

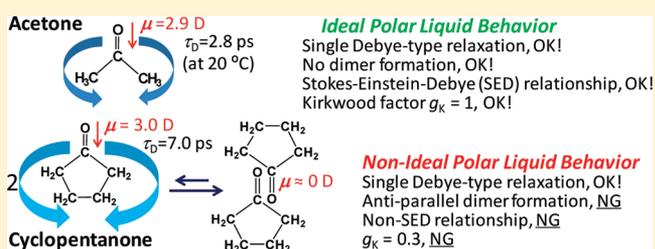
Dielectric Behavior of Some Small Ketones as Ideal Polar Molecules

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ABSTRACT: The dielectric behaviors of some small symmetric ketone molecules, including acetone, 3-pentanone, cyclopentanone, 4-heptanone, and cyclohexanone, were investigated as a function of temperature (T) over a wide frequency range from 50 MHz ($3.14 \times 10^8 \text{ s}^{-1}$, in angular frequency) to 3 THz ($1.88 \times 10^{13} \text{ s}^{-1}$). The temperature dependencies of the rotational diffusion times (τ_r) determined using ^{17}O NMR spin–lattice relaxation time (T_1) measurements and viscosities of the ketones were also examined. The

obtained temperature dependencies of the parameters for the ketones were compared with those of ideal polar molecules, which obey the Stokes–Einstein–Debye (SED) relationship without the formation of intermolecular dimeric associations and without orientational correlations between dipoles (molecular axes), that is, free rotation. Kirkwood correlation factors (g_K) of only acetone and 3-pentanone were close to unity over a wide temperature range, whereas those of other ketones were obviously less than unity. These results revealed that no correlations exist between the rotational motions of dipoles in acetone and 3-pentanone, as expected in ideal polar molecules. However, other ketones exhibited orientational correlations in their dipoles because of dipole–dipole interactions via antiparallel configurations. Furthermore, because acetone and 3-pentanone satisfied the SED relationship and because their microscopic dielectric relaxation times (τ_μ), which were calculated from the determined dielectric relaxation times (τ_D) via the relationship $\tau_\mu = \tau_D g_K^{-1}$, were identical to $3\tau_r$ and were proportional to $V\eta(k_B T)^{-1}$ over the wide temperature range examined, where V , k_B , and η represent the effective molecular volume, Boltzmann's constant, and the viscosity of the liquid molecules, respectively, these two ketone molecules behave as ideal polar molecules. In addition, other ketones not significantly larger than acetone and 3-pentanone in molecular size likely form dimeric intermolecular associations with antiparallel cyclic configurations, which demonstrates the g_K values less than unity.



■ INTRODUCTION

This year (2012) is the 100th anniversary of the publication of Debye's famous paper, in which he proposed the presence of permanent dipoles in molecules because of anisotropic distribution of electric charges. Debye's model is capable of explaining the additional relatively large, temperature-dependent electric susceptibilities that have been observed in many polar materials at lower frequencies.¹ Debye also first proposed a theoretical microscopic dielectric model. He assumed a molecule possessing a permanent dipole moment rotates freely and feels friction due to viscosities caused by the surrounding other molecules; this model describes the dielectric relaxation behavior of polar molecules in the pure liquid state.² This Debye relaxation model has only one set of a relaxation time and strength. However, the Debye relaxation model has been used as an elementary, basic model for the analysis of the dielectric relaxation phenomena for all the dielectric materials, even if a material has complicated dielectric characteristics not shown with a single relaxation time. In general, a summation of Debye relaxation models bearing a necessary number of relaxation times and strengths is able to describe any kind of complicated dielectric behavior.^{3,4} The application of Debye's polar molecule model to real polar materials in the pure liquid state requires an explicit expression that relates the applied external electric field to the local electric field felt by a polar molecule. Onsager⁵ has proposed a formula that connects the

external and local electric fields; this formula is useful for polar media that consist of polar molecules and is significantly more general than a fundamental formula proposed by Lorentz,⁶ which is useful only for nonpolar media. Kirkwood^{7,8} and Fröhlich^{3,4} modified the formulas proposed by Debye and Onsager, and obtained a general expression for polar molecules in the pure liquid state that relates a (relative) static electric permittivity, ϵ_0 , and the square of the dipole moment (μ^2) of a constituent molecule in the isolated state as follows:

$$\epsilon_0 - \epsilon_{\infty a} = \frac{\epsilon_0(\epsilon_{\infty a} + 2)^2 c N_A \mu^2 g_K}{9(2\epsilon_0 + \epsilon_{\infty a}) \epsilon_v k_B T} \quad (1)$$

where $\epsilon_{\infty a}$, c , N_A , g_K , ϵ_v , and $k_B T$ represent the apparent limiting electric permittivity observed at a high frequency limit, the molar concentration of molecules in units of $\text{mol}\cdot\text{cm}^{-3}$, Avogadro's number, the Kirkwood correlation factor, the electric permittivity in a vacuum, and the product of the Boltzmann constant and absolute temperature, respectively. The Kirkwood correlation factor,^{7,8} g_K , provides a measure of the orientational correlation between the dipoles of each constituent molecule. When the observed g_K is unity, molecules rotate freely without any intermolecular orientational correla-

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tion. Under a condition of $g_K > 1$, molecules possess dipolar orientational correlation in a parallel fashion, whereas they exhibit antiparallel-type orientational correlation when $g_K < 1$.

The combination of the Debye relaxation model and the expression of the static electric permittivity for polar molecular liquids given by eq 1 leads to the idea that simple polar molecules obey the Debye relaxation (DR) behavior with only one set of a relaxation time (τ_D) and strength governed by eq 1. However, the determined Debye dielectric relaxation time, τ_D , should be carefully handled because τ_D is a macroscopic relaxation time for the total dipole moment, which can be converted into a microscopic dipole relaxation time (τ_μ) defined at a single molecular level via some proposed theoretical equations.^{10,11} In particular, the observed dielectric relaxation time, τ_D , or τ_μ should be controlled by the viscosity of the liquid and temperature because polar molecules with a g_K value of unity show free rotation and experience friction controlled by the Stokes–Einstein–Debye (SED) relationship. Here, we refer to such polar molecules that satisfy these three criteria of single DR behavior, $g_K = 1$, and an SED relationship as *ideal polar molecules*. In this study, we investigated the dielectric behavior of some small, symmetric ketones in the pure liquid state at several temperatures and compared the dielectric behavior of the ketones with that of ideal polar molecules. The presence of ideal polar molecules is discussed not only as a conceptual model for theoretical discussion but also in practice. The reasons for dielectric behavior as nonideal polar molecules observed in some ketones are also considered.

Acetone (dimethylketone: Ac) is a typical polar, aprotic molecule that possesses a relatively large dipole moment of about 2.9 D¹² and is widely used as a solvent in many types of chemical reactions that require a solvent of relatively high polarity. Although Ancian et al.^{13,14} claimed some decades ago that Ac forms intermolecular dimeric associations on the basis of the results obtained from ¹⁷O nuclear magnetic resonance (NMR) measurements, their hypothesis has not been widely accepted. Acetone is therefore an excellent candidate as an ideal polar molecule. In the 1950s, Calderwood et al.¹⁵ reported the dielectric behavior of Ac in the pure liquid state over a relatively wide temperature range. They evaluated the magnitude of the dipole moment to be 3.06 ± 0.02 D under the assumptions that $g_K = 1$ and $\epsilon_{\infty a} \sim 1.05n^2$, where n is the refractive index of Ac (ca. 1.359). Because the validity of the assumptions used in their study was not clear, we decided to reconsider the dielectric behavior of Ac using contemporary experimental techniques over a wide frequency range up to 3 THz.

