Association Equilibria and Micelle Formation of Fatty Acid
Sodium Salts. V. Investigation of Branched Chain Salts by
Vapour Pressure Osmometry

RAUNO FRIMAN* and PER STENIUS

*Department of Physical Chemistry, Åbo Akademi, Porthansgatan 3—5, SF-20500 Åbo 50, Finland and
†The Swedish Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden

The association of sodium pentanoate, sodium 3-
methylbutyrate and sodium 2,2-dimethylpropionate
in aqueous solution was studied by vapour pressure
osmometry. The mean aggregation numbers cal-
culated from these data are in good agreement with
those calculated from previously reported deter-
minations of the stability constants of the com-
plexes. At low ionic strengths, the mean activity
coefficients of the salts follow Harned's rule. The
excess Gibbs' energies were calculated and clearly
indicate that the association decreases with increas-
ing branching of the hydrocarbon chain. Otherwise
the thermodynamic properties are not easily inter-
guished between the effects of association and the
effects of changes in the mean activity coefficients.

EXPERIMENTAL

1. Chemicals. The sodium salts of pentanoic acid,
3-methylbutyric acid and 2,2-dimethylpropionic
acid were prepared by neutralization of the acids
(Fluka Ag, puriss.) with NaOH (Merck Titrisol) at
the boiling point. The salts were dried and their
purity checked as described previously. The NaCl
and KCl (Merck zur Analyse) were dried for a week
at 200 °C. The doubly distilled and de-ionized water
has a spec. conductivity of 0.5 μS cm⁻¹.

2. Solutions. The solutions were prepared by
mixing sodium carboxylate and NaCl of equal
centrations in different volumetric proportions.
The molalities of the solutions were calculated from
known NaCl solution densities and pycnometri-
cally determined densities of the carboxylate solu-
tions. The contraction on mixing is of the order
0.1 %, which causes smaller changes in the concen-
trations than could be detected with the osmometer.
Hence, the contraction was neglected throughout
in the calculations.

3. Water activities. The activity of water was
measured using a Mechrolab Vapor Pressure
Osmometer Model 301. NaCl solutions of suitable
concentrations were used as reference solutions. The
procedure used is described in Ref. 2.

4. Conductivities. The conductivities were
measured with a Metrohm E 365 B conductoscope,
which was calibrated with 0.01 mol dm⁻³ KCl.
List of symbols

\[ A_1 = \text{integral in eqn. 5.} \]
\[ B = \text{carboxylate ion.} \]
\[ a_i = \text{activity of species } i. \]
\[ G^E = \text{excess Gibbs' energy.} \]
\[ m_i = \text{molality of species } i. \]
\[ m = \text{total molality.} \]
\[ \bar{q}_2 = \text{mean aggregation number of carboxylate ions.} \]
\[ R = \text{universal gas constant.} \]
\[ T = \text{temperature.} \]
\[ u_i = m_i/m \quad i = 1, 2. \]
\[ x_i = \frac{m_i}{m} \quad i = 1, 2. \]
\[ z_i = m_i/\phi_i \quad i = 1, 2. \]
\[ \beta_{pu} = \text{stability constant of complex } H_pB_u. \]
\[ \gamma_i = \text{mean activity coefficient of species } i. \]
\[ \phi_i = \text{osmotic coefficient of species } i. \]
\[ v_i = \text{number of ions formed by each NaCl (i = 1) or } \]
\[ \text{Na carboxylate (i = 2) molecule.} \]
\[ v = \text{mean amount of ions per unit amount of mixed electrolyte.} \]

Subscripts. 1 denotes NaCl, 2 Na carboxylate, w water and r reference solution.

