

# Molecular Dynamics in the System Methanol-Dimethylsulphoxide

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*Dedicated to Professor Hitoshi Ohtaki on the occasion of his 60th birthday*

NMR proton relaxation rates of normal and oxygen-17 enriched methanol- $d_3$  in a mixture of 71 mol% methanol and 29 mol% dimethylsulphoxide- $d_6$  (DMSO) were measured as a function of temperature between 298 and 158 K. From these data rotational correlation times of the methanol molecule in the mixture and the oxygen-proton dipolar spin-lattice coupling parameter were obtained. The latter parameter is considerably smaller than the one obtained from neutron diffraction studies of the molecular geometry of methanol. Additionally, deuterium and oxygen-17 relaxation rates were measured over the same temperature range. Using the rotational correlation times obtained from the oxygen-17 induced proton relaxation rates, the quadrupole coupling constant for deuterium was derived; it shows a temperature dependence. Application of the Pople relation yielded the oxygen-17 quadrupole coupling constants, so that oxygen correlation times could be obtained. Comparison of deuterium and oxygen correlation times indicates that the reorientation of the methanol molecule in the methanol/DMSO mixture is anisotropic.

## 1. Introduction

The dynamics of the methanol molecule in the system methanol/dimethylsulphoxide were investigated some time ago by Blicharska, Hertz, and Versmold [1]. Measuring the proton relaxation rates of  $CH_3OD$  dissolved in DMSO- $d_6$  as a function of temperature and frequency, they found fast rotation for the  $CH_3$  group. The results were evaluated on the basis of intra- and intermolecular relaxation theories. The separated intramolecular relaxation rates could describe only the internal rotation of the methyl group in the methanol molecule. To derive the rotational reorientation of the C–O–H unit they needed the framework of the Woessner theory [2, 3, 4]; a satisfactory interpretation with this model could not be achieved. Additionally, strong anisotropic motion of the methanol molecule had to be assumed in order to interpret the experimental results.

It is expected that the dynamics of the methanol molecule are mainly described by the reorientational correlation for the OH bond. Because of hydrogen bonding this correlation time can be considerably longer than the correlation time of the methyl group which describes the internal rotation [5]. It is the pur-

pose of this work to determine the rotational correlation time of the OH vector of methanol in the system methanol/DMSO. This is not a straightforward task since for the interpretation of the proton relaxation in  $CD_3OH$  [6] the reorientational vector is not clearly defined, whereas in the case of deuterium relaxation in  $CH_3OD$  [7, 8], although the direction of the principle axis of the deuterium quadrupole coupling tensor is well defined, the quadrupole coupling constant is not known for the liquid phase. We therefore prefer to obtain the reorientational correlation time for the OH vector from oxygen-17 induced relaxation in  $CD_3^{17}OH$ .

By application of the oxygen-17 method we were previously able to study the dynamics of the hydroxyl groups of water in binary mixtures [9–12], of pure methanol [13], ethanol and propanol [14], of butanol, pentanol and hexanol [15], and of binary mixtures of methanol in carbon tetrachloride and tetrahydrofuran [16, 17]. This method was first introduced by Leyte and coworkers [18, 19] and allows one to obtain reliable values of the rotational correlation time of water. Obviously it can be applied to all OH groups. Determination of the rotational correlation times from the oxygen-17 induced proton relaxation rates is feasible because this relaxation process is predominantly intramolecular and depends directly on rotational

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motion. The accuracy of the rotational correlation times obtained depends strongly on the right choice of the intramolecular OH bond distance. For pure methanol we used a bond length of 99 pm; this gives a correlation time of 5 ps [13] at room temperature. For a mixture of water and methanol the relaxation rate maximum cannot be reached in an accessible temperature range within the liquid phase. The relaxation rate maximum can, however, be attained for the methanol OH group in the methanol/DMSO mixture. The mixture of 71 mol% methanol and 29 mol% DMSO could be cooled down to 158 K without freezing.

With the experimental information obtained from the relaxation rate maximum it is possible to extract not only the rotational correlation time,  $\tau_{\text{OH}}$ , discussed above but also a value for the OH dipolar coupling parameter itself. With this correlation time,  $\tau_{\text{OH}}$ , and the measured deuteron relaxation rate we can then calculate the deuterium quadrupole coupling constant (DQCC) in methanol. This procedure is valid because for the deuteron relaxation rate the relevant vector is along the OD bond. Consequently, the problem of a possible anisotropy in the rotational motion does not arise. This is due to the fact that the principal axis of the electric field gradient tensor at the deuteron lies almost along the OD bond, and its asymmetry parameter is negligibly small [20].

