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## **Ionic Interactions in Aqueous Solutions of Organic Electrolytes: The System NaCl + NaHSucc + H<sub>2</sub>O at 25°C**

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*Electrochemistry / Galvanic Cells / Ionic Solutions / Mixing-Electrolytes / Thermodynamics*

Activity coefficients for the mixed system NaCl + NaHSucc + H<sub>2</sub>O (where Succ stands for the succinate anion) are determined from emf measurements. In all cases, the stoichiometric ionic strength was kept constant at 0.1, 0.5, 1, 2 and 3 mol kg<sup>-1</sup>, and the temperature at 25°C. At each ionic strength, different ionic strength fractions,  $y_B = m_B/(m_A + m_B)$ , are studied. The results obtained were analyzed by means of various theoretical or empiric-theoretical models (Harned, Scatchard-Rush-Johnson and Pitzer). From these, it can be

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deduced that some ionic association must have taken place in this system in which the presence of the  $\text{HSucc}^-$  anions play an important role. So, not only the  $(\text{HSucc})_2^{2-}$  dimers, but also the triple interactions between like-charged ions ( $\text{Cl}^- - \text{HSucc}^- - \text{HSucc}^-$ ) and the less important interactions between unlike-charged ions ( $\text{Na}^+ - \text{Cl}^- - \text{HSucc}^-$ ) must be taken into account in this system, if the experimental results within the experimental error are to fit properly. Because the original Pitzer model does not consider these triple interactions, it cannot adequately describe the behaviour of this mixed electrolyte and, therefore, the Chan and Khoo extension of this equation must be used.

## 1. Introduction

In the study of the thermodynamic properties of aqueous solutions of mixtures which include an organic electrolyte, triple interactions between like-charged ions must be taken into account. This is the case with the  $\text{NaCl} + \text{NaHSucc} + \text{H}_2\text{O}$  system here studied (where Succ stands for the succinate ion), for which triple interactions between the anions must be considered to fit the experimental results properly. Because the initial equations from Pitzer [1,2] do not consider these types of interactions, the Chan and Khoo extension [3] of these equations was used.

## 2. Experimental

### 2.1. Chemicals and Solutions

$\text{NaCl}$ , Merck "pro analysi", was dried in vacuo at  $150^\circ\text{C}$  for 24 hours and afterwards stored in a desiccator over silica gel.

$\text{NaHSucc}$  was prepared by semi-neutralization [4] of succinic acid, Merck "pro analysi", with Merck "pro analysi"  $\text{NaOH}$  (of K content less than 0.002%).

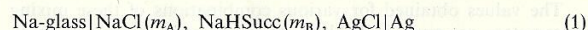
Stock solutions of both  $\text{NaCl}$  and  $\text{NaHSucc}$  were made up by direct weighing and correcting to vacuo the appropriate salt and conductivity grade water ( $\kappa_0 = 5.0 \cdot 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ ). From these, work solutions with different ionic strengths were prepared by dilution.

### 2.2. Apparatus, Cells and Electrodes

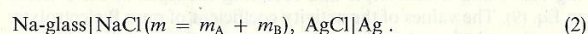
The apparatus [5], cells and electrodes [6] used were described in previous papers. The temperature inside the cells was kept constant at  $25.00 \pm 0.002^\circ\text{C}$  by using an oil thermostat bath.

## 3. Results

The emf measurements were obtained from the cell:



where  $m_i$  stands for molality. From now on,  $\text{NaCl}$  and  $\text{NaHSucc}$  will be represented by A and B, respectively. To cancel the asymmetry potential of the Na-glass electrode used, cell (1) was combined with another reference [5,7,8]:



The difference in potential of cells (1) and (2) is given by:

$$\Delta E = \frac{RT}{F} \ln \left[ \frac{m^2 \gamma_A^{\circ 2}}{(m_A + m_B) m_A \gamma_A^2} \right] \quad (3)$$

in which  $\gamma_A$  and  $\gamma_A^\circ$  stand for the ionic mean activity coefficient of  $\text{NaCl}$  in the mixed electrolyte (at  $m_A$  concentration) and the pure electrolyte (at  $m = m_A + m_B$  concentration), respectively.

