

# IR spectroscopy studies of molecular states of alkali-metal acetates in acetic acid solution

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This work presents the results of IR spectroscopic studies of the molecular states of alkali-metal (Li, Na, K, Cs) acetates in glacial acetic acid. The associates  $M(\text{Ac} \cdot n\text{HAc}) \cdot p\text{HAc}$  (I) have been shown to form with  $n \approx 8-9$  and varying number  $p$  of the outer-sphere HAc molecules, depending on the salt concentration. The anion  $\text{Ac} \cdot n\text{HAc}^-$  is symmetrical about the central fragment  $\text{O}-\text{H}-\text{O}$  with a very strong H-bond. The anion negative charge is located mainly on this fragment and on the two nearest  $\text{O} \cdots \text{H}-\text{O}$  fragments. The first coordination sphere of  $\text{M}^+$  comprises only oxygen atoms from the  $\text{O}-\text{H}-\text{O}$  group and from the anion's terminal  $\text{C}=\text{O}$  groups. Associates I form a microvolume of structured liquid phase which can be considered as a prototype of liquid-crystalline lamellar or ribbon-like structures produced by alkali acid soaps. When water is added,  $\text{H}_2\text{O}$  molecules hydrate both anions and cations,  $\text{M}^+$ , equalizing the polarizing influence of the latter on the anion. For hydrated salts the radius of the ordered liquid-phase microvolume around the cation  $\text{M}^+$  increases. On the whole, water addition produces a similar effect on the composition and structure of associates I as it does with liquid-crystalline water-free alkali acid soaps.

Aqueous and non-aqueous solutions of alkali-metal carboxylates having  $\text{C}_8-\text{C}_{12}$  carbon atoms in aliphatic chains (fatty acid soaps) have been studied extensively with regard to their surface-active properties and their ability to form lyotropic liquid-crystalline phases (see ref. 1 and 2). It has been known for a long time that fatty acid soap (MA) interactions with fatty acids (HA) reveal crystalline molecular compounds of a definite stoichiometric composition (2MA : 1HA, 1MA : 1HA, 1MA : 2HA).<sup>3</sup> It has also been found that the interaction between soaps and fatty acids in non-aqueous solutions yields molecular compounds (acid soaps) hydrated upon addition of water. These hydrated compounds form micelles and liquid-crystalline phases.<sup>4-11</sup> However, the content and structure of acid soaps which are formed in solutions with a large excess of fatty acid still remain unclear. These studies are of great importance not only for a better understanding of how acid soaps form liquid-crystalline phases, but help to determine the mechanism of extraction of alkali and other metals by fatty acids, which are used extensively as extraction solvents.<sup>12</sup> It is well known that they extract metals as acid soaps.<sup>12,13</sup>

Unlike fatty-acid soaps, the acetates of alkali metals possess no surface-active properties and hardly ever form mesophases or liquid-crystalline phases in the solution. This facilitates the studying of the content and structure of complex anions  $(\text{Ac} \cdot n\text{HAc})^-$  forming in the solutions of alkali-metal acetates in concentrated acetic acid (HAc) with and without water, as well as the interactions of cation  $\text{M}^+$  and ion  $(\text{Ac} \cdot n\text{HAc})^-$  with surrounding molecules. Such studies also help us to identify the molecular state of fatty-acid soaps in binary MA-HA and tertiary MA-HA- $\text{H}_2\text{O}$  systems (HA is  $(\text{C}_8-\text{C}_{22})$  carboxylic acid). We have already shown<sup>14</sup> that in the HAc-containing solutions of trimethylammonium acetate in  $\text{CCl}_4$ , acid salts  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  form. As the molar ratio  $\text{HAc}/\text{R}_3\text{CH}_3\text{N}^+\text{Ac}^-$  is increased to 4.6, the value of  $n$  increases to 4. We have determined the structure of these salts. However, the molecular states of MAc (M is an alkali metal) or  $\text{R}_4\text{NAc}$  salts in 100% acetic acid have not yet been studied.

In the present work IR spectroscopy was used to study molecular states of acid acetates of alkali metals Li, Na, K and Cs in acetic acid solution in the absence and in the presence of a small amount of water. We also discuss the peculiarities of the IR spectra produced by the compounds formed.

## Experimental

### Reagents and apparatus

Glacial acetic acid of chemical purity grade was used without additional purification. The solutions of MAc (M = Li, Na, K, Cs) in HAc were prepared in two ways: by dissolving the weighed portions of MAc anhydrous salts of chemical purity grade, or by dissolving metal Li (0.5 and 1 mol  $\text{dm}^{-3}$  solutions) or K (0.5 mol  $\text{dm}^{-3}$  solution) in HAc under an Ar atmosphere.

