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Dielectric Relaxation and Intermolecular Association of Alicyclic Alcohols in Liquid and Solid States

Toshiomi SHINOMIYA†
School of Pharmaceutical Sciences, Kitasato University,
5-9-1, Shirokane, Minato-ku, Tokyo 108
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The dielectric constants and losses of cyclopentanol (**CPEN**), cyclohexanol (**CHEX**), cycloheptanol (**CHEP**), and cyclooctanol (**COCT**) have been measured at frequencies from 1.35 to 4500 MHz over a temperature range of 10—35 °C. The absorption could be resolved into three Debye-like dispersion regions in liquid and solid states. The relaxation time of the first, low-frequency, dispersion region and viscosity for **CHEX** are slightly larger than those for **CHEP**. This observation can be connected with differences of the molecular geometry between a chair and a twisted chair form and an interconversion between an equatorial and an axial form. Upon solidification, the magnitude of the first dispersion region decreases from 12.67 in the liquid state to 10.25 in the solid state for **CHEX** and increases from 8.77 to 9.35 for **COCT**. A transformation from a linear chain polymer into a nonpolar cyclic polymer for **CHEX** and from a linear chain polymer into a chain dimer and trimer for **COCT**, occurs mainly upon solidification. The free energies of activation in the solid state are 26 kJ mol^{-1} for the first region, 23 kJ mol^{-1} for the second region, and 17 kJ mol^{-1} for the third region and are larger than those in the liquid state, respectively.

Upon solidification, in general, the equilibrium dielectric constant decreases abruptly to a value arising from induced polarization for polar liquids, such as nitrobenzene,[1] some ketones,[2] and higher alkanols.[2,3] If polar groups are fixed randomly in the solid state upon solidification, the dipoles in the molecules cannot be oriented by an external applied field. Therefore, the contribution of the dipoles to the dielectric constant becomes very small or zero as an average value. However, there are many compounds, such as some benzene derivatives,[4] ice,[5] and cyclohexanol,[6] whose dielectric constant does not decrease upon solidification. It is considered that the orientation of the dipoles can occur even in the solid state for these compounds, although the molecules cannot perform a translational motion. This information has been obtained from temperature dependence of the complex dielectric constants at low frequencies. There have been almost no reports on the Cole-Cole plot in the solid state. For alicyclic alcohols, moreover, different values of the thermodynamic parameters have been obtained by different methods.[6,7]

We are studying hydrogen bondings and intermolecular association in liquid alcohols.[8—11] The coexistence of three dispersion regions has been found through wide-frequency measurements of dielectric constants and losses for the liquid state of primary, secondary, and tertiary alcohols. The three dispersion regions have been assigned to a linear chain polymer, a chain dimer and trimer, and a free monomer. The concentrations of these three species and a nonpolar cyclic polymer were evaluated by means of a modified Kirkwood-Fröhlich equation by making use of the Kirkwood correlation factor and the limiting low- and high-frequency dielectric constants for each dispersion. The existence of a nonpolar cyclic polymer was proved by adding 1-butanol to the more hindered octanol isomers. It is the purpose of the present work to investigate the dielectric relaxation processes of alicyclic alcohols and to compare a composition of a monomer and three associated species in the liquid and solid states for **CHEX** and **COCT**.

Experimental

Purification of Materials. The alicyclic alcohols were fractionally distilled twice under reduced pressure at a high reflux ratio.[8] The middle portion was dried with a Molecular Sieve 4A, and water removed by reflux under reduced pressure in a grease-free apparatus during about 3 hours, and distilled before use. The melting points are 25.3 °C for **CHEX** and 20.5 °C for **COCT**. These temperatures are slightly lower than 26.1 °C for **CHEX** measured by Adachi et al.[6] and 22 °C for **COCT** measured by Shablakh et al.,[7] respectively.

