

# A Fourier Transform-Infrared Study of the Reversed Micellar Solution Phase of the Sodium Octanoate/Octanoic Acid/Water System

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A Fourier transform-infrared spectroscopy study of the L<sub>2</sub> solution phase of the system sodium octanoate/octanoic acid/water is reported. Sample series with both H<sub>2</sub>O and D<sub>2</sub>O were investigated. The methylene vibration modes showed only minor frequency changes throughout the whole L<sub>2</sub> phase. Upon addition of H<sub>2</sub>O to the nonaqueous system, a strong decrease in the frequency of the antisymmetric carboxylate mode was observed. If H<sub>2</sub>O was substituted for D<sub>2</sub>O, this frequency was almost constant and the same as in the nonaqueous sample (1553 cm<sup>-1</sup>). The band width of this mode decreased with increasing water content of the L<sub>2</sub> solution phase. From frequency shifts and band width alterations, it is proposed that the interactions between water, sodium ion and the polar head groups of the reversed micellar L<sub>2</sub> phase, involve hydrogen bonding and counterion effects. Spectra of HOD in the 3100–3700 cm<sup>-1</sup> range showed that the interior of the reversed micellar phase consisted of different types of water.

The self-assembly of amphiphiles in water has received a great deal of attention. There are many reasons for this, among which, the occurrence of amphiphiles in industry (food, detergent etc.) and in biological systems (membranes, the lungs, bile etc.) are the most important. Numerous studies have been carried out and several reviews have been reported.<sup>1–5</sup> In the present study, we used FT-IR spectroscopy in the investigation of the L<sub>2</sub> solution phase of the system sodium octanoate/octanoic acid/water as part of a research program dealing mainly with spectroscopic investigations of the physicochemical properties of lipids akin to those involved in biological membranes. Conventional IR spectroscopy in this solution phase has been carried out by Friberg et al.<sup>6,7</sup> but FT-IR is inherently more suitable in dealing with the influence of water on the spectra. FT-IR has been used in the study of the aqueous micellar solution phase (L<sub>1</sub>) in a soap/water system.<sup>8</sup> Since FT-IR is a quite new method in the

study of L<sub>2</sub> solutions, we were motivated to start the investigations on a well known model system which has been studied by a number of methods. To our knowledge, no previous FT-IR studies on a reversed micellar system have been published.

## Materials and methods

Sodium octanoate (BDH Chemicals U.K.) and n-octanoic acid (Merck AG, Germany) were used without further purification. Heavy water (99.75 %) was obtained from Merck and water was distilled twice in an all-quartz apparatus. The samples were prepared by weighing the components in test tubes which were flame-sealed and brought into solution by heating and shaking. After preparation the samples were stored for some days to ensure that they were single phase solutions.

Spectra were recorded using a Digilab FTS-14 C spectrometer in a single beam mode at 2 cm<sup>-1</sup> resolution. Dry air was used to reduce the influence of carbon dioxide and water vapour on the spectra. In an independent investigation, spectra

Dedicated to Professor Per Ekwall on his 90th birthday.

were recorded on a Bruker IFS 113 V spectrometer. 1000 Scans were combined and the resultant interferogram was Fourier transformed to obtain a resolution of  $1\text{ cm}^{-1}$  over the spectral range.

## Results and discussion

The partial phase diagram of the system sodium octanoate/octanoic acid/water is shown in Fig. 1, where only the reversed solution phase region ( $L_2$ ) is marked. The composition of the samples investigated are given by the dashed lines. For the longest line, the molar ratio between octanoic acid and sodium octanoate was about 3:1. For the other lines, the molar ratio  $\text{HC}_8/\text{NaC}_8$  varied from about 4 to 1.6 and 4 to 2.1. The content of water was kept constant at 10 and 20 weight % respectively. Sample series with both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  were used.

The infrared spectra of the present  $L_2$  system show strong absorption bands associated with (i) the methylene stretching and bending frequencies, (ii) the antisymmetric and symmetric carboxylate modes and (iii) the carbonyl stretching mode of the carboxylic acid group (Fig. 2). Figure 2 also shows that the contribution of water cannot be completely subtracted from the micellar system indicating a difference between water in pure and micellar state.