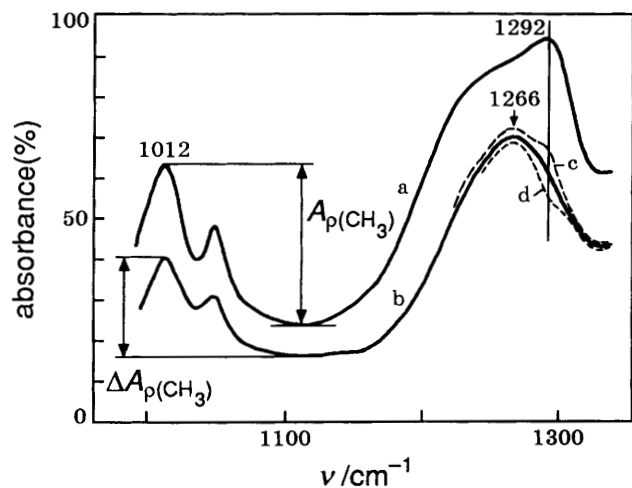
IR spectra were registered by an Specord 75 IR spectrometer within the 950–4000  $\text{cm}^{-1}$  range using capillary-layer width  $\text{BaF}_2$  cells. Cell widths were calculated using the equation  $d = A_p/(\epsilon_p C_{\text{HAc}})$ , where  $A_p$  is the absorbance of the torsional vibration band  $\rho(\text{CH}_3)$  at 1012  $\text{cm}^{-1}$ ,  $\epsilon_p$  is the molar absorption coefficient equal to 24.4 l  $\text{mol}^{-1} \text{cm}^{-1}$ ,<sup>14</sup> and  $C_{\text{HAc}}$  is the molar concentration of the HAc solution. The calculated  $d$  values were used to determine the molar absorption coefficients of other absorption bands. A curves synthesizer CS-2 (Russia) was used for deconvolution of the overlapping bands.

### Differential IR spectroscopy

We used differential IR spectroscopy to measure the concentration of those HAc molecules that experience the influence of dissolved salts and whose IR spectra thus differ from that of free HAc molecules. Let us designate the concentration of disturbed molecules by  $C_{\text{HAc}}^*$ . The procedure consists of recording of differential IR spectra of MAc in HAc solution with respect to pure HAc. The reference cell width was adjusted to calibrate one of the most typical bands,  $\nu_s(\text{CO}_2) = 1192 \text{ cm}^{-1}$  [vibration is mixed with  $\nu(\text{COH})$ ], of dimer cyclic  $(\text{HAc})_2$  molecules, thus subtracting their whole spectra together with the whole spectra of all other linear polymer  $(\text{HAc})_1$  molecules containing glacial acetic acid (Fig. 1). When compensation is attained, the following equation becomes true:

$$C_{\text{HAc}}^*/C_{\text{HAc}}^0 = \Delta A_p/A_p \quad (1)$$

where  $C_{\text{HAc}}^0$  is the total concentration of HAc molecules, and  $A_p$  and  $\Delta A_p$  are the absorbances of the torsional vibration band  $\rho_s(\text{CH}_3) = 1012 \text{ cm}^{-1}$  in the IR patterns of tested solu-



**Fig. 1** IR spectrum of 1 mol dm<sup>-3</sup> LiAc solution in HAc recorded without (a) and with (b) compensation of the spectra of solvent undisturbed molecules. Compensation was performed with respect to the absorption band 1192 cm<sup>-1</sup>. For spectrum b  $N = 7.7$ ; for sub-compensated (c) and overcompensated (d) spectra (dotted lines)  $N = 8.1$  and 7.3, respectively.

tions recorded respectively without and with  $\nu_s(\text{CO}_2) = 1192$  cm<sup>-1</sup> band compensation (see Fig. 1). We adopt the  $\rho_s(\text{CH}_3) = 1012$  cm<sup>-1</sup> band as the internal standard, since only this band is strictly proportional to the concentrations of all acetate group types in solution.<sup>14</sup>

From eqn. (1) we can determine  $C_{\text{HAc}}^*$  and the molar ratio  $N = C_{\text{HAc}}^*/C_{\text{M}^+}$ . The latter is equal to  $n + p$ , where  $n$  is the number of HAc molecules forming  $(\text{Ac} \cdot n\text{HAc})^-$  anions, and  $p$  is a number of HAc molecules solvating  $\text{M}(\text{Ac} \cdot n\text{HAc})$  salts.

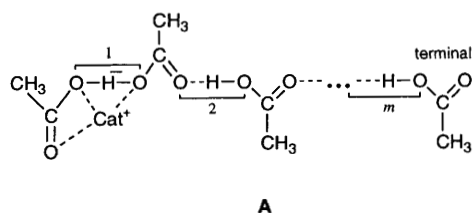
Differential IR spectroscopy allows us to separate simultaneously the spectra of  $\{\text{M}(\text{Ac} \cdot n\text{HAc})\} \cdot p\text{HAc}$  compounds (*i.e.*  $\text{MAc} \cdot n\text{HAc}$ ) from their superposition with the solvent spectra. Below we shall discuss only the differential IR spectra of  $\text{MAc} \cdot n\text{HAc}$  compounds.

## Results and Discussion

### Structure of $\text{M}(\text{Ac} \cdot n\text{HAc})$ salts and anion-cation interaction

The IR spectra of alkali-metal acetates are very similar and at first glance practically do not differ from the known spectra of  $(\text{Ac} \cdot n\text{HAc})^-$  in acid methyltrialkyl ( $\text{C}_8\text{--C}_{10}$ ) ammonium acetate  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  with  $n = 3\text{--}4$ .<sup>14</sup> This is not surprising, because a strong ionic interaction between the anions  $(\text{Ac} \cdot n\text{HAc})^-$  and the cations of the alkali metals or  $\text{R}_3\text{CH}_3\text{N}^+$  allows us to suggest that the cation nature affects only slightly the content and structure of  $(\text{Ac} \cdot n\text{HAc})^-$  anions.