Apparatus. The dielectric constants and losses were measured using three types of apparatus over a frequency range of 1.35—4500 MHz, as described in a previous paper.[8]

The refractive indices were measured using 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 dielectric constants (ε') and losses (ε'') for alicyclic alcohols are shown in Fig. 1 as a function of frequency. The limiting low-frequency dielectric constants (ε_0) are 16.81, 16.19 (at 27 °C), 13.60, and 11.77 at 25 °C for **CPEN**, **CHEX**, **CHEP**, and **COCT**, respectively. The ε' decreases from the ε_0 to about 2.7 with increasing frequency. On the other hand, the ε'' increases with increasing frequency. It reaches a maximum and then decreases with increasing frequency. By assuming that the absorption was the

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† Present address: 207-52, Shirahata kami-cho, Kanagawa-ku, Yokohama 221.

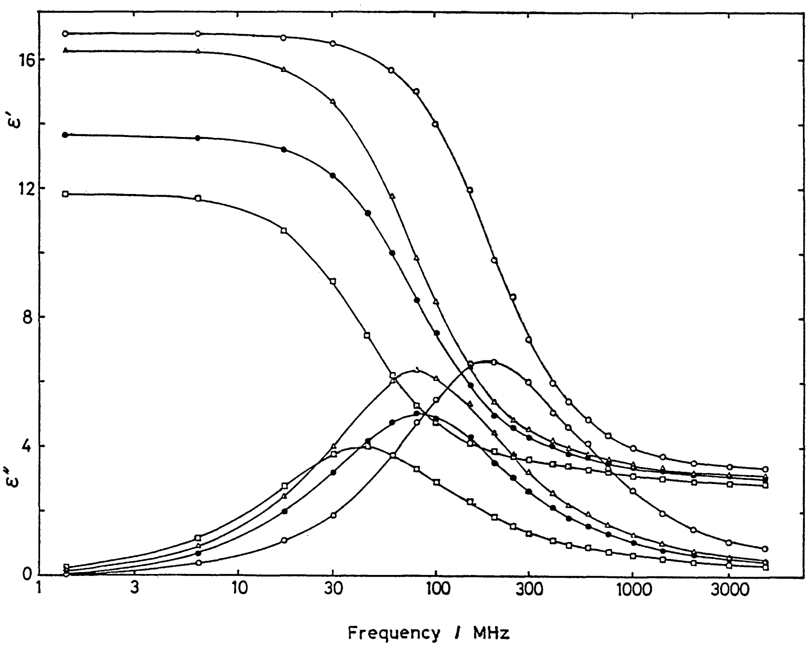

Fig. 1. Dielectric constant ε' and loss ε'' as a function of frequency at 25 °C (**CHEX** at 27 °C)
○: **CPEN**, △: **CHEX**, ●: **CHEP**, □: **COCT**.

Table 1. Dielectric Parameters, Refractive Indices, Densities, and Viscosities for Four Alicyclic Alcohols

t	Dielectric constant				Relaxation time			n_D	d	$\eta \times 10^3$
°C	ε_0	ε_1	ε_2	ε_3	τ_1 / ps	τ_2 / ps	τ_3 / ps		g cm^{-3}	N s m^{-2}
					Cyclopentanol					
15	18.38	3.60	3.29	2.65	1421	113	15.0	1.4556	0.9512	16.0
25	16.81	3.58	3.31	2.66	820	105	14.3	1.4516	0.9428	10.4
35	15.44	3.51	—	—	488	—	—	1.4478	0.9349	6.7
					Cyclohexanol					
10[a)]	16.94	4.71	3.58	2.99	10340	2471	175	—	—	—
15[a)]	16.36	4.75	3.61	3.00	7689	1823	161	—	—	—
20[a)]	15.75	4.90	3.67	3.02	5939	1447	155	—	—	—
27	16.19	3.75	3.18	2.65	1987	1684	15.0	1.4648	0.9435	53.3
30	15.84	3.75	3.20	2.64	1677	1530	14.7	1.4627	0.9412	43.4
35	15.21	3.83	—	—	1243	—	—	1.4608	0.9377	32.4
					Cycloheptanol					
15	15.08	3.63	3.06	2.65	3882	218	19.2	1.4799	0.9622	105
25	13.60	3.72	3.13	2.62	1997	189	16.4	1.4759	0.9547	53.6
35	12.30	3.90	3.35	2.86	1068	190	—	1.4720	0.9471	29.7
					Cyclooctanol					
10[a)]	15.10	5.14	3.27	2.76	24260	5253	171	—	—	—
15[a)]	14.70	5.11	3.30	2.82	17040	3337	162	—	—	—
18[a)]	14.39	4.89	3.34	2.79	12840	2248	133	—	—	—
19[a)]	14.36	4.78	3.36	2.81	11530	2002	135	—	—	—
20[a)]	14.24	4.89	3.37	2.82	10750	2025	141	—	—	—
20	12.40	3.63	3.09	2.70	5184	384	56.2	—	—	—
21	12.23	3.67	3.09	2.72	4823	396	55.5	—	—	—
22	12.11	3.75	3.17	2.73	4509	464	65.5	1.4863	0.9651	189
23	12.04	3.81	3.12	2.76	4313	410	57.9	—	—	—
25	11.77	3.77	3.08	2.67	3835	267	27.0	1.4851	0.9628	149
30	11.08	3.84	3.10	2.65	2514	297	29.5	1.4830	0.9587	100
35	10.59	3.94	—	—	2062	—	—	1.4809	0.9549	70