Calculations

Calculation of mean activity coefficients and aggregation numbers. For the system under consideration, the Gibbs-Duhem equation takes the form

\[ -m_v \text{d}(\ln a_v) = m_1 \text{d}(\ln a_1) + m_2 \text{d}(\ln a_2) \]

(1)

(for notation see the list of symbols.) We assume that the molality of free Na\(^+\) ions is \( m_{Na} = m_1 + m_2 = m, \) i.e., that no sodium ions are bound to the carboxylate aggregates. This is probably a good approximation except in solutions containing aggregates of micellar size. Then

\[ \nu m = m_{Na} + m_{c1} + m_{aggr} \]
\[ = m(2 - x_2) + m_{aggr} \]

(2)

where \( \nu \) is the number of moles of ions formed by one mol of mixed electrolyte and \( m_{aggr} \) is the molality of the aggregates formed by the carboxylate ions, including monomers. Since two ions are formed by each NaCl molecule and \( v_2 \) ions by each NaB molecule,

\[ a_1 = \gamma_1^2 m^2 x_1; \quad a_2 = [x_2(v_2 - 1)]^{v_2 - 1} \gamma_2^2 m^2. \]

Substituting in (1), we obtain for constant \( m \)

\[ -m_v \text{d}(\ln a_v) = 2x_1 m \text{d}(\ln \gamma_1) + \]
\[ + x_2 m \text{d}[\ln (v_2 - 1)] - x_1 \text{d}x_2 + \]
\[ + m(v_2 - 2) \text{d}x_2 \]

(4)

In a previous paper\(^2\) we have shown, that the following equation for \( \gamma_1 \) may be derived on the basis of (4) and the corresponding equation for a pure NaCl solution with the same vapour pressure (reference solution, quantities pertaining to this are denoted by subscript r)

\[ \ln \gamma_1 = \ln (\gamma_1^r u_1) - \frac{1}{m_{1r}} \int_0^{x_2} \left( \frac{\partial u_1}{\partial x_2} \right)_{m_{1r}} x_2 (u_1 + 1) \text{d}x_2 \]

\[ = \ln (\gamma_1^r u_1) - A_1 \]

(5)

The equation was derived on the basis of a method suggested by McKay and Perring.\(^8\) The equation is valid provided two ions are formed by every NaCl molecule dissolved. If this is the case for the sodium carboxylate, an exactly analogous equation is valid for its mean activity coefficient (\( \gamma_2 \)). However, we have good reason to believe that the carboxylate ions associate. It is experimentally found that for a given \( m, A_1 \) in eqn. (5) is close to zero\(^2\) for systems in which there is no association (e.g. sodium acetate/NaCl or sodium propionate/NaCl). We may then assume that values of \( A_1 \) that deviate substantially from 0 indicate association. It can be shown that \( v \) is given by

\[ v = 2e^{A_1} \]

(6)

if only the carboxylate ions associate.

The mean aggregation number of the carboxylate ions, including the monomers may be calculated from

\[ \bar{q}_2 = \frac{m_2}{m_{aggr}} = \frac{x_2}{v + x_2 - 2} \]

(7)

When \( v \) is known, the mean activity coefficient of NaB with the association taken into account may be calculated from

\[ \ln \gamma_2 = \ln m + \frac{1}{v_2} \left( \ln (v_2 - 1)^{y_2 - 1} m_{2r}^2 \gamma_2^{y_2} \right) \]
\[ - \int_0^{x_2} \frac{1}{m_{2r}} \left( \frac{\partial u_2}{\partial x_1} \right)_{m_{2r}} x_1 (u_2 + 1) \text{d}x_2 \]

(8)

\[ v_2, \text{ the number of ions formed by NaB in a solution without NaCl, is calculated by extrapolation of the } \]
\[ v \text{ to } x_1 = 0. \quad \gamma_1, \gamma_2, v \text{ and } \bar{q}_2 \text{ were calculated from vapour pressure data for seven different total molalities and seven equidistant } x_2 \text{ values using a numerical procedure programmed in Algol for a Univac 1108 computer.} \]

Calculation of excess Gibbs' energies. In accordance with Harned and Robinson,\(^8\) the excess Gibbs' energies are calculated from

energy of the mixed solution is defined as the Gibbs' energy possessed by the solution over and above that possessed by the single electrolytes, i.e., as the Gibbs' energy for the process

\[
\begin{align*}
&x_1 \text{ kg H}_2\text{O} \\
&x_1 \text{ I mol NaCl} + x_2 \text{ kg H}_2\text{O} \\
&x_2 \text{ I mol NaB} \\
\rightarrow \\
&1 \text{ kg H}_2\text{O} \\
&1 \text{ mol (NaCl + NaB)}
\end{align*}
\]

