

## Notes on Solvate Formation in Dimethyl Sulphoxide-Water Mixtures

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Thermodynamic, dielectric and viscosimetric data<sup>1</sup> indicate a very strong interaction between dimethyl sulphoxide (DMSO) and water, whereas no definite complex formation has been detected by cryoscopic measurements<sup>2</sup>. Furthermore, infrared spectroscopic investigations of DMSO containing traces of water<sup>3</sup> show that the water molecules are subject to strong forces tending to straighten the molecules and the transverse motion of the molecules is markedly hindered. To collect more detailed information on the nature of the solvates formed in DMSO-water mixtures, we have investigated the Raman spectra of this system over the whole range of concentrations at room temperature.

An inspection of the recorded spectra showed that all previously reported Raman bands of pure DMSO<sup>3,4</sup> except the rotational bands mentioned in Ref. <sup>3</sup> were present. The intensities of the Raman bands decrease continuously with increasing water content of the mixture. In the case of the S=O stretching frequency (located at 1046 cm<sup>-1</sup> in the spectrum of pure DMSO), a similar trend was observed, but the band splitting caused by hydrogen bond formation previously noted in the infra-red spectra of the DMSO-phenol system<sup>5</sup> was not detected. In addition, the S=O stretching frequency shifted to lower frequencies with increasing water content, in contrast to the weak, but definite increase of the frequency of most of the other bands in the spectrum under the same conditions. From Fig. 1 it is evident that the frequency of the S=O band is an approximately linear function of the dielectric constant of the solution. The extrapolated value of the S=O frequency at infinite dilution in water is about 1010 cm<sup>-1</sup>.

It is not likely that the S=O stretching frequency of the DMSO-water hydrogen bond complex is forbidden in the Raman spectrum, especially as a corresponding band splitting is observed in the Raman

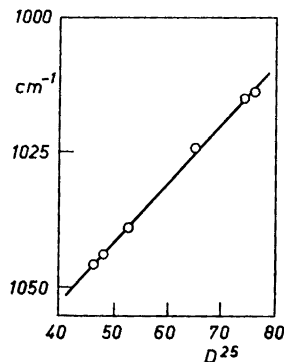


Fig. 1. System DMSO-H<sub>2</sub>O. S = O stretching frequency as a function of dielectric constant at 25°C.

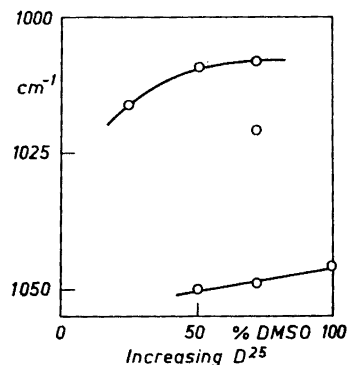


Fig. 2. System DMSO-acetic acid. S = O stretching frequency as a function of composition at 25°C.

spectra of DMSO-acetic acid mixtures where a definite hydrogen bond complex has been detected (*cf.* Fig. 2 and Ref. <sup>6</sup>). It seems therefore natural to conclude that the absence of the mentioned splitting in the spectra of DMSO-water mixtures must be a real one and that the molecular interaction in this case, especially in solutions of high water content, is primarily of a very strong dipole-dipole and possibly partly ionic type. This explanation is also in agreement with the kinetic anomalies recently observed by Holmes, Kivelson and Drinkard<sup>7</sup> in their NMR-investigations on DMSO-water mixtures and with evidence from acid-base equilibria studies<sup>8</sup> and kinetic solvent effects<sup>9</sup>.

*Experimental.* The Raman spectra were recorded photographically on Ilford Backed Zenith plates with a Model E 612 Raman spectrograph from Hilger & Watts Ltd., London. The exposure times were 30 min.

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Received May 9, 1963.

## NMR-Experiments on Solubilization in Soap Micelles

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To date apparently no investigation has been reported in which the high-resolution NMR technique has been used for studying soap solutions containing micelles. In this communication, however, some findings will be described which indicate that such investigations may give valuable information concerning the nature and structure of micelles.

Fig. 1 displays the relevant parts of the NMR-spectrum of cetyl pyridinium chloride (CPC) when dissolved in water (a) and methanol (b) to equal concentrations

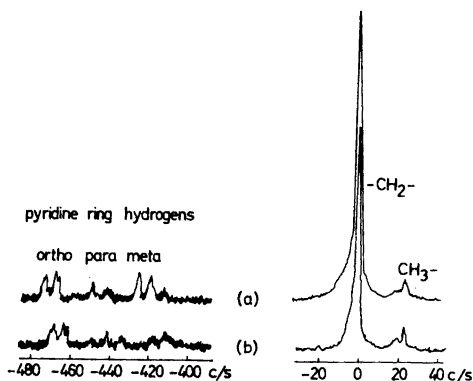


Fig. 1. The spectrum of cetyl pyridinium chloride (except the  $\alpha$ - $\text{CH}_2$ -peak) in water (a) and methanol (b).

(0.1723 M). In these solvents, the triplet of the  $-\text{CH}_2$ -group next to the pyridine ring ( $\alpha$ - $\text{CH}_2$ -) is concealed by the strong water and  $-\text{OH}$  resonance lines. The assignment of the pyridine ring proton peaks was carried out by comparison with the spectrum of methyl pyridinium iodide in water solution and with the thoroughly investigated spectrum of pure pyridine<sup>1</sup>. The critical micelle concentration of CPC in water is, according to the spectrophotometric measurements of Sata and Sasaki<sup>2</sup>,  $0.706 \times 10^{-3}$  M. Because micelles are not formed in methanol, and since a closer examination reveals that the  $-\text{CH}_2$ -peak areas in (a) and (b) are equal to within 2 %, the conclusion must be drawn that it is mainly the hydrogens of the soap molecules in the micelles which contribute to the signal intensity in the case of water solution. The fact that the resonance lines are not much broadened, due to the formation of micelles, may obviously be considered as a consequence of the commonly presumed liquid-like state of micelles in comparatively dilute solutions<sup>3,4</sup>, *i.e.* the interaction between the nuclear magnetic dipoles is effectively averaged as a result of the thermal relative motions of the paraffin chains. However, it may be questioned whether the observed line width could also be accounted for on assuming that the micelle is a microcrystallite, which reorientates under the influence of the thermal fluctuations. Accordingly, from the theory of spin-lattice relaxation given by Bloembergen, Purcell and Pound<sup>5</sup>,