Eq. (3) can be rearranged as:

$$\log \frac{\gamma_A}{\gamma_A^\circ} = \frac{1}{2} \log \frac{m^2}{(m_A + m_B) m_A} - \frac{\Delta E}{2k} \quad (4)$$

where, as usual,  $k = 2.303 RT/F$ . If  $\gamma_A^\circ$  values are known, those for  $\gamma_A$ , activity coefficient for  $\text{NaCl}$  in the mixed electrolyte solutions, can be obtained. In Table 1, the experimental  $\Delta E$  values (whose estimated error is less than  $\pm 0.07 \text{ mV}$ ) are summarized at the dif-

ferent ionic strength fractions of  $\text{NaHSucc}$ ,  $y_B = m_B/m$ , within each of the total ionic strengths studied. The values obtained for the corresponding  $\log \gamma_A$  are also presented in Table 1. The values of  $\gamma_A^\circ$  used (ionic mean activity coefficient for the pure  $\text{NaCl}$  in aqueous solution at the same total ionic strength,  $m = m_A + m_B$ ) were taken from the Ref. [9].

The results thus obtained were analyzed by using different theoretical models.

Table 1  
Summary of the  $\Delta E$  values measured and the activity coefficient values calculated for the mixed system  $\text{NaCl} + \text{NaHSucc}$

$y_B$	$\Delta E/\text{mV}$	$-\log \gamma_A$	$-\log \gamma_B^\circ$	$-\log \gamma_B^P$
$I = 0.1000 \text{ mol kg}^{-1}$				
0	0.00	0.1088 <sup>a)</sup>	0.1090	0.1104
0.2000	5.75	0.1089	0.1104	0.1119
0.4000	13.17	0.1091	0.1117	0.1133
0.6000	23.47	0.1082	0.1131	0.1148
0.8000	41.27	0.1081	0.1145	0.1162
$I = 0.5000 \text{ mol kg}^{-1}$				
0	0.00	0.1668 <sup>a)</sup>	0.1669	0.1683
0.2000	5.64	0.1660	0.1733	0.1745
0.4000	13.05	0.1675	0.1797	0.1806
0.6000	23.37	0.1653	0.1858	0.1866
0.8000	41.08	0.1645	0.1919	0.1925
$I = 1.000 \text{ mol kg}^{-1}$				
0	0.00	0.1825 <sup>a)</sup>	0.1809	0.1816
0.2000	5.57	0.1812	0.1933	0.1936
0.4000	12.89	0.1806	0.2052	0.2051
0.6000	23.18	0.1795	0.2166	0.2161
0.8000	40.96	0.1793	0.2273	0.2266
$I = 2.000 \text{ mol kg}^{-1}$				
0	0.00	0.1755 <sup>a)</sup>	0.1682	0.1688
0.2000	5.56	0.1741	0.1930	0.1931
0.4000	12.71	0.1720	0.2155	0.2153
0.6000	23.01	0.1710	0.2358	0.2355
0.8000	40.74	0.1703	0.2539	0.2536
$I = 3.000 \text{ mol kg}^{-1}$				
0	0.00	0.1463 <sup>a)</sup>	0.1355	0.1368
0.1999	5.61	0.1453	0.1744	0.1748
0.4000	12.88	0.1442	0.2082	0.2081
0.6000	23.30	0.1443	0.2370	0.2368
0.8000	41.11	0.1442	0.2606	0.2609

<sup>a)</sup> From Ref. [9].

