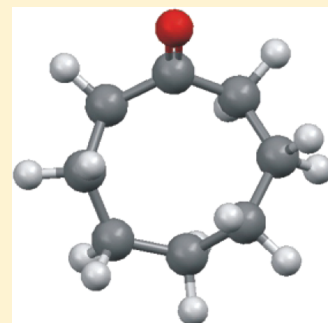


Phase Transition from Liquid to Disordered Solid Phase of Cyclooctanone Studied with Dielectric Methods

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ABSTRACT: The dielectric studies performed for cyclooctanone in its static dielectric regime have shown that at the phase transition from liquid to disordered (plastic) solid phase of the compound, the following singular phenomena occur: (a) the static permittivity (ϵ_s) exhibits a small increase at the transition, instead of that usually observed for polar liquids, a strong decrease of the permittivity at the transition to the crystalline solid phase; (b) temperature dependence of the permittivity, $\epsilon_s(T)$, is practically the same in both phases, reflecting the same dipolar orientational entropy increment induced by the probing electric field; (c) a distinct jump occurs in the slope of the frequency dependence (in log–log scale) of the dielectric losses due to an ionic current, from the “ohmic” value -1 in the liquid phase to about -0.9 just after the transition to the plastic phase; (d) a similar jump is observed in the shape of the electric modulus spectra of cyclooctanone. The results clearly show the liquid-like freedom in the molecular dynamics in the plastic phase as well as similar intermolecular interactions in both phases of cyclooctanone. The differences in the dielectric losses frequency behavior may reflect the change in the ions dynamics: from the normal translational Brownian diffusion in the liquid phase to the subdiffusional dynamics in the plastic phase.



1. INTRODUCTION

The cyclic hydrocarbons and their derivatives, due to the globular molecular shape and conformational flexibility of the rings, exhibit rich polymorphism in the solid state.^{1–3} The highest temperature solid phase, the rotor solid or plastic phase, is characterized by an orientational disorder,³ which reflects itself in anomalously high melting point and abnormally low entropy change (in general, less than 20 J/(K·mol)),⁴ measured at the plastic to liquid phase transition.

Cyclooctanone belongs to the series of compounds that undergo the transition from the liquid phase to the disordered solid phase and, next, to the ordered solid phases. Studies performed by Rudman and Post⁵ with the use of differential thermal analysis, X-ray, and nuclear magnetic resonance methods revealed that cyclooctanone forms three solid phases: at the melting temperature of about 315 K, phase I is formed with a very low entropy change, $\Delta S_I = 8.3$ J/(mol·K); next, at the temperature of 231 K, the transition to the ordered phase II is accompanied by an essentially higher entropy change, $\Delta S_{II} = 71.5$ J/(mol·K); and, finally, at 183 K the transition to phase III occurs, with the entropy change of $\Delta S_{III} = 16.6$ J/(mol·K). Very small melting entropy indicates for an existence of extensive disorder in phase I. X-ray diffraction studies have shown that the rotor phase I of cyclooctanone has cubic structure with the space group $Pm\bar{3}n$ and eight molecules per unit cell.³ That cubic structure is also observed for other cyclic molecules such as cyclooctane, cycloheptatriene, cyclononanone, and so on, and surprisingly, it is the structure identical to high-temperature phases of some diatomic molecules, such as δ -F₂ or γ -O₂.³ Disordered organic molecular crystals composed of non-spherical molecules normally adopt face-centered cubic or, sometimes, hexagonal close-packing structure.⁴

This paper concerns the phase transition from liquid cyclooctanone (Liq) to its disordered solid phase I (Sol), as seen by the dielectric spectra recorded in the frequency range much lower than the frequencies where the dipolar relaxation of the compound occurs. The main goals of the studies are as follows: (i) to investigate the temperature behavior of the static dielectric permittivity, $\epsilon_s(T)$, and hence, estimate the orientational entropy effects in the vicinity of the Liq–Sol phase transition; and (ii) to investigate the frequency behavior of the dielectric losses due to an ionic current and discuss the results in terms of possible differences in ions dynamics in the liquid and plastic phases of the compound studied.