Evaluation of the oxygen quadrupole coupling constant (OQCC) in methanol, using the same procedure as for the deuteron is much more problematic because the direction of the principal axis of the field gradient tensor at the oxygen is perpendicular to rather than along the OH bond, and the asymmetry parameter may be rather large as it is in water, where  $\eta = 0.75$  [19]. To obtain an experimental value for the OQCC we followed Leyte and used a correlation between oxygen-17 and deuterium coupling constants for crystal hydrates and ice observed by Poplett from solid-state NQR [21] (see (6) below). With this OQCC we obtained the rotational correlation time  $\tau_{\text{O}}$  along the principal axis of the oxygen field gradient tensor. A comparison of  $\tau_{\text{D}}$ , which is equal to  $\tau_{\text{OH}}$ , and  $\tau_{\text{O}}$  suggests a reorientational anisotropy of the methanol motion.

## 2. Experimental

Mixtures of 71 mol% methanol and 29 mol% DMSO were prepared by weighing the appropriate

quantities. They were degassed thoroughly by several freeze-pump-thaw cycles. Normal  $\text{CD}_3\text{OH}$  (99.9 atom% deuterium, Aldrich, Steinheim, Germany) and four charges of oxygen-17 enriched methanol were used for these mixtures with dimethylsulphoxide- $\text{d}_6$  (99.0 atom% deuterium, Aldrich, Steinheim, Germany). The isotopic compositions were 6.0, 11.7, 26.8 and 37.5 atom% oxygen-17. The preparation of methanol  $\text{CD}_3^{17}\text{OH}$  from  $\text{H}_2^{17}\text{O}$  was described previously [13]. For the deuteron measurements we prepared a sample with  $\text{CH}_3\text{OD}$  (99.5 atom% deuterium, Aldrich, Steinheim, Germany) and dimethylsulphoxide- $\text{h}_6$  (stated purity 99.9 per cent, Aldrich, Steinheim, Germany). With the same sample we measured the oxygen-17 relaxation rates (natural abundance in oxygen-17). Therefore no isotopic mass correction was needed.

The spin lattice relaxation times were measured for protons at 300.13 MHz using a Bruker CXP-300, for deuterons at 76.77 MHz and oxygen-17 at 67.80 MHz a Bruker AM-500 was used. The temperature range covered was 158–298 K.

## 3. Results and Discussion

From the experimental proton relaxation rates  $R_1^{\text{H}}$  we obtain  $(R_1)_{\text{H}}^{\text{H}}$  and  $(R_1)_{\text{H}}^{\text{O}}$ , the relaxation rates from neighboring protons and the directly bonded oxygen-17, respectively, by a least-squares fit to the equation

$$R_1^{\text{H}} = (R_1)_{\text{H}}^{\text{H}} + X_{17\text{O}}(R_1)_{\text{H}}^{\text{O}}, \quad (1)$$

where  $X_{17\text{O}}$  is the mole fraction of oxygen-17. The values of the  $(R_1)_{\text{H}}^{\text{O}}$  contribution are shown in Fig. 2 for the whole temperature range. This contribution is completely dominated by the intramolecular interaction, which has been shown by theoretical estimates to be about 98% for water [18]. For alcohols it should be even larger since the spin density is lower and the molecular diameter is larger than in water. Therefore we can use the following well-known relation [22] to determine the rotational correlation time  $\tau_{\text{OH}}$ :

$$(R_1)_{\text{H}}^{\text{O}} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{2}{15} \hbar^2 \gamma_{\text{H}}^2 \gamma_{\text{O}}^2 S(S+1) r_{\text{OH}}^{-6} \times \left\{ \frac{\tau_{\text{OH}}}{1 + (\omega_{\text{H}} - \omega_{\text{O}})^2 \tau_{\text{OH}}^2} + \frac{3\tau_{\text{OH}}}{1 + \omega_{\text{H}}^2 \tau_{\text{OH}}^2} + \frac{6\tau_{\text{OH}}}{1 + (\omega_{\text{H}} + \omega_{\text{O}})^2 \tau_{\text{OH}}^2} \right\}, \quad (2)$$

