MEAN ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE IN WATER-ETHANOL SOLVENTS AT 25 °C

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ABSTRACT

Mean activity coefficients of sodium chloride in water-ethanol mixtures were determined from potentiometric data, at 25 °C, using the classic Pitzer model, based on molalities, and the Pitzer-Simonson model, based on molar fractions. The molalities of NaCl varied from 0.1 mol kg^{-1} to near saturation, in mixed solvents with compositions of 5, 10, 15 and 20% (w/w) ethanol. The results obtained from the two models were compared.

Key Words: Pitzer equation; Pitzer-Simonson equation; ethanol-water solvents; activity coefficients; sodium chloride.

INTRODUCTION

Since the beginning of the 20th century, the study of the mean activity coefficients of electrolytes in water-alcohol mixtures has received considerable attention in the literature [1, 2]. Most of the work deals with potentiometric data, using methanol and ethanol as second solvents. Nevertheless, for the ternary system sodium chloride+water+ethanol, the reports found in the literature comprise only a few studies [3, 4, 5].

In this work, mean activity coefficients were determined from potentiometric data for NaCl in aqueous-alcoholic solvents, with 5, 10, 15 and 20% (w/w) of ethanol. The sodium chloride concentrations varied from 0.1 mol kg^{-1} to near saturation and data were collected at 25 °C. For each ethanol content in the solvent, a function describing the variation of the mean activity coefficient with salt molality was obtained using the Pitzer model [6]. A more complex model, based on molar fractions and devised by Pitzer and Simonson [7], was also applied, and both results were compared for this ternary system.

EXPERIMENTAL

The materials used were analytical grade sodium chloride, Merck, 99.5 %+, dried in an oven for 12 hours, at 110 °C, and ethanol, Pronalab R, 99.8 %+. All solutions were prepared by weight, using deionised water with specific conductivity of 1.2 μS m^{-1}. The emf ("electromotive force") measurements were made on the cell without liquid junction

$$\mathrm{Ag} \,\Big|\, \mathrm{AgCl} \,\Big|\, \mathrm{NaCl}\ (m) \,\Big|\, \mathrm{ISE\ Na^{+}\ glass\ electrode} \qquad \text{(I)}$$

where m is the molality of sodium chloride in water-ethanol solvents (5, 10, 15, 20 % (w/w) ethanol). The electrodes were a commercial glass sodium ion selective electrode, ABB Kent Taylor, and a silver / silver chloride electrode of the thermal electrolytic type prepared following the procedure described by Bates [8]. When not in use, the sodium glass electrode was stored in a 0.1 M NaCl solution, prepared with the solvent to be used in the following run, and the silver / silver chloride electrode in a 0.1 M NaCl aqueous solution.

The cell vessel was a glass double wall container, enabling the circulation of thermostated water, from a water bath (Haake, model L) and the use of a magnetic stirrer. Through the lid, the electrodes and a glass thermometer (±0.05 °C) were immersed in the solution.

The emf measurements were obtained on a Metrohm, model 713, pH/mV meter. Voltage readings were taken as final when they were constant, within 0.1 mV, for at least 5 minutes. For each run readings were taken starting from the most dilute solution, and, at the end of the run, the reading was repeated for this solution. The difference was never greater than 0.2 mV.

In order to check the response of the electrodes, readings were also taken for aqueous solutions of NaCl, with molalities ranging from 0.1 to 4 mol kg^{-1}. After the calculation of $\gamma_\pm$, at 25 °C, using the Pitzer equation for this system [9], a plot of E against lg(m $\gamma_\pm$) showed a straight line with slope 118.26 mV and standard deviation 0.07 mV.

RESULTS AND DISCUSSION

Experimental potential data (E) for each solution are given in Table 1. The potential of cell I is given by:

$$E = E^{o} + 2\,k\,(\,\lg m + \lg \gamma_\pm\,) \qquad (1)$$

where $\gamma_\pm$ is the mean activity coefficient of NaCl, k=(RT/F)ln10, with R, T and F having their usual meaning and E^{o} is the standard potential of the cell.

