

## Thermodynamic Excess Quantities in Aqueous Solutions of Short-chain Ionic Surfactants

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The excess enthalpies of mixing aqueous sodium chloride and sodium alkanooate (propanoate and pentanoate) solutions at three constant total molalities as well as the partial molar excess enthalpies on diluting pure alkanooate solutions have been determined from calorimetric measurements at 298.2 K. Further, the excess free energies of mixing aqueous sodium chloride and sodium alkanooate (methanoate to hexanoate) solutions have been determined from electrochemical measurements at the same temperature. The results are discussed in terms of chain length and molality dependence. The excess quantities can partially be understood as aggregation, disaggregation, hydration or dehydration effects.

In the discussions of micelle formation, special attention has been given to the structural changes in the state of the amphiphilic molecule as well as in surrounding medium.<sup>1–5</sup> Hydration and associated phenomena have been interpreted in terms of bound water to the amphiphiles and structural changes in neighbouring water molecules. In an earlier investigation<sup>6</sup> we have proposed a model for the different hydrations and related structural effects, *i.e.* hydrophilic, semihydrophilic and “hydrophobic” hydration of short-chain ionic surfactants. This study shows further that water electrostatically bound to the homologous alkanooate ions tends towards a limiting value at infinite dilution. We believe that the studied hydration numbers and their relationships to thermodynamic quantities in aqueous solutions together with earlier systematic investigations<sup>7,8</sup> can give useful information about micellar aggregation, even though the water structure as such has been consistently disregarded.

This work presents thermodynamic excess properties of aqueous alkanooate solutions. Earlier studies of mixed electrolyte solutions have increased the understanding of the specific ionic interactions in this kind of solutions.<sup>9–12</sup> Although the free energy and enthalpy are complex quantities reflecting the whole change in the equilibrium conditions of the solutions, we try to explain these excess functions by means of changes in aggregation as well as in the hydration numbers of the investigated alkanooates.

### EXPERIMENTAL

The experimental work involves measurements of: (i) heats of dilution of pure sodium alkanooate solutions (NaB–H<sub>2</sub>O), (ii) heats of mixing sodium chloride and sodium alkanooate solutions and (iii) mean activity coefficients of sodium chloride at different constant sodium molalities,  $m_{\text{Na}^+}$ , in the system NaCl–NaB–H<sub>2</sub>O. All measurements were made at 298.2 K.

*Chemicals.* Sodium chloride (E. Merck AG, *pro analysi* quality), sodium ethanoate, C<sub>2</sub>, (E. Merck AG, *pro analysi* quality) and sodium propanoate, C<sub>3</sub>, (Sigma Chem. Co., purity about 99%) were used without further purification. Sodium butanoate, C<sub>4</sub>, and sodium pentanoate, C<sub>5</sub>, were prepared by neutralizing the corresponding fatty acid (Fluka AG, *purissimum* quality) with sodium hydroxide (E. Merck AG “1 N Titrisol”) as described earlier.<sup>13</sup> Hydrochloric acid solutions were made from E. Merck AG “1 N Titrisol”. The water was distilled and passed through an ion exchange resin. Its conductivity was 0.5  $\mu\text{S cm}^{-1}$ .

*Calorimetric measurements.* All enthalpies for the propanoate systems were measured with an LKB

10700-1 Flow Microcalorimeter. The solutions were pumped through the mixing cell by two repeatedly calibrated peristaltic pumps (LKB 10200 Perpex). Excess enthalpies of mixing at constant  $m_{\text{Na}^+}$  were measured by a stepwise mixing procedure, *i.e.* pure solutions of NaCl and  $\text{C}_3$  were mixed and the resulting mixture was then in turn mixed with each of the pure solutions and so on. Water was used instead of NaCl solution to get the dilution enthalpies of pure  $\text{C}_3$  solutions. All enthalpies for the pentanoate systems were measured with a titration calorimeter connected to an LKB 8700 Precision Calorimetry System. Each titration at a constant sodium molality was divided into two parts. In the first part a  $\text{C}_5$  solution was added to an NaCl solution. In the second part an NaCl solution was added to a  $\text{C}_5$  solution. A known volume was removed from the titration vessel after each addition in order to keep the solution volume almost constant during the titration. Dilution enthalpy measurements were performed by addition of water to a  $\text{C}_5$  solution. Hydrochloric acid titrations were made to check the operation of both the calorimetric systems.<sup>14</sup>