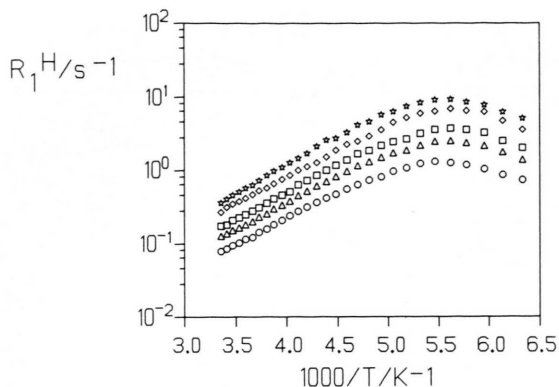


Fig. 1. Proton relaxation rates,  $R_1^H$ , of  $\text{CD}_3^{17}\text{OH}$  in the system 71 mol% methanol and 29 mol% dimethylsulphoxide as a function of temperature for different oxygen-17 mole fractions:  $x = 0$  (○),  $x = 0.06$  (△),  $x = 0.117$  (□),  $x = 0.268$  (◇) and  $x = 0.375$  (★).

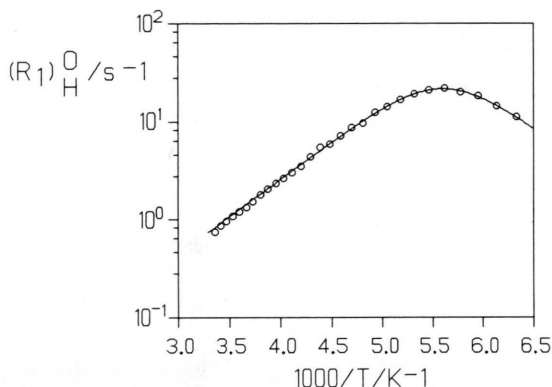


Fig. 2. The oxygen-17 dipolar contribution  $(R_1^O)_H$  to the proton relaxation rate of methanol  $\text{CD}_3^{17}\text{OH}$  in the system 71 mol% methanol and 29 mol% dimethylsulphoxide as a function of temperature.

where  $\omega_H$  and  $\omega_O$  are the Larmor frequencies of proton and oxygen-17 spins, respectively, the  $\gamma$ 's are gyromagnetic ratios,  $S = \frac{5}{2}$  is the spin of oxygen-17 and  $r_{OH}$  is the proton-oxygen bond length. The temperature dependence of  $\tau_{OH}$  is described by the Arrhenius equation

$$\tau_{OH} = \tau_0 \exp\left(\frac{E_a}{RT}\right). \quad (3)$$

With (2) and (3) we obtained an excellent fit to the experimental data, shown as solid line in Fig. 2, with an activation energy  $E_a = 14.66 \text{ kJ mol}^{-1}$ , a pre-exponential factor  $\tau_0 = 2.99 \cdot 10^{-14} \text{ s}$  and a bond length

$r_{OH} = 108.4 \text{ pm}$ . This value of  $r_{OH}$  for methanol in the methanol/DMSO mixture is surprisingly large when compared to the proton-oxygen bond lengths of 99 to 103 pm found in pure methanol from different neutron diffraction data [23, 24]. This experimentally measured maximum value for  $R_1$ , which leads to a smaller than expected dipolar coupling parameter, has also been observed for proton relaxation by other authors who measured internal rotation of the methyl groups of methanol [1] and DMSO [25] in this mixture. We found similar smaller-than-expected dipolar coupling parameter for the water hydroxyl group in the mixture water/DMSO [10].

If this experimental value of 108.4 pm for the bond length is used, one obtains values for the rotational correlation times which are rather long. Taking the Arrhenius parameters from a least squares fit, Ludwig et al. [13] obtained a value of 10.8 ps at 298 K, which is twice as long as that found in pure methanol, where  $\tau_{OH} = 5.1 \text{ ps}$ . These data then indicate that methanol in a methanol/DMSO mixture has a decreased mobility compared to the mobility in pure methanol. This result can be compared to the factor of 1.6 obtained from viscosity studies [26].

