

The Activity of the Acetate Ion in Aqueous Sodium Chloride Solutions

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In connection with studies on the association of short-chain alkali metal alkanooates in ionic media 3 molar in Na(Cl), a method has been developed for the estimation of the activity coefficients of alkanooate ions in the concentration range where no association takes place. The sodium alkanooate-sodium chloride-water systems are treated formally as systems of four components, *viz.* sodium ion, chloride ion, alkanooate ion, and water. Potentiometric data (a_{NaCl} , a_{Cl} , a_{Na}) and vapour pressure data ($a_{\text{H}_2\text{O}}$) are used to calculate the activities of the alkanooate ions from the Gibbs-Duhem law. Results for solutions of sodium acetate in the ionic medium Na(Cl) at 25°C are presented.

Despite the doubts expressed especially by Guggenheim¹ about the justification of determining the activities of individual ionic species, a great deal of work has been done to estimate such activities. The main difficulty is the experimental determination of the diffusion potential, whose magnitude cannot be estimated without knowledge of the activities of the ions under study.² However, Frank³ has claimed that physical significance can be ascribed to the activities of individual ionic species. The activities of ions, taken together with the mean activities of individual salts, provide a better idea of the properties of electrolyte mixtures than the mean activities alone.

The association of short-chain alkanooates in media of constant high ionic strength (3 *c* Na(Cl)) has been studied by determining hydrolytic equilibrium constants by potentiometric measurements in our laboratory.⁴⁻¹¹ The aim of the work described in this paper was to determine to what extent the activity of the acetate ion (Ac) varies with its concentration in such media. Such variation must occur in principle according to the studies of Harned and his co-workers,¹² on activities in concentrated solutions of mixed electrolytes.

Since Bury,¹³ and especially Hartley,¹⁴ outlined the classical theory of micelle formation in association colloid solutions, the activities of free paraffin-chain ions in such solutions have attracted the attention of investigators. Already in the forties, Ekwall and Harva,¹⁵ and later Kolthoff and Johnson,¹⁶

attempted to measure these activities by means of electrodes of second order. It has been established in many studies ^{7,8} that sodium acetate (NaAc) does not undergo association in aqueous solution, whereas its higher homologues, sodium butyrate ⁵ and sodium valerate, ⁶ do. Our studies of the activities of alkanooate ions in these associated systems are being continued.

EXPERIMENTAL

The experimental work involved the evaluation of the mean activity coefficient of sodium chloride and the activity coefficient of the chloride ion by potentiometric measurements, and the evaluation of the activity of water by osmotic measurements, all in the three-component system sodium chloride–sodium acetate–water. The total concentration range was varied from 0.1 to 3 molar.

1. *Chemicals.* Sodium chloride and sodium acetate trihydrate of guaranteed reagent grade from E. Merck AG were employed without further purification in the preparation of the solutions. The water used was twice distilled water that had been deionised; its specific conductance was $0.6 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ at 25°C.

2. *Solutions.* The prepared solutions had the following compositions:

i	Solution mol/l	$c_{\text{Na}}/c_{\text{Ac}}$	Symbol in Figs. 3, 4, 6–11
0	3 c NaCl	6/0	○
1	2.5 c NaCl + 0.5 c NaAc	6/1	×
2	2.0 c NaCl + 1.0 c NaAc	6/2	●
3	1.5 c NaCl + 1.5 c NaAc	6/3	▽
4	1.0 c NaCl + 2.0 c NaAc	6/4	●
5	0.5 c NaCl + 2.5 c NaAc	6/5	△
(6)	(Extrapolated results)	(6/6)	

c_{Na} and c_{Ac} are the molarities of Na^+ and Ac^- in the mixed electrolyte. *i* denotes the number of the mixed electrolyte. The specific gravities of the solutions were determined for the conversion of concentrations to molalities (*m*). All the solutions and the employed water were saturated with silver chloride; the resulting increase in chloride ion concentration was disregarded.

