

Spin Probe Studies on the Dynamic Structure of Dimethyl Sulfoxide—Water Mixtures

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The rotational diffusion data of free nitroxyl radicals in dimethyl sulfoxide (DMSO) indicated two transition temperatures at which changes in intermolecular arrangement occurred: There was first a steep decrease in the rotational correlation time (τ) beginning at the melting point 18.5°C. Then a steep decrease in τ at 55°C. The latter was deduced to arise from the dissociation reaction of the DMSO ordered structure.

When τ was plotted as a function of the molar composition of the DMSO—water mixture at constant temperature, ($T = 60^\circ\text{C}$) two τ -maxima were found: one at a DMSO—water ratio of 1:2 and another at a ratio of about 1:1. The very weak nature of the association complexes of DMSO with water seems to be in agreement with the experimental results obtained.

Several opinions have been given regarding the structure and kind of the bonds that are established between water and dimethyl sulfoxide (DMSO). Thus, Cowie and Toporowski assumed the formation of a stoichiometric adduct $(\text{H}_2\text{O})_2\cdot\text{DMSO}$,¹ whereas Kenttämää and Lindberg and co-workers^{2,3} proposed the presence of non-specific dipole-dipole or ionic type bonds rather than definite complexes. From NMR-studies Drinkard and Kivelson concluded in favour of mixed hydrogen and dipolar bonding.⁴ Later Rallo *et al.*⁵ inferred from calorimetric measurements an interaction without the formation of stoichiometric compounds. Recent NMR-chemical shift and Raman-spectroscopic measurements^{6,7} seem to support the non-stoichiometric structural model.

Furthermore, the measurements of Salonen,⁸ among others, of the infrared spectra of DMSO containing traces of water indicate that the water molecules are subjected to strong forces tending to straighten the molecules and the transverse motion of the molecules is markedly hindered. In addition a polymer chain structure of DMSO seems to be prevalent.^{2,9} From Raman-spectra of DMSO—water mixtures Scherer and co-workers⁷ have deduced a simple structural model in which it is assumed that water can be separated into two major species: one is symmetrically hydrogen bonded and the other asymmetrically hydrogen bonded.

Such a structural model presents several unsolved problems, especially with regard to the formation, breaking, and rotation of secondary valence bonds. In a previous report Lindberg and Hakalax¹⁰ calculated an approximate dielectric relaxation time τ_d equal to 7×10^{-12} s for DMSO-benzene mixtures. From viscosity data¹¹ the relaxation time was estimated to be 3×10^{-11} s, in rough agreement with the value above.

The above data indicate that there should be a relaxational motion of DMSO—water mixtures in the microwave region. As the recently developed spin probe method seems to be especially suitable for accurate resolution of dynamic and microviscometric problems in this region, the present authors have studied the DMSO—water system by using stable nitroxyl radicals as labels and their ESR spectra as sensitive indicators of environmental effects.

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EXPERIMENTAL

3-Carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl (I) was prepared by the method of Rozantsev *et al.*¹² Commercial DMSO was purified by distillation *in vacuo* and repeated recrystallization to a melting point of 18.52°C.¹³ Freshly distilled water was used as such.

The binary mixtures were made by weighing and traces of radical I were added. At the concentration of probe used, (8×10^{-4} M), the spin-spin exchange was absent. All measurements were made in a time interval very short as compared to the decay time of the radicals in solution.

The ESR spectra were obtained on a Varian E-4 spectrometer operating at a microwave frequency of 9.5 GHz, *i.e.* about 3.2 cm. The magnetic field was modulated with an amplitude less than one sixth of the line-width. The microwave power was 1 mW to avoid saturation effects. The measurements were made, where possible, in the temperature range 223–423 K, a Varian E-257 variable temperature accessory with an accuracy of ± 2 K, calibrated with an iron/constantan thermocouple, was employed.

RESULTS

It has been found that under conditions where intermolecular interactions between radicals are eliminated, the rotational frequencies of radicals of small molecules as indicated by ESR spectra are affected by the motions of the surrounding molecules.^{14,15}

In Fig. 1 are given some typical examples of the ESR spectra of free radicals intermixed with DMSO–water solutions at different temperatures. At room temperature the motion is so rapid that an isotropic spectrum is obtained.