Deuteron and oxygen-17 quadrupole relaxation are entirely intramolecular processes. The deuteron rate is given by [22]

$$R_1^D = \frac{3\pi^2}{10} \chi_D^2 \left(1 + \frac{\eta_D^2}{3}\right) \left\{ \frac{\tau_D}{1 + \omega_D^2 \tau_D^2} + \frac{4\tau_D}{1 + 4\omega_D^2 \tau_D^2} \right\}, \quad (4)$$

where  $\chi_D$  is the DQCC in units of  $\text{s}^{-1}$ ,  $\eta_D$  is the asymmetry parameter and  $\omega_D$  the Larmor frequency of the nucleus. For oxygen-17, which is a spin 5/2 system, there does not exist an analytical expression for the relaxation rate outside the extreme narrowing region [22, 27]. Some authors have shown that the longitudinal relaxation rate can be expressed to a good approximation in terms of a single exponential, and an approximate analytical expression is derived for  $R_1^O$  in a convenient form [28, 29, 30]:

$$R_1^O = \frac{12\pi^2}{625} \chi_O^2 \left(1 + \frac{\eta_O^2}{3}\right) \left\{ \frac{\tau_O}{1 + \omega_O^2 \tau_O^2} + \frac{4\tau_O}{1 + 4\omega_O^2 \tau_O^2} \right\}, \quad (5)$$

where  $\chi_O$  is the OQCC in units of  $\text{s}^{-1}$ ,  $\eta_O$  is the oxygen asymmetry parameter and  $\omega_O$  the oxygen Larmor frequency.

We now use the values for  $\tau_{OH}$  along with the present deuterium relaxation data and (4) to calculate values for the DQCC. This procedure is valid because

both correlation times  $\tau_{\text{OH}}$  and  $\tau_{\text{D}}$  are equal, even in the event that the water molecule should reorient anisotropically. The measured deuteron relaxation rates and the calculated DQCC values are shown in Figs. 3 and 4. At 298 K we get a value for the DQCC of about  $151 \pm 5$  kHz which is much smaller than the experimental result  $210 \pm 5$  kHz from earlier NMR investigations [13] in neat, liquid methanol. This value is even smaller than the literature value of 192 kHz in neat, solid methanol and suggests very strong DMSO-hydrogen bonds.

There is a small (17%) temperature dependence of the DQCC, the values change from 151 kHz at 298 K to 177 kHz at 158 K. The effect of an increasing DQCC with decreasing temperature was already observed in pure methanol [13]. In both cases, the change is substantially larger than the estimated error of  $\pm 5$  kHz. A linear regression (solid line in Fig. 4) gives a negative slope of 0.19 kHz/K. In the water/DMSO system [11] we found a positive slope of about 0.08 kHz/K, which agrees well with data from computer simulation studies of Huber *et al.* [20] who calculated a variation of 0.037 kHz/K.

The experimental deuteron relaxation rates can also be evaluated by a different procedure. We carry out a least-squares best fit for the deuteron relaxation rates using (4) and (3) with  $\tau_{\text{OH}}$  replaced by  $\tau_{\text{D}}$ . The result is shown in the lower curve of Fig. 3 as solid line. The best fit gives an activation energy  $E_a = 15.2$  kJ mol<sup>-1</sup>, a pre-exponential factor  $\tau_0 = 1.85 \cdot 10^{-14}$  s and a DQCC  $\chi_{\text{D}} = 175.7$  kHz. For this fitting procedure, of course, one must assume that the DQCC is temperature independent. Note that the value obtained is heavily weighted toward the value at the  $R_1$  maximum.

The measured oxygen-17 relaxation rates for the CH<sub>3</sub>OD/DMSO mixture are shown in the upper part of Figure 3. We could not obtain reliable values for the rates in the dispersion region because of systematic errors arising from the fact that the 90° pulse width (10 microseconds) became an appreciable fraction of the relaxation time (about 100 microseconds). This limits the information available since in the extreme narrowing region ( $\omega\tau_{\text{O}} \ll 1$ ), (5) reduces to one with a simple linear dependence on  $\tau_{\text{O}}$ .

In this case  $\tau_{\text{O}}$  is the correlation time for the oxygen field gradient, for which neither the direction nor the asymmetry parameter are known from experimental data in the liquid phase. Consequently, the methods described above are not a valid means for obtaining

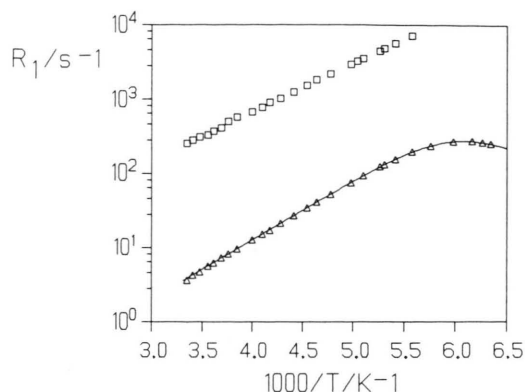


Fig. 3. Deuteron,  $R_1^{\text{D}}$  ( $\Delta$ ), and oxygen-17,  $R_1^{\text{O}}$  ( $\square$ ), relaxation rates of methanol CH<sub>3</sub>OD in the system 71 mol% methanol and 29 mol% dimethylsulphoxide as a function of temperature.