In terms of the activities of the components, this excess Gibbs' energy is given by

\[
\frac{G^E}{RT} = m_x \ln \frac{a_w} {a_{w1}} + x_2 m \ln a_2 + x_1 m \ln a_1 - \\
- x_2 m \ln \left(1 - x_2 m \right) a_{w2} - x_1 m \ln \left(1 - x_1 m \right) a_{w1} - \\
- x_2 m \ln a_2
\]

(9)

where \(a_w\) is the water activity in the solution of two electrolytes and \(a_{w1}\) and \(a_{w2}\) the water activities in the solutions of NaCl and NaB, respectively, at the molality \(m\), \(a_1\) and \(a_2\) are the activities of NaCl in the mixed and pure NaCl solutions, respectively, and \(a_1, a_2\) are the corresponding quantities for NaB.

To calculate \(G^E\), we integrate eqn. (4) (i) from a solution at molality \(m\) containing only NaCl (mean activity coefficient \(\gamma_1^m\)) to one in which the molality of NaCl is \(x_1 m\), (ii) from a solution at molality \(m\) containing only NaB (mean activity coefficient \(\gamma_2^m\)) to \(x_2 m = (1 - x_1)m\). The resulting integrals are multiplied by \(x_1\) and \(x_2\), respectively, and added; we then obtain the sum \(x_1 \ln a_w + x_2 \ln a_w \equiv \ln a_w\) which is inserted into (9). By rearrangement of terms, eqn. (9) then becomes

\[
\frac{G^E}{RT} = -x_2 m \int_0^{\ln \gamma_1} \left[ x_1 m \left( \ln \ln \gamma_1 \right) + x_1 m \left[ x_2 \left( \ln \left(1 - x_2 m \right) \right) \right] \right] dx_2
\]

\[
- x_2 m \int_0^{\ln \gamma_2} \left[ x_1 m \left( \ln \ln \gamma_1 \right) + x_1 m \left[ x_2 \left( \ln \left(1 - x_2 m \right) \right) \right] \right] dx_2
\]

\[
- x_1 m \int_0^{\ln \gamma_1} \left[ x_2 m \left( \ln \ln \gamma_1 \right) + x_2 m \left[ x_1 m \left( \ln \left(1 - x_1 m \right) \right) \right] \right] dx_2
\]

\[
+ x_1 m \ln \left( \frac{\gamma_2}{\gamma_1} \right)^2
\]

(10)

where \(\gamma_1^m\) is the value for \(\gamma_1\) at molality \(m\) when extrapolated to \(x_1 = 0\), \(\gamma_2^m\) the similarly extrapolated value for \(\gamma_2\) at \(x_2 = 0\) and \(\gamma_2^m\) the value for \(\gamma_2 \) extrapolated to \(x_2 = 0\). By partial integration, this equation becomes

\[
\frac{G^E}{RT} = \int_0^{\ln \gamma_1} \frac{(v_2 - 1)^{y_2 - 1} \gamma_2^{y_2} m^{y_2}}{(v_2 - 1)^{y_2 - 1} \gamma_2^{y_2} \gamma_1^{y_1} m^{y_1}} dx_2
\]

(11)

This equation was used to calculate \(G^E\) from the known values of \(\gamma_1, \gamma_2, v_2\) as functions of \(x_2\) at constant \(m\).

\textit{Calculation of \(\bar{q}_{2}\) from concentrations of complexes.}

The stability constants of the complexes formed by the three salts investigated here have been determined potentiometrically at ionic strength 3 mol dm\(^{-3}\) and are given in Table 1.\(^4\) Knowing these, we

\textbf{Table 1.} Complex formation by different isomers of sodium pentanoate. The stability constants are defined by eqn. (12). \(\beta_{r,s} = \) stability constant of complex \(\text{H}_r\text{B}_s\) (from Refs. 4 and 11).

