

**SODIUM, FLUORIDE AND PERCHLORATE ACTIVITY COEFFICIENTS IN  
NaF+NaClO<sub>4</sub> AQUEOUS MIXTURES AT 25 °C.**

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**Abstract**

A system of equations for the calculation of ionic activity coefficients in electrolyte mixtures is reported. The theoretical method used is the one from Robinson and Bates, already published. Our results are a generalisation of their equations. Mixtures with a common ion of two electrolytes with all ions hydrated are involved. A variation of the hydration number with molality is allowed. Equations for the calculation of upper absolute errors in  $\ln \gamma_i$  are derived.

*Keywords:* ionic activity coefficients, electrolyte mixture, common ion.

**Introduction**

Several reasons justify the necessity to collect data about single-ion activity coefficients in mixture of electrolytes. First, they are needed for the quantitative determination of ions in natural waters. Second, research about the determination of global stability constants of metal complexes in solution would progress if the activity of the ligand ions were known. Third, in the studies of specific adsorption of ions at a metal/solution interface it is necessary to know the activity of the ions in solution. Finally, after Pitzer [1], for complex mixture of electrolytes, it is better to use, in the theoretical developments, single-ion activity coefficients than mean activity coefficients.

We mentioned here four papers about the calculation of single-ion activity coefficients in mixture of two electrolytes: the papers of Robinson and Bates [2,3] and the papers of J.H. Vera and co-workers [4,5].

In this paper we follow the Robinson and Bates method in order to generalise their results. The experimental verification is done with NaF+NaClO<sub>4</sub> aqueous mixtures.

**Experimental**

The chemicals, NaF and NaClO<sub>4</sub>, were Merck GR pro analysi. Stock solutions at each ionic strength were prepared by weighing the solute and the solvent (twice distilled water). The working solutions at a given ionic strength and changing ionic strength fraction were made by weighing-in from stock solutions of single electrolytes.

The emf measurements were made with a voltmeter CRISON 2002 with an only input impedance higher than  $10^{14} \Omega$ . The indicator and reference electrodes and cell used were METROHM. The impedance of the Na<sup>+</sup>-SE and F<sup>-</sup>-SE was 100-200M $\Omega$  and 150 – 200 k $\Omega$ , respectively; a sodium saturated calomel electrode was used as reference

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electrode. The measuring cell, held to a stand rod, had ground-joint apertures and in the half cell bottom a thermostatic jacket. The working solutions were stirred at constant rate with a magnetic stirring bar. The temperature was kept constant at  $25.0 \pm 0.1$  °C by means of a HETO-HETOFRIG cooling bath model 03T623. The resolution of the voltmeter used for emf measurements is 0.1 mV (4-1/2 digit resolution), the imprecision of these measurements was valued at  $\pm 0.2$  mV and care was taken to reduce the inaccuracy to values not significantly greater than the imprecision, that is, the uncertainty was valued at  $\pm 0.2$  mV.

**Theory**

The calculation method now reported is a generalisation of the one published by Robinson and Bates [2,3]. It is applicable to mixtures of two electrolytes with a common ion where all ions are hydrated. In the derived equations it is considered that the ion hydration numbers are molality dependent. Following to Glueckauf [6], we can look at a mixture of two electrolytes in two ways. We can treat it as made up from the two components, hydrated electrolytes + free water, or from the analytical components, unhydrated electrolytes + total water. We combine the equations expressing the total free energy with those of Gibbs-Duhem for both cases and the final results can be resumed in the following system of equations:

$$\gamma_{M^+} = \gamma_A^{y_A} \gamma_B^{y_B} a_W^{\frac{1}{2} [h_{M^+} + y_A h_{X^-} + y_B h_{Y^-}]} \quad (1)$$

$$\gamma_{X^-} = \gamma_A^{y_A} \gamma_B^{y_B} a_W^{\frac{1}{2} [h_{M^+} - (2-y_A)h_{X^-} + y_B h_{Y^-}]} \quad (2)$$

$$\gamma_{Y^-} = \gamma_A^{y_A} \gamma_B^{y_B} a_W^{\frac{1}{2} [h_{M^+} + y_A h_{X^-} - (2-y_B)h_{Y^-}]} \quad (3)$$

