

Activity Coefficients of Alkanoate Ions in Aqueous Three-component Solutions Containing Sodium Alkanoate and Sodium Chloride

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In connection with studies on the self-association of alkali metal alkanoates in the ionic medium 3 M Na(Cl), a method has been developed for the estimation of the alkanoate ion activity coefficients in the three-component system sodium chloride-sodium alkanoate-water at different constant ionic strengths. The activity coefficients are calculated from the activities of the other components in the system using the Gibbs-Duhem equation. The activities have been estimated from potentiometric measurements (a_{Na^+} , a_{Cl^-} , $a_{\text{Na,Cl}}$) and vapour pressures (a_w). Results are given for propionate, butyrate, and pentanoate at total ionic strengths of 1.0 mol kg⁻¹ and 3.0 mol kg⁻¹ Na(Cl) at 25°C.

This paper reports a direct continuation of the attempts to estimate the activity coefficients of alkanoate ions in mixed solutions, which started with a determination of the activity coefficients of acetate ions in sodium chloride solutions.¹ The activity coefficients of propionate, butyrate, and pentanoate ions in sodium chloride solutions are investigated and calculated using the Gibbs-Duhem equation. The experimental part includes potentiometric titrations with a sodium responsive glass electrode, and vapour pressure osmometry determinations of the water activities in the mixtures.

Sodium propionate, butyrate, and pentanoate have previously been investigated by, among others, potentiometric studies of the hydrolytic equilibria in the ionic medium 3 M Na (Cl) (Dainelsson;² Stenius and Zilliacus³). The aim of the present investigation is to clarify to what extent the activity coefficients of the alkanoate ions change in such systems. The object is closely related to the studies of hydrolytic equilibria in that the present investigation also aims at elucidating the association of the anions in the system. A difference, however, is that there are no excess hydrogen ions in the solutions.

Danielsson,⁴ using a method developed by McKay and Perring, has calculated mean molar activity coefficients of sodium propionate and butyrate in solutions similar to those discussed here.

Note. The symbols and units in this paper follow throughout the recommendations in Ref. 5.

EXPERIMENTAL

1. *Chemicals.* The sodium chloride (E. Merck AG *p.a.* quality) was dried two days at 200°C and stored in a desiccator. The sodium alkanooates were prepared by neutralizing the corresponding fatty acids (Fluka AG *purissimum* quality) with sodium hydroxide (E. Merck AG "Titrisol") at the boiling point. The salts were dried in an evaporator over diphosphorus pentaoxide for five days at 100°C. The molar masses of the salts were checked by titration with perchloric acid in glacial acetic acid, using crystal violet as indicator. Salts with a molar mass differing more than 0.5 % from the theoretical values were rejected. The water was twice distilled and deionized. Its conductivity was 0.5 $\mu\text{S cm}^{-1}$ and its pH about 6 at 25°C.

2. *Solutions.* Sodium chloride and sodium alkanooate solutions of equal molality were prepared for each titration at a constant ionic strength. The solutions were saturated with silver chloride and stored in polyethylene bottles in darkness. Extensive precautions were taken to protect the solutions from carbon dioxide. Since all measurements of the water activities of the mixtures were made for solutions whose concentrations were measured in mol dm^{-3} at a constant molar ionic strength,⁶ these values have been recalculated as molalities at a constant molal ionic strength.

3. *Potential measurements.* The two following electrode systems were used to measure the sodium and chloride ion activities:

Cell 1: $\text{Ag, AgCl}/I_m \text{ NaCl}/I_m (\text{NaCl, NaB})/\text{Na-glass}$

Cell 2: $\text{Ag, AgCl}/I_m \text{ NaCl}/I_m (\text{NaCl, NaB})/\text{AgCl, Ag}$

where NaB is the sodium alkanooate and $I_m = \frac{1}{2} \sum_i m_i z_i^2$, (m_i = the molality of ionic species

i.) The reference electrode vessel, measuring vessel, and the bridge ("Wilhelm" type) were similar to those described by Sillén.⁷ The cells were immersed in a water bath kept at $25.00 \pm 0.05^\circ\text{C}$, an adequate temperature control for the emf measurements which were made to an accuracy of 0.1 mV. About 6 mol kg^{-1} ammonium nitrate was used in the bridge.