<table>
<thead>
<tr>
<th></th>
<th>\text{Sodium pentanoate}</th>
<th>\text{Sodium 3-methylbutyrate}</th>
<th>\text{Sodium 2,2-dimethylpropionate}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log \beta_{1,1})</td>
<td>9.20 ± 0.2</td>
<td>9.23 ± 0.02</td>
<td>8.859 ± 0.002</td>
</tr>
<tr>
<td>(\log \beta_{2,5})</td>
<td>17.40 ± 0.06</td>
<td>19.17 ± 0.05</td>
<td>9.85 ± 0.07</td>
</tr>
<tr>
<td>(\log \beta_{3,5})</td>
<td>25.26 ± 0.05</td>
<td>6.35</td>
<td>17.48 ± 0.07</td>
</tr>
<tr>
<td>(\log \beta_{1,11})</td>
<td>12.06 ± 0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. The mean activity coefficient of the sodium chloride and sodium carboxylate in mixtures of sodium chloride and sodium pentanoate ($\triangle/\bigtriangleup$), sodium 3-methylbutyrate ($\square/\blacksquare$) and sodium 2,2-dimethylpropionate ($\bigcirc/\bullet$) at constant total molality 0.5 mol kg$^{-1}$ and 25 °C.

Fig. 2. As Fig. 1, total molality 1.0 mol kg$^{-1}$.

Fig. 3. As Fig. 1, total molality 2.0 mol kg$^{-1}$.

Fig. 4. As Fig. 1, total molality 3.0 mol kg$^{-1}$.

may calculate $\bar{q}_2$ at any total concentration of carboxylate. Since the electrode system used in the potentiometric titrations was calibrated against an excess of base, the stability constants obtained are the base constants, defined for the complex $H_pB_q$ by

$$\beta_{pq} = (OH)^p(B)^{-q}(H_pB_q)$$  \hspace{1cm} (12)

(Parentheses denote concentrations (mol dm$^{-3}$);

charge signs are omitted.) For any (OH) we may calculate (B) by numerically solving the mass balance equation

$$c_B = (B) + \sum_{p,q} q(H_pB_q) = (B) + \sum_{p,q} q(OH)^{-p}(B)^{-q} \beta_{pq}$$ \hspace{1cm} (13)

for (B). We then use (B) to calculate $(H_pB_q)$ from (12) and $\bar{q}_2$ from

$$\bar{q}_2 = \frac{\sum_{p,q} q(H_pB_q)}{\sum_{p,q} (H_pB_q)}$$ \hspace{1cm} (14)

RESULTS

In Figs. 1 – 4 we give the logarithms of the mean activity coefficients for NaCl and NaB at four different total molalities, for each of the salts investigated, and with the fraction of NaB as the abscissa.

Values for $\bar{q}_2$ calculated from eqn. (7) using eqn. (6) to calculate the $v$ are given for the same total molalities in Figs. 5 – 8. Finally, we give the excess Gibbs' energies for the molalities 1 mol kg$^{-1}$ and 3 mol kg$^{-1}$ in Figs. 9 and 10.

A comparison between $\bar{q}_2$ values calculated from eqn. (7) and from eqn. (14) at $\text{pOH} = 7.5$ is given in Table 2.

Table 2. A comparison of $\bar{q}_2$ values calculated from eqn. (7) with those calculated from eqn. (14). The former are given for constant total molality 3.5 mol kg$^{-1}$, the latter for ionic strength 3 mol dm$^{-3}$ and $\text{pOH} = 7.5$.

