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Theoretical Aspects on the NMR of Quadrupolar Ionic Nuclei in Micellar Solutions and Amphiphilic Liquid Crystals

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Abstract

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A theoretical framework for the interpretation of NMR quadrupole splittings and relaxation times of alkali and halide counter-ions in amphiphile–water systems is presented. Special attention is payed to the effect of the macroscopic and microscopic anisotropies of the systems. Explicit expressions for the quadrupole splittings are given. It is stressed that in the discussion of the relaxation in an isotropic system that is locally anisotropic, one has to consider both a fast local motion and a slow isotropic motion over the dimensions of the aggregates.

Introduction

Nuclear magnetic resonance (NMR) of ionic nuclei such as e.g. Na^+, Rb^+, Cl^- and Br^- has proved to be a valuable tool in the study of the microscopic structure and the microdynamic properties of aqueous solutions containing ionic amphiphiles. NMR investigations of alkali and halide ions in micellar solutions [1–4], in lecithin vesicle systems [5] and in anisotropic liquid crystals [6–8] have been reported in recent years. In some respects these amphiphile–water systems show considerable deviations from simple fluids and the interpretation of experimental data is therefore often not straight-forward.

Although the examples in the present treatment will be taken from the field of amphiphilic systems the equations derived will give a basis for a similar analysis for other types of colloidal solutions, such as protein and polyelectrolyte solutions. On some important points the considerations presented are also relevant for ^1H, ^2H and ^{13}C NMR investigations of solutions containing molecules or aggregates of colloidal dimensions. The results obtained should also be directly applicable to NMR studies aiming at an elucidation of the interactions between small ions and biological membranes. In the field of membranology, a negligibly perturbing method like NMR is of great significance.

The NMR parameters of interest for ionic nuclei are relaxation times, chemical shifts and in anisotropic systems also quadrupolar splittings. The present work is an attempt to give a theoretical framework for the interpretation of relaxation times and quadrupole splittings.

I. Basic theory

All alkali and halogen nuclei except fluorine have spin quantum numbers, I, greater than one half and consequently possess quadrupole moments. The subsequent discussion will be concentrated on quadrupolar nuclei. The most important terms in the nuclear spin hamiltonian are then usually those representing the nuclear Zeeman interaction and the interaction between the nuclear quadrupole moment, eQ, and the electric field gradients at the nucleus. Thus in frequency units

$$H = -\nu_L I_z + \beta_Q \sum_{q=-2}^{2} (-1)^q V_{-q} A_q \tag{1}$$

Here $2\pi\nu_L = \omega_0$, the Larmor angular frequency. The anisotropic parts of the chemical shift have been neglected. V_q is a component of the irreducible electric field gradient tensor.

$$V_{\pm 2} = \frac{1}{2\sqrt{6}} \left\{ \left(\frac{\partial^2 V}{\partial x^2} \right)_N - \left(\frac{\partial^2 V}{\partial y^2} \right)_N \pm 2i \left(\frac{\partial^2 V}{\partial x \partial y} \right)_N \right\} \tag{2a}$$

$$V_{\pm 1} = \mp \frac{1}{\sqrt{6}} \left\{ \left(\frac{\partial^2 V}{\partial x \partial z} \right)_N \pm i \left(\frac{\partial^2 V}{\partial y \partial z} \right)_N \right\} \tag{2b}$$

$$V_0 = \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2} \right)_N \tag{2c}$$

The index N indicates that the derivative is taken at the nucleus in question. A_q is a component of a second rank irreducible tensor operator working on nuclear spin functions

$$A_{\pm 2} = \frac{\sqrt{6}}{2} I_{\pm}^2 \tag{3a}$$

$$A_{\pm 1} = \mp \frac{\sqrt{6}}{2} (I_{\pm} I_z + I_z I_{\pm}) \tag{3b}$$

$$A_0 = (3I_z^2 - I^2) \tag{3c}$$

$\beta_Q = \dfrac{eQ}{2I(2I-1)h}$ is a reduced matrix element as defined in connection with the Wigner–Eckart theorem [9].

The quadrupole coupling term in eq. (1) can be evaluated in any coordinate system. Due to the presence of the Zeeman term it is convenient to express the spin operators in a laboratory-fixed

coordinate system. It is more natural on the other hand to express the electric field gradients in a principal axis coordinate system fixed at the nucleus. The quadrupolar hamiltonian can then be written

$$H_Q = \beta_Q \sum_{qq'} (-1)^q V^M_{-q} A^L_{q'} D^{(2)}_{q'q}(\Omega_{LM}) \tag{4}$$

where $D^{(2)}_{q'q}$ is a Wigner rotation matrix element [9] and Ω_{LM} stands for the three eulerian angles that specify the transformation from the molecular system (M) to the laboratory system (L). In the following all D matrix elements will be of rank two and the superscript is omitted. The superscripts on V_{-q} and $A_{q'}$ indicate in which coordinate system the quantities should be taken. If molecular motion has to be taken into account, the hamiltonian in eq. (4) becomes time-dependent through the time dependence of the eulerian angles Ω_{LM}. In an isotropic[1] solution the mean values of the Wigner rotation matrix elements are zero and the quadrupole interaction gives only relaxation effects. In an anisotropic[1] medium like a lamellar or hexagonal liquid crystal the mean value of $D^{(2)}_{q'q}(\Omega_{LM})$ is not necessarily zero and one may observe quadrupole splittings in the NMR spectrum.

