Thermodynamic modeling of 2-2 aqueous electrolytes

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Abstract

The Pitzer model has been used to correlate activity coefficients of several aqueous electrolytes of 2-2 type using experimental data from literature. The model parameters are optimized using a computer code in FORTRAN language. The results show that this model can correlate the experimental data with a very good precision. Moreover, the performance of this model has been compared to the performances of several thermodynamic models available in literature. The results of the comparison indicate that the model used in this work show better quality of fitting.

Keywords: *Activity coefficient; electrolytes; Pitzer; model; Aqueous solutions.*

I. Introduction

Electrolytes are very important in many applications such as corrosion, water pollution control, salting-in and salting-out effects in extraction and distillation processes, oilfield processing and many others. Accurate models for representing thermodynamic properties of electrolyte solutions are essential for the design and control of these processes. Several models have been proposed in the literature to calculate thermodynamic properties of electrolyte solutions such as the nonrandom two-liquid model (NRTL) proposed by Chen [1], the NRTL-NRF model suggested by Haghtalab et al. [2], the Wilson model extended to electrolyte solutions proposed by Zhao et al.[3] and the modified Wilson model proposed by Xu et al.[4]. These models can correlate the mean ionic activity coefficients of electrolytes with a good precision. In this work, we have applied the Pitzer model [5] to correlate activity coefficients of several 2-2 aqueous electrolytes at 298.15 °K using experimental data from literature [6]. We have than compared the performance of this model to those of the other models developed recently.

II. Thermodynamic model

For an aqueous solution including a single electrolyte, the excess Gibbs energy is written as [5]:

$$\left(G^{ex} \big/ n_w RT \right) = f^{GX} + m^2 (2\,\nu_M\ \nu_X) B_{MX}^{GX} + m^3 \left[2\,(\nu_M\ \nu_X)^{3/2} \right] C_{MX}^{GX} \tag{1}$$

Where

$$f^{GX} = -A_\varphi \left(4\,I \big/ b \right) \ln\left(1 + b\,I^{1/2}\right) \tag{2}$$

$$B_{MX}^{GX} = \beta_{MX}^{(0)} + \frac{2\,\beta_{MX}^{(1)}}{\alpha^2\,I} \left[1 - e^{-\alpha\,I^{1/2}} \left(1 + \alpha\,I^{1/2} \right) \right] \tag{3}$$

And $C_{MX}^{GX} = (1/2)\,C_{MX}^{\varphi}$ (4)

The expression for the mean ionic activity coefficient is

$$\ln \gamma_{MX} = \left| z_M\, z_X \right| f^{\gamma} + m \left(\frac{2\,\nu_M\ \nu_X}{\nu} \right) B_{MX}^{\gamma} + m^2 \left[\frac{2\,(\nu_M\ \nu_X)^{3/2}}{\nu} \right] C_{MX}^{\gamma} \tag{5}$$

where $\nu = \nu_M + \nu_X$

$$f^{\gamma} = -A_\varphi \left[\frac{I^{1/2}}{1 + b\,I^{1/2}} + \frac{2}{b} \ln\left(1 + b\,I^{1/2}\right) \right] \tag{6}$$

$$\begin{aligned} B_{MX}^{\gamma} = 2\,\beta_{MX}^{(0)} &+ \frac{2\,\beta_{MX}^{(1)}}{\alpha_1^2\,I} \left[1 - e^{-\alpha_1 I^{1/2}} \left(1 + \alpha_1\,I^{1/2} - (1/2)\,\alpha_1^2\,I \right) \right] \\ &+ \frac{2\,\beta_{MX}^{(2)}}{\alpha_2^2\,I} \left[1 - e^{-\alpha_2 I^{1/2}} \left(1 + \alpha_2\,I^{1/2} - (1/2)\,\alpha_2^2\,I \right) \right] \end{aligned} \tag{7}$$

and

$$C_{MX}^{\gamma} = (3/2)\,C_{MX}^{\varphi} \tag{8}$$

I, is ionic strength:

$$I = \frac{1}{2} \sum_i m_i\ Z_i \tag{9}$$

is a Debye-Huckel coefficient:

$$A_\varphi = \left[\frac{1}{3}\left(2\,\pi\,N_0\,d_W\,/1000\right)^{1/2}\right]\left(e^2\,/DkT\right)^{3/2} \quad (10)$$

For each electrolyte, the adjustable parameters for the Pitzer model are $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$ and C_{MX}^{φ}. The optimal values for α1, α2 and b are 1.4, 12 and 1.2 respectively [5].