a) The data were measured in the solid state.

sum of several overlapping Debye-like dispersion regions as described for linear alcohols,[8,9] experimental data in the liquid and solid states were resolved into three dispersion regions using a least-squares method. The dielectric parameters calculated are given in Table 1, together with the refractive indices, densities, and viscosities.

Relaxation Time and Viscosity in the Liquid State. Table 1 shows that three relaxation times (τ_{1-3}) of **CPEN**, **CHEX**, **CHEP**, and **COCT** are much longer than those of normal alcohols from pentyl through octyl, respectively.[8,12] The viscosities (η) of the former are also larger than those of the latter. It is considered that these observations can be attributed to a difference of the molecular geometry between the alicyclic and normal alcohols. For alicyclic alcohols, the relaxation time (τ_1) of the first dispersion region are shown in Fig. 2 as a function of the molecular volume, together with η of the liquid. It is noticeable that both τ_1 and η of **CHEX** are slightly larger than those of **CHEP**, as shown in Fig. 2, although the molecular volume (106 cm^{3}mol^{-1}) of **CHEX** is less than that (120 cm^{3}mol^{-1}) of **CHEP**. For normal alcohols from propyl through decyl,[8,12] it is known that both τ_1 and η increase linearly with increasing molecular volume at room temperature. If it is assumed that both τ_1 and η increase with increasing molecular volume, the apparent molecular volume of **CHEX** must be slightly larger than that of **CHEP** in the dielectric relaxation and viscosity. As described by Shablakh et al.,[7] **CHEX** in the liquid state exists in about 73% of the equatorial chair in dynamic equilibrium with the axial chair. **CHEP** has probably a composition of 91% equatorial twisted chair, 8% axial twisted chair, and 1% twisted boat. More of **CHEX** exists in the axial form than **CHEP** and, therefore, an interconversion between the equatorial and axial forms occurs more extensively for **CHEX** than for **CHEP**. To exist in 91% equatorial twisted chair, **CHEP** has a flatter structure than **CHEX**. It is considered that the apparent molecular volume of **CHEP** is slightly less than that of **CHEX** because of the twisted skeleton and less interconversion.

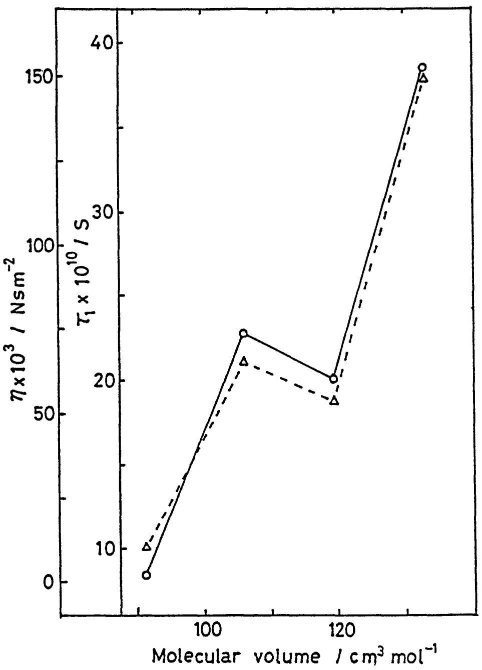

Fig. 2. Relaxation time τ_1 and viscosity η as a function of molecular volume for **CPEN**, **CHEX**, **CHEP**, and **COCT** at 25 °C.

