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Abstract—Nuclear magnetic resonance line-widths of ^{23}Na have been determined at several compositions in two isotropic solution phases and five mesomorphous phases in the sodium caprylate–decanol–water system. The results obtained demonstrate that the rate of nuclear magnetic relaxation of ^{23}Na$^+$ is primarily determined by the number of water molecules per sodium ion. This indicates that in all the phases investigated, the sodium ions are predominantly coupled to water molecules. A comparison with ^{81}Br nuclear magnetic relaxation data shows that the bonding of sodium ions is markedly different from that of bromide ions in systems containing association colloids and water. This diversity is found to be due to differences in ion–water coupling.

The phase equilibria in the system sodium caprylate (NaC$_8$)–decanol–water have been investigated by Ekwall and co-workers[1–4] who have given evidence for the presence of several mesomorphous phases and of two homogeneous isotropic solution phases (L_1 and L_2). The phase diagram is given in Fig. 1. These investigations were concerned also with the structures of the different phases. X-ray diffraction was chiefly used to study the mesophases[3–6] and the solution phases were studied with a number of physico-chemical methods.[7–9]

Recently the decanol-rich isotropic solution phase (the L_2 phase) was studied by Gillberg and Ekwall[10] by means of proton magnetic resonance. This study provided valuable information particularly regarding the coupling of the water molecules in the micelles and in the intermicellar solutions. The bonding properties of the sodium ions in the different phases are however also of great interest. For nuclei having electrical quadrupole moments, as e.g. ^{23}Na, studies of nuclear magnetic relaxation rates have been shown to give important information regarding bonding properties and microdynamic behaviour. In particular, studies of nuclear quadrupole relaxation of ionic nuclei in aqueous solutions have contributed to the understanding of the existing ion–ion and ion–water interactions (see e.g. ref. 11 and 12 where also additional references are given). In the present paper an account of studies of the line-widths of the ^{23}Na nuclear magnetic resonance in the L_1, L_2, B, C, D, E and F phases (the designations of the phases are defined in Fig. 1) will be given. (Some data concerning the L_2 phase have already been reported by Gillberg and Ekwall.[10])

Experimental

A Varian V-4200 B n.m.r. spectrometer equipped with a 12 inch V-4012 A magnet was used for the measurements. The magnetic field was controlled by a Varian Fieldial. The derivative of the absorption curve was recorded and the line-width was evaluated directly from the recorded curve as the distance between the maximum and minimum slopes of the absorption curve. The resonance frequency was stabilized at 10 MHz by means of a Hewlett Packard 5245 L electronic counter. The r.f. field was chosen sufficiently low so as to avoid saturation. Since the ^{23}Na magnetic resonance signal is rather narrow compared to the attainable homogeneity of the magnetic field we were not able to obtain absolute line-width data. (Previous determinations of ^{23}Na line-widths in electrolyte solutions have also failed to give absolute line-widths.[13, 14])

The modulation frequency was 40 Hz and the amplitude of the modulation field 28 milligauss. Since the modulation frequency is of the same order of magnitude as the line-widths, the shape of the resonance signal is influenced by modulation effects. Owing to this and to the broadening due to finite modulation amplitude and to magnetic field inhomogeneity the reported line-widths are always somewhat greater than the "natural" linewidth. An indication of the magnitude of the broadening effect due to the instrumental limitations is provided by the fact that the observed width of the ^{23}Na resonance signal in a dilute aqueous solution of sodium chloride was 22 milligauss. The "natural" line-width for this solution was calculated to be approximately 5 milligauss (this value is only approximate since the shape of the undistorted resonance signal is not known—the order of magnitude is however certain) from the

