The Activity Coefficients of Formate and Hexanoate Ions in Mixed Aqueous Solutions of Sodium Alkanoate and Sodium Chloride at Constant Sodium Molality (3.0 m)

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The activity coefficients of the sodium and chloride ions have been calculated from potentiometric measurements at 25 °C in aqueous sodium chloride and sodium formate as well as sodium chloride and sodium hexanoate. In the measurements, the sodium molality was kept constant at 3.0 mol kg⁻¹. On the basis of these data and water activities calculated from vapour pressure measurements, the activity coefficients of the alkanoate ion has been calculated using the Gibbs-Duhem equation. The results show that Harned's rule is valid for the formate mixtures. The hexanoate mixtures, however, deviate strongly from this rule. The investigation is connected with other investigations of the self association of alkali alkanoates in highly concentrated ionic media.

Previous investigations of the activity coefficients in aqueous sodium chloride media [1,2] have been continued with an investigation of the activity coefficients of the formate and hexanoate ions at the constant sodium molality 3.0 mol kg⁻¹. These investigations constitute a part of work to clarify the association and the micelle formation of the alkali salts of short-chain fatty acids.[3] The investigations of these equilibria have been conducted in a highly concentrated ionic medium, Na(Cl), in order to minimize the variations of the activity coefficients. Some caution in the interpretation of these results seems to be necessary, as the activity coefficients of the alkanoate ions change considerably when chloride ions are replaced with alkanoate ions in neutral aqueous solutions of sodium chloride and sodium alkanoate in water at constant total molality.[1,2] The purpose of this series of investigations, is to enable

variations of ionic activity coefficients to be used in investigations of the association and the formation of micelles.

EXPERIMENTAL

1. Chemicals. Sodium chloride (E. Merck AG *pro analysi* quality) and sodium formate (J. T. Baker *pro analysi* quality) were dried before use at respectively 140 °C and 90 °C, in vacuum. Sodium hexanoate was synthetized by neutralization of boiling sodium hydroxide solution (E. Merck AG "1 N Titrisol") with hexanoic acid (Fluka AG *purissimum* quality). The molar mass, as determined by titration with perchloric acid in glacial acetic acid, was not allowed to deviate more than 0.5 % from the theoretical value. The distilled water used was passed through an ion exchange resin immediately before use. Its conductivity was about 0.5 μS cm⁻¹.

2. Measurements of electromotive force. Measurements were made after each addition in titrations where a 3.0 mol kg⁻¹ sodium chloride solution was added to a sodium alkanoate (NaB) solution of the same molality and *vice versa*. The electrode systems, the bridge and the temperature control described in Ref. 2 were used. The sodium responsive electrode was an E.I.L. glass electrode, type GEA 33 B. The silver-silver chloride electrodes were prepared by a procedure slightly modified from that of Brown.[4] Emf was measured with a "Beckmann Research pH Meter".

3. Vapour pressure osmometry. The water activities a_w in mixtures of sodium chloride, sodium alkanoate and water were measured with a "Perkin-Elmer Model 115" vapour pressure osmometer. All solutions were prepared separately by direct weighing; the molalities of the reference solutions were checked after the measurements.

RESULTS

The water activities found are shown as functions of sodium alkanoate molality in Fig. 1. The water activities of these systems have been investigated previously by Danielsson et al.,[3,5] these measurements, however, were made at the constant sodium concentration 3.0 M.
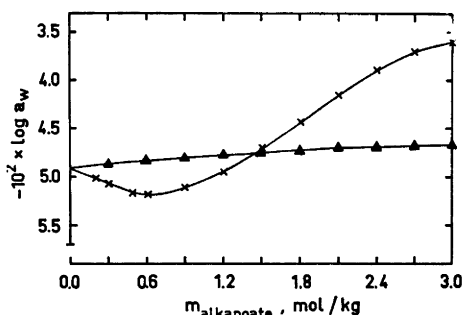

Fig. 1. The logarithm of the water activity as a function of the sodium alkanoate molality for the systems sodium chloride-sodium formate-water and sodium chloride-sodium hexanoate-water at the constant sodium molality 3.0 mol kg^{-1}, temperature 25 °C. ▲, formate; ×, hexanoate.