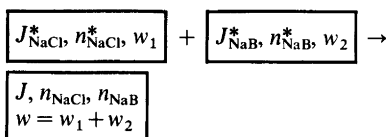
**Potentiometric measurements.** The following electrode system was used in the emf measurements

Ag, AgCl/ $m_{\text{NaCl}}$ ,  $m_{\text{NaB}}$ /Na-glass

At constant sodium molality,  $m_{\text{Na}^+}$ , the alkanooate ion molality varied between 0 and  $m_{\text{Na}^+}$ . The apparatus, electrodes and measuring methods have been described earlier.<sup>13,15</sup>

## RESULTS

1. *Excess functions of mixing.* Mixing a sodium chloride solution with a sodium alkanooate solution, NaB, can be illustrated by Scheme 1, where  $n_i$  is



Scheme 1.

the amount of solute  $i$ ,  $w$  is the mass of water and superscript \* is used to express pure aqueous solutions. If  $J$  is an arbitrary quantity, the corresponding quantity of mixing becomes eqn. (1), *i.e.* the quantity

$$\Delta J^E = J - J_{\text{NaCl}}^* - J_{\text{NaB}}^* \quad (1)$$

over and above that of the single solutions from which the mixture could be made. This quantity is usually given per mass unit of water,<sup>12</sup> eqns. (2) and (3), where  $m_i$  denotes molality of solute  $i$ .

$$J_w = J/w \quad (2)$$

$$\begin{aligned} \Delta J_w^E &= \frac{\Delta J^E}{w} = J_w - \frac{w_1}{w} J_{\text{NaCl},w}^* - \frac{w_2}{w} J_{\text{NaB},w}^* = \\ &= J_w - \frac{m_{\text{NaCl}}}{m_{\text{NaCl}}^*} J_{\text{NaCl},w}^* - \frac{m_{\text{NaB}}}{m_{\text{NaB}}^*} J_{\text{NaB},w}^* \end{aligned} \quad (3)$$

When the pure solutions are of equal molality one can write eqn. (4) and further replace  $m_{\text{NaCl}}^*$  and

$$m_{\text{NaCl}}^* = m_{\text{NaB}}^* = m_{\text{Na}^+} \quad (4)$$

$m_{\text{NaB}}^*$  in eqn. (3) with  $m_{\text{Na}^+}$ .

2. *Excess hydration number.* Eqn. (3) gives for the excess hydration number of mixing eqn. (5),

$$\Delta h_w^E = h_w - y_{\text{NaCl}} h_{\text{NaCl},w}^* - y_{\text{NaB}} h_{\text{NaB},w}^* \quad (5)$$

where  $h_w$  expresses the amount of bound water per mass unit of water and the quantity  $y_i$  is defined by  $y_i = m_i/m_{\text{Na}^+}$ . If  $h_i$  denotes the hydration number, *i.e.* amount of bound water per amount of solute  $i$ , one obtains eqns. (6) and (7).

$$h_{i,w}^* = m_i^* h_i^* = m_{\text{Na}^+} h_i^* \quad (6)$$

$$h_w = \sum_i m_i h_i \quad (7)$$

Substituting eqns. (6) and (7) into eqn. (5) yields eqn. (8).

$$\Delta h_w^E = \sum_i m_i (h_i - h_i^*) \quad (8)$$

With following approximations

(i) the hydration number of the chloride ion is zero<sup>16,17</sup>

(ii)  $h_{\text{NaB}} = h_{\text{Na}^+} + h_{\text{B}^-}$  and  $h_{\text{NaCl}} = h_{\text{Na}^+}$

(iii)  $h_{\text{Na}^+}$  is constant at constant sodium molality and independent of the anion<sup>18</sup>

eqn. (8) applied to the system NaCl–NaB– $\text{H}_2\text{O}$  takes the form (9).