Application of the Pitzer model to the emf data

The mean activity coefficient may be given by the Pitzer equation [6], which for 1-1 type electrolytes takes the form:

$$\ln \gamma_\pm = f^{\gamma} + m B^{\gamma} + m^{2} C^{\gamma} \qquad (2)$$

where

$$f^{\gamma} = -\,A^{\phi}_{mix}\,[\,m^{1/2} / (\,1+bm^{1/2}\,) + (2/b)\ln(1+bm^{1/2}\,)] \qquad (3)$$

$$B^{\gamma} = 2\,\beta^{o} + 2\,\beta^{1}\,[1-(1+\alpha m^{1/2} - \alpha^{2} m/2)\exp(-\,\alpha m^{1/2}\,)]/\alpha^{2} m \qquad (4)$$

In this equation the molality of the electrolyte, m, equals the ionic strength, I, and B^{γ} and C^{γ} represent the second and third virial coefficients, respectively. The variation of B^{γ} with the ionic strength is given by equation (4) with the parameters β^{o} and β^{1}, specific for each electrolyte. The coefficients α and b have the values 2.0 and 1.2, respectively, and the Debye-Hückel coefficient for the osmotic function, A^{ϕ}_{mix}, depends on the temperature and solvent properties. The A^{ϕ}_{mix} values for water-ethanol mixtures were taken from reference [10].

Table1. Electromotive Force Data for NaCl in Water-Ethanol Mixtures at 25 °C

m / mol kg^{-1}	E / mV				
	0 % Et.	5 % Et.	10 % Et.	15 % Et.	20 % Et.
0.1000	-17.3	-8.5	0.25	11.7	20.4
0.2348	-	-	-	-	59.3
0.2500	-	33.9	42.8	54	-
0.5000	58.9	66.5	75.3	86.15	93.9
0.7500	-	85.95	94.55	105.45	112.9
1.0000	92.15	99.8	108.6	119.3	126.7
1.2500	-	111.2	119.95	130.3	137.7
1.5000	-	120.95	129.4	139.9	146.8
1.7500	-	-	-	147.8	155.3
2.0000	128.55	136.85	145.3	155.1	162.85
2.5000	-	149.9	158.2	168.3	175.85
3.0000	-	161.25	169.7	179.8	187.35
3.5000	-	171.65	180.2	190.2	197.5
4.0000	172.75	181.15	189.7	-	-
4.5000	-	190.1	-	-	-

The values for the Pitzer parameters β^{o}, β^{1} and C^{γ} obtained by the fit of equations (1, 2) to the experimental potential data are listed in Table 2, as well as the standard potential of the cell, E^{o}, and standard deviation of the fit, SD, for each ethanol content. Figure 1 shows the variation of ln $\gamma_\pm$ with molality, for NaCl in the various solvents.

Table 2. Pitzer Parameters for Solutions of NaCl in Water-Ethanol Mixtures at 25 °C

	5 % Ethanol	10 % Ethanol	15 % Ethanol	20 % Ethanol
β^o / kg mol^{-1}	0.0848	0.0846	0.0748	0.0917
β^1 / kg mol^{-1}	0.2298	0.2800	0.3527	0.2740
C^γ / kg^2 mol^{-2}	0.0009	0.0020	0.0066	0.0016
E°/mV	123.6	133.0	145.1	155.2
SD/mV	0.07	0.06	0.10	0.13

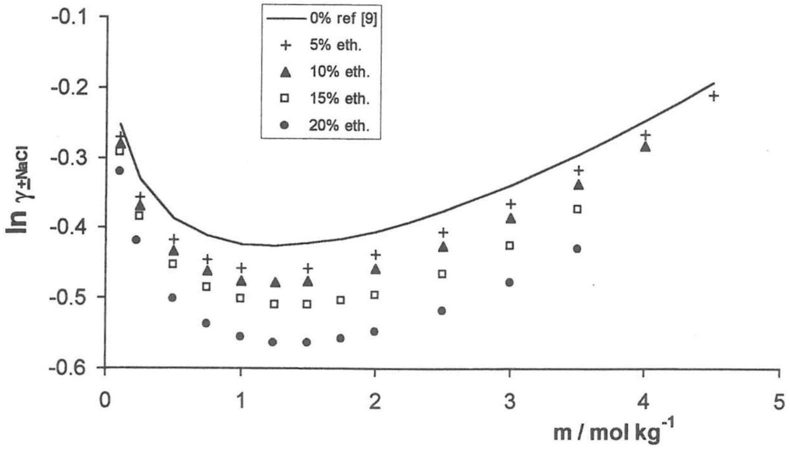

Figure 1. Variation of ln $\gamma_\pm$ with molality of NaCl at 25 °C according to the Pitzer model

