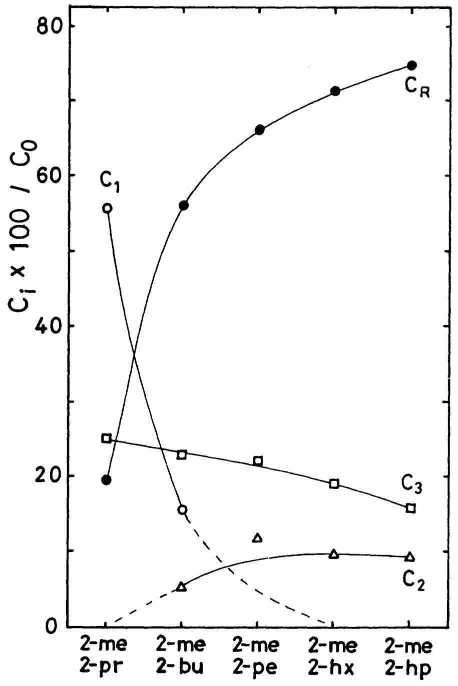

Fig. 4. Percentages of the C_{1-R} at 25 °C as a function of 2-methyl-2-alkanol (n=3—7). Dotted line shows an estimated value.

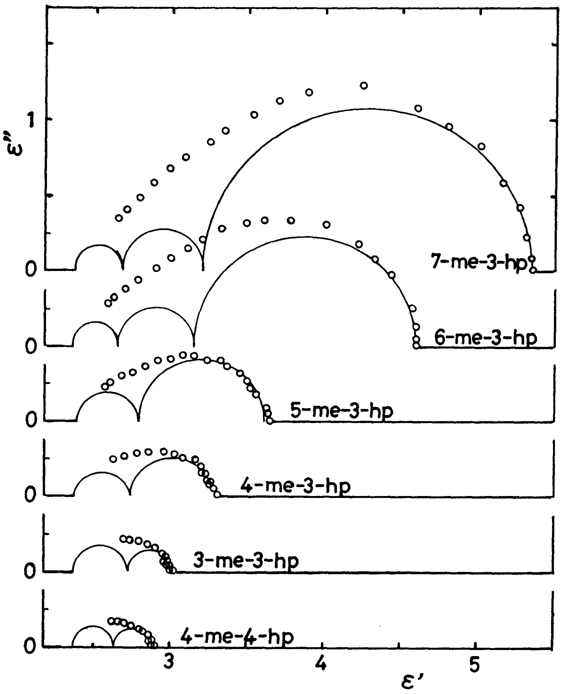

Fig. 5. Cole–Cole plots for isomeric methylheptanols at 25 °C, together with calculated behavior.

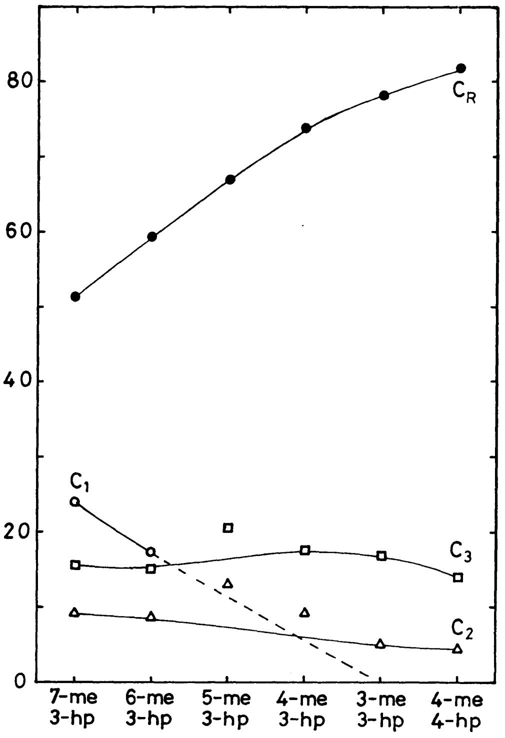

Fig. 6. Percentages of the C_{1-R} at 25 °C as a function of isomeric methylheptanols. Dotted line shows an estimated value.