The acid salt  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  with  $n = 3\text{--}4$  in  $\text{CCl}_4\text{--HAc}$  solutions has a particular structural feature. Its  $\text{O} \cdots \text{H} \cdots \text{O}$  group, most strongly interacting with cation  $\text{Cat}^+$ , is located near one end of the chain of H-bonded HAc molecules.<sup>14</sup>



The IR spectra of either  $\text{MAc} \cdot n\text{HAc}$  or  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  solutions contain the following absorption bands produced by non-equivalent OH-group oscillation: (i) wide bands  $\nu_{\text{as}}(\text{OHO}) \approx 1000$  cm<sup>-1</sup> and

$\delta(\text{OHO}) = 1520$  cm<sup>-1</sup> characterizing the centre symmetric group  $\text{O} \cdots \text{H} \cdots \text{O}$  with a very strong H-bond;<sup>16-19</sup> (ii) inten-

sive absorption at 1600-3100 cm<sup>-1</sup> (so-called continuous absorption background, cab) comprising three Fermi-resonance components A (2800 cm<sup>-1</sup>), B (2500 cm<sup>-1</sup>), C (1900 cm<sup>-1</sup>), which are called the A, B, C-structure of the cab,<sup>20-23</sup> corresponding to the quasi-symmetric group  $\text{O} \cdots \text{H} \cdots \text{O}$  with

a less strong H-bond of the  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  salt and a double-minimum proton potential;<sup>24-26</sup> (iii) a strong absorption within 2400-3400 cm<sup>-1</sup> with maximum at *ca.* 3000 cm<sup>-1</sup> and counter-deformed by a Fermi resonance for all other groups  $\text{O} \cdots \text{H} \cdots \text{O}$  (Fig. 2).

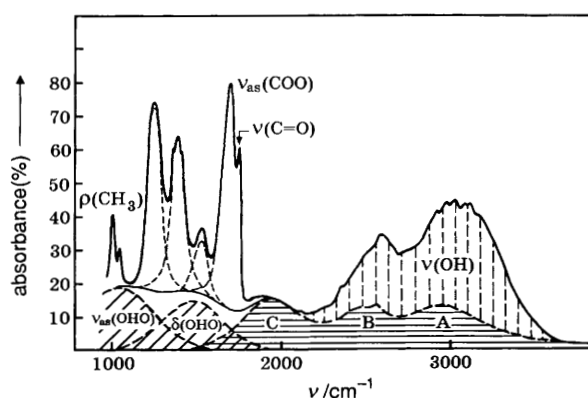
A frequency region of  $\nu_{\text{as}}(\text{CO}_2)$  contains a complex band with a maximum at 1712-1714 cm<sup>-1</sup>. It consists of the overlapping bands of non-equivalent H-bonded  $\text{CO}_2$ -groups. Band  $\nu(\text{C}=\text{O}) = 1755$  cm<sup>-1</sup> for the free terminal  $\text{C}=\text{O}$  groups is also present (Fig. 2).

Cation  $\text{M}^+$  should affect most strongly the group  $\text{O} \cdots \text{H} \cdots \text{O}$  and less strongly group  $\text{O} \cdots \text{H} \cdots \text{O}$  following the

decrease of their negative charge. To characterize such an influence in the effects produced by cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , one can use the change of absorption intensity of these groups. It is convenient to measure the absorption intensity of the Fermi resonance C band of the  $\text{O} \cdots \text{H} \cdots \text{O}$  group in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at a frequency of 1900 cm<sup>-1</sup>, where  $\text{O} \cdots \text{H} \cdots \text{O}$

groups do not absorb according to ref. 14. Similarly, the absorption intensity of the  $\nu_{\text{as}}(\text{OHO})$  band of the  $\text{O} \cdots \text{H} \cdots \text{O}$  group is measured in  $\epsilon_{1100}$  units at 1100 cm<sup>-1</sup>, where other species do not absorb.

Table 1 shows that the intensity of band C practically does not depend on the nature of cations  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$  (and increases only slightly for  $\text{Li}^+$ ). Therefore, the value  $\epsilon_{1900}$  for  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  salt should have been equal to  $\epsilon_{1900}$  for Na, K and Cs salts. However, in fact, this value is 1.9 fold less than expected. The values for the  $\epsilon_{1100}$  of  $\nu_{\text{as}}(\text{OHO})$  band for Na, K and Cs salts are practically equal to that of  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  (Table 1); we believe that, in contrast



**Fig. 2** IR spectrum of 1 mol dm<sup>-3</sup> CsAc solution in 100% HAc recorded with compensation of solvent undisturbed molecules. Hatching indicates absorption band of OHO groups, namely,  $\nu_{\text{as}}(\text{OHO})$  and  $\delta(\text{OHO})$  of the centre-symmetric  $\text{O} \cdots \text{H} \cdots \text{O}$  fragment; cab with A, B,

C-structure of  $\text{O} \cdots \text{H} \cdots \text{O}$  fragments (separation was made using spectral data of  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac} \cdot n\text{HAc})^-$  with  $n = 2\text{--}4$ );<sup>14</sup>  $\nu(\text{OH})$  of peripheral  $\text{O} \cdots \text{H} \cdots \text{O}$  groups of anion  $(\text{Ac} \cdot n\text{HAc})^-$  and of HAc molecules solvating associate  $\text{Cs}(\text{Ac} \cdot n\text{HAc})$  outerspherically.

