

Association Equilibria and Micelle Formation of Fatty Acid Sodium Salts. II. An Investigation of Straight-chain Salts by Vapour Pressure Osmometry

PER STENIUS

Department of Physical Chemistry, Åbo Akademi, Porthansgatan 3-5, SF-20500 Åbo 50, Finland

The vapour pressures of mixed aqueous solutions of sodium chloride and sodium acetate, propionate, butyrate, and hexanoate, respectively, have been measured. From these, using a method suggested by McKay and Perring¹ the mean activity coefficients of the sodium chloride and the sodium carboxylates have been calculated. The regularities shown by the changes in activity in solutions where there is no association (in these, the activity coefficients generally follow Harned's rule) make it possible to estimate the mean aggregation number of the butyrate and hexanoate anions. These agree with previously reported potentiometric determinations of association equilibria² and show that the aggregation occurs in alkaline solutions, too. The method cannot be applied to solutions containing aggregates of micellar size, due to their high vapour pressure.

It is generally accepted³ that small aggregates are formed in measurable amounts by surfactants in aqueous solutions below the critical micelle concentration, c.m.c. However, the structure and size of these aggregates is not very well established. Different suggestions have been made,²⁻⁸ most of them indicating that the submicellar aggregates, similarly to micelles, are held together mainly by forces of attraction between hydrocarbon chains in conjunction with a reduction in the water structure on association (hydrophobic bonding). The possibility that the binding of counter ions plays a role cannot, however, be ruled out. It may be expected that more could be learned about the structural changes in the solutions from a detailed examination of the association equilibria in solutions of compounds with a very high c.m.c. These give rise to the formation of appreciable amounts of smaller aggregates and, at higher concentrations, to micelles.^{1,8}

Such investigations, at least if thermodynamic properties are studied, are rendered difficult by the fact that effects caused by changes in the concentrations of different species cannot be distinguished from changes in their activity coefficients.^{9,10} In this investigation it has been found possible to make some

reasonable predictions concerning the variation in activity coefficients by utilizing the regularities shown by the activity coefficients of the different components in mixed electrolyte solutions.

Investigations of the activity of water in aqueous solutions of short-chain alkanoates were made very early in the history of surfactant science.^{11,12} Smith and Robinson¹³ made extensive isopiestic investigations of pure sodium carboxylate solutions. From their data, it is clearly seen that carboxylates with five or more carbon atoms in the chain do associate, but it is not possible to draw definite conclusions regarding the size of the aggregates formed. A few¹⁴⁻¹⁸ investigations of the activities in mixtures of short-chain carboxylates with simple electrolytes have been reported. Some of the data used for the calculations below have been published before,¹⁹ but complete tables are given here to give a comprehensive picture of the calculations and results.

LIST OF SYMBOLS

- a_i = activity of substance i
 n_i = amount of substance i
 m_i = molality of substance i
 m = total molality of NaCl and NaR in mixed solutions
 \bar{q} = mean number of anions per carboxylate aggregate
 $u_1 = m_{1r}/m, u_2 = m_{2r}/m$
 $x_{12} = m_1/m_2, x_1 = m_1/m, x_2 = m_2/m$
 $y = \ln a_w, z_1 = m_{1r}\phi_{1r}, z_2 = \nu_{2r}m_{2r}\phi_{2r}$
 ν_i = mean number of ions formed by substance i
 γ_i = mean activity coefficient of substance i (molality basis)
 ν = mean amount of ions per unit amount of mixed electrolyte

Subscripts: _w = water, ₁ = NaCl (in mixed solutions), _{1r} = NaCl (in reference solutions), ₂ = Na-carboxylate (NaR, in mixed solutions), _{2r} = NaR (in reference solutions).

METHOD OF CALCULATION

Mean activity coefficient of sodium chloride. Consider a system of sodium chloride (1) and sodium carboxylate, (2) dissolved in water (w). Application of the Gibbs-Duhem equation to this system gives, at constant temperature and pressure,

$$n_1 d \ln a_1 + n_2 d \ln a_2 + n_w d \ln a_w = 0 \quad (1)$$

where n_i is the amount of substance i and a_i its activity.

Several methods to utilize eqn. (1) to calculate the activities of different components in ternary systems have been discussed recently.²⁰⁻²⁴ For our purposes, it has been found convenient to modify the method outlined by McKay and Perring¹ in the following way, which makes it possible to estimate the relative influence of association and intermolecular interactions as the concentration of electrolyte increases.

The experimentally determined quantities in vapour pressure osmometry are the water activities a_w at different molalities of NaCl, m_1 , and NaR, m_2 .

As suggested by McKay and Perring,¹ it is convenient to transform (1) to an expression where $\ln a_w \equiv y$ and $m_1/m_2 \equiv x_{12}$ are used as independent variables. On changing to molalities, (1) can be written

$$-d \ln a_2 = x_{12} d \ln a_1 + m_w/m_2 dy \quad (2)$$

where m_w is the molality of water ($= 55.508 \text{ mol kg}^{-1}$). Differentiating $\ln a_1 = f(x_{12}, y)$ gives

$$d \ln a_1 = \left(\frac{\partial \ln a_1}{\partial x_{12}} \right)_y dx_{12} + \left(\frac{\partial \ln a_1}{\partial y} \right)_{x_{12}} dy \quad (3)$$

Introduction of (3) into (2) yields the following equation:

$$-d \ln a_2 = \left[x_{12} \left(\frac{\partial \ln a_1}{\partial y} \right)_{x_{12}} + \frac{m_w}{m_2} \right] dy + x_{12} \left(\frac{\partial \ln a_1}{\partial x_{12}} \right)_y dx_{12} \quad (4)$$

(4) is of the general form $dF(y, x_{12}) = G(y, x_{12})dy + H(y, x_{12})dx_{12}$, where dF is a total differential. Then $(\partial G/\partial x_{12})_y = (\partial H/\partial y)_{x_{12}}$ or from (4):

$$\left(\frac{\partial \ln a_1}{\partial y} \right)_{x_{12}} = -m_w \left[\frac{\partial(1/m_2)}{\partial x_{12}} \right]_y \quad (5)$$

From an experimental point of view, it is convenient to use the quantity

$$x_2 = \frac{m_2}{m_1 + m_2} = \frac{m_2}{m} = \frac{1}{1 + x_{12}} \quad (6)$$

instead of x_{12} . Introducing this variable into the right hand member of (5) gives

$$\left[\frac{\partial(1/m_2)}{\partial x_{12}} \right]_y = \frac{x_2}{m^2} \left(\frac{\partial m}{\partial x_2} \right)_y + \frac{1}{m} \quad (7)$$

The molality of Na^+ ions is $m_1 + m_2 = m$ and the molality of Cl^- ions is m_1 . The NaCl activity hence is given by $a_1 = \gamma_1^2 m_1 m$ where γ_1 is the mean activity coefficient of NaCl. But $m_1/m = 1 - x_2$ and thus

$$a_1 = \gamma_1^2 m^2 (1 - x_2); (\partial \ln a_1)_{x_2} = 2(\partial \ln \gamma_1 m)_{x_2} \quad (8)$$

Introduction of (7) and (8) into (5) yields

$$\frac{2}{m_w} \left(\frac{\partial \ln \gamma_1 m}{\partial y} \right)_{x_2} = - \frac{x_2}{m_2} \left(\frac{\partial m}{\partial x_2} \right)_y - \frac{1}{m} \quad (9)$$