$$\Delta h_w^E = m_{\text{NaB}} (h_{\text{B}^-} - h_{\text{B}^-}^*) \quad (9)$$

3. *Excess enthalpies.* Using eqn. (3), the excess enthalpies of mixing,  $\Delta H_w^E$ , are calculated from the

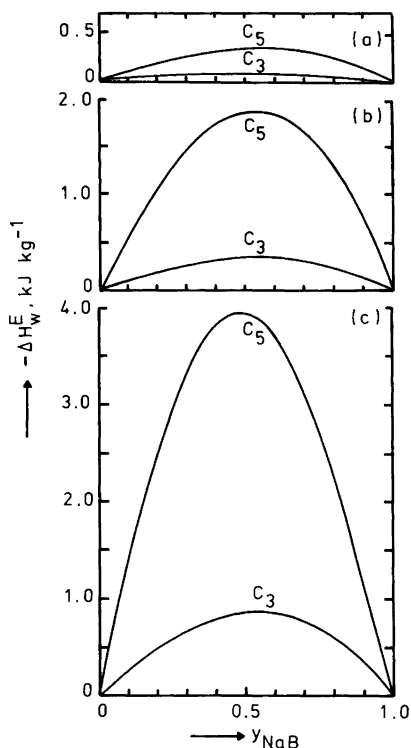


Fig. 1. Excess enthalpy of mixing ( $\Delta H_w^E$ ) aqueous sodium chloride and sodium propanoate ( $C_3$ ) or sodium pentanoate ( $C_5$ ) at 298.2 K and three constant sodium molalities (a) 1.0, (b) 2.0 and (c) 3.0 mol  $\text{kg}^{-1}$  plotted against  $y_{\text{NaB}} = m_{\text{NaB}}/m_{\text{Na}^+}$ .

calorimetric measurements. These enthalpies are shown in Fig. 1 as functions of  $y_{\text{NaB}}$  at three different constant sodium molalities,  $m_{\text{Na}^+}$ .

Molar excess enthalpies,  $H_m^{*,E}$ , in pure solutions, calculated from measured values are plotted in Fig. 2 as functions of the alkananoate molality. The excess enthalpies of sodium ethanoate by Parker<sup>19</sup> and of sodium butanoate by Lindenbaum<sup>20</sup> are also given in the same graph.

4. *Excess free energies.* We have calculated the mean activity coefficients  $\gamma_{\text{Na},B}$  from measured mean activity coefficients  $\gamma_{\text{Na},\text{Cl}}$  and earlier measured water activities<sup>21,7,22</sup> by means of Gibbs-Duhem equation.<sup>13</sup> The results are given in Table 1. When mixing sodium chloride and sodium alkananoate solutions of equal molality, the excess free energy of mixing,  $\Delta G_w^E$ , can be calculated according to Harned and Robinson<sup>10</sup> from eqn. (10).

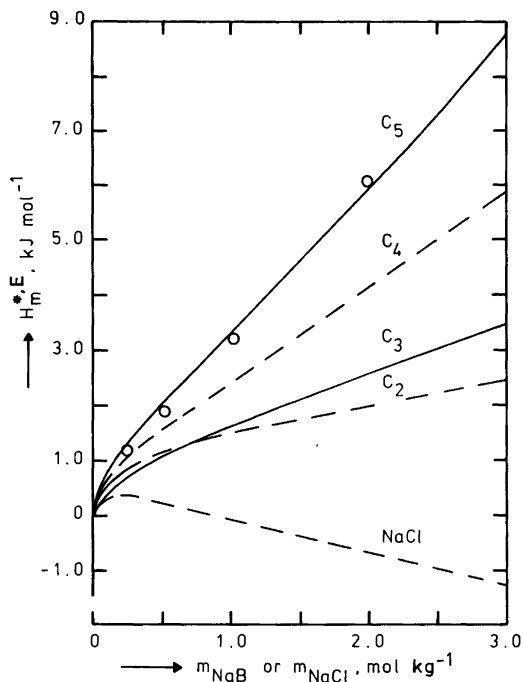


Fig. 2. Molar excess enthalpy ( $H_m^{*,E}$ ) in pure aqueous solutions of NaCl,<sup>33</sup>  $C_2$ ,<sup>14</sup>  $C_3$ ,  $C_4$ ,<sup>20</sup> and  $C_5$  plotted against molality at 298.2 K. Lindebaum's<sup>20</sup> data for  $C_5$  are denoted by (O).