The present treatment will mainly be concerned with uniaxial liquid crystalline phases and following Luckhurst [10] the symmetry axis will be referred to as the director. We now consider a phase which is macroscopically aligned in such a way that the director has the same direction throughout the sample. If the transformation from the molecular coordinate system to the laboratory system is performed via the director coordinate system (D) (cf. Fig. 1) eq. (4) reads

$$H_Q = \beta_Q \sum_{qq'q''} (-1)^q V^M_{-q} A^L_{q''} D_{q'q}(\Omega_{DM}) D_{q''q'}(\Omega_{LD}) \tag{5}$$

The angles Ω_{DM} specify the transformation from the molecular to the director system and Ω_{LD} gives the corresponding quantity for the transformation from the director to the laboratory system. All quantities except $D_{q'q}(\Omega_{DM})$ in eq. (5) remain constant over the molecular motion if the magnitude of the field gradient is assumed constant.

Generally, the amphiphilic systems are cylindrically symmetrical around the director [10, 11] which makes the averages $\overline{D_{q'q}(\Omega_{DM})}$ zero unless $q'=0$ [10]. The separation of the hamiltonian in eq. (1) into a time dependent part $H_1(t)$ and a time independent part H_0 i.e. $H = H_0 + H_1(t)$ gives

$$H_0 = -\nu_L I_z + \beta_Q \sum_{qq''} (-1)^q V^M_{-q} A^L_{q''} \overline{D_{0q}(\Omega_{DM})} D_{q''0}(\Omega_{LD}) \tag{6}$$

$$H_1(t) = \beta_Q \sum_{qq'q''} (-1)^q V^M_{-q} A^L_{q''} D_{q''q'}(\Omega_{LD}) \{D_{q'q}(\Omega_{DM}(t)) - \overline{\delta_{q'0} D_{0q}(\Omega_{DM})}\} \tag{7}$$

The condition for the division of the hamiltonian into two well-defined parts is that the motion causing averaging of the quadrupole interaction is fast compared to the interaction in frequency units. It is thus assumed that the motion around the director is much faster than a quantity of the order of

$$\beta_Q V^M_{-q} \{D_{q'q}(\Omega_{DM}) - \overline{\delta_{q'0} D_{0q}(\Omega_{DM})}\}$$

[1] The difference between isotropic and anisotropic fluids is not distinct in NMR theory. The isotropy or anisotropy of a system should be judged with reference to the interactions present. Thus a solution is considered isotropic here if the mean value, taken over a time that is short compared to the inverse of the quadrupole coupling constant, of $D^{(2)}_{q'q}(\Omega_{LM})$ is zero for all q', q. A solution is anisotropic if the mean value, taken over a time that is long compared to the inverse of the quadrupole coupling constant, of $D^{(2)}_{q'q}(\Omega_{LM})$ is non-zero for at least some q', q.

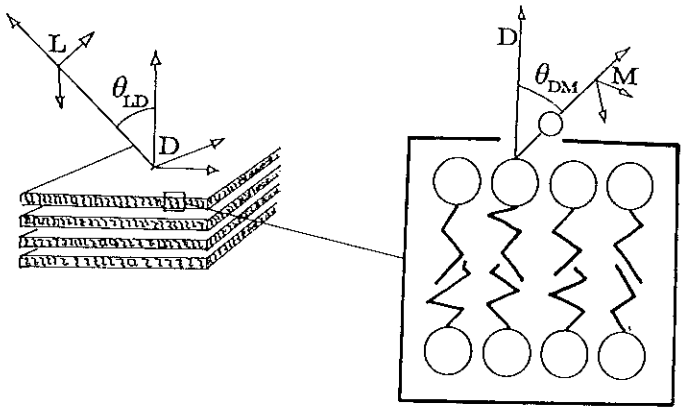

Fig. 1. Schematic drawing of the mesomorphous structure in a lamellar phase. The different coordinate systems used in text are outlined in the figure, laboratory frame (L), director frame (D) and molecular frame (M). θ_{LD} and θ_{DM} are angles between z-axis in laboratory–director systems and director–molecular systems, respectively.

and that the change of the director orientation is slower than

$$\beta_Q V^M_{-q} \overline{D_{0q}(\Omega_{DM})} D_{q'0}(\Omega_{LD})$$

So far it has been assumed that the nucleus possessing a quadrupole moment can be considered as fixed in a molecule or a complex. For alkali and halide ions in water-amphiphile systems this is probably not a valid assumption. Instead, the NMR data have to be analysed in terms of two or more sites with different quadrupole couplings and correlation times. If the fraction of the nuclei at site i is denoted p_i, eq. (6) can be generalized to

$$H_0 = \sum_i p_i H^i_0 \tag{8}$$

where H^i_0 is given by eq. (6) for site i. Here it is assumed that the exchange is fast between the sites compared to the quadrupole interaction. It has been shown [12] that relaxation in the presence of chemical exchange can be accounted for by a time-dependent hamiltonian

$$H_1(t) = \sum_i f_i(t) H^i_1(t) \tag{8}$$

where $H^i_1(t)$ is given by eq. (7). The function $f_i(t)$ is equal to unity if the nucleus considered is at site i at a time t and zero otherwise.

II. Quadrupole splittings

In an anisotropic medium the quadrupole interaction does not average to zero which gives rise to a quadrupolar term in the static hamiltonian. If this term is small compared to the Zeeman term only the secular part of H_Q needs to be considered and from eq. (6)

$$H_0 = -\nu_L I_z + \nu_Q S(3\cos^2\theta_{LD} - 1)(3I_z^2 - I^2)/6 \tag{10}$$

$$\nu_Q = 3\beta_Q V^M_0;$$

$$S = \tfrac{1}{2}\{\overline{(3\cos^2\theta_{DM} - 1)} + \eta \overline{\sin^2\theta_{DM}\cos 2\phi_{DM}}\};$$

$$\eta = \sqrt{6}\, V^M_2 / V^M_0;$$

where θ and ϕ are equal to the eulerian angles β and γ respectively. The effective electric field gradient is thus cylindrically symmetric around the director.

