

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

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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 calculated from these data are in good agreement with those calculated from previously reported determinations of the stability constants of the complexes. 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 increasing branching of the hydrocarbon chain. Otherwise the thermodynamic properties are not easily interpreted.

The aggregation processes in solutions of short-chain carboxylates have been studied extensively in order to elucidate the steps in the aggregation leading to micelle formation.^{1–6} It has been clearly established that the association to micelles is preceded by the formation of small amounts of aggregates with 3–5 monomers at concentrations below and around the c.m.c.⁵ The potentiometric method used to determine the stability constants of the complexes, however, requires the use of constant ionic strength and high concentrations of the associating species. The ionic medium method as a device to eliminate the influence of variations in the activity coefficients in this case is open to some criticism.⁷ Hence, it becomes very important to confirm the potentiometric results by other methods. In this paper we report vapour pressure osmometric studies of systems that were previously investigated by potentiometry.^{1,3} It is possible to clearly distin-

guish 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.³ 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 $\mu\text{S cm}^{-1}$.

2. *Solutions.* The solutions were prepared by mixing sodium carboxylate and NaCl of equal concentrations in different volumetric proportions. The molalities of the solutions were calculated from known NaCl solution densities¹⁴ and pycnometrically determined densities of the carboxylate solutions. The contraction on mixing is of the order 0.1 %, which causes smaller changes in the concentrations 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 = integral in eqn. 5.
 B = carboxylate ion.
 a_i = activity of species i .
 G^E = excess Gibbs' energy.
 m_i = molality of species i .
 m = total molality.
 \bar{q}_2 = mean aggregation number of carboxylate ions.
 R = universal gas constant.
 T = temperature.
 $u_i = m_{ir}/m$ $i = 1, 2$.
 $x_i = m_i/m$ $i = 1, 2$.
 $z_i = m_{ir} \phi_{ir}$ $i = 1, 2$.
 β_{pq} = stability constant of complex $H_p B_q$.
 γ_i = mean activity coefficient of species i .
 ϕ_i = osmotic coefficient of species i .
 v_i = number of ions formed by each NaCl ($i = 1$) or Na carboxylate ($i = 2$) molecule.
 v = 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

$$-m_w d(\ln a_w) = m_1 d(\ln a_1) + m_2 d(\ln a_2) \quad (1)$$

(for notation see the list of symbols.) We assume that the molality of free Na^+ ions is $m_{\text{Na}} = m_1 + m_2 = m$, 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

$$vm = m_{\text{Na}} + m_{\text{C}_1} + m_{\text{aggr}} = m(2 - x_2) + m_{\text{aggr}} \quad (2)$$

where v 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,

$$a_1 = \gamma_1^2 m^2 x_1; a_2 = [x_2(v_2 - 1)]^{v_2 - 1} (\gamma_2 m)^{v_2} \quad (3)$$

Substituting in (1), we obtain for constant m

$$-m_w d(\ln a_w) = 2x_1 m d(\ln \gamma_1) + x_2 m d[\ln(v_2 - 1)^{v_2 - 1} \gamma_2^{v_2}] + m(v_2 - 2) dx_2 \quad (4)$$

In a previous paper² we have shown, that the following equation for γ_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 it are denoted by subscript r)

$$\ln \gamma_1 = \ln(\gamma_{1r} u_1) - \int_0^{x_2} \frac{1}{m_{1r}} \left[x_2 \left(\frac{\partial u_1}{\partial x_2} \right)_{m_{1r}} - u_1 + 1 \right] dz_1 \quad (5)$$

$$= \ln(\gamma_{1r} u_1) - A_1$$

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 (γ_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 zero² 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 by²

$$v = 2e^{A_1} \quad (6)$$

if only the carboxylate ions associate.