$$\Delta G_w^E = 2m_{\text{Na}} + RT \left( \int_0^{y_{\text{NaB}}} \ln \left( \frac{\gamma_{\text{Na},B}}{\gamma_{\text{Na},\text{Cl}}} \right) dy_{\text{NaB}} - y_{\text{NaB}} \int_0^1 \ln \left( \frac{\gamma_{\text{Na},B}}{\gamma_{\text{Na},\text{Cl}}} \right) dy_{\text{NaB}} \right) \quad (10)$$

From the mean activity coefficients in Table 1 as well as our previously published data,<sup>6,13,22</sup>  $\Delta G_w^E$  is calculated and plotted in Fig. 3 as a function of  $y_{\text{NaB}}$  at four different sodium molalities.

The partial molar excess free energies,  $G_{m,j}^{*,E}$  for the ion  $j$  are given in Fig. 4 as a function of the molality. These energies were calculated from eqn. (11), where  $\gamma_j^*$  is the ion activity coefficient.<sup>23</sup>

$$G_{m,j}^{*,E} = RT \ln \gamma_j^* \quad (11)$$

Note that the sodium chloride curve in Fig. 4 represents both  $G_{m,\text{Na}^+}^{*,E}$  and  $G_{m,\text{Cl}^-}^{*,E}$  as a result of the Guggenheim convention<sup>24</sup>  $\gamma_{\text{Na}^+}^* = \gamma_{\text{Cl}^-}^* = \gamma_{\text{Na},\text{Cl}}^*$ .

Table 1. Mean activity coefficients in sodium chloride–sodium alkanooate–water systems at 298.2 K and different constant sodium molalities, *i.e.* 0.5; 1.5 and 2.0 mol kg<sup>-1</sup>. The last molality value in each  $m_{C_i}$  – column represents the constant molality,  $m_{Na^+}$ .

$m_{C_i}$ mol kg <sup>-1</sup>	Sodium ethanoate		Sodium propanoate		Sodium butanoate		Sodium pentanoate	
	$\gamma_{Na,Cl}$	$\gamma_{C_2}$	$\gamma_{Na,Cl}$	$\gamma_{C_3}$	$\gamma_{Na,Cl}$	$\gamma_{C_4}$	$\gamma_{Na,Cl}$	$\gamma_{C_5}$
0.00	0.681	0.698	0.681	0.713	0.681	0.701	0.681	0.679
0.05	0.684	0.702	0.685	0.719	0.683	0.711	0.686	0.692
0.10	0.686	0.706	0.689	0.724	0.688	0.721	0.692	0.705
0.15	0.689	0.710	0.693	0.730	0.692	0.731	0.698	0.718
0.20	0.691	0.714	0.696	0.735	0.697	0.740	0.704	0.730
0.25	0.694	0.718	0.700	0.740	0.702	0.748	0.710	0.741
0.30	0.697	0.722	0.704	0.745	0.706	0.756	0.716	0.752
0.35	0.700	0.725	0.708	0.750	0.711	0.763	0.722	0.763
0.40	0.702	0.728	0.712	0.755	0.716	0.770	0.728	0.772
0.45	0.705	0.732	0.716	0.759	0.721	0.776	0.735	0.782
0.50	0.708	0.735	0.720	0.764	0.725	0.782	0.741	0.790
0.00	0.656	0.672	0.656	0.730	0.656	0.789	0.656	0.806
0.15	0.660	0.690	0.660	0.748	0.665	0.810	0.668	0.835
0.30	0.664	0.708	0.667	0.766	0.674	0.830	0.683	0.862
0.45	0.669	0.724	0.675	0.783	0.685	0.850	0.697	0.885
0.60	0.673	0.739	0.683	0.799	0.696	0.870	0.711	0.906
0.75	0.677	0.752	0.691	0.815	0.709	0.889	0.724	0.924
0.90	0.682	0.764	0.699	0.829	0.722	0.907	0.738	0.939
1.05	0.686	0.775	0.707	0.843	0.738	0.924	0.752	0.950
1.20	0.690	0.784	0.716	0.856	0.754	0.941	0.765	0.957
1.35	0.695	0.791	0.724	0.867	0.772	0.957	0.778	0.961
1.50	0.700	0.799	0.733	0.880	0.792	0.973	0.791	0.965
0.00							0.668	0.957
0.20							0.687	0.977
0.40							0.707	0.995
0.60							0.726	1.010
0.80							0.744	1.022
1.00							0.761	1.033
1.20							0.777	1.036
1.40							0.791	1.039
1.60							0.804	1.038
1.80							0.815	1.034
2.00							0.825	1.030