Usually the counter-ions reside in different sites so that eqs. (8) and (10) have to be combined. For a sample with uniform director orientation the NMR spectrum consists of $2I$ peaks centered at the Larmor frequency and equally spaced by

$$\Delta(\theta) = |(3\cos^2\theta_{LD} - 1)\sum_i p_i \nu_Q^i S_i| = |(3\cos^2\theta_{LD} - 1)\,\overline{(\nu_Q S)}| \quad (11\,a)$$

For $I = 1$ the two peaks are of equal intensity while for $I = 3/2$ the integrated intensity ratio between the peaks is 3:4:3.

For a powder sample where all values of $\cos\theta_{LD}$ are equally probable the distance between peaks in the NMR spectrum corresponds to that for $\theta_{LD} = 90°$ in eq. (11) [13], i.e. the splitting, Δ_p, for a powder sample is given by

$$\Delta_p = |\sum_i p_i \nu_Q^i S_i| \quad (11\,b)$$

Equation (11 b) is valid provided broadening effects due to exchange and relaxation phenomena can be neglected.

For nuclei with half integral spin quantum numbers the NMR line corresponding to the transition $m = 1/2$ to $m = -1/2$ is not affected by the static quadrupole interaction to first order. In spite of this an observation of a sharp peak at the Larmor frequency deceptively has lead some authors to interpret their experimental data as if static quadrupole interactions are absent [14].

In an aligned sample the second order terms result in an orientation dependent shift of the central peak for a particular site of [13, 15]

$$\delta^i_{\frac{1}{2},-\frac{1}{2}} = (\nu_Q S)_i^2/(16\nu_L)\{I(I+1) - \tfrac{3}{4}\}(\cos^2\theta_{LD} - 1)(9\cos^2\theta_{LD} - 1) \quad (12)$$

For a powder sample this shift term gives rise to an absorption curve having two marked peaks separated by [15]

$$\Delta_i = 25(\nu_Q S)_i^2\{I(I+1) - \tfrac{3}{4}\}/(144\nu_L) \quad (13\,a)$$

and for several sites

$$\Delta = 25(\sum_i p_i \nu_Q^i S_i)^2\{I(I+1) - \tfrac{3}{4}\}/(144\nu_L) \quad (13\,b)$$

For a given θ_{LD} the magnitude of the observed quadrupole splitting is determined by the factors p_i, ν_Q^i and S_i according to eqs. (11)–(13). In concentrated micellar solutions the fraction of ions bound is known to be between 0.5 and 0.8 [16] and it seems reasonable to assume that in a corresponding liquid crystalline system the fraction of bound ions is at least that large. It must, however, be realized that an ion interacting with a charged surface can be bound in several different ways. Thus when discussing quadrupole splittings more than two types of binding sites may have to be considered.

The electrical field gradients at the centre of an ion can arise from several sources. In an electrostatic model, which we think is adequate in the present systems, the main contribution to the field gradients comes from the charges of the amphiphilic ions and the dipoles of the water [17]. A point charge Z (in atomic units) at the distance r (in m) from a nucleus with a quadrupole moment Q (in m²) gives a quadrupole coupling constant ν_Q (in Hz) of [13]

$$\nu_Q = \pm\frac{1.04\times10^6(1+\gamma_\infty)}{I(2I-1)}\left(\frac{2\varepsilon+3}{5\varepsilon}\right)\frac{QZ}{r^3} \quad (14)$$

where γ_∞ is the Sternheimer antishielding factor [17] and ε is the dielectric constant of the medium. For a dipole moment μ (in Debye) directed parallel (+) or antiparallel (−) to the dipole-nucleus vector the corresponding expression is

$$\nu_Q = \pm\frac{6.52\times10^{-5}(1+\gamma_\infty)}{I(2I-1)}\left(\frac{2\varepsilon+3}{5\varepsilon}\right)\frac{Q\mu}{r^4} \quad (15)$$

For a sodium nucleus [17] $1+\gamma_\infty = 5.1$ and $Q = 0.11\times10^{-28}$ m². Assuming that $\varepsilon \gg 1$ eq. (14) gives for a sodium ion being at a distance of 5×10^{-10} m from the charge of an univalent anionic amphiphile $\nu_Q = 62$ kHz (simple estimates give a minimal distance of 4.5–5.0×10^{-10} m between a hydrated sodium ion and an amphiphilic ion). From eq. (15) $\nu_Q = -270$ kHz for the interaction between a sodium nucleus and a single water dipole at a distance 2.4×10^{-10} m. However, in the systems under consideration any sodium nucleus will simultaneously interact with several water dipoles and their contributions to ν_Q will largely cancel. Thus it is only an asymmetric hydration sheath that can produce a net quadrupole coupling. A displacement by 0.1×10^{-10} m of one of the water molecules in the first hydration layer from the symmetrical configuration gives a net quadrupole coupling $\nu_Q = 43$ kHz.

The magnitude of the order parameter S is determined by two factors. Firstly, the degree of anisotropy of the mesophase has an effect on the order parameter. Secondly, it depends on the angles θ_{DM} and ϕ_{DM}. In lyotropic liquid crystals it appears that at least the charged amphiphilic surface is rather rigid [18] so that the normal to the surface does not alter its orientation appreciably with time. For a system rigid in this sense the value of S can change from 1 to $-1/2$ depending on the angles θ_{DM} and ϕ_{DM}. For the case when $\eta = 0$, $S = 0$ at the "magic angle", i.e. $\theta_{DM} = 54.7°$. This means that in spite of a high anisotropy of the system the splitting $\Delta(\theta)$ may be small or unobservable as a result of a very small order parameter. A further situation where $\Delta(90)$ can be small although the anisotropy of the phase is large occurs when different $(\nu_Q S)_i$'s have opposite signs causing a partial cancellation of the terms in the sum of eq. (11).

