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Research Article

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An equation of state for nonaqueous electrolyte solutions

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ABSTRACT

A two parameters equation of state (EOS) for nonaqueous electrolyte solutions system has been developed. The equation is in terms of Helmholtz free energy and incorporated with results of low density expansion of non-primitive mean spherical approximation. The EOS was tested for experimental data reported in literatures of 9 nonaqueous single electrolyte solutions of which the temperature was 298.15K, and it also has a good predictive capability for nonaqueous electrolyte solutions at different temperature in this work. The comparasions with EOSs published earlier by other researchers in literatures are carried out in detail.

Keywords: EOS; Nonaqueous; Electrolyte Solutions

INTRODUCTION

Electrolyte solutions are encountered in a wide variety of industrial processes, for example, wastewater treatment, extraction, seawater desalinization, distillation and geological processes. It is very important for us to describe the thermodynamic properties of such systems accurately. Phase equilibrium in electrolyte systems is very important to chemical industry.

Past a few decades, people made a lot of progress on describing thermodynamic properties of electrolyte systems with some models.[1-4] But most of studies in literatures were restricted in aqueous electrolyte systems. There are little attention on nonaqueous electrolyte systems until now. Although we can get some data of properties from literature, the data about nonaqueous electrolyte systems is much less than the one about aqueous electrolyte systems. So in engineering, we need a simple predictive model in order to describe phase behavior of nonaqueous electrolyte systems.

EOSs of nonaqueous electrolytes have been developed successfully since the late 1970s. Pitzer's models[5, 6] have also extended to nonaqueous electrolyte solutions and the adjustable parameters are needed in all of these models. But up to now, there are still few models to represent phase equilibria properties of nonaqueous electrolyte solution.
In general, EOS can be derived by differentiating the Helmholtz free energy with respect to the density. The helmholtz free energy is divided into several contributions, typically including solvent-solvent, ion-solvent and ion-ion terms. In this work, we expanded Helmholtz free energy as several contributions (including electrostatic contribution and association contribution) according to perturbation theory. On the other hand, the EOS proposed is tested for 9 nonaqueous solutions of alkali metal halides. The parameters can be obtained by fitting the vapor pressure of solvents. In addition, we also compared our results with the results of Mock ed al.,Youxiang Zuo and Tzujen Chou.

MODEL AND THEORY

The systems of interest in this work are limited in nonaqueous solutions (methanol solvent) of alkali metal halides.

Since the salts are fully dissociated, there are three components in the solution, including cation, anion and methanol solvent respectively. The ions are treated as charged Lennard-Jones (LJ) spheres with additional associating sites forming hydrogen bonds with methanol. A methanol molecule is regarded as the LJ sphere with embedded a point dipole and three associating sites, two of which represent lone pair electrons and the others represent protons.

At temperature T and volume V, the system consists of N particles, and the number of species i is N_i. By using the perturbation theory[7], the differences of the Helmholtz free energies (A-A^{hs}) between the system and the corresponding hard sphere system can be expanded as

$$\frac{A - A^{hs}}{NkT} = \frac{A^{LJ}}{NkT} + \frac{A^{elect}}{NkT} + \frac{A^{assoc}}{NkT} \quad (1)$$

where k is the Boltzmann constant. The superscripts hs, LJ, elect and assoc represent the contributions from hard sphere, Lennard-Jones, electrostatic (including ion-ion, ion-dipole and dipole-dipole terms) and association interactions, respectively. Then we can get this equation:

$$\frac{A}{NkT} = \frac{A^{LJ}}{NkT} + \frac{A^{elect}}{NkT} + \frac{A^{assoc}}{NkT} + \frac{A^{hs}}{NkT} \quad (2)$$

The equation of state expressed as the compressibility factor can be derived from above equations by differentiating the free energy with respect to the density,

$$Z = \rho\left[\frac{\partial}{\partial\rho}\left(\frac{A}{NkT}\right)\right] \quad (3)$$

The chemical potential of species k is derived from the following differentiation,

$$\frac{\mu_k}{kT} = \left(\frac{\partial}{\partial\rho_k}\left(\frac{\rho A}{NkT}\right)\right)_{T,\rho\neq\rho_k} \quad (4)$$

Note although the differentiations of eqs. (3) and (4) can be derived analytically, for convenience, the numerical ones are used for our calculations in this work directly.