The glass electrode was an Electronic Instruments Ltd Type GNA 33.⁸ The potential of the glass electrode was found to vary with the illumination, and so all measurements were made at constant light conditions. The silver-silver chloride electrodes were prepared according to Brown⁹ with some minor modifications. The electrode systems were checked by titration in sodium chloride solutions.

The measurements were performed as volumetric titrations with automatic recording of the potentials in the following way. Each titration at a given ionic strength was divided into two parts. In the first part, NaCl of ionic strength I_m was added to 30 cm^3 NaB of the same ionic strength. In the second, NaB was added to NaCl.

The emf values were recorded by a digital voltmeter furnished with a printout unit. When cell 1 was used, a preamplifier was connected between the cell and the digital voltmeter. The additions were made with a motor-driven burette controlled by a dial timer. The apparatus has been described previously by, *e.g.*, Danielsson¹⁰ and Backlund.¹

4. *Vapour pressure osmometry.* The water activities a_w of the mixed electrolytes have been measured by Danielsson *et al.*⁶ These measurements have been supplemented by measurements in pure sodium alkanooate solutions. The water activities of pure sodium chloride solutions were taken from Ref. 11. The measurements were performed with a Mechrolab 301 A Vapor Pressure Osmometer.

RESULTS

1. Activity coefficients of sodium and chloride ions. The mean activity coefficients of sodium chloride

The standard state was chosen to give $\lim_{m_{\pm} \rightarrow 0} \gamma_{\pm}^* = 1$. Moreover, the Guggenheim convention¹² for pure sodium chloride-water systems was used to set the mean activity coefficient $\gamma_{\text{Na,Cl}}^* = \gamma_{\text{Na}^+}^* = \gamma_{\text{Cl}^-}^*$.

The activity coefficients of sodium ion were calculated from emf values measured with cell 1. According to the Nernst equation,

$$E_1 = E^{\ominus'}_1 + k \log a_{\text{Na}^+} + E_{\text{diff } 1} \quad (1)$$

where $E^{\ominus'}_1 = E^{\ominus}_{\text{glass}} - E^{\ominus}_{\text{AgCl,Ag}} + k \log a_{\text{Cl}^-}$ and $k = RTF^{-1} \ln 10$. a_{Cl^-} is the activity of chloride ion at the molality of I_m NaCl. The diffusion potential $E_{\text{diff } 1}$ is not zero. In measurements in pure sodium chloride solutions, the diffusion potential was shown to be constant with varying $a_{\text{Na,Cl}}$ (i.e. E_1 versus $\log a_{\text{Na}^+}$ yielded a straight line of slope k).

Ekwall and Stenius¹³ found that replacing chloride by formate ions did not change the diffusion potential to any significant extent. If $E^{\ominus'}_1$ and $E_{\text{diff } 1}$ are combined into a single quantity, E^{\ominus}_1 , the following equation, which may be used to calculate the activity coefficient of the sodium ion, is obtained

$$\log \gamma_{\text{Na}^+} = (E_1 - E^{\ominus}_1 - k \log m_{\text{Na}^+})/k \quad (2)$$

E^{\ominus}_1 is calculated from the activity¹¹ in a pure sodium chloride solution of an ionic strength equal to that of the mixed electrolyte under investigation. Values of $\log \gamma_{\text{Na}^+}$ calculated at $I_m = 1.0 \text{ mol kg}^{-1}$ and $I_m = 3.0 \text{ mol kg}^{-1}$ are given in Tables 1 and 2, respectively.

