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Measuring and modeling of osmotic coefficients for $LiNO_3+2$-naphthol+ethanol at 298.15 K

Zohreh Karimzadeh [a,*], Maryam Alamdari Shendi [b], Jaber Jahanbin Sardroodi [c], Rahman Salamat-Ahangari [b], Ali Ebrahimian Pirbazari [b]

[a] Department of Chemistry, Shahid Beheshti University, G.C., Evin-Tehran, Iran
[b] Department of Chemistry, Faculty of Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran
[c] Molecular Simulation Laboratory, Azarbaijan Shahid Madani University, Tabriz, Iran

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ABSTRACT

The modeling purposes are achieved based on the experimental osmotic coefficients determination of lithium nitrate in $LiNO_3+2$-naphthol+ethanol ternary system at 298.15 K. The experimental osmotic coefficients data are correlated using the Pitzer, the modified Pitzer equation by Esteso (PE) and the Pitzer–Simonson–Clegg (PSC) equations. The present calculations are performed for lithium nitrate electrolyte molalities ranging from 0 up to about 2.3 mol kg^{-1} in 2-naphthol and ethanol with different weight fractions, $y=(0.25, 0.50, 0.75)$. Activity and vapor pressure data are also given.

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1. Introduction

2-Naphthol is widely used chemical matter in industry. It is a widely used intermediate for the production of dyes and other compounds. Thermodynamic study of 2-naphthol solutions in various solvents, especially in organic phase, is important in the design and control of industrial processes including them; furthermore, their understanding is helpful in investigation about the interactions occurring in these solutions [1–4].

Limited thermodynamic data are available for non-aqueous electrolyte systems and consequently, correlation of such data has attracted little attention. The osmotic coefficients of the solution, and activity of the solvent and activity coefficients of the 2-naphthol in ethanol were measured using the isopiestic method at 298.15 K [5]. A second study in this series [6] reports the osmotic coefficients of lithium nitrate in ethanol at 298.15 K. The present study gives the third report to compile more data on non-aqueous electrolyte systems by extending the previous studies to investigate more complex systems containing lithium nitrate, 2-naphthol and ethanol.

A survey of literature confirms that limited thermodynamic data are available. Following papers studied the lithium nitrate in ethanol: Li and co-workers performed the solubility measurements of lithium nitrate and ethanol in the range between 298.15 and 338.15 K [7]. Effects of lithium nitrate on the vapor – liquid equilibria of ethyl acetate and ethanol were reported by Topphoff et al. [8].

Isothermal vapor – liquid equilibrium data were reported for the system consisting of acetone, methanol and lithium nitrate by Yan et al. [9]. Tretyakov et al. reported phase diagrams and conductivity isotherms for lithium nitrate as solutes and sulfones ($(CH_3)_2SO_2$) as solvent [10]. Specific conductivities and viscosities of molten mixtures of lithium nitrate, acetamide, and urea were measured by Rajkhowa and co-workers [11].

Vapor pressures of lithium nitrate solutions in ethanol were reported by Verevkin et al. [12].

A valuable formalism has been presented by Pitzer, which involves a very useful extension of the Debye–Hückel (DH) theory for long range interactions, where short range effects are incorporated via a virial expansion up to three virial coefficients [13–19]. Since the virial expansion formalism at very high concentrations, like miscible fused salt becomes unsatisfactory, Pitzer and Simonson presented a new equation for systems containing ions of symmetrical charge type at very high concentration and for miscible fused salt [17,18]. In this approach a three suffix Margules expansion is used as a short-range force term and a DH term as a long-range force. This formalism correlated activity coefficient data of symmetrical charge type electrolyte over entire range.

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[*] Corresponding author.
E-mail address: z.karimzadeh@gmail.com (Z. Karimzadeh).

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Clegg and Pitzer [19,20] developed Pitzer and Simonson formalism consisting of extended DH term and four suffix Margules expansion in order to include different charge type electrolytes containing an indefinite number of ionic and neutral components.