Application of the Pitzer-Simonson model to the emf data

Recently, Pitzer and Simonson [7] developed a mole fraction based model for symmetrical electrolyte mixtures, that is applicable to the entire concentration range. The model is based on the assumption that the excess Gibbs energy of the mixture is a combination of two terms: short-range forces accounted for by a Margules expansion in mole fraction (with three suffix) and a long-range force Debye-Hückel term that is a function of the ionic strength of the solution only. If this model is applied to a ternary system of two neutral species, 1 and 2, and a strong electrolyte MX, the following equation for the mean activity coefficient is obtained [10]:

$$\ln\gamma_{x\pm} = -\frac{2}{\rho}A_x \ln(1+\rho\sqrt{I_x}) - \frac{A_x}{1+\rho\sqrt{I_x}}\sqrt{I_x}\,(1-2I_x) - x_X x_M B_{MX}\left[\frac{g(\alpha\sqrt{I}\,)}{2I_x} + \left(1-\frac{1}{2I_x}\right)\exp(-\alpha\sqrt{I_x})\right] +$$

$$+ x_X\, B_{MX}\, g(\alpha\sqrt{I_x}) + \frac{x_1x_2}{f^2}\left\{\left(1-f^2\right)w_{12} + 2\left(x_1-x_2\right)\frac{1-f^3}{f}u_{12} + \left[\left(1-2x_I\right)f^2-1\right]Z_{12MX}\right\} +$$

$$+ \frac{f^2-1}{f}\left(x_1W_{1MX}+x_2W_{2MX}\right) + \frac{x_1}{3f^2}\left[f^3\left(2-2x_1+x_I\right)+x_If^2\left(3x_1+x_2\right)-2x_2\right]U_{1MX} +$$

$$+ \frac{x_2}{3f^2}\left[f^3\left(2-2x_2+x_1\right)+x_If^2\left(3x_2+x_1\right)-2x_1\right]U_{2MX} \qquad (5)$$

where: $x_I = 1-x_1-x_2$; $f = 1-x_I$; $g(y) = 2\left[1-(1+y)\exp(-y)\right]/y^2$; $I_x = \frac{1}{2}(x_M+x_X)$; $\rho = 2150\,(\rho_s / DT)^{1/2}$, with ρ_s and D being the density and dielectric constant of the solvent; $A_x = (1/3)(2\pi N_A \rho_s / M_{mol})^{1/2}(e^2 / D k_B T)^{3/2}$ is the Debye-Huckel coefficient for the solvent; M_{mol} is the mean molar mass of the solvent, N_A and k_B are the Avogadro and Boltzman constants, respectively, and e is the electronic charge; w_{12} and u_{12} are parameters for the binary system (solvent 1 + solvent 2); W_{1MX}, U_{1MX} and W_{2MX}, U_{2MX} are parameters for the binary system (solvent 1 + MX) and (solvent 2 + MX), respectively; Z_{12MX} is a parameter that accounts for the triple interaction in the system.

The relationship between the activity coefficient on a mole fraction and molal basis, γ_x e γ, respectively, is

$$\gamma_x = \gamma\,(1 + 0.002\, M_{mol}\, m) \qquad (6)$$

In order to obtain the mean activity coefficient with this model, the activity coefficient in a molar fraction base from equation (5) has to be converted to a molal base, using equation (6), and then substituted in equation (1), before the fit with experimental data.

