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Torbjörn Wärnheim [a b] , Ulf Henriksson [a b] & Tomas Klason [a b]

[a] Department of Physical Chemistry, The Royal Institute of Technology, S-100 44, Stockholm, Sweden

[b] Institute for Surface Chemistry, P.O. Box 5607, S-114 86, Stockholm, Sweden

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Alkyl Chain Order Parameters and Phase Diagrams for Systems Containing Sodium n-Octanoate, Water, and Different Alcohols

TORBJÖRN WÄRNHEIM, ULF HENRIKSSON and TOMAS KLASON

*Department of Physical Chemistry, The Royal Institute of Technology,
S-100 44 Stockholm, Sweden and Institute for Surface Chemistry, P.O. Box 5607,
S-114 86 Stockholm, Sweden*

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Lamellar liquid crystalline phases containing sodium n-octanoate, water, and an alcohol have been studied by means of ^{2}H NMR. Order parameters have been determined for the octanoate alkyl chain in systems containing ethanol, 1-propanol, 1-butanol, 1-pentanol, benzyl alcohol or 1,8-octandiol. The straight chain alcohols yield decreasing octanoate order parameters with decreasing chain length. With 1,8-octandiol the octanoate order parameters are somewhat smaller than with 1-propanol, indicating quite flexible octanoate hydrocarbon chains. Using mono-deuteriated benzyl alcohol, C_6H_5CHDOH, the S_{CD} as well as the S_{HD} ($= S_{HH}$) order parameters were determined in the same measurement. A typical measurement yields $|S_{HD}| - |S_{CD}| = 0.04 \pm 0.04$, where the error estimation includes the uncertainties in the quadrupole and the magnetic dipole-dipole coupling constants. It is stressed that in order to ascertain a significant difference between S_{HH} and S_{CD}, it is necessary to know the coupling constants with high accuracy. The phase diagram for the system sodium n-octanoate/water/benzyl alcohol was determined, mainly by ^{2}H and ^{23}Na NMR.

INTRODUCTION

Phase equilibria in systems containing amphiphilic molecules are rather complex. Besides isotropic solution phases, several phases with liquid crystalline order usually occur. Ternary systems containing amphiphile, water, and a third weakly polar compound have been systematically studied by, among others, Ekwall *et al.*[1] Sodium n-octanoate was chosen as a model surfactant for their studies and phase diagrams for a multitude of aqueous systems containing sodium n-octanoate, water, and various additives were determined.

In the present work, a ^2H NMR investigation was undertaken in order to determine the order parameter profile of the surfactant alkyl chain in the lamellar phase in some sodium n-octanoate systems. The purpose was to compare the order parameter profiles for systems with different short chain alcohols as additives. The alcohols ethanol, 1-propanol, 1-butanol, 1-pentanol and benzyl alcohol were used. Alkyl chain order parameters have, for a given system, proved to be similar whether measured directly for different liquid crystalline phases or determined from relaxation measurements using isotropic solution phases.[2,3] Our results are therefore also of relevance for the discussion as to how steric factors affect the relative stability of the lamellar liquid crystalline phase and the isotropic solution phases. In addition, we have determined the phase diagram for the system sodium n-octanoate/benzyl alcohol/water, mainly by NMR-techniques.

EXPERIMENTAL

Chemicals: Heavy water (Merck >99.75% ^2H), 1-pentanol (Fluka >99%), 1-butanol (Merck >99.5%), 1-propanol (Merck >99.5%), ethanol (Ab Svensk Sprit >99.5%), benzyl alcohol (Merck >99%), 1,8-octandiol (Fluka >98%) and perdeuteriated sodium n-octanoate (Larodan) were used as received. Sodium n-octanoate (BDH) was washed several times with ethanol and dried at 110°C. Some samples were prepared with specially purified octanoate prepared by titration of octanoic acid (Fluka >99.5%) with aqueous (NaOH. No differences in the phase boundaries could be detected. Mono-deuteriated benzyl alcohol (C_6H_5CHDOH) was prepared by reduction of benzaldehyde with $LiAlD_4$ (CIBA) and purified by distillation. Water was twice distilled.

