MEAN ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE IN WATER-ETHANOL MIXTURES AT 25 °C

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ABSTRACT

Mean activity coefficients of KC1 in water-ethanol solvents were determined, using the Pitzer model, from electromotive force data, at 25 °C. The molalities of KC1 varied from 0.1 mol kg^{-1} to near saturation, in the range 0 to 20 % w/w ethanol. A modified model of the Pitzer equations was also applied to predict the mean activity coefficients of KC1 in water-ethanol and water-methanol mixtures. These results were compared with experimental values.

INTRODUCTION

Crystallization of inorganic salts by salting-out with organic solvents has long attracted the interest of the industry. Nevertheless, the effects of the mixed solvent upon the crystallization kinetics, size and habit of the crystals, are far from being well established. Therefore, the objective of the present work was to measure and correlate activity coefficients data of KC1 in water-ethanol mixtures, in order to study the growth and dissolution driving force for KC1 in this system. Potassium chloride was chosen because it is a salt whose morphologic characteristics of the crystals are well known in aqueous solutions, hence giving a good comparison.

In this work electromotive force data were collected for molalities of KC1 from 0.1 to near saturation and solvent composition of 5, 10, 15 and 20 % w/w ethanol at 25 °C. Mean activity coefficients of KC1 in water-ethanol were obtained from these data using the Pitzer model [1]. To overcome the necessity of substantial experimental data a new prediction method [2], based on the Pitzer model, was tested here for KC1 in water-ethanol mixtures and the results obtained were compared with those calculated from electromotive force data,

by the Pitzer model. This method was also applied to KCl in water-methanol mixtures, and compared with results obtained from electromotive force data, existing in the literature [3].

EXPERIMENTAL SECTION

The materials used were analytical-grade potassium chloride (Fluka AG, 99.5%+), dried for 12 hours, at 110 °C, and ethanol (Pronalab R, 99.8%+). The solutions were prepared by weight, using deionized water with specific conductivity of 1.2 μS cm^{-1}.

The emf measurements were made on the cell

$$Ag \mid AgCl \mid KCl\ (m) \mid K\ (glass) \qquad (I)$$

The electrodes used were a commercial potassium ion selective electrode K/NH$_4$ ABB Kent Taylor and a silver/silver chloride electrode, prepared by the thermal-electrolytic method [4]. The cell vessel was a glass double-wall container, enabling the circulation of thermostated water and the use of a magnetic stirrer. Through the lid, the electrodes and a glass thermometer (± 0.05 °C) were immersed in the solutions. When not in use, the potassium glass electrode was stored in a 0.1 M KCl solution, prepared with the solvent to be used next run, and the silver/silver chloride electrode in a 0.1 M KCl aqueous solution [3]. The emf measurements were obtained on a Metrohm model 713 pH/mV meter. Voltage readings were taken as final when they were constants, within 0.1 mV, for at least 5 minutes.

RESULTS AND DISCUSSION

Application of the Pitzer model to the efm data

Experimental data E (potential) and m (molality) are listed in Table 1. The cell potential, E, is given by

$$E = E^O + 2(RT/F)\ (\ln m + \ln \gamma_\pm) \qquad (1)$$

where E^0 is the standard potential of the cell (I) and $\gamma_\pm$ is the mean activity coefficient of KCl. One way of expressing $\ln \gamma_\pm$ as a function of molality, m, is the Pitzer equation [1], which for 1-1 type electrolytes takes the form :

