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Dipolar interactions in liquids and linear dielectric relaxation spectroscopy

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Linear dielectric relaxation studies performed on two isotropic liquids composed of the molecules of the same moment of inertia and a quite different polarity: $C_{10}H_{21}$—O—Ph—**COO**—Ph—CN (the dipole moment of about 5 D) and $C_{10}H_{21}$—O—Ph—**OOC**—Ph—CN (2.5 D) showed that, at given temperature, the relaxation times corresponding to the rotation around the short axis of the two kinds of molecules coincide to each other, regardless the polarity of the molecules and their abilities to accomplish dipolar aggregation. The studies allow one to estimate the lifetime of the intermolecular aggregates due to the dipolar interactions in liquids as no longer than 0.1 ns.

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I. INTRODUCTION

A significance of the intermolecular dipolar interactions in the dynamics of molecules, as revealed in dielectric relaxation spectroscopy, is one of the most important and still open problems of molecular physics of the liquid state. A general opinion, expressed, for example, in an excellent review by Bagchi and Chandra [1], is that conventional dielectric relaxation experiments measure the collective orientational motion of dipolar molecules rather than single-particle motion. However, as the authors had stated, it is surprising that the simple noninteracting Debye's model is so successful in describing the polar response of many strongly interacting dipolar liquids [1].

In this paper we present experimental results that seem to be important in discussion of the question as to how dipolar interactions in liquids reveal themselves in linear dielectric spectroscopy. The linearity concerns the relation between the dielectric polarization and the probing electric field strength, a condition fulfilled for low strengths of the field.

Conventional dielectric relaxation experiments on molecular liquids operate in the frequency region of the probing electric field ranging from kilohertz to gigahertz, which corresponds to relaxation time values between 10 μs and 1 ps. Some basic conditions are needed to observe the appearance of a signal in the dielectric relaxation spectrum of an entity rotating in a dense medium. First of all, the lifetime of the rotor should be sufficiently long—roughly, at least of the order of magnitude of the relaxation time. Secondly, the movement should be followed by a change of the projection of the molecular dipole moment on the direction of the probing electric field. Finally, if the frequency of the molecular rotation and that of the field are coincident, an absorption band appears in the dielectric relaxation spectrum.

Short-range intermolecular dipolar interactions lead undoubtedly to molecular aggregation, at least to a dimerization [2–7]. Numerous data based mainly on static dielectric polarization measurements have shown that in diluted solutions of dipolar compounds in a nonpolar medium, the molecular apparent dipole moment decreases as the concentration of the dipolar compound increases. The data can be quite well interpreted within a simple model of the monomer-dimer equilibrium, where the dimers are weakly polar. The model of the antiparallel dipolar aggregation of molecules in diluted solutions, which causes the compensation of the dipole moments, is well established. As the concentration of the dipolar component of the solution increases, the dipolar interactions lead certainly to the formation of aggregates more complex than dimers. However, even in pure polar liquids, the antiparallel dipolar aggregation reveals itself by a decrease of the molecular apparent dipole moment compared to that of the single molecule. Quantitatively, the process can be described by the well-known Kirkwood correlation g-factor, which, in the frame of the Onsager local field model [8], can be calculated from the following equation:

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$$g\mu^2 = \frac{9kT}{4\pi N}\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2}, \tag{1}$$

where μ denotes the dipole moment of a single molecule, ε_s and ε_∞ are the permittivities measured with the static and high frequency electric field, respectively. N is the number of molecules per unit volume, k is the Boltzmann constant, and T is the absolute temperature. The g values less than unity are rather characteristic of an antiparallel dipolar aggregation in a liquid studied.

An intuition prompts us that the dipolar molecular aggregation should influence the molecular dynamics in the liquid state. Moreover, the strongest effect is expected for the molecules having the highest polarity. In order to verify this in the frame of the linear dielectric relaxation, the experiments were performed on two liquids composed of molecules having different polarities but very similar structures (the same moment of inertia).