NMR-measurements: The NMR-measurements were performed at 26 ± 0.5 °C on a Bruker CXP-100 FT spectrometer, operating at 13.82 and 23.81 MHz for ^2H and ^{23}Na, respectively.

Microscopy: Polarization microscopy was performed using a Reichert microscope at 25 ± 0.5 °C.

Phase diagram: The existence region of the isotropic solution phase in the benzyl alcohol system was determined by inspection in plane polarized light, using crossed polarisers and a thermostatted bath at 25 ± 0.2 °C. Samples were titrated with water or benzyl alcohol until they appeared isotropic. The procedure for determining the boundaries for the mesophases is described in the text. However, the following is to be noted: In the NMR-measurements, the molar amount of ^1H_2O in each sample was replaced with an equal amount of ^2H_2O. In the phase diagram, this is presented as an equivalent weight percent of ^1H_2O. Some samples were made with ^2H_2O in order to check any isotopic substitution effects on the boundaries of the solution phase. If any isotopic effects exist, they must be in the order of one percent (w/w), *i.e.*, approximately the experimental error in the other measurements. The liquid crystalline phases were identified by means of polarization microscopy.

THEORY

NMR spectroscopy is a very convenient method for determining order parameters for liquid crystals. Order parameters have been determined from the quadrupolar splittings in ^2H NMR for many different lipid bilayers and liquid crystalline systems.[4–8] In general, an order parameter describes the average orientation of a molecule fixed vector relative to the director. For a nucleus with spin quantum number $I = 1$ experiencing a cylindrically symmetric electric field gradient, the measurable order parameter S is given by the time average

$$S = \tfrac{1}{2} \cdot \langle 3\cos^2\theta - 1 \rangle \tag{1}$$

where θ is the angle between the director and the direction of the biggest component of the electric field gradient tensor in its molecule fixed principal axes system. The relation between this order parameter and the quadrupole splitting Δ_Q measured from an unoriented sample is, provided that the asymmetry parameter η is zero, given by[9]

$$\Delta_Q = \frac{3}{4} \cdot \frac{e^2Qq}{h} \cdot |S_{CD}| = \nu_Q \cdot |S_{CD}| \tag{2}$$

where e^2Qq/h is the quadrupole coupling constant. In solid n-hexane-

d_{24}. $\nu_Q = 126$ kHz,[10] a value that is quite constant for methylene groups in different molecules. For a ^2H nucleus in a methylene group, the biggest component of the electric field gradient tensor is usually assumed to coincide with the CD-bond direction and the order parameter measured from the ^2H quadrupole splitting is denoted S_{CD}. The observed order parameter in a lyotropic lamellar liquid crystal is given relative to a director that is perpendicular to the lamella.

An important question when describing the alkyl chain motions in surfactant aggregates and biomembranes is whether one order parameter is sufficient to characterize fully each methylene segment.[11,12] This question can be answered only by determining order parameters for different molecule fixed vectors. This can be accomplished by measuring quadrupole and magnetic dipole–dipole splittings.[13] For a methylene group, the order parameter S_{HH} describing the average orientation of the proton–proton vector can be determined in this way. In order to observe a dipole–dipole splitting from a certain methylene group in an alkyl chain in ^1H NMR, it is necessary to deuteriate all other segments in the chain. Using this method, Higgs and MacKay[13] were able to determine S_{HH} for the α-methylene segment in the potassium palmitate/water system. The dipole splitting is ≈ 10 kHZ, which is readily observed in spectra from unoriented samples. It is a definite weakness that S_{CD} and S_{HH} have to be determined from different samples with chemicals prepared by different methods. Diehl and Niederberger[14] have demonstrated that S_{CD} and S_{DD} ($= S_{HH}$) can be determined from the same sample using the ^1H-decoupled ^2H NMR-spectrum from an oriented sample. The small value of the ^2H–^2H dipole–dipole splitting makes it necessary to use oriented samples, and this limits the utility of the method. In this work, we show that well resolved ^2H–^1H dipole–dipole splittings from mono-deuteriated methylene groups can be observed in ^2H spectra from unoriented samples, which makes it possible to determine simultaneously S_{CD} and S_{HD} ($= S_{HH}$). For the case of an unoriented sample, the ^1H–^2H magnetic dipole–dipole splitting Δ_D is given by[9]