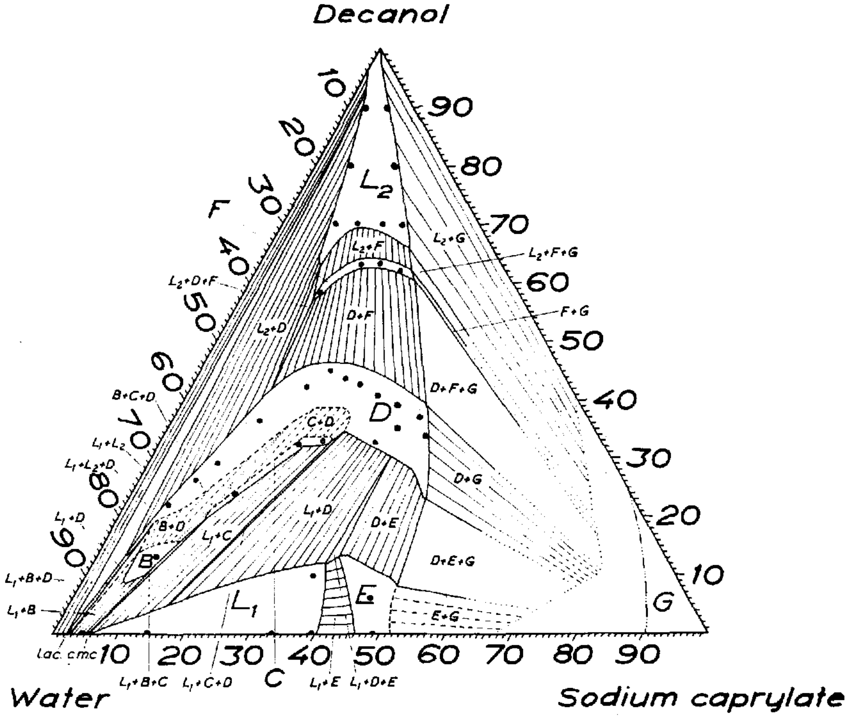

Figure 1. Phase diagram for the three-component system sodium caprylate–decanol–water at 20°C. B–F regions with homogeneous mesomorphous phases; G region with solid substances; L_1 region with homogeneous isotropic aqueous solution; L_2 region with homogeneous isotropic decanolic solution. The compositions of the samples investigated in the present work are indicated by dots in the diagram.

Table 1 Observed Line-widths of the ^{23}Na Nuclear Magnetic Resonance Signal in the Sodium Caprylate–Decanol–Water System (Temperature 25 ± 1°C)

Composition (weight %)				
NaC_8	Decanol	Water	Phase	Line-width (milligauss)
4.7	—	95.3	L_1	23
14.3	—	85.7	L_1	23
34.0	—	66.0	L_1	22
39.5	—	60.5	L_1	23
35.0	10.0	55.0	L_1	24
49.0	—	51.0	*E*	26
46.0	6.0	48.0	*E*	26
9.0	13.0	78.0	*B*	23
21.5	32.5	46.0	*C*	22
16.0	24.0	60.0	*C*	24
25.0	33.0	42.0	*C*	24
7.0	22.0	71.0	*D*	25
9.0	26.0	65.0	*D*	22
11.0	29.0	60.0	*D*	24
14.7	36.3	50.0	*D*	23
18.0	42.0	40.0	*D*	24
20.0	45.0	35.0	*D*	24
33.5	32.4	34.1	*D*	26
23.0	43.4	33.6	*D*	25
25.5	42.5	32.0	*D*	26
29.5	40.5	30.0	*D*	26
35.7	34.8	29.5	*D*	29
33.3	39.2	27.5	*D*	24
40.0	34.0	26.0	*D*	36
38.0	37.0	25.0	*D*	38
12.0	58.0	30.0	*F*	24
16.0	63.0	21.0	*F*	24
19.0	63.0	18.0	*F*	28
22.2	61.8	16.0	*F*	42
8.0	70.0	22.0	L_2	23
11.5	70.0	18.5	L_2	26
15.5	70.0	14.5	L_2	30
18.3	70.0	11.7	L_2	47
5.3	80.0	14.7	L_2	26
12.2	80.0	7.8	L_2	49
2.7	90.0	7.3	L_2	42
6.1	90.0	3.9	L_2	52

T_2-data given by Eisenstadt and Friedman.[15] The line-widths of the broader signals reported in this paper are considerably less influenced by the instrumental broadening effect. In all cases our reported data represent upper limits of the "natural" line-widths. Since our primary interest was to detect the structural changes occurring in the different phases a qualitative discussion can nevertheless be given. The relative line-widths are accurate within 10 per cent. The sweep rate was chosen sufficiently low not to produce any detectable distortion of the recorded curve. Sample temperature was 25 ± 1°C. The samples were prepared by the staff at the Laboratory for Surface Chemistry and their compositions are indicated by the dots in Fig. 1. The observed line-widths, which are given in Table 1, are usually the arithmetic means of three to four measurements. Only values greater than 26 milligauss can be considered to be broadened in excess of the broadening effect due to our instrumental limitations. No correction of the line-width data presented in Table 1 for the modulation and inhomogeneity broadening has been made since a separation of these effects is difficult. The inhomogeneity effect depends on the magnetic field distribution over the sample but is believed to give an approximately constant contribution to the observed line-width in all cases whereas the effect of the modulation broadening will decrease as the line-width increases. A discussion of these problems has been given by Lösche.[16] As described below an approximate method for correcting the line-widths has been applied to one set of data.

