Peculiar Dielectric Relaxation Behaviour of Dimethylsulfoxide in Tetrachloromethane

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The dielectric spectrum of the title mixture system, which has been studied over the whole composition range at 20 °C, exhibits an unusual relation between relaxation time and viscosity, the former passing through a maximum though the latter changes monotonously. This anomaly is discussed having regard to previous examples of similar behaviour, which concern tetrachloromethane mixtures, too.

Introduction

A liquid containing quasi-rigid polar molecules which do not experience specific interactions (as, for example, aprotic molecules) corresponds to the parent model for dielectric relaxation processes which is based on the assumption of rotational tumbling of single polar entities. From hydrodynamic considerations Debye [1] estimated the dielectric relaxation time τ to be proportional to the viscosity η,

$$\tau = \frac{4\,\pi\, r_{\mathrm{eff}}^3}{k\,T}\,\eta\,, \tag{1}$$

where r_{eff} is the effective radius of the tumbling entity. Experimental data, at least for relatively small molecules, were found to deviate from that estimation not only in the absolute values but also in showing a sublinear $\tau(\eta)$-dependence of the $\tau \sim \eta^a$ type with $a < 1$ [2–5]. The correlation

$$\tau = \tau_0 \left(\frac{\eta}{\eta_0}\right)^{(r_{\mathrm{eff}}/r_0) - k_0} \tag{2}$$

was deduced from a wealth of experimental material, comprising pure liquids as well as mixtures with nonpolar diluents [6–8]. The quantities indexed ‘0’ are empirical parameters: $\tau_0 = 0.655$ ps, $\eta_0 = 1.7 \cdot 10^{-4}$ mPa s, $r_0 = 0.6$ nm and $k_0 = 0.27$ (20 °C) [7, 8].

A marked deviation from the ‘normal’ relaxation behaviour described by (2) may be indicative of specific effects. This is particularly the case if the relaxation time τ does not even change in a parallel manner with the viscosity η. Examples of quasi-rigid, aprotic molecules which show such an extreme anomaly are sparse. Till now, it has been found for dilution series of N-cyanopiperidine and N-cyanopyrrolidine with the nonpolar, ‘inert’ component tetrachloromethane, where τ passes through a maximum though η changes monotonously [8]. The purpose of the present communication is to describe another system exhibiting a similar peculiarity, a hint at which could be gathered from previous work [9], namely tetrachloromethane (CCl_4)-dimethylsulfoxide (DMSO) mixtures.

Experimental

We have studied the dynamic dielectric properties of the CCl_4–DMSO system by measuring the frequency dependence of the complex permittivity, in particular of its imaginary part $\varepsilon''(\omega)$, at 20 °C. For moderately concentrated mixtures and the pure liquid DMSO (DMSO mole fraction $x \approx 0.3$ to 1), the instrumentation available for high loss liquids (frequencies between some ten MHz and 72 GHz) facilitated measurements over the whole relaxation spectrum. The $\varepsilon''(\omega)$ data could satisfactorily be described by a single Debye function, the fitting parameters being the relaxation time τ and relaxation strength S. For the dilute solution range ($x \approx 0.003$ to 0.05), on the other hand, the available apparatus had too low a frequency limit (below 10 to 12 GHz, depending on sample absorption) to define the $\varepsilon''(\omega)$ maximum. In that case a Debye function was fitted to the lower frequency data, assuming that the relaxation strength equals the separately measured static-optical permittivity difference.

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The viscosity was determined for the whole composition range with capillary viscometers, and the density with pycnometers or a Mohr balance or a Paar vibrating tube densimeter.

Results

To illustrate the peculiar relaxation behaviour of the system, Fig. 1 shows τ vs. η together with two lines according to (2). In the higher concentration (higher viscosity) range τ and η vary in *opposite* sense, which is quite unusual. This leads to a positive 'τ excess' in the medium concentration range. As in the above mentioned examples [8], that behaviour of DMSO is observed only with CCl_4, not with other nonpolar mixture components studied so far. Figure 2 shows some further quantities for comparison which all do not exhibit extraordinary features. The apparent moment μ_{app} was calculated from the static-optical data (*viz.* putting $\varepsilon_\infty = n^2$) by use of the Onsager relation (or the corresponding Guggenheim relation in case of very diluted systems). As customary, the excess viscosity is defined by

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (3)$$

and the excess molar volume V^E by

$$V^E = x_1\, M_1 \left(\frac{1}{\varrho} - \frac{1}{\varrho_1}\right) + x_2\, M_2 \left(\frac{1}{\varrho} - \frac{1}{\varrho_2}\right). \qquad (4)$$

Concerning V^E, similar (negative) values have been reported also for 25 °C [10].

