Counter-ion Dependent Water and Amphiphile Orientation

and Deuteron Exchange in Lyotropic Mesophases

NILS-OLA PERSSON, HÅKAN WENNERSTRÖM
and BJÖRN LINDMAN

*Division of Physical Chemistry 2, The Lund Institute of Technology, Chemical Center,
P.O.B. 740, S-220 07 Lund, Sweden*

Lamellar mesophase samples composed of alkali octanoate, decanol
and heavy water were studied by means of deuteron magnetic reson-
ance. The variations of the quadrupole splitting and of the spectral
shape with pH and temperature are ascribed to chemical exchange
of deuterons between decanol hydroxyl groups and water.

A method for treating chemical exchange phenomena in the pres-
ence of static quadrupolar effects is proposed and it is found that
the quadrupole splitted NMR signals may give otherwise not easily
accessible kinetic information. Comparison between computer-
simulated and experimental spectra permits the estimation of deuteron
exchange rates. It is found that the exchange rate depends markedly
on the counter-ion present. Water orientation changes strongly as
the counter-ion is changed whereas amphiphile orientation is almost
independent of which alkali ion is present.

It has previously been observed that deuteron NMR spectra of amphiphilic
liquid crystals containing heavy water are affected by three processes, *i.e.*
the degree of water orientation, the degree of amphiphile orientation, and the
rate of exchange of deuterons between water and amphiphile.[1-3] Since all
these factors contain pertinent information on mesophase structure and/or
motional processes it would be desirable to have a method for quantitatively
separating the different contributions to the NMR spectral shape. It is the
object of this communication to propose such a method. In this context also
preliminary information on the dependence of water and amphiphile orientation
and deuteron exchange rates on sample composition will be given.

EXPERIMENTAL

Heavy water was purchased from Norsk Hydro, Norway and had an isotopic enrich-
ment of 99.8 %. Decanol and sodium octanoate were obtained from the British Drug
Houses Ltd., Poole, England and the purity was better than 98 %. The lithium and
potassium octanoates were prepared from metal ethanolate and octanoic acid by exact

neutralization in ethanol and the purity of the salts filtered off after washing with ethanol and drying were checked by titration in glacial acetic acid with crystal violet as an indicator. The rubidium and cesium octanoates were prepared by neutralization of alkali hydroxide with octanoic acid and their purities were checked as above. The molar weights obtained were for lithium octanoate 150.5 (calculated 150.2), for potassium octanoate 181.8 (182.3) for rubidium octanoate 225.1 (228.7) and for cesium octanoate 277.2 (276.1). Samples mostly of 1 g were prepared by weight in ampoules which were then immediately sealed off. The error in sample preparation was $\pm$ 0.002 g. The lamellar phase samples were prepared by heating the samples to a temperature above the transition point to isotropic solution and samples were then shaken and cooled.

The NMR measurements were performed on a Varian V-4200 wide line spectrometer with a 12 inch V-3603 magnet. The magnetic field was regulated with a Varian Mark II Fieldial unit and the sample temperature was controlled by means of a Varian V-4540 temperature controller. Sample temperatures were checked before and after each measurement with a copper-constantan thermocouple. The accuracy was within $\pm$ 2°C. For signal intensity reasons it was necessary to use samples of 4 g, which did not fit in the temperature controller to obtain the signals from the decanol hydroxyl deuterons (see below). These spectra were recorded at probe temperature (27 $\pm$ 3°C).

Deuteron spectra were recorded at a magnetic field of 1.403 T*, and a radio-frequency field of 9.1786 MHz. The intensities of the rf field and the modulation field were kept low enough not to affect the line-shape. For intensity reasons a slight saturation and over-modulation was necessary in the case of the decanol hydroxyl spectra.

RESULTS AND DISCUSSION

If, for a nucleus with spin quantum number I greater than one half, the motion is anisotropic on a sufficiently long time-scale then the interactions between the nuclear electric quadrupole moment and the electric field gradient lead to a splitting of the NMR signal into $2I$ components. For a deuteron ($I = 1$) this results in two major absorption maxima separated by

$$\varDelta = \tfrac{1}{2} |\nu_Q S| \qquad (1)$$

and

$$\varDelta(\varOmega) = \tfrac{1}{2} |(3\cos^2 \varOmega - 1)\nu_Q S| \qquad (2)$$

for powder and oriented samples, respectively.

Here $\nu_Q = \tfrac{3}{2}(e^2qQ/h)$, where eq is the largest component of the electric field gradient tensor in the principal axes system and eQ is the quadrupole moment. $\varOmega$ is the angle between the magnetic field and the director.[4]

Recently, from the theory given by Luckhurst,[4] Lindblom [5] derived the order parameter S to be given by

$$S = \overline{D_{00}^{(2)}} + 1/\sqrt{6}\eta\ (\overline{D_{02}^{(2)}} + \overline{D_{0-2}^{(2)}}) \qquad (3)$$

The $\overline{D^{(2)}}$'s are the second rank Wigner rotation matrix elements averaged over the molecular motion and η is the asymmetry parameter for the electiric field gradient tensor. The fact that the asymmetry parameter only affects the magnitude of the splitting and not the line shape (except for relaxation) has not always been recognized previously.

