

## Properties and Structure of the Decanolic Solutions in the Sodium Caprylate-Decanol-Water System

### III. An NMR Investigation of the Solutions

GUNILLA GILLBERG

*Division of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden*

and

PER EKWALL

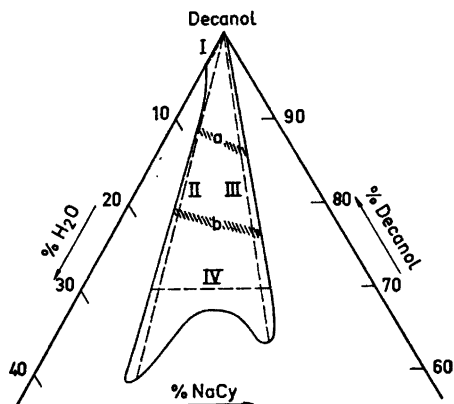
*Laboratory for Surface Chemistry (Ytkemiska Laboratoriet), the Royal Swedish Academy of Engineering Sciences, Stockholm, Sweden*

Chemical shifts have been determined for the decanolic solutions with the mole ratio  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  and 5.9 and with constant weight fraction of decanol (70 %). For the last-mentioned system the resonance line width of the  $^{23}\text{Na}^+$ -counterions was also determined. The results obtained indicate that the chemical environment of the molecules is relatively independent of the decanol concentration and of the mole ratio of  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}}$ . In the spherical micelles formed in the systems with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  and 5.9, respectively, a somewhat different interaction between the molecules seems to exist.

Previous investigations of binary water solutions of association colloids have shown that interesting information of the structure and physico-chemical qualities of micellar systems can be obtained by means of high resolution NMR-spectroscopy.<sup>1-4</sup> In the present paper an account of the studies of ternary solutions, which contain decanol as the main component besides sodium caprylate and water, will be given. These solutions have been carefully investigated by means of macroscopic methods by Ekwall and coworkers at the Laboratory for Surface Chemistry, Stockholm.<sup>5</sup> The fact that the solvent, decanol, constitutes a micelle forming component has led to considerable complications at the interpretation of the PMR results. The chemical shifts of decanolic solutions with the mole ratio  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  and 5.9 and with constant weight fraction of decanol (70 %) have been recorded. For the

Fig. 1. The area of the decanolic solutions at 30°C. a = region of c.m.c., b = limit for spherical micelles.

- I: Decanol-H<sub>2</sub>O-solutions;  
 II: Solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$ ;  
 III: » » »  $= 5.9$ ;  
 IV: » » » const. weight fraction  
 of decanol.



last-mentioned system the resonance line width of the  $^{23}\text{Na}^+$ -counterions was also determined. The examined solutions are shown in the ternary diagram (Fig. 1), in which the region of the c.m.c. and the expected appearance of reversed spherical micelles<sup>5</sup> have been entered.

#### EXPERIMENTAL

The solutions were prepared and the density determinations were made by the staff at the Laboratory for Surface Chemistry, Stockholm. The PMR measurements were carried out at about 30.5°C on a Varian A-60 spectrometer, equipped with a Hewlett Packard 202 A audio oscillator and a Hewlett Packard 5512 A electronic frequency counter. In order to let the solutions reach thermal equilibrium, the samples were placed in the probe at least 10 min before measurements. The temperature in the probe was regularly recorded. All resonance line positions were measured relative to the intense CH<sub>2</sub>-peak of decanol as an internal standard calibrated against chloroform as an external standard. The reported shifts are average values of 4 separate measurements. The accuracy of the shift determinations can in general be estimated to lie within  $\pm 0.2$  cps.

