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Dielectric Properties of the Hydrogen-Bonded Liquids. Steric Effects on Dielectric Properties in Isomeric Methylcyclohexanols

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The dielectric properties of 2- and 4-methylcyclohexanols were studied in order to elucidate the molecular geometric dependences of the dielectric properties of alcohols. The Kirkwood correlaton factors g of the trans isomers are larger than those of the cis isomers. Especially the g of *cis*-2-methylcyclohexanol at 298 K is 0.75. The dielectric relaxation of all the methylcyclohexanols studied shows the characteristics of the Debye-like behavior frequently reported for primary alcohols. The activation energy of dielectric relaxation of 2-methylcyclohexanol is much larger than that of the other methylcyclohexanols. These facts are discussed in terms of the difference of the steric hindrance for the association through the hydrogen bond.

It is well-known that alcohol molecules in a liquid state are generally self-associated by intermoleculer hydrogen bonding; therefore, the alcohols show abnormal physical properties.[1] The abnormal behaviors in dielectric properties have been revealed in earlier investigations.[2]

The dielectric susceptibility of many organic liquids can be predicted from the magnitude of their dipole moments while that of the alcohols can not. This can be explained by the fact that the dipoles of alcohol molecules do not follow an electric field independently, owing to the self-association through the hydrogen bond. Further, their dielectric relaxation times are longer than those of many organic molecules in a liquid state due to the large interaction of the hydrogen bond. In the dielectric relaxation process, the dipoles of many organic molecules reorient independently under an alternative electric field, while the dipoles of alcohol molecules reorient cooperatively for the hydrogen bond. After all, the abnormal dielectric behavior of the alcohols also results from the hydrogen bond.

The association through the hydrogen bond and the hydrogen bond network system governing the dielectric relaxation have been investigated by changing the molecular geometry of alcohols: Secondary alcohols and tertiary alcohols, with the more sterically hindered association in a liquid state, are known to have different tendencies of dielectric properties from primary alcohols. Many investigators have mainly studied linear alcohols and have discussed the steric effect for the association and the dielectric relaxation.[3,4] Most of these linear molecules, however, have a freedom of intramolecular dipolar rotation for the dipole, which is considered to denature the association and the hydrogen bond system, itself. Therefore, these investigators have neglected the significance of the change of the molecular geometry and did not separate the segmental dipolar reorientation process from the whole dielectric relaxation.

In order to discuss the different tendencies of secondary alcohols and tertiary alcohols in further detail, we studied the dielectric properties of cyclohexanol derivatives which have less freedom of the segmental dipolar reorientation motion and of changing the molecular geometry than the linear molecules.

Experimental

2-Methylcyclohexanol. The trans isomer (Guaranteed reagent, Tokyo Kasei Co.) and the cis isomer synthesized according to the literature[5] were used to prepare the isomeric mixture. The commercial isomeric mixture (Extra pure reagent, 23% cis content by GC, Tokyo Kasei Co.) was also used.

3-Methylcyclohexanol. The commercial isomeric mixture (Extra pure reagent, 67% cis content by GC, Tokyo Kasei Co.) was used.

4-Methylcyclohexanol. The trans isomer (Analytical reagent, Aldrich Chemical Co.) and the cis isomer (Analytical reagent, Aldrich Chemical Co.) were used to prepare the isomeric mixture. The commercial isomeric mixture (Extra pure reagent, 37% cis content by GC, Tokyo Kasei Co.) was also used.

Purification. Dielectric measurments are sensitive to water as an inpurity, so that all these alcohols were dried by refluxing over calcium hydride before distillation. These purities were checked using a Hitachi GC-063 gas chromatograph with a thermal conductivity detecter and a stainless-steel column (1m long, 3mm diameter) packed with PEG 20M.