$$\Delta_D = \frac{h\gamma_H\gamma_D}{4\pi^2 r_{HD}^3} \cdot |S_{HD}| = \nu_D \cdot |S_{HD}| \tag{3}$$

where γ_D and γ_H are the magnetogyric ratios for ^2H and ^1H, respectively, and r_{HD} is the deuterium-proton distance. Assuming that $r_{CH} = r_{CD} = 1.09$ Å, that the H-C-D bond angle is 109.5°, we obtain $r_{HD} = 1.78$ Å and a magnetic dipole—dipole coupling constant $\nu_D = 3.269$ kHz.

Unfortunately, quadrupole and dipole–dipole splittings yield only the magnitude and not the sign of the order parameters. The sign can be determined by measuring chemical shift anisotropies[15,16] or sometimes by geometrical considerations.[17]

RESULTS AND DISCUSSION

The existence regions of the liquid crystalline phases in the system benzyl alcohol/water/sodium n-octanoate were determined by means of ^{2}H and ^{23}Na NMR spectroscopy. This technique has proved to be efficient and reliable, and is described in detail by Khan *et al.*[18] Spectra for the hexagonal and lamellar liquid crystalline one-phase regions were recorded, as well as for three two-phase regions and two three-phase regions. Around seventy samples were used for the determination. Most samples were rechecked a few weeks after the original run. In the hexagonal phase, the ^{2}H water quadrupole splittings fall in the range 0.5–0.7 kHz and the ^{23}Na splittings in the range 1.2—2 kHz. In both cases, the splittings decrease with increasing alcohol content at constant ratio of water/octanoate. For the lamellar phase, splittings in the range 0–0.5 kHz for ^{2}H and 0–1.8 kHz for ^{23}Na were observed with no simple relation to the composition of the sample. These results are similar to the results of Rosenholm and Lindman for the system sodium octanoate/pentanol/water.[19] The phase diagram is shown in Figure 1. It is to be noted that the boundaries between the two- and three-phase regions are determined with considerably less accuracy than the boundaries between the one- and two-phase regions.

It is interesting to compare the extensions of the isotropic solution phase and the lamellar liquid crystalline phase with those found in other systems containing sodium n-octanoate and a short chain alcohol. In Figure 2, phase diagrams determined by Ekwall *et al.*[1] are presented for the 1-butanol and 1-pentanol systems. In general, for ternary surfactant systems containing straight chain alcohols, the transition from the existence of one single isotropic solution phase (extending from the water-surfactant binary axis to the alcohol corner in the phase diagram) to the occurrence of two separate solution phases occurs between 1-butanol and 1-pentanol. Even though benzyl alcohol has a mutual miscibility with water close to that of 1-pentanol, it is more similar to 1-butanol when comparing the phase diagrams. A branching of the alkyl chain of the cosurfactant has been