<table>
<thead>
<tr>
<th>$m_2$ (mol kg$^{-1}$)</th>
<th>Sodium pentanoate $\bar{q}_2$ (pot)</th>
<th>Sodium pentanoate $\bar{q}_2$ (VPO)</th>
<th>3-Methylbutyrate $\bar{q}_2$ (pot)</th>
<th>3-Methylbutyrate $\bar{q}_2$ (VPO)</th>
<th>2,2-Dimethylpropionate $\bar{q}_2$ (pot)</th>
<th>2,2-Dimethylpropionate $\bar{q}_2$ (VPO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.00</td>
<td>1.09</td>
<td>1.01</td>
<td>1.05</td>
<td>1.00</td>
<td>1.07</td>
</tr>
<tr>
<td>1.0</td>
<td>1.02</td>
<td>1.15</td>
<td>1.05</td>
<td>1.14</td>
<td>1.02</td>
<td>1.18</td>
</tr>
<tr>
<td>1.5</td>
<td>1.08</td>
<td>1.35</td>
<td>1.13</td>
<td>1.24</td>
<td>1.05</td>
<td>1.29</td>
</tr>
<tr>
<td>2.0</td>
<td>1.17</td>
<td>1.50</td>
<td>1.22</td>
<td>1.36</td>
<td>1.10</td>
<td>1.41</td>
</tr>
<tr>
<td>2.5</td>
<td>1.29</td>
<td>1.65</td>
<td>1.31</td>
<td>1.50</td>
<td>1.16</td>
<td>1.50</td>
</tr>
<tr>
<td>3.0</td>
<td>1.42</td>
<td>1.74</td>
<td>1.41</td>
<td>1.63</td>
<td>1.22</td>
<td>1.52</td>
</tr>
<tr>
<td>3.5</td>
<td>1.55</td>
<td>1.78</td>
<td>1.52</td>
<td>1.73</td>
<td>1.28</td>
<td>1.51</td>
</tr>
</tbody>
</table>

DISCUSSION

A comparison of the aggregation numbers calculated from the potentiometric and osmometric measurements, respectively, (see Table 2) shows that these agree very satisfactorily, in particular considering the lengthy calculations needed to obtain the osmometric aggregation numbers from the primary experimental data. The osmometric aggregation numbers are consistently somewhat higher than the potentiometric, but both vary with concentration in the same way. Moreover, both investigations show an increasing tendency to associate in the order 2,2-dimethylpropionate < 3-methylbutyrate < pentanoate. It is also obvious from both investigations that the association is so weak that there are no dramatic changes in the mean aggregation numbers. Hence, we conclude that the two independent methods both indicate association of the salts to polynuclear aggregates. The osmometric results, of course, do not allow us to draw any conclusions concerning the size distribution of the aggregates. The potentiometric measurements show a formation of aggregates with 4 — 5 anions as well as small micelles in 3-methylbutyrate and pentanoate solutions.

As is clearly seen from Figs. 1 — 4, the changes in the mean activity coefficients at lower ionic strengths follow the wellknown Harned’s rule:

\[
\log \gamma_i = \log \gamma_i^m + \alpha m_i
\]

where \( \gamma_i^m \) denotes the trace mean activity coefficient, i.e., the value of the mean activity coefficient of the salt \( i \) at infinite dilution at this ionic strength. Figs. 1 — 4 also show that the slope \( \alpha \) of the log \( \gamma \) vs. \( x_2 \) for 39.5

Table 2. Since we know the stability constants at ionic strength 3 mol dm\(^{-3}\) only, we have used the \( \nu \) values at the highest total molality investigated by vapour pressure measurements to calculate the \( \bar{q}_2 \) for the comparison.

Fig. 9. The excess Gibbs’ energy of mixing sodium pentanoate (\( \triangle \)), sodium 3-methylbutyrate (\( \square \)) and sodium 2,2-dimethylpropionate (\( \bigcirc \)) with NaCl at constant total molality 1.0 mol kg\(^{-1}\).

Fig. 10. As Fig. 9, total molality 3.0 mol kg\(^{-1}\).

