Dielectric Relaxation of Hexadeutero Dimethylsulfoxide

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The dielectric relaxation parameters of the title substance (DMSO-d_6) in its pure liquid state are determined from measurements up to 72 GHz at 20 °C in comparison to protonated DMSO. While the relaxation strengths do not differ, the relaxation time of DMSO-d_6 is significantly longer (21.3 ps) than that of DMSO (19.5 ps).

Key words: Dielectries; Isotopic Substitution; Liquids; Relaxation.

Dimethylsulfoxide (DMSO) is a liquid exhibiting some peculiar physical properties which point to specific intermolecular interactions, the nature of which is a matter of continuing debate. Such a peculiarity is also found in the dielectric relaxation behaviour inasmuch as the relaxation time is longer than to be expected from a comparison with other liquids consisting of quasi-rigid molecules for which the main relaxation contribution is due to the reorientational tumbling motion of single molecules [1]. Thus some kind of transient associative effect is likely to be operative, on average slowing down the reorientational motion (note that, in principle, dielectric spectroscopy observes molecular collectives rather than single molecule motion). In that context it seems worthwhile to regard the alteration of the relaxation behaviour caused by isotopic substitution H → D, thus comparing DMSO with DMSO-d_6. For a small, rigid molecule like water it is known that deuteration leads to a noticeable increase in relaxation time τ [2]: At 20 °C, the ratio for deuterated/protonated water is $\tau(D)/\tau(H) = 1.25$. Concerning DMSO, the far-infrared absorption spectra of DMSO and DMSO-d_6 have been studied with respect to the librational modes effective in that region [3], but such a comparison has not yet been published for the "classical" dielectric relaxation process, viz. the microwave region. Therefore we report here the respective relaxation data.

We have studied both DMSO and DMSO-d_6 (Merck, deuteration >99%) at 20 °C over the frequency range between 90 MHz and 72 GHz, paying particular attention to the differences in the (negative) imaginary part of permittivity, ε'', in dependence on the frequency ν. In both cases, the $\varepsilon''(\nu)$ spectra can satisfactorily be fitted by a Debye function, disregarding the indication of an additional but very weak contribution on the high frequency side of the spectrum. The parameters of the main relaxation region, that is the relaxation time τ and relaxation strength S, are given in Table 1.

Table 1. Relaxation time τ and relaxation strength S for DMSO and DMSO-d_6 at 20 °C.

	τ ps	S
DMSO	19.5	44.2
DMSO-d_6	21.3	44.2

In view of the only slight increase of molar concentration on deuteration (less then 0.5 percent) it is not unexpected that the relaxation strength S stays practically unaltered. The relaxation time τ, on the other hand, is significantly increased: $\tau(D)/\tau(H) = 1.09$. It is interesting to compare that finding with NMR results from which the correlation time τ_c of the single molecule tumbling motion can be obtained. The respective ratio is $\tau_c(D)/\tau_c(H) = 1.12$ [4]. Even taking into account experimental uncertainties, this value seems to be slightly larger than $\tau(D)/\tau(H)$. If so, this would be not inconsistent with the above-mentioned conjecture that the dielectrically observed process comprises some kind of associative effect, which here may cause a reduction of the collective characteristic $\tau(D)/\tau(H)$ in comparison to the single molecule isotopic correlation time ratio.

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