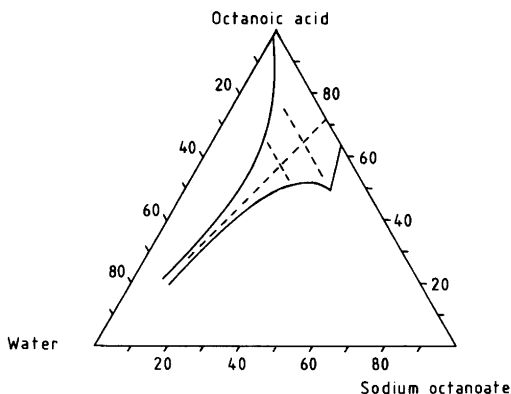


Fig. 1. Partial phase diagram of the system sodium octanoate/octanoic acid/water, showing the  $L_2$  phase investigated. The compositions of the samples are shown by dashed lines.

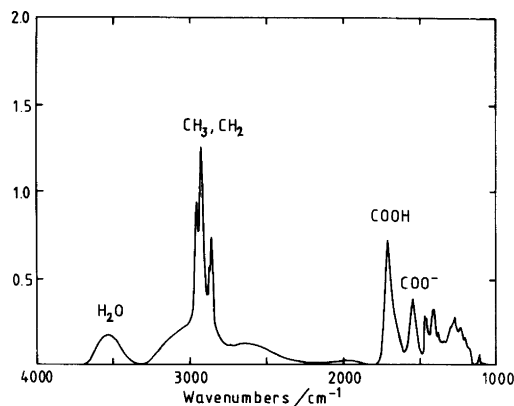


Fig. 2. Infrared spectrum of the system sodium octanoate/octanoic acid/water, where  $\text{H}_2\text{O}$  (30 wt.%) has been subtracted. The spectrum shows that water cannot be completely subtracted indicating a difference between  $\text{H}_2\text{O}$  in the micellar and pure state.

**Methylene modes.** In recent studies of aqueous n-alkanoate  $L_1$  solutions, the frequencies of the methylene stretching band were determined.<sup>8,9</sup> The frequency of the asymmetric methylene band was found to increase with increasing water content. This effect was explained by a difference in interaction of the methylene group in hydrocarbon-water and hydrocarbon-hydrocarbon milieu. In the frequency range of the CH stretching modes of the present  $L_2$  solutions, symmetric methylene stretching vibrations were found at the wave numbers 2928 and 2857  $\text{cm}^{-1}$ . This is quite close to the values  $\nu_s-\text{CH}_2 = 2930\text{ cm}^{-1}$  and  $\nu_s-\text{CH}_2 = 2858\text{ cm}^{-1}$  obtained for the pure liquid octanoic acid. However, our experimental findings showed only minor frequency changes in the asymmetric and the symmetric methylene bands. There was no shift in the symmetrical methylene bending vibration at 1467  $\text{cm}^{-1}$  or in the symmetrical methylene deformation band at 1379  $\text{cm}^{-1}$ . Therefore, it is reasonable to conclude that the hydrocarbon chains "feel" nearly the same environment throughout the whole  $L_2$  phase region.

**1800–2700  $\text{cm}^{-1}$  Range.** The spectral pattern in the 1800–2700  $\text{cm}^{-1}$  range was quite different for  $\text{D}_2\text{O}$ - and  $\text{H}_2\text{O}$ -containing samples as demonstrated in Figs. 3 and 4. Figure 3 shows that at least three absorption bands are formed when  $\text{D}_2\text{O}$  is added to the solution of soap in nonaque-