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

$$\bar{q}_2 = \frac{m_2}{m_{\text{aggr}}} = \frac{x_2}{v + x_2 - 2} \quad (7)$$

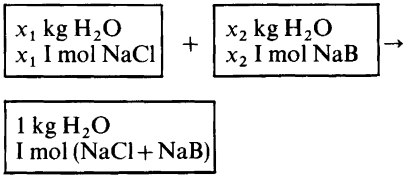
When v is known, the mean activity coefficient of NaB with the association taken into account may be calculated from

$$\ln \gamma_2 = \ln m + \frac{1}{v_2} \left\{ \ln \frac{(v_{2r} - 1)^{v_{2r} - 1} (m_{2r} \gamma_{2r})^{v_{2r}}}{(v_2 - 1)^{v_2 - 1}} - \int_0^{x_2} \frac{1}{m_{2r}} \left[\left(\frac{\partial u_2}{\partial x_1} \right)_{m_{1r}} x_1 - u_2 + 1 \right] dz_2 \right\} \quad (8)$$

v_{2r} , the number of ions formed by NaB in a solution without NaCl, is calculated by extrapolation of the v to $x_1 = 0$. γ_1 , γ_2 , v and \bar{q}_2 were calculated from vapour pressure data for seven different total molalities and seven equidistant x_2 values using a numerical procedure programmed in Algol for a Univac 1108 computer.

Calculation of excess Gibbs' energies. In accordance with Harned and Robinson,⁹ the excess Gibbs'

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



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

$$\begin{aligned} G^E/RT = & m_w \ln a_w + x_2 m \ln a_2 + x_1 m \ln a_1 - \\ & - x_2 m_w \ln a_{w(2)} - x_2 m \ln a_2^0 - x_1 m_w \ln a_{w(1)} - \\ & - x_1 m \ln a_1^0 \end{aligned} \quad (9)$$

where a_w is the water activity in the solution of two electrolytes and $a_{w(1)}$ and $a_{w(2)}$ the water activities in the solutions of NaCl and NaB, respectively, at the molality m . a_1 and a_1^0 are the activities of NaCl in the mixed and pure NaCl solutions, respectively, and a_2 , a_2^0 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 γ_1^0) 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 γ_2^0) to $x_2 m \equiv (1-x_1)m$. 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

$$\begin{aligned} \frac{G^E}{RT} = & -2x_1 m \int_{\ln \gamma_1^0}^{\ln \gamma_1} x_1 d(\ln \gamma_1) \\ & - x_1 m \int_{\ln[(v_2^0-1)^{v_2^0-1} \gamma_2^{v_2^0}]}^{\ln[(v_2-1)^{v_2-1} \gamma_2^{v_2}]} x_2 d[\ln(v_2-1)^{v_2-1} \gamma_2^{v_2}] \\ & - 2x_2 m \int_{\ln \gamma_2^0}^{\ln \gamma_2} x_2 d(\ln \gamma_2) \\ & - x_2 m \int_{\ln[(v_2^0-1)^{v_2^0-1} \gamma_2^{v_2^0}]}^{\ln[(v_2-1)^{v_2-1} \gamma_2^{v_2}]} x_2 d[\ln(v_2-1)^{v_2-1} \gamma_2^{v_2}] \\ & - x_1 m \int_0^{x_2} (v_2-2) dx_2 - x_2 m \int_0^{x_2} (v_2-2) dx_2 \\ & + x_1 m \ln \frac{\gamma_1^2}{\gamma_1^0}
 \end{aligned}$$

$$+ x_2 m \ln \frac{(v_2-1)^{v_2-1} \gamma_2^{v_2} m^{v_2}}{(v_2^0-1)^{v_2^0-1} \gamma_2^{v_2^0} m^{v_2^0}} \quad (10)$$

where γ_1^* is the value for γ_1 at molality m when extrapolated to $x_1=0$, γ_2^* the similarly extrapolated value for γ_2 at $x_2=0$ and v_2^* the value for v_2 extrapolated to $x_2=0$. By partial integration, this equation becomes

$$\begin{aligned} \frac{G^E}{RT} = & m \int_0^{x_2} \ln \frac{(v_2-1)^{v_2-1} \gamma_2^{v_2}}{\gamma_1^2} dx_2 \\ & - x_2 m \int_0^1 \ln \frac{(v_2-1)^{v_2-1} \gamma_2^{v_2}}{\gamma_1^2} dx_2 \\ & - m \int_0^{x_2} (v_2-2) dx_2 + x_2 m \int_0^1 (v_2-2) dx_2 + x_2 m \ln \frac{m^{v_2}}{m^{v_2^0}} \end{aligned} \quad (11)$$

This equation was used to calculate G^E from the known values of γ_1 , γ_2 , v_2 as functions of x_2 at constant m .