3. *Potential measurements.* The measurements consisted of automatically recorded volumetric titration data. The emf's of the following two cells were measured:

Cell 1: Ag,AgCl/3 c NaCl//NaCl,NaAc/Na-glass.

Cell 2: Ag,AgCl/3 c NaCl//NaCl,NaAc/AgCl,Ag.

The reference cell and the "Wilhelm" bridge were similar to those described by Sillén.¹⁷ The bridge solution was about 6 molal in ammonium nitrate. The measuring cell, reference cell, and the bridge were immersed in a water bath at $25.00 \pm 0.05^\circ\text{C}$.

a. *Electrodes.* The glass electrode was one of type GNA 33, manufactured by Electronic Instruments Ltd.¹⁸ The electrode was conditioned in 0.1 c sodium chloride, and stored in a sodium chloride solution of the same concentration. The time taken by the electrode to attain a constant potential is shown in Fig. 1.

The silver-silver chloride electrodes were prepared mainly as described by Brown.¹⁹ These were conditioned in 3 c sodium chloride about 48 h, before they were taken into use. The potentials of the electrodes became constant almost instantaneously.

b. *Apparatus.* The volumetric titrations were performed using a titration unit, designed in this department, that has been described by Danielsson.²⁰ The apparatus was slightly modified and increased with two components. The essential parts of the apparatus are shown in the block diagram in Fig. 2.

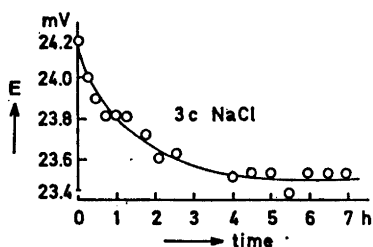


Fig. 1. The time taken by a sodium-sensitive glass electrode to attain constant potential in 3 c NaCl in cell 1.

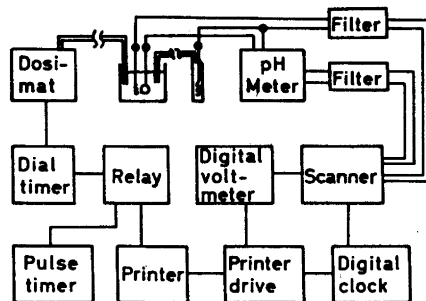


Fig. 2. Block diagram of the apparatus need for automatic potentiometric volumetric titrations.

The new components that made automatic titrations possible were an Atcotrol 305-B dial timer and a Dosimat E 412 motor burette. The dial timer, manufactured by Automatic Timing & Controls, Inc., Pennsylvania, was an interval or delay relay, driven by a synchronized motor. For our purposes, the dial timer was connected, so that it allowed current to pass to the motor burette once every hour. The accuracy of volume measurements with the motor burette was 0.03 ml, according to the manufacturer, Metrohm AG, Herisau, Switzerland. The burette was held at $25.0 \pm 0.1^\circ\text{C}$. The reproducibility of a potentiometer reading was 0.1 mV.

c. Procedure. Every titration was performed in two stages. In one stage, water was added to 30 ml of the 3 molar electrolyte mixture. The molar ionic strength I varied from 3 molar to about 1 molar. In the second stage, the 3 molar electrolyte mixture was added to 30 ml of water, whereupon the ionic strength increased from 0.05 to 1.5 c.