In Fig. 2 the logarithms of the mean activity coefficients of sodium chloride, $\gamma_{Na,Cl}$, are shown as functions of the alkanoate molality m_{NaB}. These are calculated directly from measured emf values. From $\gamma_{Na,Cl}$, and a_w for the two systems investigated it is possible to calculate the mean activity coefficients for the sodium alkanoates, using the equation

$$2m_{NaCl}d(\log \gamma_{Na,Cl}) + 2m_{NaB}d(\log \gamma_{Na,B}) + m_w d(\log a_w) = 0 \qquad (1)$$

where m_w is the molality of water. This equation is the Gibbs-Duhem equation as applied to the system $NaCl - NaB - H_2O$; it has been given by Harned[6] and developed further by Backlund et al.[2] The final equation used for calculating the mean activity coefficients, $\gamma_{Na,B}$, of sodium alkanoate was

$$\log \gamma_{Na,B} = \log \gamma^*_{Na,B} + b_0 \ln 10 \log m_{NaB}/m_{Na}$$
$$+ \sum_{i=1}^{n}[b_i(i+1)/i](m^i_{NaB} - m^i_{Na}) \qquad (2)$$

$\gamma^*_{Na,B}$ are the mean activity coefficients in the binary system $NaB - H_2O$. The values for these, according to Robinson and Stokes[7] are $\gamma^*_{Na,Fo} = 0.678$ for the formate and $\gamma^*_{Na,Hex} = 0.612$ for the hexanoate. b_i are constants ($i = 0, 1, ...n$) which are determined by fitting the polynomial to experimental values of $\gamma_{Na,Cl}$ and a_w by regressional analysis. m_{Na} is the constant sodium molality and thus $m_{Na} = 3.0$ mol kg^{-1}. The standard states are chosen to give

$$\lim_{\substack{m_{NaCl} \to 0 \\ a_w \to 1}} \gamma^*_{Na,Cl} = \lim_{\substack{m_{NaB} \to 0 \\ a_w \to 1}} \gamma^*_{Na,B} = 1. \text{ It is also}$$

assumed that, as postulated by Guggenheim,[8] $\gamma^*_{Na,Cl} = \gamma^*_{Cl^-} = \gamma^*_{Na^+}$ in pure sodium chloride-water systems.

Table 1. Single ion activity coefficients in mixed aqueous solutions of sodium chloride and sodium alkanoate at the constant sodium molality $m_{Na} = 3.0$ mol kg^{-1}, temperature 25 °C.

$m_{alkanoate}$ mol kg^{-1}	Formate			Hexanoate		
	γ_{Na^+}	γ_{Cl^-}	γ_{Fo^-}	γ_{Na^+}	γ_{Cl^-}	γ_{Hex^-}
0.00	0.714	0.714	0.658	0.714	0.714	2.985
0.30	0.694	0.723	0.676	0.723	0.770	2.447
0.60	0.674	0.733	0.695	0.719	0.830	1.996
0.90	0.655	0.741	0.714	0.702	0.886	1.632
1.20	0.637	0.749	0.733	0.675	0.938	1.349
1.50	0.618	0.756	0.753	0.640	0.990	1.137
1.80	0.601	0.762	0.774	0.600	1.044	0.984
2.10	0.584	0.768	0.795	0.558	1.105	0.883
2.40	0.567	0.773	0.816	0.517	1.177	0.827
2.70	0.551	0.776	0.838	0.478	1.267	0.815
3.00	0.535	0.779	0.860	0.441	1.381	0.852

The logarithms of the activity coefficients calculated from eqn. (2) are shown as functions of m_{NaB} in Fig. 3. The experimentally estimated single ion activity coefficient γ_{Na^+} now makes it possible to calculate the alkanoate single ion activity coefficient γ_{B^-} from the defining equality

$$\log \gamma_{B^-} = 2 \log \gamma_{Na,B} - \log \gamma_{Na^+} \qquad (3)$$

The calculated values of γ_{B^-} are given in Table 1, together with the experimentally estimated values of γ_{Na^+} and γ_{Cl^-} for both three component systems.