The NMR measurements on the  $^{23}\text{Na}^+$ -counterions were performed by using a Varian V-4200 B NMR spectrometer equipped with a 12 inch V-4012 A magnet at 22–23°C. The magnetic field was controlled by a Varian Fieldial. The r.f. field was chosen so as to avoid saturation. The line width was evaluated directly as the peak to peak distance of the observed adsorption band derivative, each value being the mean of 2–3 runs. Experiments with 1.0 M NaBr solutions showed that the magnet inhomogeneity determined the width of the  $^{23}\text{Na}^+$ -resonance line (*cf.* Ref. 6), which is equal to about 0.03 gauss.

#### CORRECTIONS

The chemical shifts reported are given relative chloroform used as an external standard. The shift values have been corrected for the bulk susceptibility differences between pure decanol and the solutions.

The only resonance line positions which had to be corrected for the observed small temperature deviations from 30.5°C were those of the OH-groups. A temperature coefficient of 0.5 c/sec, °C (*cf.* Ref. 7) was used for both types of OH-protons.

## RESULTS

Fig. 2 shows the corrected chemical shifts obtained for the decanol-H<sub>2</sub>O solutions at 30.5°C. One signal is observed for the water protons and one for the alcohol OH-protons, indicating phase separation or that the rate of proton exchange is very low. In the figure there is also given the average resonance line position of the exchanging protons, calculated according to the formula  $\nu_{\text{H}_2\text{O,OH}} = p\nu_{\text{R-OH}} + (1-p)\nu_{\text{H}_2\text{O}}$  where  $p$  = the proton fraction =  $n_{\text{R-OH}} / (n_{\text{R-OH}} + 2n_{\text{H}_2\text{O}})$ . This is the resonance line position of the OH-protons which would have been obtained if traces of an acid or base had been present in the solutions. From Fig. 2 it is evident that the resonance line position of the water protons is the only one which is shifted to any considerable extent with an increasing water fraction in the decanol-water solutions. The resonance line position of pure water is +162.0 cps relative to chloroform at 30.5°C and at decanol bulk susceptibility. If all of the hydrogen bonds were broken, the resonance signal would be up-field shifted by an amount of about 220 cps.<sup>8</sup> Thus the observed shifts indicate that a relatively high degree of hydrogen bonding exists for the water molecules already at low water fractions and that this increases with an increasing amount of water. The resonance line position of the decanol OH-protons is, however, nearly independent of the water proportion of the system, which indicates that the total amount of hydrogen bonds for the decanol molecules remains constant over the whole concentration range of water, thus quite in opposition to the water molecules. A possible explanation of this behaviour is that the water molecules form association complexes in such a way that the original decanol structure is left

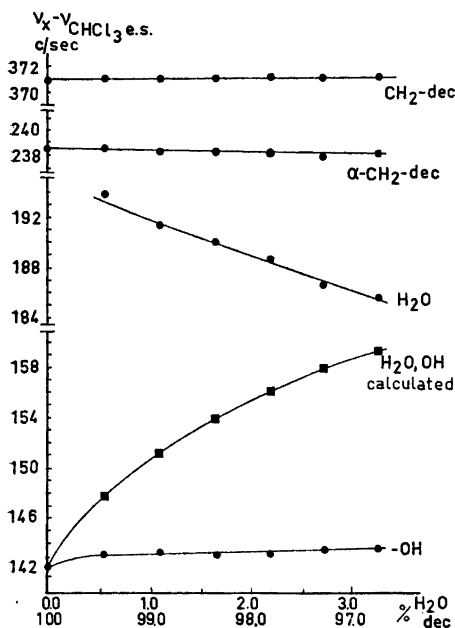


Fig. 2. The chemical shifts in decanol-H<sub>2</sub>O solutions at 30.5°C.

rather intact. The observed down-field shift of the water protons should thus originate only from an increased amount of intermolecular hydrogen bonds.