Discussion

The ^{23}Na nucleus has a spin quantum number $I = 3/2$ and an electric quadrupole moment. The interaction between the latter and the fluctuating electric field gradients at the nucleus will, under most circumstances, provide the dominant nuclear magnetic relaxation mechanism (cf. ref. 11 and 15). The relaxation of nuclei having quadrupole moments has been studied previously for electrolyte solutions by several workers (see e.g. ref. 11 and 12). A theory of quadrupole relaxation in liquids has been developed by

Abragam and Pound[17] who derived the following expression for the inverse spin-lattice relaxation time:

$$T_1^{-1} = \frac{3}{40} \cdot \frac{2I+3}{I^2(2I-1)} \cdot \left(\frac{eQ}{\hbar}\right)^2 \left\langle \left(\frac{\partial^2 V}{\partial z^2}\right)^2 \right\rangle \tau_c \qquad (1)$$

where eQ is the electric quadrupole moment of the nucleus, $\langle(\partial^2 V/\partial z^2)^2\rangle$ is the mean square electric field gradient at the nucleus and τ_c is a correlation time describing the random molecular motions producing the electric field gradients, while $\hbar = h/2\pi$ (h the Planck constant).

Since the ^{23}Na resonance signals observed in this work are rather narrow it seems to be reasonable to describe the situation by the case of extreme narrowing (this has been verified for ^{23}Na for some electrolyte solutions[15]). In this case T_1 is equal to T_2 and the nuclear magnetic resonance line-width is proportional to the inverse spin-lattice relaxation time. According to Eq. (1) the variable factors that determine the width of the resonance line of a given nucleus should be the mean square electric field gradient and the correlation time. These quantities are of great interest since they are determined by the bonding properties of the sodium ion and by its microdynamic behaviour. Previous investigations of the nuclear magnetic relaxation of ions have been shown to give information regarding changes in bonding properties due to e.g. ion-pairing,[12] complex formation[18, 19] and reinforced coupling to the solvent.[12] The correlation time in Eq. (1) has been found, experimentally and theoretically, to be roughly proportional to the viscosity.[20]

A discussion of the structural implications given by our findings will be undertaken for the different phases which were investigated.

In the water-rich solution phase (the L_1 phase) no broadening of the ^{23}Na resonance above that determined by the instrumental limitations is found. A comparison with the data of Eriksson *et al.*[21] on the ^{81}Br resonance in the octylamine hydrobromide–water system seems to be appropriate for this case. Eriksson *et al.*[21] found that above the critical micelle concentration (c.m.c.) the line-width of ^{81}Br was approximately 20 times the line-width at low concentrations (i.e. under the c.m.c.). This was interpreted as being due to an adsorption of part of the counter-ions in a Stern layer next to the ionic groups of the surfactant molecules. For the system sodium caprylate–water we have found that the "natural" line-width of ^{23}Na in the concentration range above c.m.c. (0.38 moles NaC_8/1000 g H_2O) was less than 5 times (no broadening was observed) the natural line-width in ordinary electrolyte solutions, thus in marked contrast to what was found for ^{81}Br in the system octylamine hydrobromide–water. Neither at sodium caprylate concentrations above 1.1 moles of NaC_8/1000 g H_2O, where Ekwall and Stenius[22] have shown that the bonding of sodium ions to the micelles increases, has any broadening been observed. This indicates that the counter ion bonding is less effective in our case, viz. that the sodium ions seem to be surrounded by a water sheath also at the surface of the micelles. Ekwall *et al.* have previously reached the same conclusion based upon other measurements, chiefly viscosity studies.[7, 22, 23] The difference between the binding in the cases mentioned is that to be expected from the differences in ion–water coupling shown to exist between sodium and bromide ions, e.g. by Bergqvist and Forslind[24] from proton magnetic resonance chemical shifts. Thus sodium ions have a structure-stabilizing effect on the water lattice whereas bromide ions are structure-breaking. This difference makes an adsorption of sodium ions directly on the "naked" ionic surface of the micelles existing in the system sodium caprylate–water energetically less favourable as compared to an adsorption of bromide ions on the micelles which are formed in mixtures of octylamine hydrobromide and water. The electric field gradients in the micelles containing caprylate ions may also be smaller due to charge-delocalization in the carboxyl groups. As can be inferred from Table 1 addition of decanol to aqueous sodium caprylate solutions does not broaden the signal. This indicates that the sodium ion–water coupling in the L_1 phase is rather independent on the decanol weight fraction. The most likely explanation is that most of the decanol molecules are solubilized in the micelles, thus leaving the intermicellar solutions relatively unaffected. The same conclusion has been drawn from other experimental studies.[7]