Infrared (IR) absorption and Raman scattering (RS) have been used to investigate the structures of ketones in relation to the formation of intermolecular dimeric associations in the pure liquid state and in solution. IR and RS signals at a wavenumber (or Raman shift) of approximately 1700 cm⁻¹ are assigned to a characteristic vibration band of carbonyl, C=O, stretching. Vaz et al.^{16–18} clearly confirmed that the self-association of some small cyclic ketones, such as cyclopentanone (cP) and cyclohexanone (cH) in the pure liquid state and in tetrachloromethane (CCl₄) solution. They concluded that the self-association of the ketones is limited to the formation of intermolecular dimeric associations. These dimers have a few types of antiparallel (C=O group) cyclic configurations with dipole–dipole intermolecular interactions between the C=O groups sustained by hydrogen bonding between the molecules in the form of C=O⋯H–C in accordance with the results obtained via ab initio quantum chemical calculations. Although

all of the antiparallel cyclic configurations reduce the total dipoles to values less than the summation of the two dipole moments of the constituent C=O groups, one antiparallel cyclic configuration has no total dipole moment because of the completely opposite configuration of the two C=O groups. The dielectric behavior of the small cyclic ketones cP and cH is therefore not identical to that of ideal polar molecules because of the formation of intermolecular dimeric associations. These two cyclic ketones will clearly demonstrate how nonideal dipolar compounds exhibit behavior different from that of ideal polar molecules with respect to their Kirkwood parameters, g_K , the distribution of dielectric relaxation times, and also activation energies of their dielectric relaxation times, rotational relaxation times, and viscosities.

The presence of ideal polar molecules based on Debye's ideas^{1–8} is therefore confirmed experimentally in real compounds 100 years after the publication of his ideas.

EXPERIMENTAL SECTION

Materials. Highly purified acetone, Ac, (purity >99.8%), 4-heptanone (4H) (>98%), and cyclopentanone, cP, (>95%) were purchased from Wako Pure Chemical Industries (Osaka) and were used without any further purification. High-purity 3-pentanone (3P) (>99%) and cyclohexanone, cH, (99.8%) were purchased from Sigma-Aldrich (St. Louis) and were also used without further purification.

Methods. A dielectric-probe kit (8507E, Agilent Technologies, Santa Clara) equipped with a PNA-L network analyzer (N5230C, Agilent Technologies) and a 50 GHz performance probe was employed to measure the real and imaginary parts (ϵ' and ϵ'') of the relative electric permittivity over a frequency, ν , range from 50 MHz to 50 GHz (3.14×10^8 to 3.14×10^{11} s⁻¹ in angular frequency; $\omega = 2\pi\nu$). After the standard calibration process using open, short, and water¹⁹ as the standard load material over a temperature (T) range of 5 to 60 °C, dielectric spectra for 3P were precisely determined in the form of single Debye-type relaxation. The resulting data were employed as sets of parameters necessary for a three-load calibration process and also for analysis and discussion. The three-load calibration process was performed at each temperature prior to the dielectric measurements for samples other than 3P using three load liquids (*n*-hexane, 3P, and water) because temperature control of the probe was easier and more precise than the standard calibration process using open and short conditions. The electric permittivities of *n*-hexane at several temperatures were obtained from the literature.²⁰ To test the accuracy of the measurement system, we measured dielectric spectra of a typical nonpolar liquid, CCl₄, at 20 °C prior to the measurements of the sample liquids. For CCl₄, values of $\epsilon' = 2.25 \pm 0.10$ and $\epsilon'' = 0.00 \pm 0.05$ were obtained with no dielectric dispersion, irrespective of the frequency, ω , when $\omega > 3 \times 10^9$ s⁻¹. This static electric permittivity, $\epsilon_0 (= \epsilon')$, of CCl₄ agreed reasonably well with the value of 2.23 reported in the literature.²¹ On the basis of these results, our measurement system performed dielectric relaxation measurements on the sample liquids with an uncertainty of less than 2.0%, at least in the range of $\omega > 10^9$ s⁻¹. The temperature, T , of the samples was adjusted to 10 to 60 °C with an accuracy of ± 0.1 °C using a temperature-control system equipped with a Peltier device.

A TR-1000 system (Otsuka Electronics, Osaka), a time-domain reflectometric spectroscopic system for the THz region utilizing a femtosecond laser, was used to measure ϵ' and ϵ'' of

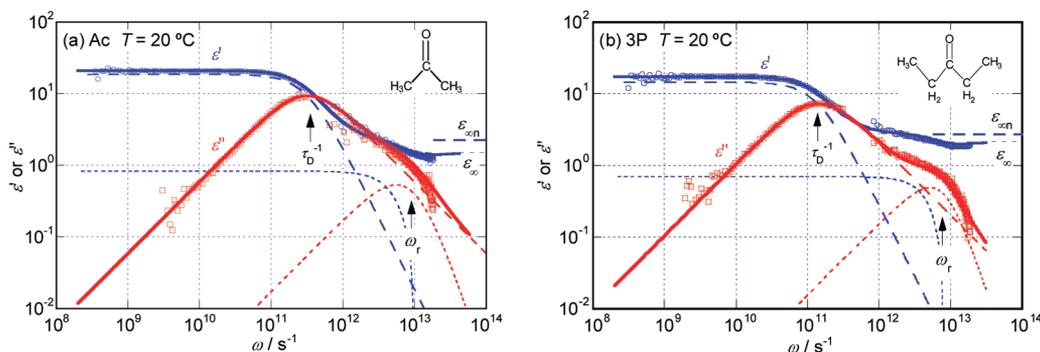


Figure 1. Frequency, ω , dependencies of ϵ' and ϵ'' for acetone, Ac, (a) and 3-pentanone, 3P, (b) in the pure liquid state determined at $T = 20$ °C. Solid lines indicate the summation of a constituent Debye-type relaxation (DR) function (broken lines) and a damped harmonic oscillation (DHO) function (dotted lines). The chemical structures of Ac and 3P are also inserted in the figures.

Ac and 3P in the pure liquid state at $T = 20$ °C in a frequency range of $\nu = 100$ GHz to 3 THz ($\omega = 6.28 \times 10^{11}$ to 1.88×10^{13} s $^{-1}$). Liquid samples were sandwiched between two polyethylene window plates with a 10 mm aperture radius and a thickness of 1.0 mm using an O-ring-type Teflon spacer of 0.2 mm thickness for Ac and 0.5 mm for 3P, respectively. The refractive index, n , and the absorption coefficient (α) were automatically calculated as functions of ω via the standard software installed on the TR-1000 system and were converted to ϵ' and ϵ'' using the relationships $\epsilon' = n^2 - (\alpha\chi\omega^{-1})^2/4$ and $\epsilon'' = n\alpha\chi\omega^{-1}$, where χ is the velocity of light.⁹

For spin–lattice relaxation time (T_1) measurements for the ^{17}O nuclei of Ac, 3P, cP, and cH, a Varian 600 NMR system (Agilent Technologies, Santa Clara) was operated without a field/frequency lock at a temperature range of $T = 10$ to 60 °C (50 °C for Ac) and at a resonance frequency of 81.27 MHz for ^{17}O nuclei.

The viscosities and densities of the ketones were measured as functions of T using a Stabinger SVM3000 (Anton Paar, Graz) viscosity–density meter.

Raman scattering (RS) spectra for Ac, 3P, and 4P were recorded on a JASCO (Tokyo) NR1800 micro-Raman spectrometer equipped with an argon ion, Ar^+ , laser with a wavelength of 514.5 nm. RS measurements were performed in a temperature range from 0 to 40 °C for Ac and 3P and from -30 to 60 °C for 4P using a cryostat sample holder.