For the decanolic solutions with sodium caprylate present a rapid exchange of protons occurs between the decanol OH-groups and the water molecules, and therefore only an average resonance signal of the exchanging protons is observed in these solutions. Since only one resonance signal for each kind of protons is observed within the whole concentration range it is also concluded that a rather rapid exchange of molecules occurs between the micelles and the intermicellar solution. The observed peak position is thus determined by the chemical shifts of the micelle-forming molecules and the "free" molecules according to the formula  $\nu^{\text{obs}} = p \cdot \nu^{\text{m}} + (1-p)\nu^{\text{s}}$ , where  $\nu^{\text{m}}$  is the chemical shift for molecules engaged in micelle formation while  $\nu^{\text{s}}$  refers to molecules dispersed in the intermicellar solution,  $p$  being the proton fraction, *i.e.* the ratio of protons of a particular kind present in the micelles and the total amount of protons present of the same kind. At a high relative amount of micelle-forming molecules, *i.e.* at a low weight fraction of decanol, the average peak position will therefore almost entirely be determined by the chemical shifts of the protons present in the micelle molecules and vice versa. For the solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  (Fig. 3) the chemical shifts agree with those observed for the pure water-decanol solutions down to a decanol fraction of

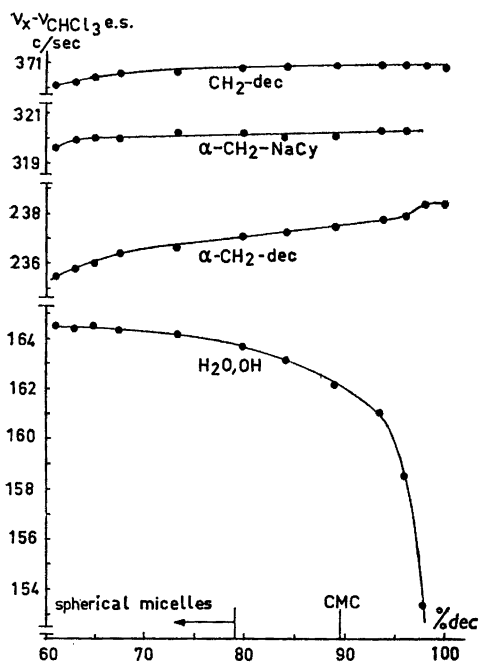


Fig. 3. The chemical shifts in the decanolic solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$ .

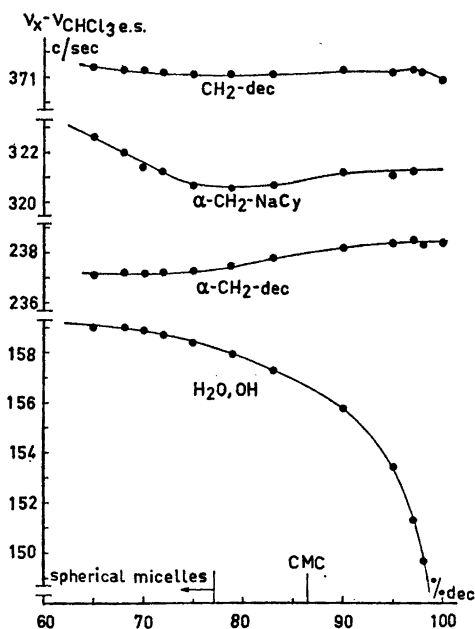


Fig. 4. The chemical shifts in the decanolic solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$ .

95–96 %. At further decrease of the decanol content the resonance lines of  $\alpha$ -CH<sub>2</sub>-NaCy,  $\alpha$ -CH<sub>2</sub>-dec and CH<sub>2</sub>-dec are shifted very smoothly to various degrees towards lower applied magnetic fields. From density, viscosity, and low-angle X-ray measurements<sup>5</sup> we know that a change in the structure of the decanolic solutions occurs in the concentration range 83–95 % of decanol. This indicates that already before the formation of real micelles smaller aggregates of decanol, sodium caprylate, and water molecules exist and this explains the smooth change of the slope of the recorded shift curves. (The c.m.c. value given in the diagram should thus not be regarded as a well-defined limit for the existence of micelles.<sup>5</sup>) The obtained down-field shifts, especially the shift of the  $\alpha$ -CH<sub>2</sub>-decanol protons indicate that the outer CH<sub>2</sub>-groups of the carbon chains are exposed to an environment in the micelles that reduces the screening as compared to that occurring in the intermicellar solution. The rather large change in the H<sub>2</sub>O,OH-resonance line position is due to the fact that at high decanol fractions the shifts are essentially determined by the decanol OH-resonance line position (142.0 cps) while at low decanol fractions the water proton signal position predominates (164.8 cps, see Table 1).