The course of a volumetric titration was as follows. The pulse timer sent an impulse by way of the relay to the dial timer, which in turn connected the current to the motor burette. The motor burette delivered a preselected volume of titrant through a tube to the titration cell. One ml of titrant was delivered during each period of addition. Another

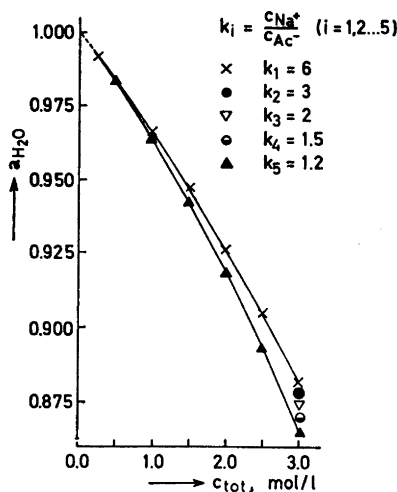


Fig. 3. Activity of water as a function of the total electrolyte concentration containing different ratios of sodium acetate and sodium chloride.

impulse from the pulse timer then put the dial timer back, and the measuring circuit was switched on by the relay.

4. *Osmotic measurements.* The activities of water in the electrolyte mixtures were determined previously by Danielsson *et al.*²¹ The measurements were performed with a Mechrolab 301 A Vapor Pressure Osmometer. In principle, the apparatus measures the temperature difference required to equalize the vapour pressures of a reference sodium chloride solution and the electrolyte solution under study. The variation of the water activity with total concentration c_{tot} is shown in Fig. 3.

RESULTS

1. Activity coefficients of sodium chloride

a. *Theoretical.* A 3 molar sodium chloride solution was used as a reference solution in the potentiometric measurements. The potentials of interest here are

- (i) the difference between the potential of cell 1 and the potential of cell 2 (containing electrolyte mixtures), which we denote by E , and
- (ii) the potential of cell 1 (containing 3 molar sodium chloride solution), denoted by E_{ref} .

The mean activity coefficient of sodium chloride in an electrolyte mixture can then be calculated from the potential differences by the Nernst equation

$$\Delta E = E - E_{\text{ref}} = k \log \frac{m_{\text{Na}} m_{\text{Cl}} \gamma_{\text{NaCl}}^2}{a_{\text{ref}}^2}$$

where $k = RT \ln 10/F$, and a_{ref} is the mean activity of sodium chloride at a concentration of 3 c. When this mean activity is taken to be 2.325, as given in the book by Robinson and Stokes,²² it is found that $k \log a_{\text{ref}}^2 = 43.3$ mV at 25°C. Values of the molal activity coefficients of sodium chloride in solutions,

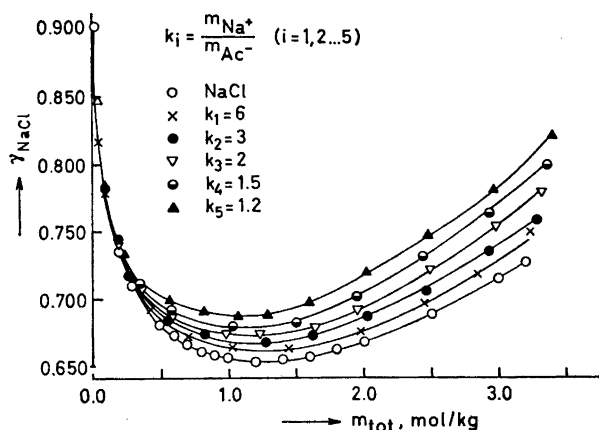


Fig. 4. Molal mean activity coefficient of sodium chloride as a function of total electrolyte concentration in solutions containing sodium acetate and sodium chloride in different ratios. The lowermost curve is a plot of Robinson and Stokes' data for sodium chloride solutions.²²

containing different ratios of sodium chloride and sodium acetate, are plotted against the total salt concentration in Fig. 4.

b. Applicability of Harned's rule to sodium chloride. Comparison with isopiestic data. For comparison with previously reported data, the logarithms of the activity coefficients of sodium chloride at ionic strengths 3.0, 1.0, and 0.1 molal are plotted against m_{Cl} ($m_{\text{Cl}}/m_{\text{tot}}$) and m_{Ac} in Figs. 5 and 6. The