RESULTS AND DISCUSSION

Dielectric Behaviors of Ideal Polar Molecules. The angular frequency, ω , dependencies of ϵ' and ϵ'' for the Ac and 3P determined at $T = 20$ °C are presented in Figures 1(a) and (b) as examples of the typical dielectric behaviors of the smallest two symmetric ketones. The spectra, which are presented as plots of ϵ' and ϵ'' vs ω in Figure 1(a), were reasonably decomposed into two constituent functions as given by eq 2; the first component is a Debye-type relaxation (DR) function, and the second one is a damped harmonic oscillation (DHO) function that shows resonance characteristics:

$$\epsilon' = \frac{\epsilon}{1 + \omega^2\tau_D^2} + \frac{A\omega_r^2(\omega_r^2 - \omega^2)}{(\omega_r^2 - \omega^2)^2 + \omega^2\gamma^2} + \epsilon_\infty \quad \text{and}$$

$$\epsilon'' = \frac{\epsilon\omega\tau_D}{1 + \omega^2\tau_D^2} + \frac{A\omega_r^2\omega\gamma}{(\omega_r^2 - \omega^2)^2 + \omega^2\gamma^2} \quad (2)$$

where ϵ and τ_D represent the relaxation strength and time of the DR function. Moreover, A , ω_r , and γ represent the

resonance amplitude, the resonance frequency, and the damping constant of the DHO function, respectively, and ϵ_∞ is the ω -independent constant of electric permittivity. Although Vij et al.^{22,23} used three DHO functions to describe the dielectric spectra of Ac and its solutions in the same ω range used in this study, only one DHO function was necessary in this study. Because the value of $\omega_r = 9.8 \times 10^{12}$ s $^{-1}$ ($= 52$ cm $^{-1}$ in wavenumbers) was identical to the peak frequency of a broad absorption band of Ac in the far-infrared region, this DHO mode was assigned to a libration motion of Ac molecules in cages formed by the surrounding other Ac molecules.²⁴ The determined relatively large damping constant, γ , of 20×10^{12} s $^{-1}$ ($\sim 2\omega_r$) corresponded well to the broad absorption band that bears a half-width value of ~ 80 cm $^{-1}$.²⁴ The half-width value for the absorption band, which has been assigned to the ordinary intramolecular scissors bending mode of C–C–C observed at 393 cm $^{-1}$, was evaluated to be about 20 cm $^{-1}$ and was much smaller than that observed at ω_r .²⁴ The origin of the DHO mode at ω_r therefore appears to be different from the ordinal intramolecular vibration modes, such as the scissors mode at 393 cm $^{-1}$, the in-plane wagging mode of C=O observed at 520 cm $^{-1}$, the out-of-plane wagging modes of C=O at 530 cm $^{-1}$, and other many vibration modes observed at higher wavenumbers. These intramolecular vibration modes contribute to the dielectric spectra as DHO modes with damping constants that are much smaller than those of the mode at ω_r . The value of ϵ_∞ includes the summation of the amplitudes of these fast, sharp, intramolecular DHO modes.

In the case of 3P, the dielectric spectrum obtained at 20 °C, which is presented in Figure 1(b), was reproduced by the combination of a Debye-type relaxation, DR, function and a DHO function as given by eq 2; the spectrum of Ac was reproduced in a similar manner. The evaluated parameters of the DHO function for 3P were similar to those of Ac. Although the amplitude, $A \sim 0.7$, of 3P was 90% of that of Ac, the values of ω_r were nearly identical to each other. The decrease in A likely results from the difference in the molecular sizes between 3P and Ac. Vij et al.^{22,23} have already discussed the DHO resonance mode in ketone homologues, including Ac and its solutions dissolved in cyclohexane, in detail. They have concluded that the mode is a libration one and that its amplitude, A , is governed by the magnitudes of the dipole moment and the inertia moment of Ac. The frequency, ω_r , however, is proportional to $(V_0I_r^{-1})^{1/2}$, where V_0 and I_r represent the height of a local energy barrier of a cage that

surrounds a dipole (of an Ac molecule) and the reduced inertia moment of Ac, respectively.

Although the DR and DHO functions in eq 2 are derived from fundamentally different physical origins, the ω dependence of the DHO function becomes similar to that of the DR function when the value of the damping factor, γ , significantly increases. This similarity arises, if the inertia moments of portions that possess electric charges in the mentioned system could be neglected.⁹ However, in the case of this study, the ω dependence of the second part of the dielectric response in eq 2 was obviously resonant and was still described with the DHO function. This observation means that librational, intermolecular motions of Ac (and 3P) molecules in cages formed by other Ac (and 3P) molecules are highly restricted by strong restoring forces due to the potential energy, V_{θ} , and due to frictions in the frequency range down to ω_r . Therefore, rotational molecular motions of Ac (and 3P) molecules occur in the frequency range below ω_r .

With respect to the Kirkwood correlation factors, g_K , of these ketones, which are a measure of the orientational correlation of dipole moments of molecules over the entire frequency range, the choice of an apparent high frequency limiting electric permittivity ($\epsilon_{\infty a}$) is important. The g_K factor is evaluable via eq 1 using the dipole moment (ca. 2.9 D for Ac¹² and 2.7 D for 3P^{25,26}). Two options exist for the selection of $\epsilon_{\infty a}$, that is, $\epsilon_{\infty a} = \epsilon_{\infty}$ and $\epsilon_{\infty a} = \epsilon_{\infty} + A$, which is identical to the apparent high frequency limiting electric permittivity ($\epsilon_{\infty n}$) determined through the dielectric relaxation measurements up to 50 GHz using the network-analyzer system. The former selection implies that the g_K factor includes information related to the orientational correlation of the dipole moments in both the rotational and the librational modes and leads to the relationship $g_K = 1.45$ and 1.34 for Ac and 3P, respectively. The latter selection implies that the factor includes only information related to the rotational modes and leads to the relationship $g_K = 0.93$ and 0.95 at 20 °C for Ac and 3P, respectively.

The condition of $g_K = 1$ means perfectly free rotation without orientational correlation in the dipole moments. The condition of $g_K > 1$ implies not-free rotation with parallel interactions between dipoles, and the condition of $g_K < 1$ implies not-free rotation with antiparallel interactions between dipoles. Consequently, a g_K value of greater than 1.0 for the former condition revealed that the dipole moments of these small ketones are confined in a parallel configuration in the librational molecular motion. In the frequency range below ω_r , where the librational intermolecular motion completes, the rotational motion of these ketones is perfectly free, without the formation of intermolecular-associations like dimers.

Because the $\epsilon_{\infty a}$ was not previously determined correctly because of technical reasons, the conventional expression of $\epsilon_{\infty a} = 1.05n^2 \sim 1.1n^2$ and $n = 1.359$ for Ac at 20 °C has been used in many dielectric studies; this expression results in $\epsilon_{\infty a} = 1.94$ –2.03 for Ac. Furthermore, the obtained static electric permittivity of $\epsilon_0 = 20.8$ at 20 °C results in a g_K value of 1.02–1.07. This value of g_K indicates weak orientational correlation in the parallel configuration. Therefore, researchers have widely believed that the g_K of Ac is close to unity. This conventional consideration of the $\epsilon_{\infty a}$ value for Ac corresponds well to the results obtained in this study based on the choice of $\epsilon_{\infty a} = \epsilon_{\infty} + A$. Consequently, the approximate expression for $\epsilon_{\infty a}$ is incidentally useful for Ac.