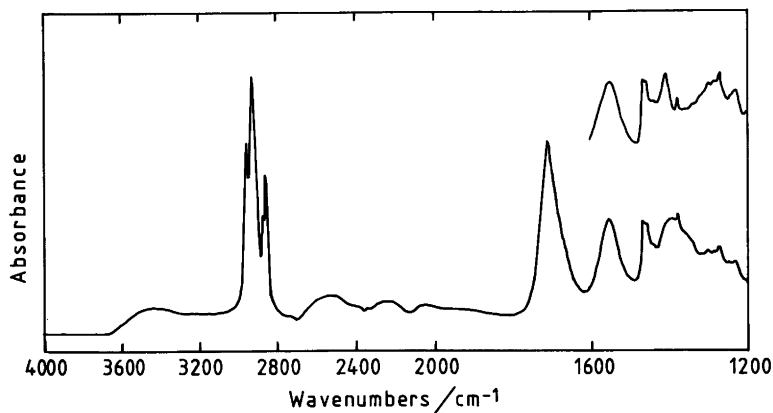


Fig. 3. Infrared spectrum of the system sodium octanoate/octanoic acid/water, at 10 weight %  $D_2O$ . The spectrum of the water-free solution is included to show the effect of  $D_2O$  in the  $1300\text{--}1500\text{ cm}^{-1}$  range.

ous octanoic acid. The origin of these bands is unclear. The spectra in Fig. 4 show the variation in the absorption pattern with addition of ordinary water to the same nonaqueous solution as in Fig. 3. The spectrum of pure octanoic acid is in-

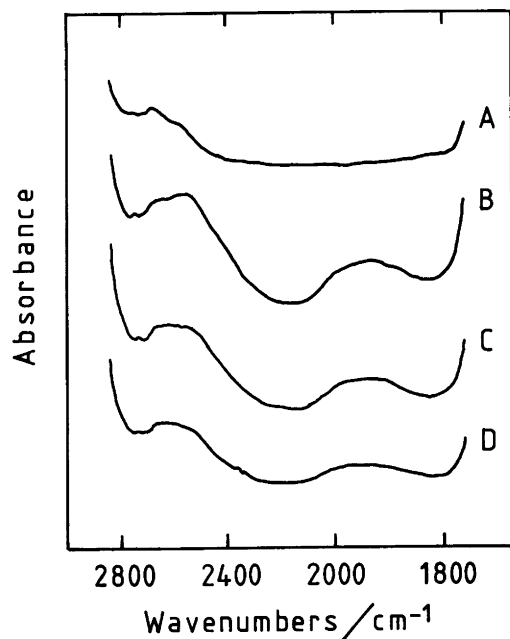


Fig. 4. Some infrared spectra of the  $L_2$  solution phase; (A) pure octanoic acid, (B) a solution of soap in nonaqueous carboxylic acid, (C)  $HC_8/NaC_8 = 3$  at 10 weight-%  $H_2O$  and (D)  $HC_8/NaC_8 = 3$  at 30 weight %  $H_2O$ . The spectra are shifted along the absorbance scale.

serted in the figure for comparison. The pure acid has an absorption maximum at  $2670\text{ cm}^{-1}$ . This shifted to  $2550\text{ cm}^{-1}$  when sodium octanoate was added and a new band at  $1927\text{ cm}^{-1}$  formed. Upon addition of 30 weight % of water, these two bands shifted to  $2635$  and  $1935\text{ cm}^{-1}$ , respectively. The intensity of the two bands decreased when the water content increased. This effect has been attributed to the formation of hydrogen bonded compounds with stronger bonds than those of carboxylic acid dimers.<sup>6</sup> The observed frequency shifts upon addition of water can be interpreted as a loosening of the hydrogen bonded structure.

*Antisymmetric carboxylate mode.* For the water-free solution, the antisymmetric carboxylate vibration  $\nu_a - COO^-$  was  $1553\text{ cm}^{-1}$  at the ratio  $HC_8/NaC_8 = 3$ . On addition of heavy water at this ratio, the frequency approached the value  $1552\text{ cm}^{-1}$  at high  $D_2O$  contents. If on the other hand, ordinary water was added to the nonaqueous system ( $HC_8/NaC_8 = 3$ ) there was a strong decrease in  $\nu_a - COO^-$  (the water content was increased to 40 weight %) (Fig. 5). In the series with 10 weight % of  $D_2O$ , the frequency increased from  $1552$  to  $1558\text{ cm}^{-1}$  when the molar ratio  $HC_8/NaC_8$  varied from 4 to 1.6 (Fig. 6). The corresponding figures for the series with constant content of  $H_2O$  were  $1544\text{ cm}^{-1}$  and  $1551\text{ cm}^{-1}$ . Decreasing molar ratio of  $HC_8/NaC_8$ , led to an increase in the band width. In the series with 20 weight % of  $D_2O$  or  $H_2O$ , the difference in the wave number was less than  $3\text{ cm}^{-1}$  for the molar ratios of  $HC_8/NaC_8$  investigated, and the band

width was almost unchanged. In order to understand the observed frequency changes that have to do with the antisymmetric carboxylate stretching vibration of the reversed micelles, we consider below some possible models of the interaction.