II. EXPERIMENT

The measurements were performed in the *isotropic phase* of two mesogenic compounds: 4-cyanophenyl—4′-*n*-decyloxybenzoate (CPDOB), $C_{10}H_{21}$—O—Ph—COO—Ph—CN, and 4-*n*-decyloxyphenyl-4′-cyanobenzoate (DOPCB), $C_{10}H_{21}$—O—Ph—OOC—Ph—CN with the sequence of the phase transitions: (Cr) 70 °C (S_A) 78 °C (N) 86 °C (I), and (Cr) 69 °C (S_A) 99.3 °C (I), respectively. A change of the mutual arrangement of the polar groups —COO— and —CN, leads here to an essential change in the resultant dipole moment of the molecules (from 5 D for CPDOB to about 2.5 D for DOPCB), whereas the moment of inertia remains practically unchanged. For comparison, the dielectric relaxation was measured for 4-cyanophenyl — 4′-*n*-decylbenzoate, $C_{10}H_{21}$PhCOOPhCN, the compound analogous to CPDOB, in which the oxygen is removed from the tail of the molecule.

The compounds were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The dielectric relaxation measurements were realized in the frequency range of 1 MHz to 1 GHz by using a HP 4291B impedance analyzer.

III. RESULTS AND DISCUSSION

Figure 1 presents, as an example, the real and imaginary parts of the dielectric permittivity of both compounds as a function of frequency, at 100 °C. The spectra were resolved into two elementary contributions corresponding to the molecular rotation around the short (1) and long (2) axes with the use of the Cole-Cole formula [9]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_i \frac{A_i}{1 + (j\omega\tau_i)^{1-\alpha_i}}. \tag{2}$$

For the limiting value of the parameter $\alpha_i = 0$, the ith reorientational process is described by a single relaxation time (the Debye type process). A_i and τ_i denote, respectively, the dielectric strength and the relaxation time, and together with α_i, they are the adjustable parameters in the procedure of the fitting of Eq. (2) to the experimental spectrum. The best fit gave us for α_i the values of the order of 10^{-2} for all resolved spectra, what means that the bands 1 and 2 are very close to the Debye type. The temperature dependences of the remaining parameters (τ_i and A_i) obtained, are presented in Fig. 2.

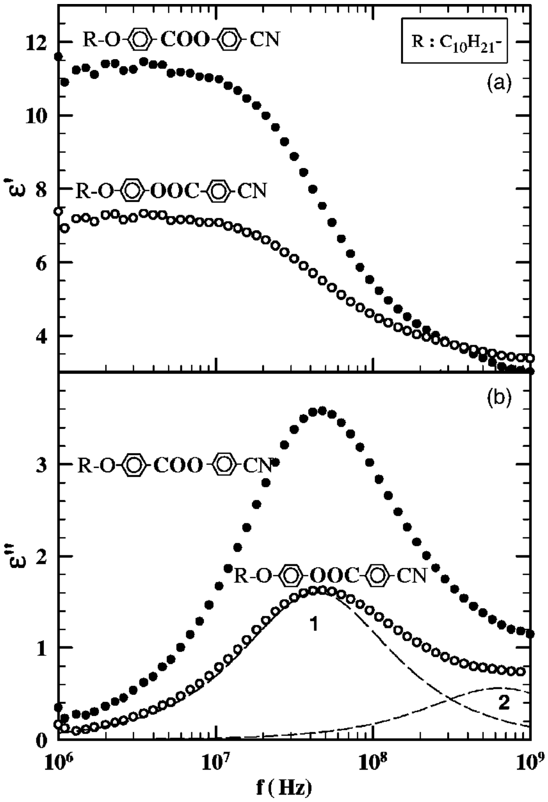

FIG. 1. Dispersion (a) and absorption (b) dielectric relaxation spectrum of CPDOB (●) and DOPCB (○), at 100 °C. In (b) the spectrum is resolved into two components corresponding to the molecular rotation around the short (1) and long (2) axes.

