Quadrupole Splittings of Alkali NMR Signals in Decylammoniumchloride Mesophases

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In lyotropic mesophases of decylammoniumchloride the NMR signals of the alkali nuclei ^{6}Li, ^{7}Li, ^{23}Na, ^{39}K, ^{85}Rb, ^{87}Rb and ^{133}Cs solubilized in these mesophases have been observed. The linewidths of the signals are comparable with the linewidths in aqueous solutions. Apart from ^{6}Li and ^{39}K for all other alkali nuclei in the mesophases first-order quadrupole splitted spectra have been observed. For the rubidium isotopes ^{85}Rb and ^{87}Rb a ratio of the quadrupole splitting of 2.01 ± 0.05 has been determined. Further the chemical shifts of the solubilized alkali nuclei relative to infinitely diluted aqueous solutions have been measured.

Introduction

Lyotropic liquid crystals have been proposed as model systems for biological membranes [1—10]. Since small molecules or ions can be dissolved in amphiphilic mesophases, interactions of these particles with the host can be studied. Though such ions are not chemically bound to the soap molecules forming the liquid crystal, the electric field gradient is not averaged out on the whole also at the position of the ionic nuclei. Therefore quadrupolar nuclei are very sensitive probes since in addition to the Zeeman splitting a quadrupole splitting can sometimes be observed.

The mechanism of the interaction, is however, not well understood [11—16]; the lineshape of the NMR spectra of quadrupolar nuclei depends on a lot of different parameters. Hence it is very difficult to draw conclusions on the structure of the mesophase from spectra of dissolved ions. But at this state of knowledge it is interesting to see what ions can be embedded in a certain mesophase and what types of spectra can be expected. Further it is important to know whether the interactions which can be observed are the same for two different isotopes of the same element or not. It has been shown for instance that for the isotopic pair ^{35}Cl and ^{37}Cl the ratio of the observed quadrupole splittings agrees with the ratio of the quadrupole moments [17].

Some qualitative conclusions are possible from measurements of chemical shifts of the Larmor frequencies of the dissolved alkali nuclei. For instance the isotropic chemical shift can give some information of the averaged chemical environment of the ions [8, 12]. As the molecules or ions can be dissolved in the lyotropic liquid crystal only to a limited extent without destroying the mesophase, sometimes very long measuring times must be taken into account. NMR investigations of anionic and cationic counterions have been performed in some mesophases [1, 4—9, 12—23]. In this paper NMR spectra of isotopes of all alkali elements were observed in mesophases basing on decylammoniumchloride. For almost all nuclei first-order quadrupole splitted spectra could be observed. For the isotopic pair ^{85}Rb and ^{87}Rb a ratio of the quadrupole moments from the observed quadrupole splittings was calculated. Further the isotropic chemical shifts of these signals relative to aqueous solutions were determined.

Experimental

The NMR measurements of the alkali nuclei were performed on a multi-nuclei Bruker pulse spectrometer SXP 4-100 at (300 ± 3) K in a magnetic field of 2.114 T, produced by a Bruker high-resolution magnet, which was externally stabilized. Cylindrical sample tubes of 10 mm outer diameter were used. The free induction decays were accumulated and Fourier transformed by a B-NC 12 data unit. The absorption signals were evaluated. The NMR parameters of the observed alkali nuclei are given in Table 1.

The liquid crystals, which were investigated by NMR in this work, were prepared according to Ref. [22]. The composition of the various samples is given in Table 2*. By trial and error mesophases were prepared, as to our knowledge for the decyl-

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Table 1. NMR parameters of the observed alkali nuclei.

Nucleus	Natural abundance in %	Spin	Quadrupole moment* in 10^{-24} cm^2	Larmorfreq. at 2.11 T in MHz	Receptivity
^{6}Li	7.4	1.0	-0.0008	13.2	$6.3 \cdot 10^{-4}$
^{7}Li	92.6	3/2	-0.04	35.0	$2.7 \cdot 10^{-1}$
^{23}Na	100.0	3/2	$+0.10$	23.8	$9.3 \cdot 10^{-2}$
^{39}K	93.1	3/2	$+0.049$	4.2	$4.7 \cdot 10^{-4}$
^{85}Rb	72.2	5/2	$+0.26$	8.7	$7.6 \cdot 10^{-3}$
^{87}Rb	27.8	3/2	$+0.13$	29.5	$4.9 \cdot 10^{-2}$
^{133}Cs	100.0	7/2	-0.0030	11.8	$4.7 \cdot 10^{-2}$

* averaged values taken from G. H. Fuller [25].

ammoniumchloride mesophases no phase diagrams exist and such phase diagrams would change for dissolved alkali ions. A decision, whether a prepared sample was a liquid crystal or not, was made by observing the birefringence of the sample. With this optical method further the temperature range for the liquid crystal phase could easily be determined.