DISCUSSION

Previous investigations of sodium hexanoate in aqueous solutions [9] and in aqueous sodium chloride solutions [3,10] have shown that the hexanoate forms micelles. In a sodium chloride solution of total sodium ion concentration 3.0 M the critical micelle concentration (c.m.c.) of sodium hexanoate is about 0.4 M. In a sodium chloride ionic medium with the same total concentration of sodium ions, Ödberg et al.[11] have found a considerable change in the spin relaxation rate of the protons bound to the hydrocarbon chain when the sodium hexanoate concentration exceeds 0.3 M.

Figs. 1 and 2 show that $\log a_w$ and $\log \gamma_{Na,Cl}$ both depend linearly on molarity up to 0.5 mol kg^{-1} sodium hexanoate. The same linearity is
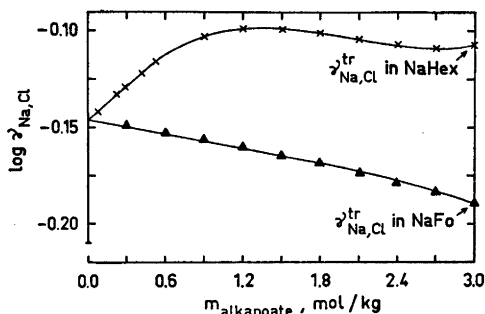
Fig. 2. The logarithm of the mean activity coefficient of sodium chloride as a function of the sodium alkanoate molality in the systems sodium chloride-sodium formate-water and sodium chloride-sodium hexanoate-water at the constant sodium molality 3.0 mol kg^{-1}, temperature 25 °C. ▲, formate; ×, hexanoate.
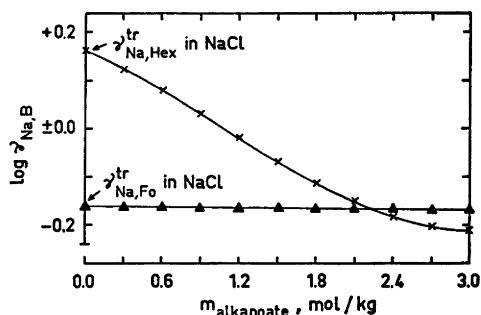
Fig. 3. The logarithm of the mean activity coefficient of sodium alkanoate as a function of the sodium alkanoate molality in the systems sodium chloride-sodium formate-water and sodium chloride-sodium hexanoate-water at the constant sodium molality 3.0 mol kg^{-1}, temperature 25 °C. ▲, formate; ×, hexanoate.

found for molalities < 0.5 mol kg^{-1} if $\log \gamma_{Na^+}$ (Table 1) is plotted against the sodium hexanoate molality. These linear relationships indicate that the components in the mixture behave as simple $1-1$ electrolytes, i.e., Harned's rule [7] is valid. At the sodium molality 3.0 mol kg^{-1} Na(Cl), an increasing deviation from this rule is observed as the sodium hexanoate molality increases above 0.5 mol kg^{-1}. This is in good agreement with the values for c.m.c. of sodium hexanoate given above. Considering the relatively high aggregation numbers of sodium hexanoate (about 17 anions [3]) one might expect that the deviations from Harned's rule should manifest themselves as well defined breaks in the curves giving $\log \gamma_{Na,Hex}$ or $\log \gamma_{Hex^-}$ as functions of the alkanoate molality. This, however, is not the case, as can be seen from Fig. 3 or Table 1. This can be attributed to the method of treatment of the experimental data. These have all been fitted to eqn. (2) using one polynomial in the whole molality range, giving slightly high values for $\gamma^{tr}_{Na,Hex}$ and $\gamma^{tr}_{Hex^-}$. The deviation is probably about 0.02 logarithmic units. γ^{tr} is the trace activity coefficient as defined by $\lim_{m_{NaB} \to 0} \gamma = \gamma^{tr}$ at constant total molality.

The activity coefficients of the chloride ions follow Harned's rule in the whole range of molalities. This is clearly because the chloride ions do not participate in micelle formation, see, among others, Danielsson.[10] Figs. 2 and 3 as

well as Table 1 show that Harned's rule is valid for all formate molalities and that the formate ion behaves quite analogously to singly charged anions of ordinary dimensions. The inclusion of the formate into this investigation is justified by the possibilities of obtaining information about the influence of the carboxylic group (COO^-) on water, an effect which may apply for the higher homologues, acetate, propionate, butyrate, pentanoate, and hexanoate.