We have recorded deuteron NMR spectra for lamellar mesophase samples composed of heavy water, alkali octanoates and decanol.[6] As exemplified in Fig. 1 the spectra taken at room temperature consist of two signals, each split
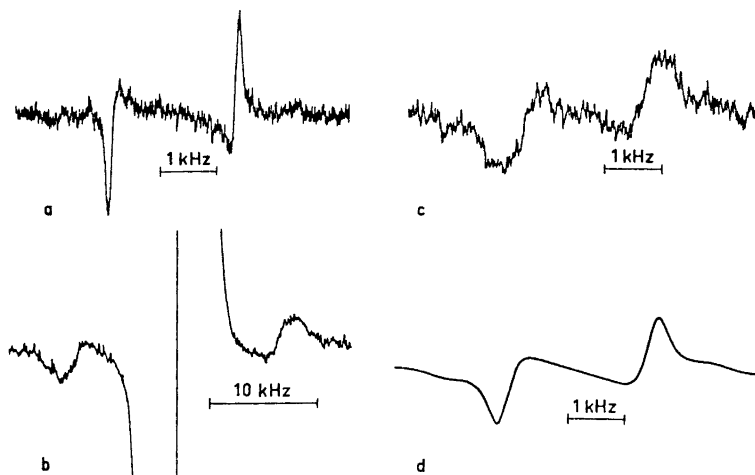
---

* 1 T (tesla) = 10 000 Gauss.

Fig. 1. Deuteron NMR spectra for a sample with the molar ratio D_2O:lithium octanoate: decanol being 83.0:6.8:10.2. a) Water deuteron spectrum at $27 \pm 2°C$. b) Spectrum for the decanol OD-group at $27 \pm 2°C$. c) Experimental spectrum at 40°C showing deuteron exchange effects. d) Corresponding computer simulated spectrum (*cf.* text) with intermediate exchange rate ($\tau = 23$ μs)

into two components. The signal of high intensity and small splitting is caused by the water deuterons, whereas the signal from the decanol deuterons gives a splitting one order of magnitude larger.

The distances between the intense peaks in the spectra are given in Fig. 2 as a function of temperature. As may be seen the splitting at first increases and then decreases with increasing temperature. Furthermore, at intermediate temperatures the NMR-signals are considerably broadened (*cf.* Fig. 2). Only
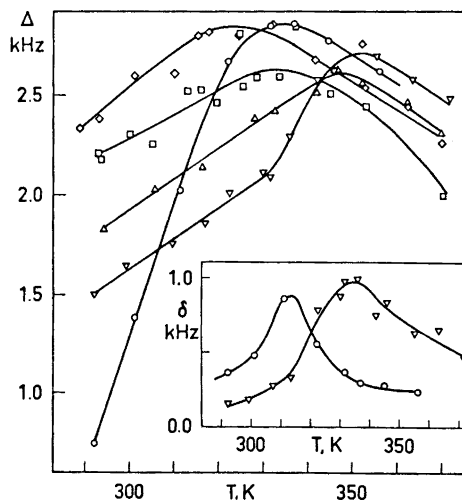
Fig. 2. Temperature dependence of the splitting corresponding to the intense deuteron signal (*cf.* text) and, inserted, the temperature dependence of the width at half height above the baseline of the inner peaks in the derivative of the NMR absorption spectrum. Samples investigated were (with molar ratios D_2O:soap:decanol given in parentheses). ☐ D_2O:lithium octanoate:decanol (83.0:6.8:10.2). ○ D_2O: sodium octanoate:decanol (77.5:10.8:11.7). ▽ D_2O:potassium octanoate:decanol (77.5: 10.8:11.7). △ D_2O:rubidium octanoate: decanol (77.5:10.8:11.7). ◇ D_2O:cesium octanoate:decanol (77.5:10.8:11.7).

one split signal can be detected at high temperatures in contrast to the room temperature spectra. All these facts strongly indicate that an exchange of deuterons between water and decanol takes place at a rate comparable to the splitting difference between the two sites. Such an exchange is base-catalyzed [7] and, as expected, additions of alkali hydroxide to the samples produce qualitatively the same changes as a temperature increase.

The effect of chemical exchange on the NMR spectrum of quadrupole split signals has, to the authors' knowledge, not previously been treated quantitatively. Lynden-Bell[8] has shown that if one neglects those terms in the quadrupole spin hamiltonian that do not commute with I_z, i.e. the secular approximation, then the transitions $m = 1 \to m = 0$ and $m = 0 \to m = -1$ are independent at low intensity radio frequency fields. (m is the magnetic quantum number.) If this is the case the problem is reduced to calculate the lineshape for each transition separately and then simply superimpose them to get the total lineshape. For each of these transitions the well known exchange equations from proton magnetic resonance [9] can be used. The shape of the deuteron signal is obtained by first solving the exchange equations for a given orientation of the microcrystallite. Then the average over all equally probable orientations is taken followed by adding the intensities from the two independent transitions. The formal expression for the lineshape $L(\nu)$ in the presence of exchange is (cf. Ref. 9. eqns. 13 – 15 where also symbols are defined)