2. EXPERIMENTAL SECTION

Cyclooctanone was purchased from Aldrich with stated purity of minimum 98% and was stored over the 4 Å molecular sieves before investigation. The melting point of the compound is equal to 317.5 K and its chemical structure is presented in Figure 1.

The impedance spectra of the compounds were recorded with the use of an HP 4194A impedance/gain phase analyzer in the frequency range from 500 Hz to 1 MHz and in the temperature range from 253 to 343 K. The details on the apparatus and the measuring capacitor used are described in ref 6.

Experimental results presented in this paper concern the measurements performed for an increasing and decreasing temperature. In the latter case the supercooling of the liquid

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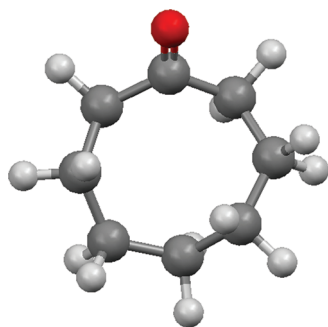


Figure 1. Molecular structure of cyclooctanone.

cyclooctanone was recorded. The ionic conductivity of studied cyclooctanone results only from some thermally activated ionic impurities present in the compound.

3. RESULTS AND DISCUSSION

As the dipolar relaxation of cyclooctanone occurs at about 5 GHz,⁷ the frequency of the electric stimulus used in our experiments certainly corresponds to the static dielectric regime of the compound. Then, the real, ϵ' , and imaginary, ϵ'' , parts of the complex permittivity, $\epsilon^* = \epsilon' - j\epsilon''$, ($j = (-1)^{1/2}$), are the simplest possible;⁸ namely, the real part is equal to the static permittivity, $\epsilon' = \epsilon_s$, and the dielectric losses ϵ'' are only due to the ionic conductivity and can be presented in the following general form,

$$\epsilon''(\omega) = \frac{\sigma_{0\text{ion}}}{\epsilon_0(\omega)^n} \quad (1)$$

where $\sigma_{0\text{ion}}$ is the dc conductivity, $\omega = 2\pi f$ denotes the angular frequency of the measuring electric field, f is the linear frequency, and $\epsilon_0 = 8.85 \text{ pF/m}$ is the permittivity of free space. The exponent n is an empirical quantity which represents the slope of the linear dependence of ϵ'' vs frequency (in log–log scale). In the simplest case, when an ionic current fulfills Ohm's law, that is, the current density (j) is a linear function of the electric field strength (E), the exponent n is equal to 1.⁹ For most of the molecular liquids one records for n the values somewhat less than 1 (the lowering amounts, in general, of a few percent). However, the precise and reliable determination of the exponent n is possible only in the case of the static dielectric regime of the compound under investigation; otherwise, the contribution of the dipolar relaxation (i.e., the displacement current¹⁰) in ϵ'' makes the n determination difficult or even impossible.

Figure 2 presents the dielectric spectra recorded for cyclooctanone in its static dielectric regime when the temperature was rising. The real part of the spectra (a) presents the static permittivity of cyclooctanone in its liquid (Liq) and solid (Sol) states, and only in the low frequencies does one observe in the liquid phase a significant increase of the permittivity due to the electrodes polarization effects. As seen in panel (b) of the figure, the imaginary dielectric spectra have a form of straight lines, indicating the ionic current as a source of the dissipation energy in the studied dielectric material. At the transition to the liquid phase one observes not only an increase of the ionic conductivity (a usual effect) but also a distinct increasing of the lines slopes. As depicted in Figure 3, in liquid cyclooctanone the slope is equal to about -0.99 (± 0.01), so here the ionic current fulfills Ohm's law quite perfectly. From the macroscopic electric point of view, that liquid is a linear