Interestingly, the simple but vague approximate expression for $\epsilon_{\infty a}$ ($= 1.05n^2 \sim 1.1n^2$) leads to g_K values close to unity for DMSO in both the pure liquid state and in solution, whereas DMSO forms dimeric molecular associations in an antiparallel configuration, and the correct $\epsilon_{\infty a}$ values determined at sufficiently high frequencies leads to $g_K \sim 0.5$. This value of g_K indicates the presence of dimers.^{27,28} Researchers should therefore exercise caution when they encounter situations in which they must use the approximate expression for $\epsilon_{\infty a}$ to evaluate g_K values.

The dependencies of the values of g_K on T , as evaluated by the condition of $\epsilon_{\infty a} = \epsilon_{\infty} + A$ ($= \epsilon_{\infty n}$), are plotted in Figure 2

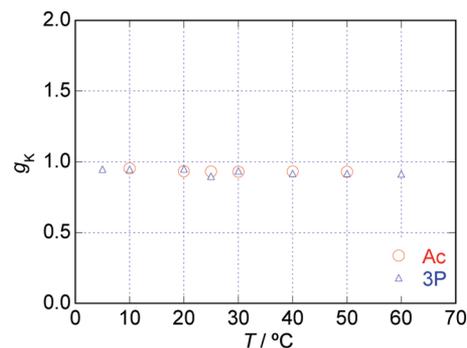


Figure 2. Temperature, T , dependence of Kirkwood factors, g_K , for Ac and 3P.

for Ac and 3P. Nearly constant values close to unity are observed in the figure for both of the ketones, irrespective of T . We conclude that Ac and 3P exhibit free rotation without the formation of intermolecular associations, such as dimers, over the examined temperature range. Because taking $\epsilon_{\infty n}$ as $\epsilon_{\infty a}$ appears to provide adequate results for the evaluation of g_K in Ac and 3P, we also used $\epsilon_{\infty n}$ to evaluate the g_K values for other ketone samples.

The dependencies of dielectric relaxation strength, ϵ and $\epsilon_{\infty n} - 1$, on T for both Ac and 3P are plotted in Figures 3(a) and (b), respectively. The T dependencies of ϵ and $\epsilon_{\infty n} - 1$ are slightly different, as seen in the figures. An increase in T decreased ϵ but decreased $\epsilon_{\infty n}$ to a lesser extent in both the Ac and 3P systems. According to theoretical considerations of the dielectric behavior of a polar molecular liquid, the dielectric relaxation strength, ϵ , decreases with increasing T in proportion to ρT^{-1} , where ρ is the density of the sample liquid, if the polar molecules behave as ideal polar particles that show free rotation without the formation of intermolecular associations.^{1,49} The solid lines in the figures represent the T dependence of ρT^{-1} for Ac and 3P and coincide well with the experimental ϵ data. On the other hand, the T dependence of $\epsilon_{\infty n} - 1$, almost constant irrespective of T as shown in Figures 3(a) and (b), is typical for liquid substances. The parameter $\epsilon_{\infty n} - 1$ represents the dielectric contribution that results from both the intramolecular vibration modes in the IR range and the librational intermolecular mode observed at ω_r , as previously described. The magnitude of $\epsilon_{\infty n} - 1$ might be governed by the number density of constituent molecules, ρ , of the system because precise investigations in nonpolar liquids,²⁰ such as n -hexane, confirmed the relationship. The broken lines in Figures 3(a) and (b) indicate values proportional to ρ , which are almost constant over the examined temperature range.

For the analysis of relaxation times determined using different methods, we converted the (macroscopic) dielectric

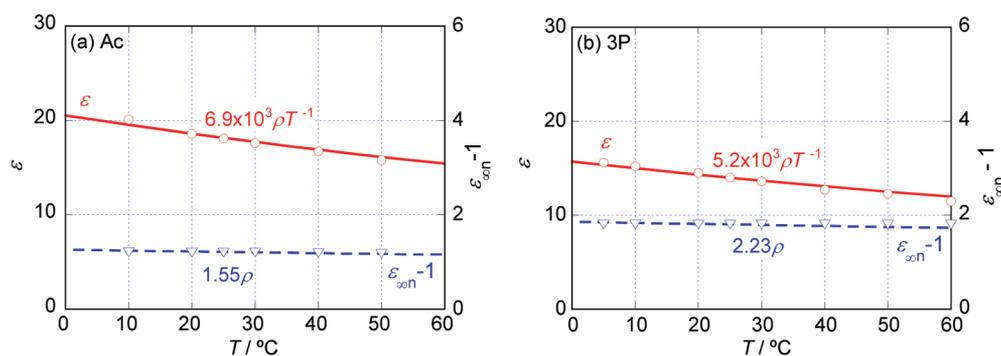


Figure 3. T dependence of dielectric relaxation strength, ϵ , and the difference of the apparent high frequency limiting permittivity from the value of vacuum, $\epsilon_{\infty n} - 1$, for Ac (a) and 3P (b).

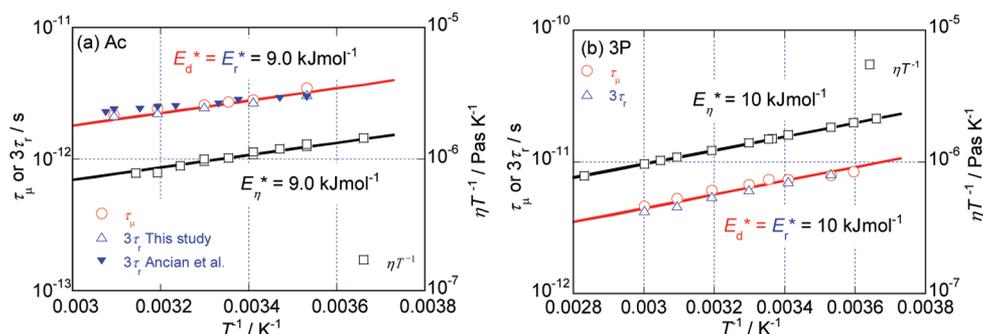


Figure 4. T^{-1} dependence of microscopic dielectric relaxation time, τ_{μ} , temperature reduced viscosity, ηT^{-1} , and 3 times the value of rotational relaxation time, $3\tau_r$, for Ac (a) and 3P (b).

relaxation time, τ_D , to a microscopic dielectric relaxation time (τ_{μ}) which corresponds to a characteristic decay time of single molecular dipole, by using eq 3 proposed by Kivelson et al.¹¹

$$\tau_D = f \frac{g_K}{\dot{g}} \tau_{\mu} \quad (3)$$

where f and g represent a local electric field correction, for example, $f = 3\epsilon_0(2\epsilon_0 + \epsilon_{\infty})^{-1}$,¹⁰ and a dynamic correlation factor, respectively. However, the relationship $\tau_D = g_K \tau_{\mu}$ which is simpler than eq 3, has been frequently used²⁹ because \dot{g} is not obtained in an explicit form. We therefore used this simpler relationship in this study, that is, essentially $\tau_D = \tau_{\mu}$ because $g_K = 1$ for an ideal polar molecule (like Ac and 3P). The relationship between the microscopic dielectric relaxation times, τ_{μ} , and T^{-1} for Ac and 3P are shown in Figures 4(a) and (b), respectively. The slopes of the plots represent the activation energies (E_d^*) for the microscopic dielectric relaxation time, τ_{μ} , about 9.0 kJ·mol $^{-1}$ for Ac and 10 kJ·mol $^{-1}$ for 3P. For ideal polar molecules showing a free rotational relaxation mode without the formation of molecular associations, the microscopic dielectric relaxation time, τ_{μ} , is described by the Stokes–Einstein–Debye (SED) relationship:

$$\tau_{\mu} \propto \frac{V\eta}{k_B T} \quad (4)$$

where V and η represent the effective molecular volume and the viscosity of the liquid, respectively.^{1,4,9} Because the value of V should be a weak function of T , the ratio of ηT^{-1} exhibits the same T dependence as τ_{μ} . Figures 4(a) and (b) also show the relationship between ηT^{-1} and T^{-1} , which provides an activation energy (E_{η}^*) for the ratio of ηT^{-1} that is identical to E_d^* . This agreement between E_{η}^* and E_d^* reveals that both

Ac and 3P adhere to the SED relationship and behave as ideal polar molecules.