The activity coefficients of the chloride ion are calculated from the emf values of cell 2. Use of the Nernst equation and application of the same argument to cell 2 as to cell 1, gives the following expression

$$\log \gamma_{\text{Cl}^-} = (E^{\ominus}_2 - E_2 - k \log m_{\text{Cl}^-})/k \quad (3)$$

E^{\ominus}_2 consists of the constant terms $E_{\text{diff } 2}$, $k \log a_{\text{Cl}^-}$, and E' , the difference between the standard potentials of the two silver-silver chloride electrodes. E^{\ominus}_2 is determined in the same way as E^{\ominus}_1 . Values of $\log \gamma_{\text{Cl}^-}$ at $I_m = 1.0 \text{ mol kg}^{-1}$ and $I_m = 3.0 \text{ mol kg}^{-1}$ are given in Tables 1 and 2, respectively.

The mean activity coefficients of sodium chloride in the mixed electrolyte solutions were calculated from the defining equation

$$\log \gamma_{\pm} = \frac{1}{2}(\log \gamma_+ + \log \gamma_-) \quad (4)$$

Calculated mean activity coefficients $\gamma_{\text{Na,Cl}}$ at $I_m = 1.0 \text{ mol kg}^{-1}$ and $I_m = 3.0 \text{ mol kg}^{-1}$ are shown in Figs. 1 and 2, respectively.

Table 1. Coefficients of the polynomial $\log \gamma_x = \sum_{i=0}^3 g_i m^i_{\text{NaB}}$, where $x = \text{Na}^+$, Cl^- and B^- , in mixtures of sodium chloride and sodium alkanooate at ionic strength $I_m = 1.0 \text{ mol kg}^{-1}$.

Alkanooate	$\log \gamma_{\text{Na}^+}$			$\log \gamma_{\text{Cl}^-}$			$\log \gamma_{\text{B}^-}$					
	g_0	g_1	g_2	g_0	g_1	g_2	g_0	g_1	g_2			
Propionate	-0.1831	-0.0466	0.0135	0.0000	-0.1827	0.0767	0.0290	0.0000	-0.1174	0.1560	0.0000	0.0000
Butyrate	-0.1847	-0.1210	0.1419	-0.0608	-0.1815	0.1166	0.0342	0.0000	-0.0860	0.3479	-0.3275	0.1680
Pentanoate	-0.1829	0.0106	-0.0166	0.0000	-0.1836	0.0956	0.0380	0.0000	-0.1207	0.1908	0.0000	0.0000

Table 2. Coefficients of the polynomial $\log \gamma_x = \sum_{i=0}^3 g_i m^i_{\text{NaB}}$, where $x = \text{Na}^+$, Cl^- and B^- , in mixtures of sodium chloride and sodium alkanooate at ionic strength $I_m = 3.0 \text{ mol kg}^{-1}$.

Alkanooate	$\log \gamma_{\text{Na}^+}$			$\log \gamma_{\text{Cl}^-}$			$\log \gamma_{\text{B}^-}$					
	g_0	g_1	g_2	g_0	g_1	g_2	g_0	g_1	g_2			
Propionate	-0.1469	-0.0043	-0.0015	0.0000	-0.1464	0.0580	0.0030	0.0000	0.0839	0.0727	0.0000	0.0000
Butyrate	-0.1464	-0.0091	-0.0019	0.0000	-0.1466	0.0866	-0.0008	0.0000	0.2042	0.0187	0.0277	-0.0039
Pentanoate	-0.1476	0.0417	-0.0182	0.0009	-0.1485	0.0885	-0.0036	0.0000	0.3083	-0.0796	0.0145	0.0000

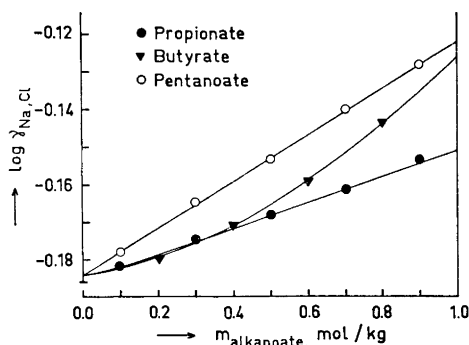


Fig. 1. The logarithm of the mean activity coefficient of the sodium chloride as a function of the alkanolate molality in mixed solutions of sodium chloride and sodium alkanolate at ionic strength $I_m = 1.0 \text{ mol kg}^{-1}$.