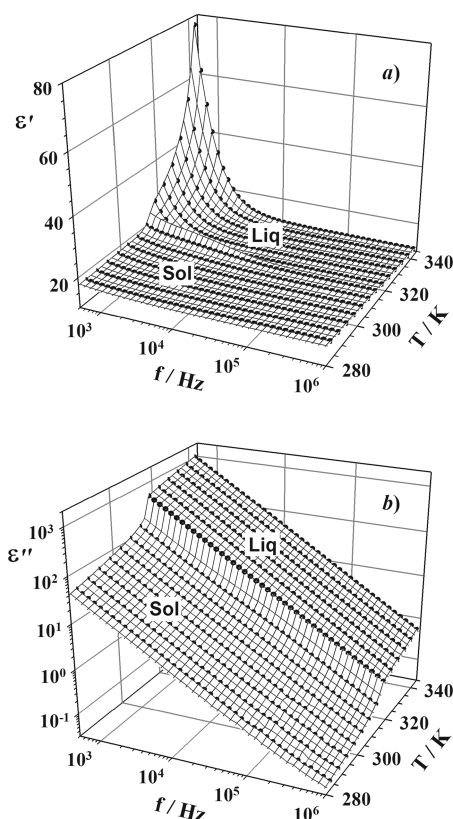


Figure 2. Dielectric spectra of cyclooctanone, the real (a) and imaginary (b) parts, recorded in the liquid and solid phases of the compound for decreasing temperature.

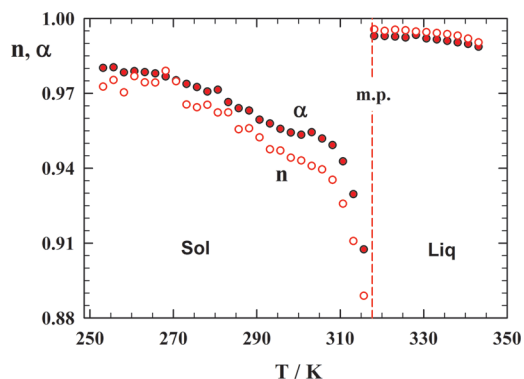


Figure 3. Temperature dependencies of the exponent n in eq 1 (representing the slope of the dielectric losses in Figure 2b and the exponent α in eq 6 (representing the shape of the electric modulus spectra) (see text) in the liquid and solid phases of cyclooctanone.

resistor. What does it mean from the microscopic point of view? It seems to be obvious and natural that the simplest macroscopic response of the molecular/ionic system should reflect the simplest microscopic mechanism of the phenomenon studied. For example, Debye has shown¹¹ that the simplest possible rotational dynamics of polar molecules in liquids—the normal Brownian rotational diffusion—leads to the simplest (exponential) macroscopic dielectric response of the relaxing dipoles after perturbation of their equilibrium by an external electric field. As was shown in many papers,^{12–21} any deviation from that Brownian rotational diffusion (usually it is the subdiffusion) reflects itself as a dielectric response of an exceptional complexity in its theoretical description.

So it seems to be natural that the simplest response of the ionic system to the applied electric field strength (Ohm's law) results from the perturbation by that field of the normal Brownian translational diffusion of the charge carriers in a given medium. It is the simplest possible dynamics of ions in liquids (and not only). An appearance of some traps of the charge carriers or other obstacles in the movement of ions must lead to an effective slowing down in ionic dynamics, that is, to the subdiffusion. The process must manifest itself in the deviation from Ohm's law and consequently lead to decreasing of the exponent n . The data presented in Figure 3 show that at the Liq to Sol phase transition the exponent n exhibits a decreasing jump of about 10%. Next, with decreasing temperature the exponent gradually recovers its value up to about $n = 0.98$ at the temperatures of about 65 °K below the transition to the plastic phase. In the frame of the discussion presented above, the results in Figure 3 show that the maximum of the (probable) subdiffusional effect in ions dynamics reflects the greatest disorder in the plastic phase, occurring just after the transition to that phase from the liquid state.