Fig. 11. The limiting slopes of the log \( \gamma \) vs. \( x_2 \) plots extrapolated to \( x_2 = 0 \) for the sodium pentanoate (\( \triangle \)), sodium 3-methylbutyrate (\( \square \)) and sodium 2,2-dimethylpropionate (\( \bigcirc \)) as a function of the total molality in mixtures with NaCl.
Table 3. The trace mean activity coefficients for sodium chloride and sodium carboxylates at ionic strength 2.0 mol kg⁻¹, the molar conductivity at infinite dilution and the Stokes’ radii for sodium pentanoate, sodium 3-methylbutyrate and sodium 2,2-dimethylpropionate at 25 °C.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda^\infty ) (cm² Ω⁻¹ mol⁻¹)</th>
<th>( r_{\text{Stokes}} ) (nm)</th>
<th>( \gamma_1^\infty )</th>
<th>( \gamma_2^\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium pentanoate</td>
<td>78.7</td>
<td>0.116</td>
<td>0.815</td>
<td>1.060</td>
</tr>
<tr>
<td>Sodium 3-methylbutyrate</td>
<td>87.3</td>
<td>0.105</td>
<td>0.859</td>
<td>1.070</td>
</tr>
<tr>
<td>Sodium 2,2-dimethylpropionate</td>
<td>83.5</td>
<td>0.110</td>
<td>0.830</td>
<td>1.004</td>
</tr>
</tbody>
</table>

plot increases with increasing ionic strength. This is more clearly seen in Fig. 11 where we have plotted the slopes as functions of the total molality. There is no obvious explanation to this systematic variation. At very high total molalities the 3-methylbutyrate and the pentanoate show deviations from the linear dependence. This may be due to the formation of micelles, i.e., the assumption that no sodium ions are bound in aggregates is probably no longer valid and, consequently, the procedure of calculating the mean activity coefficients with the association taken into account is no longer valid.

A comparison of the \( \gamma_1 \) values when the chloride ion is replaced with the carboxylate ion in the three systems shows that they are roughly equal for pentanoate and 3-methylbutyrate at low ionic strengths, while they are higher for the latter salt at higher ionic strength. The mean activity coefficients are lowest for the 2,2-dimethylpropionate throughout. This probably reflects differences in the way straight and branched hydrocarbon chains affect the water structure.

The excess Gibbs’ energies of mixing chloride with carboxylate is shown in Fig. 9 for ionic strength 1 mol kg⁻¹. These curves clearly reflect the differences in the interaction with the surrounding water between linear and branched hydrocarbon chains with the same number of carbon atoms. The excess energy is positive throughout for the almost spherical 2,2-dimethylpropionate, and for pentanoate passes from negative to positive for the 3-methylbutyrate. At ionic strength 3 mol kg⁻¹ the 2,2-dimethylpropionate and pentanoate excess energies behave similarly as at 1.0 mol kg⁻¹, but are roughly ten times higher. The excess energy of the 3-methylbutyrate behaves quite differently: this is now strongly positive. This certainly partially is an effect of the dissociation of micelles and pre-micellar aggregates when the solutions are mixed; this may also be the cause of the inflection points in the curve for ionic strength 1 mol kg⁻¹. The excess energies thus clearly show the increasing tendency to associate with decreasing branching of the hydrocarbon chains. All the same, they also serve to stress the complicated nature of the hydrophobic interactions in water. Excess energies are often interpreted in terms of changes in solvent-solute interactions rather than association. We have shown, however, that by assuming that all effects are due to association of the carboxylate ions we arrive at aggregation numbers that are in good agreement with independent potentiometric results.

Backlund¹² has correlated the trace ionic activity coefficients for straight-chain carboxylates with the hydrocarbon chain length, calculated according to Tanford.¹³ From the linear relationship between these two quantities, he concluded that the energy of interaction between the ions and the surrounding solvent is proportional to the size of the hydrocarbon moiety of the ions. In order to investigate whether this correlation could be extended to branched hydrocarbon chains we have calculated the Stokes’ radii of the three carboxylate ions discussed here from measurements of their molar conductivities at infinite dilution.¹⁰ The results are given in Table 3, together with \( \gamma_1^\infty \) and \( \gamma_2^\infty \). \( \gamma_1^\infty \) is inversely proportional to the radius, but there is no correlation between the carboxylate mean activity coefficient, \( \gamma_2^\infty \), and the radius of the ion.

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