This equation might be used to calculate γ_1 from y and x_2 . The integrand in the right hand member of (9), however, becomes uncertain as $m \rightarrow 0$. This difficulty can be circumvented by utilizing the known activity coefficients γ_{1r} in an isopiestic pure sodium chloride solution of molality m_{1r} . The Gibbs-Duhem equation for this solution gives²⁵

$$\frac{2}{m_w} \frac{d \ln \gamma_{1r} m_{1r}}{dy} = - \frac{1}{m_{1r}} \quad (10)$$

Since a_w is the same in this reference solution and the mixed electrolyte solution, subtraction of (10) from (9) gives

$$\frac{2}{m_w} \left[\frac{\partial \ln (\gamma_1 m / \gamma_{1r} m_{1r})}{\partial y} \right]_{x_1} = - \frac{x_2 (\partial m)}{m^2 (\partial x_2)_y} - \frac{1}{m} + \frac{1}{m_{1r}} \quad (11)$$

This equation now is integrated at constant x_2 , yielding values for γ_1 at a given ratio m_1/m . In the limit, $m \rightarrow 0$, $\gamma_1 m \rightarrow \gamma_{1r} m_{1r}$ and $a_w \rightarrow 1$; (11) then can be written

$$\frac{2}{m_w} \ln \frac{\gamma_1 m}{\gamma_{1r} m_{1r}} = - \int_0^y \left[\frac{x_2 (\partial m)}{m^2 (\partial x_2)_y} + \frac{1}{m} - \frac{1}{m_{1r}} \right]_{x_1} dy \quad (12)$$

(12) is McKay's and Perring's equation (6) in our notation.

The osmotic coefficient of the reference solution, ϕ_{1r} , is defined by

$$y \equiv \ln a_w = - \frac{2}{m_w} m_{1r} \phi_{1r} \quad (13)$$

For convenient calculations, (12) is further modified by introducing (13) and the symbols

$$m_{1r} \phi_{1r} = z_1; m_{1r}/m = u_1 \quad (14)$$

giving the final equation for γ_1 :

$$\ln \gamma_1 = \ln (\gamma_{1r} u_1) - \int_0^{z_1} \frac{1}{m_{1r}} \left[x_2 \left(\frac{\partial u_1}{\partial x_2} \right)_{m_{1r}} - u_1 + 1 \right]_{x_1} dz_1 \quad (15)$$

This equation contains no approximation except the assumption that the free Na^+ -ion molality is $m_1 + m_2$, *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.

Mean aggregation number of the carboxylates. If it is assumed that the carboxylate dissociates completely into two ions, *i.e.* the association to polynuclear aggregates is disregarded, an equation exactly analogous to (15) is valid for the activity coefficient of NaR, γ_2' :

$$\ln \gamma_2' = \ln (\gamma_{2r}' u_2) - \int_0^{z_1} \frac{1}{m_{2r}} \left[x_1 \left(\frac{\partial u_2}{\partial x_1} \right)_{m_{2r}} - u_2 + 1 \right]_{x_1} dz_2 \quad (16)$$

where γ_{2r}' and m_{2r} are the activity coefficient (disregarding association) and molality, respectively, of an isopiestic reference solution of NaR, and

$$u_2 = \frac{m_{2r}}{m}; x_1 = \frac{m_1}{m}; z_2 = m_{2r} \phi_{2r} \quad (17)$$

However, it is possible to estimate the effects of association upon γ_2' . It is experimentally found that in solutions where there is no association, m_{1r} and m_{2r} are linear functions of x_2 and x_1 at constant m :

$$m_{1r}/m = 1 + a'x_2 \quad (18)$$

$$m_{2r}/m = 1 + a''x_1 \quad (19)$$

where a' and a'' are constants which are different for different values of m . These relationships are illustrated for sodium acetate in Figs. 1 and 2, which

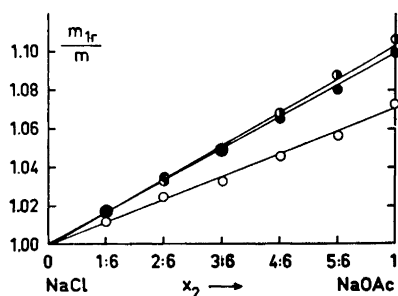


Fig. 1. The molality of an isopiestic solution of NaCl, m_{1r} , as a function of the fraction of sodium acetate x_2 in a mixed aqueous solution of NaCl and NaOAc for different total molalities m . \circ 1.0, \bullet 2.0 and \bullet 3.0 mol kg⁻¹.

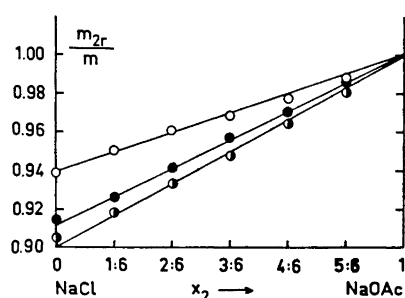


Fig. 2. The molality of an isopiestic solution of NaOAc, m_{2r} , as a function of the fraction of sodium acetate, x_2 , in a mixed aqueous solution of NaCl and NaOAc for different total molalities m . Symbols as in Fig. 1.

show that straight lines are obtained within experimental error. If (18) is introduced into (15), the integrand becomes zero.

The condition of vapour pressure equilibrium between the reference solution and the mixed solution demands that²⁶

$$\phi_{1r}m_{1r}v_{1r} = \phi m v \quad (20)$$

where v_{1r} is the mean amount of ions formed per unit amount of reference electrolyte, v the corresponding quantity for the mixed electrolyte and ϕ the osmotic coefficient of the mixed electrolyte solution. Then

$$\phi v / \phi_{1r} v_{1r} = u_1 \quad (21)$$

If the integral in (15) is denoted by A_1 , (15) may be transformed to

$$\gamma_1 / \gamma_{1r} = u_1 e^{-A_1} \quad (22)$$

and thus

$$\phi v / \phi_{1r} v_{1r} = (\gamma_1 / \gamma_{1r}) e^{A_1} \quad (23)$$

If there is no association $v = v_{1r} = 2$. If this is combined with the experimental fact that $A_1 = 0$ under these circumstances, (23) becomes

$$\phi / \phi_{1r} = \gamma_1 / \gamma_{1r} \text{ (no association)} \quad (24)$$

It seems reasonable to assume that (24) will hold for the non-associating component, *i.e.* for the NaCl, even in solutions where the other component does form aggregates. This implies that the term e^{A_1} just reflects the effect

of the association of the other component upon the ratio $\phi\nu/\phi_{1r}\nu_{1r}$, *i.e.* the fact that ν is less than 2. Introducing (24) into (23) gives

$$\nu = 2 e^{A_1} \quad (25)$$

since it can be assumed that $\nu_{1r} = 2$ for all m_{1r} .