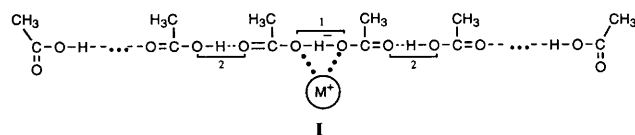
**Table 1** Molar absorption coefficients of  $\nu_{as}(\text{O}-\text{H}-\text{O})$  band ( $\epsilon_{1100}$ ) and C Fermi resonance component of the  $\text{O} \cdots \text{H}-\text{O}$  fragment ( $\epsilon_{1900}$ )

IR spectra of 1.0 and 0.5 mol dm<sup>-3</sup> water-free solutions of Cat<sup>+</sup>Ac<sup>-</sup> salts in HAC, and of the same solutions but containing water in the molar ratio H<sub>2</sub>O : MA = 4

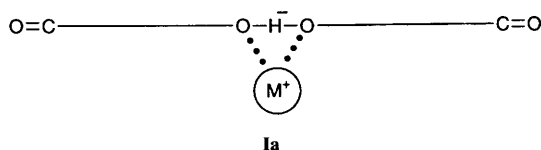
Cat <sup>+</sup>	$\epsilon_{1100}/\text{l mol cm}^{-1}$		$\epsilon_{1900}^a/\text{l mol}^{-1} \text{cm}^{-1}$
	water-free	hydrated	
Li	132 ± 3	170 ± 4	158 ± 6
Na <sup>+</sup>	160 ± 2	171 ± 4	146 ± 5
K <sup>+</sup>	168 ± 4	172 ± 4	150 ± 5
Cs <sup>+</sup>	169 ± 7	173 ± 4	146 ± 5
R <sub>3</sub> CH <sub>3</sub> N <sup>+</sup> <sup>b</sup>	161 ± 1	—	77.4 ± 3

<sup>a</sup> No dependence on water presence in solutions. <sup>b</sup> Data from ref. 14 for 0.061 mol l<sup>-1</sup> solutions of R<sub>3</sub>CH<sub>3</sub>N<sup>+</sup>Ac<sup>-</sup> in 0.20–0.26 mol l<sup>-1</sup> solutions HAC in CCl<sub>4</sub>.

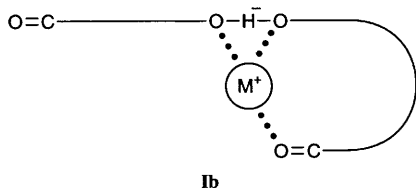
to R<sub>3</sub>CH<sub>3</sub>N<sup>+</sup>(Ac · nHAc)<sup>-</sup> in MAC · NHAc salts, not one but two groups of  $\text{O} \cdots \text{H}-\text{O}$  relate to one cation and their structures are as follows:



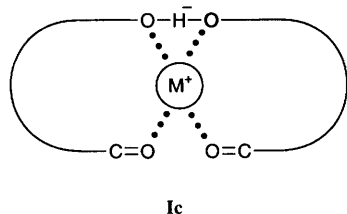
or in short form



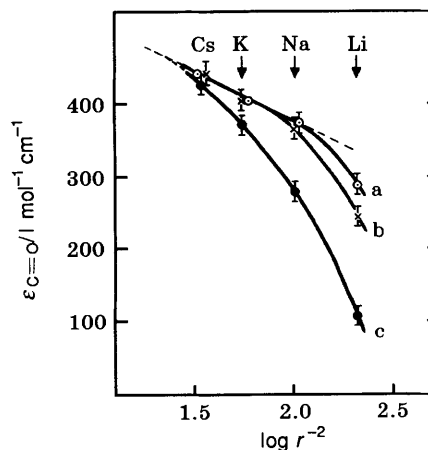
If the terminal C=O groups interact with the cation, then the following structures can also form:



and



Then the ratio of free and bonded terminal C=O groups should depend on the nature of the cation M<sup>+</sup>. As the anion-cation interaction can be considered to be purely ionic, the strength of this interaction depends on the M<sup>+</sup> cation charge density which is proportional to 1/r<sup>2</sup>, where r is the ionic radius of M. Fig. 3b, c shows the band intensity of  $\nu(\text{C}=\text{O}) = 1755 \text{ cm}^{-1}$  versus log(1/r<sup>2</sup>) for the solutions with C<sub>MAc</sub> = 0.5 and 1.0 mol dm<sup>-3</sup> ( $\epsilon_{\text{C}=\text{O}}$  was determined from the ratio  $A_{\text{C}=\text{O}}/(dC_{\text{MAc}})$ , where  $A_{\text{C}=\text{O}}$  is the absorbance at 1755 cm<sup>-1</sup>, d is the cell thickness, C<sub>MAc</sub> is the salt concentration). Obviously, the higher the charge density of the M<sup>+</sup> cation, the



**Fig. 3** Dependence of the intensity of band  $\nu(\text{C}=\text{O}) = 1755 \text{ cm}^{-1}$  of free terminal C=O groups on the logarithm of charge density of M<sup>+</sup> for solutions with C<sub>MAc</sub> = 0.5 mol dm<sup>-3</sup> (a, b) and 1 mol dm<sup>-3</sup> (c), without water (b, c) and with 2 mol dm<sup>-3</sup> of water (a)

more terminal C=O groups interact with M<sup>+</sup> and the stronger the equilibria

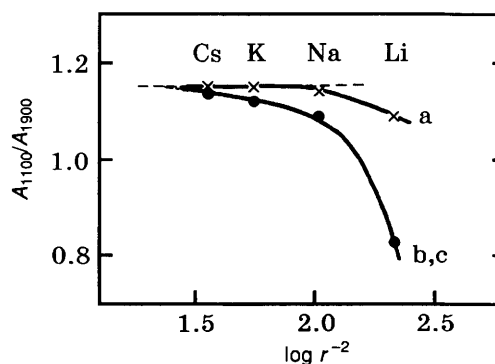


shift to the right.