For the solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  the shift curves exhibit a somewhat different dependence on the decanol concentration (Fig. 4). Down to a decanol fraction of about 90 % the shifts of the CH<sub>2</sub>-protons are relatively constant. The resonance line position of  $\alpha$ -CH<sub>2</sub>-dec (238.4 cps) corresponds to that observed in pure decanol, which seems to indicate that in these solutions the water molecules are mainly coupled to the sodium caprylate molecules. For smaller decanol fractions the down-field shifts obtained both for the  $\alpha$ -CH<sub>2</sub>-NaCy,  $\alpha$ -CH<sub>2</sub>-dec, and to a certain degree also for the CH<sub>2</sub>-dec protons, may be interpreted as being due to the formation of micelles. For decanol fractions below 75 %, *i.e.* in the region where spherical micelles are supposed to dominate,<sup>5</sup> the  $\alpha$ -CH<sub>2</sub>-NaCy and to a smaller degree the CH<sub>2</sub>-dec resonance signals are shifted up-field while the  $\alpha$ -CH<sub>2</sub>-dec resonance line position is constant again (Fig. 4). This indicates the presence of different types of interaction in the initial and the spherical micelles.

A calculation of the micellar resonance line positions may give a better information of the molecular interactions in the micelles. However, we must emphasize that the results obtained from these calculations will be afflicted by quite a great uncertainty due to the fact that the shifts of the observed resonance line positions are small and that rather loose assumptions have to be made about the distribution of molecules between micelles and solvent. As already mentioned the observed shifts obey the expression

$$\nu^{\text{obs}} = p \cdot \nu^{\text{m}} + (1-p)\nu^{\text{s}} = (\nu^{\text{m}} - \nu^{\text{s}}) p + \nu^{\text{s}}$$

If the micelle composition and the relative amounts of free sodium caprylate and water were approximately constant in the whole concentration range of the respective system, constant values of  $\nu^{\text{s}}$  and  $\nu^{\text{m}}$  would be expected. Straight lines should thus be obtained, when  $\nu^{\text{obs}}$  is plotted against the respective proton fraction  $p$ . In order to simplify the calculations of the different proton fractions we assume that the micelle compositions are constant from  $p = 0$  (*i.e.* from the estimated c.m.c. values) up to  $p = 1$ , *i.e.* 1 mole NaCy/3.6