It is interesting (and maybe important) to see how the postulated subdiffusion in the ionic dynamics in the plastic phase of cyclooctanone manifests itself in the electric modulus spectra of the compound. The dielectric spectra presented in Figure 2 can be easily transformed into the electric modulus spectra, $M^*(\omega) \equiv M'(\omega) + jM''(\omega) = 1/\epsilon^*(\omega)$, where the real (M') and imaginary (M'') parts are given by the following general relations:

$$M'(\omega) = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2}, \quad M''(\omega) = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (2)$$

The electric modulus spectra of cyclooctanone in the liquid and plastic phases, obtained with the use of eq 2, are presented in Figure 4. As was shown in our recent paper,⁸ in the particular case of the ionically conducting molecular material being in the static dielectric regime and when the material fulfills Ohm's law ($n = 1$), the general eq 2 can be easily transformed into the following expressions for the frequency dependence of the modulus,

$$M'_{\text{ion}}(\omega) = \epsilon_s^{-1} - \frac{\epsilon_s^{-1}}{1 + \omega^2 \tau_{\text{ion}}^2}, \quad M''_{\text{ion}}(\omega) = \frac{\epsilon_s^{-1} \omega \tau_{\text{ion}}}{1 + \omega^2 \tau_{\text{ion}}^2} \quad (3)$$

or in the complex notation:

$$M^*_{\text{ion}}(\omega) = \epsilon_s^{-1} - \frac{\epsilon_s^{-1}}{1 + j\omega \tau_{\text{ion}}} \quad (4)$$

where

$$\tau_{\text{ion}} = \epsilon_0 \frac{\epsilon_s}{\sigma_{0\text{ion}}} \quad (5)$$

is the conductivity relaxation time.²² The above relations show that, in the static dielectric regime of the ohmic conducting dielectric materials, the electric modulus exhibits the relaxational behavior of the Debye-type and its spectral characteristics are determined by the static dielectric permittivity (ϵ_s) and the dc ionic conductivity ($\sigma_{0\text{ion}}$). The relaxation process of $M^*_{\text{ion}}(\omega)$ is characterized by the time constant, τ_{ion} , which is proportional to the ratio of the static permittivity to the dc conductivity (eq 5).

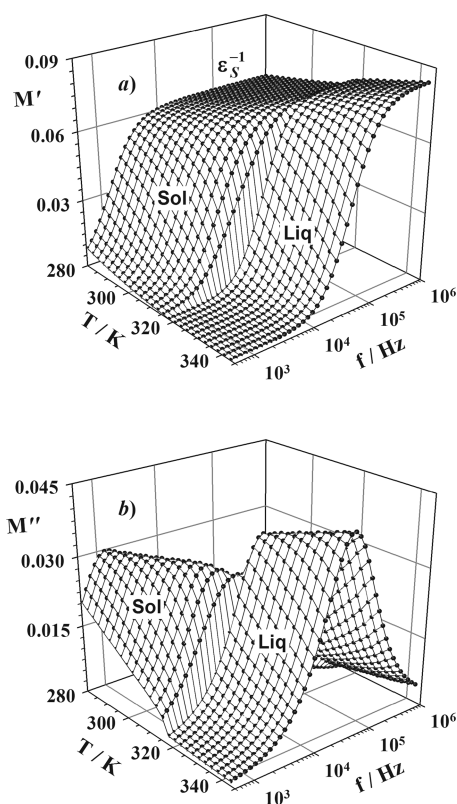


Figure 4. Electric modulus spectra of cyclooctanone resulting from transformation of the dielectric spectra from Figure 2, with the use of relations (2). The solid lines represent the best fit of the Cole–Cole type eq 6 to the experimental modulus data (points).

Before the analytical treatments of the modulus spectra it is useful to present the spectra in a form of the master curve, as shown in Figure 5. As can be seen in the figure, only in the liquid phase of cyclooctanone all the modulus spectra can be incorporated into the one common spectrum which, in practice, points out that the spectra shapes are the simplest, that is, the

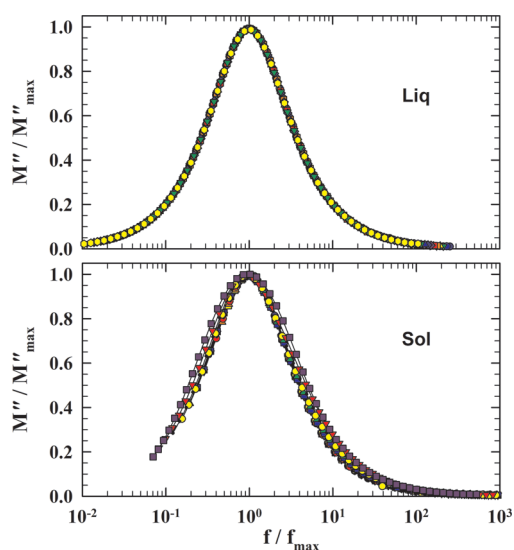


Figure 5. Presentation of the imaginary part of the electric modulus spectra of cyclooctanone in the scale normalized with respect to the maxima of the spectra. The spectra form a master curve only in the liquid phase of the compound.