So, only the terminal C=O group and the O-H-O fragment (note the change of absorption  $\epsilon_{1100}$  of the latter, Table 1) experience the polarizing influence of M<sup>+</sup>. The ratio  $A_{1100}/A_{1900}$  can serve as a more sensitive detector of the M<sup>+</sup> polarizing effect on group O-H-O because, as the effect increases,  $\epsilon_{1100}$  decreases, but  $\epsilon_{1900}$ , if it changes at all, increases (see Table 1). The dependence of  $A_{1100}/A_{1900}$  on log(1/r<sup>2</sup>) (Fig. 4) demonstrates that the polarizing effect of Li<sup>+</sup> on O-H-O differs drastically from that of Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>.

#### Hydration and solvation of M<sup>+</sup> cations

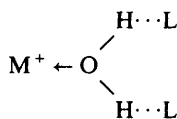
The alkali-metal soaps of fatty acids are known to dissolve in aliphatic alcohols only in the presence of water, and the minimum amount of water needed is just sufficient to hydrate the M<sup>+</sup> cations.<sup>4,5,27–30</sup> This fact is considered as strong evidence in favour of hydration in MA salts.<sup>1</sup> If one adds a small amount of water to the solutions studied here and adjusts the molar ratio H<sub>2</sub>O : M<sup>+</sup> = 4, then values  $\epsilon_{1100}$  for all the salts increase in the order of Cs<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> cations and become practically equal, but values for  $\epsilon_{1900}$  remain unchanged (Table 1). As a result, the ratios  $A_{1100}/A_{1900}$  approach a constant value (except for Li<sup>+</sup>, see Fig. 4). The



**Fig. 4** Dependence of absorbance ratio  $A_{1100}/A_{1900}$  on the logarithm of charge density of cations M<sup>+</sup> for solutions with C<sub>MAc</sub> = 0.5 mol dm<sup>-3</sup> (a, b) and 1 mol dm<sup>-3</sup> (c), without water (b, c) and with 2 mol dm<sup>-3</sup> of water (a). Curves b and c coincide exactly.

intensity of the  $\nu(\text{C}=\text{O})$  band at  $1755\text{ cm}^{-1}$  of the free terminal  $\text{C}=\text{O}$  groups grows in the same manner, *i.e.* most strongly for the Li-salt solution, slightly for Na salts, and remains virtually the same for K and Cs salts. As a result,  $\epsilon_{\text{C}=\text{O}}$  versus  $\log(1/r^2)$  approaches a linear function (Fig. 3). Even when only small amounts of water are added,  $\text{H}_2\text{O}$  molecules enter into the first coordination sphere of  $\text{M}^+$ , decrease the effective charge of cations and their polarizing effect on the anion, thus completely confirming the data of ref. 1, 4, 5, 27–30. This shifts equilibria (2) to the left for Li-salt solutions, does so only slightly for Na salts, but produces no effect in the case of K and Cs. Evidently, the ability of cations to be hydrated decreases following the same order.

The IR spectra of water exhibit a wide absorption band with the maximum at  $3430\text{--}3540\text{ cm}^{-1}$  typical for  $\text{H}_2\text{O}$  molecules forming weak H bonds. However, the band of free OH groups at *ca.*  $3680\text{ cm}^{-1}$  is absent. So,  $\text{H}_2\text{O}$  molecules bond to  $\text{M}^+$  having the following coordination type:



where L stands for solvent molecules. The presence of only one wide band of water stretching OH vibrations indicates that this band is complex and arises from non-equivalent  $\text{H}_2\text{O}$  molecules, as discussed below, only some of the added  $\text{H}_2\text{O}$  molecules enter into the first coordination sphere of the metal cation with the remainder interacting in an outerspherical manner with the complex anion.

For the water-free solutions of MAC in acetic acid, ratios  $A_{1100}/A_{1900}$  do not depend on  $C_{\text{MAC}}$  in the range from  $0.5\text{ mol dm}^{-3}$  to complete saturation ( $1.2\text{--}1.3\text{ mol dm}^{-3}$ ), forcing almost all HAC molecules to enter  $\text{MAC}\cdot n\text{HAc}$  associates. This indicates that HAC molecules do not solvate  $\text{M}^+$  cations or do so very slightly, almost not affecting the cation effective charge. So, oxygen atoms from groups  $\text{O}-\text{H}-\text{O}$  and bonded terminal groups  $\text{C}=\text{O}$  remain most closely to the  $\text{M}^+$  cation in its first coordination sphere.

#### Content of anions ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup>

The ratio of free and cation-bounded terminal  $\text{C}=\text{O}$  groups depend not only on the charge density of cation  $\text{M}^+$  but also on the length of the H-bonded HAC molecule chain in the ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup> anions, *i.e.* on their content. Indeed, in the salts  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac}\cdot n\text{HAc})^-$  dissolved in  $\text{CCl}_4\text{-HAc}$ , the portion of free terminal  $\text{C}=\text{O}$  groups grows linearly as  $n$  increases from 1 to 4.<sup>14</sup>

One can expect that in binary systems  $\text{MAC-HAc}$  the  $n$  values of anion ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup> will decrease in going from diluted solution ( $n$  is maximum) to concentrated or saturated solutions, as the excess of free HAC molecules decreases. Indeed, the difference in  $\epsilon_{\text{C}=\text{O}}$  vs.  $1/r^2$  for  $0.5$  and  $1.0\text{ mol dm}^{-3}$  solutions (Fig. 3b, c) shows unambiguously that the amount of free terminal  $\text{C}=\text{O}$  groups decreases in going from dilute to concentrated solutions following the decrease of  $n$  in anions ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup>.