A temperature dependence of the splitting $\Delta(\theta)$ can be interpreted in terms of a temperature dependence of the p_i's or the S_i's. Furthermore, a transition from slow to rapid exchange conditions will give rise to temperature dependent quadrupole split spectra as described for deuterons [19]. This type of exchange effects could lead to sufficient extra line-broadening to be identifiable from the spectral shape.

The S values of hexagonal and lamellar mesophases of the same system can easily be related to each other if the microscopic structure at the water–amphiphile interface can be assumed identical for the two phases. For the hexagonal phase the quadrupole hamiltonian can be written

$$H_h = \beta_Q \sum_{qq'q''q'''} (-1)^q V^M_{-q} A^L_{q''} D_{q'q}(\Omega_{SM})\, D_{q''q'}(\Omega_{DS})\, D_{q'''q''}(\Omega_{LD}) \quad (16)$$

since $\overline{D_{q''0}(\Omega_{DS})} = \delta_{q''0} D_{00}(\Omega_{DS})$ (cf. ref. [10]), averaging over the molecular motion yields

$$\overline{H_h} = \beta_Q \sum_{qq'''} (-1)^q V^M_{-q} A^L_{q'''}\, \overline{D_{0q}(\Omega_{SM})}\, D_{00}(\Omega_{DS})\, D_{q'''0}(\Omega_{LD}) \quad (17)$$

The subscript S denotes a coordinate system fixed at the charged amphiphilic surface. This coordinate system is coincident with the director system in a lamellar phase having planar lamellae. For a hexagonal phase, built up of long rods in a hexa-

gonal array the D and S coordinate systems are perpendicular to each other and $\bar{H}_h = -1/2\bar{H}_l$ (cf. ref. [20]) where $\bar{H}_l$ is the time-independent quadrupolar hamiltonian for the lamellar mesophase. When the lamellae are not planar but form concentric cylinders as e.g. in a myelin type structure the splittings of the lamellar and the hexagonal phases should be the same [21], if the molecular motion along the amphiphile surfaces is fast enough.

The treatment given so far is intended to provide a general basis for the interpretation of static quadrupole effects of counterions in anisotropic amphiphile–water systems. In addition the calculation of quadrupole couplings for a simple electrostatic model has been performed. Several amphiphile–water systems have been investigated experimentally to test the validity of the theoretical results and to utilize the equations to obtain information on amphiphile–counterion and counterion–water interactions in such systems. Here some general results will be presented.

Table I summarizes some of our results obtained by means of ^{23}Na NMR for "powder" samples in two systems where the amphiphiles have a sulphate end-group. It can be inferred that for both systems the concentration dependence of the first-order quadrupole splitting, Δ_p, is weak. This indicates that both the p_i's and the S_i's are only slightly affected by concentration changes. The temperature dependence of the quadrupole splitting in the sodium octyl sulphate–decanol–heavy water system was investigated and found to be only slightly temperature dependent. This indicates that the p_i's and S_i's also are insensitive to temperature changes. From these findings it seems that the observed quadrupole splitting is determined by the structure of the phase, which does not change much with temperature and concentration. The experimental splittings given in Table I are clearly compatible with the splittings calculated from eqs. (14) and (15). Also as implied by the above considerations Δ_p of the hexagonal phase is close to half the value in the lamellar phase, which is consistent with a planar structure of the lamellae. Clearly, it appears possible to rationalize all observations on these two systems by the theoretical treatment given above.

Experimentally observed quadrupole splittings in the systems octylammonium chloride–decanol–water (^{35}Cl and ^{37}Cl NMR) [15], dodecyltrimethylammonium chloride–water (^{35}Cl NMR) [22], cetyltrimethylammonium bromide–hexanol–water (^{81}Br NMR) [30] and sodium octyl sulphonate–decanol–heavy water (^{23}Na NMR) [7] also appear consistent with our treatment. In the system sodium octanoate–decanol–water the phase denoted C [7] gives a ^{23}Na splitting close to that estimated for an electrostatic model. The lamellar D phase in this system gives a considerably smaller ^{23}Na splitting and for high water contents no splitting was observed [7]. We are not able to give a well founded explanation to this observation.

Table I. *Observed ^{23}Na quadrupole splittings for some unoriented mesophase samples with sulphate amphiphilic endgroup (the NMR measurements were performed as in ref. [7])*

Sample composition (mole %)	Phase	^{23}Na splitting Δ_p (kHz)
Sodium octylsulphate/decanol/water		
4.0 : 8.8 : 87.2	Lamellar	24.0
7.2 : 15.9 : 76.9	Lamellar	27.4
9.8 : 13.3 : 76.9	Lamellar	32.0
8.3 : 14.8 : 76.9	Lamellar	32.3
8.7 : 0.0 : 91.3	Hexagonal	18.0
Aerosol OT[a]/water		
1.7 : 98.3	Lamellar	53.4
2.6 : 97.4	Lamellar	53.0
4.0 : 96.0	Lamellar	53.4

[a] Aerosol OT stands for sodium di-2-ethylhexylsulphosuccinate.