The NMR signals of all samples were observed about 1 day after the preparation. All systematic measurements were performed about 1 month later. No strong changes in the NMR parameters could be observed. The chemical shifts of the signals were measured relative to an aqueous solution by the sample exchange technique and extrapolated to infinitely diluted aqueous solutions. As most of the mesophases are fast reoriented in the magnetic field no long waiting times were necessary.

Results and Discussion

In a first measurement the NMR signal of ^{14}N has been observed in the liquid crystal number 1 (see Table 2). The quadrupole splitting is (817 ± 3) Hz, this is somewhat different from the splitting reported by Chen and Glickson [22] in a very similar sample. The linewidth of the different signals is about 20 Hz. In addition to the indirect spin-spin coupling between ^{1}H and ^{14}N a small contribution of direct dipole-dipole coupling can be observed [22].

In liquid crystal number 2 by ^{2}H NMR the development of the macroscopic orientation in the magnetic field could be seen. The lineshape changes within a few minutes from a powder pattern to a sharp doublett. The linewidth of the two lines is about 25 Hz. The macroscopic orientation is perpendicular to the static magnetic field and the observed quadrupole splitting about 200 Hz.

For ^{17}O in the liquid crystal number 3 a quintett was measured. The intensities of the different lines do not agree with the theoretical intensity of a first-order quadrupole splitted signal for a nucleus with spin 5/2, indicating that different molecular arrangements in the mesophase exist. The line-

Table 2. Composition of the mesophases* used for the NMR investigations.

	Components				
Number	Decylammonium-chloride in weight %	NH_4Cl in weight %	0.1 n HCl in weight %	0.1 n DCl in weight %	Solute
1	41	5	54	—	—
2	39	3	—	54	4 wt% KCl
3	41	5	54**	—	—
4	37	4	55	—	4 wt% LiCl
5	40	5	50	—	5 wt% NaCl
6	37	4	55	—	4 wt% RbCl
7	40	3	52	—	5 wt% CsCl

* We like to thank Dr. J. D. Glickson and Dr. D. M. Chen for the private communication of the components of liquid crystal number 1 prior to publication [22].

** For this liquid crystal the used 0.1 n HCl was 10% enriched in ^{17}O.

width of the central line was about 200 Hz and the observed quadrupole splitting (2040 ± 50) Hz.

The ^{2}H and ^{17}O NMR signals were also observed by Fujiwara et al. [3] in a mesophase with decylammoniumchloride of similar composition. The quadrupole splitting was for both nuclei about a factor 1.2 stronger. Recently Niederberger and Tricot [24] have reported ^{2}H and ^{17}O spectra of a mesophase with sodiumdecylsulfate, they got different values for the quadrupole splitting. This can be explained by an other structure of the mesophase. An absorption signal of ^{7}Li in the liquid crystal number 4 is given in Figure 1. The intensities of the 3 lines are about 3 : 4 : 3 as one expects for a first-order quadrupole splitted signal of a nucleus with spin 3/2. The measured quadrupole splitting, values of the linewidth of the central line and of the chemical shift of the ^{7}Li signal relative to an infinitely diluted aqueous solution are given in Table 3.

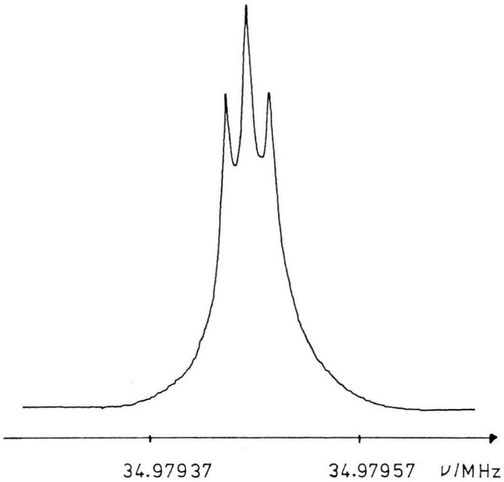

Fig. 1. First-order quadrupole splitted absorption signal of ^{7}Li in liquid crystal number 4 (see Table 2). Experimental spectrum width: 1 kHz; number of pulses: 1300; measuring time: 65 min. 1024 data points were accumulated followed by 3072 points of zero-filling before Fourier transformation.