In spite of the widespread success of the Pitzer model for aqueous solutions, the application of the Pitzer ion-interaction approach in non-aqueous media is still scarce. This approach is a valuable method for correlation and prediction of thermodynamic properties of electrolytes in mixed solvent media [21–26].

After successfully modeling of electrolytes in mixed solvent systems using PSC equation [22–26], the present investigation reports modeling of lithium nitrate and 2-naphthol in ethanol solutions with Pitzer [13–16], PSC [19,20] and a modified form of Pitzer ion-interaction approaches [27] using the experimental osmotic coefficients data. Scope of work is non-aqueous phase study of osmotic coefficient based on Pitzer approaches modeling.

2. Experimental

The alcohol and salts (NaI, (GR., Min. 99.5%) and $LiNO_3$ (GR., Min. 99.5%)) are obtained from Merck. They are all superior reagents. Ethanol (GR. 99.8%) is dried by the method described by Vogel [28]. 2-Naphthol is also obtained from Merck (GR. Min. 99%). All the salts are used without further purification. All the salts are dried in an electrical oven at about 393 K for 24 h prior to use. We have to dry the $LiNO_3$ at more 473 K, but our $LiNO_3$ is dried at about 393 K, so the process of $LiNO_3$ weighting involves maximum error as ± 0.025. The isopiestic apparatus employed here, is essentially the same as the one used for the osmotic coefficient measurements in non-aqueous solutions of various electrolytes and polymers by Zafarani-Moattar and co-workers [6]. This apparatus consisted of a five-leg manifold attached to round-bottom flasks. The five flasks are typically used are as follows: two flasks contained the standard NaI solutions, two flasks contained the solutions of 2-naphthol and lithium nitrate in ethanol and the central flask is used as an ethanol reservoir. The apparatus is held in a constant temperature bath for at least 140 h for equilibration at (298.15 ± 0.005) K. On the basis of the activity measurements, the maximum error has been verified as ± 0.0002 for the isopiestic technique used [29].

3. Modeling

3.1. Pitzer approach

In the Pitzer ion-interaction approach, the non-ideal behavior of the electrolyte system is conveniently described by the related activity and osmotic coefficients, or excess Gibbs energies. For a single $M_{\nu+}X_{\nu-}$ electrolyte ($L=LiNO_3$) in solvent (E=ethanol), the corresponding Pitzer equation is written as [16]:

$$\phi-1=(2/\sum m_i)[-A_f(I^{1.5}/(1+bI^{1.5}))+m_{Li}m_{NO_3}(B^{\phi}_{LiNO_3}+ZC_{LiNO_3})]. \tag{1}$$

where

$$B^{\phi}_{LiNO_3}=\beta^{(0)}_{LiNO_3}+\beta^{(1)}_{LiNO_3}\exp(-\alpha_1 I^{0.5})+\beta^{(2)}_{LiNO_3}\exp(-\alpha_2 I^{0.5}). \tag{2}$$

$$Z=m_{Li}|z_{Li}|+m_{NO_3}|z_{NO_3}|. \tag{3}$$

$$C_{LiNO_3}=C^{\phi}/(2|z_{Li}z_{NO_3}|^{0.5}). \tag{4}$$

and ϕ is the molality-scale osmotic coefficient of the electrolyte $M_{\nu+}X_{\nu-}$; z is the charge number of an ion; $\upsilon=\upsilon_+ + \upsilon_-$ is the number of ions dissociated in one unit electrolyte formula; m is the molality of electrolyte (mol kg^{-1}); I is the ionic strength on a molality scale; $\beta^{(0)}$ (kg mol^{-1}), $\beta^{(1)}$ (kg mol^{-1}), $\beta^{(2)}$ (kg mol^{-1}) and C^{ϕ} (kg $mol^{-1})^{0.5}$ are the parameters of the Pitzer equations; $b=3.2$ $kg^{1/2}$ $mol^{-1/2}$; $\alpha_1=2$ $kg^{1/2}$ $mol^{-1/2}$ and $\alpha_2=1.4$ $kg^{1/2}$ $mol^{-1/2}$. Investigation the non-aqueous electrolyte systems are often allowed to consider the $\beta^{(2)}$ parameter in Eq. (2) [16].