Bonding between a sodium ion and a carboxylate group will lower the symmetry of the latter, if the cation is off the  $C_2$  axis of the carboxylate ion. The following sketch (I) shows a structure where we have a reduction of the symmetry from  $C_{2v}$  to  $C_s$ . An analysis of possible fundamental infrared active transitions shows that the number of possible absorption bands will be unchanged, so it will not be possible to detect if a lower symmetry influences the frequency of the carboxylate modes. With increasing covalent character of the interaction between the oxygen and the sodium ion in (I), we should expect the vibrational frequency,  $\nu_a - \text{COO}^-$ , to increase and vice versa.<sup>10</sup>

In the series with increased content of  $\text{H}_2\text{O}$ , the antisymmetric stretching frequency ( $\sim 1550 \text{ cm}^{-1}$ ) of the carboxylate group decreases (Fig. 5) whereas the frequency is approximately constant with  $\text{D}_2\text{O}$ . Assuming an interaction between the sodium ion and the carboxylate group, with a solvated sodium ion forming a solvent-separated ion pair according to sketch (II) this model should also lead to a decrease in the frequency of the stretching mode with increasing hydrogen bonding.

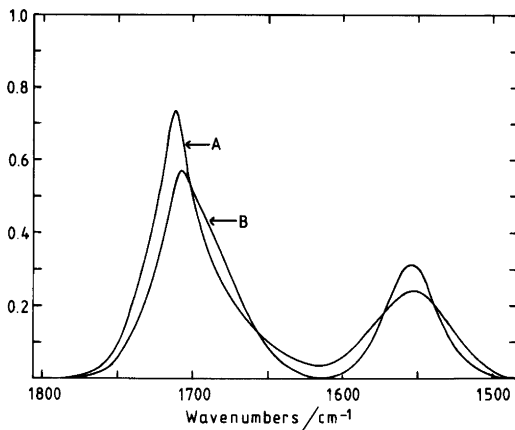


Fig. 6. Infrared spectra of a nonaqueous sample (A) and a sample with 30 weight-%  $\text{D}_2\text{O}$  (B), showing the shoulder formed at the low frequency side of the carbonyl peak. The molar ratio  $\text{HC}_8/\text{NaC}_8 = 3$ .

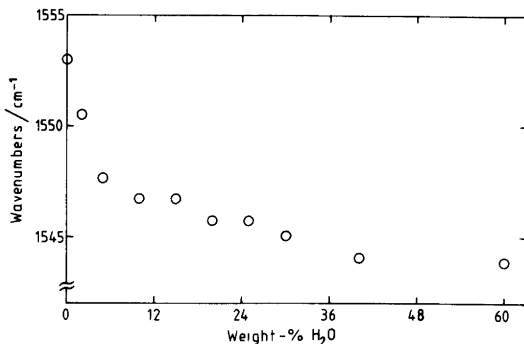
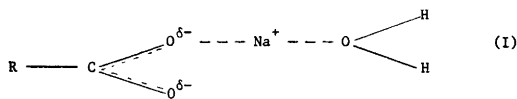
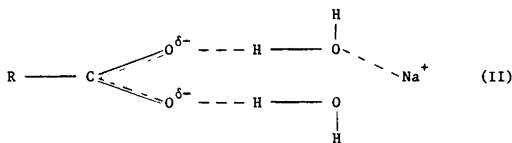


Fig. 5. The antisymmetric carboxylate stretching frequency versus weight %  $\text{H}_2\text{O}$ .



