

VAPOR PRESSURE AND OSMOTIC COEFFICIENTS USING BROMLEY EQUATION FOR 1:1 ELECTROLYTES IN METHANOL AT 298.15K

KARAMAT NASIRZADEH

Department of Chemistry, Faculty of Science, Azerbaijan University of Tarbiat Moallem, P.O.Box 51745-406, Tabriz, IRAN

In this study the Bromley model was developed for the non-aqueous electrolyte solutions. This model contains four adjustable parameters (ρ , B , B° and a) and has been used to estimate osmotic coefficients and vapor pressures of LiCl, LiBr, LiCH₃COO, KCH₃COO, NaCH₃COO, KI, NH₄SCN, NaSCN and NaBr in methanol at 298.15 K. In addition, comparisons were made to the model of Pitzer and Mayorga for the osmotic coefficients and vapor pressures of these electrolytes.

Keywords: Osmotic coefficient; Vapor pressure; Bromley Model; Mixtures; Methanol; Inorganic salts

INTRODUCTION

Simple methods for representing deviations from ideality in electrolyte solution are needed to design industrial processes, especially for transformation of raw materials and pollution control. In the past few decades, considerable progress has been made in measuring and modeling of thermodynamic properties of electrolyte systems. However, most of studies have been restricted by aqueous systems. Much less attention has been given to non-aqueous electrolyte solutions. In this article, the Bromley equations [1] is proposed for prediction of osmotic coefficients and vapor pressures of LiCl, LiBr, LiCH₃COO, NaCH₃COO, KCH₃COO, KI, NH₄SCN, NaSCN and NaBr in methanol based on the experimental isopiestic data of these electrolytes at 298.15 K. In our previous works [2,3] the Pitzer and Mayorga model [4,5] was used for the prediction of activity and osmotic coefficients of methanol + LiCl, LiBr and +LiCH₃COO and self-consistent local composition [6] model (SCLC) was used for the prediction of osmotic coefficients and vapor pressures of CaCl₂ and Ca(NO₃)₂ in methanol at 298.15 K.

The Bromley model [1] contains four adjustable parameters (ρ ; B , B° and a). In some aqueous and nonaqueous electrolyte solutions the parameter $\rho=1$ were used and three remaining parameters were calculated [1, 7]. In this study, the four parameters of the Bromley equations were calculated for methanol solutions of LiCl, LiBr, LiCH₃COO, NaCH₃COO, KCH₃COO, KI, NH₄SCN, NaSCN and NaBr. Furthermore, comparisons were made for osmotic coefficients and vapor pressures of investigated systems obtained with Bromley model to the model of Pitzer and Mayorga and experimental isopiestic measurements of our previous works.

BASIC DEFINITION AND THEORETICAL TREATMENTS

The isopiestic method is the most accurate, simple experimental technique available for measuring of the solvent activity of solutions that contain nonvolatile solutes. It is the base of phenomenon when different solutions, connected through the vapor space, approach to equilibrium by transfer of solvent mass by distillation. The accuracy of the method depends on the standard solutions that are used, sample mixing during the equilibration period, temperature stability, and the time allowed for the equilibration process. Equilibrium has been established one, the temperature and

pressure are uniform through out the system, provided that no concentration gradients exist in the liquid phases. At the equilibrium the chemical potentials of the solvent in each of the solutions in the closed system are identical:

$$\mu_s^{\alpha} = \mu_s^{\beta} = \dots \mu_s^{\omega} \quad (1)$$

where μ_s is the chemical potentials of the solvent in each of the solutions α through ω . The solvent activity is related to the solvent chemical potential by

$$\ln a_s = \frac{(\mu_s - \mu_s^\circ)}{RT} \quad (2)$$

where a_s is the solvent activity, R is the gas constant, μ_s° is the standard state chemical potential of the solvent, and T is the absolute temperature. After the equilibrium, the solvent activity equals between the investigated solutions. Since the solvent activity is known for one or more standard solutions, it will be known for each solution within the isopiestic system.

