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 × 10^8 s⁻¹, in angular frequency) to 3 THz (1.88 × 10^13 s⁻¹). The temperature dependencies of the rotational diffusion times (τr) determined using 17O NMR spin–lattice relaxation time (T1) 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 (gK) 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 (τr,fi), which were calculated from the determined dielectric relaxation times (τr,fi) via the relationship τr,fi = τ0gK−1, were identical to 3τr, and were proportional to V0/kT−1 over the wide temperature range examined, where V, k0, 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 gK 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. 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. 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. The application of Debye’s polar molecule model to real polar molecules 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. Onsager 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, which is useful only for nonpolar media. Kirkwood and Fröhlich 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, ε0, and the square of the dipole moment (μ²) of a constituent molecule in the isolated state as follows:

$$\varepsilon_0 - \varepsilon_{\infty} = \frac{\varepsilon_0(\varepsilon_{\infty} + 2)^2 c N A \mu^2 g_k}{9(2\varepsilon_0 + \varepsilon_{\infty})cK_0k_BT}$$

(1)

where ε∞, ε0, N, A, gK, ε0, c, and k0T represent the apparent limiting electric permittivity observed at a high frequency limit, the molar concentration of molecules in units of mol·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 gK provides a measure of the orientational correlation between the dipoles of each constituent molecule. When the observed gK is unity, molecules rotate freely without any intermolecular orientational correla-
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 ($\tau_{\text{D}}$) and strength governed by eq 1. However, the determined Debye dielectric relaxation time, $\tau_{\text{D}}$, should be carefully handled because $\tau_{\text{D}}$ is a macroscopic relaxation time for the total dipole moment, which can be converted into a microscopic dipole relaxation time ($\tau_{\text{m}}$) defined at a single molecular level via some proposed theoretical equations.\textsuperscript{10,11} In particular, the observed dielectric relaxation time, $\tau_{\text{D}}$, or $\tau_{\text{m}}$ 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 D\textsuperscript{12} 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.\textsuperscript{13,14} claimed some decades ago that Ac forms intermolecular dimeric associations on the basis of the results obtained from $^{17}$O 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.\textsuperscript{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 $e_{\text{r,na}} ≈ 1.05n^2$, 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\textsuperscript{-1} are assigned to a characteristic vibration band of carbonyl, C=O, stretching. Vaz et al.\textsuperscript{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 (CCl\textsubscript{4}) 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\textsuperscript{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\textsubscript{4} (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 (5230C, Agilent Technologies) and a 50 GHz performance probe was employed to measure the real and imaginary parts ($\varepsilon'$ and $\varepsilon''$) of the relative electric permittivity over a frequency, $\nu$, range from 50 MHz to 50 GHz (3.14 × 10\textsuperscript{8} to 3.14 × 10\textsuperscript{11} s\textsuperscript{-1} in angular frequency; $\omega = 2\pi\nu$). After the standard calibration process using open, short, and water\textsuperscript{19} 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.\textsuperscript{20} To test the accuracy of the measurement system, we measured dielectric spectra of a typical nonpolar liquid, CCl\textsubscript{4}, at 20 °C prior to the measurements of the sample liquids. For CCl\textsubscript{4}, values of $\varepsilon'$ = 2.25 ± 0.10 and $\varepsilon'' = 0.00 ± 0.05$ were obtained with no dielectric dispersion, irrespective of the frequency, $\omega$, when $\omega > 3 \times 10^9$ s\textsuperscript{-1}. This static electric permittivity, $\varepsilon_0$ ($=\varepsilon'$), of CCl\textsubscript{4} agreed reasonably well with the value of 2.23 reported in the literature.\textsuperscript{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 $\omega > 10^8$ s\textsuperscript{-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 $\varepsilon'$ and $\varepsilon''$ of
Ac and 3P in the pure liquid state at $T = 20 \, ^\circ C$ in a frequency range of $\nu = 100 \, \text{GHz} \text{ to } 3 \, \text{THz}$ ($\omega = 6.28 \times 10^{11} \text{ to } 1.88 \times 10^{13} \, \text{s}^{-1}$). 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 ($\alpha$) were automatically calculated as functions of $\omega$ via the standard software installed on the TR-1000 system and were converted to $\varepsilon'$ and $\varepsilon''$ using the relationships $\varepsilon' = n^2 - (\alpha \omega \tau_0)^2/4$ and $\varepsilon'' = n \alpha \omega \tau_0^{-1}$, where $\gamma$ is the velocity of light.