0% for 2-methyl-2-heptanol at 25 °C. C_1 vanishes into nothing and C_R increases to 74% of the gross concentration for 2-methyl-2-heptanol. Figure 4 shows the equilibrium between a linear chain polymer and a free monomer for 2-methyl-2-propanol and that between a nonpolar cyclic polymer and a free monomer for 2-methyl-2-heptanol.

For six isomeric methylheptanols shown in Figs. 5

and 6 at 25 °C, the absorption could be resolved into three regions for 7-methyl-3-heptanol and 6-methyl-3-heptanol. However, it could not be resolved into three regions for 5-methyl-3-heptanol and 4-methyl-3-heptanol. For both alcohols there was no distinction between the first and second regions. As shown in Fig. 6, therefore, the percentages of C_2 and C_3 become slightly large because of the existence of a small first region. The first region becomes small in magnitude. This indicates that the formation of a linear chain polymer becomes difficult and a nonpolar cyclic polymer is formed as the methyl group approaches the hydroxyl group fixed on the third carbon atom in a molecule. The first region could not be observed in the tertiary alcohols of 2-methyl-2-heptanol (shown in Figs. 3 and 4), 3-methyl-3-heptanol, and 4-methyl-4-heptanol (shown in Figs. 5 and 6). The magnitude of the second region also decreases as both the hydroxyl and the methyl groups approach the center of a molecule. The percentage of C_R is favorable and becomes 74% of the gross concentration for 2-methyl-2-heptanol, 78% for 3-methyl-3-heptanol, and 82% for 4-methyl-4-heptanol. The large value for C_R is one remarkable feature of tertiary alcohols. Figure 6 shows that a nonpolar cyclic polymer is in equilibrium with a linear chain polymer for 7-methyl-3-heptanol and with a free monomer for 3-methyl-3-heptanol.

For five isomeric nonanols at 25 °C, the absorption could be resolved into three dispersion regions, as shown in Figs. 7 and 8. C_1 is large and, accordingly, C_R is small for normal alcohols from propyl through decyl.[8] C_1 decreases rapidly and C_R increases inversely with C_1 as the hydroxyl group approaches the center of a molecule. When the hydroxyl group approaches the center of a molecule (such as 5-nonanol), the formation of a linear chain polymer is hindered by the alkyl groups at both sides of the hydroxyl group. Figure 8 shows that a free monomer is in equilibrium with a linear chain polymer for 1-nonanol and with a nonpolar cyclic polymer for 5-nonanol.

The magnitude of the first region is in proportion to C_1 and becomes small for more hindered alcohols. Both the magnitude and C_1 decrease as the temperature increases.[5] As pure normal alcohol is diluted with a nonpolar solvent[5,11,12] and as the hydroxyl group is more sterically hindered, both the magnitude and C_1 also decrease. Therefore, any decrease in C_1 indicates that the length of a hydrogen-bonded chain shortens, namely, that the number of hydroxyl groups decreases in this polymer. The separation between the first and second regions becomes difficult as the length of a hydrogen-bonded chain approaches that of a chain dimer and trimer. The first region at last vanishes into nothing for the more hindered species (such as several tertiary alcohols), since a long linear chain polymer cannot exist. The hydrogen bond in a long chain polymer is broken by the repulsion between the terminal methyl and the alkyl groups for these more hindered alcohols, although a chain dimer and trimer can be formed. A nonpolar cyclic polymer is stably formed and becomes a preferred species for these alcohols. The second region is due to the chain dimer and trimer and is always small in magnitude. It may, therefore, be considered to be formed as an intermediate.