III. Relaxation

For nuclei possessing quadrupole moments it is the time-dependence of the quadrupole interaction that normally gives the dominant relaxation mechanism. For a nucleus with $I \geq 3/2$ it is only in the limit of "extreme narrowing", i.e. $J(\omega_0) = J(0)$ (cf. below), that the longitudinal, T_1, and transverse, T_2, relaxation times are well defined and [23]

$$1/T_1 = 1/T_2 = 24\pi^2(2I-1)(2I+3)J_{00}(0)_2 = 8\pi^2(2I-1)(2I+3)\nu_Q^2(1+\eta^2/3)\tilde{J}_{00}(0)/15 \quad (18)$$

where the spectral densities are defined through

$$J_{q\,q}(\omega) = \beta_Q^2 \overline{V_q^L(0)\, V_q^{L*}(0)}\tilde{J}_{q'q}(\omega) = \tfrac{1}{2}\beta_Q^2 \int_{-\infty}^{+\infty} \overline{V_q^L(0)\, V_q^{L*}(\vartheta)} \exp(-i\omega\tau)\, d\tau \quad (19)$$

In this simple case the observed NMR signal is a lorentzian curve and the linewidth gives a measure of the spin relaxation rates through $\Delta\nu_{1/2} = 1/(\pi T_2)$, where $\Delta\nu_{1/2}$ is the full width at half height of the NMR absorption curve.

For the case where $J(0) \neq J(\omega_0)$ and $I = 3/2$, Hubbard [24] has given explicit expressions for the decay of the magnetization in the z-direction and in the rotating xy-plane. A fourier transformation of the xy-decay gives a NMR signal consisting of two superimposed lorentzian curves a and b with the relative intensities of 3 : 2 and linewidths given by

$$\Delta\nu_{\frac{1}{2}}^a = (16\pi/5)\nu_Q^2(1+\eta^2/3)\{\tilde{J}_{00}(0) + \tilde{J}_{-11}(\omega_0)\} \quad (20\,a)$$

$$\Delta\nu_{\frac{1}{2}}^b = (16\pi/5)\nu_Q^2(1+\eta^2/3)\{\tilde{J}_{-11}(\omega_0) + \tilde{J}_{-22}(2\omega_0)\} \quad (20\,b)$$

If the molecular motion can be described by a rotation diffusion equation with an isotropic rotation diffusion constant D_r the spectral densities are [23]

$$\tilde{J}_{-qq}(\omega) = \tau_c\{1+(\omega\tau_c)^2\}^{-1};\ \tau_c = 6/D_r \quad (21)$$

In the discussion of the relaxation of quadrupolar nuclei in amphiphilic systems the assumption of a simple isotropic diffusion is so crude that the results obtained from eq. (21) can only provide a qualitative analysis of the data. A more realistic model is needed in the evaluation of the spectral densities if a deeper insight into the relaxation process is to be obtained.

In the presence of chemical exchange the expressions for the relaxation times have to be modified. There are three limits when the exchange rates do not influence the relaxation rates explicitly:

(*a*) If exchange is slow compared to the relaxation in the different sites, the NMR spectrum is a superposition of the spectra characterizing the different sites.

(*b*) If on the other hand exchange is fast compared to the relaxation but slow relative to the inverse correlation times the spectral densities are given by

$$J_{-qq}(\omega) = \sum_i p_i J^i_{-qq}(\omega) \quad (22)$$

where $J^i_{-qq}(\omega)$ is the spectral density at site i.

(*c*) The third case arises when the exchange time can be considered as infinitely short. Then the correlation function is

$$\overline{V_q^L(0)\, V_{-q}^L(\tau)} = \overline{\left(\sum_i p_i\, V_q^{iL}(0)\right)\left(\sum_j p_j\, V_q^{jL}(\tau)\right)} \tag{23}$$

that is, the field gradients are averaged over sites at each instant and it is the correlation between the mean values that counts.

In the transition ranges between these three regions of exchange rates the theoretical treatment is more complicated. The case when the exchange and relaxation rates are of the same order of magnitude has for $I=3/2$ been examined by Bull [25]. For the case when the correlation times and the life-times in the different sites are of comparable magnitude one has to make specific assumptions about the nature of the motion in the system. If the direction of the electric field gradient tensor is completely randomized at the exchange process and if exponential correlation functions in the different sites are assumed [12], e.q. (24) is obtained

$$J(\omega) = \sum_i p_i J^{il}(\omega) \tag{24}$$

where the spectral density $J^{il}(\omega)$ of site i is modified so that the effective correlation time is given by

$$\tau_{\mathrm{eff},i} = 1/(1/\tau_{c,i} + 1/\tau_{l,i}) \tag{25}$$

where $\tau_{c,i}$ is the rotational correlation time and $\tau_{l,i}$ the life-time in site i.

IIIA. *Relaxation in liquid crystals*

In an anisotropic liquid crystal, which is macroscopically aligned, the time-dependent hamiltonian in eq. (7) gives the relaxation. This hamiltonian can be used to derive an equation of motion for the spin density operator. Such a derivation does not differ markedly from that for isotropic systems. One difference is that the orthogonality relations for correlation functions of irreducible tensor operators derived by Hubbard [26] can not be used. For a spin system consisting of a single nucleus this does not give rise to any severe problems. The equation of motion for the density matrix in the rotating frame, σ^*, is [27]

$$\frac{d}{dt}\sigma^*_{\alpha\alpha'} = \sum_{\beta\beta'} \exp\{i(\alpha-\alpha'-\beta+\beta')\,t\}\, R_{\alpha\alpha'\beta\beta'}\, \sigma^*_{\beta\beta'} \tag{26}$$

R is the relaxation super matrix and α and β denote both the eigenstates of the time-independent hamiltonian (H_0) and their energies. Due to the exponential term in eq. (26), substantial contributions to the relaxation is obtained only when $\alpha-\alpha' = \beta-\beta'$. With this restriction on $\beta-\beta'$ it follows that only correlation functions of the type $\overline{V_q^L(0)\, V_{-q}^L(\tau)}$ enter into the relevant elements of R [28].