II. Optimization of model parameters

The Pitzer model was applied to correlate the mean ionic activity coefficients of several systems including aqueous solutions of bi-bivalent electrolyte type. Using the experimental data available in the literature [6], the model parameters are obtained by minimizing the following objective function:

$$OBJ = \sum_{i}^{NP}\left(\ln \gamma_{MX}^{cal} - \ln \gamma_{MX}^{\exp}\right)^2 \quad (11)$$

where NP is the number of data points.
We have elaborated for this purpose a computer code in FORTRAN language.
The standard deviation of the fit is defined as,

$$\sigma = \left[\frac{\sum_{i}^{NP}\left(\ln \gamma_{MX}^{cal} - \ln \gamma_{MX}^{\exp}\right)^2}{NP}\right]^{1/2} \quad (12)$$

III. Results

Some of the results are shown in figures 1 and 2. As presented in these figures, it can be seen that the calculated values using Pitzer model are in good agreement with the experimental data.

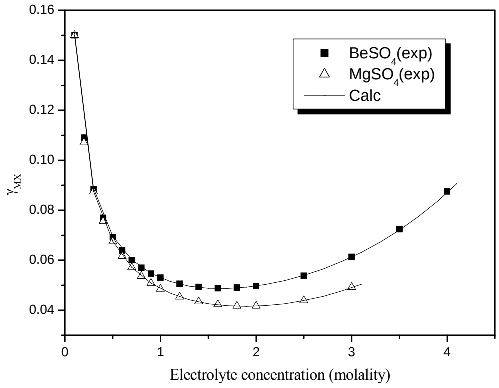

Figure 1: Measured and calculated mean ionic activity coefficients for the electrolytes: BeSO4, and MgSO4 in aqueous solutions at 298.15°K.

Figure 3 illustrate the mean average standard deviation of the fit by several models. The standard deviation of the fit indicates the precision of the model used. As presented in figure 3. The model used in this work shows an average standard deviation less than those of other models developed recently.

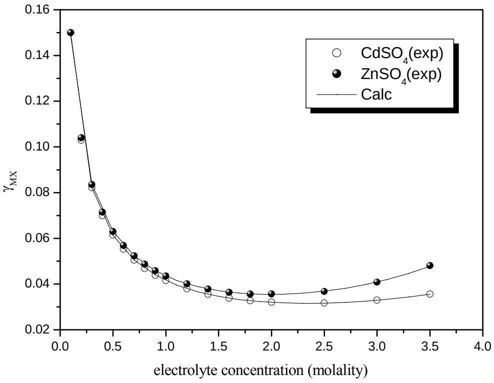

Figure 2: Measured and calculated mean ionic activity coefficients for the electrolytes: CdSO4 and ZnSO4 in aqueous solutions at 298.15°K.

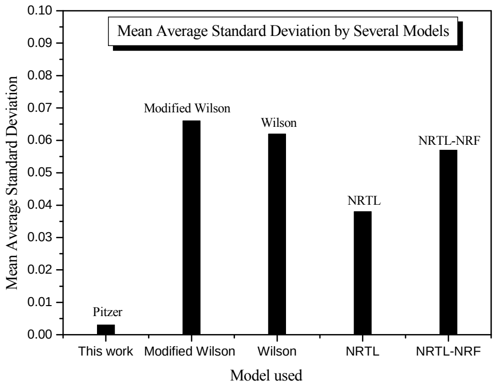

Figure 3: Mean Average Standard Deviation by different models

IV. Conclusion

In this work, we have applied the Pitzer model to correlate activity coefficient of several aqueous electrolytes of type 2-2. The results show that this model can correlate the experimental data with a very good precision. By comparing the performance of this model to other models developed in literature, this model shows better quality of fitting.

List of symbols

Aφ	Debye-Huckel constant
dW	density of water
D	dielectric constant of solvent
e	electronic charge

G	Gibbs energy
I	ionic strength
k	Boltzman constant
m	molality
NA	Avogadro number
NP	number of experimental data points
T	Absolute temperature
Z	charge number of ionic species

Greek Letters

α	Pitzer parameter
β	Pitzer parameter
γ	activity coefficient
φ	osmotic coefficient
ν	stoechiometric number
σ	standard deviation

Subscripts

MX	electrolyte formula

Superscripts

cal	calculated
exp	experimental
ex	notation of excess quality

References

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