Dielectric Measurements. The measurements were carried out using a ratio-arm transformer bridge (TR-1C, Ando Electric Co.) and a glass cell with a platinum concentric electrode over a frequency range from 100 Hz to 3 MHz. Dipole measurements were carried out by the Halverstadt-Kumler method[6] in CCl_4 using another more precise ratio-arm transformer bridge (TR-10C, Ando Electric Co.). The accuracy of the temperature control was maintained within 0.1 K. All data regarding dielectric relaxation were analyzed with a least-square method.

Viscosity Measurement. Measurements were carried out with an Ostwald-type viscometer calibrated with the "standard liquid" (Cosmo Oil Co.). The accuracy of the temperature control was maintained within 0.1 K.

Results and Discussion

Static Dielectric Constants and the Association. The temperature dependences of static dielectric constants of 2-methylcyclohexanol and 4-methylcyclohexanol studied are shown in Fig. 1. There are linear correlations between the static dielectric constants and the reciprocal absolute temperature for the trans isomer of these two isomers, while small deviations from the linear correlation can be seen for the cis isomers. Such deviations have been frequently found in the neighborhood of the melting temperature. The melting temperature of a cis isomer is generally higher than that of the trans isomer.[7] The maximum point is found for *cis*-2-methylcyclohexanol, whose melting temperature is ca. 280 K.[8]

As is shown in Fig. 1, a very weak dependence of the dielectric constant on temperature was found for *cis*-2-methylcyclohexanol. This phenomenon is peculiar for the alcohols, i.e. associated molecules, though it is generally found for nonpolar molecules. Upon mixing one substance with an associated one, a correlation between the dielectric constant and its mole fraction maintains an experimentally linear relationship since the density is almost the same.[9] Figure 2 shows the change in the dielectric constants with the mixing ratio of the cis isomer and the trans isomer. x is the mole fraction of the cis isomer. A linear correlation was also found in a mixture of these two isomers. This fact shows that the cis isomer associates with the trans isomer and that such a self-association of these alcohols could also be confirmed by an IR spectroscopic study.

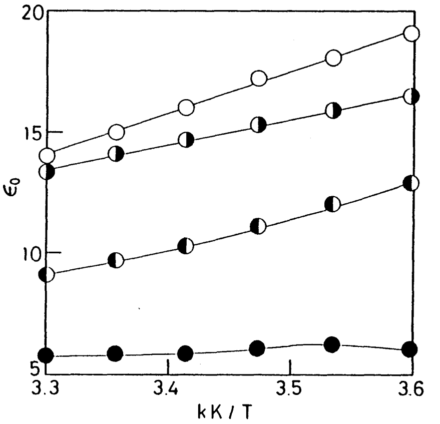

Fig. 1. Dielectric constants for some methylcyclohexanols as a function of T^{-1}. ○: *trans*-2-methyl, ○: *trans*-4-methyl, ○: *cis*-4-methyl, ●: *cis*-2-methyl.

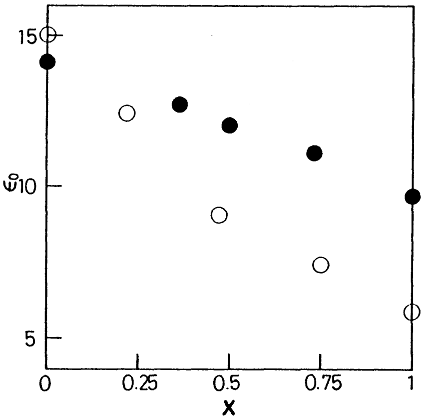

Fig. 2. Dielectric constants for some methylcyclohexanols as a function of x at 298 K. ○: 2-methyl, ●: 4-methyl.