For spin–lattice relaxation time ($T_1$) measurements for the $^{17}$O nuclei of Ac, 3P, $^3$P, and $^4$P, 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 $^\circ C$ ($50 \, ^\circ C$ 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 $^\circ C$ for Ac and 3P and from −30 to 60 $^\circ C$ for 4P using a cryostat sample holder.

## RESULTS AND DISCUSSION

### Dielectric Behaviors of Ideal Polar Molecules

The angular frequency, $\omega_0$, dependencies of $\varepsilon'$ and $\varepsilon''$ for the Ac and 3P determined at $T = 20 \, ^\circ C$ 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 $\varepsilon'$ and $\varepsilon''$ vs $\omega$ 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 show resonance characteristics:

\[
\varepsilon' = \frac{\varepsilon}{1 + \omega^2 \tau_0^2} + \frac{\omega_0^2}{(\omega_0^2 - \omega^2)^2 + \omega'^2} + \varepsilon_\infty
\]

\[
\varepsilon'' = \frac{\varepsilon \tau_0}{1 + \omega^2 \tau_0^2} + \frac{\omega_0^2 \omega' \gamma}{(\omega_0^2 - \omega^2)^2 + \omega'^2}
\]

where $\varepsilon$ and $\tau_0$ represent the relaxation strength and time of the DR function. Moreover, $\omega_0$, $\omega_0$, and $\gamma$ represent the resonance amplitude, the resonance frequency, and the damping constant of the DHO function, respectively, and $\varepsilon_\infty$ is the $\omega$-independent constant of electric permittivity. Although Vij et al.\textsuperscript{22,23} used three DHO functions to describe the dielectric spectra of Ac and its solutions in the same $\omega$ range used in this study, only one DHO function was necessary in this study. Because the value of $\omega_0 = 9.8 \times 10^{12} \, \text{s}^{-1}$ ($= 52 \, \text{cm}^{-1}$ 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.\textsuperscript{24} The determined relatively large damping constant, $\gamma$, of $20 \times 10^{12} \, \text{s}^{-1}$ ($\sim 20 \, \text{cm}^{-1}$) corresponded well to the broad absorption band that bears a half-width value of $\sim 80 \, \text{cm}^{-1}$.\textsuperscript{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 $20 \, \text{cm}^{-1}$ and was much smaller than that observed at $\omega_0$.\textsuperscript{24} The origin of the DHO mode at $\omega_0$, therefore appears to be different from the ordinary intramolecular bending 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 $\omega_0$. The value of $\varepsilon_\infty$ includes the summation of the amplitudes of these fast, sharp, intramolecular DHO modes.

In the case of 3P, the dielectric spectrum obtained at $20 \, ^\circ C$, 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, $A = 0.7$, of 3P was 90% of that of Ac, the values of $\omega_0$ 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.\textsuperscript{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, $\omega_0$, however, is proportional to $(V_0 I_0)^{-1/2}$, where $V_0$ and $I_0$ represent the height of a local energy barrier of a cage that

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**Figure 1.** Frequency, $\omega_0$, dependencies of $\varepsilon'$ and $\varepsilon''$ for acetone, Ac, (a) and 3-pentanone, 3P, (b) in the pure liquid state determined at $T = 20 \, ^\circ C$. 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.
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 \( \omega \) dependence of the DHO function becomes similar to that of the DR function when the value of the damping factor, \( \gamma \), 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 \( \omega \) 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, \( V_r \), and due to frictions in the frequency range down to \( \omega_r \). Therefore, rotational molecular motions of Ac (and 3P) molecules occur in the frequency range below \( \omega_r \).