$$L(\nu) = \int_{-1}^{1} (G(\nu) + G(-\nu))\, \mathrm{d}(\cos \Omega) \tag{4}$$

$$G(\nu) = \frac{i\tau[2p_A p_B - \tau(p_A \alpha_B + p_B \alpha_A)]}{p_A p_B - \tau^2 \alpha_A \alpha_B} \tag{5}$$

$$\alpha_{A,B} = -[i2\pi((\Delta(\Omega))_{A,B}/2 - \nu) + 1/T_2 + p_{B,A}/\tau] \tag{6}$$

$$\tau = p_B/k_{A \to B} = p_A/k_{B \to A} \tag{7}$$

$\nu = 0$ corresponds to the resonance frequency without splitting. A computer simulated spectrum using the lineshape equation (4) is included in Fig. 1. Eqn. (4) gives an approximate rationalization of the variation of lineshape with temperature. It does not, however, reproduce the experimental spectra quantitatively. This is probably due to either the neglect of the non-secular terms in the hamiltonian or to the use of an intense radio frequency field.

The procedure outlined above for handling deuteron exchange has been utilized to determine exchange rates and the quadrupole splittings of water deuterons and of amphiphile hydroxylic deuterons and in particular how these quantities depend on the counter-ion.

As may be inferred from Fig. 2 the "coalescence temperature" depends significantly on which alkali ion is present. It is interesting to note for example that the deuteron exchange proceeds at a markedly higher rate with sodium as counter-ion than with potassium. Detailed calculations which are in progress are hoped to yield the activation parameters for the different cases.

Water deuteron splittings can be obtained from the signals observed at low temperatures by correcting for the effect of exchange. This was accomlished by comparing the increase in splitting obtained on hydroxide addition with the

Table 1. Water deuteron splittings for samples with molar composition 83.0 %, 6.8 % and 10.2 % of water, alkali octanoate and decanol respectively.

Counter-ion	Li^+	Na^+	K^+	Rb^+
Δ, kHz	2.21	1.14	1.50	1.46

splitting for the amphiphilic deuterons. As shown in Table 1 the water orientation depends markedly on the counter-ion present and is largest with lithium. The relation between the other counterions depends on sample composition. Besides lithium the water orientation increases with increasing atomic number of the counter-ion at least at the lowest water contents. The difference between the effect of potassium, rubidium and cesium on water orientation is small at low amphiphile concentrations.

In contrast to these observations, the degree of amphiphile orientation depends very little on the counter-ion present (Table 2). On the other hand, amphiphile splitting increases drastically with decreasing water content as well as with increasing molar ratio between soap and decanol.

Table 2. Decanol-OD deuteron splittings for samples with molar composition 83.0 %, 7.6 % and 9.5 % of water, alkali octanoate and decanol respectively.

Counter-ion	Li^+	Na^+	K^+	Rb^+
Δ, kHz	20.6	23.7	21.9	21.8

It may be concluded from this preliminary account that if deuteron exchange is not too rapid, information on both water and amphiphile orientation may be obtained from deuteron NMR studies on heavy water containing lyotropic mesophase samples. Furthermore, the rate of deuteron exchange may be estimated. Detailed studies of this type on a large number of systems, including model membrane systems, are in progress and will be presented at a later date.

An interesting aspect on studying chemical exchange in the presence of static quadrupolar interactions is the possibility of continuously varying the splitting difference in the case of macroscopically oriented samples by varying Ω (*cf.* eq. 2). Thus for oriented samples the range of exchange rates possible to investigate may be quite large.

REFERENCES

1. Johansson, Å. and Drakenberg, T. *Mol. Cryst. Liquid Cryst.* 14 (1971) 23.
2. Persson, N.-O. and Johansson, Å. *Acta Chem. Scand.* 25 (1971) 2118.
3. Johansson, Å. and Lindman, B. In Gray G. W. and Winsor, P. A., Eds., *Liquid Crystals and Plastic Crystals*, Ellis Horwood Publishers, Chichester, Vol. 2, Chapter 8. *In press.*
4. Luckhurst, G. R. In Gray, G. W. and Winsor, P. A., Eds., *Liquid Crystals and Plastic Crystals*, Ellis Horwood Publishers, Chichester, Vol. 2, Chapter 7. *In press.*

5. Lindblom, G. *Acta Chem. Scand.* **26** (1972) 1745.
6. For phase diagrams see Ekwall, P., Mandell, L. and Fontell, K. *Mol. Cryst. Liquid Cryst.* **8** (1969) 157.
7. Luz, Z. and Meiboom, S. *J. Chem. Phys.* **30** (1959) 1540.
8. Lynden-Bell, R. M. *Mol. Phys.* **22** (1971) 837.
9. Binsch, G. In Eliel, E. L. and Allinger, N. L., Eds., *Topics in Stereochemistry*, John Wiley & Sons, New York 1968, Vol. 3, p. 106.