RESULTS AND DISCUSSION

As all the ions are removed, the system is regressed to pure methanol, i.e., LJ spheres with a point dipole and three associating sites. Its Helmholtz free energy can be expressed by equations. The dipole moment is set as 2.49 Debye to reproduce the experimental dielectric constant of methanol, which is predicted as 32.49 for our EOS and is very close to the experimental value 32.70 at 298.15K.

There are still two kinds of parameters need to be fixed. The first one is the effective average ionic diameter (σ_i), which is assumed adjustable here for each salt. Another one is the ion-methanol association parameter for each ion. This parameter can be obtained by fitting it as a salt-dependent parameter. Furthermore, it is found that the association of the anion and methanol can be ignored in this model without notable losses of accuracies. The anion-methanol association term was therefore removed from our EOS either. Consequently, only two parameters are required in our model.

The EOS proposed was tested for 9 nonaqueous electrolyte solutions of alkali metal halides. The parameters were obtained by fitting the experimental data of the vapor pressure and activity of electrolyte solutions at 1 bar and 298.15K. The regressed parameters and the average absolute deviations (AADs, see definitions in Table 1) of the vapor pressure data are listed in Table 1.

Table 1: Regressed parameters for EOS in this work and the average absolute deviations (AADs) in the vapor pressure (*P*) and activity (*a*), from this work and other models at 1bar and 298.15K

Salt	EOS parameters[a]		AAD%[b]					Molarity range (mol/kg)
	σ_i (Å)	ε^{assoc}/k (K)	Zuo, P[c]	Mock et al., P[d]	Chou, P[e]	This work		
						P	a	
LiCl	5.326	3215.46	2.33	2.90	0.42	1.825	0.387	0-4.580
LiBr	5.316	3137.97	1.99	3.17	0.59	1.800	0.282	0-4.345
NaCl	6.126	2106.30	0.17	0.19	0.01	0.942	0.023	0.041-0.219
NaBr	5.651	3623.06	0.36	0.22	0.08	0.839	0.053	0.042-0.649
NaI	5.111	2717.21	0.84	0.84	0.26	0.907	0.063	0.024-0.755
KBr	6.992	4471.59	0.19	0.12	0.00	0.961	0.016	0.044-0.134
KI	6.008	5129.05	0.24	0.25	0.06	0.889	0.066	0.022-0.735
RbI	6.473	5241.23	0.20	0.24	0.01	0.945	0.045	0.02-0.436
CsI	7.421	5787.42	0.21	0.16	0.00	0.975	0.020	0.033-0.130
Average			0.99	1.63	0.26	1.120	0.106	

[a] *There are two parameters for each salt. One is the effective average ion diameter, σ_i, and the other is the cation-methanol associating parameter, ε^{assoc}. The two parameters are all salt dependent.*

[b] $AAD\% = \frac{100}{NP}\sum_{i=1}^{NP}\left|\frac{f^{cal} - f^{exp}}{f^{exp}}\right|$, *where NP is the number of the experimental points and f is the property of interest (P and a). The superscripts cal and exp indicate the value is from the calculation and experiment, respectively.*

[c] *The AADs% were reported for the electrolyte EOS proposed by Julian Youxiang Zuo, Dan Zhang and Walter Furst.*[8]

[d] *The AADs% were reported for the electrolyte NRTL model proposed by Mock et al.*[9]

[e] *The AADs% were reported for the two-parameter ACM proposed by Tzu-Jen Chou and Akihiko Tanioka.*[10]

As can be seen from Table 1, our EOS gives a good correlation of vapor pressure and activity with an average AAD of 1.120% and 0.106%. Meanwhile, it is obvious to see that the predicted activities are in good agreement with the experimental data over from low molality ranges to high molality ranges. And the agreement with experimental data is very good when the maximum molality up to 4.58 mol/kg methanol. So it reveals that our EOS is very successful in activity calculation over molality range about 0-5 mol/kg methanol in general although the AADs about vapor pressure are little higher than the ones obtained by Zuo.

The predictive capability of EOS in this work can be demonstrated by extrapolating the temperature to a little higher value. For example, Fig. 1(a) and (b) show the predictive vapor pressures by using the parameters given in Table 1, which are correlated from experimental vapor pressures with a temperature of 298.15K. Strikingly, even up to 308.15K, our EOS can still accurately represent the non-ideality of the nonaqueous electrolyte solutions and the AADs are shown in Table 2.