moles decanol/26.2 moles H<sub>2</sub>O and 1 mole NaCy/1.8 moles decanol/5.9 moles H<sub>2</sub>O, respectively. The amount of sodium caprylate not engaged in micelle formation has been calculated from the estimated c.m.c. values, *viz.* 89 % of decanol for the system with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  and 86–87 % of decanol for that with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$ . For the solutions with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  good adaption to straight line was obtained in all cases, while the case  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  a linear representation of the  $\alpha\text{-CH}_2\text{-NaCy}$ ,  $\alpha\text{-CH}_2\text{-dec}$  and  $\text{CH}_2\text{-dec}$  shifts could only be obtained by way of two straight lines with different slopes intersecting at about 74 % decanol and corresponding to different values of  $(\nu^m - \nu^s)$ . If the above-said assumptions were right,  $\nu^s$  should be constant and the difference in slope would only depend on  $\nu^m$ . It should also follow that the molecular interaction within the first formed micelles and within the spherical micelles which predominate at low decanol fractions would not be the same. The extrapolated resonance line positions at  $p = 1$  are given in Table 1 as well as those of some other solutions required for a comparison. For the micelles in the system with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 26.2$  the  $\alpha\text{-CH}_2\text{-dec}$  resonance appears at a field about 4 cps lower than in the case of the decanol solution saturated with water. This may be taken to indicate that the group has a lower internal energy and that the water molecules are thermally stabilized by the formation of a clathrate cage around the outer  $\text{CH}_2$ -groups of the carbon chains<sup>9</sup> of these micelles. The presence of water molecules which are hydrogen bonded to the carboxylate and hydroxyl groups, would dispense with the need for sodium counterions at localized sites at the water core surface. In the system corresponding to  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  the calculated shifts of the  $\text{CH}_2$ -group protons imply that in the first formed micelles a similar bonding exists as in the micelles of the previous system. However, in the case of spherical micelles, the relatively high resonance line positions of the  $\text{CH}_2\text{-dec}$ ,  $\alpha\text{-CH}_2\text{-dec}$  and  $\alpha\text{-CH}_2\text{-NaCy}$  protons (see Table 1) indicate that very few water molecules are present at the carbon chains. However, due to the low mole ratios of water to sodium caprylate (5.9, *i.e.* approximately 10 M) and decanol to caprylate (1.8) it is most probable that on the average, a quite large amount of the sodium ions are adsorbed at the water core surface since this would lead both to a smaller disturbance of the water structure and to a decrease of the repulsion between the negative carboxylate groups. An interesting observation regarding the spherical micelles at  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  is that resonance is obtained at about the same applied magnetic field as with the mesomorphous F-phase samples,<sup>10</sup> which is in equilibrium with these micelles (Table 1). A different behaviour is, however, observed for the resonance signal of the exchanging groups. At 30.5°C one observes two signals overlapping each other, one relatively sharp with resonance at 159.0 cps and one which is very broadened (the ratio between the relative line widths is about 1/14) but with resonance at about the same place. An intensity analysis showed that the sharp signal originates from the protons of the decanol-OH groups and the broadened one from the water protons. At 20°C one single very broad resonance signal is obtained and at 37°C the same sharp resonance signal as in the other decanolic solutions. A resonance line broadening will be obtained for protons, if the nuclear dipole-dipole interaction is not averaged by the thermal motions of the molecules which is generally the case in solutions at room

Table 1. The chemical shifts relative to  $\text{CHCl}_3$  and corrected to decanol's susceptibility and  $30.5^\circ\text{C}$ .

Solution	$\frac{n_{\text{H}_2\text{O}}}{n_{\text{NaCy}}}$	$\text{CH}_3\text{-dec}$	$\alpha\text{-CH}_2\text{-dec}$	$\alpha\text{-CH}_2\text{-NaCy}$	$\text{H}_2\text{O,OH}$	$\text{H}_2\text{O}$	Conc. of NaCy in $\text{H}_2\text{O M}$
$\text{H}_2\text{O}$						162.0	0
$\text{NaCy-H}_2\text{O}$ :							
before 1:st c.m.c.	555	—	—	316.4	—	162.1	0.1
after 2:nd c.m.c.	26.2	—	—	318.3	—	164.8	2.1
$\text{NaCy-dec-H}_2\text{O}$ :							
micelles	26.2	369.6	233.5	319.6	164.8	166	2
first formed micelles	5.9	371.1	234.5	320.4	160.6	163	~10
spherical micelles	5.9	371.9	237.0	324.3	160.6	163	~10
Phase F: 61.1 % dec	5.9	371.5	237.3	324.3	159.0	163	~10
Decanol saturated with $\text{H}_2\text{O}$		371.1	237.7	—	159.6	185	0