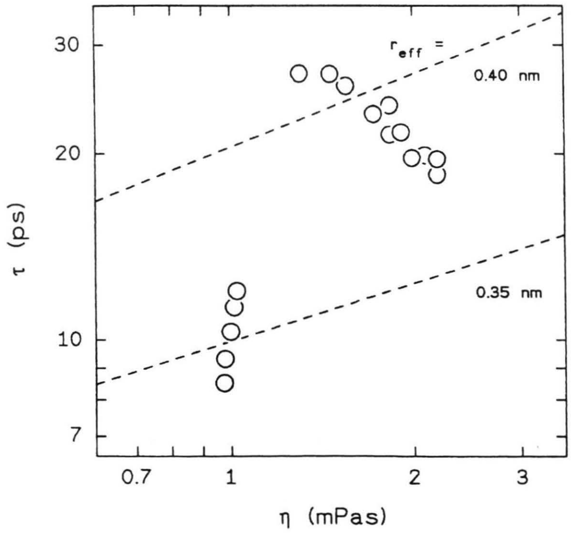

Fig. 1. The DMSO/CCl_4 system: Relaxation time τ against viscosity η (double log representation). Viscosity increases monotonously with increasing DMSO mole fraction x. Data in the left part correspond to $x = 0.0035$ to 0.045, data in the right part to $x = 0.3$ to 1 (including some values from [12]). The straight lines represent (2) for exemplary effective radii r_{eff}.

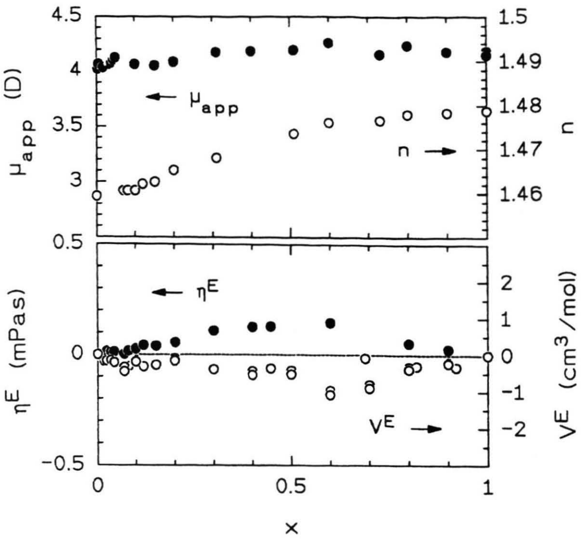

Fig. 2. Some properties of the DMSO/CCl_4 system against DMSO mole fraction x. – Above: Apparent (Onsager) moment μ_{app} (full symbols) and refractive index n (open symbols). – Below: Excess viscosity η^E after (3) (full symbols) and excess molar volume V^E after (4) (open symbols).

Discussion

Since (2) describes merely a correlation, the effective radii appearing in that equation are to be understood as rough estimates. Nonetheless it seems significant that the relaxation time of pure DMSO is somewhat longer than to be expected from its radius, which from space filling molecular models is estimated to be $r_{eff} \approx 0.33$ nm. This is perhaps because some dipole–dipole interaction is operative which delays the molecular tumbling motion but does not lead to the formation of long-lived 'complexes'. In the dilute solution limit, on the other hand, τ is consistent with the model value of r_{eff}. It should be stressed in this context that for the two comparable examples mentioned above, that is N-cyanopiperidine and N-cyanopyrrolidine in CCl_4 [8], the effective radii deduced from the relaxation time are in accord with molecular dimensions in both the pure liquid and the dilute solution limit. Thus the effects causing the relaxation time of pure DMSO to appear longer than expected cannot be essential for the anomalous relaxation behaviour in mixtures with CCl_4. They may therefore remain disregarded here.