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

Table 1. Complex formation by different isomers of sodium pentanoate. The stability constants are defined by eqn. (12). $\beta_{p,q}$ = stability constant of complex $H_p B_q$ (from Refs. 4 and 11).

Sodium pentanoate	
$\text{CH}_3(\text{CH}_2)_3\text{COO}^- \text{Na}^+$	
-log $\beta_{1,1}$	9.20 ± 0.2
-log $\beta_{2,5}$	17.40 ± 0.06
-log $\beta_{3,5}$	25.26 ± 0.05
-log $\beta_{1,11}$	12.06 ± 0.20
Sodium 3-methylbutyrate	
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{COO}^- \text{Na}^+$	
-log $\beta_{1,1}$	9.23 ± 0.02
-log $\beta_{1,4}$	9.17 ± 0.05
-log $\beta_{0,15}$	6.35
Sodium 2,2-dimethylpropionate	
$(\text{CH}_3)_3\text{C}-\text{COO}^- \text{Na}^+$	
-log $\beta_{1,1}$	8.859 ± 0.002
-log $\beta_{1,4}$	9.85 ± 0.07
-log $\beta_{2,4}$	17.48 ± 0.07

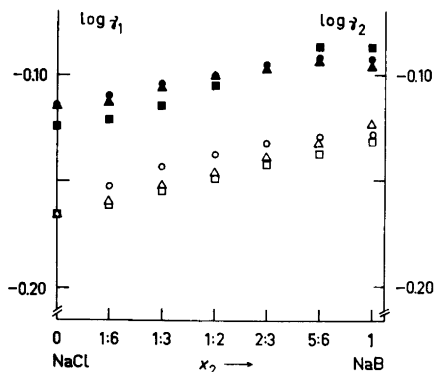


Fig. 1. The mean activity coefficient of the sodium chloride and sodium carboxylate in mixtures of sodium chloride and sodium pentanoate (Δ/\blacktriangle), sodium 3-methylbutyrate (\square/\blacksquare) and sodium 2,2-dimethylpropionate (\circ/\bullet) at constant total molality 0.5 mol kg^{-1} and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

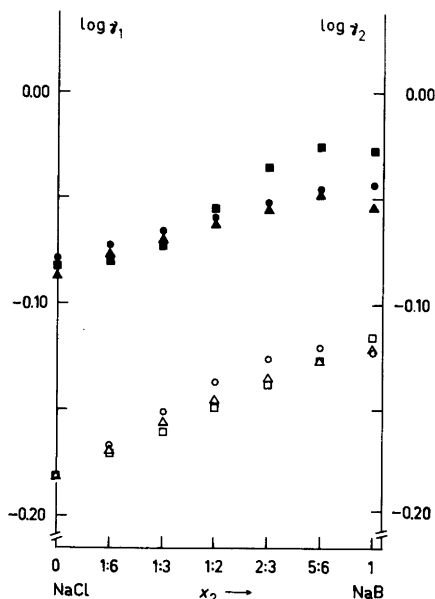


Fig. 2. As Fig. 1, total molality 1.0 mol kg^{-1} .

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

$$\beta_{pq} = (\text{OH})^p (\text{B})^{-q} (\text{H}_p\text{B}_q) \quad (12)$$

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

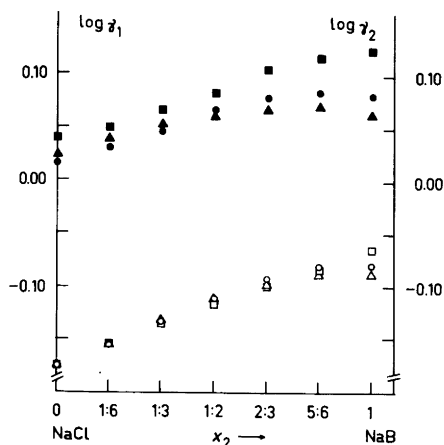


Fig. 3. As Fig. 1, total molality 2.0 mol kg^{-1} .