For ^{6}Li only a single line was observed with a linewidth of about 9 Hz. From the splitting measured for ^{7}Li and from the ratio of the quadrupole moments $\frac{Q(^7\text{Li})}{Q(^6\text{Li})} = 50$ (Ref. [25]) a splitting of 2.8 Hz for ^{6}Li can be calculated, which was not resolved.

In the liquid crystal number 5 a powder pattern of ^{23}Na was detected, which did not show a macroscopic orientation even after being a long time in the magnetic field. An example of such a spectrum is given in Figure 2. By integrating the different parts of the spectrum it could be shown, that the ratios of the intensities are 1 : 4 : 1 instead of 3 : 4 : 3. Chen and Reeves [18] found a similar behaviour of the intensities in a mesophase with sodiumdecylsulfate. The results of our measurement are given in Table 3.

Rotating the liquid crystal number 5 around a rotation axis perpendicular to the magnetic field yields a spectrum, which consists of a central line with a linewidth of 15 Hz and two broad satellites, the frequency of which indicates, that the crystal now is macroscopically oriented perpendicular to the magnetic field.

Although optical measurements and NMR investigations of ^{2}H of the liquid crystal number 2 confirmed the existence of a mesophase, for ^{39}K in this system only a single signal was observed. The NMR data are given in Table 3. In a further mesophase of similar composition with 0.1 n HCl the same results were found. Potassium seems to be in

Table 3. Results of NMR measurements of alkali nuclei in decylammoniumchloride mesophases.

Nucleus	Liquid crystal number*	Quadrupole splitting** in Hz	Linewidth of the central line in Hz	Chemical shift***
^{6}Li	4	—	8 ± 2	0.2 ± 0.2
^{7}Li	4	23 ± 1	23 ± 3	0.1 ± 0.2
^{23}Na	5	1360 ± 37	23 ± 3	0.3 ± 0.2
^{39}K	2	—	12 ± 1	− 3.6 ± 1.1
^{85}Rb	6	3596 ± 83	317 ± 47	—
^{87}Rb	6	5966 ± 74	170 ± 7	9 ± 1
^{133}Cs	7	33 ± 2	13 ± 1	27 ± 1

* The composition of the liquid crystals is given in Table 2.
** The given quadrupole splitting is the frequency separation of the different lines of the observed multipletts.
*** The chemical shift is given as $[(\nu_{\text{Liq cryst}} - \nu_0)/\nu_0] \cdot 10^6$ where $\nu_{\text{Liq cryst}}$ is the frequency of the central line and ν_0 the Larmor frequency in infinitely diluted aqueous solutions (see References [27—31].

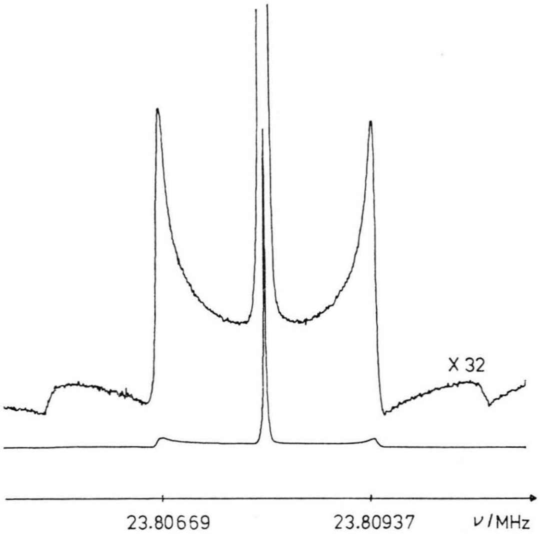

Fig. 2. Powder pattern of ^{23}Na in liquid crystal number 5 (see Table 2). The splitting is due to a quadrupole interaction. Experimental spectrum width: 10 kHz; number of pulses: 13000; measuring time: 30 min. 1024 data points were accumulated, the following 3072 points were filled with zeros before Fourier transformation.

a molecular aggregation, in which the quadrupole coupling is very small.