The Debye–Hückel coefficient for the osmotic coefficient (A_{ϕ}) is defined as

$$A_{\phi}=(1/3)(2\pi N_A d_s)^{0.5}(e^2/4\pi\varepsilon_0 D_s kT)^{1.5}. \tag{5}$$

where the constants ε_o, k, N_A, D_s and d_s are the vacuum permittivity, Boltzmann constant, Avogadro constant, dielectric constant and density of the solvent, respectively.

The experimental data are fitted by considering $A_{\phi}=2.006$ $kg^{1/2}$ $mol^{-1/2}$ as a fixed value.

For a neutral species (N) in solvent (E), the corresponding Pitzer equations are written respectively as

$$\phi-1=(2/m_N)[0.5m_N^2\lambda_{NN}+m_N^3\mu_{NNN}]. \tag{6}$$

Finally, for a single $M_{\nu+}X_{\nu-}$ electrolyte (L) including neutral species (N) in solvent (E) the corresponding Pitzer equation is written as

$$\begin{aligned}\phi-1=(2/\sum m_i)[&-A_f(I^{1.5}/(1+bI^{1.5}))+m_{Li}m_{NO_3}(B^{f}_{LiNO_3}+ZC_{LiNO_3})\\&+m_N m_{Li}\lambda_{NLi}+m_N m_{NO_3}\lambda_{NNO_3}+0.5m_N^2\lambda_{NN}+m_N^3\mu_{NNN}\\&+3m_N^2 m_{Li}\mu_{NNLi}+3m_N^2 m_{NO_3}\mu_{NNNO_3}\\&+m_N m_{Li} m_{NO_3}\zeta_{NLiNO_3}].\end{aligned} \tag{7}$$

where λ_{NLi}, λ_{NNO_3}, λ_{NN}, μ_{NNN}, μ_{NNLi}, μ_{NNNO_3} and ζ_{NLiNO_3} are the parameters of the Pitzer equation including neutral species.

3.2. Pitzer–Simonson–Clegg approach

In the PSC model, the excess Gibbs energy per mole as well as the derived activity coefficient relations are expressed by the contributions of short-range (g^s) and long-range (g^{DH}) forces [19,20]:

$$g^E=g^S+g^{DH}. \tag{8}$$

The contributions of long-range forces are defined in terms of an extended DH expression including composition dependent terms. Similarly, a four-suffix Margules expansion is used for the contribution of short-range forces, including parameters for the interactions of solvent–anion and solvent–cation. The corresponding activity coefficient equation is written as [19]:

$$\ln f_i^*=\frac{1}{RT}(\partial(\sum_i n_i g^E)/\partial n_i)_{T,P}. \tag{9}$$

The dissociation of all electrolytes are considered as complete and the following relation is used to convert the mole-fraction-based activity coefficient f_i^* to the molal-based activity coefficient (γ_i) [16]:

$$f_i^*=\gamma_i(1+(M_s/1000)\sum_i m_i) \tag{10}$$

where γ_i, M_s and m_i are the molal activity coefficient, the mean molar mass of the solvent and the molal concentration of the solute species i, respectively. When the ethanol is treated as the solvent, the related values and subscripts of s=E and $M_s=M_E$ (ethanol molar mass) are substituted in the above relation.

Using the following equations:

$$\ln(a_E)=-(M_E/1000)\phi\sum_i m_i. \tag{11}$$

$$\begin{aligned}\ln f_E^*=(2A_x I_x^{1.5}/(1+\rho I_x^{0.5}))-x_{Li}x_{NO_3}B_L\exp(-\alpha I_x^{0.5})+x_I^2(W_{EL}\\+(x_I-x_E)U_{EL})+x_E x_I^2(2-3x_E)V_{EL}.\end{aligned} \tag{12}$$

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