### 3.1. Harned's Rule

The simplest model used was the Harned rule. The equation for the electrolyte A in a mixture with the electrolyte B, at a constant ionic strength, is [10]:

$$\log \frac{\gamma_A}{\gamma_A^\circ} = -\alpha_A m_B - \beta_A m_B^2 \quad (5)$$

which relates this  $\log(\gamma_A/\gamma_A^\circ)$  to the sodium bisuccinate concentration (electrolyte B) in the mixture, when the total ionic strength



( $m = m_A + m_B$ ) in the solution remains constant. In this study, at all the ionic strengths here used, the results obtained for  $\log \gamma_A$  can be fitted, within the limits of the experimental error, with  $\beta_A = 0$ , i.e., by using only the linear term of Eq. (5). The values found for the adjustable parameter  $\alpha_A$  at each ionic strength studied are given in Table 2 together with those of the standard deviation of the fitting for these  $\log \gamma_A$  values.

Table 2  
Summary of the Harned parameter values for NaCl in the mixed NaCl + NaHSucc system

$I/\text{mol kg}^{-1}$	$\alpha_A$	$\sigma/\text{mV}$
0.1	-0.0059	0.04
0.5	-0.0052	0.03
1.0	-0.0046	0.04
2.0	-0.0036	0.05
3.0	-0.0011	0.05

### 3.2. Scatchard-Rush-Johnson Treatment

Due to the fact that the values of the parameter  $\alpha$  depend on the ionic strength and also on the nature of the electrolyte under consideration, it is usual to use theoretical or empiric-theoretical equations (which include parameters related to the mixture only instead of to the electrolyte) to fit these  $\log \gamma_A$  values. One of these is the Scatchard-Rush-Johnson [11,12] equation.

In the case of a mixture of two 1:1 electrolytes, A and B, the equation for electrolyte A is given by:

$$\ln \frac{\gamma_A}{\gamma_A^\circ} = y_B (\phi_B^\circ - \phi_A^\circ) + \frac{1}{2} y_B (b_{01} I + b_{02} I^2 + b_{03} I^3 + b_{12} I^2 + b_{13} I^3) - \frac{1}{2} y_B^2 \left( \frac{1}{2} b_{02} I^2 + \frac{2}{3} b_{03} I^3 + b_{13} I^3 \right) + \frac{3}{2} b_{12} I^2 + 2 b_{13} I^3 + \frac{1}{3} y_B^3 b_{13} I^3 \quad (6)$$

where  $b_{ij}$  represents the interaction parameters which are characteristic of the mixture and can be related to the different kinds of interaction between the ions.  $\phi_i^\circ$  is the osmotic coefficient of the  $i$  electrolyte, when it is pure in a solution at the same total ionic strength,  $m$ , of the mixture. This osmotic coefficient, for a single electrolyte, is given by [12]:

$$2(\phi_i^\circ - 1) = \frac{2S}{a_i^\circ I} [(1 + a_i I^{1/2}) - (1 + a_i I^{1/2})^{-1} - 2 \ln(1 + a_i I^{1/2})] + \sum_{n=1}^4 a_i^{(n)} I^n \quad (7)$$

where  $S$ , the Debye-Hückel limiting-law slope constant, is  $-1.17202$ , and the values of the parameters  $a_i$  and  $a_i^{(n)}$  of the pure electrolyte are given in Table 3 together with the standard deviation found for the values of  $\phi_i^\circ$ .

The results obtained for the fitting of the experimental data to Eq. (6) by using different combinations of  $b_{ij}$  parameter values are given in Table 4 together with the standard deviation of these fit-

tings. As can be seen, the combination which leads to the best fitting, within the experimental error, and moreover uses the least number of these  $b_{ij}$  parameters, is that which includes  $b_{01}$ ,  $b_{02}$  and  $b_{12}$ .

Once the values of the  $b_{ij}$  parameters are known, the activity coefficient values for the second electrolyte ( $B = \text{NaHSucc}$ ) can be calculated [12] by interchanging, in Eq. (6), the A and B subscripts and reversing the signs of the terms in  $b_{12}$  and  $b_{13}$ . The value of the activity coefficient for pure NaHSucc,  $\gamma_B^\circ$ , necessary for this calculation, can be obtained from [12]:

$$\ln \gamma_B^\circ = \frac{1}{2} \left[ \frac{2S I^{1/2}}{1 + a I^{1/2}} + \sum_{n=1}^4 a_B^{(n)} I^n \right] \quad (8)$$

The values of  $\log \gamma_B^\circ$  thus calculated are given in the fourth column in Table 1.