The mean aggregation number of the carboxylate anions is defined by

$$\bar{q} = m_2/m_{\text{aggr}} \quad (26)$$

where m_{aggr} is the molality of the aggregates, including monomers. Assuming that no sodium ions are bound to the aggregates, $\nu m = m_{\text{Na}} + m_{\text{Cl}} + m_{\text{aggr}}$; $m_{\text{Na}} = m$ and $m_{\text{Cl}} = (1 - x_2)m$, giving

$$\bar{q} = x_2/(\nu + x_2 - 2) \quad (27)$$

Mean activity coefficient of the carboxylate. It is, as can be seen from Fig. 3, which shows ν for sodium hexanoate, possible to extrapolate the values for

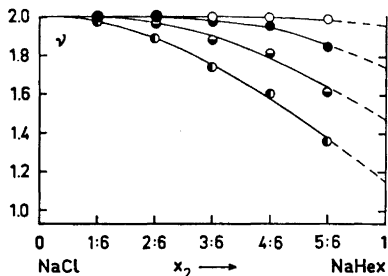


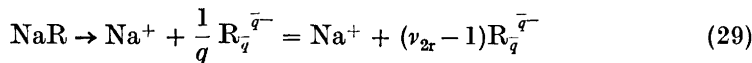
Fig. 3. The mean amount of ions ν formed per unit amount of mixed electrolyte in aqueous NaCl–Na hexanoate mixtures at different total molalities m as a function of the fraction of Na hexanoate. \circ 0.5, \bullet 1.0, \bullet 2.0, and \bullet 3.0 mol kg^{-1} .

ν calculated from (25) to $x_2 = 1$, *i.e.* to pure carboxylate solutions. These extrapolated values, ν_{2r} , may then be utilized to calculate the activity coefficient of the carboxylates in pure solutions *with the association taken into account* in the following way:

From the Gibbs-Duhem equation,

$$m_{2r} d \ln a_{2r} = -m_w d \ln a_w = -m_w dy \quad (28)$$

If the carboxylate dissociation is written



the mean carboxylate activity is defined by

$$a_{2r} = (\nu_{2r} - 1)^{\nu_{2r}-1} (\gamma_{2r} m_{2r})^{\nu_{2r}} \quad (30)$$

and the mean activity coefficient is given by

$$\gamma_{2r} = (\gamma_{\text{R}}^{\nu_{2r}-1} \gamma_{\text{Na}})^{1/\nu_{2r}} \quad (31)$$

where γ_{R} and γ_{Na} are the single ionic activity coefficients of the $\text{R}_{\bar{q}}^-$ and Na^+ ions, respectively. Introducing (30) and the osmotic coefficient

$$\phi_{2r} = - \frac{m_w y}{\nu_{2r} m_{2r}} \quad (32)$$

into (28) gives, after slight rearrangement

$$d \ln [(\nu_{2r} - 1)^{\nu_{2r}-1} (\gamma_{2r} m_{2r})^{\nu_{2r}}] = \frac{1}{m_{2r}} dz_{2r} \quad (33)$$

where $z_{2r} = \nu_{2r} m_{2r} \phi_{2r}$. As $m_{2r} \rightarrow 0$, the integration of (33) becomes uncertain. This difficulty may be circumvented by using a value of γ_{2r} at a concentration which is low enough to make the assumption $\nu_{2r} = 2$ certain, as an integration constant. This integration constant, γ_{2r}° at $m_{2r} = m_{2r}^\circ$ may be calculated in the conventional way from osmotic coefficients.²⁶ Introducing γ_{2r}° and m_{2r}° , the integrated form of (33) is

$$\ln \gamma_{2r} = - \ln m_{2r} + \frac{2}{\nu_{2r}} \ln m_{2r}^\circ \gamma_{2r}^\circ - \frac{1}{\nu_{2r}} \ln (\nu_{2r} - 1)^{\nu_{2r}-1} + \frac{1}{\nu_{2r}} \int_{z_{2r}^\circ}^{z_{2r}} \frac{dz_{2r}}{m_{2r}} \quad (34)$$

where $z_{2r}^\circ = 2 m_{2r}^\circ \phi_{2r}^\circ$. If $\nu_{2r} = 2$ throughout, (34) reduces to

$$\ln \gamma_{2r}' = - \ln m_{2r} + \ln m_{2r}^\circ \gamma_{2r}^\circ + \int_{\phi_{2r}^\circ m_{2r}^\circ}^{\phi_{2r} m_{2r}} \frac{d(\phi_{2r} m_{2r})}{m_{2r}} \quad (35)$$

In the mixed solutions, the association may be taken into account in a similar way. The sodium ion activity is $a_{Na} = \gamma_{Na} m$ and the carboxylate ion activity is $a_R = \gamma_R \nu_R m_2 = \gamma_R (\nu_2 - 1) x_2 m$, giving the mean carboxylate ion activity

$$a_2 = \gamma_{Na} m [\gamma_R m x_2 (\nu_2 - 1)]^{\nu_2-1} = [x_2 (\nu_2 - 1)]^{\nu_2-1} (\gamma_2 m)^{\nu_2} \quad (36)$$

where

$$\gamma_2 = (\gamma_{Na} \gamma_R^{\nu_2-1})^{1/\nu_2} \quad (37)$$

is the mean activity coefficient of the carboxylate with the association taken into account. Using this activity, an equation for the calculation of γ_2 from a_w may now be derived in a way exactly analogous to the derivation of (15). In analogy with (7),

$$\left[\frac{\partial(1/m_1)}{\partial x_{21}} \right]_y = \frac{x_1}{m^2} \left(\frac{\partial m}{\partial x_1} \right)_y + \frac{1}{m} \quad (38)$$

where $x_1 = 1 - x_2$ and $x_{21} = m_2/m_1$. Differentiation of (36) after taking logarithms and introducing $x_1 = 1 - x_2$ yields

$$(\partial \ln a_2)_{x_1} = [\ln(\nu_2 - 1)^{\nu_2-1} (\gamma_2 m)^{\nu_2}]_{x_1} \quad (39)$$

and the equation analogous to (9) is

$$\frac{1}{m_w} \left(\frac{\partial \ln [(\nu_2 - 1)^{\nu_2-1} (\gamma_2 m)^{\nu_2}]}{\partial y} \right)_{x_1} = - \frac{x_1}{m^2} \left(\frac{\partial m}{\partial x_1} \right) - \frac{1}{m} \quad (40)$$

To avoid uncertainty in the integration of (40), activity coefficients calculated from (34) may be utilized.

Introducing $m_w(\partial y)_{x_2} = -\partial(\nu_2 m_2 \phi_2)_{x_2} = -\partial z_2$ and subtracting (33) from (40) gives

$$d \ln \frac{(\nu_2 - 1)^{\nu_2 - 1} (\gamma_2 m)^{\nu_2}}{(\nu_2 - 1)^{\nu_{2r} - 1} (\gamma_{2r} m_{2r})^{\nu_{2r}}} = \left[\frac{x_1}{m^2} \left(\frac{\partial m}{\partial x_1} \right)_{x_1} + \frac{1}{m} - \frac{1}{m_{2r}} \right]_{x_1} dz_2 \quad (41)$$

As $m \rightarrow 0$, the logarithm also becomes 0. The final expression for $\ln \gamma_2$ then is

$$\ln \gamma_2 = \ln m + \frac{1}{\nu_2} \left\{ \ln \frac{(\nu_{2r} - 1)^{\nu_{2r} - 1} (m_{2r} \gamma_{2r})^{\nu_{2r}}}{(\nu_2 - 1)^{\nu_2 - 1}} - \int_0^{x_2} \frac{1}{m_{2r}} \left[\left(\frac{\partial u_2}{\partial x_1} \right)_{m_{1r}} x_1 - u_2 + 1 \right]_{x_1} dz_2 \right\} \quad (42)$$

where $u_2 = m_{2r}/m$.

