A Dielectric Relaxation Study of Diethylsulfoxide/ Tetrachloromethane Binary Mixtures

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Z. Naturforsch. **56a,** 785–787 (2001); received September 27, 2001

The dielectric spectra of diethylsulfoxide (DESO)/tetrachloromethane mixtures have been measured from 0.5 to 72 GHz at 20 °C. On the basis of the relation between the relaxation time and the DESO concentration a complex formation between DESO and tetrachloromethane is suggested.

Key words: Association; Dielectric Spectroscopy; Liquids.

Introduction

Diethylsulfoxide (DESO), like dimethylsulfoxide (DMSO), has unique physicochemical properties [1, 2] and could find biomedical applications [3]. The relatively long relaxation time obtained from dynamic dielectric measurements indicates the occurence of strong associative effects in pure DESO [1], even stronger than in DMSO. Moreover these results lead to the conclusion that not only dipole-dipole interactions between SO groups but also intermolecular hydrogen bonds of the type SO···HC are responsible for self-association of DESO molecules.

It is known that CCl_4 reveals an ability to form charge-transfer complexes with various electron-donor organic compounds [4, 5]. Such a possibility has also been considered for DMSO [6]. Early, on the basis of dielectric relaxation measurements on the DMSO/CCl_4 system it was concluded that some kind of transient 'associates', or in other words, donor-acceptor complexes between molecules of DMSO and CCl_4 could be formed [7]. Indeed, our re-investigation of the dielectric properties of the DMSO/CCl_4 system has shown that the relaxation time τ exhibits a maximum at a mole fraction $x_{DMSO} = 0.5$ (with $\tau \approx 24$ ps). These results confirm, on one hand, the formation of DMSO–CCl_4 complexes with 1 : 1 stoichiometry and show, on the other hand, that those complexes are relatively short-living.

In view of the results on DMSO/CCl_4 it seemed worthwhile to study also the DESO/CCl_4 system. In the present work the dynamic dielectric properties of the latter have been investigated in order to gain information on self-association of DESO molecules as well as on complex formation between molecules of DESO and CCl_4.

Experimental

The dielectric loss spectra $\varepsilon''(\nu)$ of the systems DESO/CCl_4 and DMSO/CCl_4 were measured at 20 °C in the frequency range from $\nu = 500$ MHz up to 72 GHz, using various apparatus. The DESO/CCl_4 mixtures were studied over the mole fraction range $x_{DESO} \approx 0.1$ to 1, and the DMSO/CCl_4 mixtures from $x_{DMSO} \approx 0.3$ to 1. The conductivity was determined with a conductivity meter 'Jenway 4330', and the viscosity was measured with a capillary viscometer. DESO and DMSO were previously dried over anhydrous sodium sulfate, then over barium oxide, and finally distilled under vacuum. Tetrachloromethane was used after distillation.

Results and Discussion

The density d, conductivity κ, viscosity η and refractive index n_D of DESO/CCl_4 for the whole concentration range of the mixtures are summarized in Table 1. For comparison the corresponding data for DMSO/CCl_4 are also presented.

As can be seen from Table 1, the conductivity of pure DESO as well as of its solutions is higher than that of DMSO, whereas the values of the viscosities are closely similar. One may suppose that the participation of hydrogen atoms of the α-CH_2 group in chain intermolecular associates causes that increase of conductivity.

Table 1. Some properties of the binary mixtures DESO/CCl$_4$ (**a**) and DMSO/CCl$_4$ (**b**) against mole fraction of dialkylsulfoxide x_{DASO} at 20 °C: Density d, viscosity η, conductivity κ, and refractive index n_{D}.

x_{DASO}	d g/cm^3		η mPa s		κ μS/cm		n_{D}	
	a	**b**	**a**	**b**	**a**	**b**	**a**	**b**
0.0	1.58	1.58	0.95	0.95	0.016	0.016	1.4606	1.4606
0.1	1.53	*	1.08	*	0.026	*	1.4642	*
0.2	1.48	*	1.25	*	0.81	*	1.4680	*
0.3	1.43	1.48	1.43	1.44	2.52	0,50	1.4703	1.4650
0.5	1.31	1.42	1.78	1.69	5.63	1.23	1.4736	1.4725
0.7	1.19	1.31	2.07	1.96	8.29	2.23	1.4735	1.4763
0.8	1.13	1.25	2.17	2.09	9.77	2.73	1.4735	1.4763
0.9	1.08	1.20	2.23	2.26	11.27	3.30	1.4725	1.4761
1.0	1.01	1.10	2.31	2.37	13.07	4.00	1.4715	1.4755

* These data are omitted because of heterogeneity of DMSO/CCl$_4$ observed at $x_{\mathrm{DMSO}} \approx 0.1 \cdots 0.2$.