The dielectric constant generally depends on the temperature, density and dipole moment. For associated molecules, however, an estimation of the orientational angle between the two neighboring dipoles is important for a determination of the dielectric constant. The Kirkwood theory for liquid dielectrics includes this correlation factor, g, which is used to evaluate the dipole-dipole correlation:[10]

$$g = 1 + z\langle\cos\theta\rangle = \frac{9kTV}{4\pi N\mu^2}\ \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \quad (1)$$

where z is the number of nearest-neighbor dipoles, θ the orientational angle between a dipole and its nearst neighbors, k the Boltzmann constant, T the absolute temperature, V the molar volume, N Avogadro's number, and μ the gas-phase dipole moment ε_0 and ε_∞ are, respectively, the static dielectric constant and the high-frequency limiting value of ε, and the bracket indicates the average over the ensemble. We used $\varepsilon_\infty = 1.1\, n_D^2$ according to Dannhauser and Bahe,[11] and μ in CCl_4 solution instead of that in gas phase. Since z is not known for almost all organic molecules, g was used to estimate and discuss the dipole-dipole correlation. It is difficult to estimate the degree of aggregation of dipoles from g, but it gives a criterion for cluster formation. The calculated experimental g is shown in Table 1.

The g of both trans isomers in this table is larger than unity, indicating a parallel alignment of these dipoles. This phenomenon is similar to that of primary alcohols, which generally form a linear chain multimer of various lengths. On the other hand, the g of these cis isomers does not have the same characteristic as that of their trans isomers. The g of *cis*-4-methylcyclohexanol is larger than unity, that is the same case of the trans isomer. The g of *cis*-2-methylcyclohexanol, however, is smaller than unity, which indicates the possibility that *cis*-2-methylcyclohexanol forms a cyclic multimer.

In order to discuss the steric hindrance for the association through the hydrogen bonding, we took the

Table 1. Dielectric Properties for Some Methylcyclohexanols at 298 K

Isomer	$d^{a)}$/g cm^{-3}	ε_0	n_D	μ/D$^{b)}$	g
cis-2-Methyl	0.93181	5.85	1.4608	1.88	0.75
trans-2-Methyl	0.92085	15.0	1.4589	1.74	2.91
cis-4-Methyl	0.9147	9.68	1.4578	1.76	1.73
trans-4-Methyl	0.9080	14.1	1.4535	1.85	2.46
Cyclohexanol$^{a)}$	0.9684	15.0	1.4684	1.86	2.10

a) From Ref. 25. b) 1 D=3.3356×10^{-30} C m.

role of the conformation of these methylcyclohexanols into account.

Cyclohexane skeletons have been well-studied in stereo chemistry. The structure of such a molecule can be roughly divided into the two types of conformations: a boat and a chair form. The latter conformation is more stable than the former one. Here, we consider only the chair conformation while discussing the dielectric properties of this alcohol since this form is predominant at room temperature. A substituent has two positions: axial and equatorial. The former position has an "1,3-diaxial" interaction, a large steric repulsion of a methyl substituent with the two axial hydrogen atoms on the same side of a cyclohexane skeleton. For this reason a large substituent prefers the equatorial position to the axial one.

There have been many conformational studies of these methylcyclohexanols.[12–14] The predominant position of the two substituents is determined as follows: The hydroxyl group has an axial position and the methyl group, which is larger than hydroxyl group, has an equatorial position for the cis isomer, while both these substituents have an equatorial position for the trans isomer. Therefore, the cis isomer, having an 1,3-diaxial interaction, can be said to have a larger steric hindrance for the association than the trans isomer. 2-Methyl isomer evidently has a larger steric hindrance for the hydroxyl group than the 4-methyl isomer, which is considered to have the absence of a direct steric hindrance.[7]

Alcohols with a strong steric hindrance have the tendency to form a cyclic dimer or trimer.[15,16] The position of the methyl group attached to the same or the neighboring carbon with the hydroxyl group has been reported to make the g smaller than unity for the case of secondary alcohols.[3,4] Therefore, the g of *cis*-2-methylcyclohexanol is smaller than unity. However, that of *cis*-4-methylcyclohexanol, having the 1,3-diaxial interaction as well as *cis*-2-methylcyclohexanol, is larger than unity. It can be, therefore, considered that the steric hindrance of the 1,3-diaxial interaction enlarges the average dipolar orientation angle, though this hindrance is not sufficient to form a cyclic multimer.