The calculation of γ_2 is limited to solutions which have a vapour pressure which is equal to the pressure of a reference solution of the pure carboxylate. This limits the possibilities to calculate γ_2 to cases where there is not very extensive association. It is thus, unfortunately, not possible to calculate γ_2 in micellar solutions. However, in such solutions the assumption that no sodium ions are bound is probably not correct, *i.e.* the calculation of ν from (25) becomes very questionable and the whole method breaks down for this reason, too.

The calculation of γ_1 from (15), \bar{q} and ν from (26) and (25), and γ_2 from (42) were performed by numerical integration and differentiation using a program written in Algol for a Univac 1108 computer.

The calculation of the derivatives in (15), (16), (42) was performed by fitting a cubic polynomial to the functions $u_1(x_2)$ and $u_2(x_1)$ at constant m_{2r} and m_{1r} , respectively. The values for u_1 and u_2 used for this fitting were obtained by quadratic interpolation from the experimental values of u_1 and u_2 which may be calculated from the points given in Tables 2–5.

Table 1. Densities of sodium carboxylates in aqueous solution at 25°C.

c_{NaR} mol dm ⁻³	Sodium acetate	Sodium propionate	ρ_{NaR} , g cm ⁻³ Sodium butyrate	Sodium hexanoate
0.250	1.0072	1.0094	1.0083	1.0064
0.400	1.0134	1.0149	1.0137	1.0120
0.500	1.0176	1.0187	1.0174	1.0155
0.700	1.0257	1.0263	1.0248	1.0226
1.000	1.0377	1.0376	1.0361	1.0327
1.300	1.0496	1.0490	1.0476	1.0419
1.500	1.0573	1.0566	1.0557	1.0475
1.800	1.0688	1.0679	1.0661	1.0554
2.100	1.0842	1.0793	1.0770	1.0627
2.400	1.0927	1.0906	1.0872	1.0695
2.700	1.1030	1.1020	1.0961	1.0760
3.000	1.1140	1.1133	1.1053	1.0822

Table 2. Experimental results for sodium acetate/sodium chloride solutions. x_2 = (carboxylate molality): (total molality); m = total molality of the sample solution; m_{1r} = molality of a NaCl solution with the same water activity as the sample solution.

$x_2 = 0.1667$: (m, m_{1r}): 0.252, 0.254; 0.405, 0.408; 0.507, 0.511; 0.713, 0.720; 1.020, 1.040; 1.237, 1.251; 1.558, 1.576; 1.884, 1.916; 2.215, 2.250; 2.552, 2.590; 2.894, 2.940; 3.243, 3.289.
 $x_2 = 0.3333$: (m, m_{1r}): 0.252, 0.255; 0.405, 0.411; 0.508, 0.515; 0.715, 0.729; 1.030, 1.055; 1.243, 1.270; 1.567, 1.607; 1.898, 1.958; 2.234, 2.306; 2.577, 2.655; 2.926, 3.021; 3.283, 3.377.
 $x_2 = 0.5000$: (m, m_{1r}): 0.253, 0.256; 0.406, 0.414; 0.509, 0.520; 0.717, 0.737; 1.034, 1.069; 1.249, 1.292; 1.577, 1.639; 1.911, 2.004; 2.253, 2.363; 2.603, 2.723; 2.959, 3.107; 3.325, 3.474.
 $x_2 = 0.6667$: (m, m_{1r}): 0.253, 0.257; 0.407, 0.417; 0.510, 0.524; 0.719, 0.745; 1.038, 1.087; 1.255, 1.316; 1.586, 1.659; 1.925, 2.048; 2.273, 2.422; 2.628, 2.798; 2.993, 3.197; 3.368, 3.580.
 $x_2 = 0.8333$: (m, m_{1r}): 0.253, 0.258; 0.407, 0.420; 0.511, 0.529; 0.721, 0.752; 1.042, 1.104; 1.261, 1.340; 1.596, 1.713; 1.939, 2.097; 2.292, 2.485; 2.655, 2.877; 3.028, 3.292; 3.412, 3.693.
 $x_2 = 1.000$: (m, m_{1r}): 0.253, 0.259; 0.408, 0.423; 0.512, 0.534; 0.723, 0.760; 1.046, 1.122; 1.267, 1.368; 1.606, 1.750; 1.954, 2.148; 2.313, 2.550; 2.683, 2.958; 3.064, 3.390; 3.457, 3.819.

Table 3. Experimental values for sodium propionate/sodium chloride solutions. Symbols: as in Table 2.

$x_2 = 0.1667$: (m, m_{1r}): 0.400, 0.408; 0.508, 0.512; 0.714, 0.727; 1.241, 1.263; 1.564, 1.595; 1.892, 1.935; 2.227, 2.283; 2.567, 2.636; 2.914, 2.994; 3.268, 3.368.
 $x_2 = 0.3333$: (m, m_{1r}): 0.400, 0.413; 0.509, 0.519; 0.718, 0.736; 1.250, 1.299; 1.579, 1.650; 1.915, 2.010; 2.258, 2.376; 2.621, 2.757; 2.968, 3.123; 3.336, 3.526.
 $x_2 = 0.5000$: (m, m_{1r}): 0.400, 0.418; 0.511, 0.527; 0.721, 0.749; 1.260, 1.334; 1.594, 1.703; 1.938, 2.075; 2.290, 2.470; 2.660, 2.870; 3.024, 3.251; 3.407, 3.675.
 $x_2 = 0.6667$: (m, m_{1r}): 0.400, 0.422; 0.513, 0.534; 0.724, 0.763; 1.270, 1.370; 1.610, 1.757; 1.961, 2.153; 2.323, 2.565; 2.696, 2.982; 3.082, 3.389; 3.418, 3.835.
 $x_2 = 0.8333$: (m, m_{1r}): 0.400, 0.428; 0.514, 0.542; 0.727, 0.777; 1.280, 1.410; 1.626, 1.814; 1.985, 2.234; 2.357, 2.670; 2.742, 3.110; 3.143, 3.527; 3.558, 3.995.
 $x_2 = 1.000$: (m, m_{1r}): 0.410, 0.433; 0.516, 0.550; 0.730, 0.792; 1.290, 1.447; 1.625, 1.875; 2.010, 2.316; 2.392, 2.774; 2.790, 3.249; 3.205, 3.668; 3.639, 4.177.

Table 4. Experimental values for sodium butyrate/sodium chloride solutions. Symbols: as in Table 2.