Debye type. However, in the solid phase the situation is not so clear. The modulus spectra are somewhat broadened in comparison to those recorded in the liquid state, and also, the shape of the spectra exhibit the temperature evolution, shown in the bottom panel of Figure 5. Here, the spectra cannot be presented in the form of a master curve. The effect is not too large, but explicitly shows that the Debye-type eq 4 will not be adequate for theoretical analysis of the modulus spectra in the plastic phase of cyclooctanone.

Similarly to the dielectric formalism, where the simplest empirical modification of the Debye's relaxation equation was introduced by K.S. Cole and R.H. Cole in 1941²³ for description of the symmetrically broadened dielectric relaxation spectra, we propose a similar modification of eq 4 by introducing (the Cole–Cole-type) exponent α :

$$M_{\text{ion}}^*(\omega) = \epsilon_s^{-1} - \frac{\epsilon_s^{-1}}{1 + (j\omega\tau_{\text{ion}})^\alpha} \quad (6)$$

For $\alpha = 1$ the above equation has a form of the Debye type.

The Cole–Cole equation was widely used in the dielectric relaxation spectroscopy as an empirical equation, and only quite recently, the molecular basis of the equation and the physical meaning of the exponent α have been given. Namely, it was shown in numerous theoretical papers^{16–21} that the Cole–Cole relaxational behavior is a direct consequence of the *anomalously slow transport process*, namely, the process of the rotational subdiffusion of dipolar molecules in a liquid under investigation. Then the equilibration way in the system could not be accounted for by the traditional Brownian description of the random walks with an exponential decay, but by the continuous–time random walks theory with a power–law distribution of the waiting times between the consecutive jumps of the rotating object.

Analogous to the interpretation of the Cole–Cole behavior of the dielectric relaxation phenomenon, it may be postulated that the Cole–Cole-type eq 6 corresponds to the subdiffusional translational motion of the ions in a given medium. Of course, such a postulate requires a theoretical grounding. The experimental data presented in this paper give some, seem to be important, arguments for such assumption.

The solid lines in Figure 4 represent the best fit of eq 6 to the experimental modulus data (points) recorded in both the liquid and solid phases of cyclooctanone. The temperature dependence of the exponent α , resulting from the fitting procedure, is presented in Figure 3. A similarity in the temperature behavior of the exponent n [from eq 1] and the exponent α [from eq 6] is really striking and quite possible not accidental. The convergence of the values of these two exponents seems to be an argument for the supposition that eqs 1 and 6 concern the same physical object—the ions immersed in the studied liquid.

In the liquid phase of cyclooctanone, the shape of the electric modulus spectra (represented by exponent α) exhibits only traces of the deviation from the simplest, that is, the Debye-like behavior, in the whole temperature range used. It is why all the spectra recorded in the liquid phase can be represented by the master curve. In microscopic language, the translational diffusion of ions in liquid cyclooctanone is practically of the normal Brownian type. However, it is not the case of the plastic phase of the compound. Here, the ions dynamics is (probable) subdiffusional and the extent of the ionic slowing down depends on the temperature distance from the transition to the

plastic phase. One can roughly estimate the effect as about 10% of ionic translation slowing down just after the transition to the plastic phase and it is the maximal value of the effect observed in the studied compound.