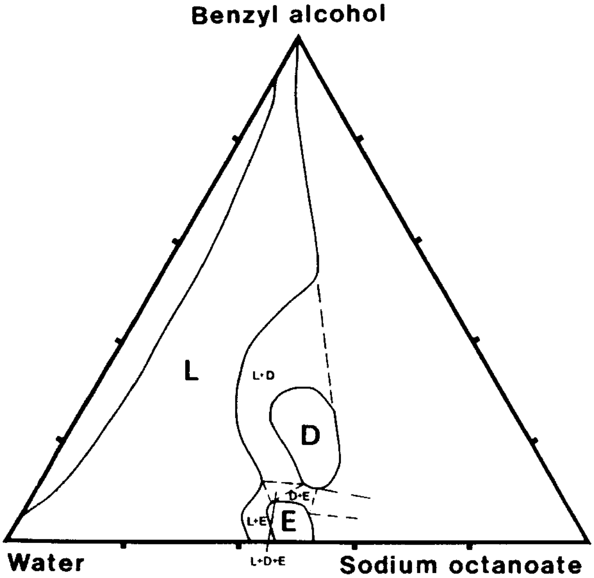

FIGURE 1 Phase diagram of the tenary system sodium n-octanoate/water/benzyl alcohol at 25°C. Compositions are given in weight percent. L denotes isotropic solution phase, D lamellar phase and E hexagonal phase, respectively.

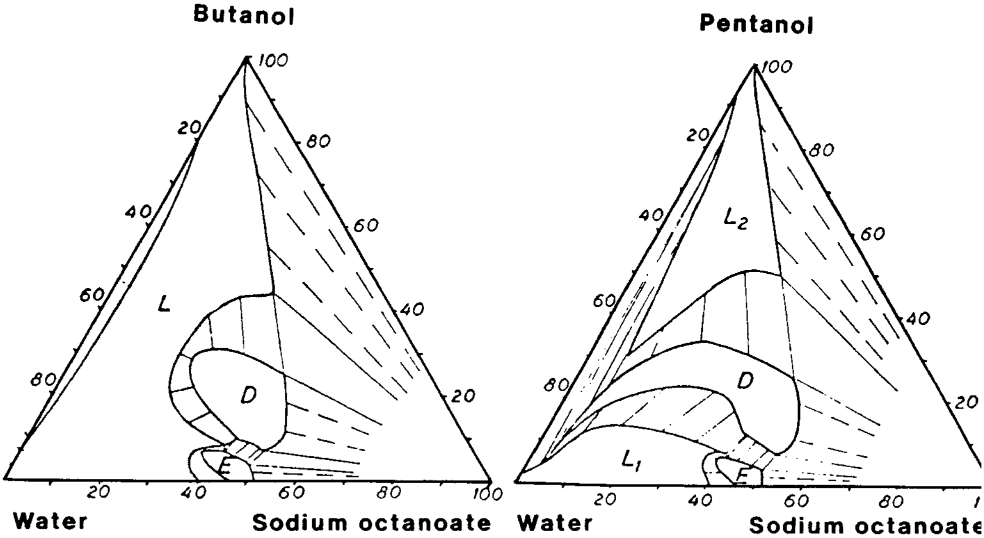

FIGURE 2 Phase diagram for two ternary systems sodium n-octanoate/water/alcohol at 20°C. Compositions are given in weight percent. Notations as in Fig. 1. Taken from ref. 1.

shown to give a smaller existence region for the lamellar phase in similar systems.[20] Benzyl alcohol with a hydrocarbon volume similar to pentanol, but a length more close to that of butanol, has the same effect. In a previous paper[20] this effect has been discussed in the light of changes in the "packing ratio" introduced by Israelachvili *et al.*[21]

Among the straight chain alcohol systems, a cubic phase occurs for ethanol and propanol.[1] No evidence was found for the existence of a cubic phase in the benzyl alcohol system. However, rather few samples were investigated in the relevant area.

The S_{CD} order parameter profile of the perdeuteriated octanoate chain has been determined from the quadrupole splittings in the ^2H NMR spectra from the lamellar liquid crystalline phases containing different alcohols. The results are shown in Figure 3. The assignment of an observed splitting to a particular methylene segment has been made in accordance with previous work,[3,22,23] using the following principles: i) The order parameter profile decreases along the chain, starting from the polar group. Using selectively deuteriated octanoate, it has been shown in other systems that the α-methylene segment has the biggest order parameter.[3,23] ii) The "plateau region" of the profile cannot be unambiguously resolved for perdeuteriated alkyl chains and the assignments have been made by estimation of the peak intensities.