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 \( (\varepsilon_{\infty}) \) is important. The \( g_K \) factor is evaluable via eq 1 using the dipole moment \( (ca. 2.9 \, D \) for Ac\(^{12}\) and 2.7 \, D \) for 3P\(^{25,26}\)). Two options exist for the selection of \( \varepsilon_{\infty} \) that is, \( \varepsilon_{\infty} = \varepsilon_{\infty}^0 \) and \( \varepsilon_{\infty} = \varepsilon_{\infty}^0 + A \), which is identical to the apparent high frequency limiting electric permittivity \( (\varepsilon_{\infty}) \) 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 rotational 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 \, \text{°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 \( \omega_r \), 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 \( \varepsilon_{\infty} \) was not previously determined correctly because of technical reasons, the conventional expression of \( \varepsilon_{\infty} = 1.05n^2 \sim 1.1n^2 \) and \( n = 1.359 \) for Ac at 20 \, \text{°C} \) has been used in many dielectric studies; this expression results in \( \varepsilon_{\infty} = 1.94 \)–2.03 for Ac. Furthermore, the obtained static electric permittivity of \( \varepsilon_0 = 20.8 \) at 20 \, \text{°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 \( \varepsilon_{\infty} \) value for Ac corresponds well to the results obtained in this study based on the choice of \( \varepsilon_{\infty} = \varepsilon_{\infty}^0 + A \). Consequently, the approximate expression for \( \varepsilon_{\infty} \) is incidentally useful for Ac.

Interestingly, the simple but vague approximate expression for \( \varepsilon_{\infty} = 1.05n^2 \sim 1.1n^2 \) 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 \( \varepsilon_{\infty}^0 \) values determined at sufficiently high frequencies leads to \( g_K \sim 0.5 \). This value of \( g_K \) indicates the presence of dimers.\(^{25,28}\) Researchers should therefore exercise caution when they encounter situations in which they must use the approximate expression for \( \varepsilon_{\infty} \) to evaluate \( g_K \) values.

The dependencies of the values of \( g_K \) on \( T \), as evaluated by the condition of \( \varepsilon_{\infty} = \varepsilon_{\infty}^0 + A (= \varepsilon_{\infty}) \), are plotted in Figure 2.
relaxation time, $\tau_{\text{D}}$, to a microscopic dielectric relaxation time ($\tau_{\mu}$) which corresponds to a characteristic decay time of single molecular dipole, by using eq 3 proposed by Kivelson et al.:\textsuperscript{11}

$$\tau_{\text{D}} = \frac{N_{\text{d}}}{g} \tau_{\mu}$$  \hspace{1cm} (3)

where $f$ and $g$ represent a local electric field correction, for example, $f = 3\varepsilon_0(2\varepsilon_0 + \varepsilon_\infty)^{-1}$,\textsuperscript{10} and a dynamic correlation factor, respectively. However, the relationship $\tau_{\text{D}} = 8\delta\tau_{\mu}$ which is simpler than eq 3, has been frequently used\textsuperscript{25} because $g$ is not obtained in an explicit form. We therefore used this simpler relationship in this study, that is, essentially $\tau_{\text{D}} = \tau_{\mu}$ because $\delta g = 1$ for an ideal polar molecule (like Ac and 3P). The relationship between the microscopic dielectric relaxation times, $\tau_{\mu}$, 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 ($E_\eta^*$) for the microscopic dielectric relaxation time, $\tau_{\mu}$ 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, $\tau_{\mu}$ is described by the Stokes–Einstein–Debye (SED) relationship:

$$\tau_{\mu} \propto \frac{V\eta}{k_B T}$$  \hspace{1cm} (4)

where $V$ and $\eta$ represent the effective molecular volume and the viscosity of the liquid, respectively.\textsuperscript{1,4,9} Because the value of $V$ should be a weak function of $T$, the ratio of $\eta T^{-1}$ exhibits the same $T$ dependence as $\tau_{\mu}$. Figures 4(a) and (b) also show the relationship between $\eta T^{-1}$ and $T^{-1}$, which provides an activation energy ($E_{\eta}^*$) for the ratio of $\eta T^{-1}$ that is identical to $E_\mu^*$. This agreement between $E_\eta^*$ and $E_\mu^*$ reveals that both Ac and 3P adhere to the SED relationship and behave as ideal polar molecules.

The rotational relaxation times ($\tau_r$) 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, $\tau_{\mu}$; 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, $\tau_r$, of the molecules via eq 5:

$$\frac{1}{T_1} = \frac{3\pi^2}{10} \frac{2I + 3}{I(I + 1)} \left(1 + \frac{\kappa^2}{3}\right) \left(\frac{c^2 qQ}{h}\right)^2 \tau_r$$  \hspace{1cm} (5)

where $I$, $\varepsilon$, $\kappa$, $q$, $Q$, 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.\textsuperscript{14} The parameter $c^2 qQ/h$ 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 $NQCC = 11.3 \pm 0.1$ MHz evaluated for acetone.\textsuperscript{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 $\tau_r$ values for both Ac and 3P appear to be perfect. Because the $3\tau_r$ data in Figure 4(a) taken from the literature\textsuperscript{14} were calculated from $T_1$ data.
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 for 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.