Now, let us analyze the static dielectric permittivity of cyclooctanone in the liquid²⁴ and plastic phases of this compound. The experimental permittivity data depicted in Figure 2a are presented in Figure 6a as a function of the

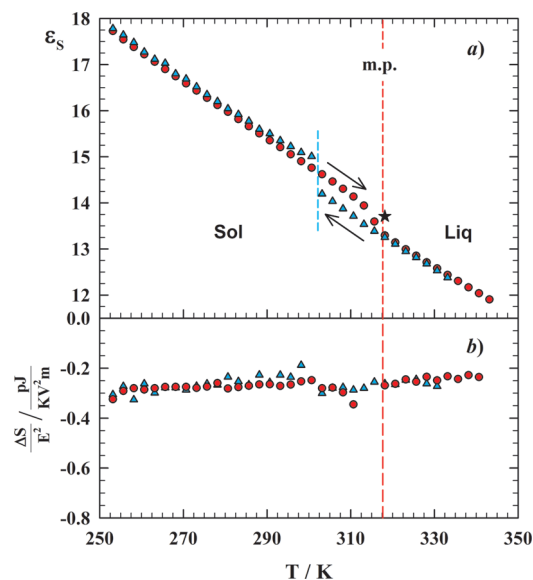


Figure 6. Temperature dependence of the static dielectric permittivity (a) of cyclooctanone in its liquid and plastic phases, measured with increasing (●) and decreasing (▲) temperature. The literature⁷ permittivity value is denoted as ★; panel (b) presents the corresponding orientational entropy increment calculated with eq 7.

(increasing) temperature. In the figure are presented also the permittivity data measured when the temperature was decreasing and when a quite important supercooling effect (of about 15 °C) is recorded. A relatively small increasing jump (ca. 3%) of the permittivity value, observed at the transition from the liquid to the plastic phase, corresponds mainly to the contraction of the compound, that is, an increasing of the dipoles density number in the plastic phase. The effect is illustrated in Figure 7, where the temperature dependence of the molar volume (V_M) of cyclooctanone, obtained on the basis

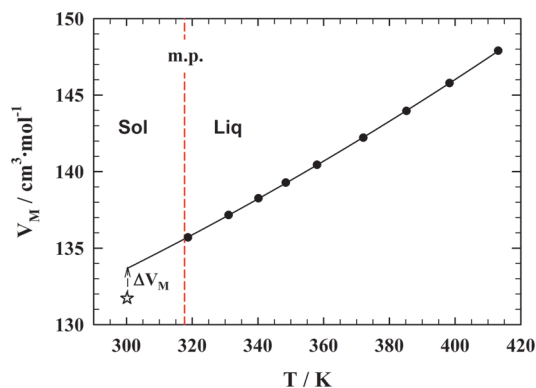


Figure 7. Temperature dependence of the molar volume of cyclooctanone resulting from the density measured in the liquid²⁵ and solid²⁶ phases of the compound.

of the density values published in the literature,^{25,26} is shown. One can roughly estimate the molar volume change at the transition as about 2%, close to the permittivity change.

Let us consider the permittivity temperature dependence recorded in the liquid and the plastic phases of cyclooctanone. As was shown first by Fröhlich,²⁷ the static permittivity temperature dependence reflects an efficiency of the dipoles ordering, forced by the probing electric field. Namely, the temperature derivative of the static permittivity is directly related to the orientational entropy increment (ΔS) induced by the measuring electric field of intensity E :

$$\frac{\Delta S(T)}{E^2} \equiv \frac{S(T, E) - S_0(T)}{E^2} = \frac{\epsilon_0}{2} \frac{\partial \epsilon_s}{\partial T}(T) \quad (7)$$

S_0 denotes the entropy of the liquid under investigation in the absence of the electric field and T is the absolute temperature. Two features of the entropy increment are important: the sign and the dependence on the temperature. A negative ΔS corresponds to the dipolar ordering action of the electric field and it is a typical behavior of dipolar liquids. Anomalous entropy behavior was observed for some highly polar mesomorphic liquids in the vicinity of the phase transitions from the isotropic phase to the liquid crystalline phases.^{28,29} The temperature dependence of ΔS , in turn, reflects the structural changes in the liquid studied, leading, at different temperatures, to the different dipolar orientational effects.