### 3.3. Pitzer Treatment

A simpler equation whose parameters have, in principle, a physical meaning clearer than that of the S-R-J parameters, is the Pitzer equation [1,2]. Nevertheless, the usefulness of this equation is limited since it does not take into consideration triple interactions between like-charged ions. Fortunately, this equation was extended by Chan and Khoo [3], to take into account these types of interactions. In this last case, the activity coefficient for NaCl in the mixture with another 1:1 electrolyte, NaHSucc, is given by [3,5]:

$$\ln \frac{\gamma_A}{\gamma_A^\circ} = m_B [(\beta_B^\circ - \beta_A^\circ) + (\beta_B^1 - \beta_A^1) e^{-2I^{1/2}} + m(C_B^\phi - C_A^\phi) + \theta_{\text{Cl-HSucc}} + m(\psi_{\text{Na-Cl-HSucc}}^* + \delta_{\text{Cl-HSucc}})] - m_B^2 \frac{1}{2} (\psi_{\text{Na-Cl-HSucc}}^* + 3\delta_{\text{Cl-HSucc}}) \quad (9)$$

in which  $\theta_{\text{Cl-HSucc}}$  is considered constant (and so,  $\theta_{\text{Cl-HSucc}}^\circ = 0$ ). The parameters  $\beta_i^\circ$ ,  $\beta_i^1$  and  $C_i^\phi$  for the pure electrolytes are given in Table 5. In this Eq. (9)  $\psi^*$  and  $\delta$  stand for:

$$\psi_{\text{Na-Cl-HSucc}}^* = \psi_{\text{Na-Cl-HSucc}} + \frac{1}{2} (\delta_{\text{Cl-Cl-HSucc}} + \delta_{\text{Cl-HSucc-HSucc}}) \quad (9a)$$

and

$$\delta_{\text{Cl-HSucc}} = \frac{1}{2} (\delta_{\text{Cl-Cl-HSucc}} - \delta_{\text{Cl-HSucc-HSucc}}) \quad (9b)$$

When  $\delta = 0$  and  $\psi^* = \psi$ , Eq. (9) becomes the original Pitzer equation.

The values obtained for various combinations of these mixing parameters, are given in Table 6. As can be seen, it is necessary to consider triple interactions between like-charged ions to fit these data properly, within the experimental error.

Once the mixing parameters are known, activity coefficient values for NaHSucc in the mixture can be calculated [3,5] by interchanging the A and B subscripts and reversing the signs of the  $\delta$  terms in Eq. (9). The values of the activity coefficient of pure B electrolyte,  $\gamma_B^\circ$ , to be substituted in that calculation are obtained from [1]:

$$\ln \gamma_B^\circ = -A_\phi \left[ \frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2 I^{1/2}) \right] + B_B^\phi m + \frac{3}{2} C_B^\phi m^2 \quad (10)$$

Table 3  
Values of the parameters for osmotic and activity coefficients of pure NaCl and NaHSucc

Electrolyte	$a_i$	$a_i^{(1)}$	$a_i^{(2)}$	$a_i^{(3)}$	$a_i^{(4)}$	$\sigma(\phi, \ln \gamma)$
NaCl <sup>a)</sup>	1.4323	0.049210	0.016525	-0.000684	-0.000025	0.0004
NaHSucc <sup>b)</sup>	1.3879	-0.096299	0.065254	-0.014350	0.001191	0.0009

<sup>a)</sup> From Ref. [9].

<sup>b)</sup> From Refs. [4] and [9].