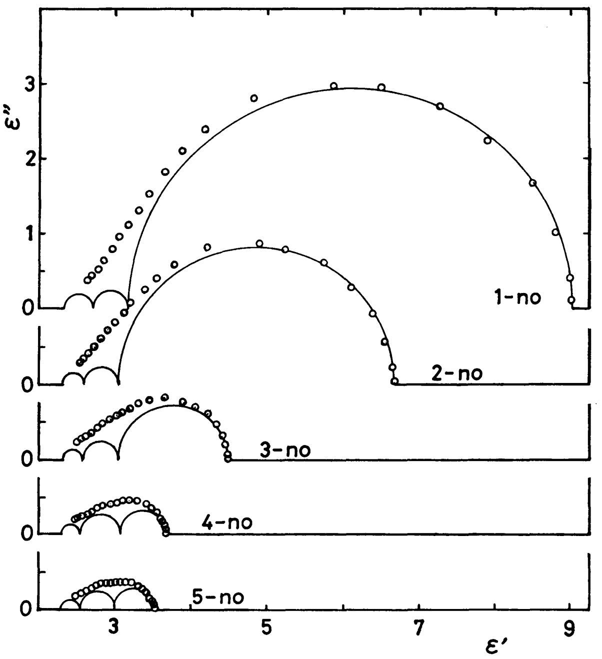

Fig. 7. Cole-Cole plots for isomeric nonanols at 25 °C, together with calculated behavior. Nonanol is abbreviated to no.

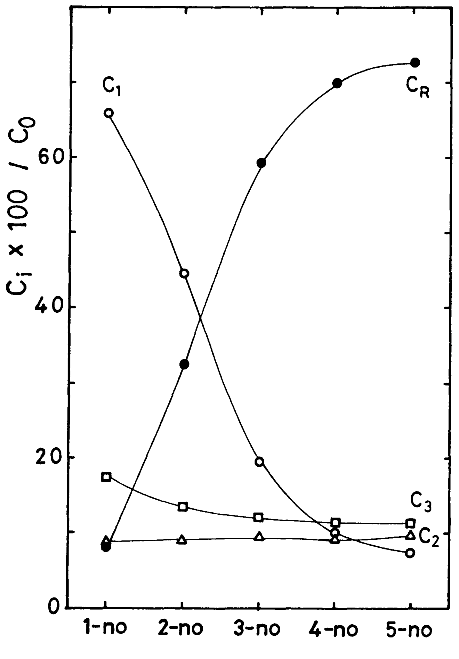

Fig. 8. Percentages of the C_{1-R} at 25 °C as a function of isomeric nonanols.

For the first region of some normal and secondary alcohols (n=3—10),[2,8] the relaxation time (τ_1) becomes long and C_1 decreases with increasing alkyl chain length in a molecule. τ_1 also becomes long with increasing viscosity of the liquid. τ_1 depends on both the alkyl chain length and the viscosity of the liquid. As pointed out by Smyth et al.,[2,13] therefore, it is considered that overall rotation of a molecule is closely associated with the relaxation process. In this work, τ_1 shortens and C_1 decreases for isomeric methylheptanols (in which the alkyl chain length and the viscosity are approximately equal) as the methyl group approaches a hydroxyl group fixed on the third carbon atom in a molecule. For the isomeric nonanols (in which the alkyl chain length and the viscosity also are approximately equal) τ_1 shortens and C_1 also decreases as the hydroxyl group approaches the center of a molecule. These observations show that τ_1 has an immediate association with C_1, namely, that τ_1 becomes shorter with decreasing length of a linear hydrogen-bonded chain. Therefore, τ_1 is considered to be dependent on the alkyl chain length in a molecule, the viscosity of the liquid, and the length of a linear hydrogen-bonded chain. The mechanism of the relaxation process may be envisioned from these relationships, as follows. After one hydrogen bond of a chain-end molecule is broken, the overall rotation of the molecule (which now becomes free) occurs; then, the overall rotation of the next molecule (which is now at the chain end) occurs successively by breaking one hydrogen bond between the molecule and a neighboring molecule. All molecules in this hydrogen-bonded chain are turned over successively. The time of the overall rotation for one molecule depends on the alkyl chain length and the viscosity of the liquid. The magnitude of the dispersion is determined by the concentration of the hydroxyl group in the linear chain polymer. The orientated molecules are rearranged so as to form a linear chain polymer by new hydrogen bondings.