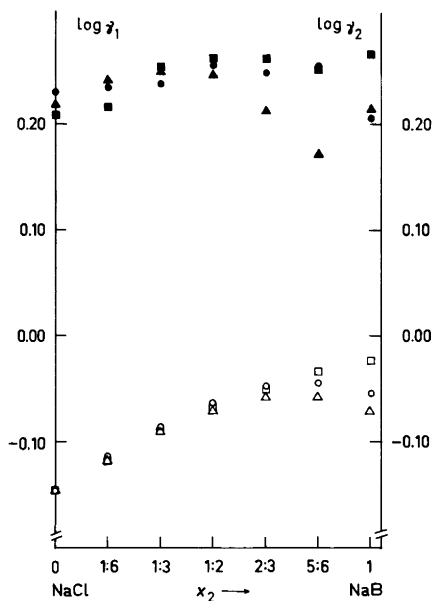


Fig. 4. As Fig. 1, total molality 3.0 mol kg^{-1} .

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

$$c_{\text{B}} = (\text{B}) + \sum_{p,q} q(\text{H}_p\text{B}_q) = (\text{B}) + \sum_{p,q} q(\text{OH})^{-p} (\text{B})^{-q} \beta_{pq} \quad (13)$$

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

$$\bar{q}_2 = \frac{\sum_{p,q} q(\text{H}_p\text{B}_q)}{\sum_{p,q} (\text{H}_p\text{B}_q)} \quad (14)$$

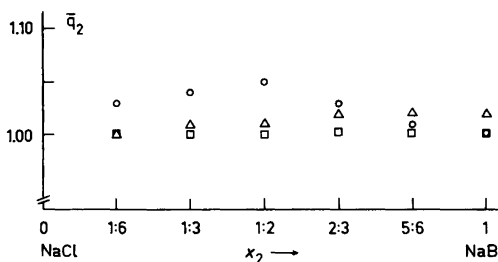


Fig. 5. The mean aggregation number of sodium pentanoate (Δ), sodium 3-methylbutyrate (\square) and sodium 2,2-dimethylprionate (\circ) in mixtures with NaCl at constant total molality, 0.5 mol kg^{-1} .

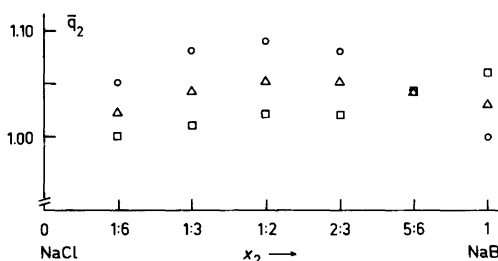


Fig. 6. As Fig. 5, total molality 1.0 mol kg^{-1} .

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 ν are given for the same total molalities in Figs. 5–8. Finally, we give the excess

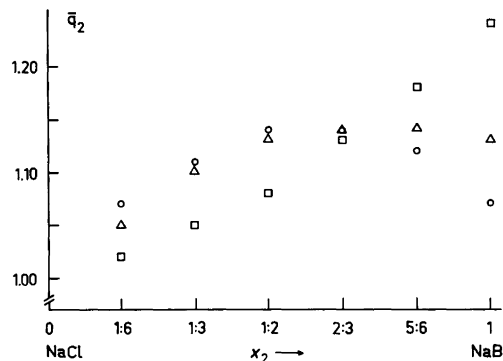


Fig. 7. As Fig. 5, total molality 2.0 mol kg^{-1} .