The order parameters are quite similar to the 1-pentanol and 1-butanol systems, while 1-propanol and especially ethanol give smaller order parameters. It is tempting to ascribe this to different packing conditions in the lamellae. However, due to differing compositions in the interlamellar solution, the amount of dissolved octanoate may differ. An increased surfactant concentration in the interlamellar solution reduces the observed other parameter S_{obs} according to

$$S_{obs} = (1 - P) \cdot S_{lam} \tag{4}$$

where S_{lam} is the order parameter for the octanoate in the lamellae and P is the fraction of the octanoate present in the interlamellar solution. P is not known, but in order to account for all the difference between the pentanol and ethanol systems, as much as ~30% of the octanoate has to be present in the interlamellar water/ethanol mixture. This is rather unlikely, and a large part of the observed difference must obviously be attributed to differences in the conformational state of the octanoate chains.

The lamellar phase in the system sodium n-octanoate/1,8-

octandiol/water, denoted D_s ("single layered lamellar type") by Ekwall *et al.*,[24] shows an anomalous feature; it has a lamellar thickness of approximately one extended octanoate chain. It was suggested that the diol is oriented with one hydroxyl group on each side of lamella with the octanoate chains aligned parallel to the diol molecules. This proposed structure should give high S_{CD} order parameters, as well as a rather slow decrease in S_{CD} along the chain. The observed order parameter profile (Figure 3) is quite different. The shape of the profile does not differ from that of the other systems and the absolute values of the order parameters are rather small, somewhere between the 1-propanol and the ethanol systems. This is clearly not consistent with the ordered structure previously suggested[24] and indicates that although the lamellae are thin the octanoate alkyl chains do not on average penetrate through the whole lamella.

A more detailed investigation has been performed with the sodium n-octanoate/benzyl alcohol/water system. Samples were prepared with mono-deuteriated benzyl alcohol, C_6H_5CHDOH, and S_{CD} as

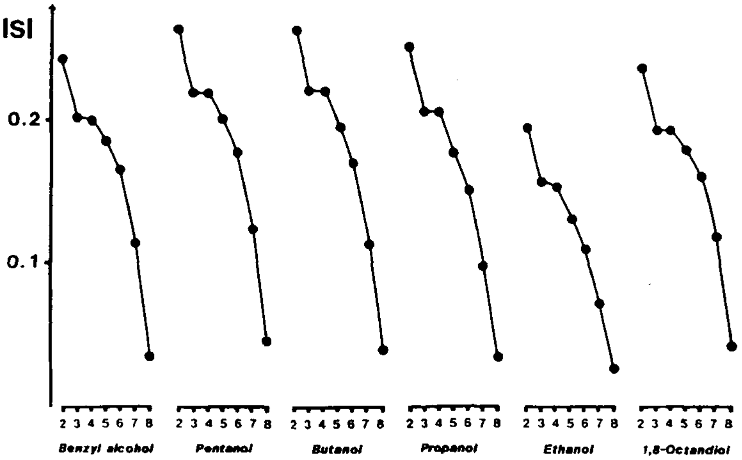

FIGURE 3 S_{CD} order parameter profiles for the octanoate chain in different ternary systems sodium n-octanoate/water/alcohol determined from the quadrupolar splittings of a sample in the lamellar phase. The methylene groups of the octanoate alkyl chain are numbered starting from the polar head group.

Composition of the samples (given as weight ratios): sodium n-octanoate : water : benzyl alcohol = 0.456 : 0.374 : 0.163; sodium n-octanoate : water : pentanol = 0.466 : 0. 372 : 0.162; sodium n-octanoate : water : butanol = 0.465 : 0.373 : 0.162; sodium n-octanoate : water : propanol = 0.465 : 0.375 : 0.160; sodium n-octanoate : water : ethanol ≈ 0.466 : 0.372 : 0.162; sodium n-octanoate : water : 1, 8-octandiol = 0.41 : 0. 41 : 0.18.