Nor in the mesomorphous *E* phase was any broadening in excess of the inhomogeneity and modulation broadening observed. This phase has been shown to be built up of cylinders consisting of a hydrocarbon core and a surface layer of hydrophilic end groups surrounded by water.[5,6] Since the line-width of the ^{23}Na resonance is small it can be assumed that the sodium ions are predominantly coupled to water and that the local (or microscopic) viscosity in the regions between the cylinders is rather low (as mentioned above the correlation time has been found to be approximately proportional to the viscosity). This is in concordance with the good electrical conductance of this mesophase. If the sodium ions were strongly coupled to the ionic surface of the cylinders (i.e. a sort of ion-pair formation on the surface) the line-width should be large due to greater field gradients and correlation times.

Also in the mesomorphous *B* and *C* phases the signal was unbroadened which is what is to be expected in view of the high water content and the above mentioned strong coupling between sodium ions and water.

More interesting are the observations concerning the mesomorphous *D* phase. This has been shown to have a layer structure with alternating double layers of amphiphilic ions and molecules separated by water layers.[3, 5, 6] In the water-rich part of this phase the ^{23}Na resonance signal is unbroadened whereas in the water-poor part the signal becomes broader as the sodium caprylate–water ratio is increased. This broadening effect runs parallel with the reduction of the thickness of the water layers. A result of this is a decrease of the distance between the sodium ions and the charged part of the amphiphilic ions and thus an increase of the electric field gradient at the place of the ^{23}Na nucleus. An increase in the correlation time due to an attenuation of the thermal amplitudes of the sodium ions is certainly also of importance as the water layers become more narrow. In conformity with this model the line-width seems to be primarily determined by the water–caprylate ratio and rather independent on the decanol weight fraction. The X-ray diffraction studies have previously shown that the increase in the Bragg spacing with water content markedly changes when the decanol-to-caprylate molar ratio exceeds about 2.0–2.6:1. The maximum water content that the mesophase in question is able to incorporate at this point increases over the maximum amount that can be bound by the hydrophilic groups of the amphiphile molecules. The extension of the *D* phase to very high water contents is believed to be caused by the decreasing charge density in the amphiphile-water interface. Consequently the firmness of the binding of the sodium ions to the amphiphile layers will decrease. This will ultimately result in the liberation of a part of these ions, thus providing conditions for a Donnan distribution, which enables increasing amounts of unbound water to be incorporated in the mesophase. On the other hand theoretical considerations have led to the conclusion[6] that at lower water contents the sodium ions are linked *via* water molecules to the carboxylate groups of the soap, but that there at the lower boundary of the mesophase region *D* seems to be a limit for the linking of the sodium ions in this manner at a decanol-to-caprylate molar ratio of about 1.3:1. The present measurements confirm that the sodium ions are relatively firmly bound at low decanol-to-caprylate ratios and low water contents and that the firmness decreases with increasing water content still at a decanol-to-caprylate molar ratio of 1.0–1.3:1. The changes in the sodium ion binding at higher decanol-to-caprylate ratios are shown only indistinctly in these measurements.

The mesomorphous *F* phase has been shown to be built up of cylinders with a water core surrounded by a layer of hydrophilic groups of the amphiphile ions and molecules.[3, 5, 6] The hydrocarbon parts of these ions and molecules are oriented outwards from the water core forming a continuous hydrocarbon region between the cylinders. For this phase the line-width of the ^{23}Na signal shows a similar dependence on the sodium caprylate–water ratio as for the *D* phase. The interpretation of the results is believed to be analogous, i.e. as the water content is decreased a reduction of the dimensions of the water cores takes place. This makes the solvation of the sodium ions in the water cores less effective. The sodium ions are thus forced to approach the charged surfaces of the cylinders where they experience a greater electric field gradient and also become less mobile.