Neither structure (I) nor structure (II) can however explain the observed frequency shifts of the antisymmetric stretching frequency of the carboxylate group, since the models are independent of the type of water present. Furthermore, the infrared spectra from the 1800–2700  $\text{cm}^{-1}$  range indicate that octanoic acid may also have some influence on the antisymmetric carboxylate mode. The appropriate model could be a combination of (I) and (II) with the octanoic acid molecules hydrogen-bonded to sodium octanoate.

The band width of the antisymmetric carboxylate stretching mode decreased with increasing amount of water. For the water-free solution, this band width was  $64 \text{ cm}^{-1}$  decreasing to  $42 \text{ cm}^{-1}$  at a water content of 30 weight % (Fig. 6). From Fig. 6 we can also see that the relative absorbance  $A_{\text{C=O}}/A_{\text{COO}^-}$  decreased when 30 weight %  $\text{D}_2\text{O}$  was added to the nonaqueous sample but also that a shoulder was formed on the low frequency side of the carbonyl peak. This observation can be interpreted as being caused by different sur-



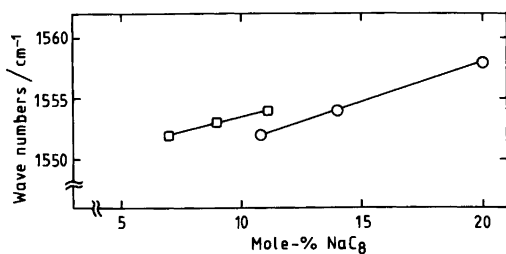


Fig. 7. The influence of different micellar compositions on the asymmetric carboxylate stretching frequency. The water content of the samples was kept constant at 10 weight % (○) and 20 weight % (□) D<sub>2</sub>O.

roundings of the carbonyl group. Band shapes and band widths result from atomic and molecular motions, and they are described by reorientational and vibrational relaxation.<sup>11-14</sup> Kato et al.<sup>15,16</sup> have performed band shape analysis of the symmetric stretching mode of nitrate ions in aqueous LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> solutions. They observed a broadening of infrared band profiles and shifts to higher frequency with increasing solute concentration. According to their conclusion, the vibrational band width of the stretching mode must be attributed to vibrational relaxation and more precisely to the pure vibrational dephasing analogous to a T<sub>2</sub> process in nuclear magnetic relaxation. For large molecules, the vibrational relaxation processes seem to dominate the observed band profiles as shown by Rothschild<sup>17</sup> and also by Bulkin and Brezinsky,<sup>18</sup> who investigated vibrational spectra of liquid crystals.

The observed band widths of the  $\nu_a$ -COO<sup>-</sup> vibration in the present system may then reflect different perturbations of the vibration caused by the environment. For the nonaqueous solution, the interaction between the sodium ion and the carboxylate group should be strong compared to the situation in aqueous solutions. The addition of water to the nonaqueous system results in hydration of the sodium ions leading to a diminished interaction. Thus, the observed narrowing of the band width of  $\nu_a$ -COO<sup>-</sup> with increasing amount of water may be due to changes in the counterion association. This explanation may also be valid for the increase of about 7 cm<sup>-1</sup> in the antisymmetric COO<sup>-</sup> frequency at 10 weight % H<sub>2</sub>O or D<sub>2</sub>O, when the molar ratio of HC<sub>8</sub>/

NaC<sub>8</sub> is changed from 4 to 1.6 (Fig. 7). The number of anions and cations are almost doubled for this change in the molar ratio and, since the water concentration is constant, the observed frequency increase probably reflects changes in counterion association.