## DISCUSSION

1. *Free energy.* The excess free energy,  $\Delta G_w^E$ , of mixing sodium chloride and sodium alkanooate is negative and decreases with increasing chain length of the alkanooate ion as shown in Fig. 3a at  $m_{Na^+} = 0.5$  mol kg<sup>-1</sup>. At 1.5 mol kg<sup>-1</sup> the opposite effect can be observed, *i.e.*  $\Delta G_w^E$  increases with increasing chain length. Higher sodium molalities still result in increasing  $\Delta G_w^E$  for ethanoate and propanoate systems, the values of which gradually become positive. Butanoate and especially penta-

noate and hexanoate form aggregates above a definite molality.<sup>7</sup> The high positive values of  $\Delta G_w^E$  for the aggregating alkanooates in Figs. 3c and d reflect, among other effects, the breaking up of aggregates. The same conclusion was drawn by Friman and Stenius<sup>25</sup> from  $\Delta G_w$  in sodium chloride and sodium pentanoate mixtures.

A clearer picture of the above discussed aggregation phenomena is given in Fig. 4, where the partial molar excess free energies,  $G_{m,j}^{*,E}$ , of the sodium and alkanooate ions are given. The curves for butanoate

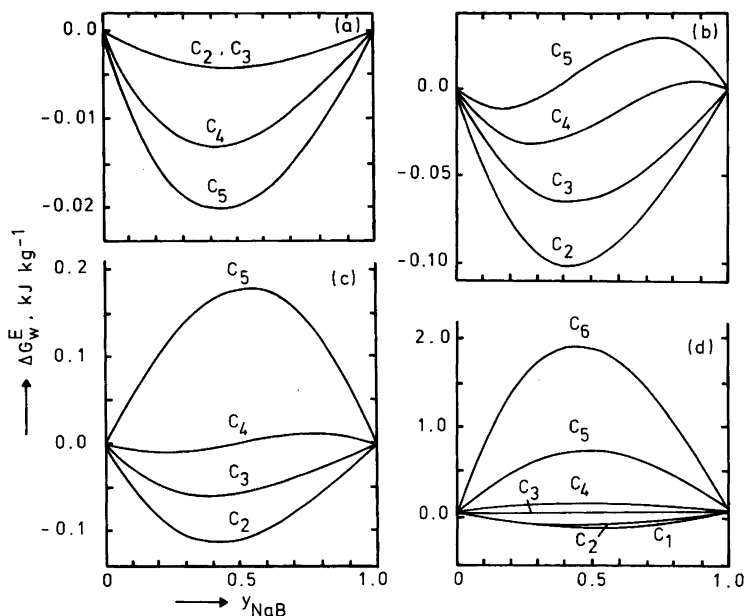


Fig. 3. Excess free energy of mixing ( $\Delta G_w^E$ ) aqueous sodium chloride and sodium methanoate ( $C_1$ ),  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$  or sodium hexanoate ( $C_6$ ) solutions at four constant sodium molalities (a) 0.5, (b) 1.5, (c) 2.0 and (d) 3.0 mol  $\text{kg}^{-1}$  plotted against  $y_{\text{NaB}}$  at 298.2 K.