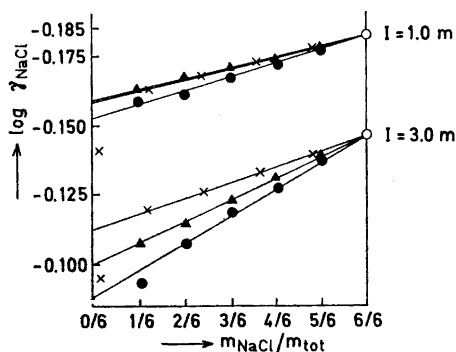


Fig. 5. Logarithm of the mean activity coefficient of sodium chloride as a function of sodium chloride concentration in solutions containing sodium acetate and sodium chloride in different ratios at total ionic strengths of 1.0 m and 3.0 m (NaCl). γ_{NaCl} : O, Robinson and Stokes;²³ x, Lanier;²³ ●, Danielsson;²⁴ ▲, data of present author.

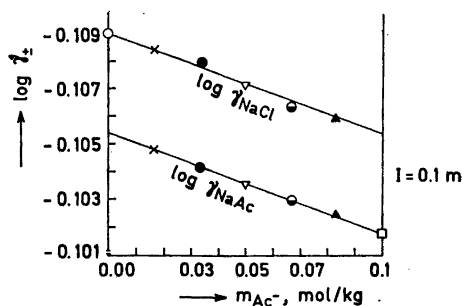


Fig. 6. Logarithms of the mean activity coefficients of sodium chloride and sodium acetate as functions of acetate ion concentration in solutions of ionic strength 0.1 m (NaCl) containing sodium acetate and sodium chloride.

activity coefficients reported by Lanier were determined by potentiometry,²³ and those reported by Danielsson *et al.* by osmometry.²⁴ Our results are summarised in Table 1.

Table 1. Activity coefficients of sodium chloride in solutions containing sodium chloride and sodium acetate.

$\frac{m_{\text{Na}}}{m_{\text{Ac}}}$	$\log \gamma_{\text{NaCl}}$		
	$I = 0.1 \text{ m}$	$I = 1.0 \text{ m}$	$I = 3.0 \text{ m}$
6/0	-0.1090	-0.1820	-0.1460
6/1	-0.1084	-0.1783	-0.1387
6/2	-0.1079	-0.1740	-0.1310
6/3	-0.1072	-0.1705	-0.1232
6/4	-0.1065	-0.1675	-0.1149
6/5	-0.1059	-0.1629	-0.1071
(6/6)	(-0.1054)	(-0.1590)	(-0.1000)

2. Activity coefficients of the chloride ion

Activity coefficients of the chloride ion were evaluated from emf's of cell 2. It was assumed that, as postulated by Guggenheim,²⁵ $\gamma_{\text{NaCl}}^\circ = \gamma_{\text{Na}}^\circ = \gamma_{\text{Cl}}^\circ$ in the additive free sodium chloride-water system.

$$E = E' + k \log a_{3 \text{ Cl}} - k \log a_{\text{Cl}} + E_{\text{diff}}$$

$a_{3 \text{ Cl}}$ is the activity of the chloride ion at a concentration of 3 c NaCl, and E' is the difference between the standard potentials of the two silver-silver chloride electrodes. By combining the constant terms E' , E_{diff} , and $k \log a_{3 \text{ Cl}}$, and call this magnitude E° , we get

$$\log \gamma_{\text{Cl}} = \frac{E^\circ - E - k \log m_{\text{Cl}}}{k}$$

The values of E° were determined previously by potentiometric measurements on solutions of constant ionic strength (3 c Na(Cl)).²⁴ The results of our measurements are presented in Fig. 7. The logarithms of the activity coefficients