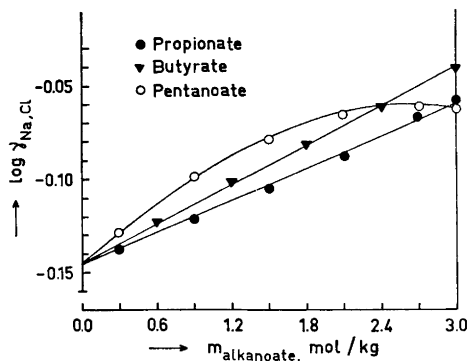


Fig. 2. As Fig. 1, but $I_m = 3.0 \text{ mol kg}^{-1}$.

2. The mean activity coefficient of the sodium alkanolate. The activity coefficient of the alkanolate ion

Application of the Gibbs-Duhem equation to the three-component system $\text{NaCl}-\text{NaB}-\text{H}_2\text{O}$ gives

$$m_{\text{NaCl}} d[\ln(a_{\text{Na}} a_{\text{Cl}})] + m_{\text{NaB}} d[\ln(a_{\text{Na}} a_{\text{B}})] + m_w d(\ln a_w) = 0 \quad (5)$$

where m_w is the molality of water. All the solutions investigated have the cation in common, and the sodium molality $m_{\text{Na}} = m_{\text{Cl}} + m_{\text{B}}$ is constant. Therefore, according to Harned,¹⁴

$$2 m_{\text{NaCl}} d(\log \gamma_{\text{Na,Cl}}) + 2 m_{\text{NaB}} d(\log \gamma_{\text{Na,B}}) = -m_w d(\log a_w) \quad (6)$$

Integration of (6), from pure NaB to a mixed solution of a given composition, gives

$$\int_{\log \gamma_{\text{Na,B}}^*}^{\log \gamma_{\text{Na,B}}} m_{\text{NaB}} d(\log \gamma_{\text{Na,B}}) = \frac{m_w}{2} \log \frac{a_{\text{wNaB}}^*}{a_w} - \int_{\log \gamma_{\text{Na,Cl}}^{\text{tr}}}^{\log \gamma_{\text{Na,Cl}}} m_{\text{NaCl}} d(\log \gamma_{\text{Na,Cl}}) \quad (7)$$

where, following Harned and Robinson,¹⁵ $\gamma_{\text{Na,Cl}}^{\text{tr}} = \lim_{m_{\text{NaCl}} \rightarrow 0} \gamma_{\text{Na,Cl}}$ is called the "trace activity coefficient". a_{wNaB}^* is the water activity of pure sodium alkanolate solution. Eqn. (7) makes it possible to calculate the mean activity coefficients of sodium alkanolate in mixtures of sodium chloride and sodium alkanolate at a constant sodium molality.