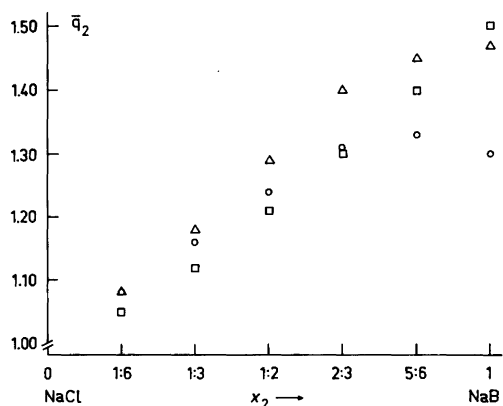


Fig. 8. As Fig. 5, total molality 3.0 mol kg^{-1} .

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. 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 $\text{pOH} = 7.5$.

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

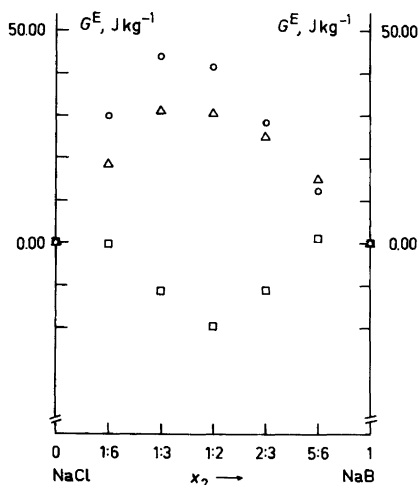


Fig. 9. The excess Gibbs' energy of mixing sodium pentanoate (Δ), sodium 3-methylbutyrate (\square) and sodium 2,2-dimethylpropionate (\circ) with NaCl at constant total molality 1.0 mol kg^{-1} .

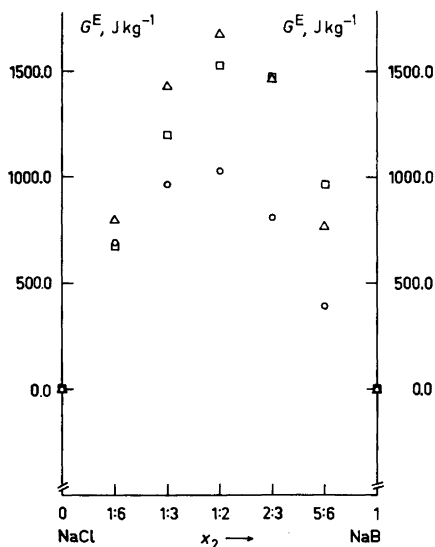


Fig. 10. As Fig. 9, total molality 3.0 mol kg^{-1} .

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

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.^{4,11}

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:

$$\log \gamma_i = \log \gamma_i^{\text{tr}} + \alpha m_i \quad (15)$$

where γ_i^{tr} 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 α of the $\log \gamma_1$ vs. x_2

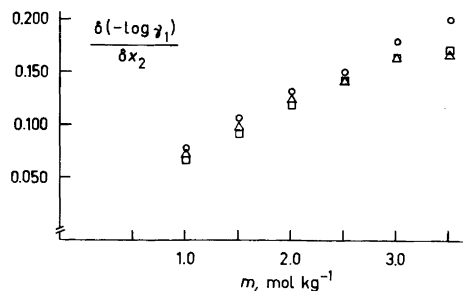


Fig. 11. The limiting slopes of the $\log \gamma_1$ vs. x_2 plots extrapolated to $x_2 = 0$ for the sodium pentanoate (Δ), sodium 3-methylbutyrate (\square) and sodium 2,2-dimethylpropionate (\circ) as a function of the total molality in mixtures with NaCl.

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 .

	λ^∞ ($\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$)	r_{Stokes} (nm)	γ_1^{tr}	γ_2^{tr}
Sodium pentanoate	78.7	0.116	0.815	1.060
Sodium 3-methylbutyrate	87.3	0.105	0.859	1.070
Sodium 2,2-dimethylpropionate	83.5	0.110	0.830	1.004

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 γ_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 γ_1^{tr} and γ_2^{tr} . γ_1^{tr} is inversely proportional to the radius, but there is no correlation between the carboxylate mean activity coefficient, γ_2^{tr} , and the radius of the ion.

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