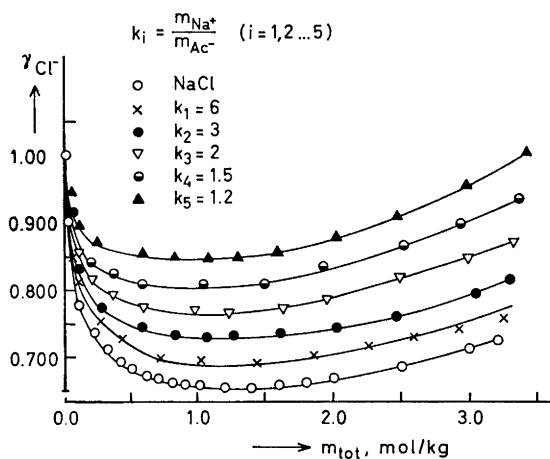
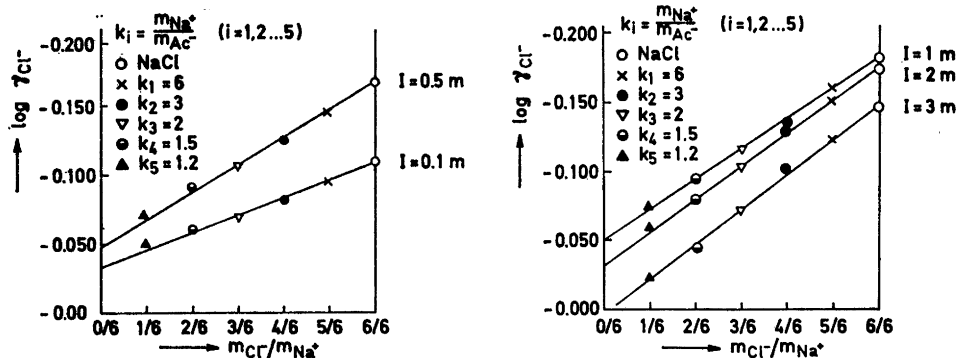


Fig. 7. Molal activity coefficient of chloride ion as a function of the total electrolyte concentration in solutions containing sodium acetate and sodium chloride in different ratios. The curve for sodium chloride is based on data of Robinson and Stokes.²²

of chloride ion are plotted against $m_{\text{Cl}}/m_{\text{Na}}$ at ionic strengths 3.0, 2.0, 1.0, 0.5, and 0.1 molal in Figs. 8 and 9. The values are given in Table 2.

3. Activity coefficient of the acetate ion

a. Theoretical. When the Gibbs-Duhem equation $\sum_{j=1}^4 X_j d\mu_j + SdT - VdP = 0$ is applied to the four-component system $\text{Na}^+ - \text{Cl}^- - \text{Ac}^- - \text{H}_2\text{O}$, one



Figs. 8 and 9. Logarithm of the molal activity coefficient of chloride ion as a function of the molal ratio of chloride to sodium ions in solutions of ionic strengths 0.1, 0.5, 1.0, 2.0, and 3.0 m (Na(Cl)) containing sodium acetate and sodium chloride.

Table 2. Activity coefficients of the chloride ion in solutions containing different ratios of sodium chloride and sodium acetate.

$\frac{m_{\text{Na}}}{m_{\text{Ac}}}$	$\log \gamma_{\text{Cl}}$				
	$I=0.1 \text{ m}$	$I=0.5 \text{ m}$	$I=1.0 \text{ m}$	$I=2.0 \text{ m}$	$I=3.0 \text{ m}$
6/0	-0.110	-0.167	-0.182	-0.175	-0.146
6/1	-0.094	-0.144	-0.160	-0.150	-0.122
6/2	-0.082	-0.126	-0.137	-0.129	-0.100
6/3	-0.070	-0.107	-0.116	-0.102	-0.071
6/4	-0.060	-0.090	-0.094	-0.079	-0.045
6/5	-0.049	-0.069	-0.073	-0.058	-0.021
(6/6)	(-0.033)	(-0.048)	(-0.050)	(-0.031)	(-0.005)

Table 3. Activity coefficients of the acetate ion in solutions containing mixtures of sodium acetate and sodium chloride.