Several models are available in the literature for the correlation of osmotic coefficients as a function of molalities. The model of Pitzer and Mayorga [4,5] has been successfully used for aqueous, in a few cases, for non-aqueous electrolyte solutions [2,3]. The experimental osmotic coefficients data were correlated with the model of Pitzer and Mayorga [6] for solutions of LiCl, LiBr, LiCH₃COO, KCH₃COO, NaCH₃COO, KI, NH₄SCN, NaSCN and NaBr in methanol. For 1:1 electrolytes, this model has the following form

$$\ln f = \ln f^\circ + mB^\circ + m^2 C^\circ \quad (3)$$

where

$$f^\circ = -A m^{1/2} / (1 + b m^{1/2}), \quad (4)$$

$$A = (1/3)(2 \rho N_A d_s)^{1/2} (e^2 / 4 \rho \epsilon_0 D k T)^{3/2}, \quad (5)$$

and

$$B^\circ = b^{(0)} + b^{(1)} \exp[-a_1 m^{1/2}]. \quad (6)$$

For some aqueous and non-aqueous electrolyte solutions, it was found that by adding a $\beta^{(2)}$ term to equation (6) better

agreement with the experimental results could be obtained with the Pitzer model [2].

$$B^f = b^{(0)} + b^{(1)} \exp[-a_1 I^{1/2}] + b^{(2)} \exp[-a_2 I^{1/2}] \quad (7)$$

In these equations $b^{(0)}$, $b^{(1)}$, $b^{(2)}$ and C^f are Pitzers ion-interaction parameters, a_1 , a_2 and b are adjustable parameters, and A_f is Debye-Hückel (DH) constant for the osmotic coefficient on the molal basis. The remaining symbols have their usual meaning. For methanol solutions $A_f = 1.294 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$ was calculated using equation (5).

From the analysis of the experimental osmotic coefficient data, Zafarani-Moattar and Nasirzadeh [2] found that the values of $b = 3.2 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$, $a_1 = 2.0 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$ and $a_2 = 1.4 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$ were satisfactory at 298.15 K. Ion-interaction parameters were obtained from the fitting experimental osmotic coefficient data for the investigated systems and are shown in Table 1. In this table $b^{(0)}$, $b^{(1)}$, $b^{(2)}$ and C^f are the Pitzer parameters, $s(\phi)$ and $s(p)$ are the standard deviation for the osmotic coefficients and vapor pressures, respectively.

Table 1.

Pitzer parameters for methanol solutions of LiCl, LiBr, LiCH₃COO, KCH₃COO, NaCH₃COO, KI, NH₄SCN, NaSCN and NaBr calculated from osmotic coefficients at 25°C.

No. of data	molality range	β^o	β_1	β_2	$C\phi$	$\sigma(\phi)$	$\sigma(p) / \text{kPa}$
LiCl							
32	0.22-4.18	-0.11458 0.02167	-3.95303 0.09548	3.421 0	0.06478 0.01431	0.006 0.015	0.008 0.021
LiBr							
27	0.19-3.90	0.00275 0.24842	-2.6665 0.06083	2.238 0	0.05542 0.01649	0.005 0.009	0.003 0.005
LiCH ₃ COO							
20	0.24-3.01	0.19224 0.05542	1.39440 0.06113	-1.202 0	-0.01017 0.014365	0.004 0.005	0.005 0.008
KCH ₃ COO							
23	0.18- 2.51	0.008128 0.114109	-0.687219 0.200517	0.838449 0	0.004572 -0.016451	0.0001 0.001	0.0002 0.0005
NaCH ₃ COO							
26	0.26 -1.76	-0.128391 0.174060	-2.118794 -0.165151	1.9988 0	0.026218 -0.047509	0.002 0.003	0.005 0.008
KI							
19	0.13 -0.98	-0.983997 0.215944	-5.000851 0.109784	6.0448 0	0.322375 -0.079194	0.001 0.002	0.0002 0.0004
NH ₄ SCN							
24	0.36 -4.35	0.056495 0.141341	-1.085211 0.079836	0.9453 0	-0.00583 -0.018001	0.008 0.009	0.009 0.002
NaSCN							
24	0.16-3.36	0.184719 0.283717	-0.904255 0.020163	0.8182 0	-0.007136 -0.022223	0.005 0.006	0.007 0.009
NaBr							
18	0.18 -1.57	0.757993 -0.027613	5.607655 0.838263	-4.98352 0	-0.098082 0.102425	0.002 0.004	0.002 0.005

^a $A_\phi = 1.294 \text{ kg}^{1/2} \text{ mol}^{-1/2}$; $b = 3.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$; $\alpha(1) = 2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$; $\alpha(2) = 1.4 \text{ kg}^{1/2} \text{ mol}^{-1/2}$.