The rotational relaxation times (τ_r) of molecules determined using techniques other than dielectric measurements, such as NMR relaxation measurements, are classified as second-order rotational correlation times. The quantity of $3\tau_r$ has the same physical meanings as the microscopic dielectric relaxation time, τ_{μ} , that is, the first-order rotational correlation time, if the molecules rotate freely without the formation of molecular associations. The NMR longitudinal (spin–lattice) relaxation time, T_1 , for ^{17}O nuclei of Ac and 3P molecules is related to the rotational relaxation time, τ_r , of the molecules via eq 5:

$$\frac{1}{T_1} = \frac{3\pi^2}{10} \frac{2I + 3}{I^2(2I - 1)} \left(1 + \frac{\kappa^2}{3} \right) \left(\frac{e^2 q Q}{h} \right)^2 \tau_r \quad (5)$$

where I , e , κ , q , Q , and h represent the elementary electric charge, the spin quantum number of $S/2$ for ^{17}O nuclei, the asymmetry parameter of the field gradient tensor, the largest component of the field gradient tensor in its principal axis system, the nuclear quadrupole moment, and Planck's constant, respectively.¹⁴ The parameter $e^2 q Q/h$ is called the nuclear quadrupole coupling constant (NQCC). The $3\tau_r$ values for Ac and 3P in the pure liquid state were determined from the experimental T_1 (^{17}O NMR) values measured by the inversion–recovery pulse sequence via eq 5 assuming parameters of $\kappa = 0.5$ and $\text{NQCC} = 11.3 \pm 0.1$ MHz evaluated for acetone.³⁰

The temperature dependencies of the $3\tau_r$ values determined for ^{17}O of Ac and 3P are also shown in Figures 4(a) and (b). The agreements between the $3\tau_r$ and τ_{μ} values for both Ac and 3P appear to be perfect. Because the $3\tau_r$ data in Figure 4(a) taken from the literature¹⁴ were calculated from T_1 data

determined from the results of line-width measurements, the data appear to include additional experimental errors due to the minimum line-width resolution. This error represents an essential reason for the slight difference in the low T^{-1} region between the $3\tau_r$ values determined in this study and those reported in the literature,¹⁴ whereas the agreement between the two $3\tau_r$ values for Ac appears reasonable. The agreement between the $3\tau_r$ and τ_μ values in Figures 4(a) and (b) reveals that the evaluated activation energy values (E_r^*) of $3\tau_r$ are identical to the E_d^* values and the E_η^* values for both Ac and 3P. Consequently, these experimental results strongly support that Ac and 3P behave as ideal polar molecules that show free rotation without the formation of molecular associations in both the parallel and the antiparallel configurations. Furthermore, the agreement between $3\tau_r$ and τ_μ observed in Figures 4(a) and (b) supports the validity of the use of the simpler relationship of $\tau_D = g_K\tau_\mu$.

The Raman scattering, RS, spectra for Ac and 3P showed few changes in the values of the Raman shifts and in the half-width values of the C=O stretching vibration bands observed at about 1709 cm^{-1} for Ac and at about 1713 cm^{-1} for 3P, irrespective of temperature as observed in Figures 5(a) and (b).

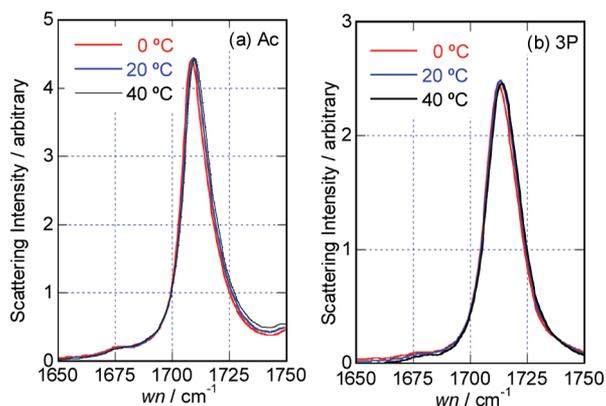


Figure 5. T dependence of Raman scattering spectra in a wavenumber region around $wn = 1700\text{ cm}^{-1}$ for Ac (a) and 3P (b).

The data in the figures are normalized by the peak heights observed at 1430 and 1460 cm^{-1} , respectively, which are assigned to HCH bending modes not affected by the formation of intermolecular dimeric associations. The RS spectra of the C=O stretching bands for both Ac and 3P were slightly asymmetric and well decomposed into two Lorentzian functions. Then, the determined relative area-intensity ratios between the two decomposed functions at each temperature were kept at constant values irrespective of temperature, T . The C=O stretching vibration band is sensitive to the formation of intermolecular dimers for small carbonyl compounds.^{16–18} If the two decomposed Lorentzian functions correspond to the C=O stretching modes due to monomers and dimers and the populations of monomers and dimers alter depending on T , the value of the relative area-intensity ratio changes with T . Consequently, the T dependence of RS data for both AC and 3P observed above reveals that no intermolecular dimeric associations occur in either Ac or 3P. Schindler et al.³¹ discussed the C=O stretching mode split into two Lorentzian functions observed in Ac, and they concluded that intermolecular dipole–dipole coupling between Ac molecules is responsible for the observed split signals.

Dielectric Behaviors of Non-Ideal Polar Molecules. Vaz et al.^{16–18} have clearly shown that, based on the results of RS experiments, the presence of intermolecular dimeric associations in the small ring carbonyl compounds cP and cH change the shape of the C=O stretching bands as a function of temperature and as a function of the composition of the solutions dissolved in carbon tetrachloride (CCl_4). They also proposed some realistic configurations of intermolecular dimeric associations of cP and cH based on ab initio quantum chemical calculations, which included dimers bearing antiparallel cyclic configuration in dipoles.^{16–18} Therefore, the presence of dimers in cP and cH is certain. However, Vaz et al. were not interested in the association behavior in nonring carbonyls and did not report RS data for the C=O stretching bands of small symmetric ketones, such as 4H. The temperature dependence of the RS spectra for 4H at approximately 1710 cm^{-1} related to the C=O stretching band is shown in Figure 6(a). The data in this figure are

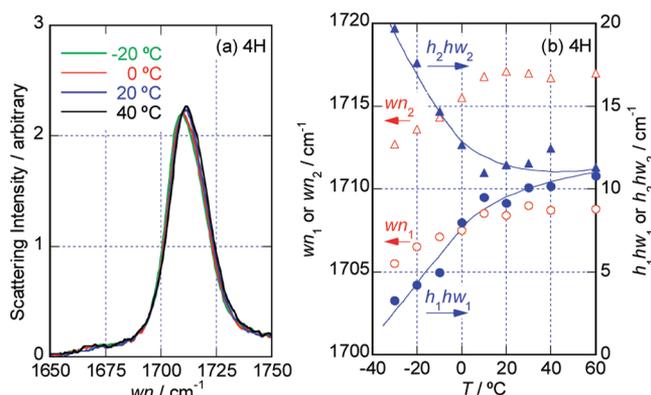


Figure 6. (a) T dependence of Raman scattering, RS, spectra for 4-heptanone, 4H, in the wavenumber (or Raman shift) region of approximately $wn = 1700\text{ cm}^{-1}$, and (b) the relationship between T and wavenumbers, wn_1 and wn_2 , and the products of height and half-width value, h_1hw_1 and h_2hw_2 , of two constituent Lorentz functions necessary to reproduce the RS data seen in (a).