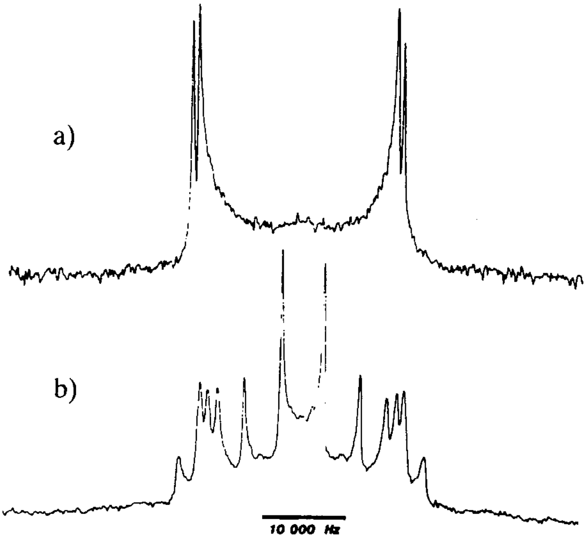

FIGURE 4 ^{2}H NMR spectra from two samples in the ternary system sodium n-octanoate/water/benzyl alcohol. a) Monodeuteriated benzyl alcohol, showing a quadrupolar splitting of 25100 Hz and a dipolar splitting of 750 Hz. Weight ratio n-octanoate : water : benzyl alcohol = 0.379 : 0.332 : 0.289. b) Perdeuteriated sodium n-octanoate, showing the quadrupolar splitting corresponding to the order parameter profile in Fig. 3.

well as S_{HD} were evaluated from the observed quadrupole and dipole–dipole splittings in the ^{2}H spectrum (Figure 4a) using Eqs. (2) and (3). The results are presented in Table I, where some results for α-deuteriated alcohols obtained by Seelig and Niederberger[17] for some sodium n-octanoate/alcohol/water systems are also presented. As mentioned above, it is a matter of theoretical interest to compare the

TABLE I

Order parameters for α-methylene groups of alcohols in the systems sodium n-octanoate/alcohol/H_2O

Alcohol	w% alcohol	w% octanoate	w% H_2O	$\lvert S^{\alpha}_{CD} \rvert$	$\lvert S^{\alpha}_{HD} \rvert$
Benzyl alcohol	14.9	44.6	40.5	0.169 ± 0.005	0.191 ± 0.03
Benzyl alcohol	20.0	42.5	37.5	0.191 ± 0.006	0.232 ± 0.04
Benzyl alcohol	28.9	37.9	33.2	0.200 ± 0.006	0.229 ± 0.04
Butanol	21	40	39	0.187[a]	
Hexanol	25	37	38	0.216[a]	
Octanol	30	35	35	0.222[a]	
Decanol	35	32	33	0.225[a]	

[a] Data taken from Ref. 17.

magnitude of S_{CD} and S_{HH}; are they equal or not? The orientation of a methylene segment is most conveniently described by means of a coordinate system with one axis (x) bisecting the H-C-H angle and one axis (z) perpendicular to the H-C-H plane. The -CH$_2$-group is rigid with approximately tetrahedral symmetry and it is thus sufficient to describe the orientations of this molecule fixed coordinate system relative to the director. This can be done with an order parameter tensor expressed in either Cartesian or spherical coordinates. The measured order parameters S_{CD} and S_{HD} can then be expressed as different linear combinations of these tensor elements:[11]

$$S_{HD} = S_{yy} = -\frac{1}{2} \cdot S^{(2)}_{00} - \frac{1}{\sqrt{24}} \cdot (S^{(2)}_{20} + S^{(2)}_{-20}) \tag{5}$$

$$S_{CD} = \frac{1}{3} \cdot S_{xx} + \frac{2}{3} \cdot S_{yy} = -\frac{1}{2} \cdot S^{(2)}_{00} - \frac{1}{\sqrt{24}} \cdot (S^{(2)}_{20} + S^{(2)}_{-20}) \tag{6}$$