**Carbonyl mode.** For the nonaqueous solution, the stretching vibration of the carbonyl group of the carboxylic acid was 1712 cm<sup>-1</sup> for the molar ratio 3 between octanoic acid and sodium octanoate (HC<sub>8</sub>/NaC<sub>8</sub> = 3). If the molar ratio was kept constant and water was added, no significant change in the frequency was detected. Substituting water for heavy water, however, resulted in a frequency decrease from 1712 to 1707 cm<sup>-1</sup> at higher contents of heavy water (60 weight % D<sub>2</sub>O). At constant 10 weight % of D<sub>2</sub>O, there was a decrease in the frequency of the carbonyl group stretching vibration from 1709 to 1705 cm<sup>-1</sup> when the molar ratio varied from 4 to 1.6. The corresponding frequency values were independent of the molar ratio HC<sub>8</sub>/NaC<sub>8</sub>, at 20 weight % of D<sub>2</sub>O (1707 cm<sup>-1</sup>). The decrease in the frequency of the carbonyl group stretching with increasing D<sub>2</sub>O content seems to be an isotope effect. Experimental values of CH<sub>3</sub>COOH and CH<sub>3</sub>COOD<sup>19</sup> reveal a frequency shift of 9 cm<sup>-1</sup> for the carbonyl stretching vibration. Due to the exchange between proton and deuterium in the octanoic acid, we observed COOD instead of COOH. This isotope exchange was obvious from our spectra where the  $\delta$ -OH in-plane bending frequency at 1410 cm<sup>-1</sup> disappeared when D<sub>2</sub>O was added to a water-free solution (Fig. 3). Unfortunately, the frequency of  $\delta$ -OH and the symmetric stretching vibration of the carboxylate group as well as the symmetric methylene bending frequency at the  $\alpha$ -carbon all occur at about the same frequency. We have not made any attempt to separate these bands so that their dependence on composition could be followed.

**HOD modes.** It is possible to use HOD as a hydrogen bonding probe. In HOD, the stretching motions of the OH or OD vibrations are not coupled<sup>20</sup> and the OH group stretching transition is narrower than in pure liquid H<sub>2</sub>O. This facilitates the interpretation of the observed spectrum. The absorption spectra of traces of HOD in pure D<sub>2</sub>O show an absorption maximum for  $\nu$  OH at 3409

$\text{cm}^{-1}$ . This is in good agreement with the value  $3410 \text{ cm}^{-1}$  obtained by Bayly et al.<sup>21</sup> At low  $\text{D}_2\text{O}$  concentrations, the OH stretching frequency was significantly higher.

At 10 weight %  $\text{D}_2\text{O}$ , e.g., the absorbance maximum was at  $3445 \text{ cm}^{-1}$ . This value decreased with increasing amount of  $\text{D}_2\text{O}$  and at 60 weight %  $\text{D}_2\text{O}$  a maximum was obtained at  $3412 \text{ cm}^{-1}$ . Typical spectra are shown in Fig. 8. From the figure, where the nonaqueous system ( $\text{HC}_8/\text{NaC}_8 = 3$ ) has been subtracted from the aqueous system, we can see the aforementioned shift in the OH frequency and the broader absorption band forming a shoulder on the low frequency side of the absorption maximum (10 weight %  $\text{D}_2\text{O}$ , mole ratio  $\text{D}_2\text{O}/\text{NaC}_8 \approx 3$ ). Increasing the  $\text{D}_2\text{O}$  content, resulted in a narrowing of the absorption band.

In our system, strong interactions occurred not only among the water molecules but also between water and lipid polar headgroups as well as between water and cations. From the infrared spectra, we can obtain some information about this variation in the environment of a water molecule. The high frequency side of the OH band (Fig. 8) indicates that, in comparison with bulk water, the water in the interior of the reversed micelles becomes less tightly bound with decreasing water content while the low frequency side indicates the micellar water to be more tightly bound with decreasing water content. If the

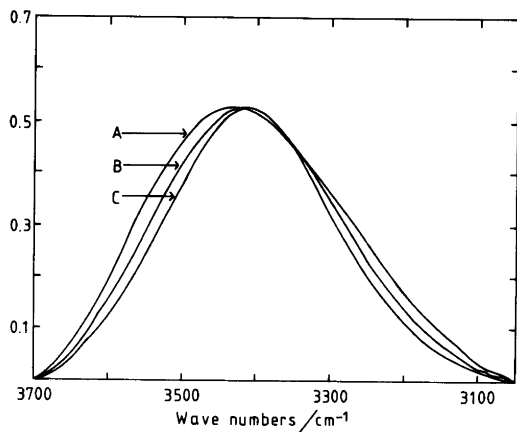


Fig. 8. Infrared spectra of the OH stretching region for HOD, at 10 weight %  $\text{D}_2\text{O}$  (A), 30 weight %  $\text{D}_2\text{O}$  (B) and 60 weight % (C). The spectra are scaled to the same absorbance.