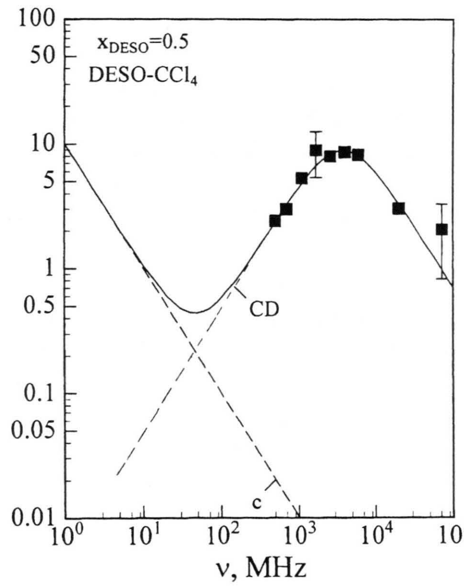

Fig. 1. Dielectric loss spectrum, ε'' against frequency ν, for the binary DESO/CCl$_4$ mixture with $x_{\mathrm{DESO}} = 0.5$ (double log plot). – c: Conductivity contribution; CD: Cole-Davidson type component.

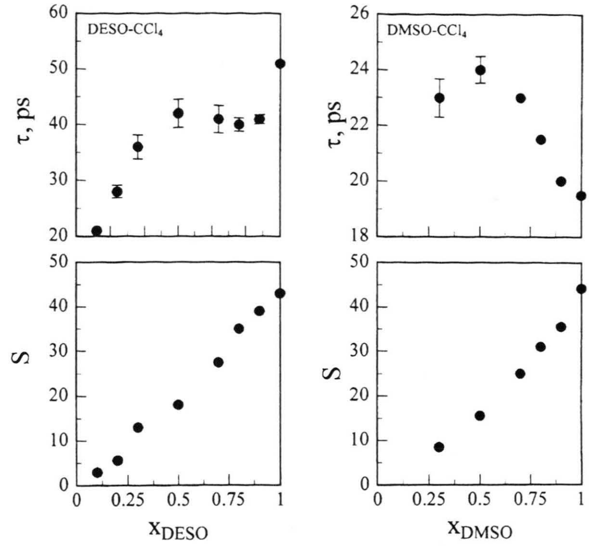

Fig. 2. Relaxation parameters τ and S for the binary mixture systems DESO/CCl$_4$ and DMSO/CCl$_4$ against mole fraction of dialkylsulfoxide.

Figure 1 shows the dielectric loss spectrum, viz. ε'' against frequency ν, for a typical DESO/CCl$_4$ mixture. Apart from the conductivity contribution $\varepsilon'' = \kappa/(2\pi\varepsilon_0\nu)$, the spectrum can be described by a relaxation contribution of Cole-Davidson (CD) type, but ony slightly broadened in comparison to a Debye type curve. A corresponding analysis is possible for all mixtures studied. The CD character increases (the skewness parameter β decreases) with increasing mole fraction x_{DESO}.

The relaxation parameters, viz. relaxation times τ and relaxation strengths S, for both binary systems are represented in Figure 2. The CD parameter β changes from 1 (i.e. Debye type) for low DESO concentrations to 0.88 for pure DESO [1].

Like DMSO/CCl$_4$ [7], also in the case of DESO a deviation from the well-known correlation between relaxation time τ and viscosity η is found inasmuch as the relaxation time does not change in parallel manner with the viscosity. This striking observation, which seems to be peculiar to the systems studied here, points to the occurence of specific interactions between dialkylsulfoxide (DASO) and CCl$_4$ molecules.

Since tetrachloromethane is a non-polar molecule, the observed relaxation component can essentially be ascribed to the highly polar sulfoxide molecules. Accordingly the relaxation contribution becomes more intense as the sulfoxide concentration increases.