Ternary systems  $\text{MAC-HAc-H}_2\text{O}$  with a low content of water differ from binary systems  $\text{MAC-HAc}$ , as noted above, by a substantial increase in the number of free terminal  $\text{C}=\text{O}$  groups only when  $\text{M} = \text{Li}$  (Fig. 3a). Therefore, the hydration of cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$  (and maybe  $\text{Li}^+$ ) does not change the content of anions  $\text{Ac}\cdot n\text{HAc}$ <sup>-</sup>.

We interpret the character of  $\epsilon_{\text{C}=\text{O}}$  vs.  $\log(1/r^2)$  change in the following manner. At low  $C_{\text{MAC}}$  the  $n$  values of anions ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup>, if at all dependent on the nature of the  $\text{M}^+$  cation, decreases in the order Cs, K, Na, Li. Meanwhile the fraction of terminal  $\text{C}=\text{O}$  groups bonded to  $\text{M}^+$  increases

**Table 2** Molar ratio  $N = C_{\text{HAc}}^*/C_{\text{MAC}}$  for water-free solutions of MAC in 100% HAC and for the same solutions after water addition (in brackets) in the molar ratio  $\text{H}_2\text{O} : \text{MAC} = 4$

M	$C_{\text{MAC}}/\text{mol dm}^{-3}$		
	1.0	0.5	0.3
Li	7.70 <sup>b</sup> (9.80) 6.53 (11.94) <sup>c</sup> 6.46	14.3 <sup>b</sup> (18.2) 14.5 <sup>b</sup> 8.7 (11.9) <sup>c</sup>	— <sup>d</sup>
Na	8.80	9.1 (15.5) 9.0	— <sup>d</sup>
K	10.50	12.3 <sup>b</sup> (21.4) 12.4 <sup>b</sup>	— <sup>d</sup>
Cs	9.68 (11.40) 9.59 (11.40)	13.2 (19.7)	22

<sup>a</sup> The error of  $N$  is  $\pm 0.05$  ( $1.0\text{ mol dm}^{-3}$ );  $\pm 0.15$  ( $0.5\text{ mol dm}^{-3}$ );  $\pm 1$  ( $0.3\text{ mol dm}^{-3}$ ). <sup>b</sup> The solutions are obtained by the reaction of the metal with HAC; all other solutions are obtained by dissolving MAC in HAC. <sup>c</sup> Molar ratio  $\text{H}_2\text{O} : \text{MAC} = 2$ . <sup>d</sup> Not studied.

almost proportionally to the increase of the cation charge density logarithm.

Values of  $\epsilon_{\text{C}=\text{O}}$  for  $1.0$  and  $0.5\text{ mol dm}^{-3}$  solutions of CsAc practically coincide (their difference  $\Delta\epsilon_{\text{C}=\text{O}}$  is only  $13.9\text{ l mol}^{-1}\text{ cm}^{-1}$ ; for reference, in  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac}\cdot n\text{HAc})^-$  solutions an increase of  $n$  by 1 results in  $\Delta\epsilon_{\text{C}=\text{O}} = 898\text{ l mol}^{-1}\text{ cm}^{-1}$ ),<sup>14</sup> that is the composition of ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup> anions in these solutions is the same. Therefore, experimentally determined  $N$  values for  $1\text{ mol dm}^{-3}$  CsAc solutions (Table 2) are closest to  $n$  and can serve as an upper limit, *i.e.*  $n < 9.6$ .

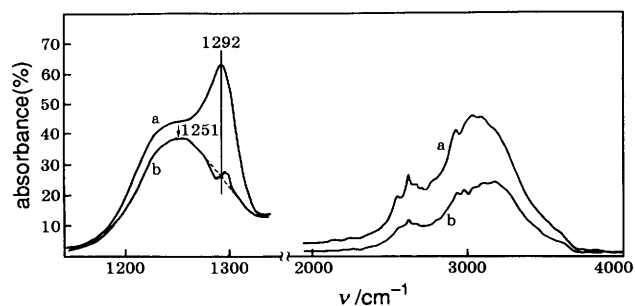
We can estimate the lower limit of  $n$  by considering the composition and structure of the asymmetric anion of  $\text{R}_3\text{CH}_3\text{N}^+(\text{Ac}\cdot n'\text{HAc})^-$  with  $n' = 4$  (see structure A), which forms in  $\text{CCl}_4\text{-HAc}$  solutions at a molar ratio  $\text{HAc} : \text{R}_3\text{CH}_3\text{N}^+ = 4.7$ . In neat HAC this anion becomes symmetric with  $n > 2n' - 1$ , *i.e.*  $n > 7$ . Consequently,  $7 < n < 9.6$ , and for  $\text{Cs}(\text{Ac}\cdot n\text{HAc})$  the most probable statistical mean  $n$  should be 8–9 as well. In the case of  $1\text{ mol dm}^{-3}$   $\text{Li}(\text{Ac}\cdot n\text{HAc})$  solutions (attaining saturation) the  $n$  value is significantly lower than that for  $0.5\text{ mol dm}^{-3}$  solutions and should approach  $N = 6.5$  (Table 2). As for dilute solutions,  $n > 6.5$ . Therefore, in dilute solutions of MAC in HAC the composition of ( $\text{Ac}\cdot n\text{HAc}$ )<sup>-</sup> either does not depend on the nature of  $\text{M}^+$  and  $n$  equals 8–9, or does so only slightly, and  $n$  decreases insignificantly (within 9–7) in going from Cs to Li.