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

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 carboxyls 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 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 (\(\omega_n\)), the magnitude (\(h_1\)), and the half-width value (\(\omega_w1\)); and \(\omega_n2\), \(h_2\), and \(\omega_w2\). Figure 6(b) demonstrates the temperature, \(T\), dependence of \(\omega_n1\) and \(\omega_n2\) and also that of the integrated signal strength (or area-intensity) for each Lorentzian mode evaluated in the form of the product as \(h_1\omega_{w1}\) and \(h_2\omega_{w2}\). Because an increase in \(T\) strengthened the signal strength of \(h_1\omega_{w1}\) observed at a lower Raman shift of \(\omega_n1 = 1705\) 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 4H.\(^{16}\) 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, \(\varepsilon'\) and \(\varepsilon''\) vs \(\omega\), for 4H at \(T = 20^\circ C\). The spectra were perfectly decomposed into two

DR functions and a high frequency limiting electric permittivity determined by the network-analyzer system, \(\varepsilon_\infty\). 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. 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 \(\varepsilon_\infty\) and they agree perfectly with the experimental data. Although the relaxation times, \(\tau_{D1}\) and \(\langle \tau \rangle_{D2}\), and strengths, \(\varepsilon_1\) and \(\varepsilon_2\), for each relaxation mode and \(\varepsilon_\infty\) were determined as functions of \(T\), the slow mode with \(\tau_{D2}\) and \(\varepsilon_2\) was necessary only for spectra obtained at \(T = 10\) and \(20^\circ C\) (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 \(\varepsilon_\infty = \varepsilon_\infty\) and \(\mu_1 = 2.66\) D is shown in Figure 8. The obtained \(g_K\) values are close to unity in the temperature range above \(30^\circ C\), 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 \(30^\circ C\) because of the presence of intermolecular dimeric associations. This decrease 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 \(\varepsilon_1, \varepsilon_2, \text{ and } \varepsilon_\infty - 1\) on \(T\) for 4H. The behavior of \(\varepsilon_\infty - 1\) appears normal and is proportional to the density, \(\rho\), over the entire examined temperature range. Finite nonzero values were determined for \(\varepsilon_2\) assigned to the contribution of dimeric associations at temperatures of 10 and \(20^\circ C\). In the case of \(\varepsilon_1\), the relationship \(\varepsilon_1 \propto \rho^2\) holds in the \(T\) range above \(25^\circ C\), similar to the previously discussed behavior of the ideal dipolar liquids Ac and 3P. However, the \(\varepsilon_1\) value downwardly deviates from the proportionality line in the temperature range below \(25^\circ C\), 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 \(\varepsilon_\infty = 1.05n^2 \sim 1.1n^2\) results in an \(\varepsilon_\infty\) value of 2.05 at \(20^\circ C\), which is considerably smaller than the \(\varepsilon_\infty\) value of 2.8 for 4H, 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, \(\tau_{D1}\) and \(\tau_{D2}\), which were converted from \(\tau_{D1}\) and \(\tau_{D2}\) using the relationship \(\tau_{D1} = g_K\tau_{D2}\), are shown in Figure 10. In a low

Figure 8. \(T^{-1}\) dependence of \(\tau_{D2}\), \(\eta T^{-1}\), and \(3\tau_{D2}\) for 4H.