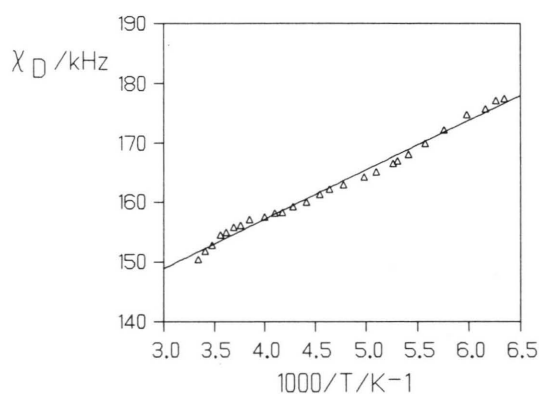


Fig. 4. Deuteron quadrupole coupling constants of methanol in the system 71 mol% methanol and 29 mol% dimethylsulphoxide as a function of temperature.

values for the oxygen-17 correlation time. However, Poplett has observed a correlation between the deuteron and oxygen quadrupole coupling constants for crystal hydrates and different forms of ice from solid-state NQR [21]; it is given by

$$\chi_{\text{O}} = (38.214 \pm 1.293) \chi_{\text{D}} - (1650 \pm 302), \quad (6)$$

where  $\chi_{\text{O}}$  is in units of MHz and  $\chi_{\text{D}}$  is in units of kHz. Given a value for the DQCC, the OQCC may be obtained from the above equation.

From the data in Fig. 4 we have calculated the OQCC for exactly the same temperatures used in the oxygen-17 relaxation rate measurements and determined the rotational correlation times  $\tau_{\text{O}}$ . Their temperature dependence is described by an Arrhenius



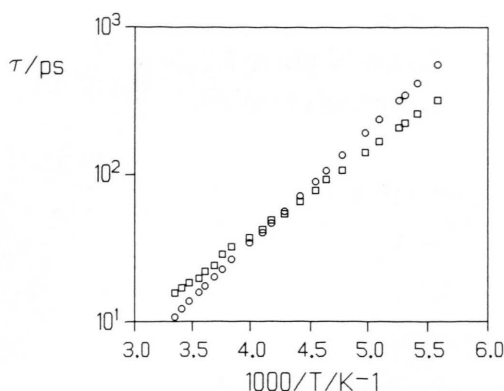


Fig. 5. Rotational correlation times for deuterium,  $\tau_D$  ( $\circ$ ), and oxygen,  $\tau_O$  ( $\square$ ), of methanol in the system 71 mol% methanol and 29 mol% dimethylsulphoxide as a function of temperature.

activation law. From a least-squares fit we obtained an activation energy  $E_a = 12.4 \text{ kJ mol}^{-1}$  and a pre-exponential factor of  $\tau_0 = 7.4 \cdot 10^{-14} \text{ s}$ . In the temperature range between 298 K and 158 K the ratio  $\tau_O/\tau_D$  decreases from 1.45 to 0.57 which indicates a strong anisotropic reorientation of the methanol molecule in the methanol/DMSO mixture (Figure 5). Since the error in a given DQCC value is  $\pm 5 \text{ kHz}$ , and a statistical error of  $\pm 0.2 \text{ MHz}$  arises from the Poplett relation, the total error in a given OQCC value is about  $\pm 0.4 \text{ MHz}$ . This error in the QCC leads to an error in

the correlation time  $\tau_O$  of about 10 percent, which is smaller than the measured effect. We must also consider the possibility of a systematic error in the Poplett relation, since the latter was found from experimental values at 77 K. Here we have used it for a different molecule and at higher temperatures. A possible change in the asymmetry parameter (in water  $\eta_O$  ranges from 0.75 for the gas phase to 0.93 for ice) over the whole temperature range would also lead to a small systematic error, and this would increase even more the effect of anisotropy, that is, the error resulting from the value we have used for the asymmetry parameter would make the ratio  $\tau_O/\tau_D$  larger.

We have shown clearly here that the deuterium quadrupole coupling constant in methanol is sensitive to both temperature and solvent. It is reasonably clear that both of these effects are related to hydrogen bonding interactions. This observation is not too surprising, given the fact that the hydroxyl proton (or deuterium) isotropic chemical shift in alcohols is also sensitive to both temperature and solvent [31].

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