Table 4  
Values obtained for the Scatchard-Rush-Johnson parameters of the mixed NaCl + NaHSucc system

$b_{01}$	$b_{02}$	$b_{03}$	$b_{12}$	$b_{13}$	$\sigma/\text{mV}$
—	—	—	—	—	2.26
0.1052	—	—	—	—	0.29
0.1433	-0.0226	—	—	—	0.16
0.1665	-0.0603	0.0106	—	—	0.15
0.1547	-0.0293	—	0.0119	—	0.06
0.1695	-0.0539	0.0070	0.0114	—	0.05
0.1729	-0.0596	0.0085	0.0229	-0.0050	0.04

Table 5  
Values for the Pitzer parameters for pure NaCl and NaHSucc

Electrolyte	$\beta_1^0$	$\beta_1^1$	$C_1^*$	$\sigma(\phi, \ln \gamma)$
NaCl <sup>a)</sup>	0.0754	0.2770	0.0014 <sub>0</sub>	0.000 <sub>5</sub>
NaHSucc <sup>b)</sup>	0.0334	0.1843	0.0008 <sub>3</sub>	0.002 <sub>3</sub>

<sup>a)</sup> From Ref. [14].

<sup>b)</sup> From Refs. [4] and [9].

Table 6  
Summary of the values obtained for the Pitzer parameters of the mixed NaCl + NaHSucc system

$\theta$	$\psi^*$	$\delta$	$\sigma/\text{mV}$
—	—	—	2.27
0.0529	—	—	0.26
0.0699	-0.0101	—	0.15
0.0751	-0.0131	0.0055	0.06

$A_\phi = 0.3915$  [13, 14] and:

$$B_B^\gamma = 2\beta_B^0 + \frac{\beta_B^1}{2I} [1 - (1 + 2I^{1/2} - 2I) e^{-2I^{1/2}}]. \quad (10a)$$

The values calculated for  $\log \gamma_B^\beta$  are collected in the last column in Table 1.

#### 4. Discussion

It is necessary to take into account three mixing parameters in both the S-R-J ( $b_{01}$ ,  $b_{02}$  and  $b_{12}$ ) and the Pitzer ( $\theta$ ,  $\psi^*$  and  $\delta$ ) fittings to describe properly the behaviour of this mixture of electrolytes within the experimental error. Hence, some type of ionic association must occur in this system. A test of this assumption can be made by using the relations between the S-R-J and the Pitzer mixing parameters:

$$b_{01} = 2\theta_{\text{Cl-HSucc}} \quad (11a)$$

$$b_{02} = 2\psi_{\text{Na-Cl-HSucc}}^* \quad (11b)$$

$$b_{12} = 2\delta_{\text{Cl-HSucc}} \quad (11c)$$

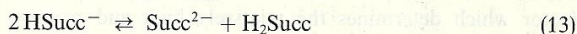
which are derived from the Eqs. (6) and (9) with only three parameters different from zero. The comparison of the values of these mixing parameters, collected in Tables 4 and 6,

agrees well with these relations, within the experimental error.

In aqueous solutions, pure NaHSucc presents ionic association. In fact, by looking at the activity coefficient values reported in the Refs. [4,15], it can be seen that they are lower than those of other 1:1 sodium salts of weak organic acids like formic, acetic or propionic acid. This fall-off of such parameters indicates that some ionic association or chemical equilibrium must be present in the aqueous solution of this electrolyte. Ionic association between the  $\text{Na}^+$  and the  $\text{HSucc}^-$  ions is unlikely due to the weakness of the acid yielding this salt. Consequently chemical equilibria must be responsible for the decrease of the activity coefficient values. In fact, due to the existence of a carboxylic group in the bisuccinate anion, which is not dissociated, hydrogen bonding between these groups should occur like in aqueous solutions of other carboxylic acids [16,17], leading to the formation of dimeric ions  $(\text{HSucc})_2^{2-}$ , in accordance with:



On the other hand, disproportionation according to:



may occur, this equilibrium being displaced to the right side depending on the ratio  $K_{a2}/K_{a1}$  ( $K_{ai}$  being the acidity equilibrium constants of the di-carboxylic acid).