It is strange to say that the larger the number of carbon atoms for the homolog of the primary alcohol, the larger is g.[17] This suggests that the steric hindrance is favorable for making the g larger upon forming a linear multimer. This may be the reason why *trans*-2-methylcyclohexanol has a larger g than *trans*-4-methylcyclohexanol. It is interesting to see how strong the association is sterically hindered to form the cyclic multimer.

Dielectric Relaxation. The typical dielectric relaxation for the methylcyclohexanol investigated is shown in Fig. 3. In general, the dielectric relaxation for monohydric alcohol is reported as a Debye type, formulated in Eq. 2, while a dielectric relaxation for diol and triol is reported as a Davidson-Cole type, formulated in Eq. 3:

$$\varepsilon^* = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau_m} \tag{2}$$

and

$$\varepsilon^* = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau_m)^\beta} \tag{3}$$

where ε^* is the complex dielectric constant, ω the angular frequency, $\tau_m = (2\pi f_m)^{-1}$ the relaxation time, and β the Davidson-Cole parameter. The Davidson-Cole type is used in the following discussion because the standard deviation of the residual of the Davidson-Cole type is smaller than that of the Debye type with an analysis by the least-square method.

Fitted parameters are shown in Table 2. The β are nearly equal to unity, indicating a "Debye-like" behavior of the relaxation frequently reported for the

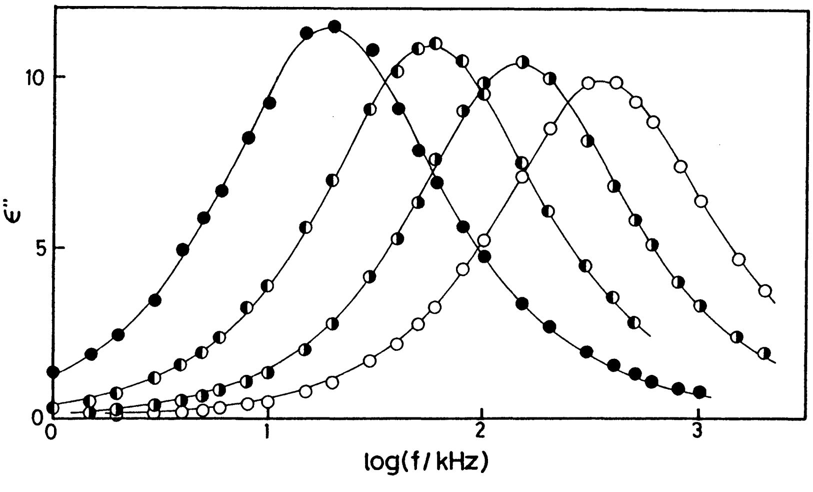

Fig. 3. Dielectric losses for 2-methylcyclohexanol (x=0.23) as a function of frequency. Circles show observed values and real lines are estimated by using observed values. ○: at 253 K, ○: at 248 K, ○: at 243 K, ●: at 238 K.