For our problem, the crucial result concerns the relaxation time τ_1: the rotation around the short axis of both molecules studied performs with the same frequency, disregarding a quite different degree of the dipolar aggregation occurring in the both liquids. This degree can be evaluated on the basis of the Kirkwood g factor value calculated from Eq. (1). At 100 °C, the static permittivity is equal to 11.25 and 7.25 for CPDOB and DOPCB, respectively (see Fig. 1). Assuming the same density of the two liquids and the same value for the high-frequency permittivity $\varepsilon_\infty = 2.5$, and taking into account the value of the dipole moment of single molecules 5 D and 2.5 D for CPDOB and DOPCB, respectively, one obtains from Eq. (1) that $g_{\mathrm{CPDOB}} \approx 0.5 g_{\mathrm{DOPCB}}$; i.e., the degree of the antiparallel dipolar aggregation in more polar liquid is roughly twice as higher as that existing in the less polar one. Figure 3 shows that, in the limits of the experimental errors, the rotation around the short axis of CPDOB and DOPCB molecules occurs with the same activation energy. Some deviation from the Arrhenius behavior, observed for the nematogenic CPDOB in the low-temperature region, points out for the beginning of the pretransitional effects discussed in our recent paper [10].

The results presented show undoubtedly that the dynamics of the molecules studied, observed in the frequency win-

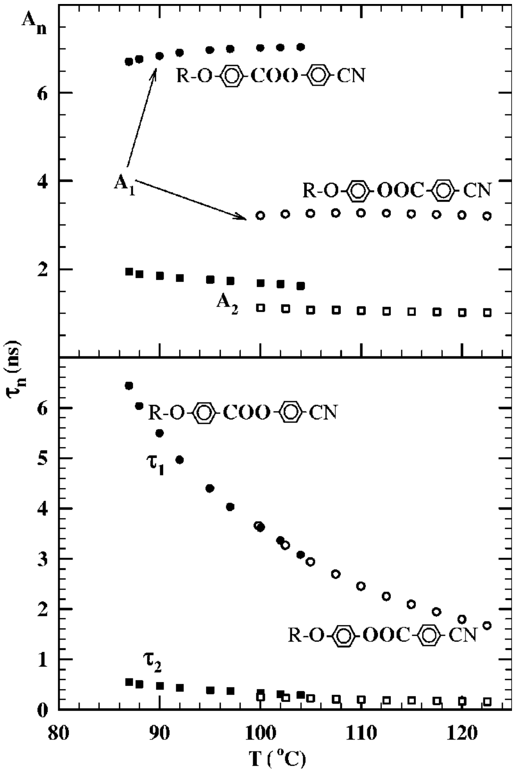

FIG. 2. Temperature dependences of the dielectric strengths (A_n) and the dielectric relaxation times (τ_n) corresponding to the rotation of CPDOB and DOPCB molecules around their principal axes.

dow used by the conventional linear dielectric spectroscopy, is not influenced by the intermolecular dipolar aggregation. The main factor that determines the dynamics of the particle is its moment of inertia. The conclusion is convergent to that of Budo *et al.* [11], who more than 60 years ago argued the importance of the moment of inertia of individual molecules in their dynamics in isotropic liquids. It is shown in Fig. 3 that the decrease of the moment of inertia by removing the oxygen atom from the tail of CPDOB molecule, quite decidedly accelerates the molecular rotation around the short axis of decylo-derivative, though the ability for the dipolar aggregation remains practically unchanged (only a small change of the dipole moment) in comparison to the corresponding decyloxy-derivative compound.