temperature. A calculation of the resonance line position of the water protons gives the value 163 cps, *i.e.* the same as in the micellar solution with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  (see Table 1). Addition of electrolytes generally shifts the water resonance up-field due to the positive shift contribution from the disruption of hydrogen bonds which will be dominating.<sup>11,12</sup> For this very concentrated solution ( $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$ , *i.e.* approximately 10 M) resonance at a considerably higher magnetic field should be expected. (Compare the chemical shifts of the water protons for the other sodium caprylate solutions in Table 1). The obtained chemical shift (163 cps) can be interpreted as if the real ion-concentration is lower, *i.e.* the sodium ions and the carboxylate groups mainly form ion-pairs. However, as the water molecules are few the negative shift contribution originating from the polarization of those water molecules which are dipolarly orientated to sodium ions will also cause a lower chemical shift of the water protons than first expected.<sup>11,12</sup> Hydrogen bonding to carboxylate and hydroxyl groups combined with a certain degree of dipolar orientation to the sodium ions might be expected to prevent free rotation of the water molecules and thus to explain the observed resonance line broadening of the water proton signal. In the micelle solutions the rapid exchange of molecules between the solvent decanol and micelles should tend to prevent such an effect.

For the solutions with constant weight fraction decanol (70 %) (Fig. 5) a calculation shows that the amount of caprylate bound to micelles is approximately the same ( $p_{\text{NaCy}} = 0.75$  to 0.76) and from Fig. 1 we can see that spherical micelles are dominating. The observed small positive shifts of the  $\alpha\text{-CH}_2\text{-dec}$  and  $\alpha\text{-CH}_2\text{-NaCy}$  proton resonances with an increasing weight fraction of sodium caprylate or rather with a decreasing mole ratio of

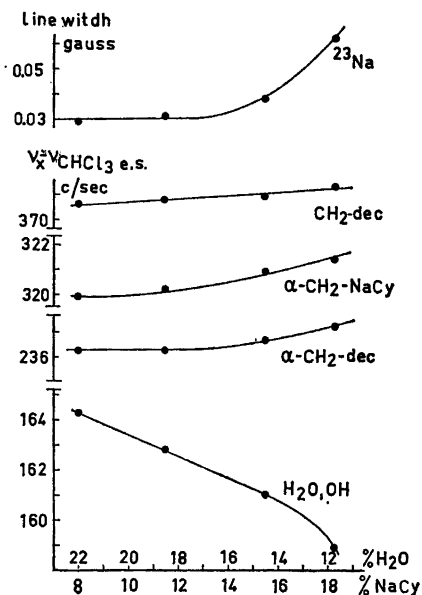


Fig. 5. The line width of  $^{23}\text{Na}$ -resonance and the chemical shifts in the decanolic solutions with constant weight fraction of decanol (70 %).



$n_{\text{H}_2\text{O}}/n_{\text{NaCy}}$  may indicate that a relatively smooth change occurs in the molecular interactions. These changes are accompanied by a parallel but stronger change of the resonance line width of the sodium resonance signal. (For the solutions with a weight fraction of sodium caprylate smaller than 13 % the real line width of the sodium resonance can not be determined due to the broadening caused by the magnetic field inhomogeneities). For  $^{23}\text{Na}$  with spin quantum number  $I = 3/2$  the resonance line width mainly depends on quadrupole relaxation. The resonance line width is thus proportional to the inverse relaxation time  $T_1^{-1} = \text{const.} \langle q^2 \rangle \tau_c$ , where the constant is determined by the nuclear properties,  $\langle q^2 \rangle$  is the mean square electric field gradient at the nucleus, and  $\tau_c$  is the correlation time characterizing the random molecular motions. The observed line width broadening can thus depend both on an increase of  $\langle q^2 \rangle$  and  $\tau_c$ . A larger  $\langle q^2 \rangle$  will be obtained if the sodium ions are partly adsorbed at the water core surface and this will also lead to a larger  $\tau_c$  as the thermal amplitudes of the ions will then be attenuated. The observed strong resonance line broadening for the solution with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$  seems therefore to confirm the assumption that the sodium ions are mainly adsorbed at the water core surface in the system with  $n_{\text{H}_2\text{O}}/n_{\text{NaCy}} = 5.9$ .

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