The thermodynamic parameters, the free energy of activation $\Delta F^{\neq}$, the heat of activation $\Delta H^{\neq}$, and the entropy of activation $\Delta S^{\neq}$, were calculated by means of Eyring equations[8,13] from temperature dependences of the τ_{1-3} and η, and are given in Table 2. $\Delta F_{\tau}^{\neq}$ and $\Delta F_{\eta}^{\neq}$ for **CHEX** also are nearly equal to those for **CHEP**. These values are larger than those of **CPEN** and less than those of **COCT**.

Comparison of CHEX and COCT in the Liquid and Solid States. The Cole-Cole plots are shown in Fig. 3 for **CHEX** and in Fig. 4 for **COCT** to indicate a comparison of the dielectric dispersion between in the liquid and solid states. The Cole-Cole plots show that experimental data at higher frequencies could not be explained by a Davidson-Cole skewed arc, $\varepsilon^{*}-\varepsilon_{\infty}$

Table 2. Thermodynamic Parameters of the Three Dispersion Regions and the Viscous Flow in the Liquid State at Room Temperature

Compound	Three dispersion region and viscous flow											
	$\Delta F_{\tau 1}^{\neq}$[a)]	$\Delta H_{\tau 1}^{\neq}$	$\Delta S_{\tau 1}^{\neq}$	$\Delta F_{\tau 2}^{\neq}$[a)]	$\Delta H_{\tau 2}^{\neq}$	$\Delta S_{\tau 2}^{\neq}$	$\Delta F_{\tau 3}^{\neq}$[a)]	$\Delta H_{\tau 3}^{\neq}$	$\Delta S_{\tau 3}^{\neq}$	$\Delta F_{\eta}^{\neq}$[a)]	$\Delta H_{\eta}^{\neq}$	$\Delta S_{\eta}^{\neq}$
	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{JK}^{-1}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{JK}^{-1}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{JK}^{-1}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{kJ}}{\text{mol}}$	$\frac{\text{JK}^{-1}}{\text{mol}}$
Cyclopentanol	21.2	37.2	53.7	16.1	2.47	−45.6	11	1.1	−34	19.3	31.2	40.0
Cyclohexanol	23.7	42.8	64.2	17.4	21.9	15.2	11	3.4	−26	24.0	47.2	77.8
Cycloheptanol	23.4	45.2	73.1	17.6	2.73	−50.0	11	9.1	−7.8	24.1	46.1	74.1
Cyclooctanol	24.9	45.5	69.2	19.0	27.1	27.1	14	60	155	26.8	56.9	101

a) The values were calculated at 298 K.

