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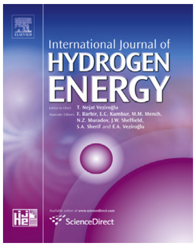

Use of the Pitzer model for correlating thermodynamic phase behavior of salts in water–ethanol mixed solvent solutions

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ABSTRACT

Hydrogen can be produced from Ethanol through many industrial processes which may involve electrolyte species in some cases. The thermodynamic phase behavior of electrolyte solutions is very important for the design of such processes.

The Pitzer model, initially designed for aqueous electrolyte solutions, has been adapted to the case of electrolytes in mixed solvent solutions. This approach was applied for calculating activity coefficients of the electrolytes KCl, CsCl, NaCl and NaBr in water–ethanol mixtures at 25 °C. The Pitzer parameters have been evaluated for each salt in both aqueous and ethanol–water mixed solvent by minimizing the objective function using experimental data from literature.

The values of the standard deviations show that the Pitzer model can be used successfully in modeling activity coefficients of the electrolytes studied in both aqueous and ethanol-water mixed solvent solutions.

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Introduction

Alcohols, in particular, methanol and ethanol are fuels which can be converted into hydrogen to be used in fuel cells. These alcohols are easily decomposed in the presence of water and generate mixture rich in hydrogen suitable for feeding fuel cells [1,2]. However this hydrogen production route may involve electrolytes at certain stages of the process as well as liquid and gas phases and one can be able to predict the phase equilibria which may take place by means of reliable and efficient thermodynamic models such as the electrolyte-NRTL model developed by Chen [3,4] which combines the Pitzer-Debye-Hückel model [5] for long-range ion–ion electrostatic interactions with the NRTL theory [6] for short-range energetic interactions among the species in electrolyte solutions.

The knowledge of thermodynamic properties of electrolyte in both aqueous and mixed solvent systems is important for understanding the nature of various ion-interactions and for controlling many industrial processes. Different models exist to calculate thermodynamic properties of electrolyte

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Nomenclature

A_φ	Debye-Huckel coefficient
d	Density of the solvent, g/cm^3
D	Dielectric constant of the solvent
I	Ionic strength in molality basis
m	Molality, mol/kg
NP	Number of experimental data points
Z	Ionic charge number
ARD	Average relative deviation

Greek letters

α	Pitzer parameter
β	Pitzer parameter
γ	Activity coefficient in molality basis
φ	Osmotic coefficient
ν	Stoechiometric number
σ	Standard deviation

Subscripts

MX	Electrolyte formula

Superscripts

cal	Calculated
exp	Experimental

solutions. They can be classified into equations of state [7,8] and excess Gibbs energy models [3,4,9–11]. In general the excess Gibbs energy of the electrolyte solution can be separated into two contributions: the long-range ion–ion interactions and short-range interactions. The long-range contribution is often described by a Debye-Huckel type term whereas the description of the short-range contribution represents the main difference between the models.

The Pitzer model [9] extended the Debye-Huckel method, using a virial expansion to account for the ionic strength dependence of the short-range forces in binary and ternary ion interactions. The model is applicable to solutions of high ionic strength. It provides the simplest and most coherent procedure for calculating the properties of electrolyte components. The Pitzer ion interaction theory was particularly successful in modeling thermodynamic properties of electrolytes in aqueous media, its application for the investigation of electrolytes in nonaqueous or in mixed solvent solutions was also found to be successful [12–15].

The results concerning modeling the non ideal behavior of the electrolytes LiCl, CsCl, RbCl, HCl, NaCl and NaBr in methanol–water mixed solvent at 25 °C using Pitzer model have been reported [13]. The objective of the present work is to carry out a similar study for some electrolytes in water + ethanol mixtures.

The experimental values for the activity coefficients are reported for different electrolytes in ethanol-water mixtures in the literature, for KCl and CsCl [16], for NaCl [17], and for NaBr [18,19]. The Pitzer model has been applied in this work for correlating the mean ionic activity coefficients of the salts KCl, CsCl, NaCl, and NaBr in water + ethanol mixed solvent solutions using the experimental data from the literature cited [16–19].

Thermodynamic model

The Pitzer model

Pitzer's equations [9] for the activity coefficient of an electrolyte $M_{\nu M}X_{\nu X}$ in a solution of molality m and ionic strength I is given by:

$$\ln\,\gamma_{MX} = |\,z_M\,z_X|\,f^\gamma + m\left(\frac{2\,\nu_M\,\nu_X}{\nu}\right)B^\gamma_{MX} + m^2\left[\frac{2\,(\,\nu_M\,\nu_X)^{3/2}}{\nu}\right]C^\gamma_{MX} \tag{1}$$

where $\nu = \nu_M + \nu_X$

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1+b\,I^{1/2}} + \frac{2}{b}\,\ln\,(\,1+b\,I^{1/2})\right] \tag{2}$$

$$B^\gamma_{MX} = 2\,\beta^{(0)}_{MX} + \frac{2\,\beta^{(1)}_{MX}}{\alpha^2\,I}\left[1 - e^{-\alpha\,I^{1/2}}\,(1+\alpha\,I^{1/2} - (1/2)\,\alpha^2 I)\right] \tag{3}$$

$$C^\gamma_{MX} = (3/2)\,C^\varphi_{MX} \tag{4}$$

and

$$I = \frac{1}{2}\sum_i m_i\,Z_i \tag{5}$$

The optimal values for α and b are respectively 2.0 and 1.2 [9].

For 1-1 electrolyte, Equation (1) can be written as:

$$\ln\,\gamma_{MX} = \,f^\gamma + m\,B^\gamma_{MX} + m^2\,C^\gamma_{MX} \tag{6}$$

A_ϕ is the Debye-Huckel coefficient for the osmotic function. At 25 °C, the value of this coefficient is found to be [12]:

$$A_\varphi = 272.058\,d^{1/2}\,D^{-3/2} \tag{7}$$

where d and D are, respectively, the density and the dielectric constant of the solvent.A_ϕ has the value 0.392 at 25 °C for water [18].

Application of the Pitzer equation to single electrolyte solutions requires three parameters:

$\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and C^γ_{MX}.

Table 1 – Values of dielectric constants and densities as a function of the percentage of Ethanol in the mixture at 298.15 K [18].

%EtOH	D	d (g/cm3)
0	78.3	0.99707
20	67.0	0.96638
40	55.0	0.93147
60	43.4	0.88698
70[a]	38.0[a]	0.86340[a]
80	32.8	0.83910
90	28.1	0.81361
100	24.3	0.78505

[a] From Ref. [19].

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