The correlation functions obtained from eq. (7) are

$$\overline{V_{q''}^L(0)\, V_{-q''}^L(\tau)} = \sum_{pqq'} (-1)^{p+q}\, V_{-q}^M\, V_{-p}^M\, D_{q''q'}(\Omega_{LD})\, D_{-q''-q'}(\Omega_{LD})$$
$$\overline{\{D_{q'q}(\Omega_{DM}(0))\, D_{-q'p}(\Omega_{DM}(\tau))} - \overline{\delta_{q'0} D_{0q}}\, \overline{D_{0p}}\} \tag{27}$$

In the derivation of eq. (27) the result that the cylindrical symmetry requires that $\overline{D_{q'q}(\Omega_{DM}(0))\, D_{p'p}(\Omega_{DM}(\tau))}$ is zero unless $p' = -q'$ has been used. The factor $D_{q''q'}(\Omega_{LD})\, D_{-q''-q'}(\Omega_{LD})$ makes the correlation functions orientation dependent. This in turn implies that the relaxation times depend on the orientation of the director with respect to the applied magnetic field.

The expressions for the linewidths in a spectrum with quadrupole splittings are somewhat different from the ones valid for isotropic solutions. For $I=3/2$ the central peak corresponding to the transition $m=1/2 \rightarrow m=-1/2$ has the same linewidth as the narrow component in eq. (20a). The linewidths of the two satellites have been calculated from eq. (26). It is only one element of the super matrix R that contributes and

$$\Delta\nu_{\frac{1}{2}} = (6\pi/5)\,\nu_Q^2(1+\eta^2/3)\left\{\tilde{J}_{00}(0) + \tilde{J}_{-11}(\omega_0) + \tilde{J}_{-22}(2\omega_0)\right\} \tag{28}$$

One possible cause of the time dependence of the quadrupole interaction is a chemical exchange between sites having different quadrupole coupling constants. For a two-site case where the motion around the director is fast compared to the exchange, the equations of section 2.3 of ref. [12] can be used to derive an expression for the spectral densities. These are

$$J^{ex}_{-qq}(\omega) = (p_1 p_2/9)\, D_{q0}(\Omega_{LD})\, D_{-q0}(\Omega_{LD})\left\{(\nu_Q S)_1 - (\nu_Q S)_2\right\}^2 \tau_{ex}$$
$$\times\left\{1+(\omega\tau_{ex})^2\right\}^{-1} \tag{29}$$

here $\tau_{ex} = p_2\tau_{l,1} = p_1\tau_{l,2}$.

For an unoriented sample where all values of Ω_{LD} are represented the observed relaxation behaviour is a superposition of the relaxation of all the different microcrystallites. For such a sample the decay of the M_z-magnetization, in principle, is described by a continuous distribution of time constants.

IIIB. *Relaxation in isotropic systems*

Micellar and vesicle solutions and cubic liquid crystals give, in contrast to anisotropic liquid crystals, NMR spectra with a resolution similar to that of simple solutions. The reason for this is that these systems are isotropic over a distance of the order of 100 Å, which is short enough for the diffusion motion to average out the static quadrupole and dipole–dipole interactions. Locally these isotropic systems should be very similar to the corresponding anisotropic liquid crystalline systems, leading to a local anisotropy. This local anisotropy can be very important for the understanding of the relaxation.

It is often reasonable to treat the averaging of the quadrupolar interaction in these isotropic systems as a two-step process. Let us take a micellar solution as an example. In the first step there is a fast local motion partially averaging the quadrupole interaction to $\overline{(\nu_Q S)}$. If this were the only motion we could describe the system in terms of the time-independent hamiltonian of eq. (6) and the time-dependent hamiltonian of eq. (7). The second step leads to a time-dependence also in H_0 of eq. (6) due to the normally slower motion that requires diffusion over the distance of a micellar diameter. This gives a set of hamiltonians

$$H_0 = -\nu_L I_z; \qquad H_1^s(t) = \overline{(\nu_Q S/3)} \sum_q D_{q0}(\Omega_{LD}(t))\, A_q^L \tag{30}$$

and a hamiltonian $H_1^f(t)$ as in eq. (7). The relaxation in isotropic systems can thus be caused either by $H_1^s(t)$ or by $H_1^f(t)$.

We can get a picture of the relaxation process described by $H_1^s(t)$ by introducing as a local "director" the direction perpendicular to the amphiphilic surfaces of the aggregates present in the solution. Then the relaxation corresponding to $H_1^s(t)$ can be described in terms of a time-dependence of the local director orientation. This time-dependence can be due to aggregate (e.g. micellar) rotation, to counter-ion diffusion along the curved aggregate surface or to counter-ion exchange between aggregates. Obviously, processes such as those described here by $H_1^s(t)$ may be significant also in the case of anisotropic liquid crystals and the considerations above should apply to e.g. hexagonal phases.

For lamellar phases we expect the orientation of the director to change so slowly with time that the relaxation effects from this process should be negligible. On the other hand, exchange of counter-ions between microcrystallites with different director orientations and counter-ion translational motion along curved lamellae as in a myeline type structure may well have significant relaxation effects.

It is expected that $H_1^f(t)$ is of similar magnitude for isotropic and anisotropic samples, whereas $H_1^s(t)$ should be quite different for these two cases. Therefore, a comparison of relaxation times for isotropic and anisotropic phases should make it possible to decide whether $H_1^s(t)$ or $H_1^f(t)$ gives the dominant contribution to the relaxation.