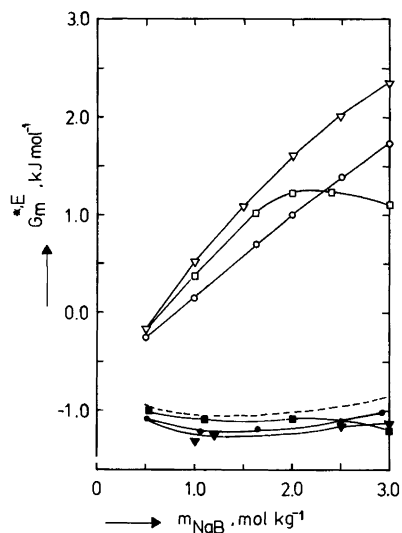


Fig. 4. Partial molar excess free energy ( $G_m^{*,E}$ ) of alkanate and sodium ions in pure aqueous solutions plotted against molality at 298.2 K. The symbols for the alkanate anions are:  $C_3$  ( $\circ$ );  $C_4$  ( $\nabla$ ) and  $C_5$  ( $\square$ ). Corresponding filled symbols are used for the sodium ions. The dashed line represents NaCl

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and pentanoate ions deviate from linearity at about 1.5 mol  $\text{kg}^{-1}$ . This agrees well with the observed effects in  $\Delta G_w^E$  in Fig. 3. The data in Fig. 4 further show that  $G_{\text{m,Na}^+}^{*,E}$  is almost constant in the interval from 0.5 to 3.0 mol  $\text{kg}^{-1}$ , when no aggregation occurs. The major contribution to the change in the partial molar free energy of NaB is thus derived from the change in free energy of the alkanate anion.

2. *Enthalpy.* The excess enthalpy,  $\Delta H_w^E$ , of mixing sodium chloride and sodium alkanate solutions is always negative at the investigated molalities (Fig. 1). The magnitudes of  $\Delta H_w^E$  agree well with corresponding values in literature.<sup>26</sup>

According to Young's sign rule<sup>11</sup> a negative enthalpy of mixing means that the participating anions have different effects on the structure of water.<sup>12</sup> Previous investigations have shown that  $\text{Cl}^-$  is a structure breaker,<sup>27</sup> propanoate a structure maker<sup>28</sup> and pentanoate a hydrophobic structure maker.<sup>29</sup> Thus our results in Fig. 1 are in accordance with Young's rule. It can also be noted that our  $\Delta G_w^E$  in Fig. 2 obeys this rule for non-associating systems. Because the classification structure breaker/maker sometimes depends on the physical

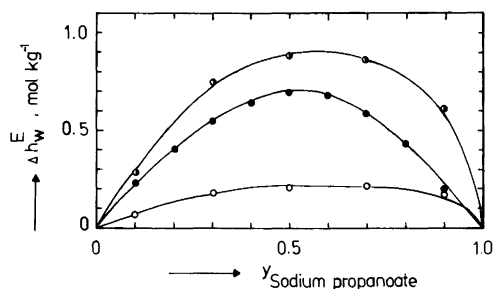


Fig. 5. Excess hydration numbers of mixing ( $\Delta h_w^E$ ) aqueous sodium chloride and  $C_3$  solutions at sodium molalities 2.0 (○), 3.0 (●) and 3.5 mol  $\text{kg}^{-1}$  (●) plotted against  $y_{C_3}$  at 298.2 K.

property under examination it has, however, been criticized.<sup>20,30</sup>

The excess enthalpies of mixing obtain the largest negative values for pentanoate systems at all investigated constant sodium molalities. Further  $\Delta H_w^E$  decreases with increased  $m_{Na+}$  for both alkanates. At  $m_{Na+}$  equal to 2.0 and 3.0 mol  $\text{kg}^{-1}$  the disaggregation certainly contributes to  $\Delta H_w^E$  in the pentanoate system. Fig. 2 shows, however, that the measured molar excess enthalpies,  $H_m^{*,E}$  for the pure sodium alkanate solutions have almost a linear dependence of the molality. Only a slight deviation due to aggregation can be observed for sodium pentanoate. One can therefore assume that the aggregation has also a negligible effect upon the investigated  $\Delta H_w^E$  in Fig. 1.