Equations (1-3) are applicable for any mixture of two 1:1 electrolytes with a common cation. In our system,  $M^+ = Na^+$ ,  $X^- = F^-$ ,  $Y^- = ClO_4^-$ ,  $A = NaF$  and  $B = NaClO_4$ . The ionic strength fractions of A and B in the mixture are represented by  $y_A$  and  $y_B$ , respectively. The water activity is designed by  $a_W$ . The hydration numbers are symbolised by  $h_j$ . The equation for the dependence of  $h_j$  versus ionic strength can be derived, according to the papers of Goldsack and those of Mussini [7-10], and the final derived equation is:

$$h_j^0(I) = \frac{h_j^0}{1 + M_W I (h_{Na^+}^0 + (1-y)h_{F^-}^0 + y h_{ClO_4^-}^0)} \quad (4)$$

$h_j^0$  and  $M_W$  being the hydration numbers at infinite dilution and the molecular weight of water in  $kg \cdot mol^{-1}$ , respectively, and I is the molal ionic strength of the mixture.

**Results and discussion**

The activity coefficient of NaF in mixtures with NaClO<sub>4</sub> can be obtained by emf measurements in the following electrochemical cells:



$I_A$  and  $I_B$  being the molal ionic strength of NaF and NaClO<sub>4</sub> in the mixtures of the cell (5). The molal ionic strength of NaF in cell (6) is numerically equal to  $I_A+I_B$ . Two cells are necessary because of the application of electrochemical thermodynamics to cells (5) and (6) results in two equations with a same molality independent term that cancels when one is subtracted from the other.

Table 1 collects the different ionic strengths and the ionic strength fractions for the NaClO<sub>4</sub> in the mixtures ( $y_B$ ). The experimental potentials and the NaF activity coefficients determined are also gathered.

Table 1. Experimental data for the aqueous mixture NaF+NaClO<sub>4</sub> at 25 °C.

$I/(mol/kg)$	$y_B$	$\Delta E/(mV)$	$\ln \gamma_A$	$I/(mol/kg)$	$y_B$	$\Delta E/(mV)$	$\ln \gamma_A$
0.1	0.0	0.0	-0.2693	0.3	0.0	0.0	-0.3919
	0.1	2.6	-0.2673		0.1	2.8	-0.3947
	0.2	5.8	-0.2716		0.2	5.6	-0.3903
	0.3	9.3	-0.2720		0.3	9.3	-0.3946
	0.4	13.1	-0.2689		0.4	13.2	-0.3934
	0.5	17.9	-0.2711		0.5	17.5	-0.3869
	0.6	23.7	-0.2724		0.6	23.2	-0.3863
	0.7	31.3	-0.2764		0.7	30.6	-0.3864
	0.8	41.3	-0.2692		0.8	41.3	-0.3919
	0.9	59.0	-0.2662		0.9	59.1	-0.3908
0.5	0.0	0.0	-0.4584	0.6	0.0	0.0	-0.4835
	0.1	2.7	-0.4583		0.1	2.8	-0.4863
	0.2	5.8	-0.4597		0.2	5.8	-0.4854
	0.3	9.0	-0.4552		0.3	9.0	-0.4803
	0.4	13.2	-0.4608		0.4	13.1	-0.4830
	0.5	17.6	-0.4553		0.5	17.5	-0.4775
	0.6	23.0	-0.4488		0.6	23.0	-0.4723
	0.7	30.4	-0.4479		0.7	30.4	-0.4732
	0.8	40.7	-0.4467		0.8	40.7	-0.4708
	0.9	58.8	-0.4513		0.9	58.4	-0.4700
0.7	0.0	0.0	-0.5053	0.9	0.0	0.0	-0.5417
	0.1	2.7	-0.5051		0.1	2.4	-0.5358
	0.2	5.2	-0.4959		0.2	5.0	-0.5284
	0.3	8.3	-0.4894		0.3	8.1	-0.5218
	0.4	12.4	-0.4921		0.4	12.0	-0.5212
	0.5	17.1	-0.4925		0.5	16.4	-0.5123
	0.6	22.7	-0.4899		0.6	22.0	-0.5125
	0.7	29.8	-0.4842		0.7	29.2	-0.5093
	0.8	40.0	-0.4780		0.8	39.4	-0.5038
	0.9	57.6	-0.4748		0.9	57.2	-0.5046