For small values of S in eq. (30) the interaction strength represented by $H_1^s(t)$ is much smaller than the one represented by $H_1^f(t)$. So if the slow motion is to contribute to the relaxation rate its correlation time must be longer by a factor $1/S^2$ than the correlation time for the fast motion. Since the transverse but not the longitudinal relaxation time depends on the spectral density at zero frequency the transverse relaxation is expected to be most sensitive to the slow motion.

If the fast and the slow motions are assumed independent the spectral densities in the expressions for the relaxation times are

$$J_{-qq}(\omega) = J^s_{-qq}(\omega) + \overline{J^f_{-qq}(\omega)} \tag{31}$$

where the superscripts s and f refer to the slow and fast motions respectively. The mean value of J^f is

$$\overline{J^f_{-qq}(\omega)} = \int J^f_{-qq}(\omega, \Omega_{LD})\, d\Omega_{LD} \tag{32}$$

III C. *Relaxation effects of different motional processes*

By means of the results obtained in the previous sections it is possible to estimate the effects of different motions on the counterion quadrupole relaxation rates in surfactant systems. The magnitude of the relaxation times are determined by the strength of the quadrupole coupling, which can be estimated as in section II, and by the correlation times.

In solutions containing spherical micelles an upper limit for the correlation time of the slow motion can be obtained from the Stokes' formula for the rotational diffusion coefficient [23] and

$$\tau_c = \frac{r^2}{6D_s} = \frac{4\pi}{3}\frac{r^3\eta}{kT} \tag{33}$$

where r is the hydrodynamic radius of the micelle and η is the viscosity of the medium. With $r = 14 \times 10^{-10}$ m and $T = 298$ K eq. (33) gives in water $\tau_c = 2.8 \times 10^{-9}$ s. This is the correlation time that is obtained when the ion is considered as fixed at the micelle surface. It is probable though that the counter-ions diffuse at, or in the vicinity of, the micelle surface which leads to a shortening of the correlation time. If the diffusion normal to the micelle surface is neglected the correlation time can be calculated from a value of D_s in eq. (33). For a free sodium ion in water solution $D_s \simeq 1.2 \times 10^{-9}$ m²/s [29]. If it is assumed that 60% of the ions are bound so strongly to the micelle that they do not move independently and the remaining ones diffuse as free ions one obtains with $r = 14 \times 10^{-10}$ m and $T = 298$ K $\tau_c = 6.7 \times 10^{-10}$ s, when the exchange between the sites is fast compared to the diffusional motion.

From the observed splitting in a lamellar phase and from a correlation time as estimated above, the contribution from the slow motion to the relaxation times can be calculated, using eqs. (8) and (30). In the system water–sodium octyl sulphate–decanol the splitting is about 30 kHz in the lamellar phase (cf. Table I). For a corresponding solution with higher water content containing spherical micelles having a hydrodynamic radius $\sim 14 \times 10^{-10}$ m, the calculated relaxation times for slow motion only with $\tau_c = 6.7 \times 10^{-10}$ s are T_1^s and $T_2^s = 26$ ms which is slightly longer than the observed value.

The contribution to the relaxation from the local motion is more difficult to estimate. Here we will consider the exchange between a site where the ion is bound to the surface and a site where the ion is free. The correlation time for this motion is estimated to be comparatively long. If for the water–sodium octyl sulphate–decanol system the splitting is explained through a two-site model with $p_1 = 0.4$, $(\nu_Q S)_1 = 0$ and $p_2 = 0.6$, $(\nu_Q S)_2 = 50$ kHz the contribution to the relaxation from exchange can be obtained from eq. (29). The orientation dependent factor $D_{q0}(\Omega_{LD}) D_{-q0}(\Omega_{LD})$ is replaced by its isotropic mean value 1/5 and one obtains

$$\frac{1}{T_1^f} = \frac{1}{T_2^f} = 3.8 \times 10^{10}\, \tau_{ex}$$

A value $\tau_{ex} = 8.2 \times 10^{-10}$ s makes $1/T_2^f$ compatible with the experimentally observed relaxation rate.

These order of magnitude estimates show that both the local motion and the overall slow motion can be responsible for the relaxation. Experimentally it is often found that the relaxation times T_1 and T_2 are nearly the same in micellar and liquid crystalline solutions [6, 30, 31], indicating that it is the local motion that is most important in determining the relaxation rates. In the system water–cetyltrimethylammonium bromide the relaxation rate was found to decrease significantly in going from rodshaped micelles to a hexagonal liquid crystalline phase [30]. This finding is hard to explain if the slow motion does not contribute to the relaxation rate in the micellar solutions.

IV. Concluding remarks

It has been our aim to present a theoretical framework for the interpretation of quadrupole splittings and relaxation times of alkali and halide ions in amphiphile–water systems. The experimental data are so far not extensive enough to permit general statements on the applicability of the derived theoretical expressions. However, above we have attempted to compare experimental quadrupole splittings and relaxation rates with those given by the theory, for some systems, where experimental measurements have been performed. It was found, for example, that observed ^{23}Na quadrupole splittings in systems where the surfactant has a sulphate endgroup are in excellent agreement with those obtained from a simple electrostatic model.

Changes in counter-ion quadrupole relaxation rates at phase transitions are generally small which indicates that a fast local motion is dominant in determining the relaxation. Using experimentally determined quadrupole splittings and assuming the critical local motion to be a translation of the ions perpendicular to the surface a reasonable agreement between theory and experiment was obtained. Other possible local motional processes involve the rotational and translational motion of the water molecules in the hydration sheath of the counter-ion. For one system a significant reduction in relaxation rate at the transition from an isotropic solution to a mesophase has been observed. Our calculations show that a motional process, involving lateral counter-ion diffusion gives a contribution to the relaxation rate in reasonable agreement with this observation. Systematic studies concerning the changes in relaxation rate at

phase transitions have been initiated in order to provide more information on the importance of the slow motions in the systems.