Table 2. The Davidson-Cole Parameters for Some Methylcyclohexanols

T/K	x	f_m/kHz	β	ε_0	ε_∞
		2-Methylcyclohexanol			
228	0.62	8.43	0.78	24.9	3.73
233	0.23	5.85	0.91	28.4	4.07
	0.62	28.9	0.80	22.8	3.10
238	0.23	17.4	0.89	27.3	3.30
	0.62	87.7	0.81	21.0	3.00
243	0.23	52.8	0.91	26.2	3.51
248	0.23	135	0.92	24.7	3.03
253	0.23	340	0.94	23.3	3.14
		4-Methylcyclohexanol			
228	0.36	25.9	0.85	24.8	2.83
	0.50	15.9	0.89	25.4	3.00
	0.73	19.9	0.80	24.7	3.37
233	0.36	46.3	0.90	24.0	3.04
	0.50	39.1	0.90	24.3	3.19
	0.73	50.6	0.83	23.5	3.16
238	0.36	104	0.91	23.0	3.08
	0.50	94.5	0.91	23.2	3.08
	0.73	121	0.86	22.2	3.31
243	0.36	213	0.90	22.1	2.86
	0.50	203	0.93	22.2	3.19
	0.73	262	0.86	21.1	3.22
248	0.36	428	0.91	21.2	2.80
	0.50	402	0.90	21.3	2.83
	0.73	502	0.82	20.1	2.86

monohydric alcohols. The relaxation time of 2-methylcyclohexanol is larger than that of the 4-methyl isomer, but the dependence of that on the fraction of the cis isomer cannot be estimated because of a lack of data points. Activation parameters of the dielectric relaxation process are shown in Table 3. The activation energy and the preexponential factor of 2-methylcyclohexanol are larger than those of 4-methyl isomers, although they depend on the fraction of the cis isomer. The spectral shape parameters,[19] m and n, are shown in Table 4. m is the index of "correlation of the intercluster exchange of relaxation motions," and n is that of "the intracluster correlation of relaxation motions." These parameters of all the methylcyclohexanol investigated are approximately the same regardless of the fraction of the cis isomer; this fact shows that the motion of an intercluster exchange of the dipole is almost free and that the motion of the dipole in its local environment couples weakly.

The Debye-like behavior for monohydric alcohols is explained on "the dipole relaxation of clusters of alcohol molecules hydrogen-bonded with each

Table 3. Dielectric and Viscous Activation Parameters for Some Methylcyclohexanols

Isomer	x	$\Delta E^{\neq}_{\varepsilon}$ / kJ mol^{-1}	A_ε / Hz	$\Delta E^{\neq}_{\eta}$ / kJ mol^{-1}	A_ε / Hz
2-Methyl	0.23	99.8	8×10^{26}	54.7	1×10^{14}
	0.62	106	9×10^{28}		
3-Methyl	0.67	67.2	5×10^{20}	40.9	6×10^{11}
4-Methyl	0.36	67.0	4×10^{20}	47.9	7×10^{12}
	0.50	76.3	3×10^{22}		
	0.73	76.3	4×10^{22}		
Cyclohexanol		55.0[a]	10^{18}[a]		
		49.2[b]	6×10^{16}[b]		

a) From Ref. 26. b) From Ref. 27.

Table 4. Spectral Shape Parameters with Standard Deviations of Residual for Some Methylcyclohexanols

Isomer	x	m	n
2-Methyl	0.23	1.04(0.07)	0.21(0.03)
	0.62	0.92(0.03)	0.31(0.04)
3-Methyl	0.67	0.99(0.02)	0.19(0.02)
4-Methyl	0.36	0.91(0.01)	0.25(0.02)
	0.50	0.97(0.02)	0.26(0.04)
	0.73	0.97(0.02)	0.29(0.03)
Cyclopentanol[a]		0.85	0.28
Cyclohexanol[a]		0.61	0.41

a) From Ref. 26.