$\frac{m_{\text{Na}}}{m_{\text{Ac}}}$	$\log \gamma_{\text{Ac}}$			
	$I=0.5 \text{ m}$	$I=1.0 \text{ m}$	$I=2.0 \text{ m}$	$I=3.0 \text{ m}$
6/1	-0.120	-0.116	-0.050	-0.038
6/2	-0.099	-0.084	-0.003	-0.069
6/3	-0.077	-0.042	0.035	0.100
6/4	-0.048	-0.005	0.079	0.142
6/5	-0.020	0.031	0.118	0.182
(6/6)	(0.006)	(0.068)	(0.160)	(0.213)

obtains the following relationship when the temperature and pressure are constant, and the concentrations are molalities:

$$-d(\ln a_{\text{Ac}}) = \frac{m_{\text{Na}}}{m_{\text{Ac}}} d(\ln a_{\text{Na}}) + \frac{m_{\text{Cl}}}{m_{\text{Ac}}} d(\ln a_{\text{Cl}}) + \frac{m_{\text{w}}}{m_{\text{Ac}}} d(\ln a_{\text{w}}) \quad (1)$$

μ_j denotes the chemical potential of the component j , and m_{w} the molality of water. In each series of measurements, the ratio $m_{\text{Na}}/m_{\text{Ac}}$ was held constant. According to the electroneutrality condition $m_{\text{Na}} = m_{\text{Cl}} + m_{\text{Ac}}$, we have the constant ratios $m_{\text{Cl}}/m_{\text{Ac}} = k_i - 1$, and $m_{\text{Na}}/m_{\text{Cl}} = k_i/(k_i - 1)$, where $k_i = m_{\text{Na}}/m_{\text{Ac}}$ and $i = 1, 2, 3, 4$, and 5 . All quantities in eqn. (1), except a_{Na} and a_{Cl} , can be measured accurately and can hence be combined. Introducing the activity coefficients $\gamma_j = a_j/m_j$ and mean activity coefficient $\gamma_{\text{NaCl}} = a_{\text{NaCl}}/m_{\text{NaCl}} = (a_{\text{Na}}a_{\text{Cl}})^{1/2}/m_{\text{NaCl}}$, we have

$$\begin{aligned} -d(\ln \gamma_{\text{Ac}}) &= 2 k_i d(\ln \gamma_{\text{NaCl}}) - d(\ln \gamma_{\text{Cl}}) + \\ &+ d [k_i \ln m_{\text{Na}} + (k_i - 1) \ln m_{\text{Cl}} + \ln m_{\text{Ac}}] + \frac{m_{\text{w}}}{m_{\text{Ac}}} d(\ln a_{\text{w}}) \end{aligned} \quad (2)$$

If we note that the data of each series of experiments relate to a constant salt concentration ratio, we may write

$$\begin{aligned} -d(\ln \gamma_{\text{Ac}}) &= 2 k_i d(\ln \gamma_{\text{NaCl}}) - d(\ln \gamma_{\text{Cl}}) + \\ &+ 2 k_i d(\ln m_{\text{Cl}}) + \frac{m_{\text{w}}}{m_{\text{Ac}}} d(\ln a_{\text{w}}) \end{aligned} \quad (3)$$

If we write

$$d(\ln a_{\text{w}}) = \frac{d(\ln a_{\text{w}})}{d(\ln m_{\text{Cl}})} d(\ln m_{\text{Cl}})$$

and then combine the last two terms in this equation and change over to Briggsian logarithms, we obtain

$$\begin{aligned} d(\log \gamma_{\text{Ac}}) &= d(\log \gamma_{\text{Cl}}) - 2 k_i d(\log \gamma_{\text{NaCl}}) \\ &- \frac{2}{\ln 10} \left\{ \frac{2 k_i + m_{\text{w}}(k_i - 1) \frac{d(\ln a_{\text{w}})}{d(\ln m_{\text{Cl}})}}{\sqrt{m_{\text{Cl}}}} \right\} d \sqrt{m_{\text{Cl}}} \end{aligned} \quad (4)$$

In our calculations, we took as the lower integration limit the one, where the total salt concentration is $0.1 c \approx 0.1$ m. This presumes that the value of the activity coefficient of acetate ion can be estimated in all solutions in which the total salt concentration has this value.