$x_2 = 0.1667$: (m, m_{1r}): 0.405, 0.410; 0.716, 0.728; 1.030, 1.066; 1.352, 1.391; 1.570, 1.617; 1.902, 1.991; 2.239, 2.322; 2.585, 2.680; 2.938, 3.062; 3.298, 3.446.
 $x_2 = 0.3333$: (m, m_{1r}): 0.407, 0.418; 0.721, 0.747; 1.040, 1.093; 1.368, 1.445; 1.592, 1.694; 1.934, 2.104; 2.284, 2.449; 2.645, 2.840; 3.016, 3.257; 3.398, 3.675.
 $x_2 = 0.5000$: (m, m_{1r}): 0.408, 0.425; 0.725, 0.761; 1.050, 1.127; 1.385, 1.503; 1.614, 1.774; 1.967, 2.219; 2.330, 2.569; 2.708, 3.000; 3.097, 3.446; 3.505, 3.915.
 $x_2 = 0.6667$: (m, m_{1r}): 0.410, 0.431; 0.730, 0.778; 1.060, 1.164; 1.402, 1.557; 1.637, 1.850; 2.002, 2.329; 2.379, 2.690; 2.774, 3.147; 3.188, 3.628; 3.619, 4.130.
 $x_2 = 0.8333$: (m, m_{1r}): 0.411, 0.438; 0.734, 0.797; 1.070, 1.120; 1.419, 1.615; 1.660, 1.916; 2.037, 2.440; 2.430, 2.809; 2.843, 3.294; 3.281, 3.800; 3.741, 4.325.
 $x_2 = 1.000$: (m, m_{1r}): 0.412, 0.441; 0.739, 0.822; 1.080, 1.244; 1.437, 1.683; 1.684, 2.011; 2.074, 2.495; 2.483, 2.935; 2.916, 3.490; 3.380, 3.937; 3.870, 4.640.

EXPERIMENTAL

I. Chemicals. The sodium acetate was *p.a.* grade from E. Merck. Other fatty acid salts were synthesized by neutralization of the acids (*purissimum* grade from Fluka) with sodium ethylate in dry ethanol. The salts were dried in vacuum at 110°C and their molecular weights then checked by titration with HClO_4 in glacial acetic acid. Only salts with a molecular weight differing less than 0.25% from the theoretical weight were accepted.

The sodium chloride was *p.a.* grade from E. Merck. It was dried before use in vacuum at 110°C.

The water was doubly distilled and passed through an ion exchanger (Dowex) immediately before use. Its conductivity was about $0.5 \mu\text{S cm}^{-1}$.

II. Preparation of solutions. Mixed electrolyte solutions were prepared by mixing appropriate volume proportions of stock sodium chloride and sodium carboxylate solutions of the same concentration. The molalities were calculated from the densities given for NaCl solutions in Ref. 27 and the pycnometrically determined carboxylate densities given in Table 1; the densities of mixed electrolyte solutions were assumed to change linearly with the amount of carboxylate in a solution of constant concentration. By checking the densities of some solutions this was shown to hold to an accuracy which was better than the difference in molality that could be detected with the vapour pressure osmometer. To all solutions were added 10^{-4} mol/l NaOH to suppress effects of hydrolysis. This amount is too small to affect the water activities to a measurable extent.

III. Measurement of water activities. Water activities were measured with a Mechrolab model 301 Vapour Pressure Osmometer, using sodium chloride solutions of suitable concentration as standards. The resistance difference ΔR between the two thermistors was calibrated as a function of the difference in water activity between the solutions surrounding the drops by using NaCl solutions of known water activity (taken from Ref. 28). At least six ΔR values were taken for each point. The standard deviation in ΔR is ± 0.2 ohm corresponding to a difference in water activity of about ± 0.001 . Fig. 4

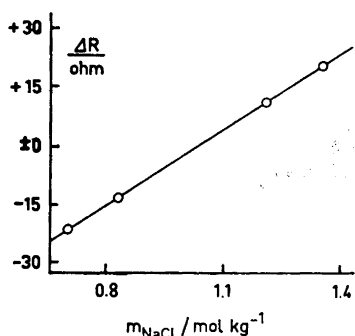


Fig. 4. A sample calibration curve showing the resistance difference ΔR between the VPO thermistors as a function of the NaCl molality using 1.0 mol kg^{-1} NaCl as a reference solution.

exemplifies a calibration curve. Measurements of the vapour pressures of the sample solutions were made in the same way and the molality of the isopiestic NaCl solution was read directly from the ΔR versus m_{NaCl} curve.

All measurements were performed at $(25 \pm 0.01)^\circ\text{C}$.

Table 5. Experimental values for sodium hexanoate/sodium chloride solutions. Symbols: as in Table 2.

$x_2 = 0.1667$: (m, m_{1r}); 0.253, 0.256; 0.406, 0.414; 0.510, 0.520; 0.718, 0.737; 1.037, 1.070; 1.362, 1.413; 1.583, 1.645; 1.920, 2.001; 2.266, 2.370; 2.619, 2.753; 2.982, 3.120; 3.360, 3.549.
 $x_2 = 0.3333$: (m, m_{1r}); 0.254, 0.263; 0.409, 0.422; 0.513, 0.533; 0.726, 0.762; 1.052, 1.115; 1.388, 1.482; 1.619, 1.730; 1.974, 2.115; 2.341, 2.500; 2.721, 2.876; 3.116, 3.190; 3.527, 3.557.
 $x_2 = 0.5000$: (m, m_{1r}); 0.255, 0.267; 0.411, 0.430; 0.517, 0.544; 0.733, 0.784; 1.068, 1.157; 1.416, 1.540; 1.656, 1.789; 2.030, 2.168; 2.422, 2.503; 2.834, 2.810; 3.267, 3.107; 3.724, 3.456.
 $x_2 = 0.6667$: (m, m_{1r}); 0.255, 0.271; 0.413, 0.436; 0.521, 0.555; 0.740, 0.804; 1.084, 1.190; 1.443, 1.574; 1.696, 1.822; 2.092, 2.129; 2.512, 2.402; 2.959, 2.663; 3.435, 2.955; 3.946, 3.327.
 $x_2 = 0.8333$: (m, m_{1r}); 0.256, 0.273; 0.416, 0.442; 0.525, 0.565; 0.748, 0.823; 1.100, 1.220; 1.475, 1.577; 1.739, 1.775; 2.159, 2.008; 2.610, 2.244; 3.096, 2.476; 3.624, 2.772; 4.198, 3.140.
 $x_2 = 1.000$: (m, m_{1r}); 0.257, 0.267; 0.418, 0.432; 0.528, 0.560; 0.756, 0.872; 1.118, 1.240; 1.508, 1.600; 1.785, 1.793; 2.231, 2.003; 2.718, 2.180; 3.253, 2.450; 3.841, 2.790; 4.493, 3.250.

Table 6. Activity coefficients of sodium chloride (1) and sodium acetate (2) in mixed aqueous solutions at different ionic strengths.

m mol kg ⁻¹	x ₂ =0		x ₂ =1:6		x ₂ =1:3		x ₂ =1:2		x ₂ =2:3		x ₂ =5:6		x ₂ =1	
	γ ₁ ^a	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂
0.500	0.681	0.713	0.686	0.718	0.692	0.719	0.697	0.723	0.700	0.727	0.704	0.731	0.707	0.736
1.000	0.657	0.718	0.665	0.720	0.673	0.729	0.681	0.733	0.689	0.742	0.696	0.750	0.699	0.757
1.500	0.660	0.748	0.667	0.726	0.678	0.755	0.690	0.764	0.700	0.775	0.708	0.787	0.712	0.800
2.000	0.668	0.789	0.681	0.782	0.695	0.792	0.707	0.806	0.720	0.820	0.730	0.835	0.736	0.851
2.500	0.688	0.840	0.702	0.827	0.719	0.840	0.732	0.856	0.746	0.872	0.758	0.892	0.767	0.914
3.000	0.714	0.896	0.728	0.896	0.745	0.889	0.760	0.910	0.777	0.933	0.791	0.958	0.803	0.982
3.500	0.746	0.953	0.757	0.926	0.772	0.940	0.789	0.963	0.807	1.004	0.824	1.025	0.843	1.057

^a From Ref. 29.