As seen in Figure 6b, the entropy increment of cyclooctanone is negative, practically temperature independent, and maintains the same value in both the liquid and the plastic phases of the compound. So, a simple (in principle) experiment in which one measures temperature dependence of the static dielectric permittivity leads to the following important conclusions related to the molecular structure and dynamics in the investigated dielectric material: (i) the negative entropy increment and its practical temperature independence reflects the orientational dipolar ordering as the only effect induced in the system by an applied electric field, so (ii) the temperature-induced conformational changes of cyclooctanone molecules, leading to their dipole moment modification, is excluded; (iii) there are no differences in the field-induced dipolar orientation effects in the liquid and the plastic phase of cyclooctanone. In both phases the molecules exhibit the same rotational abilities leading to the plasticity of the solid phase I of cyclooctanone.

However, the experimental results just presented above give no exact information on the intermolecular dipolar coupling in the system investigated. That type of interaction, in general, does not reflect itself in the orientational entropy increment,²⁷ and as was mentioned above, only in the exceptional cases of some mesogenic polar molecules, in the vicinity of the phase transition from isotropic liquid to the nematic phase, one observes an anomalous $\Delta S(T)$ dependence, including the increment sign change to the positive. In "normal" dipolar liquids, the dipolar coupling can be quite easily detected by determination of the Kirkwood correlation factor g_k .³⁰

$$\frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \frac{9kT}{4\pi N_A} V_M = \mu_1^2 g_k \quad (8)$$

where μ_1 is the dipole moment of a single molecule (determined in the gaseous phase of the compound or in diluted solutions in nonpolar solvent), k is Boltzmann's constant, N_A is Avogadro's number, T is the absolute temperature, and ϵ_∞ is the dielectric permittivity measured in

frequencies high enough to prevent the dipolar reorientation. The factor g_k was introduced by Kirkwood³¹ for expressing the intermolecular dipolar coupling in liquids; namely, the fractional values of the factor, $g_k < 1$, corresponds to the antiparallel dipolar self-association leading to the reduction of the apparent dipole moment of the molecule, $g_k > 1$ corresponds to parallel association leading to an increase of the moment, and $g_k = 1$ means a lack of the dipolar coupling in the liquid under investigation.

The values of the permittivity ϵ_∞ , necessary for use of eq 8, were estimated by a simple method³² on the basis of the literature data on the refraction index (Merck data) and the density of cyclooctanone.^{25,26} The value of the dipole moment of single cyclooctanone molecules were taken as $\mu_1 = 2.9$ D.³³

Figure 8 presents the temperature dependence of the Kirkwood correlation factor of cyclooctanone calculated from

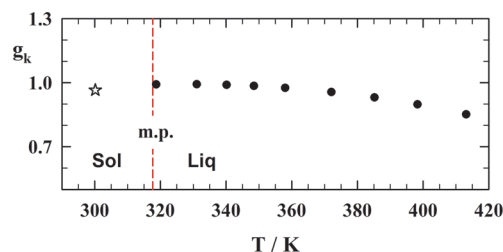


Figure 8. Temperature dependence of the Kirkwood correlation factor of cyclooctanone calculated with eq 8.

eq 8. The obtained values of the g_k factor, which are not far from unity in the whole temperature range, decidedly point out for a very limited antiparallel dipolar coupling both in the liquid and the plastic phases of cyclooctanone. The result was expected taking into account the peculiar structure of cyclooctanone molecules which makes the intermolecular dipolar aggregation process not too favorable.

CONCLUSIONS

The dielectric behavior of cyclooctanone belongs to rather exceptional cases when one can investigate the real part (static permittivity) and the imaginary part (ionic conductivity) of the complex dielectric permittivity in both the liquid and solid phases of the compound in the same, a relatively high, frequency range, where the electrodes polarization effects are marginal. The experimental data presented in this paper show several important facts concerning the dynamics of the molecules and the ions as well as the intermolecular interactions in the compound in its liquid and plastic phases: (i) there are no differences in the dynamics of cyclooctanone molecules and the interactions between them in both phases; the conclusions result from the analysis of the orientational entropy increment and the Kirkwood correlation factor temperature behavior; (ii) there is a noticeable difference in the ionic manifestation in the dielectric losses in the liquid and plastic phase of cyclooctanone which can result from the difference in the dynamics of ions in the both phases: very close to normal Brownian translational diffusion of ions in the liquid phase and the subdiffusional dynamics in the plastic phase of cyclooctanone.

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Notes

The authors declare no competing financial interest.

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