If we apply Harned's rule²² to mixtures, in which the ionic strength is 0.1 molal, we have

$$\begin{cases} \log \gamma_{\text{NaCl}} = \log \gamma_{\text{NaCl}}^{\circ} - \alpha m_{\text{NaAc}} \\ \log \gamma_{\text{NaAc}} = \log \gamma_{\text{NaAc}}^{\circ} - \beta m_{\text{NaCl}} \end{cases}$$

α was determined experimentally (Fig. 6), and $\gamma_{\text{NaCl}}^{\circ}$ and $\gamma_{\text{NaAc}}^{\circ}$ are, as given by Robinson and Stokes,²² the mean activity coefficients of sodium chloride and sodium acetate, respectively, in the additive free salt-water systems. Kortüm² has given the following equation for the evaluation of the constant β :

$$\beta = \alpha - \frac{2}{m_{\text{tot}}^2} \int_0^{0.1} m \, d \left(\frac{\ln \gamma_{\text{NaCl}}^\circ}{\ln \gamma_{\text{NaAc}}^\circ} \right)$$

Values of $\gamma_{\text{NaAc}}^\circ$ at ionic strengths below 0.1 molal have not been reported, and hence we calculated the values from the equation proposed by Guggenheim²²

$$\log \gamma_{\text{NaAc}}^\circ = -A|z_+||z_-| \frac{\sqrt{I}}{\sqrt{1 \text{ mol/kg} + \sqrt{I}}} + \lambda m_{\text{NaAc}}$$

where z is the ionic charge, $A = 0.5091$ at 25°C , and $\lambda = 0.185 \text{ mol}^{-1}\text{kg}$ (Harned and Owen²⁶ give the value $\lambda = 0.252 \text{ mol}^{-1}\text{kg}$). Values so calculated are plotted in Fig. 6.

The values of γ_{Na} at the ionic strengths in question were calculated from emf data for cell 1, assuming that γ_{Ac} at 0.1 m can be estimated with sufficient accuracy from the expression

$$\gamma_{\text{Ac}} = \gamma_{\text{NaAc}}^2 / \gamma_{\text{Na}}$$

When eqn. (4) is integrated between total concentrations 0.1 m and m , one obtains the expression

$$\log \gamma_{\text{Ac}} = \log \gamma_{\text{Cl}} - 2k_i \log \gamma_{\text{NaCl}} + K_i - 2 \log e \int_{\sqrt{m_{0.1\text{Cl}}}}^{\sqrt{m_{\text{Cl}}}} \left\{ \frac{2k_i - m_w (k_i - 1) \frac{d(\ln a_w)}{d(m_{\text{Cl}})}}{\sqrt{m_{\text{Cl}}}} \right\} d \sqrt{m_{\text{Cl}}} \quad (5)$$

where $K_i = \log \gamma_{\text{Ac}} + 2k_i \log \gamma_{\text{NaCl}} - \log \gamma_{\text{Cl}}$ at a total concentration of 0.1 molal, and is hence known at each value of $k_i (= m_{\text{Na}}/m_{\text{Ac}})$. $m_{0.1\text{Cl}}$ is the concentration of the chloride ion at the same total concentration. The quotient $d(\ln a_w)/d(m_{\text{Cl}})$ was evaluated from the slope of the plot of $\ln a_w$ against m_{Cl} .