The parameters w_{12}, u_{12}, W_{1MX} and U_{1MX} can be calculated from existing data in the literature for the two different binary system (water + ethanol) and (water + sodium chloride). They were obtained from reference [10], and they are shown in Table 3. The remaining parameters, W_{2MX}, U_{2MX} and Z_{12MX}, obtained for this ternary system, are also listed in Table 3, as well as the standard deviation of the fit. The standard potentials of the cell, for each solvent, obtained by the Pitzer-Simonson model, are given in Table 4. Figure 2 shows the variation of the calculated ln $\gamma_\pm$ with molality, for NaCl, in the various water-ethanol mixtures.

The difference, in ln $\gamma_\pm$, between the two model calculations, is shown in Figure 3, for the various solvent compositions. The activity coefficients are higher when calculated by the Pitzer-Simonson equation. However this difference corresponds to an equivelent shift in the E° values, as these were also obtained from the fit of the experimental data, in both models. This has also been observed for KCl in the same solvents [10].

The cell emf can be calculated from equation (1), after substitution of ln $\gamma_{\pm}$ by the expressions (2) or (5 and 6), and Figure 4 shows the difference between these values, E_{calc}, and the experimental ones, E_{exp} (Table 1).

Table 3. Pitzer-Simonson Parameters for the System NaCl+Water+Ethanol at 25 °C

B_{MX}	8.0034
w_{12}	1.2051
u_{12}	0.2583
W_{1MX}	-6.2870
U_{1MX}	-4.5350
W_{2MX}	-7.8806
U_{2MX}	-35.0460
Z_{12MX}	15.8138
SD/mV	0.17

Table 4. Standard Potentials of Cell (I) from the Pitzer-Simonson Model

% Ethanol	E° / mV
0	114.2
5	122.9
10	132.4
15	144.1
20	153.3

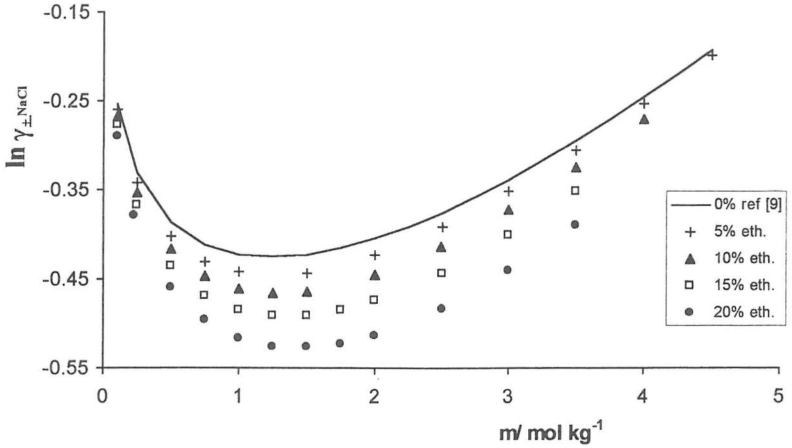

Figure 2. Variation of ln $\gamma_{\pm}$ with molality of NaCl at 25 °C according to the Pitzer-Simonson model