Although the amounts of these last ionic species are not very large, they are important. By taking into account both (12) and (13) chemical equilibria, the relation between the stoichiometric activity coefficient for pure NaHSucc,  $\gamma_B^0$ , and the mean ionic one for the free ions in the solution,  $\gamma_B^\circ$ , is given by:

$$\gamma_B^\circ = \left(1 - 2 \frac{m' + m''}{m}\right)^{1/2} \gamma_B^0 \quad (14)$$

where  $m'$  and  $m''$  are the molal concentrations of  $\text{Succ}^{2-}$  and  $(\text{HSucc})_2^{2-}$ , respectively, in a solution of the stoichiometric molality  $m$ . By using this equation, an estimation of the concentration of the ionic species present in the solution can be made. For instance, if the concentration of the solution is 0.1 molal, the values which must be inserted into Eq. (14) are:  $\gamma_B^0 = 0.764$  [15] and  $\gamma_B^\circ = 0.778$  [9] (the latter equals that of a strong electrolyte, like NaCl, at 0.1 molality). From these, concentration values around 96% in  $\text{HSucc}^-$  and 4% in the rest of the species ( $\text{H}_2\text{Succ}$  and, overall,  $(\text{HSucc})_2^{2-}$  and  $\text{Succ}^{2-}$ ) are obtained. Hence, the value calculated for the real ionic strength of the medium is approximately 1.5% higher than the stoichiometric one.

As was indicated at the beginning of this section, some ionic association must take place in the mixed system NaHSucc + NaCl. Because pure NaCl does not present ionic association in the concentration range here studied, this phenomenon must be caused by the presence of NaHSucc in the mixture. According to Robinson et al. [19], the  $b_{ij}$  parameters (Eq. (6)) can be expressed in terms of the association constants that can be considered to take place in the mixture:



$$b_{01} = K_{XX} + K_{YY} - K_{XY} \quad (15a)$$

$$b_{02} = 3(K_{XXX} + K_{YYY}) + 2(K_{MXX} + K_{MYX} - K_{MXY}) - (K_{XXY} + K_{XYY}) \quad (15b)$$

$$b_{12} = K_{XXX} - K_{YYY} + K_{XYY} - K_{XXY} \quad (15c)$$

In the present case,  $M = \text{Na}^+$ ,  $X = \text{Cl}^-$  and  $Y = \text{HSucc}^-$ ;  $K_{YY}$  must be the global equilibrium constant which includes both Eqs. (12) and (13), and will be written as  $K'_{\text{HSucc}-\text{HSucc}}$ . Eq. (15a) can now be written as:

$$b_{01} = K_{\text{Cl}-\text{Cl}} + K'_{\text{HSucc}-\text{HSucc}} - K_{\text{Cl}-\text{HSucc}} \quad (16)$$

with

$$K'_{\text{HSucc}-\text{HSucc}} = K_{\text{HSucc}-\text{HSucc}} + K_{\text{disp}} \quad (17)$$

where  $K_{\text{HSucc}-\text{HSucc}}$  is the equilibrium constant of Eq. (12) and  $K_{\text{disp}}$  that for Eq. (13).

From these Eqs. (15), an estimation of the possible aggregates formed in the solution can be made. Given that  $K_{\text{Cl}-\text{Cl}} \approx 0$ , it can be deduced that  $K'_{\text{HSucc}-\text{HSucc}}$  must be the factor which determines the relatively high and positive value of  $b_{01}$ . Because  $K_{\text{disp}}$  can be estimated equal to 0.037 (from the value of the acidity constants for the succinic acid [9]),  $K_{\text{HSucc}-\text{HSucc}} \gg K_{\text{disp}}$  and, therefore,  $K_{\text{HSucc}-\text{HSucc}}$  is the most important term in  $b_{01}$ . On the other hand, the  $b_{12}$  parameter is also positive, so the sum of the  $K_{\text{Cl}-\text{Cl}-\text{Cl}}$  (equal to zero because  $K_{\text{Cl}-\text{Cl}} \approx 0$ ) and  $K_{\text{Cl}-\text{HSucc}-\text{HSucc}}$  must be larger than the sum of  $K_{\text{HSucc}-\text{HSucc}-\text{HSucc}}$  and  $K_{\text{Cl}-\text{Cl}-\text{HSucc}}$ . Therefore, the main contribution to the value of  $b_{12}$  is  $K_{\text{Cl}-\text{HSucc}-\text{HSucc}}$ . Finally, due to the fact that  $b_{02}$  is negative,  $K_{\text{Na}-\text{Cl}-\text{HSucc}}$  and  $K_{\text{Cl}-\text{HSucc}-\text{HSucc}}$  must be the most important terms in this  $b_{02}$ . In summary, triple interactions between like-charged ions ( $K_{\text{Cl}-\text{HSucc}-\text{HSucc}}$ ) must predominate over