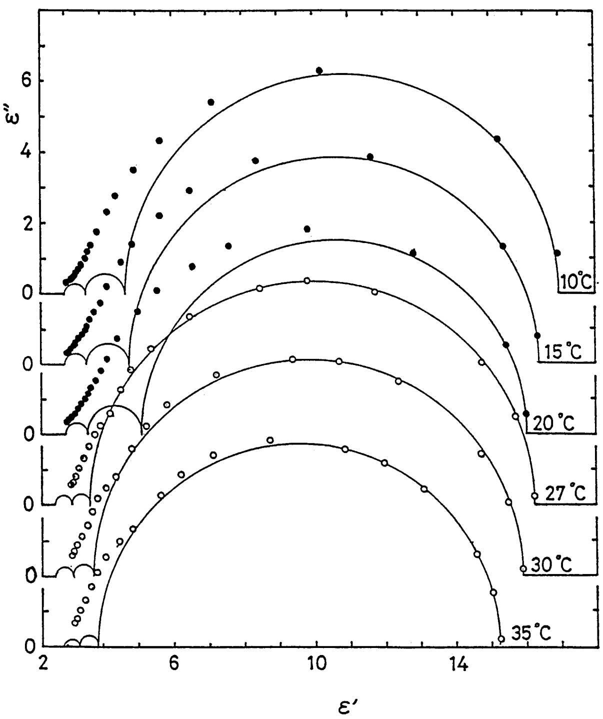

Fig. 3. Cole-Cole plots for **CHEX** at various temperatures. For clarity, the plots have been displaced along the ordinate. Three Debye-like dispersion regions calculated are shown as a solid line. ●: Data points in solid state at 10, 15, and 20 °C. ○: Data points in liquid state at 27, 30, and 35 °C.

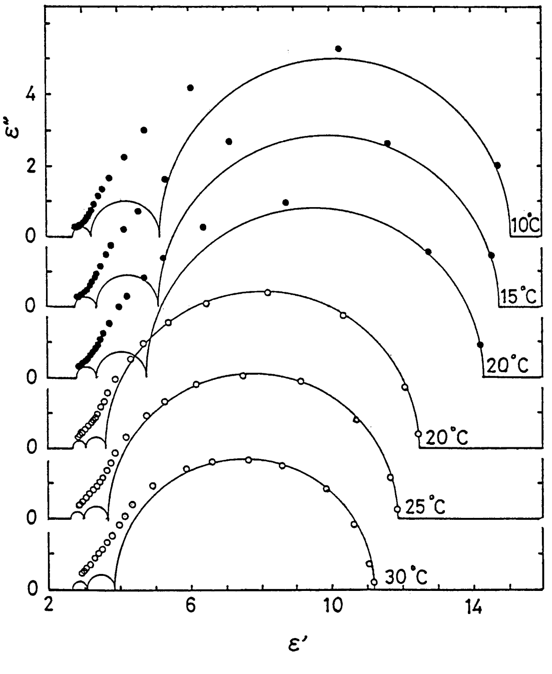

Fig. 4. Cole-Cole plots for **COCT** at various temperatures. For clarity, the plots have been displaced along the ordinate. Three Debye-like dispersion regions calculated are shown as a solid line. ●: Data points in solid state at 10, 15, and 20 °C. ○: Data points in liquid state at 20, 25, and 30 °C.

$=(\varepsilon_0-\varepsilon_\infty)/(1+i\omega\tau)^\alpha$, or a Cole-Cole depressed-center semicircular arc, $\varepsilon^*-\varepsilon_\infty=(\varepsilon_0-\varepsilon_\infty)/(1+(i\omega\tau)^\beta)$. It is considered that the absorption for alicyclic alcohols could be best explained by several overlapping Debye-like semicircular arcs, $\varepsilon^*-\varepsilon_\infty=(\varepsilon_0-\varepsilon_\infty)/(1+i\omega\tau)$, as described for linear alcohols.[8,9] 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 $\beta <1$. The absorptions in the liquid and solid states could be resolved into three dispersion regions as shown by solid lines in Figs. 4 and 5. It is obvious that the orientation of the dipoles takes place in the solid state below the melting point on application of an external field.

The magnitude($\varepsilon_{i-1}-\varepsilon_i$) for i-th dispersion change discontinuously at a melting point. For **CHEX** at a melting point, the ε_0 obtained by extrapolation decreases from 16.42 in the liquid state to 15.45 in the solid state. The magnitude of the first dispersion region also decreases from 12.67 to 10.25. For **COCT** at a melting point, however, the ε_0 increases from 12.40 in the liquid state to 14.24 in the solid state. The magnitude of the first region also increases from 8.77 to 9.35. This observation for **COCT** is contrary to the results for **CHEX**. The different results between **CHEX** and **COCT** must be due to the difference of formation of the hydrogen-bonded species upon solidification. For the second and third regions in both **CHEX** and **COCT**, the magnitudes in the solid state are larger than those in the liquid state, respectively. Notably, the increase in magnitude for the second region is a remarkable feature in the solid state.