\(T^{-1}\) (high \(T\)) region, the \(\tau_{D1}\) value obeys an Arrhenius-type temperature dependence, with an activation energy of \(E_a = 12.3\) kJ·mol\(^{-1}\). However, the \(\tau_{D1}\) data obviously deviate downwardly from the Arrhenius-type temperature dependence line in the \(T^{-1}\) range above 0.0033 K\(^{-1}\) (\(T > 25^\circ C\)) at the onset of the slow mode bearing \(\tau_{D2}\). The physical meaning of the fast mode with \(\tau_{D1}\) should be the rotational relaxation process of monomeric 4H molecules, as discussed below. However, the origin of the slow mode with \(\tau_{D2}\) would be related to the lifetime of the formed intermolecular dimeric
ideal polar molecules. Other dielectric spectra for cP resemble that of a single
DR function with only one relaxation time, which is one of the
contrast, the dielectric behavior of cP resembles that of a single
molecule in the temperature range above 30 °C, whereas a marked steep depression was observed
in ε∞ - 1, 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 ε_∞ = ε_∞ and μ =
3.0 D for cP52,53 and 3.25 D for CH3,54 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_1, ε_1, ε_2 and ε_∞ - 1 on T for cP and cH, respectively. The behavior of ε_∞ - 1 appears normal, and the ε_∞ - 1 values are proportional to the density, ρ, over the entire examined temperature range. Finite values were determined for ε_1 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 ε_1 ∝ ρT^-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 ε ∝ ρT^-1 appears to be satisfied over the entire temperature range, and cP appears to behave as an ideal polar
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 3τ_c values determined from the 17O NMR T_1 measurements for 4H are also plotted in Figure 10. The parameters k and NρC necessary to calculate τ_c are assumed to be the same as those of acetone,30 as in the case of Ac and 3P. Both the ηT^-1 and 3τ_c data show Arrhenius-type temperature dependencies over the entire examined T^-1 range, with activation energies, E_a and E_a, that are identical to the value of E_a = 12.3 kJ mol^-1 for τ_μ 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.

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 ε_∞ - 1, for cP (a) and cH (b).
molecule. The conventional approximation relationship \( \varepsilon_{\infty} = 1.0s^2 \sim 1.1s^2 \) provides an \( \varepsilon_{\infty} \) value of 2.18 at 20 °C, which is considerably smaller than the \( \varepsilon_{\infty} \) value of 3.3 for cH. Then, this relationship is not useful for the evaluation of \( \mu_0 \) similar to the case for 4H.

The dependencies of the dielectric relaxation times, \( \tau_\mu \), \( \tau_{\mu_{21}} \), and \( \tau_{\mu_{12}} \) on \( T \) are shown in Figures 13(a) and (b) for cP and CH, respectively. For cH, in the low \( T \) region, the \( \tau_{\mu_{12}} \) value exhibits an Arrhenius-type temperature dependence, with an activation energy of \( E_{\mu_{12}} \approx 5.0 \) kJ mol\(^{-1}\). In contrast, the value of \( \tau_{\mu_{21}} \) for cH appears to be almost constant, irrespective of \( T \), that is, \( E_{\mu_{21}} \approx 0 \) kJ mol\(^{-1}\). The value of \( \tau_{\mu_{12}} \) should be proportional to the rotational relaxation time of monomeric cH molecules. The origin of the slow mode with \( \tau_{\mu_{12}} \) 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 \( \eta T^{-1} \) and \( 3\tau_\eta \) for cH calculated from the \( \eta \) and \( T_1 \) data of \( ^{17}\)O NMR on the assumption that the values of \( \kappa \) and NQCC are identical to those of acetone\(^{30} \) are also plotted in Figure 13(b). Both the \( \eta T^{-1} \) and \( 3\tau_\eta \) values seem to exhibit Arrhenius-type temperature dependencies over the entire examined \( T^{-1} \) range with different activation energies of \( E_{\eta}^{\mp} = 17 \) kJ mol\(^{-1}\) and \( E_{\eta}^{\pm} = 11.5 \) kJ mol\(^{-1}\). These activation energies are significantly greater than the value of \( E_{\mu_{21}} = 5.0 \) kJ mol\(^{-1}\) determined for \( \tau_{\mu_{21}} \). This disagreement between activation energies indicates that cH never behaves as an ideal dipolar molecule over the examined temperature range. The \( \eta T^{-1} \) and \( 3\tau_\eta \) 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 \( \tau_\eta \) 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 \( E_{\eta}^{\pm} = 10.5 \) kJ mol\(^{-1}\) (Figure 13(a)). The temperature dependencies of \( \eta T^{-1} \) and \( 3\tau_\eta \) 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 \( \eta T^{-1} \) and \( 3\tau_\eta \) values satisfy the Arrhenius-type temperature dependence over the entire examined \( T^{-1} \) range, with remarkably different activation energies, \( E_{\eta}^{\pm} = 13.5 \) kJ mol\(^{-1}\) and \( E_{\eta}^{\pm} = 10.0 \) kJ 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, \( \tau_\mu \), and simpler DR behavior than that of cH or 4H exhibiting two relaxation times is not clear at present.
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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shikata@chem.sci.osaka-u.ac.jp.

Notes

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