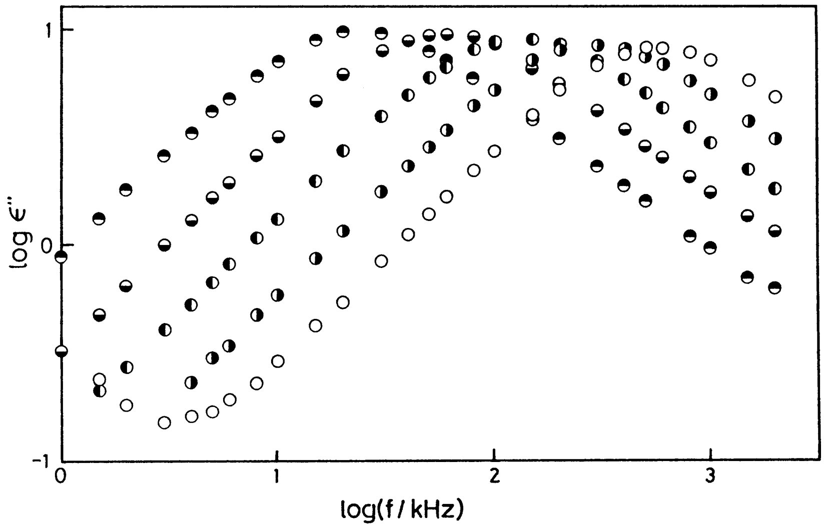

Fig. 4. Dielectric losses for 4-methylcyclohexanol (x=0.73) as a function of frequency. ○: at 248 K, ◑: at 243 K, ◐: at 238 K, ◒: at 233 K, ◓: at 228 K.

Table 5. Dielectric and Viscous Activation Energies for Some Alcohols

Alcohol	$\Delta E_{\varepsilon}^{\neq}$ / kJ mol^{-1}	Ref.	$\Delta E_{\eta}^{\neq}$ / kJ mol^{-1}	Ref.
1-Propanol	23.0	21	18.5	22
1-Pentanol	34.2	4	20.9	23
2-Methyl-2-butanol	52.1	4	30.5	23
1-Octanol	36.8	21		
2-Octanol	56.6	24		
3-Octanol	71.2	24		
5-Methyl-3-heptanol	82.1	24		
6-Methyl-3-heptanol	79.7	24		

other."[20] The relaxation time of primary alcohols can be evaluated by Bertolini et al. using the hydrogen bond lifetime and the probability that the bond is randomly intact.[4] The relaxation time of secondary alcohols and tertiary alcohols, however, could not be evaluated; this suggests an additional intramolecular relaxation of dipoles with the intermolecular one.

Secondary and tertiary alcohols have the same tendencies for the dielectric relaxation in that the activation energy and the preexponential factor are larger than primary alcohols having the same number of carbon atoms, as shown in Table 5. At first glance, the activation energy and the preexponential factor become larger with the increasing size of the alkyl group and the increasing degree of branching. Our results in Table 3 are similar to this tendency with respect to the point of the degree of the branching. The large activation energy cannot be attributed to the additional intramolecular relaxation because the activation entropy of the relaxation of these methylcyclohexanols, ca. 400—500 J mol^{-1} K^{-1}, is too large for such an additional intramolecular relaxation motion of the dipole. There seems to be another reason for the large activation energy.

Crossely et al. found a large Eyring activation enthalpy, ca. 60—100 kJ mol^{-1} for the dielectric relaxation of some simple hydrocarbons at temperatures just above their glass temperatures, T_g.[28] They concluded that this phenomenon resulted from a dipolar cooperative reorientation in the amorphous clusters and that the activation enthalpy reflected the ability of the molecules to interact. However, the activation enthalpy of methylcyclohexane in their work is almost equal to that of 3- and 4-methylcyclohexanol which clearly have a larger interaction than methylcyclohexane.

The dielectric relaxation process, which can be regarded as a molecular rotation process, is often discussed in contrast with viscosity or a shear process. The activation energies of the shear process are also listed in Table 3. The dependence on the fraction of the cis isomer cannot be evaluated due to the small quantity to be measured. The difference between the dielectric activation energy and the viscous activation energy of 2-methylcyclohexanol is larger than that of 3- or 4-methyl isomer. The difference between the two activation energies may be explained by the difference of hydrogen-bond breaking and reforming mechanisms between rotation and translation. From this point of view, the larger activation energy and the longer relaxaton time of 2-methylcyclohexanol are attributed to the steric effect of the neighboring methyl group for the hydrogen bond as well as the association.

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