In the isotropic solution phase L_2, measurements were performed at three different weight fractions of decanol, viz. 70%, 80% and 90%. At 70 and 80% weight fractions of decanol the line-widths of the ^{23}Na signal show essentially the same dependence on the caprylate–water ratio as noted for the D- and F-phases. At 90% weight fraction of decanol the ^{23}Na resonance signal is considerably broader in the water-rich part of the phase than at lower decanol weight fractions. In the water-poor part of the L_2 phase the ^{23}Na line-width is on the other hand relatively independent on the decanol concentration. It is known from density, viscosity and small-angle X-ray measurements that micelles are not formed at higher decanol concentrations than about 86–89% (the actual value is also dependent on the caprylate–water ratio). When we are in the region where micelles are found the ^{23}Na line-width depends on the caprylate–water ratio in much the same way as for the F- and D-phases. Again the interpretation is believed to be similar; i.e. as the water content is decreased the sodium ions approach the ionic surface surrounding the water core of the micelles. This will increase the field gradients experienced by the ^{23}Na nuclei and also the correlation time. At 90% decanol weight fraction also the solution in the water-rich part of the phase gives a broadened ^{23}Na resonance signal and this is certainly due to a diminished interaction between sodium ions and water. It is clear that this cation–water coupling in the absence of micelles should be less effective and that the sodium ions are then also surrounded by caprylate ions and decanol molecules. On the other hand the signal is more narrow than what could be expected where the sodium ions are predominantly coupled to decanol molecules and caprylate ions (cf. the discussion given below). Thus we may conclude that also at decanol concentrations higher than the c.m.c. smaller aggregates of water, sodium caprylate and decanol exist. The same conclusion has been drawn from proton magnetic resonance chemical shift data.[10]

We have not yet considered the possibility of occurrence of undissociated sodium caprylate (i.e. ion-pairs) or free sodium ions not surrounded by water molecules. Unfortunately, the solubility of sodium caprylate in water-free decanol is too low to permit line-width measurements. An indication of the magnitudes involved may however be given by the line-width of ^{23}Na observed for a solution of sodium caprylate in caprylic acid. In a water-free mixture the line-width was approximately 6 gauss[25] which is more than a hundred times the greatest line-width reported in this paper. For comparison it might be mentioned that the line-width of ^{81}Br in the hexanol-rich solutions of the system cetyltrimethylammonium bromide–hexanol–water is in the range 25 to 50 gauss[25] (dependent on the composition). The ^{81}Br line-width in ordinary aqueous solutions is only about 0.25 gauss. As shown by Lindman, Forsén and Forslind[12] ion-pairing has a profound influence on the rate of quadrupole relaxation of ionic nuclei.

If sodium ions not surrounded by water molecules were present the signal should also be strongly broadened, as may be inferred from the theoretically predicted[26] and experimentally observed[14] dependence of the spin-spin relaxation time on the dielectric constant of the medium.

Our conclusion is therefore that in all the phases investigated cation–water coupling dominates. A support for this view is the dependence of the line-width on the sodium caprylate–water ratio at a constant weight fraction of decanol. As shown in Fig. 2 the line-width is highly dependent on this ratio and, below 90% weight fraction of decanol, rather independent on the amount of decanol and the particular phase concerned, i.e. the number of water molecules per sodium ion is the main factor that determines the line-width. The solid curve in Fig. 2 is drawn to approximately represent the dependence of the line-width on the sodium caprylate–water ratio. We have attempted to correct the line-widths represented by this curve for broadening due to finite amplitude of the modulation field and magnetic field inhomogeneity by the following procedure. First we have assumed that the modulation broadening depends only on the ratio between modulation field amplitude and resonance line-width (cf. Haworth and Richards[27]). The magnitude of the correction has been obtained by deliberately overmodulating a resonance signal with a known line-width. Our choice was $^{79}Br^-$ in aqueous solution since ^{79}Br has its resonance at approximately the same magnetic field strength as ^{23}Na (i.e. the magnetic field inhomogeneity can be assumed to be the same as for ^{23}Na). Correction for the magnetic field inhomogeniety was made on the assumption that the field inhomogeneity gives rise to a Larmor-frequency distribution which can be approximated by a Lorentzian-type curve. In this case the field inhomogeneity over the sample simply