Table 7. Activity coefficients of sodium chloride (1) and sodium propionate (2) in mixed aqueous solutions at different ionic strengths.

m mol kg ⁻¹	x ₂ =0		x ₂ =1:6		x ₂ =1:3		x ₂ =1:2		x ₂ =2:3		x ₂ =5:6		x ₂ =1	
	γ ₁ ^a	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂	γ ₁	γ ₂
0.500	0.681	0.721	0.687	0.740	0.696	0.748	0.703	0.756	0.710	0.758	0.720	0.764	0.745	0.771
1.000	0.657	0.731	0.667	0.754	0.678	0.768	0.690	0.781	0.705	0.788	0.723	0.800	0.740	0.812
1.500	0.660	0.759	0.671	0.792	0.685	0.816	0.702	0.833	0.721	0.848	0.740	0.864	0.765	0.882
2.000	0.668	0.804	0.686	0.843	0.705	0.877	0.724	0.899	0.747	0.920	0.770	0.942	0.797	0.969
2.500	0.688	0.861	0.709	0.909	0.731	0.944	0.753	0.973	0.779	1.002	0.804	1.029	0.832	1.064
3.000	0.714	0.927	0.739	0.982	0.764	1.023	0.788	1.056	0.813	1.081	0.847	1.113	0.866	1.151
3.500	0.746	1.005	0.789	1.069	0.808	1.114	0.835	1.142	0.857	1.170	0.883	1.196	0.902	1.232

^a From Ref. 29.

Table 8. Mean aggregation number (\bar{q}) of the butyrate anions and activity coefficients of the sodium chloride (γ_1) and the sodium butyrate (γ_2) in mixed aqueous solution at different total molalities. γ_2' = activity coefficient of sodium butyrate without association taken into account.

x_2		m, mol kg ⁻¹						
		0.500	1.000	1.500	2.000	2.500	3.000	3.500
0	γ_1^a	0.681	0.657	0.656	0.668	0.688	0.714	0.746
	γ_2	0.731	0.755	0.807	0.897	0.999	1.119	1.235
1:6	γ_1	0.690	0.673	0.680	0.696	0.721	0.755	0.796
	γ_2	0.736	0.772	0.843	0.933	1.035	1.155	1.283
	ν	2.00	1.99	1.97	1.96	1.96	1.96	1.95
	\bar{q}	1.00	1.03	1.04	1.04	1.04	1.05	1.05
1:3	γ_1	0.694	0.689	0.704	0.726	0.754	0.794	0.841
	γ_2	0.750	0.792	0.868	0.958	1.061	1.189	1.329
	ν	2.00	1.97	1.96	1.94	1.95	1.93	1.90
	q	1.00	1.02	1.04	1.04	1.04	1.05	1.06
1:2	γ_1	0.699	0.706	0.716	0.752	0.786	0.833	0.890
	γ_2	0.758	0.808	0.900	0.987	1.092	1.223	1.385
	ν	2.00	1.98	1.96	1.93	1.93	1.91	1.88
	\bar{q}	1.00	1.02	1.04	1.05	1.07	1.11	1.13
2:3	γ_1	0.708	0.719	0.744	0.777	0.817	0.869	0.933
	γ_2	0.761	0.825	0.919	1.024	1.131	1.263	1.425
	ν	2.00	1.99	1.98	1.94	1.94	1.91	1.89
	\bar{q}	1.00	1.02	1.04	1.05	1.08	1.12	1.15
5:6	γ_1	0.718	0.729	0.757	0.794	0.841	0.895	0.963
	γ_2	0.766	0.847	0.954	1.060	1.171	1.302	1.450
	ν	2.00	1.99	1.97	1.97	1.96	1.91	1.88
	\bar{q}	1.00	1.01	1.04	1.05	1.07	1.11	1.16
1	γ_1	0.740	0.751	0.756	0.824	0.853	0.918	0.979
	γ_2	0.784	0.849	0.927	1.106	1.206	1.332	1.577
	γ_2'	0.786	0.869	0.962	1.095	1.185	1.307	1.380
	ν	2.00	1.98	1.97	1.96	1.93	1.90	1.87
	\bar{q}	1.00	1.01	1.04	1.04	1.05	1.08	1.16
	$\gamma_2'^a$	0.782	0.868	0.982	1.083	1.182	1.278	1.368

^a From Ref. 29.

RESULTS AND DISCUSSION

The experimental results (total molalities, and molalities of isopiestic NaCl solutions for different $m_{\text{NaR}}/m_{\text{NaCl}}$ ratios) are given in Tables 2–5.

From these data values of γ_1 , γ_2 , γ_2' , ν , and \bar{q} have been calculated; these are given in Tables 6–9. The logarithms of γ_1 and γ_2 at a few constant molalities are given in Figs. 5–12.

The results are in good agreement with previously determined activity coefficients,¹⁸ as can be seen from the figures. This gives strong support to the applicability of the method to systems of this type. The values obtained

Table 9. Mean aggregation number (\bar{q}) of the hexanoate anions and activity coefficients of the sodium chloride (γ_1) and sodium hexanoate (γ_2) in mixed aqueous solutions at different total molalities. γ_2' = activity coefficient of sodium hexanoate without association taken into account.

x_2		m, mol kg ⁻¹						
		0.500	1.000	1.500	2.000	2.500	3.000	3.500
0	γ_1^a	0.681	0.657	0.656	0.668	0.688	0.714	0.746
	γ_2	0.787						
1:6	γ_1	0.694	0.677	0.684	0.702	0.739	0.771	0.811
	γ_2	0.805	0.895	1.021				
	ν	2.00	2.00	2.00	2.00	1.99	1.97	1.95
	\bar{q}	1.00	1.00	1.01	1.02	1.07	1.20	1.40
1:3	γ_1	0.708	0.698	0.711	0.734	0.765	0.787	0.825
	γ_2	0.854	1.043					
	ν	2.00	1.99	1.98	1.96	1.93	1.89	1.84
	\bar{q}	1.00	1.02	1.06	1.12	1.26	1.57	2.00
1:2	γ_1	0.718	0.720	0.739	0.765	0.780	0.783	0.808
	γ_2	0.866	1.089					
	ν	1.99	1.97	1.96	1.88	1.81	1.74	1.64
	\bar{q}	1.01	1.07	1.15	1.26	1.59	2.03	2.67
2:3	γ_1	0.735	0.746	0.763	0.784	0.798	0.806	0.821
	γ_2	0.867	1.053					
	ν	1.99	1.95	1.92	1.80	1.76	1.60	1.55
	\bar{q}	1.07	1.14	1.27	1.50	2.10	2.96	4.25
5:6	γ_1	0.757	0.775	0.782	0.782	0.784	0.804	0.844
	γ_2	0.851	0.993					
	ν	1.98	1.84	1.75	1.61	1.48	1.36	1.26
	\bar{q}	1.11	1.24	1.47	1.74	2.68	4.81	10.13
1	γ_1	0.769	0.801	0.826				
	γ_2	0.799	0.869	0.916	0.898	0.854	0.857	
	ν	1.92	1.73	1.60	1.47	1.30	1.16	
	\bar{q}	1.20	1.38	1.64	2.00	3.38	11.28	
	γ_2'	0.801	0.858	0.847	0.769	0.678	0.617	0.583
	$\gamma_2'^a$	0.794	0.858	0.850	0.763	0.673	0.612	0.576

^a From Ref. 29.

for the activity coefficients of pure carboxylates in aqueous solution, as calculated without taking the association into account, are in close agreement with those reported by Smith and Robinson,^{13,29} as can be seen from Tables 6–9.

