

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 298.15 K, and it also has a good predictive capability for nonaqueous electrolyte solutions at different temperature in this work. The comparisons with EOSs published earlier by other researchers in literatures are carried out in detail.

Keywords: EOS; Nonaqueous; Electrolyte Solutions

1. 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 is 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 *et al.*, Youxiang Zuo and Trogen Chou.

2. 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 [7-10], the differences of the Helmholtz free energies ($A - A^{hs}$) between the system and the corresponding hard sphere system can be expanded as

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

where k is the Boltzmann constant. The superscripts hs , LJ , $elec$ and $assoc$ represent the contributions from hard

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The Properties of Electrically Conducting Systems Charles August Kraus, 1922 *Nonaqueous Electrolytes Handbook* G.J. Janz, 2012-12-02 Nonaqueous Electrolytes Handbook Volume I is an authoritative and updated information source for nonaqueous solvent systems The information in this handbook covers the literature to 1972 and includes data for some 210 solvents The book has been organized into eight well defined areas Physical Properties of Solvents Solvent Purification Electrical Conductance Diffusion Density Viscosity Transference Numbers and Additional References and Data Sources The latter section covers additional data sources and reviews not adequately described in the preceding sections recent data and references are also found in this section The method of presentation of material is briefly described in the

introduction to each section to facilitate the use of the tabulated information Bibliographies are given at the end of each section A Compound Index is included Electrical conductance is the property most widely investigated In view of the wealth of data this section has been organized by solutes as follows acids and alkali metal compounds including ammonium compounds quaternary ammonium salts and amines solvent systems electrolyte systems and finally all other solutes For each the data are reported not only for single component nonaqueous solvents but also for mixed solvents Journal of the American Chemical Society American Chemical Society,1914 Proceedings of the Society are included in v 1 59 1879 1937

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