According to Harned,¹¹ there are rather simple relationships between the composition and the activity coefficients of solutions of two electrolytes at a constant ionic strength. The right-hand member of eqn. (7) is known for all values of m_{NaB} , and it may thus be assumed that it can be expressed as

a polynomial $\sum_{i=0}^n b_i m_{\text{NaB}}^{i+1}$, where b_i are constants which can be determined, e.g. by regression analysis. The units of the b_i are $(\text{kg mol}^{-1})^i$, ($i=0, 1, \dots, n$). Eqn. (7) may now be written

$$\int_{\log \gamma_{\text{Na,B}}^*}^{\log \gamma_{\text{Na,B}}} m_{\text{NaB}} d(\log \gamma_{\text{Na,B}}) = \sum_{i=0}^n b_i m_{\text{NaB}}^{i+1} \quad (8)$$

Differentiating with respect to m_{NaB} and multiplying the result by m_{NaB}^{-1} gives

$$d(\log \gamma_{\text{Na,B}}) = \sum_{i=0}^n b_i (i+1) m_{\text{NaB}}^{i-1} d(m_{\text{NaB}}) \quad (9)$$

On integration, (9) gives

$$\int_{\log \gamma_{\text{Na,B}}^*}^{\log \gamma_{\text{Na,B}}} d(\log \gamma_{\text{Na,B}}) = \sum_{i=0}^n b_i (i+1) \int_{m_{\text{NaB}}=m_{\text{Na}}}^{m_{\text{NaB}}} m_{\text{NaB}}^{(i-1)} d(m_{\text{NaB}})$$

$$\log \gamma_{\text{Na,B}} = \log \gamma_{\text{Na,B}}^* + b_0 \ln 10 \log \frac{m_{\text{NaB}}}{m_{\text{Na}}} + \sum_{i=1}^n \frac{b_i (i+1)}{i} (m_{\text{NaB}}^i - m_{\text{Na}}^i) \quad (10)$$

According to the definition $\lim_{m_{\text{NaB}} \rightarrow 0} \gamma_{\text{Na,B}} = \gamma_{\text{Na,B}}^{\text{tr}}$, a finite value of $\gamma_{\text{Na,B}}$ will be obtained on "infinite dilution" of sodium alkanooate in sodium chloride. The values of $\gamma_{\text{Na,B}}^*$ are taken from Robinson and Smith.¹⁶

Values of mean activity coefficients $\gamma_{\text{Na,B}}$, calculated from (10), are illustrated at $I_m = 1.0 \text{ mol kg}^{-1}$ and $I_m = 3.0 \text{ mol kg}^{-1}$ in Figs. 3 and 4, respectively. γ_{B^-} has been calculated from (4) and (2). Values of this quantity are given at the same ionic strengths in Tables 1 and 2, respectively.

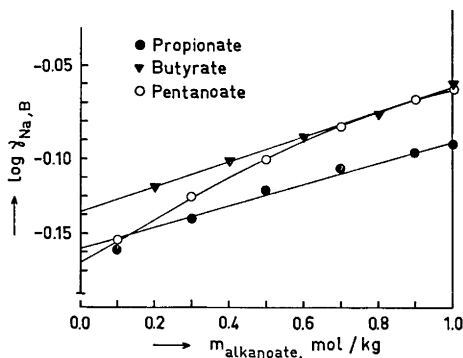


Fig. 3. The logarithm of the mean activity coefficient of the sodium alkanooate as a function of the alkanooate molality in mixed solutions of sodium chloride and sodium alkanooate at ionic strength $I_m = 1.0 \text{ mol kg}^{-1}$.

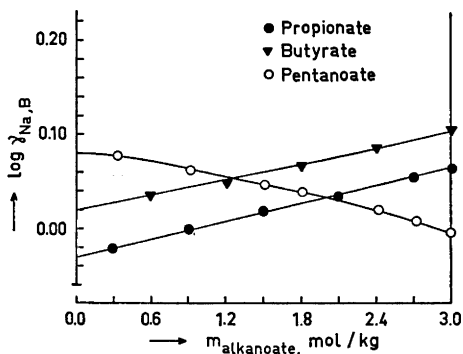


Fig. 4. As Fig. 3, but $I_m = 3.0 \text{ mol kg}^{-1}$.