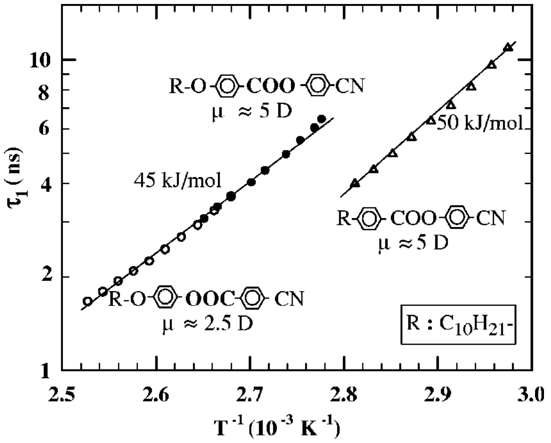

FIG. 3. Arrhenius plots for the relaxation time τ_1 for decyloxy-derivative compounds studied. The results obtained for decylo-derivative compound are shown for the comparison. The values of the dipole moment of single molecules and the activation energy are indicated in the figure.

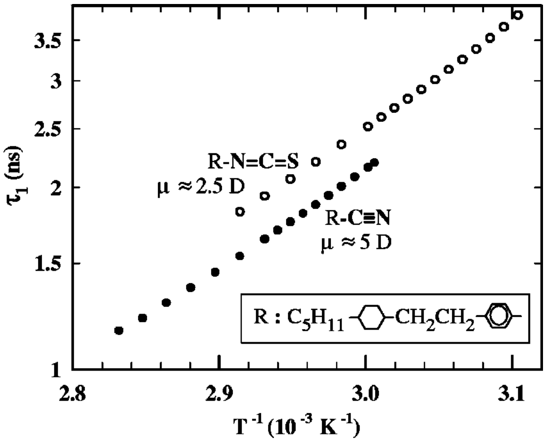

FIG. 4. Arrhenius plots of the dielectric relaxation time corresponding to the molecular rotation around the short axis of two compounds with different polar group [10].

Up to now, our discussion concerned the liquids composed of molecules belonging to the cyano-derivative family. One can suspect that, despite an essential difference in the resultant dipole moment of CPDOB and DOPCB molecules, the strongly polar —C≡N group plays a decisive role in the molecular aggregation and hence the relaxation times of the compounds are so similar. The first evidence that it is not the case is shown in Fig. 3 and was discussed just above. The second one is presented in Fig. 4. Two molecules of very similar structure and essentially different polarity due to the different ending polar group attached to the molecular core, relax at different frequencies [10]. However, the longest relaxation time corresponds not to the most aggregated compound (R—C≡N), as can be expected, but to the molecules having the highest value of the moment of inertia (R—N═C═S).

Therefore, the lack of influence of dipolar interactions on molecular motion as observed in the conventional dielectric spectroscopy, leads without fail to the conclusion on the lifetime of the intermolecular aggregates due to the dipole-dipole interactions in pure polar liquids. To our best knowledge there are no experimental data in this matter. The data presented here point out that as the relaxation time τ_1 of the studied compounds is of the order of 10^{-9} s and corresponds to the rotation of the molecules around their short axis, the lifetime of the intermolecular entities in polar liquids must be shorter than 10^{-9} s, and cannot reveal in the linear dielectric spectroscopy by using the ordinary frequency range up to 1 GHz.

Still, as was shown in recent papers [12,13], the collective molecular orientational motions in dipolar isotropic liquids can be detected by using dielectric spectroscopy, but an additional static electric field of high strength, causing a nonlinearity in the polarization—field strength relation, must be applied to the system. Then, in the nonlinear dielectric spectrum *a new dielectric absorption band* appears in the frequency region of about one order of magnitude lower than that recorded in the linear dielectric spectrum as a band corresponding to the rotation of mesogenic molecules around their short axis. The nonlinear dielectric spectroscopy was successfully used for studies of the reorientational dynamics of the multi-molecular prenematic effects in the isotropic mesogenic liquids.

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