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

where

$$f^\gamma = -A_{mix}\ (m^{1/2}\ /\ (1+bm^{1/2}) + (2/b)\ln(1+bm^{1/2}))$$

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

$$C^\gamma = 3\ C^\phi/2 \qquad with \quad \alpha=2 \qquad b=1.2.$$

Table 1 - Molality-emf data for KCl in water-ethanol solvents

5% Ethanol		10% Ethanol		15% Ethanol		20% Ethanol	
m	E/mV	m	E/mV	m	E/mV	m	E/mV
0.1000	33.2	0.1000	41.0(5)	0.1000	54.1(5)	0.1000	66.5
0.4000	97.4	0.2500	84.2	0.2500	95.1	0.2500	106.0
0.6000	115.2	0.5000	115.1	0.5000	125.8(5)	0.5000	136.6(5)
0.8000	127.5	0.7500	133.3	0.7500	144.1	0.7500	154.0
1.000	138.0	1.000	146.4	1.000	157.8(5)	1.000	166.1
1.250	148.1(5)	1.250	157.3	1.200	165.4(5)	1.250	175.8
1.500	156.6	1.500	166.0	1.300	169.5	1.500	184.2
2.000	170.6	1.750	173.2	1.500	175.8	1.600	186.9
2.500	181.6	2.000	180.0	1.600	178.8(5)	1.750	191.6
2.750	186.8(5)	2.250	185.3	1.750	183.2	1.900	194.4
3.000	191.2(5)	2.500	189.9(5)	2.000	189.8	2.000	197.7
3.250	165.9	2.750	196.0	2.250	195.5(5)	2.100	199.7
3.500	200.0	3.000	200.6	2.500	200.9(5)	2.250	202.8(5)
3.750	203.5	3.250	204.7	2.750	205.6	2.400	206.4
4.000	207.4	3.500	208.3(5)	3.000	209.6	2.500	208.8(5)

The Debye-Hückel coefficient, A_{mix}, for each solvent, was obtained from the equation :

$$A_{mix} = A_w\ (\rho_{mix}\ /\ \rho_{water})^{1/2}\ (\varepsilon_{water}\ /\ \varepsilon_{mix})^{3/2} \qquad (3)$$

where A_w is the Debye-Hückel parameter for water [1]. The densities for the water-ethanol mixtures, ρ_{mix}. were taken from reference [5] and the dielectric constants, ε_{water} and ε_{mix} , were calculated using Eq. (4). This equation was established from literature data [6] and gives ε_{mix} as a function of the solvent composition and temperature:

$$\varepsilon_{mix} = (\ a +\ b/(1-X_E) + c\ (1-X_E))\exp((d + e\ X_E)\ T) \qquad (4)$$

where a=379.2482 , b=-67.5072 , c=4.5825 , d=-4.676E-03, e=-1.641E-03 and X_E is the mass fraction of ethanol in the solvent. The values for the Pitzer parameters, β^o, β^1 and C^ϕ , adjusted to the electromotive force data of this work, for water-ethanol mixtures, and to those existing in the literature [3], for water-methanol mixtures, are listed in Table 2. Those parameters were obtained by means of a curve-fitting programme (Excel 5.0).

Table 2 - Pitzer parameters for KCl in water-ethanol (this work) and KCl in water-methanol [3]

	% Ethanol				% Methanol			
	5	10	15	20	10.2	20.6	40.3	60.3
β^0	0.0306	0.0535	0.0735	0.0357	0.0716	0.0434	0.0792	1.230
β^1	0.3509	0.3047	0.1614	0.2009	0.221	0.400	0.283	-2.067
C^ϕ	0.0048	-0.0004	-0.006	-0.007	-0.005	-0.0004	-0.007	-1.006
σ/mV	0.42	0.37	0.20	0.35	0.47	0.34	0.49	0.58

Modification of the Pitzer model

Ye et al. [2] proposed a modification of the Pitzer model, involving the substitution, at the calculation stage, of the mixed solvent by a single equivalent solvent. For this equivalent solvent one has to calculate an equivalent temperature, T', based on the principle of corresponding states:

$$T' = T / T_{cm} * T_c \qquad (5)$$

where T is the experimental temperature, T_c the critical temperature of the water and T_{cm} is the critical temperature of the mixed solvent, and is given by

$$T_{cm} = \Sigma_i \Sigma_j \ x_i x_j (T_{ci} * T_{cj})^{1/2}$$

where i,j are refered to water and alcohol. Equivalent molalities m' and m'' have also to be calculated

$$m' = m * (\rho_{water} / \rho_{mix}) \qquad (6)$$

$$m'' = m' * (\varepsilon_{water} / \varepsilon_{mix}) \qquad (7)$$

The next step is to calculate, $\beta^{0'}$, $\beta^{1'}$ and $C^{\phi'}$ for T', using expressions that give these parameters as a function of T [7]. The modified Pitzer model may now be used:

