A Thermodynamic Model for Aqueous Solutions of Sodium Sulfate from 473 K to 773 and Compositions up to the Saturated Solution SLV Line

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A thermodynamic model for the system Na_2SO_4 - H_2O is required for understanding the deposition process of this salt in supercritical water oxidation applications [1]. We have adapted models developed by Anderko and Pitzer (AP) for NaCl - H_2O [2] and by Jiang and Pitzer (JP) for $CaCl_2$ - H_2O [3]. The Na_2SO_4 - H_2O differs from the NaCl - H_2O system in the following respects: the solidus intrudes into the critical regime; the Na_2SO_4 molecule does not carry a dipole moment; and the data for Na_2SO_4 - H_2O are scarce.

In the AP and JP models, the Helmholtz free energy is a sum of a hard-sphere, and electrostatic and perturbative parts, the latter an empirically truncated virial expansion. The first two parts are theory-based, with few adjustable parameters. The AP model includes dipolar interactions, the JP model includes quadrupolar interactions as well. Dissociation of the salt is not taken into account. For the present application, water was treated as a dipolar fluid, and Na_2SO_4 as a quadrupolar one.

Experimental data by Khaibulin and Novikov for the LV phase boundaries at concentrations up to the SLV line [4] were used for temperatures up to 630 K. For guidance at higher temperatures, we included estimates by Armellini [1] of LV concentrations at two temperatures, based on data by Ravich and Borovaya [5].

The parameters of the mixture model were found through the use of methods similar to those used by AP, but, given the sparsity and limited range of the available data, simpler expressions and far fewer parameters were used than in the case of AP. The predictions of the model are compared with the experimental data used in the fit, and also with single-phase, low-concentration density data between 10 and 30 MPa, and from 517 to 668 K, from recent vibrating-tube densimetry by Majer. An attempt has been made to include a representation of the fluid-solid phase boundary.

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