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Recent Advances in Study on Thermodynamic Models for Real Systems Including Electrolytes*

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Abstract: A comprehensive review of recent advances in study on thermodynamic models for real electrolyte solutions is presented. The differences between primitive and non-primitive electrolyte models are demonstrated. Some new thermodynamic models for electrolyte solutions based on the mean spherical approximation and perturbation theory are introduced. An extended scaled-particle theory and modified Clegg-Pitzer equation are presented for physical and chemical absorption processes with mixed solvents, respectively. A pseudo one-component two-Yukawa equation of state is used for the aqueous two-phase extraction process in charged colloidal systems.

Key words: primitive and non-primitive electrolyte models; mean spherical approximation; scaled-particle theory; Clegg-Pitzer equation; physical absorption; chemical absorption; aqueous two-phase extraction; two-Yukawa potential

Introduction

Various electrolyte solutions are widely used in hydrometallurgy, solvent extraction, chemical absorption, biological separation, salt lake development, geological chemistry, and green process. Many authors have paid particular attention to the study on thermodynamic models for systems including electrolytes in order to make the optimization of process design. Although the Pitzer equation[1] and Chen-NRTL equation[2] have been popularly used in industry, in recent years the theoretical researches for electrolyte solutions based on advanced statistical mechanics (such as integral equation theory, perturbation theory, density functional theory, and molecular simulation) are still focused by many scientists. There exists the long-range electrostatic interaction force between ionic species, which makes the theoretical treatment more complicated and difficult than short-range dispersion interaction for non-ionic systems. In this paper, a comprehensive review of recent advances of real electrolyte solutions is presented. A comparison between primitive and non-primitive electrolyte models is demonstrated by use of the mean spherical approximation and the perturbation theory. An extended scaled-particle theory and modified Clegg-Pitzer equation are presented for physical and chemical absorption processes with mixed solvents. The equation of state (EOS) with two-Yukawa potentials is used for the aqueous two-phase extraction process in charged colloidal systems.

1 Primitive and Non-Primitive Electrolyte Models Based on Integral Equation and Perturbation Theories

In the electrolyte primitive model, only the electrostatic interaction between ions is included. The solvent

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molecules are not considered as interacting particles and are treated as a dielectric continuum. The Debye-Huckel theory[3], the Pitzer equation[1], and Blum primitive electrolyte mean spherical approximation (MSA)[4] are all primitive models. They have the advantages of being simple and that only electrostatic ion-ion interactions need to be considered. However, in the primitive model, the ion-solvent and the solvent-solvent interactions are included in the solvent dielectric constant D in the electrostatic term as follows:

$$u_{ij}^{\text{cc}}(r)=\frac{z_i z_j e^2}{Dr} \tag{1}$$

Here, D=78.54 in aqueous solution at 25℃ and e is electronic charge. The above expression is called the electrostatic potential of mean force in the McMillan-Mayer osmotic statistical theory, which was proved to be true by molecular simulation[5].

In the non-primitive model, the solvent molecules, such as water, are treated as interacting particles. The Chen-NRTL[2], Blum-Wei MSA[6], and Henderson-Blum-Tani (HBT) electrolyte perturbation theory-based EOS[7] are all non-primitive models. Among these equations, only Blum-Wei electrolyte MSA can use vacuum dielectric constant (D=1) in its electrostatic term while the others cannot.

Considering the interactions for ion-ion (cc), ion-dipole (cd), and dipole-dipole (dd) contributions as follows:

$$u_{ij}^{\text{cc}}(r)=\frac{z_i z_j e^2}{r} \tag{2}$$

$$u_{ij}^{\text{cd}}(r)=-\frac{z_i e\mu_j\cos\theta}{r^2} \tag{3}$$

$$u_{ij}^{\text{dd}}(r)=-\frac{\mu_i\mu_j}{r^3}[2\cos\theta_i\cos\theta_j-\sin\theta_i\sin\theta_j\cos(\phi_i-\phi_j)] \tag{4}$$

Liu et al.[8] compared the equations from mean spherical approximation and perturbation theory and found that the ion-dipole interaction term is very complicated. Only two perturbation terms including two-body and three-body interactions are not enough. So in these equations, except the non-primitive MSA, the solvent dielectric constant in electrostatic interaction term should still be used instead of vacuum dielectric constant. There is a very complicated mathematic derivation by the use of MSA and perturbation theory to illustrate this relationship, which has been done by Liu et al.[8]

Yu et al.[9] modified the primitive MSA, only including ion-ion and hard-sphere repulsive terms, to correlate the mean ionic activity coefficients for 85 real single electrolyte aqueous solutions (including 1:1, 1:2, 2:2, and 1:3 types of electrolyte) with deviations mostly less than 1% up to very high concentrations when the effective hydration diameters of the cations were treated as three adjustable parameters as a function of ionic strength. The prediction for mixed electrolyte solutions from primitive MSA is better than the Pitzer equation. In recent years, Yu et al. have used the modified primitive MSA to correlate the surface tensions for aqueous electrolyte solutions[10]. Liu et al.[11] used the Blum-Wei non-primitive three MSA equations, including hard-sphere repulsive, ion-ion, ion-dipole, dipole-dipole terms and adding hydrogen-bonding association term from the statistical associating fluid theory (SAFT)[12] to consider hydrogen bonding of water molecules, to correlate the mean ionic activity coefficients for 46 (1:1) real electrolyte solutions up to 3 mol/L with vacuum dielectric constant and a correlation deviation of 1.46%. The equations can be used to predict the mean ionic activity coefficients up to 6 mol/L with a prediction deviation of 3.87%. These non-primitive MSA equations were, however, not successful for asymmetric electrolytes. Each electrolyte only needs two-size parameters (one cation and one anion hard sphere diameters). It can be concluded that compared with the primitive MSA, the non-primitive MSA is less accurate and more complicated to solve in practical use.

Liu et al.[13] used the non-primitive HBT electrolyte perturbation theory with SAFT association term and primitive MSA as reference term to establish a new EOS with solvent dielectric constant for 49 (1:1 and 1:2 types) real electrolyte aqueous solutions. For each electrolyte, only one cation size parameter is adjustable and the Pauling anion diameters are used. There are only 6 interaction terms: hard sphere repulsive, Lennard-Jones (LJ) dispersion, dipole-dipole, ion-ion, ion-dipole, and hydrogen-bonding association terms. In their ion-ion term, they used the electrolyte primitive MSA equation instead of the tedious ion-ion term in original HBT theory. They used the Cotterman perturbation equation[14] to calculate the LJ dispersion interaction in system. The average relative deviation