The interactions between the species in an electrolyte solution are complex. At molalities  $\geq 0.5$  mol  $\text{kg}^{-1}$  thermodynamic quantities reflect

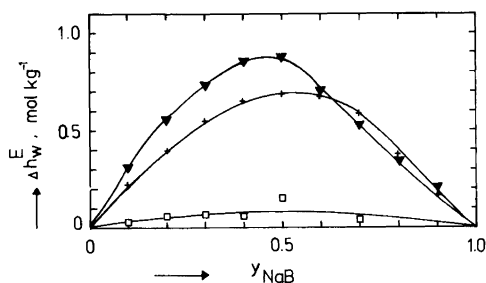


Fig. 6. Excess hydration numbers of mixing ( $\Delta h_w^E$ ) aqueous sodium chloride and  $C_2$  (□),  $C_3$  (+) or  $C_4$  (▽) at  $m_{Na+} = 3.0$  mol  $\text{kg}^{-1}$  plotted against  $y_{NaB}$  at 298.2 K.

quite a number of effects, among them long-range Coulombic forces, short-range forces of van der Waals' type, ion-water interactions, excluded volume effects, water structure effects and, due to the hydration of ions, a reduction in the number of water molecules available to the ions.<sup>31</sup> The interactions between ions and water can be described by, among others, the following parameters: Free energy of hydration, entropy of hydration, heat of hydration, radii and volumes of hydrated ions and hydration numbers.<sup>31</sup> In order to specifically elucidate the changes in these interactions we used eqn. (9) to calculate the excess hydration numbers of mixing,  $\Delta h_w^E$ . In a previous investigation<sup>6</sup> we have determined the hydration numbers of the alkanate ions in pure solutions,  $h_B^*$  (Table 2) and in sodium chloride solutions,  $h_B^-$ . The quantity  $\Delta h_w^E$  expresses the difference in amount of bound water per mass unit of water between the mixture and the pure solutions. Fig. 5 shows that  $\Delta h_w^E$  is positive and increases with the total sodium molality for the sodium chloride–sodium propanoate–water system. A lengthening of the hydrocarbon chain results in an increase in  $\Delta h_w^E$  as shown in Fig. 6 at a constant  $m_{Na+}$ .

We want to point out that  $\Delta H_w^E$  (Fig. 1) shows a similar trend as  $\Delta h_w^E$  in Figs. 5 and 6, *i.e.*  $\Delta H_w^E$  is always negative and decreases with increased  $m_{Na+}$  and chain length. A possible interpretation is that an increase of bound water gives an enthalpy decrease. This is in accordance with the observation that the transfer of a water molecule from the bulk to the hydrated region is an exothermic process.<sup>32</sup> This observation can also be applied to pure solutions, *i.e.* the observed dehydration with molality (Table 2). However, as pointed out earlier, the enthalpy certainly reflects many other effects than hydration or dehydration.

## CONCLUDING REMARKS

The present investigation deals with the thermodynamic quantities, *i.e.*  $\Delta H_w^E$ ,  $\Delta G_w^E$  and  $H_{m,i}^{*,E}$ ,  $G_{m,j}^{*,E}$ , respectively, in aqueous sodium alkanate solutions with and without sodium chloride. The aggregation of the investigated higher alkanates somewhat complicates the interpretation of the results. The excess free energies of mixing are sensitive for disaggregation. This is manifested as a pronounced difference with increasing sodium molality between homologues forming aggregates and those behaving as normal electrolytes.

Table 2. Hydration numbers of alkanooate anions in sodium alkanooate–water systems as a function of molality at 298.2 K.

$m_{\text{Ci}}$ mol kg <sup>-1</sup>	Hydration number			
	Ethanoate	Propanoate	Butanoate	Pentanoate
0.25	4.9	7.0	8.5	7.6
0.50	4.8	7.0	8.5	7.5
1.00	4.9	6.7	7.7	7.2
1.50	4.7	6.2	6.8	6.5
2.00	4.0	5.2	5.9	5.3
2.50	3.7	4.6	5.4	3.9
3.00	3.3	4.2	5.0	2.2

The aggregation process seems to have a negligible influence on the studied excess enthalpies of dilution and mixing. Qualitatively the trend in  $\Delta H_{\text{w}}^{\text{E}}$  can be attributed to a molecular change in the hydration conditions of the alkanooate anion as presented. We have not undertaken quantitative estimations of the heat arising from changes in the hydration of the alkanooate anions, because the enthalpy contributions from different interactions are unknown.

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