As described in a previous paper,[9] we have reported that the first dispersion region can be attributed to a linear chain polymer ($n\geqq4$), the second region to a chain dimer and trimer ($n=2$ and 3), and the third region to a free monomer ($n=1$). Four concentrations of 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 by making use of the Kirkwood correlation factor and the experimental values of ε_{i-1} and ε_i for the i-th dispersion.[8,9] The percentages of C_1, C_2, C_3, and C_R against the gross stoichiometric concentration C_0($C_0=d\times10^3/M$), $C_i\times 100/C_0$, are shown in Fig. 5 as a function of temperature, where d is the density and M the molecular weight. For **CHEX** at a melting point, the percentage of C_1 decreases from 66% in the liquid state to 39% in the solid state. The percentages of C_R, C_3, and C_2 increase from 16, 13, and 6% in the liquid state to 38, 14, and 9% in the solid state, respectively. These changes of the percentages of C_i show that a transformation of a linear chain polymer into a nonpolar cyclic polymer mainly occurs, when **CHEX** is frozen. For **COCT** at a melting point, on the other hand, the

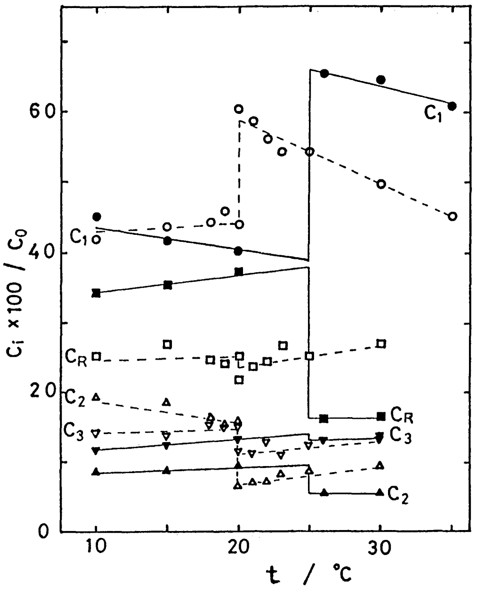

Fig. 5. Concentrations (C_i×100/C_0) for **CHEX** and **COCT** as a function of temperature. **CHEX** are shown by solid lines.
●: a linear chain polymer (C_1), ■: a nonpolar cyclic polymer (C_R), ▲: a dimer and trimer (C_2), ▼: a free monomer (C_3). **COCT** are shown by dotted lines.
○: a linear chain polymer (C_1), □: a nonpolar cyclic polymer (C_R), △: a dimer and trimer (C_2), ▽: a free monomer (C_3).

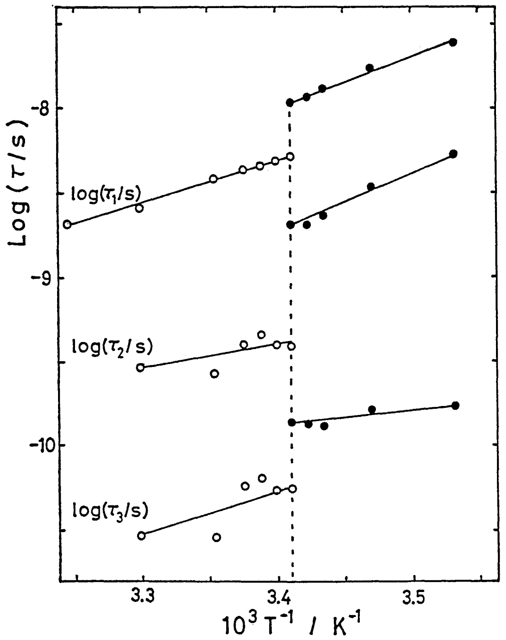

Fig. 6. Logarithm of the three relaxation times, $\log(\tau/s)$, for **COCT** as a function of reciprocal absolute temperature.
●: Experimental data in solid state. ○: Experimental data in liquid state.