According to the well-known empirical equation called Harned's rule,³⁰

$$\log \gamma_1 = \log \gamma_1^{\text{tr}} + \alpha m_1$$

where γ_1 is the activity coefficient of electrolyte 1 in a mixture of electrolytes 1 and 2 at constant molality, m_1 is the molality of 1 in this mixture and

γ_1^{tr} is the activity coefficient of 1 in infinite dilution at this ionic strength. As can be seen from Figs. 5, 7, 9 and 11, Harned's rule is valid for the NaCl in all solutions except those at high ionic strengths and high hexanoate concentrations.

In these regions, aggregation is quite extensive (Table 9) and the assumptions made are probably too crude, especially as regards the binding of sodium ions to the aggregates.

Harned's rule is also valid for the carboxylates except for butyrate at very high concentrations and for hexanoate. This is to be expected since the assumptions made are not valid in these solutions. Moreover, it can be seen

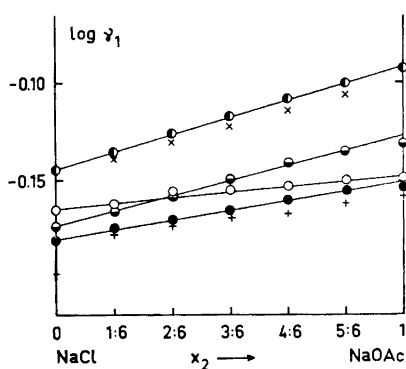


Fig. 5. The logarithm of the activity coefficient of sodium chloride in aqueous NaCl-Na acetate mixtures as a function of $x_2 = m_{\text{NaOAc}}/m$ at different total concentrations m . \circ 0.5, \bullet 1.0, \odot 2.0, \bullet 3.0, \times 3.0 (Ref. 18), and $+$ 1.0 mol kg^{-1} . (Ref. 18).

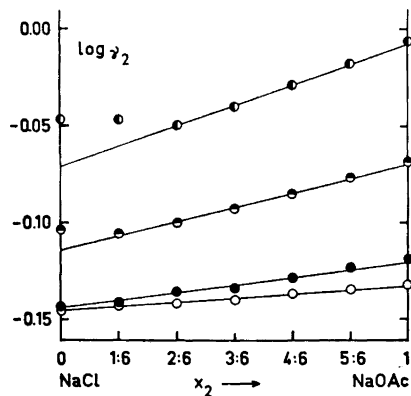


Fig. 6. The logarithm of the activity coefficient of sodium acetate in aqueous NaCl-Na acetate mixtures as a function of $x_2 = m_{\text{NaOAc}}/m$ at different total concentrations m . \circ 0.5, \bullet 1.0, \odot 2.0, and \bullet 3.0 mol kg^{-1} .

that γ^{tr} and $|\alpha|$ are equal for the sodium chloride and sodium acetate in NaCl/NaOAc mixtures, for the sodium chloride and sodium propionate in NaCl/NaPr mixtures and for the sodium chloride and sodium butyrate in NaCl/NaBu mixtures. Some theoretical justification for this phenomenon has been given by Guggenheim;³¹ since one of the main assumptions of his theory is that the ionic radii are equal, it seems very reasonable that the hexanoate deviates quite drastically from the rule.

The aggregation numbers are in good agreement with those found previously.^{2,32} It should be remembered, that the numbers given here include monomers. It is clearly seen that aggregation becomes noticeable in butyrate solutions at total molalities above 1.5 m; this agrees quite well with previous potentiometric results which indicate aggregation at concentrations higher than 1.0 mol/l at the ionic strength 3 mol/l. Considerable aggregation is indicated at high hexanoate concentrations; however, the actual mean aggregation numbers obtained should be regarded as indicative only because of the uncertainty of the extrapolations.

Fig. 7. The logarithm of the activity coefficient of sodium chloride in aqueous NaCl–Na propionate mixtures as a function of $x_2 = m_{\text{NaPr}}/m$ at different total molalities m . Symbols as in Fig. 5.

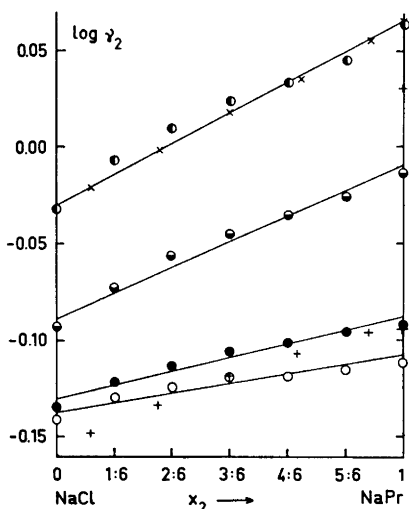
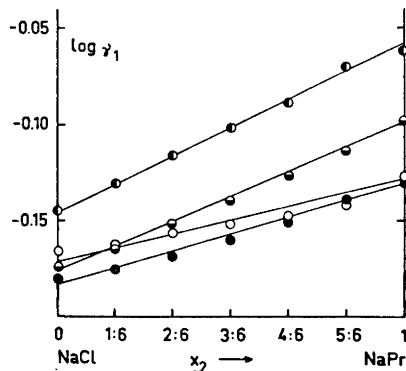


Fig. 8. The logarithm of the activity coefficient of sodium propionate in aqueous NaCl–Na propionate mixtures as a function of $x_2 = m_{\text{NaPr}}/m$ at different total molalities m . \circ 0.5, \bullet 1.0, \ominus 2.0, \bullet 3.0, \times 3.0 (Ref. 24), and $+$ 1.0 (Ref. 24).

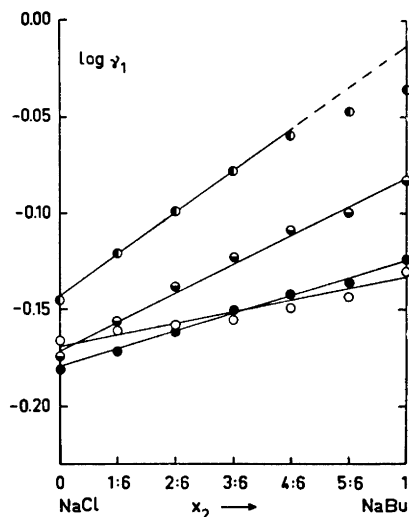


Fig. 9. The logarithm of the activity coefficient of sodium chloride in aqueous NaCl–Na butyrate mixtures as a function of $x_2 = m_{\text{NaBu}}/m$ at different total molalities m . Symbols as in Fig. 8.

