Modeling for Aqueous Alkali-Earth Metal Solutions Based on the Synergistic Action of Association and Hydration under Supercritical Conditions

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The thermodynamic properties and phase behavior of aqueous ion solutions under supercritical conditions is very important to the supercritical water oxidation process and these properties depend on the microscopic behavior of solutions. In previous works on electrolyte solutions, it is widely considered that the hydration of ions under supercritical conditions could be neglected, which has been proved correct for alkali metal solutions by Rasaiah's work (J. Am. Chem. Soc. 2000). That means only the effect of association should be added to thermodynamic models for electrolyte solutions under supercritical conditions. But it does not agree with Valyashko's experimental data (Russ. J. Inorg. Chem., 1983, 1984), which suggests that hydration also affects the behavior of the solution in addition to the association effect. In our previous work, detailed molecular dynamics simulation on aqueous alkali-earth metal chloride solutions has been carried out. It is found from our simulation results that the microscopic behavior of ions in water depends upon the synergistic action of hydration and association. We believe that both association and hydration should be taken into account in modeling for aqueous alkali-earth metal solutions under supercritical conditions. The model we present here comprises the electrostatic effect based on the Debye-Huckel equation, the association effect and the hydration effect. Association equilibrium is used to get the contribution of ionic association, and the equilibrium constants are calculated from Helgeson model (Computers & Geosciences, 1992). The hydration effect is calculated from an adjustable hydration parameter that is obtained from our MD simulation. With this combined model, some thermodynamic properties, especially the solubility of highly concentrated aqueous alkali and alkali-earth metal chloride solutions, have been calculated from 523.15K to 623.15K. The results agree well with the experimental data.