An apparent DESO dipole moment μ_{app} was calculated from the static-optical data (viz. putting $\varepsilon_\infty = n_{\mathrm{D}}^2$) by use of the Onsager relation. The apparent moment increases slightly with increasing DESO mole fraction x_{DESO}, roughly to be described as linearly varying from 4.2 to 5.0 D (the corresponding values for DMSO/CCl$_4$ are lower: 3.9 to 4.5 D).

Table 2. Effective radii (r_{eff}) estimated from the relaxation time, and geometrical radii (r_g) for pure DASO and for their 1 : 1 mixtures with CCl_4. The uncertainty of r_{eff} is ±0.05 nm.

	DESO	DESO · CCl_4	DMSO	DMSO · CCl_4
r_{eff}/nm	0.44	0.42	0.38	0.40
r_g/nm	0.34	0.49	0.23	0.48

An interesting feature already mentioned above is the dependence of the relaxation time τ on the mole fraction of DESO or DMSO, Figure 2. The position of the plateau or maximum of τ corresponds to a DASO mole fraction of 0.5. Thus one can conclude that a 1 : 1 complex formation between sulfoxide and tetrachloromethane is a common feature for both the DESO/CCl_4 and DMSO/CCl_4 system. However, as to be seen from Fig. 2 there are some differences between these systems. At $x_{DASO} = 0.5$, the relaxation times are 42 and 24 ps for DESO and DMSO, respectively, whereas at $x_{DASO} = 1$ (pure sulfoxide) the respective values are increased to 51 ps (DESO) but decreased to 19.5 ps (DMSO).

Under the assumption that the relaxation process consists in the tumbling motion of quasi-rigid entities, the relaxation times found may be used for an estimation of the effective radius r_{eff} of those entities. For that purpose an empirical correlation derived from studies on non-associating polar molecules can be used [7]. As it follows from Table 2, the effective radii r_{eff} are not consistent with the geometrical radii r_g. For the pure substances the r_{eff} values are clearly larger than r_g of single DASO molecules, by this indicating self-association. The opposite order, as (within uncertainty limits) apparent for the assumed DASO · CCl_4 complexes (Fig. 3), could be considered a hint at an additional 'chemical' relaxation mechanism acting on those complexes. Such a mechanism, by which the relaxation time is generally influenced also by the lifetime of a 'complex', should be taken into consideration for the DASO self-associates, too. Comparison of the differences between relaxation times of the pure substances and of the 1 : 1 mixtures with CCl_4 gives rise to the suspicion that (unlike DMSO) the self-associates of DESO are long-lived in comparison to the DESO-CCl_4 hetero-associates.

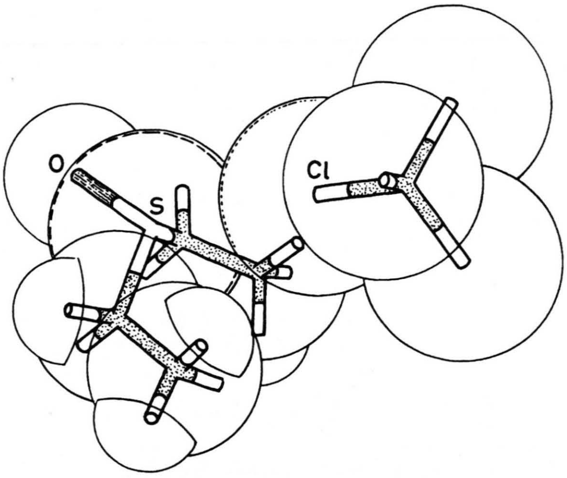

Fig. 3. Space filling model of the DESO · CCl_4 complex.

In conclusion, in case of the DASO/CCl_4 mixtures we can suppose the presence of two competitive processes, i.e. interaction between DASO and CCl_4 and self-association of DASO:

$$\mathrm{DASO} + \mathrm{CCl_4} \rightleftharpoons \mathrm{DASO} \cdot \mathrm{CCl_4}, \quad (1)$$

$$n\mathrm{DASO} \rightleftharpoons (\mathrm{DASO})_n . \quad (2)$$

The more probable DESO–CCl_4 interaction could act via a negative chlorine atom of CCl_4 and the positive sulfur atom of the sulfoxide, $Cl^{\delta-} \cdots S^{\delta+}$. Figure 3 shows the corresponding space filling model of the DESO · CCl_4 complex.

Acknowledgement

This work has been supported by the International Science and Technology Center (ISTC), project No. A–199.

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