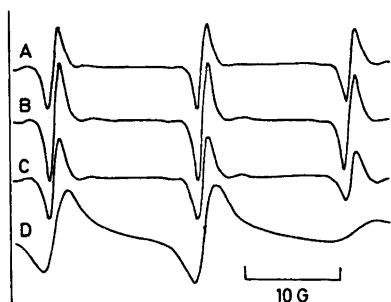


Fig. 1. ESR spectra of pyrroline nitroxyl radicals (I) in DMSO–water solution ($x_{\text{DMSO}} = 0.25$) at different temperatures. (A) $T = 55^\circ\text{C}$; (B) $T = 27^\circ\text{C}$; (C) $T = 0^\circ\text{C}$; (D) $T = -50^\circ\text{C}$.

However, with decreasing temperature and increasing viscosity it goes gradually over to a non-isotropic spectral pattern. A marked change in spectral behaviour is observed only at the respective melting points in pure DMSO and water.

DISCUSSION

A more quantitative picture of the results was obtained by estimating the rotational correlation times (τ) of the radicals from the ESR spectra. Here it is significant that the values of τ also are related to the microviscosity of the surroundings of the spin probe. In the region of rapid rotations ($\sim 5 \times 10^{-9} - 5 \times 10^{-11}$ s), τ could be calculated by the alternative eqns. (1) and (2) which are based on Kivelson's theory.¹⁶⁻¹⁷

$$\tau_1 = 8.7 W_0 [(h_0/h_1)^{\frac{1}{2}} - (h_0/h_{-1})^{\frac{1}{2}}] \times 10^{-10} \text{ s} \quad (1)$$

$$\tau_2 = 7.9 W_0 [(h_0/h_1)^{\frac{1}{2}} + (h_0/h_{-1})^{\frac{1}{2}} - 2] \times 10^{-10} \text{ s} \quad (2)$$

Here W_0 is the line width (Gauss) of the centre line in the ESR spectrum and h_1 , h_0 and h_{-1} are the intensities of the low, centre, and high field components. In general a mean value of τ_1 and τ_2 is used.¹⁷ The numerical parameters are dependent on the magnetic field and on the \bar{g} and \bar{T} tensors for which values given by Ohnishi *et al.* were used.¹⁸ The difference between the two values of τ was, as a rule, less than 10 % and they can be roughly explained as the time required for a nitroxyl radical to turn a complete rotation around its axis. The calculation of τ is reviewed more thoroughly elsewhere.^{19,20} A relative accuracy of about ± 2 % was achieved, as deduced from the variation in the experimental data.

Although there is still not found any simple physical connection between the correlation times obtained by spin relaxation measurements and macroscopically observed viscosities, it is evident that the rotation of the spin probe must be strongly influenced also by the viscous behaviour of neighbour molecules.^{19,20} This is also manifested by the approximate validity of the Stokes-Einstein relation,

$$\tau = 4\pi\eta r^3/3kT \quad (3)$$

for the tumbling probe in a viscous medium. Therefore it is possible, at least qualitatively,

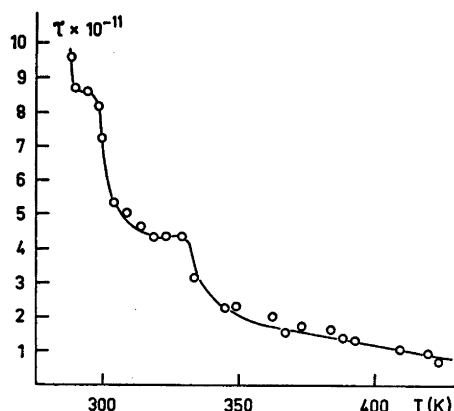


Fig. 2. Rotational correlation time τ or radicals in DMSO vs. temperature.

to correlate structural changes in the surrounding medium with changes in correlation times of the spin probes. A similar correlation has also been observed between δ and γ relaxations and spin label and probe data.^{26,27}

A closer inspection of the results presented reveals therefore the following details regarding the dynamic (microviscosimetric) structure and thus also the structural changes of the surroundings of the probe.