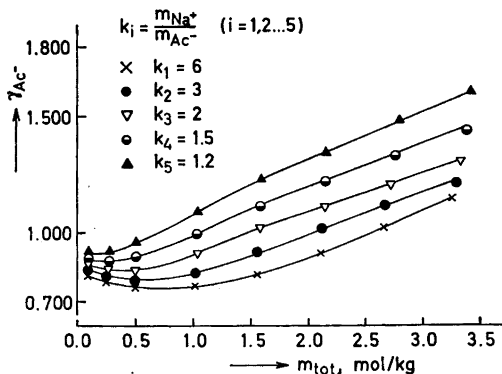
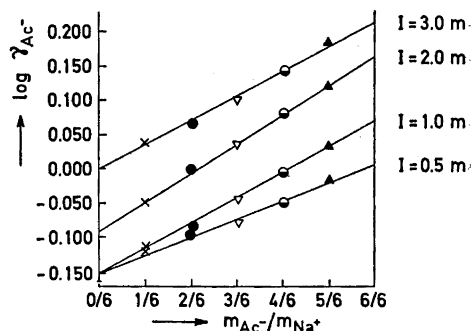


Fig. 10. Molal activity coefficient of acetate ion as a function of total electrolyte concentration in solutions containing sodium acetate and sodium chloride in different ratios.

Fig. 11. Logarithm of the molal activity coefficient of acetate ion as a function of the molal ratio of acetate to sodium ions in solutions of ionic strengths 0.5, 1.0, 2.0, and 3.0 m (NaCl) containing sodium acetate and sodium chloride.



The value of the integral was determined by a graphical method. m_w is the concentration of water in mol kg^{-1} . Values of the activity coefficient of the acetate ion thus calculated are plotted in Fig. 10.

Values of the activity coefficient of the acetate ion in different salt solutions of ionic strengths 0.5, 1.0, 2.0, and 3.0 molal are plotted against the ratio m_{Ac^-}/m_{Na^+} in Fig. 11. As the plots are linear for all ionic strengths, Harned's rule can be applied to the acetate ion as expected on the basis of earlier studies of the hydrolysis of sodium acetate.⁸

DISCUSSION

The electromotive forces of the cells were measured with an accuracy of ± 0.1 mV. If this were the only source of error, the values of the mean activity coefficients of sodium chloride and the activity coefficient of the chloride ion would be accurate to about 0.5 %. The greatest source of error is probably the diffusion potentials which are assumed to remain constant in each series of measurements. The reason why we chose to determine the activity coefficients of the chloride ion, and not the activity coefficients of the sodium ion, was that sodium ions in solutions of higher homologues of the acetate take part in complex and micelle formation, whereas chloride ions do not.

Estimation of the accuracy of the calculated activity coefficients of the acetate ion is difficult. According to Harned and Owen,²⁶ the error in the theoretically calculated activity coefficients of sodium acetate in additive free sodium acetate solutions is only ≈ 0.5 %. It seems to be a reasonable assumption that the errors in the calculated values of the activity coefficients in the 0.1 molal mixed electrolyte solutions are of the same order of magnitude. In addition, we have the uncertainties in the experimental data and in the complicated graphical estimations. A comparison with potentiometrically and osmotically determined activity coefficients of the acetate ion in solutions containing mixtures of sodium chloride and sodium acetate of ionic strength 3 c NaCl, reported by Danielsson and Öhman,²⁷ reveals that the agreement is good. This suggests that the errors in the activity coefficients of the acetate ion evaluated in this work do not exceed ± 1 %.

A series of experiments with the aim of evaluating the activities of the propionate, butyrate, and pentanoate ions in the ternary systems sodium chloride–sodium alkanoate–water is in progress. In these experiments, the ionic strengths of the studied solutions are being held constant at one level only, and the ratios of concentrations of the various ionic species are not being varied, as was done in the present study. In this way it is expected that the laborious calculations will be simplified.

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