For both rubidium isotopes ^{85}Rb and ^{87}Rb in the liquid crystal number 6 NMR spectra were measured. An absorption signal is given for ^{85}Rb in Fig. 3, this is a typical signal of a first-order quadrupole splitted spectrum of a nucleus with spin 5/2. The NMR data for both nuclei ^{85}Rb and ^{87}Rb are given in Table 3. Since the relative chemical shift for two isotopes of the same element is the same [26], only for ^{87}Rb chemical shift measurements were undertaken. From the measurement of the quadrupole splitting of both nuclei a ratio of the quadrupole moments can be derived. Assuming an equal field gradient at both nuclei a value

$$\frac{Q(^{85}\mathrm{Rb})}{Q(^{87}\mathrm{Rb})} = 2.01 \pm 0.05$$

was evaluated, which is in agreement with optical results [25].

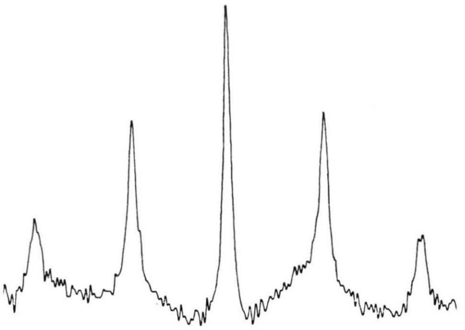

Fig. 3. First-order quadrupole splitted absorption signal of ^{85}Rb in liquid crystal number 6 (see Table 2). Experimental spectrum width: 20 kHz; number of pulses: 21000; measuring time 36 min. 300 data points were accumulated followed by 3796 points of zero-filling before Fourier transformation. The signal-to-noise ratio of the ^{87}Rb spectrum is much higher due to the more favourable receptivity (see Table 1).

Figure 4 shows the NMR signal of ^{133}Cs in the liquid crystal number 7. Because of overlapping signals the experimental intensities are somewhat different from the predictions of the theory for a first-order quadrupole splitted signal of a nucleus with spin 7/2. The NMR data of this measurement are also given in Table 3.

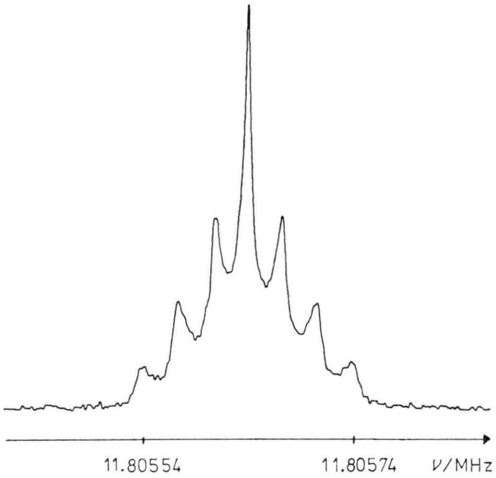

Fig. 4. First-order quadrupole splitted absorption signal of ^{133}Cs in liquid crystal number 7 (see Table 2). Experimental spectrum width: 1 kHz; number of pulses: 200; measuring time: 33 min. 1024 data points were accumulated followed by 3072 points of zero-filling before Fouriertransformation.

For the alkali nuclei already some NMR measurements have been performed in liquid crystals, mainly in mesophases with decylsulfates [5, 9, 14, 18, 21], octylsulfates and heptanoates [8, 12, 13, 15, 16, 20]. There have been measured dependencies of the quadrupole splitting on the composition of the mesophases and on the temperature. But no measurements of alkali ions were reported in mesophases with decylammoniumchloride, as far as we know.

Conclusion

It could be shown that in a decylammoniumchloride mesophase alkalichlorides can be dissolved and that NMR spectra of the alkali nuclei can be observed in the mesophases. The linewidths of the alkali signals in the liquid crystals are comparable with the corresponding linewidths in aqueous solutions.

In the mesophases there is a quadrupole interaction which is not wholly averaged out in course of time, yielding for almost all alkali nuclei first-order quadrupole splitted spectra. Compared with other mesophases, for which similar measurements have been done, the quadrupole splitting is smaller for the decylammoniumchloride liquid crystal (see f.e. Ref. [12—16]). It could be shown that the ratio of the quadrupole splitting of the rubidium isotopes ^{85}Rb and ^{87}Rb is the same as the ratio of the quadrupole moments. Apart from the influence of the quadrupole moments there is no isotopic influence on the splitting. This is not true for the quadrupole splitting of different alkali nuclei. It seems that the dissolved alkali nuclei influence the structure of the mesophases themselves.