#### Outersphere solvation and hydration of $\text{M}(\text{Ac}\cdot n\text{HAc})$ salts compared with alkali fatty acid soaps in the liquid-crystalline state

Table 2 shows  $N = n + p$  of associates  $[\text{M}(\text{Ac}\cdot n\text{HAc})] \cdot p\text{HAc}$  in acetic acid determined without and with water. From the data we can see the following. (i) In water-free solutions  $N$  increases as  $C_{\text{MAC}}$  decreases, since the number of outer-sphere molecules,  $p$ , grows at a constant  $n$ . For instance, as the concentration of CsAc solutions decreases from  $1.0$  to  $0.3\text{ mol dm}^{-3}$ ,  $N$  increases from  $9.7$  to  $21.9$  and is likely to rise further as  $C_{\text{MAC}}$  decreases. (ii) As a small amount of water is added,  $N$  increases substantially, that is,  $p$  grows at a constant  $n$ . (iii) The value of  $N$  depends on the solution preparation history.

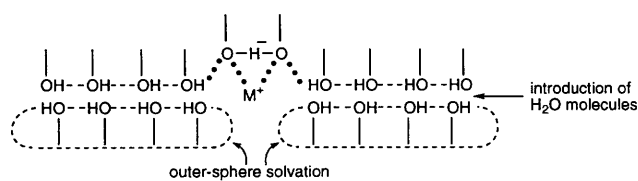
Let us consider these aspects in more detail. An increase of  $N$  within 9–20 is followed by a growth in intensity of only those bands in the IR spectra that coincide with the absorption bands of linear polymers ( $\text{HAc}$ )<sub>1</sub> comprising 100% acetic acid<sup>†</sup> [the most typical are  $\delta(\text{COH}) + \nu(\text{C}-\text{O})$  at  $1260\text{ cm}^{-1}$

<sup>†</sup> The formation of linear polymers of (MAC)<sub>1</sub> in  $\text{HAc-CCl}_4$  solution was proved by Bulmer and Shurvell,<sup>31</sup> based only on the  $\nu(\text{C}=\text{O})$  frequency region.



**Fig. 5** IR spectra of undiluted HAC: a, conventional, and b, that recorded for a 80% HAC solution in  $\text{CCl}_4$  [where the equilibrium  $(\text{HAc})_2 \leftrightarrow (\text{HAc})_1$  is strongly shifted to the left], with the cell width being selected to compensate the band at  $1292 \text{ cm}^{-1}$  of  $(\text{HAc})_2$ . Therefore, spectrum b corresponds to linear polymers  $(\text{HAc})_1$ , comprising undiluted HAC.

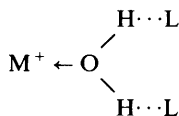
and  $\nu(\text{OH}) = 3000\text{--}3100 \text{ cm}^{-1}$ , see Fig. 5]. Therefore, outersphere-bounded HAC molecules form the same linear H-bonded chains as do  $(\text{HAc})_1$  polymers. As the cation is not solvated, then solvation should affect the anion. Anion solvation is possible due to the interaction between polar  $\text{CO}_2$  groups from HAC molecules and  $(\text{Ac} \cdot n\text{HAc})^-$  anions according to:



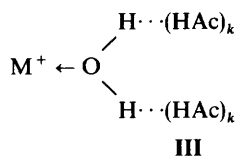
where  $\text{O} = \text{CH}_3\text{CO}_2^-$ . Simultaneously, HAC molecules form H bonds producing linear chains with IR spectra identical to those of  $(\text{HAc})_1$  linear polymers of acetic acid itself.

One can define the intermolecular events of **II** as  $(\text{Ac} \cdot n\text{HAc})^-$  anion solvation. On the other hand, **II** is likely to have much in common with the building blocks of lyotropic liquid-crystalline phases of lamellar or ribbon-like types formed by fatty-acid alkali soaps.<sup>1,32</sup> Thus, in systems  $\text{MAc-HAc}$  there is no dramatic difference between the solvation of the  $(\text{Ac} \cdot n\text{HAc})^-$  anion and the formation of ordered molecular structures, modelling the liquid-crystalline state.

In the ternary systems  $\text{MAc-HAc-H}_2\text{O}$  the growth of  $N$  (or  $p$ ) is dictated by two factors. First, water molecules intrude into the polar zones of the double molecular chains (see structure **II**) owing to dipole-dipole interactions with polar  $\text{CO}_2$  groups and H-bond formation, just as it occurs in the ternary systems alkali soaps-carboxylic ( $\text{C}_8\text{--C}_{18}$ ) acid- $\text{H}_2\text{O}$ .<sup>1</sup> This helps to stabilize structure **II**. The second factor is the hydration of cation  $\text{M}^+$  according to the type of species



If  $\text{H}_2\text{O}$  molecules form H bonds with  $\text{C}=\text{O}$  groups from  $(\text{HAc})_2$  dimers, then one OH group of the latter becomes free and can add to the next HAC molecule. This proceeds yielding chains of H-bonded HAC molecules:



Molecular chains  $\cdots(\text{HAc})_k$  can react simultaneously with  $\text{Ac} \cdot n\text{HAc}^-$  anions according to structure **II**. Thus, the  $\text{M}^+$  bonded  $\text{H}_2\text{O}$  molecules create a more dense outer-sphere solvate envelope comprising ordered  $(\text{HAc})_k$  molecules, thus helping to form a liquid crystalline type structure.