$$\ln \gamma_{\pm} = f^{\gamma} + m'' B^{\gamma} + m''^2 \ C^{\gamma} \qquad (8)$$

where
$$f^{\gamma} = - A_{mix} (m'^{1/2} / (1+bm'^{1/2}) + (2/b) \ln (1+bm'^{1/2}))$$

$$B^{\gamma} = 2 \beta^{0'} + 2 \beta^{1'} (1-(1+\alpha m''^{1/2} -\alpha^2 m''/2) \exp(- \alpha m''^{1/2}))/\alpha^2 m''$$

$$C^{\gamma} = 3 C^{\phi'}/2 \qquad \text{with} \qquad \alpha=2 \qquad b=1.2.$$

Table 3 lists the values obtained for these parameters, for water-ethanol and water-methanol systems, as well as the equivalent temperature. The standard deviation, σ, is refered to activity coefficients, calculated by Pitzer equations.

Table 3 - Parameters for KCl in water-ethanol (this work) and KCl in water-methanol [3] for the Pitzer modified model

	% Ethanol				% Methanol			
	5	10	15	20	10.2	20.6	40.3	60.3
T'	299.4	300.8	302.3	303.9	302.1	306.7	316.9	330.4
$\beta^{0'}$	0.0488	0.0496	0.0504	0.0512	0.0503	0.0526	0.0571	0.0616
$\beta^{1'}$	0.221	0.222	0.224	0.226	0.224	0.230	0.242	0.257
$C^{\phi'}$	-0.0009	-0.0009	-0.0010	-0.0011	-0.0010	-0.0013	-0.0018	-0.0023
σ	0.016	0.023	0.003	0.026	0.018	0.016	0.009	0.020

Figures 1 shows the results obtained by both methods (Pitzer model and the modified model) for the water-ethanol solvent.

The Pitzer modified method enables the calculation of activity coefficients of salts in mixed solvents, based only on the properties of the solvent (density and dielectric constant) and the knowledge of the Pitzer parameters for the aqueous solution of the salt. For these systems, it gives a good approximation of the necessary values and this seems to be of great interest in crystallization studies.
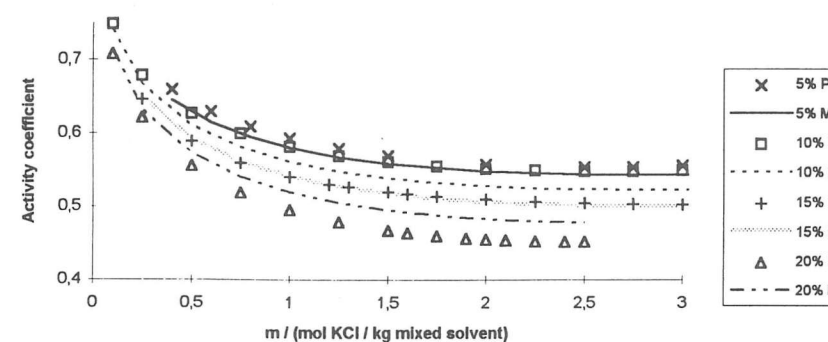

Figure 1 - Activity coefficients vs. molality for KCl in water-ethanol mixtures (P- Pitzer model ; M- Modified model)

LITERATURE CITED

1. Pitzer, S. K., Activity Coefficients in Electrolyte Solutions, 2nd ed., CRC Press, Boca Raton, London (1991).

2. Ye, S.; Xans, P.; Lagourette, B., J. Solution Chem., 23, 1301, (1994).

3. Malahias, L. and Popovych, O., J. Chem. Eng. Data, 27, 105 (1982).

4. Bates, R.G., Determination of pH, Theory and Practice, 2nd ed., Wiley, New York (1973).

5. Perry, J.H. and C. Chilton, Chemical Engineers' Handbook, 5th ed., McGraw-Hill, New York (1973).

6. Franks, F., Water: A Comprehensive Treatise, Vol.2, 1st ed., Plenum Press (1963).

7. Holmes, H.F.; Mesmer, R.E., J. Phys. Chem., 87, 1242, (1983).