DISCUSSION

A method has been developed to estimate single ion activity coefficients and mean activity coefficients in three-component systems. The method includes experimental determinations as well as theoretical calculations. The advantage of this method compared with those used earlier^{1,4} is that it is unnecessary to work over the whole molality range, from zero to a given total molality, in the mixed solution. The mean activity coefficient of one of the components can be calculated from the water activities and the activity coefficients of the other component at a single ionic strength. The method is theoretically correct if it is possible to consider the electrolyte as a 1-1 electrolyte at all the molalities investigated. The weakness of this method, as compared to the method described previously,¹ is that the effects of aggregation on the vapour pressure data for alkanooate solutions without added sodium chloride¹⁶ will influence the activity coefficients and the trace activity coefficients of the same alkanooates in molality regions where there is no association at the same ionic strength.

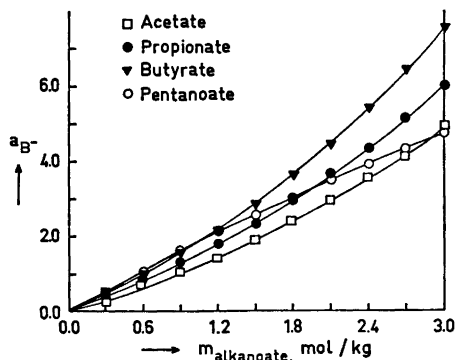
The largest source of error in experimental determinations is the diffusion potential, which has been assumed to be constant during each titration. However, a comparison with the activity coefficients calculated by Danielsson⁴ from vapour pressure data only shows a difference of less than $\pm 1\%$. This indicates that the accuracy of the activity coefficients of the sodium and chloride ions, respectively, are of the same order of magnitude.

The accuracy of the calculation of the mean activity coefficients of the sodium alkanooate is highly dependent on the experimental accuracy of the water activity. In this case too, the differences from Danielsson's⁴ values are less than $\pm 1\%$. The activity coefficients of the alkanooate ions studied so far, as well the corresponding activities, are presented for $I_m = 3.0 \text{ mol kg}^{-1}$ in Table 3. The values of the acetate ion are taken from Ref. 1. The ion activities are also given in Fig. 5. The results cannot directly be compared to the values calculated from the combination of gas chromatography and hy-

Table 3. The logarithm of the alkanooate activity coefficient and the alkanooate activity in mixtures of sodium chloride and sodium alkanooate at ionic strength $I_m = 3.0 \text{ mol kg}^{-1}$.

m_{NaB} mol kg^{-1}	Acetate		Propionate		Butyrate		Pentanoate	
	$\log \gamma_{\text{Ac}^-}$	a_{Ac^-}	$\log \gamma_{\text{Pr}^-}$	a_{Pr^-}	$\log \gamma_{\text{Bu}^-}$	a_{Bu^-}	$\log \gamma_{\text{Va}^-}$	a_{Va^-}
0.00	0.000	0.000	0.083	0.000	0.204	0.000	0.308	0.000
0.30	0.021	0.315	0.105	0.383	0.212	0.489	0.285	0.579
0.60	0.042	0.666	0.127	0.805	0.224	1.006	0.265	1.106
0.90	0.063	1.040	0.149	1.269	0.240	1.566	0.248	1.595
1.20	0.085	1.459	0.171	1.780	0.259	2.183	0.233	2.056
1.50	0.106	1.916	0.193	2.339	0.281	2.867	0.221	2.499
1.80	0.127	2.413	0.214	2.950	0.304	3.631	0.212	2.934
2.10	0.149	2.959	0.236	3.620	0.329	4.481	0.205	3.368
2.40	0.170	3.550	0.258	4.351	0.354	5.426	0.200	3.811
2.70	0.191	4.139	0.280	5.146	0.379	6.464	0.199	4.271
3.00	0.213	4.899	0.302	6.012	0.403	7.593	0.200	4.758

Fig. 5. The activity of the alkanolate ion as a function of the alkanolate molality in mixed solutions of sodium chloride and sodium alkanolate at ionic strength $I_m = 3.0 \text{ mol kg}^{-1}$.



dolytic equilibrium data given by Backlund and Danielsson.¹⁷ Neither the standard state nor the ionic strength is equal in the two cases. Moreover, the experimental uncertainty is larger in the latter case.