normalized by the peak height observed at 1430 cm^{-1} , which is assigned to the HCH bending mode and is independent of the formation of dimeric associations. The shape of the RS spectra was obviously broader than that of Ac and 3P (cf. Figures 5) and changed with increasing temperature a little. The RS spectra for 4H were perfectly decomposed into two Lorentzian functions with two sets of parameters: the Raman shift (wn_1), the magnitude (h_1), and the half-width value (hw_1); and wn_2 , h_2 , and hw_2 . Figure 6(b) demonstrates the temperature, T , dependence of wn_1 and wn_2 , and also that of the integrated signal strength (or area-intensity) for each Lorentzian mode evaluated in the form of the product as h_1hw_1 and h_2hw_2 . Because an increase in T strengthened the signal strength of h_1hw_1 observed at a lower Raman shift of $wn_1 = 1705$ to 1709 cm^{-1} , this signal is assigned to the C=O stretching band of monomeric 4H molecules, and the other is assigned to that of dimeric molecular associations. This behavior is unlike that of Ac and 3P described above (cf. Figures 5(a) and (b)), but was similar to that previously observed for cH.¹⁸ Consequently, we conclude that 4H is a mixture of monomers and dimeric associations over the entire examined temperature range and that the composition of the monomeric 4H molecule increases with increasing temperature, T .

Figure 7 shows the dielectric spectra, ϵ' and ϵ'' vs ω , for 4H at $T = 20^\circ\text{C}$. The spectra were perfectly decomposed into two

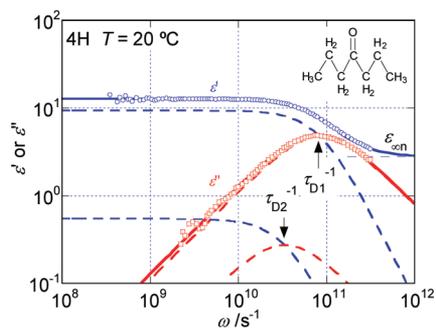


Figure 7. Dependencies of ϵ' and ϵ'' on ω for 4H in the pure liquid state at $T = 20^\circ\text{C}$. The chemical structure of 4H is also inserted in the figures.

DR functions and a high frequency limiting electric permittivity determined by the network-analyzer system, $\epsilon_{\infty n}$. To demonstrate the distribution of dielectric relaxation times, other methods based on conventional empirical models, such as a Cole–Cole and Davidson–Cole model, have been widely accepted.⁹ However, we employed a summation of DR functions, since each decomposed DR mode has distinct physical meanings in this study, such as the rotational relaxation of monomers and the lifetime of dimeric associations. The solid lines are a summation of the two DR functions, which are shown with thin broken lines, and $\epsilon_{\infty n}$, and they agree perfectly with the experimental data. Although the relaxation times, τ_{D1} and $\langle \tau_{D2} \rangle$, and strengths, ϵ_1 and ϵ_2 , for each relaxation mode and $\epsilon_{\infty n}$ were determined as functions of T , the slow mode with τ_{D2} and ϵ_2 was necessary only for spectra obtained at $T = 10$ and 20°C (cf. Figures 9 and 10). Because 4H has intermolecular dimeric associations, especially in the lower-temperature region, the slow DR mode observed in Figure 7 results from the presence of dimeric associations in accordance with the previously drawn conclusion based on the RS spectra.

The temperature dependence of the g_K factor for 4H evaluated via eq 1 under the assumptions that $\epsilon_{\infty a} = \epsilon_{\infty n}$ and $|\mu| = 2.66 \text{ D}^{23}$ is shown in Figure 8. Because the obtained g_K values are close to unity in the temperature range above 30°C , free rotation without any correlations between the orientations of the dipoles is dominant in 4H. However, a slight decrease was observed at temperatures less than 30°C because of the presence of intermolecular dimeric associations. This decrease

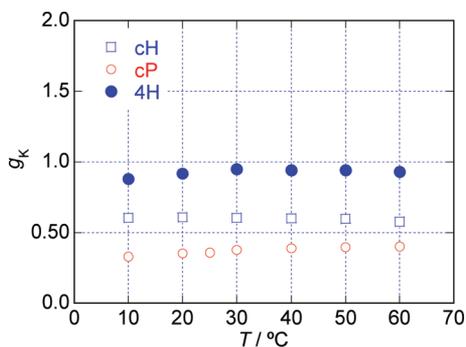


Figure 8. T dependence of g_K for 4H, cyclopentanone, cP, and cycloheptanone, cH, in the pure liquid state.

in the g_K values suggests that the intermolecular dimeric association has an antiparallel cyclic configuration that reduces the total dipole moment as a result of the dimerization.

Figure 9 shows the dependence of ϵ_1 , ϵ_2 , and $\epsilon_{\infty n} - 1$ on T for 4H. The behavior of $\epsilon_{\infty n} - 1$ appears normal and is

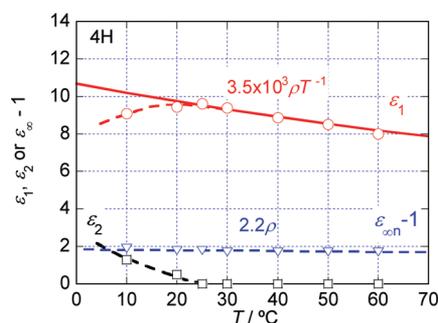


Figure 9. T dependence of dielectric relaxation strengths, ϵ_1 , ϵ_2 , and $\epsilon_{\infty n} - 1$, for 4H.

proportional to the density, ρ , over the entire examined temperature range. Finite nonzero values were determined for ϵ_2 assigned to the contribution of dimeric associations at temperatures of 10 and 20°C . In the case of ϵ_1 , the relationship $\epsilon_1 \propto \rho T^{-1}$ holds in the T range above 25°C , similar to the previously discussed behavior of the ideal dipolar liquids Ac and 3P. However, the ϵ_1 value downwardly deviates from the proportionality line in the temperature range below 25°C , as seen in Figure 9. This deviation indicates that the number density of monomeric 4H molecules decreases with decreasing T and is consistent with the conclusion based on the T dependence of the RS spectra. Because the conventional approximation relationship of $\epsilon_{\infty a} = 1.05n^2 \sim 1.1n^2$ results in an $\epsilon_{\infty a}$ value of 2.05 at 20°C , which is considerably smaller than the $\epsilon_{\infty n}$ value of 2.8 for 4H,¹⁵ the relationship is not useful for the evaluation of g_K , unlike the case of Ac and 3P.

The temperature dependencies of the dielectric relaxation times, $\tau_{\mu 1}$ and $\tau_{\mu 2}$, which were converted from τ_{D1} and τ_{D2} using the relationship $\tau_{D1} = g_K \tau_{\mu 1}$, are shown in Figure 10. In a low

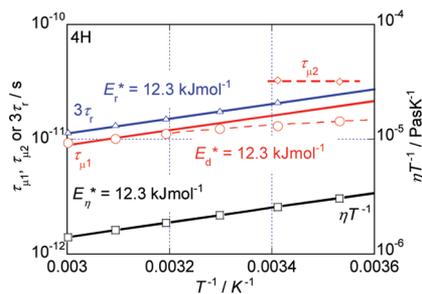


Figure 10. T^{-1} dependence of $\tau_{\mu 1}$, $\tau_{\mu 2}$, and $3\tau_r$ for 4H.