Keeping the comparable examples in mind, it seems permissible to start from the assumption that the relaxation times in the pure liquid and in the dilute solution limit are explicable. One has then to discuss only the peculiar τ excess in the medium mixture range, *viz.* a feature with the general character of a positive τ deviation which vanishes for the limiting mixture compositions.

It may be seen from the effective radii given in Fig. 1 that the maximum of τ is not high enough to be ascribed to the tumbling motion of any kind of long-lived (molecule-like) associated species, neither self nor hetero-associated DMSO species. The nearly constant apparent moments (Fig. 2) point in the same direction. Thus one has to invoke CCl_4–DMSO interactions of dynamic character, perhaps leading to some kind of transient 'associates'. The positive sign of η^E and the negative sign of V^E (Fig. 2) as well as the isentropic compressibility (from ultrasonics [11]) are indicative of additional attracting interactions in the medium mixture range, too.

The remainder of this discussion section will deal with some qualitative considerations concerning the minimum number of molecules involved in, and the nature of, those interactions.

Some simple assumptions may be made to describe the τ excess as originating from CCl_4–DMSO interactions. We assume that $CCl_4 = A$ and $DMSO = B$ form a relaxing moiety $A_a B_b = C$. Since it was already concluded above that C is unlikely to be a long-lived 'complex', its relaxation may be governed by internal motions, that means motions of its polar B constituents, and/or by the lifetime of B molecules in the transient 'associates'. The experimental findings suggest that the respective relaxation time should be longer than the time expected for single B type molecules according to (2), lengthened, however, not too much, so that the superposition of Debye type functions attributable to the single molecules and to the relaxing moieties results in a function of practically Debye type again. Then the observed relaxation time τ will be a weighted average of the times characterizing the single molecule tumbling motion and the relaxation of the assumed moieties. The τ excess as compared to the 'normally' expected value will be an indicator of the fraction ξ of B type molecules which are involved in the C type moieties; there may be even a proportionality between both. The quantity ξ as a function of the mixture composition (DMSO mole fraction x) shall briefly be regarded.

Having presupposed the equilibrium

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons \mathrm{C}; \quad \mathrm{C} = \mathrm{A}_a \mathrm{B}_b, \tag{5}$$

the concentration c_C of relaxing moieties C can be calculated according to the law of mass action,

$$\frac{c_C}{c_A^a \, c_B^b} = K, \tag{6}$$

from the known total concentrations $c_{A,0} = c_A + a c_C$ and $c_{B,0} = c_B + b c_C$ of A and B, respectively. (K is the equilibrium constant.) The fraction ξ is defined as

$$\xi = \frac{b \, c_C}{c_{B,0}}, \tag{7}$$

whereas the mixture composition is described by

$$x = \frac{c_{B,0}}{c_{A,0} + c_{B,0}}. \tag{8}$$

Here we are not interested in details of the function $\xi(x)$ as obtainable numerically from (6) but give only the necessary and sufficient conditions that $\xi(x)$ be of the same general character as the τ excess, which implies that

$$\xi(x) \to 0 \quad \text{if} \quad x \to 0, 1. \tag{9}$$

This is the case if the conditions

$$a \geq 1, \quad b \geq 2 \tag{10}$$

are met. Consequently, the presumed C moieties must be pictured by at least one CCl_4 plus two DMSO molecules interacting with each other.

Concerning the nature of interactions, it may be noticed that in the anomalous cases observed so far one mixture component has a strong dipole moment (as DMSO), which leads to the expectation of electrostatic effects. With regard to the τ excess, however, direct dipole–dipole interactions have already been ruled out. Dipole induced dipole interactions are conceivable, but since (*i*) tetrachloromethane is comparable in its mean polarizability (as obtained from the molar refraction in the liquid state) to many other organic molecules while the anomaly is observed only with CCl_4, and since (*ii*) other highly polar molecules behave 'normal' in CCl_4, this assumption is unlikely to be tenable. It appears that the anomaly should be put down to more specific, 'chemical' rather than general, 'physical' properties. Donor-acceptor interactions may play a role; DMSO is known to act as a strong electron pair donor (donor number for DMSO: 29.8, for CCl_4: 0).

In summary, dielectric spectroscopy seems to be a suitable tool to reveal specific interactions as in the present and related examples. However, in consideration of the fact that only few dielectrically anomalous systems have been found hitherto, there remains uncertainty as to the origin of the peculiar relaxation behaviour.

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