Apart from ^{133}Cs the observed isotropic chemical shifts relative to infinitely diluted aqueous solutions are small, though this isotropic interaction is not influenced by the order parameters of the mesophases and therefore should be sensitive to changes in the chemical environment of the ions. This means that the alkali ions are not attached to the decylammoniumchloride molecules, but have to a good approximation only an aqueous neighbourhood although only about 50 weight % of the mesophase consists of water.

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[1] L. W. Reeves and A. S. Tracey, J. Amer. Chem . Soc. **96**, 365 (1974).

[2] L. W. Reeves, M. Suzuki, A. S. Tracey, and J. A. Vanin, Inorg. Chem. **13**, 999 (1974).

[3] F. Fujiwara, L. W. Reeves, A. S. Tracey, and L. A. Wilson, J. Amer. Chem. Soc. **96**, 5249 (1974).

[4] F. Fujiwara, L. W. Reeves, and A. S. Tracey, J. Amer. Chem. Soc. **96**, 5250 (1974).

[5] D. M. Chen, K. Radley, and L. W. Reeves, J. Amer. Chem. Soc. **96**, 5251 (1974).

[6] D. M. Chen, L. W. Reeves, A. S. Tracey, and M. M. Tracey, J. Amer. Chem. Soc. **96**, 5349 (1974).

[7] G. Lindblom, N.-O. Persson, and B. Lindman, Ber. Bunsenges. **78** ,955 (1974).

[8] H. Gustavsson and B. Lindman, J. Amer. Chem. Soc. **97**, 3923 (1975).

[9] K. Radley, L. W. Reeves, and A. S. Tracey, J. Phys. Chem. **80**, 174 (1976).

[10] N.-O. Persson and B. Lindman, Mol. Cryst. Liq. Cryst. **38**, 327 (1977).

[11] H. Wennerström, G. Lindblom, and B. Lindman, Chemica Scripta **6**, 97 (1974).

[12] H. Gustavsson, G. Lindblom, B. Lindman, N.-O. Persson, and H. Wennerström, NMR Studies of the Interaction between Sodium Ions and Anionic Surfactants in some Amphiphile-Water Systems, in: Liquid Crystals and Ordered Fluids, Vol. 2, p. 161. Editors: J. F. Johnson and R. S. Porter, Plenum Press, New York 1974.

[13] H. Wennerström, N.-O. Persson, and B. Lindman, ACS Symposium Series **9**, 253 (1975).

[14] K. Radley and L. W. Reeves, Can. J. Chem. **53**, 2998 (1975).

[15] G. Lindblom, H. Wennerström, and B. Lindman, ACS Symposium Series **34**, 372 (1976).

[16] J. B. Rosenholm and B. Lindman, J. Colloid Interface Sci. **57**, 362 (1976).

[17] G. Lindblom, H. Wennerström, and B. Lindman, Chem. Phys. Lett. **8**, 489 (1971).

[18] D. M. Chen and L. W. Reeves, J. Amer. Chem. Soc. **94**, 4384 (1972).

[19] N.-O. Persson and B. Lindman, J. Phys. Chem. **79**, 1410 (1975).

[20] G. Lindblom, H. Wennerström, and B. Lindman, J. Magn. Res. **23**, 177 (1976).

[21] J. Charvolin, A. Loewenstein, and J. Virlet, J. Magn. Res. **26**, 529 (1977).

[22] D. M. Chen and J. D. Glickson, J. Magn. Res. **28**, 9 (1977).

[23] C. L. Khetrapal, A. C. Kunwar, A. S. Tracey, and P. Diehl, Nuclear Magnetic Resonance Studies in Lyotropic Liquid Crystals, in: NMR Basic Principles and Progress, Vol. 9, Editors: P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin 1975 and references therein.

[24] W. Niederberger and Y. Tricot, J. Magn. Res. **28**, 313 (1977).

[25] G. H. Fuller, Nuclear Spins and Moments, J. Phys. Rev. Data **5**, 835 (1976).

[26] H. Krüger, O. Lutz, A. Nolle, A. Schwenk, and G. Stricker, Z. Naturforsch. **28a**, 484 (1973).

[27] G. Heckmann, Diplomarbeit, Tübingen 1966.

[28] C. Deverell and R. E. Richards, Mol. Phys. **10**, 551 (1966).

[29] W. Sahm and A. Schwenk, Z. Naturforsch. **29a**, 1754 (1974).

[30] O. Lutz and A. Nolle, Z. Naturforsch. **27a**, 1577 (1972).

[31] O. Lutz Z. Naturforsch. **23a**, 1202 (1968).