T^{-1} (high T) region, the $\tau_{\mu 1}$ value obeys an Arrhenius-type temperature dependence, with an activation energy of $E_d^* = 12.3 \text{ kJ}\cdot\text{mol}^{-1}$. However, the $\tau_{\mu 1}$ data obviously deviate downwardly from the Arrhenius-type temperature dependence line in the T^{-1} range above 0.0033 K^{-1} ($T > 25^\circ\text{C}$) at the onset of the slow mode bearing $\tau_{\mu 2}$. The physical meaning of the fast mode with $\tau_{\mu 1}$ should be the rotational relaxation process of monomeric 4H molecules, as discussed below. However, the origin of the slow mode with $\tau_{\mu 2}$ would be related to the lifetime of the formed intermolecular dimeric

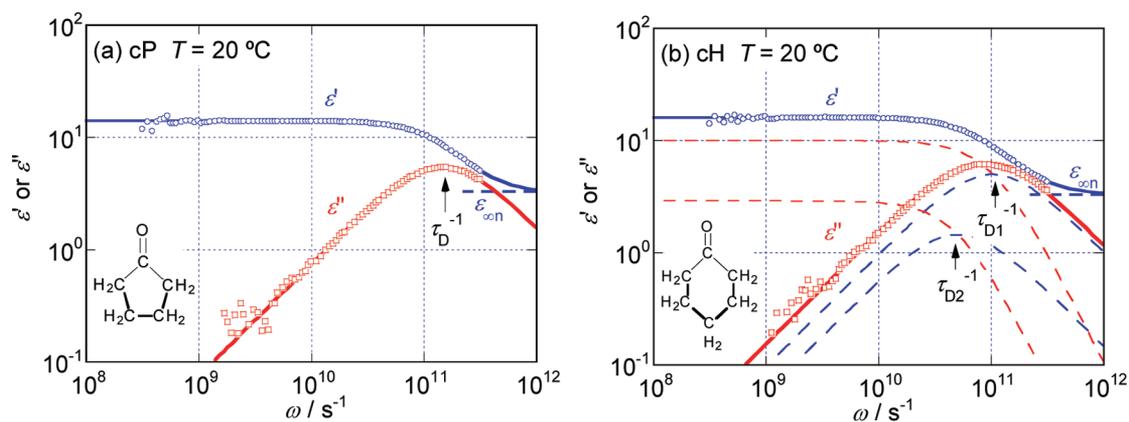


Figure 11. Dependencies of ϵ' and ϵ'' on ω for cP (a) and cH (b) in the pure liquid state at $T = 20$ °C. The chemical structures of cP and cH are also inserted in the figures.

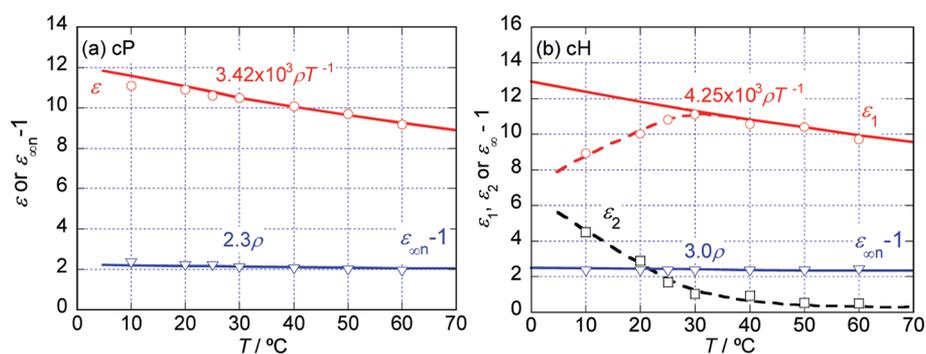


Figure 12. T dependence of dielectric relaxation strengths, ϵ_1 , ϵ_2 , and $\epsilon_{\infty} - 1$, for cP (a) and cH (b).

associations if the dimeric associations have perfect antiparallel cyclic configurations that possess a total dipole moment of zero, as in the case of DMSO.^{27,28} The perfect antiparallel cyclic dimers possessing zero total dipole moment exhibit dielectric relaxation when they are destructed and generated monomers quickly rotate after the lifetime of the dimers.

The temperature dependencies of ηT^{-1} that resulted from the viscosity measurements and the $3\tau_r$ values determined from the ^{17}O NMR T_1 measurements for 4H are also plotted in Figure 10. The parameters κ and $NQCC$ necessary to calculate τ_r are assumed to be the same as those of acetone,³⁰ as in the case of Ac and 3P. Both the ηT^{-1} and $3\tau_r$ data show Arrhenius-type temperature dependencies over the entire examined T^{-1} range, with activation energies, E_{η}^* and E_r^* , that are identical to the value of $E_d^* = 12.3 \text{ kJ}\cdot\text{mol}^{-1}$ for $\tau_{\mu 1}$ in the low T^{-1} range. These results indicate that 4H behaves as an almost ideal polar molecule in the temperature range above 30 °C and that the dielectric behavior is much more sensitive to the presence of intermolecular dimeric associations than viscometric and NMR behaviors.

The dielectric spectra for cP and cH obtained at 20 °C are shown in Figures 11(a) and (b), respectively, as typical examples. Because the dielectric spectra for cH were clearly decomposed into two DR functions that are responsible for the presence of intermolecular dimeric associations as observed in 4H in the temperature range below 30 °C, the dielectric behavior of cH is far from that of an ideal polar molecule. In contrast, the dielectric behavior of cP resembles that of a single DR function with only one relaxation time, which is one of the essential characteristics necessary for compounds to behave as ideal polar molecules. Other dielectric spectra for cP

determined at different temperatures were also described with only one DR function as well as data at $T = 20$ °C, as seen in Figure 11(a), even in the low-temperature regions. However, cP does not behave as an ideal polar molecule, as discussed below.

In accordance with the previously reported RS experiments,^{16–18} cP and cH form intermolecular dimeric associations over the entire temperature range investigated using dielectric measurements. The g_K values for both of the compounds, under the assumptions that $\epsilon_{\infty} = \epsilon_{\infty n}$ and $|\mu| = 3.0 \text{ D}$ for cP^{32,33} and 3.25 D for cH,³⁴ clearly differ from unity as observed in Figure 8. Antiparallel dipole interactions are dominant in both compounds because the g_K values are less than unity. Consequently, the formed dimeric associations in both cP and cH exhibit antiparallel cyclic configurations.