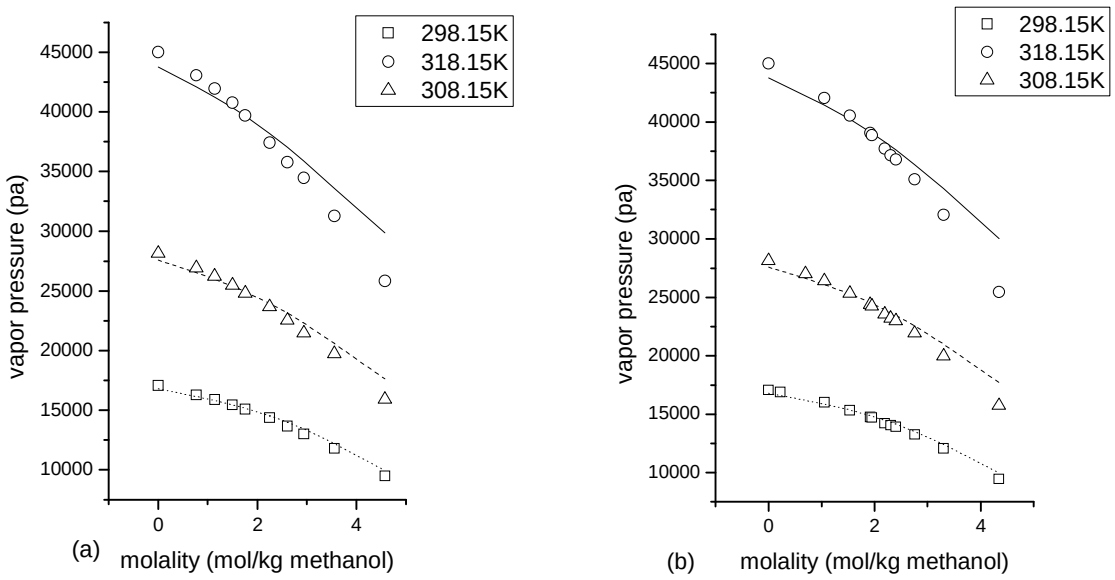

Figure 1. Predicted vapor pressure of (a) LiCl and (b) LiBr nonaqueous electrolyte solutions as a function of salt molality. The lines are calculated from equation of state with the parameters in Table 1, which were obtained by fitting the experimental data at 298.15K. The points represent the experimental data. For average absolute deviations (ADDs), see Table 2.

Table 2: The average absolute deviations (AADs) about the vapor pressure (P) for same regressed parameters of EOS in different temperature, from this work at 1bar

Salt	EOS parameters[a]		Molarity range (mol/kg)	AAD%[b] for P	T (K)
	σ_i (Å)	ε^{assoc}/k (K)			
LiCl	5.326	3215.46	0-4.580	1.825	298.15
				2.802	308.15
				4.045	318.15
LiBr	5.316	3137.97	0-4.345	1.800	298.15
				2.733	308.15
				3.630	318.15

[a] *There are two parameters for each salt. One is the effective average ion diameter σ_i, and the other is the cation- methanol associating parameter: ε^{assoc}. The two parameters are all salt dependent.*

[b] $AAD\% = \frac{100}{NP}\sum_{i=1}^{NP}\left|\frac{f^{cal} - f^{exp}}{f^{exp}}\right|$ *, where NP is the number of the experimental points and f is the property of interest (P). The superscript cal and exp indicate the value is from the calculation and experiment, respectively.*

CONCLUSION

A fundamental two-parameter equation of state for nonaqueous electrolyte solutions is proposed by incorporation of low density expansion of nonprimitive mean spherical approximation and statistical associating fluid theory. The EOS has been tested for 9 nonaqueous alkali halide solutins at ambient condition. The parameters are obtained by fitting the vapor pressures and activities with the average absolute deviation (AAD, see definition in Table 1) of 1.120% and 0.106%. With the parameters given by 298.15K, the EOS can also well predict the vapor pressure data of nonaqueous electrolyte solutions at different temperature points and over the same molality range accurately.

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