percentage of C_1 decreases from 59% in the liquid state to 44% in the solid state in spite of the increase in the magnitude of the first region. The percentages of C_R, C_3, and C_2 increase from 22, 12, and 7% in the liquid state to 25, 15, and 16% in the solid state, respectively. Therefore, a transformation of a linear chain polymer into a chain dimer and trimer mainly occurs, when **COCT** is frozen. The density in the liquid at a melting point was used as those in the solid state. In both **CHEX** and **COCT**, C_1 decreases and C_R, C_3, and C_2 increase, respectively. The different results between **CHEX** and **COCT** for the ε_0 or for the magnitude of the first region can be connected with changes of the percentages of C_i. When **CHEX** and **COCT** are frozen, a nonpolar cyclic polymer increases mainly for **CHEX**, although a chain dimer and trimer increases for **COCT**. It is interesting to investigate the increase in ε_i of the i-th dispersion region in the solid state. ε_3 at 20 °C is about 3.0 for **CHEX**. Information concerning the magnitude of $\varepsilon_3-n_D^2$ could not be obtained and must await further accuracy measurements at higher frequencies.

The three relaxation times also indicate the discontinuity at a melting point, as shown in Fig. 6 for **COCT**. The orientation of dipoles can occur slowly in the solid state because of the increase in hindrance. Adachi et al.[6] reported a relaxation in a supercooled crystal I of **CHEX**. The characteristic frequencies of the relaxation are about 300 kHz at 226 K, 30 kHz at 210 K, 3 kHz at 192 K, and 300 Hz at 177 K. The relaxation frequencies of the first dispersion region in the present work are on the extension of the straight line of $\log(\tau_1/s)$ vs. $(1/T)$, where T is the absolute temperature. The peak corresponding to the second or third dispersion could not be found in their loss peak diagram. Even in the solid state, **CHEX** and

Table 3. Thermodynamic Parameters of the Three Dispersion Regions for **CHEX** and **COCT** in the Liquid and Solid States

	$\Delta F_{\tau 1}^{\neq}$ a)	$\Delta H_{\tau 1}^{\neq}$	$\Delta S_{\tau 1}^{\neq}$	$\Delta F_{\tau 2}^{\neq}$ a)	$\Delta H_{\tau 2}^{\neq}$	$\Delta S_{\tau 2}^{\neq}$	$\Delta F_{\tau 3}^{\neq}$ a)	$\Delta H_{\tau 3}^{\neq}$	$\Delta S_{\tau 3}^{\neq}$
	kJ mol^{-1}	kJ mol^{-1}	J K^{-1}mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J K^{-1}mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J K^{-1}mol^{-1}
Cyclohexanol									
Liquid	24.0	42.8	64.2	17.4	21.9	15.2	11	3.4	−26
Solid	25.6	35.6	34.2	22.1	34.7	43.0	17	6.3	−35
Cyclooctanol									
Liquid	25.2	45.5	69.2	19.2	27.1	27.1	14	60	155
Solid	27.1	54.5	93.6	23.0	68.1	154	17	15	−6

a) The values were calculated at 293 K.

COCT have a composition of 42% (as an average value) of a linear chain polymer and 31% of a nonpolar cyclic polymer against the gross concentration. It is, therefore, concluded that the hydroxyl group in **CHEX** and **COCT** can be oriented by an external applied field and that the molecules can associate into the hydrogen-bonded species even in the solid state.

The thermodynamic parameters, $\Delta F_\tau^{\neq}$, $\Delta H_\tau^{\neq}$, and $\Delta S_\tau^{\neq}$, are shown in Table 3 to compare the values in the liquid and solid states. $\Delta F_\tau^{\neq}$ at 20 °C for **CHEX** in the liquid state was evaluated by an extrapolation. For three relaxation times of **CHEX** and **COCT**, $\Delta F_\tau^{\neq}$ in the solid state is larger than that in the liquid state, respectively. The difference of $\Delta F_\tau^{\neq}$ between in the liquid and solid states is about 2 kJ mol^{-1} for the first region and about 4 kJ mol^{-1} for the second and third regions.

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