Figures 12(a) and (b) show the dependencies of ϵ , ϵ_1 , ϵ_2 and $\epsilon_{\infty} - 1$ on T for cP and cH, respectively. The behavior of $\epsilon_{\infty} - 1$ appears normal, and the $\epsilon_{\infty} - 1$ values are proportional to the density, ρ , over the entire examined temperature range. Finite values were determined for ϵ_2 assigned to the contribution of dimeric associations over the entire examined temperature range in cH, in contradiction to the behavior of 4H (cf. Figure 9). The relationship $\epsilon_1 \propto \rho T^{-1}$ holds in the temperature range above 30 °C, whereas a marked steep depression was observed in ϵ_1 with decreasing T , in conjunction with a considerable increase in ϵ_2 . This behavior reveals that the number density of monomeric cH molecules decreases with decreasing T and is consistent with the reported behavior based on the temperature dependence of the RS spectra.^{16–18} In the case of cP, the relationship $\epsilon \propto \rho T^{-1}$ appears to be satisfied over the entire temperature range, and cP appears to behave as an ideal polar

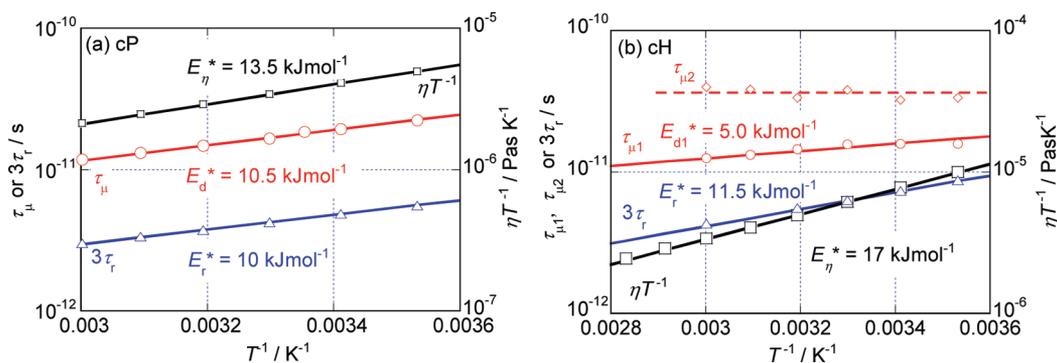


Figure 13. T^{-1} dependence of τ_{μ} , ηT^{-1} , and $3\tau_r$ for cP (a) and $\tau_{\mu 1}$, $\tau_{\mu 2}$, ηT^{-1} , and $3\tau_r$ for cH (b).

molecule. The conventional approximation relationship $\varepsilon_{\infty a} = 1.05n^2 \sim 1.1n^2$ provides an $\varepsilon_{\infty a}$ value of 2.18 at 20 °C,¹⁵ which is considerably smaller than the $\varepsilon_{\infty n}$ value of 3.3 for cH. Then, this relationship is not useful for the evaluation of g_K , similar to the case for 4H.

The dependencies of the dielectric relaxation times, τ_{μ} , $\tau_{\mu 1}$, and $\tau_{\mu 2}$, on T are shown in Figures 13(a) and (b) for cP and cH, respectively. For cH, in the low T^{-1} region, the $\tau_{\mu 1}$ value exhibits an Arrhenius-type temperature dependence, with an activation energy of $E_{d1}^* = 5.0 \text{ kJ}\cdot\text{mol}^{-1}$. In contrast, the value of $\tau_{\mu 2}$ for cH appears to be almost constant, irrespective of T^{-1} , that is, $E_{d2}^* \sim 0 \text{ kJ}\cdot\text{mol}^{-1}$. The value of $\tau_{\mu 1}$ should be proportional to the rotational relaxation time of monomeric cH molecules. The origin of the slow mode with $\tau_{\mu 2}$ would be related to the lifetime of the formed intermolecular dimeric associations in relation to the previous discussion of the slow mode of 4H.

The temperature dependencies of ηT^{-1} and $3\tau_r$ for cH calculated from the η and T_1 data of ^{17}O NMR on the assumption that the values of κ and $NQCC$ are identical to those of acetone³⁰ are also plotted in Figure 13(b). Both the ηT^{-1} and $3\tau_r$ values seem to exhibit Arrhenius-type temperature dependencies over the entire examined T^{-1} range with different activation energies of $E_{\eta}^* = 17 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_r^* = 11.5 \text{ kJ}\cdot\text{mol}^{-1}$. These activation energies are significantly greater than the value of $E_d^* = 5.0 \text{ kJ}\cdot\text{mol}^{-1}$ determined for $\tau_{\mu 1}$. This disagreement between activation energies indicates that cH never behaves as an ideal dipolar molecule over the examined temperature range. The ηT^{-1} and $3\tau_r$ values include information related to the rotational relaxation times of both monomeric cH molecules and intermolecular dimeric associations and to the lifetimes of the dimeric associations in complicated ways.

The relationship between τ_{μ} and T^{-1} for cP was well described by the Arrhenius-type temperature dependence over the entire examined T^{-1} range, with an activation energy of $E_d^* = 10.5 \text{ kJ}\cdot\text{mol}^{-1}$ (Figure 13(a)). The temperature dependencies of ηT^{-1} and $3\tau_r$ for cP calculated from the T_1 data of ^{17}O NMR under the same assumptions used for other compounds are also plotted in Figure 13(a). Both the ηT^{-1} and $3\tau_r$ values satisfy the Arrhenius-type temperature dependency over the entire examined T^{-1} range, with remarkably different activation energies, $E_{\eta}^* = 13.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $E_r^* = 10.0 \text{ kJ}\cdot\text{mol}^{-1}$. This disagreement in the activation energies for cP again confirms that cP never behaves as an ideal polar molecule over the examined temperature range. The reason why cP showed only one relaxation time, τ_D , and simpler DR behavior than that of cH or 4H exhibiting two relaxation times is not clear at present.

However, it is possible that the lifetime of the intermolecular dimeric associations in cP is incidentally not significantly different from the rotational relaxation time of monomeric cP molecules. In this case, both the rotational process of the monomers and the dissociation process of the intermolecular dimers are observed simultaneously and show one macroscopic dielectric relaxation time, τ_D , which is the averaged relaxation time between the two distinct relaxation times that correspond to the two processes.

Finally, we conclude that an ideal polar molecule exhibits single DR function type dielectric spectra possessing a microscopic dielectric relaxation time that has activation energies identical to that of both the temperature-reduced viscosity, ηT^{-1} , and the rotational relaxation time, τ_r . The value of the Kirkwood factor, g_K , for an examined compound that has been carefully calculated from the high frequency limiting electric permittivity determined at sufficiently high frequency, such as 50 GHz, is a sensitive, critical factor to discriminate the dielectric behavior of ideal polar molecules from other behaviors of nonideal polar molecules.

CONCLUSIONS

The dielectric behaviors of some small symmetric ketone molecules over a wide frequency range of 50 MHz up to 4 THz were investigated and discussed. In this study, we define an *ideal polar molecule* as a polar molecule that obeys the Stokes–Einstein–Debye relationship, with neither intermolecular association formation nor orientational correlation between dipoles. Therefore, the ideal polar molecule is expected to exhibit single Debye-type dielectric spectra with an activation energy determined from the microscopic dielectric relaxation time identical to that determined from the temperature-reduced viscosity and the rotational relaxation time. A Kirkwood correlation factor close to unity is also expected.

Acetone and 3-pentanone exhibited the dielectric behavior of ideal polar molecules over a temperature range from 10 °C up to their boiling points. 4-Heptanone, a slightly larger ketone than 3-pentanone, behaved as an ideal polar molecule in the temperature range above 30 °C. However, 4-heptanone exhibited behavior of nonideal polar molecules because its dielectric spectra showed two distinct relaxation times in the temperature region below 30 °C. Cyclohexanone exhibited dielectric spectra with two distinct relaxation times and a Kirkwood factor that was obviously less than unity over the entire examined temperature range. Although cyclopentanone exhibited single Debye-type dielectric relaxation with only one relaxation time over the entire examined temperature range, its Kirkwood factor was less than 0.4, and the activation energy for

the dielectric relaxation time was not identical to that of the temperature-reduced viscosity and rotational relaxation time. Consequently, cyclopentanone did not behave as an ideal polar molecule. The essential reason for the deviation from ideal behavior observed in 4-heptanone, cyclohexanone, and cyclopentanone is the formation of intermolecular dimeric associations in an antiparallel cyclic configuration, which reduce the total dipole moment because of the dimerization.

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Notes

The authors declare no competing financial interest.

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