If, as a very rough approximation, it is assumed that Harned's rule¹¹

$$\begin{aligned}\log \gamma_{\text{Na,Cl}} &= \log \gamma_{\text{Na,Cl}}^{\text{tr}} + \alpha m_{\text{NaCl}} \\ \log \gamma_{\text{Na,B}} &= \log \gamma_{\text{Na,B}}^{\text{tr}} + \beta m_{\text{NaB}}\end{aligned}$$

is valid for the systems investigated, then

- (i) for propionate and butyrate, $\alpha = -\beta$ and $\gamma_{\text{Na,Cl}}^{\text{tr}} = \gamma_{\text{Na,B}}^{\text{tr}}$
- (ii) for pentanoate, $\alpha \neq -\beta$ and $\gamma_{\text{Na,Cl}}^{\text{tr}} \neq \gamma_{\text{Na,B}}^{\text{tr}}$

The first case has been treated thermodynamically for 1-1 electrolytes by Guggenheim.¹⁸

The second is called the "general case"; its thermodynamic treatment is very difficult. The failure of Guggenheim's model to describe the pentanoate can probably be ascribed primarily to the great difference in size between the sodium ion and the pentanoate ion.

The trace activity coefficient of sodium pentanoate seems surprisingly high if it is compared to the trace activity coefficients of sodium propionate and butyrate at $I_m = 3.0 \text{ mol kg}^{-1}$. A possible explanation for this deviation might be the uncertainties in the activity coefficients of sodium pentanoate in chloride-free solutions, as mentioned above.

For this reason, a quantitative estimation of the degree of association of sodium pentanoate from the calculated activity coefficients does not seem to be justified at this stage. However, the results are qualitatively fully compatible with earlier investigations³ into the structure of sodium pentanoate solutions.

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REFERENCES

1. Backlund, S. *Acta Chem. Scand.* **25** (1971) 2070.
2. Danielsson, I. *Proc. IVth Intern. Congr. Surface Active Substances, Brussels 1964*, Gordon and Breach Science Publishers, New York 1967, Vol. II, p. 555.
3. Stenius, P. and Zilliacus, C.-H. *Acta Chem. Scand.* **25** (1971) 2232.
4. Danielsson, I. *Proc. Vth Intern. Congr. Surface Active Substances, Barcelona 1968*, Ediciones Unidas, S.A., Barcelona 1969, Vol. II, p. 869.
5. McGlashan, M. L. *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, Butterworths, London 1971.
6. Danielsson, I. *Proc. 3rd Scandinavian Symp. Surface Chemistry, Fredensborg 1967*, Nordforsk, pp. 1-7.
7. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 901.
8. Electronic Instruments Ltd. *TDS-ELECT-9. ISSUE 16th February* (1962) pp. 1-6.
9. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
10. Danielsson, I. *Kemian Teollisuus* **23** (1966) 1081.
11. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1959.
12. Guggenheim, E. A. *J. Phys. Chem.* **34** (1930) 1758.
13. Ekwall, P. and Stenius, P. *Acta Chem. Scand.* **21** (1967) 1643.
14. Harned, H. S. *J. Am. Chem. Soc.* **57** (1935) 1865.
15. Harned, H. S. and Robinson, R. A. *Multicomponent Electrolyte Solutions*, Pergamon, Glasgow 1968.
16. Smith, E. R. B. and Robinson, R. A. *Trans. Faraday Soc.* **38** (1942) 70.
17. Backlund, S. and Danielsson, I. *Proc. VIth Intern. Congr. Surface Active Substances, Zürich 1972. In press.*
18. Guggenheim, E. A. *Phil. Mag.* [7] **19** (1935) 588.

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