The order parameters for the molecule fixed system are defined as the following time averages:

$$S_{ij} = \frac{1}{2} \cdot \langle 3\cos\theta_i \cos\theta_j - \delta_{ij} \rangle \tag{7}$$

$$S^{(2)}_{mo} = \langle D^{(2)}_{mo}(\alpha, \beta, \gamma) \rangle \tag{8}$$

where i,j = x, y, z, $\cos\theta_i$ is the direction of cosine of coordinate axis "i" with respect to the director and δ_{ij} is the Kroenecker symbol. $D^{(2)}_{mo}(\alpha, \beta, \gamma)$ is a Wigner rotation matrix element for the transformation from the molecule fixed system to the director system. The difference

$$S_{CD} - S_{HH} = \frac{1}{3} \cdot (S_{xx} - S_{yy}) = \frac{1}{\sqrt{6}} \cdot (S^{(2)}_{20} + S^{(2)}_{-20}) \tag{9}$$

is zero if the molecular motion of the methylene segment is such that there is at least threefold symmetry around the z-axis.[25]

Earlier measurements by Petersen and Chan[26] gave $|S_{CD}| = 0.20 \pm 0.01$ and $|S_{HH}| = 0.17 \pm 0.04$ in unsonicated lecithin bilayers, while Higgs and MacKay[13] report a typical difference $|S_{HH}| - |S_{CD}| = 0.04$ for the α-methylene group in the potassium palmitate/water lamellar phase. Diehl and Niederberger[14] studied the system sodium n-decanoate/1-decanol/water and found $|S_{CD}| = 0.230 \pm 0.002$, $|S_{DD}| = 0.26 \pm 0.04$ for the decanol α-methylene group and $|S_{CD}| = 0.294 \pm 0.002$, $|S_{DD}| = 0.33 \pm 0.04$ for the α-methylene group of the decanoate ion. Fujiwara and Reeves[27] have measured S_{CD} and S_{DD} for lauric acid-d_{23} in decylammonium chloride disc micelles. Within the errors of the measurement, they obtained $S_{CD} = S_{DD}$. Our results for the α-methylene group in the benzyl alcohol molecule are presented in Table I. Prior to comparing the different order parameters, it is necessary to make an assessment of the errors in the measurements. There are two possible sources of error; firstly, the inherent errors in the quadrupole and magnetic dipole–dipole coupling constants, and secondly the errors in the measurement of the splittings. Determinations of ν_Q yield values that normally range between 123–131 kHz.[10,28] As for the dipole coupling constant, by far the largest source of error is the uncertainty of the distance between the hydrogen nuclei. We have used a probable error of 0.05 Å (assuming a C-H bond length of 1.09 ± 0.005 Å and a H-C-H bond angle of 109.5 ± 2^0). The error in S_{CD} is dominated by the uncertainty in the quadrupole coupling constant, while the errors in S_{HD} are equally attributable to the uncertainty in the measured splittings and in the deuterium-proton distance.

As can be seen from Table I, $|S_{HD}| - |S_{CD}| \approx 0.04 \pm 0.04$ for all three samples studied. This result is consistent with previous measurements for other systems.[13,14,27] According to the analysis above $|S_{HD}|$ is significantly bigger than $|S_{CD}|$ if $\nu_Q = 126$ kHz and $r_{HH} = 1.78$ Å are used, and only the errors in the measurement of the splittings are considered. However, it should be stressed that in order to guarantee that the observed difference really is significantly different from zero, it is necessary to know the quadrupole coupling constant and the H-H distance with higher accuracy.

Order parameters for the CF$_2$-group of potassium 4,4-difluoromyristate in the lamellar phase have been determined by Post, James, and Berendsen from the ^{19}F-^{19}F dipole-dipole coupling and the ^{19}F chemical shift anisotropy.[16] They obtained $S_{xx} - S_{yy} = 0.054$ which is of the same sign as that obtained for benzyl alcohol in the present work, provided that S_{CD} and S_{HD} are negative.[13,17]

The small values for the difference between S_{HH} and S_{CD} obtained in this and other studies are in good agreement with results from recent simulations of hydrocarbon chain conformations in bilayers[29] which give $S_{xx} - S_{yy} = 0.035$ for a head group area of 0.276 nm^2.

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