those involving unlike-charged ions ( $K_{\text{Na}-\text{Cl}-\text{HSucc}}$ ), although the latter are important in this mixed system.

Finally, in Fig. 1 the trace values,  $\log \gamma_{\text{A}}^{\text{tr}}$  and  $\log \gamma_{\text{B}}^{\text{tr}}$ , are plotted against  $I^{1/2}$  together with those of the pure electrolytes,  $\log \gamma_{\text{A}}^{\circ}$  and  $\log \gamma_{\text{B}}^{\circ}$ . The behaviour of these plots agrees with previous considerations. Firstly, it can be seen that  $\gamma_{\text{A}}^{\text{tr}}$  and  $\gamma_{\text{A}}^{\circ}$  present the same outlines (curves a and b), which correspond to a strong electrolyte, although the former is slightly higher than the latter (0.011 units of  $\gamma$  in the most unfavourable case). This small difference can be explained in terms of the real ionic strength of the solution containing NaHSucc plus traces of NaCl. This real ionic strength is a little greater than the stoichiometric one, as was made clear during this discussion, which causes a shortening effect on the development of curve a. On the contrary, curves c and d develop differently. In fact, while curve c has an outline characteristic of a strong electrolyte, curve d is typical of an electrolyte which presents ionic association ( $K'_{\text{HSucc}-\text{HSucc}}$ ). This can be explained by the fact that curve c corresponds to a solution containing NaCl plus traces of NaHSucc. In this solution, all the ionic strength is provided by NaCl and so, the association equilibria predicted by Eqs. (12) and (13) cannot be produced. Consequently, the values that can be obtained for the traces of NaHSucc must correspond to those of a strong electrolyte.

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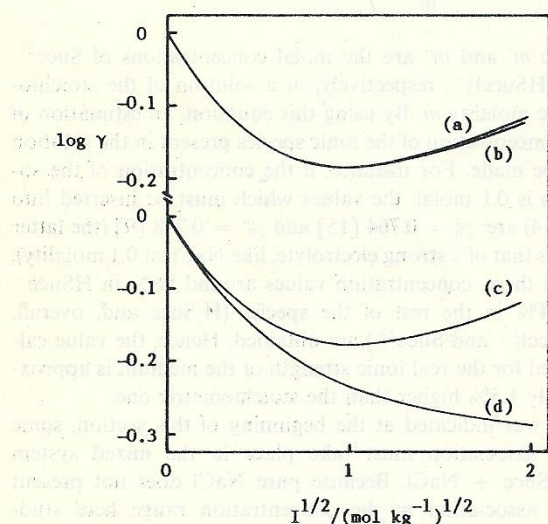


Fig. 1

Plot of  $\log \gamma^{\circ}$  and  $\log \gamma^{\text{tr}}$  against  $I^{1/2}$  for the mixture NaCl + NaHSucc:  
(a)  $\log \gamma_{\text{NaCl}}^{\circ}$ ; (b)  $\log \gamma_{\text{NaCl}}^{\text{tr}}$ ; (c)  $\log \gamma_{\text{NaHSucc}}^{\circ}$ ; (d)  $\log \gamma_{\text{NaHSucc}}^{\text{tr}}$