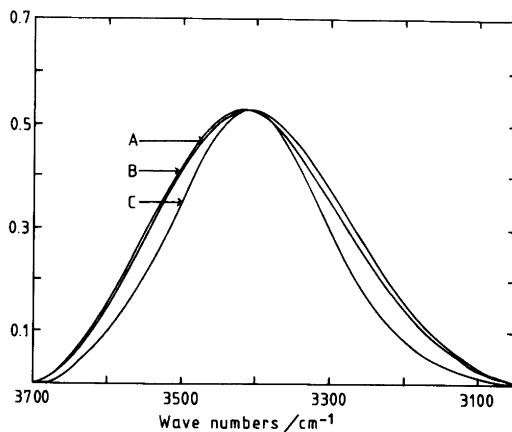


Fig. 9. Infrared spectra of the OH stretching region for the systems lithiumoctanoate/octanoic acid/water (A) and sodium octanoate/octanoic acid/water (B) at 30 weight %  $\text{D}_2\text{O}$ . The spectrum of HOD in  $\text{D}_2\text{O}$  (C) is included for comparison. The spectra are scaled to the same absorbance.

amount of water is increased, the high and low frequency shoulders are reduced and the bonding situation approaches that of bulk water. If the observed band profile is influenced by the cation, this would be recognized if lithium were substituted for sodium. It is reasonable to expect that the electric field of the cation would lower the OH vibrational frequency, the polarized bond being a better hydrogen bonding donor.<sup>22</sup> This is supported by the HOD spectrum in Fig. 9, obtained for a sample where lithium octanoate had been substituted for sodium octanoate at a  $\text{D}_2\text{O}$  content of 30 weight %. The OH band then shifted to lower frequency and the absorption maximum located at  $3410 \text{ cm}^{-1}$ .

The observed frequency dependence of  $\nu_a \text{COO}^-$  on the  $\text{D}_2\text{O}$  concentration may be explained as follows. The different behaviour of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  with respect to this vibrational frequency reflects the difference between the two hydrogen bonds  $\text{COO}^- \cdots \text{D}$  and  $\text{COO}^- \cdots \text{H}$ . If we consider  $\text{COO}^- \cdots \text{D}$  to represent a weaker hydrogen bond as compared to  $\text{COO}^- \cdots \text{H}$ , it would imply an increased frequency of the anti-symmetric carboxylate stretching mode when  $\text{H}_2\text{O}$  is substituted for  $\text{D}_2\text{O}$ , assuming that the hydration ability of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are equal. However, from quantum chemical calculations, we know that the binding energy of  $\text{Li}^+ \cdot \text{OH}_2$  is

about 5 kJ mol<sup>-1</sup> higher than that of Li<sup>+</sup> · OD<sub>2</sub>.<sup>23</sup> Kistenmacher et al.<sup>24</sup> have calculated the heats of formation for some ion-H<sub>2</sub>O complexes. They obtained the values -142.8 kJ mol<sup>-1</sup> and -97.6 kJ mol<sup>-1</sup> for the formation of Li<sup>+</sup> · OH<sub>2</sub> and Na<sup>+</sup> · OH<sub>2</sub> respectively, which was in good agreement with the experimental values -142.3 kJ mol<sup>-1</sup> and 100.4 kJ mol<sup>-1</sup>. Unfortunately, the difference in binding energy of Na<sup>+</sup> · OH<sub>2</sub> and Na<sup>+</sup> · OD<sub>2</sub> is not available, but on the assumption that  $-\Delta H_{\text{Na}^+ \cdot \text{OH}_2} < -\Delta H_{\text{Na}^+ \cdot \text{OD}_2}$ , the observed frequency dependence of the carboxylate stretching vibration,  $\nu_a \text{COO}^-$ , on the D<sub>2</sub>O content of the L<sub>2</sub> solution phase can be concluded to be a cooperative counterion and hydrogen bonding effect.

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