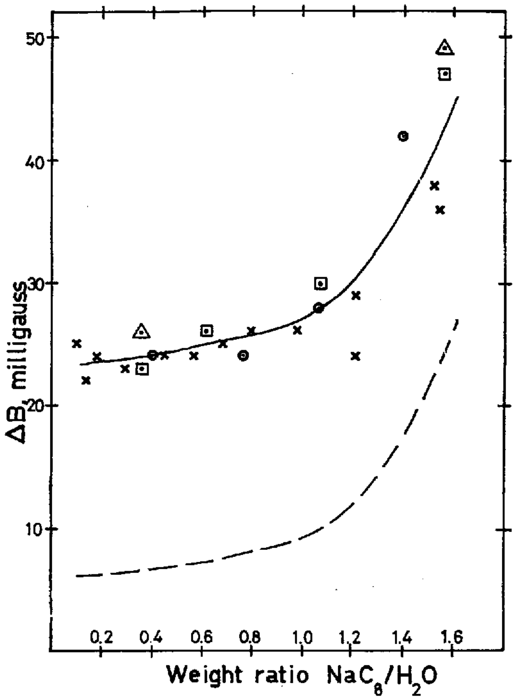

Figure 2. The line-width (in milligauss) of the ^{23}Na nuclear magnetic resonance as a function of the sodium caprylate–water ratio in the *D*, *F* and L_2-phases. (× = *D* phase, ⊙ = *F* phase, ▣ = L_2 phase, 70% decanol, △ = L_2 phase, 80% decanol.) The solid curve is drawn to approximately represent the dependence of the ^{23}Na line-width on the sodium caprylate–water ratio. The dashed curve has been obtained from the solid curve by correcting the line-widths by a procedure described in the text.

adds to the natural line-width. The value of the field inhomogeneity was obtained by assuming that the line-width of ^{23}Na in dilute aqueous solution of sodium chloride is 5 milligauss (cf. above). The dashed curve in Fig. 2 represents the line-widths obtained in this way. It must be emphasized that the method used for correcting the line-widths is very crude since no correction for the high modulation frequency has been applied and since the magnetic field distribution over the sample is not known. The corrected line-widths obtained in this way may however give an illustration of the magnitudes involved. In Fig. 3 the corrected line-widths, represented by the dashed curve in Fig. 2, are given as a function of

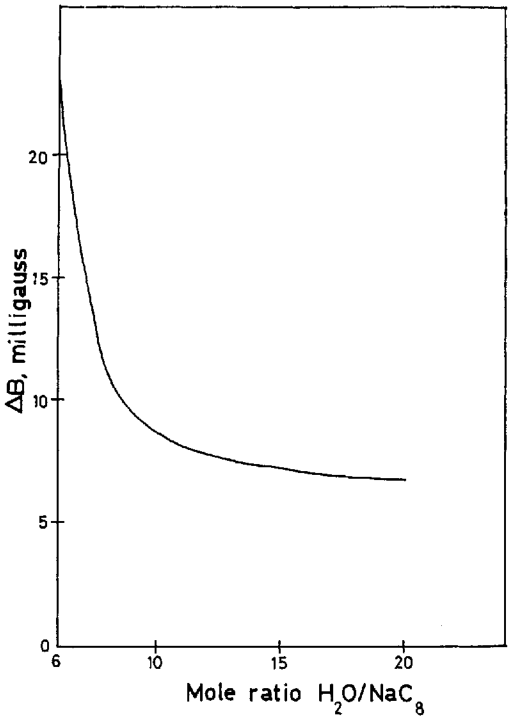

Figure 3. The corrected ^{23}Na line-widths as represented by the dashed curve in Fig. 2 given as a function of the number of water molecules per sodium ion.

the number of water molecules per sodium ion. Here it is clearly shown that the ^{23}Na line-width is highly dependent on the water content when the number of water molecules per sodium ion is low.

Our inference that the sodium ions are predominantly coupled to water molecules is in agreement with the conclusions drawn by Ekwall and Mandell from studies with other methods.[1, 2, 8, 28, 29] Thus Mandell[28, 29] found that the substitution of other alkali ions for sodium ion displaced the water-poor limit of the L_2-, F- and D-phases exactly in the direction which could be predicted from the known differences in the cation–water interactions in ordinary aqueous solutions. The water-rich limit was on the other hand practically independent on the nature of the alkali ion. The temperature dependence of the region of existence of isotropic decanolic solutions also lends support for our opinion. Whereas the left limit of the L_2-phase is independent on temperature, the right limit is displaced towards lower water contents when the temperature is increased.[28]

Acknowledgments

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