There are no experimental data directly comparable to the present investigation. The results, however, are in good agreement with the general picture of the structure of the solutions of other homologues that has been obtained in earlier investigations.[1,2]

The differences in the activity coefficients of formate and hexanoate at low alkanoate molalities (e.g., Table 1 and Fig. 3) merit a short discussion.

Gurney[12] divides ions into structure makers and structure breakers, that is, ions that increase and decrease the hydrogen bonding of water, respectively. Snell and Greyson[13] investigated the whole series of homologues from sodium formate to sodium hexanoate. On the basis of transfer entropies from heavy to normal water they concluded that the formate is a structure breaker and hexanoate is a structure maker. Gurney[12] considers the chloride ion a weak structure breaker. The almost constant water activity shown in Fig. 1 for mixtures of sodium chloride and sodium formate indicates that the formate ion is weakly structure-breaking too. This is also seen from the transfer entropies tabulated by Snell and Greyson.[13] From these it may be concluded that the hexanoate ion is a strong structure maker. On the basis of apparent molal enthalpy data, an increase in structure making effects has also been found by Lindenbaum[14] for the homologues acetate < butyrate < pentanoate. From investigations of the near-infrared spectra of $H_2O - D_2O$ solutions of sodium alkanoates, Worley and Klotz[15] have concluded that the sodium formate has a weakly structure-breaking effect. They found no effect at all for the sodium acetate and an increasing structure-making effect as the number of carbon atoms in the hydrocarbon chain increases.

Gurney[12] considers the sodium ion a weak structure maker. However, it must be stressed that the structure-making effect of the sodium ion is caused by ion-dipole attraction of the water molecules, whereas the structure-making effect of, for example, the hexanoate ion implies the stabilization of water cages around the hydrocarbon chain. Gurney also concludes that the more similar the anion and the cation are with respect to their effects on the structure of water, the smaller is the activity coefficient. Accordingly, $\gamma^{tr}_{Na,B}$ for the formate should be smaller than for the hexanoate, since there is a large difference between the structure-making effect of the sodium ion and that of the hexanoate ion. Since the sodium ion is common for both salts, $\gamma^{tr}_{Fo^-}$ should also be smaller than $\gamma^{tr}_{Hex^-}$. The results of this investigation show that this is the case.

This discussion of the relation between the activity coefficients of the anions and their effect on the structure of the solvent does not, of course, pertain to higher hexanoate molalities where the association to smaller and larger polynuclear aggregates completely dominates the dependence of the activity coefficients on the molalities.

REFERENCES

1. Backlund, S. *Acta Chem. Scand.* 25 (1971) 2070.
2. Backlund, S., Eriksson, F. and Friman, R. *Acta Chem. Scand.* 27 (1973) 3234.
3. Danielsson, I. and Stenius, P. *J. Colloid Interface Sci.* 37 (1971) 264.
4. Brown, A. S. *J. Amer. Chem. Soc.* 56 (1934) 646.
5. Danielsson, I. *Proc. 3rd Scandinavian Symp. Surface Chemistry, Fredensborg 1967*, Nordforsk, pp. 1 – 7.
6. Harned, H. S. *J. Amer. Chem. Soc.* 57 (1935) 1865.
7. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1959, pp. 492 – 493 and 438 – 450.
8. Guggenheim, E. A. *J. Phys. Chem.* 34 (1930) 1758.
9. Markina, Z. N., Tsikurina, N. N. and Kostovo, N. Z. *Kolloid. Zh.* 26 (1964) 76.
10. Danielsson, I. *Proc. 5th Intern. Congr. Surface Active Substances, Barcelona 1968*, Ediciones Unidas, Barcelona 1969, Vol. II, p. 869.
11. Ödberg, L., Svens, B. and Danielsson, I. *J. Colloid Interface Sci.* 41 (1972) 298.

12. Gurney, R. W. *Ionic Processes in Solution,* McGraw, New York 1953, pp. 248–261.
13. Snell, H. and Greyson, J. *J. Phys. Chem.* 74 (1970) 2148.
14. Lindenbaum, S. *J. Phys. Chem.* 74 (1970) 3027.
15. Worley, J. D. and Klotz, I. M. *J. Chem. Phys.* 45 (1966) 2868.

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