The thermodynamic parameters, the free energy of activation ΔF, the heat of activation ΔH, and the entropy of activation ΔS, were calculated by applying the Eyring's equation[14] to the temperature dependences of the two or three relaxation times τ_{1-3} and the viscosity η. The ΔH and ΔS were calculated from the values at the proper temperatures of 15, 25, and 35 °C in cases where the same dispersion region could not be obtained at all the temperatures investigated. ΔF was obtained at 25 °C. ΔH and ΔS increase with increasing alkyl chain length and also increase for more sterically hindered species. Figure 9 shows that ΔF also increases with increasing alkyl chain length. For isomeric methylheptanols, as shown in Fig. 10, $\Delta F_{\tau 1}$ decreases and approaches $\Delta F_{\tau 2}$ as the methyl group approaches the hydroxyl group. $\Delta F_{\tau 1}$ vanishes into nothing in the vicinity of 3-methyl-3-heptanol, as shown by a dotted line. If the magnitude of the first region would be large for more hindered methylheptanols, the curve of $\Delta F_{\tau 1}$ would be parallel to that of $\Delta F_{\tau 2}$. It is necessary to consider that the thermodynamic parameters should be calculated in terms of the temperature dependence of the same dispersion region for the more hindered alcohols.

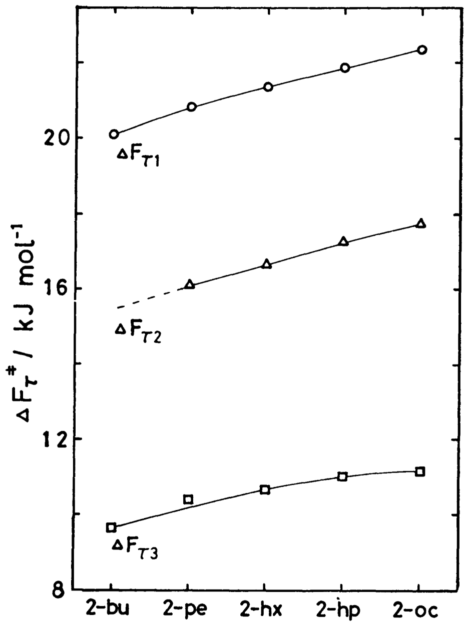

Fig. 9. Free energies of activation as a function of 2-alkanol (n=4—8).

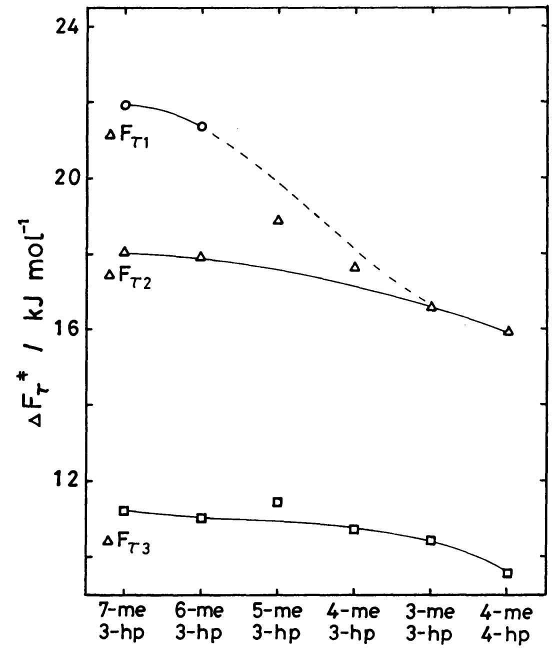

Fig. 10. Free energies of activation as a function of isomeric methylheptanols. Dotted line shows an estimated value.

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