The "experimental" values of NaF activity coefficients have been fitted to the Pitzer's equation. By applying the equation (68) of chapter 3 of the Pitzer monograph [1] to the NaF+ NaClO<sub>4</sub> mixtures, we have:

$$\ln \gamma_{NaF} = \ln \gamma_{NaF}^{\circ} - y_B I \Sigma + y_B I \Phi_{FP} + y_B (1 - y_B) I^2 \Phi'_{FP} + (y_B (2 - y_B) I^2 / 2) \Psi_{SFP} \quad (7)$$

where

$$\Sigma = \Delta \beta^{(0)} + \Delta \beta^{(1)} \exp(-\alpha I^{1/2}) + \Delta C^{\gamma} (2I/3) \quad (8)$$

$$\Delta \beta^{(0)} = \beta_{NaF}^{(0)} - \beta_{NaClO_4}^{(0)} \quad (9)$$

$$\Delta \beta^{(1)} = \beta_{NaF}^{(1)} - \beta_{NaClO_4}^{(1)} \quad (10)$$

$$\Delta C^{\gamma} = C_{NaF}^{\gamma} - C_{NaClO_4}^{\gamma} \quad (11)$$

$\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^{\gamma}$ ,  $\Phi$ , and  $\Psi$  being the Pitzer parameters for the single electrolytes forming the mixture and the Pitzer mixing parameters, respectively. At first, following to Pitzer [1], the main treatment for symmetrical mixing is given on the basis that each  $\Phi_{ij}$  at a given T is a constant which will be written as  $\Theta_{ij}$  following the equation (72) of Pitzer monograph. Also,  $\Phi'_{ij}$  is zero in this case. Likewise, the equation (7) has been derived assuming that the parameters for triple interaction,  $\mu_{ijk}$ , are not ionic strength dependant. Therefore, according to the equation (61) of the Pitzer monograph [1], the mixing parameter  $\Psi_{ijk}$  is not ionic strength dependant. Hence, the final form to be employed to fit the experimental activity coefficient data is:

$$\ln \gamma_{NaF} = \ln \gamma_{NaF}^{\circ} - y_B I \Sigma + y_B I \Theta_{FP} + (y_B (2 - y_B) I^2 / 2) \Psi_{SFP} \quad (12)$$

Likewise, the application of equation (69) of chapter three of [1] to the other component of the mixture, NaClO<sub>4</sub>, gives with the assumptions of the above paragraph, the following equation:

$$\ln \gamma_{NaClO_4} = \ln \gamma_{NaClO_4}^{\circ} + (1 - y_B) I \Sigma + (1 - y_B) I \Theta_{FP} + ((1 - y_B^2) I^2 / 2) \Psi_{SFP} \quad (13)$$

Equation (13) was used to calculate the activity coefficients of the sodium perchlorate in the different mixtures, once the parameters of mixing have been determined by the fit of the "experimental" activity coefficients to the equation (12).

An exhaustive derivation of the equations (7-13) and also the equation to calculate the "experimental" activity coefficients, derived from the application of electrochemical thermodynamics to cells (5) and (6), can be found in [11].

With the equations (1-4) we calculated the ionic activity coefficients collected in Table 2 for I = 0.5 and 1.0 molal ionic strengths. More exhaustive calculations were made for all ionic strengths. Likewise, different sets of hydration numbers were used but always the used set was determined by the same experimental method used in the determination of the hydration numbers. It is well known the scattering in  $h_j$  data, resulting from different measuring techniques, because they measure different hydration

number definitions. Even with the same measuring method, scattering is observed and this affected the calculated ionic activity coefficients. Calculation was made also with the hydration numbers at infinite dilution without consider the variation of  $h_j$  with molality. Finally, it must be underlined that Marcus [12] collects a great deal of hydration numbers. All  $h_j$  data were taken from the collections compiled in the mentioned reference.

Table 2. Ionic activity coefficients for the ions in the mixture NaF+NaClO<sub>4</sub> at 25 °C.

I	y <sub>B</sub>	γ <sub>Na<sup>+</sup></sub>	γ <sub>F<sup>-</sup></sub>	γ <sub>NaClO<sub>4</sub><sup>-</sup></sub>	I	y <sub>B</sub>	γ <sub>Na<sup>+</sup></sub>	γ <sub>F<sup>-</sup></sub>	γ <sub>NaClO<sub>4</sub><sup>-</sup></sub>
0.5	0.0	0.633	0.631	0.617	1.0	0.0	0.574	0.571	0.546
0.5	0.1	0.637	0.635	0.620	1.0	0.1	0.584	0.581	0.555
0.5	0.2	0.640	0.638	0.623	1.0	0.2	0.594	0.590	0.564
0.5	0.3	0.644	0.642	0.627	1.0	0.3	0.602	0.599	0.572
0.5	0.4	0.648	0.646	0.631	1.0	0.4	0.611	0.607	0.580
0.5	0.5	0.652	0.650	0.635	1.0	0.5	0.618	0.615	0.587
0.5	0.6	0.657	0.655	0.639	1.0	0.6	0.625	0.622	0.593
0.5	0.7	0.661	0.659	0.644	1.0	0.7	0.632	0.628	0.599
0.5	0.8	0.666	0.664	0.649	1.0	0.8	0.638	0.634	0.604
0.5	0.9	0.672	0.670	0.654	1.0	0.9	0.643	0.639	0.609
0.5	1.0	0.677	0.675	0.659	1.0	1.0	0.647	0.643	0.613