As for the effect of the solution preparation history on  $N$  (or  $p$ ), the salts resulting from metal  $\text{M}$  reaction with HAC always possess a higher  $N$  than those obtained *via*  $\text{MAc}$  dissolving in HAC (Table 2). The reason is that in the first case dissolving causes local heating, thus possibly favouring structures of type **II** with a higher density of  $(\text{HAc})_1$  molecules than at room temperature. When the solution is cooled the structure produced remains stable for a long time. A similar relationship between thermal history of sample preparation and their liquid-crystalline state has been found by others<sup>33,34</sup> with other carboxylate salts.

Structure **II** and its simplified analogue **Ia** representing the structure of  $[\text{M}(\text{Ac} \cdot n\text{HAc})] \cdot p\text{HAc}$  associates in water-free solutions show both terminal  $\text{C}=\text{O}$  groups to be free. If we fix one of them or both onto  $\text{M}^+$ , then structure **II** will transform into **Ib** and **Ic**, respectively (not shown), which are the more detailed analogues of **Ib** and **Ic**. Finally, if we complete Schemes **(II)**, **(IIb)** and **(IIc)** with fragments **(III)**, we will obtain the full structural schemes of associates forming in ternary systems  $\text{MAc-HAc-H}_2\text{O}$  at low water content.

## Conclusion

$[\text{M}(\text{Ac} \cdot n\text{HAc})] \cdot p\text{HAc}$  associates with  $n \approx 8\text{--}9$  and variable  $p$  form in the dilute water-free solutions of  $\text{MAc}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$ ) in HAC. The structure of associates is shown in **Ia-c** and **II**. The first coordination sphere of cation  $\text{M}^+$  contains only oxygen atoms from fragment  $\text{O}-\overset{1}{\text{H}}-\text{O}$  and from the

terminal  $\text{C}=\text{O}$  groups of anion  $(\text{Ac} \cdot n\text{HAc})^-$ , but no  $\text{CO}_2$  groups of solvent molecules HAC. The fraction of terminal  $\text{C}=\text{O}$  groups bonded to the  $\text{M}^+$  cation increases as the  $\text{M}^+$  charge density grows in going from  $\text{Cs}^+$  to  $\text{Li}^+$ . The anion structure is symmetric with respect to the  $\text{O}-\overset{1}{\text{H}}-\text{O}$  fragment in contrast to the asymmetrical anion of  $\text{R}_3\text{CH}_3\text{N}^+$   $(\text{Ac} \cdot n\text{HAc})^-$  in dilute solutions of HAC in  $\text{CCl}_4$ .

When water is added some  $\text{H}_2\text{O}$  molecules enter the first coordination sphere of  $\text{M}^+$ , thus increasing the number of outersphere HAC molecules,  $p$  (structure **III**). Other  $\text{H}_2\text{O}$  molecules enter the polar side of the double molecular chains produced by the  $\text{CO}_2$  groups of the  $(\text{Ac} \cdot n\text{HAc})^-$  anions and the HAC molecules solvate the latter. This further stabilizes these molecular chains.

HAC and  $\text{H}_2\text{O}$  molecules solvating and hydrating in the outer sphere (**Ia-Ic**) associates produce the same ordered molecular structures, that can be regarded as pregenerators of ribbon-like and lamellar liquid-crystalline structures typical of the system alkali soaps-fatty acid- $\text{H}_2\text{O}$ .

It is impossible to distinguish clearly between the inner- and outer-solvation in the studied molecular associates. Indeed, one can represent the acid anion  $\text{Ac} \cdot n\text{HAc}^-$  as  $(\text{Ac} \cdot 3\text{HAc})^- \cdot (n-3)\text{HAc}$ , where the structural unit  $(\text{Ac} \cdot 3\text{HAc})^-$  with two types of groups,  $\text{O}-\overset{1}{\text{H}}-\text{O}$  and  $\text{O} \cdots \overset{2}{\text{H}}-\text{O}$  can be considered as solvated by  $(n-3)\text{HAc}$

molecules. The IR spectra of the latter are almost identical to those of all other  $p$  outersphere HAC molecules. The reason is that the charge of  $\text{Ac} \cdot n\text{HAc}^-$  localizes primarily on the central fragment  $\text{O}-\overset{1}{\text{H}}-\text{O}$  and two neighbouring fragments  $\text{O} \cdots \overset{2}{\text{H}}-\text{O}$  and hardly ever affects other  $\text{O} \cdots \overset{1}{\text{H}}-\text{O}$  fragments.

So, the liquid-phase microvolume, surrounding the  $\text{M}^+$  cation, possesses an ordered structure similar to that of a

liquid crystal. The microvolume radius increases in going from concentrated to dilute solutions, and also on water addition.

In general, the data obtained should comply with other binary and ternary systems MA–HA and MA–HA–H<sub>2</sub>O produced by carboxylic acids HA with a long (C<sub>8</sub>–C<sub>18</sub>) aliphatic radical. As the surface-active properties of acids and their salts are enhanced with increasing radical length, so does the ability of the acid salts to form liquid-crystalline solutions and mesophases. Therefore, in the dilute solutions of such systems the radius of the microvolume of the ordered liquid phase surrounding the M<sup>+</sup> cation should exceed that in the solutions of MAc in HAC.

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