Pure DMSO. In Fig. 2 the correlation time τ in pure DMSO is plotted as a function of temperature in the range 285–425 K (*i.e.* from +10 to +150°C). The curve obtained shows a steep decrease beginning at the melting point, 18.5°C, and ending in a plateau at

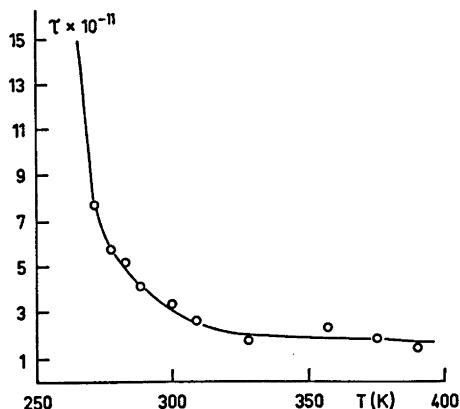


Fig. 3. τ of radicals in H₂O vs. temperature.

about 40°C. There is another steep decrease at about 55°C, again followed by a linear, slow decrease in the whole last part of the region investigated, *i.e.* 60–150°C.

One may interpret the first transition region from 18.5°C onwards as corresponding to the breaking up of the ordered network into an assembly of free DMSO chains. Such a breaking up is also indicated by dipole and calorimetric measurements.^{3,9}

The similarity of the intermolecular frequencies in the neutron elastic scattering spectra of solid and liquid DMSO²¹ suggests that the degree of association arising from dipole interactions in liquid DMSO is high and that there is a quasisolid ordering in liquid DMSO. From IR spectra of solutions of DMSO in carbon tetrachloride, Figueroa, Roig and Szmant²² concluded that dimethyl sulfoxide exists primarily in the form of cyclic dimers in the concentration range from 0.1 to 0.3 M, but may exist in the form of chains at higher concentrations. These conclusions are in accordance with the data of Lindberg, Kenttämää and Nissema.⁹ It seems evident therefore that the second transition region mentioned above corresponds to a dissociation reaction of the DMSO ordered structure and that above 60°C DMSO is chiefly present as a monomolecular species, which also is manifested by a smaller microviscosity.

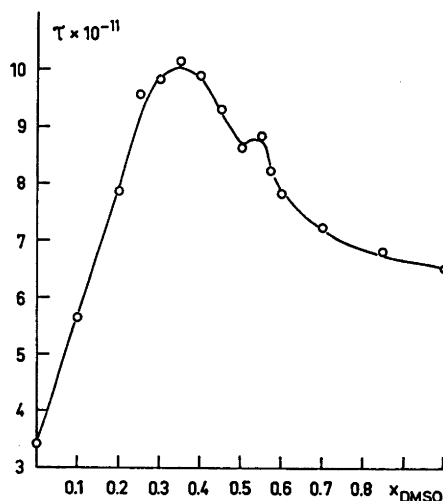


Fig. 4. τ of radicals in DMSO—water solutions of different molar compositions.

Pure water. In Fig. 3 the correlation time τ for pure water is plotted as a function of temperature in the range from -50 to $+117^\circ\text{C}$. It is evident that the steep decrease in τ sets in at the melting point. It is directly followed by the uniform liquid region up to the boiling point. The structure of water has been reported by previous authors^{23,24} and is, as expected, markedly different from that of pure DMSO. The three-dimensional hydrogen bond network of H_2O gives the substance quite other dynamic properties than does the stiff chain structure of DMSO, which is also deduced from spectral data.^{3,7-8}

DMSO—water mixtures. The correlation times in DMSO—water mixtures of various molar composition were measured at -50 , -17 , $+15$, $+27$, $+40$, $+55$, $+84$, $+103$, and $+117^\circ\text{C}$. In Fig. 4, by way of example, the correlation times in DMSO—water mixtures of various molar composition at 27°C are plotted. From the curves it was found that at all temperatures investigated a marked relaxation time maximum is observed in the region of 1:2 DMSO—water molar composition. In addition, a corresponding maximum at about 1:1 DMSO—water molar composition is observed at lower temperatures. The intensity of the latter maximum in respect to the former decreases rapidly with increasing temperature and is only slightly observable at higher temperatures, *i.e.* $> 60^\circ\text{C}$. Therefore, the above result also indicates the weakness and instability of the latter complex in respect to the former.

Acknowledgement. The authors are grateful to the National Research Council for Sciences and to the Finnish Society of Science for financial aid.

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Received May 25, 1974.