By applying the error theory [13], the upper absolute errors in  $\ln \gamma_j$ ,  $\Delta_{\ln \gamma_j}$ , can be estimated from the following equations:

$$\Delta_{\ln \gamma_{M^+}} = 0.018015 \Delta_h (2) I \phi \quad (14)$$

$$\Delta_{\ln \gamma_{X^-}} = 0.018015 \Delta_h (3 - y_A + y_B) I \phi \quad (15)$$

$$\Delta_{\ln \gamma_{Y^-}} = 0.018015 \Delta_h (3 + y_A - y_B) I \phi \quad (16)$$

$\Delta_h$  being the common upper absolute error in the hydration number of any of the three ions. The other symbols have their usual meanings, namely, the molal ionic strength (I) and the osmotic coefficient ( $\phi$ ).

Likewise, the upper absolute errors in  $\gamma_{MX}$  and  $\gamma_{MY}$  ( $\Delta_{\gamma_{MX}}$  and  $\Delta_{\gamma_{MY}}$ ) can be calculated from data in Table 2 (for the ionic activity coefficients) with the following equations derived by application of the error theory [13], namely:

$$\Delta_{\gamma_{MX}} = 0.0180152 \Delta_h (2 + y_B) I \phi \sqrt{(\gamma_{M^+} \gamma_{X^-})} \quad (17)$$

$$\Delta_{\gamma_{MY}} = 0.0180152 \Delta_h (3 - y_B) I \phi \sqrt{(\gamma_{M^+} \gamma_{Y^-})} \quad (18)$$

The experimental upper absolute errors can be calculated by making the subtraction between the experimental activity coefficients of Table 1 and the mean activity coefficients determined with Table 2 data and the definition of mean activity coefficient. Comparing these errors with the ones calculated from equations (17) and (18) it is found that both are in good agreement. The corresponding tabulations are omitted.

### Conclusion

It is necessary to study in deep the methodology applied in order to determine ionic activity coefficients from the mean ionic activity coefficients of the electrolytes. The hydration numbers are parameters of extraordinary importance for these studies. The literature compiles very much tabulations about  $\gamma_{\pm}$  with sufficient accuracy and precision but this is not the case with the  $h_j$  values where the scattering on the data is very significant even with a same measurement method.

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## STUDY OF THE REDUCTION OF MALEIC ACID BY ELECTROCHEMICAL SEMIINTEGRAL TECHNIQUES.

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### Abstract

The reduction of maleic acid at a spherical mercury electrode from solutions containing  $1 \text{ mol}\cdot\text{m}^{-3}$  acid has been studied at  $25^\circ\text{C}$ . The pH of solutions was controlled to 2.2 with Britton-Robinson buffer and ionic strength was adjusted with  $500 \text{ mol}\cdot\text{m}^{-3}$  NaCl. The electrochemical semiintegral methods have been employed for the data processing. The derivation of i-q-m-t equations was made following the procedure used by Oldham in the case of planar electrodes. The diffusion coefficients of each components of O/R couple have been considered to share a common value D. The mathematical methods used were those of the semicalculus.

*Keywords:* semiintegral methods, quasi-reversible reactions, maleic acid.

### Introduction

There are very much electrochemical studies about the maleic acid, but in the paper now reported, we pay attention to the references [1-3]. These papers have been analysed to fix the composition of the solutions where the reduction of maleic acid take place, essentially, as a quasi-reversible simple electrode reaction. It must be underlined that the theoretical derivations are made for this type of mechanism occurring at a spherical electrode.

The K.B. Oldham's paper [4] is the basis of the present paper. Also based in his paper, we have published yet another work for the totally irreversible simple electrode reaction case [5]. The mathematical methods employed are based in the fractional calculus [6,7].

We started with the i-t equation reported by K.B. Oldham [8] and the corresponding q-t equation for  $D_O = D_R$  case of a quasi-reversible reduction. The methods of the semicalculus were applied to both equations.

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