The results given in part I² of this series indicate that all complexes formed by carboxylates bind hydrogen ions. It was asserted that this was probably a result of using hydrogen ion activity measurements for the investigation of the aggregation. The vapour pressure measurements have been made at a pH of about 9, which is well above the highest pH at which any binding of hydrogen ions is indicated by potentiometric measurements. One may conclude, that

(a) small aggregates are formed by butyrate and hexanoate anions; the hexanoate forms quite large aggregates (micelles) at high concentration;

(b) hydrogen ions are not necessary to stabilize these aggregates, *i.e.*, they are probably not held together by hydrogen bonding. This conclusion is supported by recent NMR investigations;³³

(c) this does not exclude the possibility that the sodium ions play an important part in forming ion pairs with the aggregates; some indication of this is given by independent sodium ion activity measurements⁸ which show a decrease in activity as aggregates are formed. This is also supported by the results of this work, which indicate that the assumption that sodium ions are not bound to the aggregates leads to strongly decreasing sodium chloride activity coefficients when the hexanoate association becomes extensive;

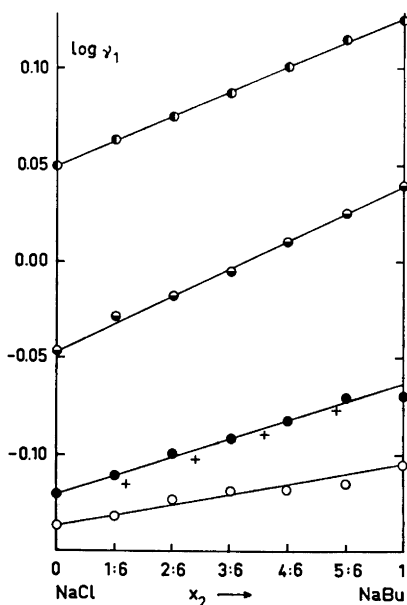


Fig. 10. The logarithm of the activity coefficient of sodium butyrate in aqueous NaCl-Na butyrate mixtures as a function of $x_2 = m_{\text{NaBu}}/m$ at different total molalities m . Symbols as in Fig. 8.

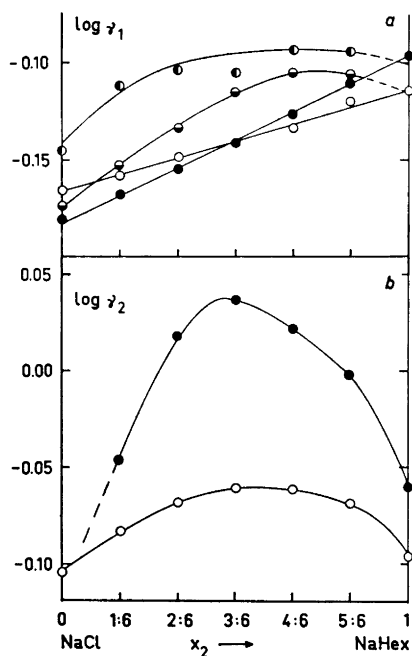


Fig. 11. The logarithms of the activity coefficient of (a) sodium chloride and (b) hexanoate in aqueous NaCl-Na hexanoate mixtures as a function of $x_2 = m_{\text{NaHex}}/m$ at different total molalities m . Symbols as in Fig. 8.

(d) the very slow rise in mean aggregation number as the concentration increases indicates quite low formation constants. This lends some support to the view that the hydrocarbon chains in the small aggregates are held together by hydrophobic bonding; there does not seem to be any strong and specific attraction between the carboxylate anions.

Acknowledgements. Professor Ingvar Danielsson, Ph. D., Mrs. Ann-Marie Öhman and Mr. Sune Backlund, Ph. L. are thanked for discussions of the theoretical parts of this work and invaluable aid in the calculations. This work has been partly financed by the *State Commission for Natural Sciences in Finland*.

REFERENCES

1. McKay, H. A. C. and Perring, J. K. *Trans. Faraday Soc.* **49** (1953) 163.
2. Stenius, P. and Zilliacus, C. H. *Acta Chem. Scand.* **25** (1971) 2232.
3. Mukerjee, P. *Advan. Colloid Interface Sci.* **1** (1967) 241.
4. Franks, F. and Smith, H. T. *J. Phys. Chem.* **68** (1964) 3581.
5. Franks, F., Quickenden, M. J., Ravenhill, J. R. and Smith, H. T. *J. Phys. Chem.* **72** (1968) 2668.
6. Stead, J. A. and Taylor, H. *Australasian J. Pharm.* **51** (1970) 51.
7. Proust, J. and Ter-Miniassan-Saraga, L. *Compt. Rend.* **270** (1970) 1354.
8. Danielsson, I. and Stenius, P. *J. Colloid Interface Sci.* **37** (1971) 264.
9. van Voorst Vader, F. *Trans. Faraday Soc.* **57** (1961) 110.
10. Birch, B. J. and Hall, D. G. *J. Chem. Soc. Faraday Trans. 1* **1972** 2350.
11. Krafft, F. and Strutz, A. *Ber.* **29** (1896) 1329.
12. McBain, J. W. and Salmon, C. S. *J. Am. Chem. Soc.* **43** (1920) 426.
13. Smith, E. R. B. and Robinson, R. A. *Trans. Faraday Soc.* **38** (1942) 70.
14. Ekwall, P. and Harva, O. *Finska Kemistsamfundets Medd.* **52** (1943) 257.
15. Kolthoff, I. M. and Johnson, W. F. *J. Phys. Chem.* **52** (1948) 22.
16. Lanier, R. D. *J. Phys. Chem.* **69** (1965) 3993.
17. Persson, H. *Acta Chem. Scand.* **25** (1971) 1775.
18. Backlund, S. *Acta Chem. Scand.* **25** (1971) 2070.
19. Danielsson, I. *Chim. Phys. Appl. Prat. Ag. Ag. Surface, C. R. Congr. Int. Deterg., 5th*, **2** (1968) 1041.
20. Robinson, R. A., Wood, R. H. and Reilly, P. J. *J. Chem. Thermodyn.* **3** (1971) 461.
21. Rush, R. M. and Johnson, J. S. *J. Chem. Thermodyn.* **3** (1971) 779.
22. Pepela, C. N. and Dunlop, P. *J. Chem. Thermodyn.* **4** (1972) 115.
23. Downes, C. J. *J. Chem. Soc. Faraday Trans. 1* **1972** 1964.
24. Backlund, S., Eriksson, F. and Friman, R., *Acta Chem. Scand.* **27** (1973) 3234.
25. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Revised Ed., Butterworths, London 1965, p. 34.
26. *Ibid.* p. 179.
27. Landolt-Börnstein, *Physikalisch-Chemische Tabellen, III Erg. Bd.* Springer, Berlin 1935.
28. Ref. 25, p. 476.
29. Ref. 25, pp. 492–933.
30. Ref. 25, p. 438.
31. Guggenheim, E. A. *Phil. Mag.* **19** (1935) 588.
32. Danielsson, I. and Koivula, T. In Ekwall, P. and Runnström-Reio, V., Eds., *Surface Chemistry*, Munksgaard, Copenhagen 1965, p. 137.
33. Ödberg, L., Svens, B. and Danielsson, I. *J. Colloid Interface Sci.* **41** (1972) 298.

Received May 14, 1973.