The Bromley equations [1] are:

$$f - 1 = A_f \left[Z_+ Z_- \sqrt{I} s(r\sqrt{I}) + 2.303(B^o - B) \left(\frac{I}{2} \right) j(al) + 2.303 \left(\frac{I}{2} \right) \right], \quad (8)$$

where

$$s(r\sqrt{I}) = \left(\frac{3}{r^3 \sqrt{I}} \right) \left[1 + r\sqrt{I} - \frac{1}{1 + r\sqrt{I}} - 2 \ln(1 + r\sqrt{I}) \right] \quad (9)$$

$$Y(al) = \left(\frac{2}{al} \right) \left[\frac{1 + 2al}{(1 + al)} - \ln \frac{1 + al}{al} \right] \quad (10)$$

In these equations F is the osmotic coefficient and other parameters have the usual meaning.

The Bromley model contains four adjustable parameters (r , B , B° and a). These parameters for the LiCl, LiBr, LiCH₃COO, KCH₃COO, NaCH₃COO, KI, NH₄SCN, NaSCN

and NaBr in methanol solutions were calculated and are shown in table 2. In this table ρ , B , B° and a are the Bromley parameters, $\sigma(\phi)$ and $\sigma(p)$ are the standard deviation for the osmotic coefficients and vapor pressures of this solutions, respectively.

Table 2.
Bromley parameters of LiCl, LiBr, LiCH₃COO, KCH₃COO, NaCH₃COO, KI, NH₄SCN, NaSCN and NaBr in methanol solutions at 25°C

salts	no. of points	r	B°	B	A	$s(f)$	$s(p)$
LiCl	32	1.4345	-7.488×10^7	0.22	83.836	0.0234	0.006
LiBr	27	1.4676	-2.245×10^9	0.2463	3.7026×10^8	0.0020	0.004
LiCH ₃ COO	20	1.5517	-7.3676×10^6	0.0634	5.1877×10^9	0.0103	0.015
KCH ₃ COO	23	2.1762	588.7344	0.0197	6.2388×10^4	0.0027	0.006
NaCH ₃ COO	27	1.9307	469.3899	0.0249	2.6746×10^4	0.0045	0.012
KI	19	2.167	0.0545	0.0548	-0.8615	0.0021	0.005
NH ₄ SCN	24	2.3069	5.1258×10^4	0.0213	1.7539×10^7	0.0146	0.021
NaSCN	24	2.1806	5.5277×10^5	0.1347	1.0294×10^8	0.0115	0.017
NaBr	18	1.9985	-1.9702×10^8	0.1072	39.616	0.0125	0.019

Bromley also has presented a one-parameter version of his model for aqueous systems by setting

$$(B^\circ - B) = (0.06 - 0.6B) / (Z_+ Z_-) \quad (11)$$

and

$$a = \frac{1.5}{Z_+ Z_-}$$

Use of equations (11) and (12) with the Bromley model for the methanol systems gave, as expected, very poor results [7] and didn't present in this paper.

CONCLUSION

Tables 1 and 2 shows the Pitzer and Bromley parameters for the electrolytes of LiCl, LiBr, LiCH₃COO, KCH₃COO,

NaCH₃COO, KI, NH₄SCN, NaSCN and NaBr in methanol solutions at 25°C respectively.

The Bromley model was found to correlate the experimental data with good accuracy.

The application of both forms of the Pitzer model has been shown to correlate the experimental osmotic coefficient data with very good accuracy, especially using the Pitzer model with the $B^{(2)}$ term. Data analysis shows that the values of $b = 3.2 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$, $a_{(1)} = 2.0 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$ and $a_{(2)} = 1.4 \text{ Kg}^{1/2} \text{ mol}^{-1/2}$, based on the optimum representation of the Lithium salts+methanol systems, also give the better overall results for other salts in methanol systems. For some of the electrolytes studied in this work, relatively large negative numbers were found for $B^{(2)}$, which may indicate significant ion-pairing of these electrolytes in methanol.

[1] L.A. Bromley; AICHE J; 19, 1973, 313-320

[2] M. T. Zafarani-Moattar and K. Nasirzadeh, J. Chem. Eng. Data, 43, 1998, 215-219.

[3] M. T. Zafarani-Moattar, J. Jahanbin, K. Nasirzadeh; Fluid Phase Equilibria; 2002, (In press)

[4] K.S. Pitzer; G. Mayorga; J. Phys. Chem.; 77(19), 1973, 2300-2308.

[5] K.S. Pitzer, , "Activity coefficient in Electrolyte solutions", 2nd ed., CRC Press, 1991.

[6] M.S. Ananth and S. Ramachandran, AICHE J., 36, 1990, 370-386.

[7] Tamasula, P.; Czerwiński, J. Gregory; P. Tassions; Fluid Phase Equilibria, 38, 1987, 129-153.

Received: 29.04.02