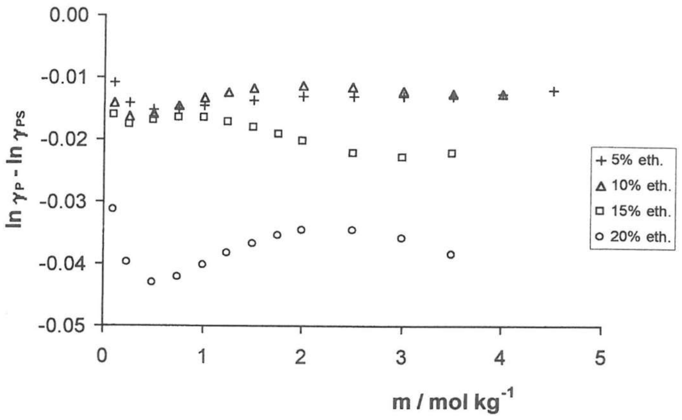

Figure 3. Difference between Pitzer-Simonson and Pitzer model calculations

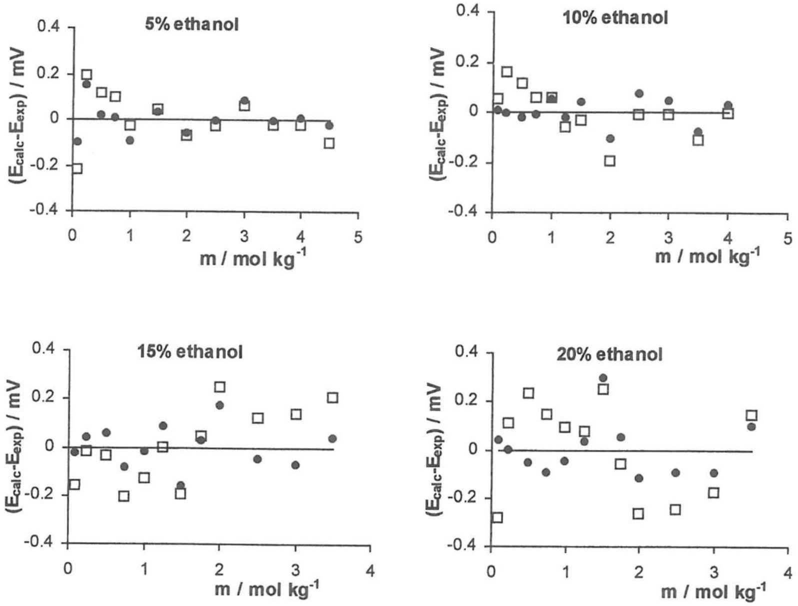

Figure 4. Residuals between calculated and experimental emf from Pitzer-Simonson (□) and Pitzer (●) models

Although both models show a good fit of the experimental data, the Pitzer-Simonson equation enables the calculation of the activity coefficients of the NaCl in solvents of any composition, within this range (0 – 20% eth.), whereas the Pitzer model would require a smooth variation of the second and third virial coefficients with solvent composition in order to perform the calculations.

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ELECTROCHEMICAL DETECTION OF BIOFILMS

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Biofilms are the result of adhesion and growth of microorganisms, creating microenvironments – a polymeric matrix – where several microbial reactions take place [1]. Usually, biofilms are divided in two groups: the ones that are beneficial, as in wastewater treatment or production of specific products, and the detrimental biofilms such as the ones that appear in drinking water pipes and heat exchangers. In any case it is very important to detect the biofilm as soon as possible, to increase its growth or to avoid the risks associated with its presence.

The ideal detector must allow the easy detection of biofilms in the early stages of formation and on line.

Electrochemical techniques are well known for their role in analytical chemistry, allowing the determination and quantification of a large number of organic, inorganic and biological compounds. These techniques have largely proved to provide an efficient means for detection *in situ* and on line of a variety of compounds [2].

In the present work, the development of a detector to function *in situ* in flow systems is described. The technique used is repetitive cyclic voltammetry applied to a platinum planar electrode of small area introduced in the system, which together with an auxiliary electrode and a reference electrode constitute an electrochemical cell. When the solution where the electrode is immersed is air-free aqueous sulfuric acid, and the platinum electrode surface is clean, the current plotted *versus* electrode potential is a cyclic voltammogram depicted in figure 1 [3]. This is a very well-known pattern and

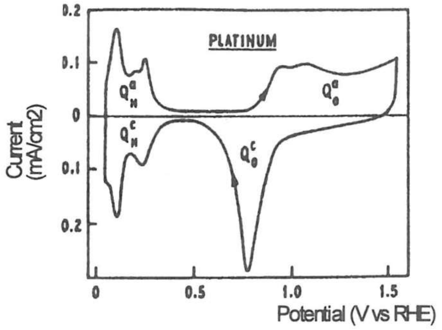

Figure 1 – Voltammogram at a platinum electrode in 1 M sulfuric acid at 25 °C; continuous triangular potential sweeps at 40 mVs^{-1}. Q_H^c and Q_H^a correspond, respectively, to the adsorption and desorption of hydrogen, and Q_O^a and Q_O^c to the adsorption and desorption of oxygen (reprinted from Woods, R., 1976).