Dielectric Relaxation of Diethylsulfoxide

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The dielectric loss spectrum of the title substance has been measured in its pure liquid state between 10 MHz and 72 GHz at 20 °C. In comparison to the Debye function, it is slightly broadened towards the high frequency side. The maximum corresponds to a relaxation time of 51 ps. In view of the molecular size and viscosity, this is relatively long and thus indicative of associative intermolecular effects as in the case of the homologous compound dimethylsulfoxide.

Key words: Association; Dielectric Relaxation; Liquids.

Among organic electron donor compounds not only dimethylsulfoxide (DMSO) but also its nearest homologues exhibit a number of unique physicochemical properties, mostly due to their self-associative structure [1–4]. Dynamic dielectric studies of liquid DMSO [5, 6] as well as its hexadeutero derivative [7] have shown that the relaxation time is relatively long in comparison to other aprotic liquids, indicating some kind of transient associative effect slowing down the reorientational molecular motion. Moreover, it was shown that DMSO does not strictly obey Debye behaviour [5]. Corresponding dielectric data for homologous compounds did not come to our knowledge. Therefore we report here the dielectric relaxation data for diethylsulfoxide (DESO) in its pure liquid state.

The total dielectric loss spectrum $\varepsilon''_{\mathrm{tot}}(\omega)$ was measured at 20 °C over the frequency range from 10 MHz to 72 GHz. After correction for the conductivity contribution $\varepsilon''_{\mathrm{c}}(\omega)=\kappa/(\varepsilon_0\,\omega)$ (κ: dc conductivity; ε_0: electric field constant), the relaxational contribution $\varepsilon''(\omega)=\varepsilon''_{\mathrm{tot}}(\omega)-\varepsilon''_{\mathrm{c}}(\omega)$ appears approximately as a Debye type spectrum but slightly broadened towards the high frequency side (as in the case of DMSO). It can satisfactorily be fitted by either a main plus a minor (higher frequency) Debye type component or, alternatively, by one component of Cole-Davidson (CD) type (with skewness parameter $0<\beta\leq 1$, where $\beta=1$ means Debye type). The relaxation time τ and relaxation strength S according to the latter description are given in Table 1. For comparison, the table presents also the corresponding data for DMSO [7], disregarding here the slight broadening (which could be accounted for by a CD spectrum with $\beta=0.88_8$ [6]). The $\varepsilon''(\omega)$ maximum of the DESO spectrum corresponds to $\tau\beta=51$ ps. The same value is found for the main term is two Debye type components are used for fitting.

Table 1. Relaxation time τ, relaxation strength S, and CD parameter β for DMSO and DESO at 20 °C. (* Main Debye term only.)

	τ (ps)	S	β
DMSO [7] *	19.5	44.2	–
DESO	58	41.7	0.88

The relaxation time may be compared with values found with quasi-rigid, non-associating polar molecules using an empirical correlation between τ, the effective molecular radius r_{eff} and the viscosity η [8]. The effective radius for DESO estimated from $\tau\beta$ according to this correlation is $r_{\mathrm{eff}}\approx 0.44$ nm, that is much larger than the DESO molecular radius of about 0.35 nm. The corresponding values for DMSO differ in a similar manner, they are 0.37 and 0.25 nm, respectively [9]. In other words, the relaxation times of both dialkylsulfoxides are longer than to be expected, thus transient associative effects are likely to be operative in DESO, too. This is in accord with spectroscopic [2, 3] and X-ray structural [4] investigations which have shown that DESO tends to form an even more associative structure than DMSO. Probably not only dipole-dipole interactions between the SO groups but also intermolecular hydrogen bonding of the type SO · · · HC are responsible for self-association of DESO molecules. This conclusion is supported by the higher conductivity of DESO as compared to DMSO [1] although their viscosities do practically not differ ($\eta\approx 2.2$ mPa s).

Dielectric relaxation studies of aqueous and non-aqueous solutions of DESO will be carried out in the future.

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