On certain points the results can be applied to the interpretation of NMR experiments on the same type of systems using other nuclei. The formulae concerning the quadrupole splittings can e.g. be applied to deuteron splittings, the only difference being that the field gradients are mainly of a covalent nature. In the analysis of ^{1}H and ^{13}C relaxation data in isotropic systems it is often necessary to make a distinction between the fast and slow motions as discussed in section IIIB. This was done by Charvolin and Rigny [20] for a cubic liquid crystalline phase but it is equally important for micellar and vesicle solutions.

References

1. Eriksson, J. C., Johansson, Å. and Andersson, L. O., Acta Chem. Scand. *1966*, 20, 2301.
2. Robb, I. D., J. Colloid Interface Sci. *1971*, 37, 521.
3. Lindman, B. and Danielsson, I., J. Colloid Interface Sci. *1972*, 39, 349.
4. Lindblom, G. and Lindman, B., J. Phys. Chem. *1973*, 77, 2531.
5. James, T. L. and Noggle, J. H., Anal. Biochem. *1972*, 49, 208.
6. Lindblom, G. and Lindman, B., Mol. Cryst. Liquid Cryst. *1971*, 14, 49.
7. Lindblom, G. and Lindman, B., Mol. Cryst. Liquid Cryst. *1973*, 22, 45.
8. Shporer, M. and Civan, M. M., Biophys. J. *1972*, 12, 114.
9. Rose, M. E., Elementary Theory of Angular Momentum. Wiley, New York, 1957.
10. Luckhurst, G. R., *in* Liquid Crystals and Plastic Crystals (ed. G. W. Gray and P. A. Winsor), Vol. 2. Ellis Horwood Publ., Chichester, Chap. 8, in press.
11. Wennerström, H., Chem. Phys. Lett. *1973*, 18, 41.
12. Wennerström, H., Molec. Phys. *1972*, 24, 69.
13. Cohen, M. H. and Reif, F., Solid State Phys. *1957*, 5, 321.
14. Cope, F. W., J. Gen. Physiol. *1967*, 50, 1353.
15. Lindblom, G., Wennerström, H. and Lindman, B., Chem. Phys. Lett. *1971*, 8, 489.
16. Ekwall, P., Danielsson, I. and Stenius, P., *in* Surface Chemistry and Colloids, MTP International Review of Science. Physical Chemistry Series One, Vol. 7, p. 97, 1972.
17. Hertz, H. G., Ber. Bunsenges. Physik. Chem. *1973*, 77, 531.
18. Charvolin, J., Manville, P. and Deloche, B., Chem. Phys. Lett. *1974*, in press.
19. Persson, N.-O., Wennerström, H. and Lindman, B., Acta Chem. Scand. *1973*, 27, 1667.
20. Charvolin, J. and Rigny, P., J. Chem. Phys. *1973*, 58, 3999.
21. Persson, N.-O., Lindblom, G., Lindman, B. and Arvidsson, G., Chem. Phys. Lipid., in press.
22. Lindblom, G., Persson, N.-O. and Lindman, B., *in* Chemie, Physikalische Chemie und Anwendungstechnik der grenzflächenaktiven Stoffe. Proc. VIth International Congress on Surface Active Substances, Zürich, 1972, Vol. II, p. 939. Carl Hanser Verlag, München, 1973.
23. Abragam, A., The Principles of Nuclear Magnetism, Chap. 8. Oxford University Press, London, 1961.
24. Hubbard, P. S., J. Chem. Phys. *1970*, 53, 985.
25. Bull, T. E., J. Magn. Reson. *1972*, 8, 344.
26. Hubbard, P. S., Phys. Rev. *1969*, 180, 319.
27. Redfield, A. G., Adv. Magn. Reson. *1965*, 1, 1.
28. Hoffman, R. A., Adv. Magn. Reson. *1970*, 4, 87, eq. (92).
29. Mills, R., J. Amer. Chem. Soc. *1955*, 77, 6116.
30. Lindblom, G., Lindman, B. and Mandell, L., J. Colloid Interface Sci. *1973*, 42, 400.
31. Lindblom, G. and Lindman, B., *in* Chemie, Physikalische Chemie und Anwendungstechnik der grenzflächenaktiven Stoffe. Proc. VIth International Congress on Surface Active Substances, Zürich, 1972, Vol. II, p. 925. Carl Hanser Verlag, München, 1973.

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Erratum

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Article by H. Wennerström, G. Lindblom and B. Lindman: *Theoretical Aspects on the NMR of Quadupolar Ionic Nuclei in Micellar Solutions and Amphiphilic Liquid Crystals.*

An omission of a factor 1/2 has been made in deriving eqs. (14) and (15) which should read

$$\nu_Q = \frac{5.2 \times 10^5 (1+\gamma_\infty)}{I(2I-1)} \left(\frac{2\varepsilon+3}{5\varepsilon}\right) \frac{QZ}{r^3} \tag{14}$$

and

$$\nu_Q = \mp \frac{3.26 \times 10^{-5} (1+\gamma_\infty)}{I(2I-1)} \left(\frac{2\varepsilon+3}{5\varepsilon}\right) \frac{Q\mu}{r^4} \tag{15}$$

The theoretically calculated quadrupole coupling constants are as a consequence of this too large by a factor of 2. The conclusions are not affected.

The following printing errors have also been detected on page 101 right column: (20a) on line 5 should be corrected to (20b) and the factor in eq. (28) $6\pi/5$ should be $16\pi/5$.