

EXCESS THERMODYNAMIC PROPERTIES OF CONCENTRATED AQUEOUS SOLUTIONS AT HIGH TEMPERATURES

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Measurements of the vapor pressure of the solvent in wide ranges of concentration and temperature provide information on solute solvation and ion pairing - the two phenomena most often invoked for description of dilute solutions. Even in moderately concentrated solutions, as interionic distances become comparable to ionic diameters, these simple concepts gradually lose their meaning and solutions behave like molten salts.

The usefulness of experimental vapor pressure results increases rapidly with their accuracy, since derived properties, such as solution enthalpies and heat capacities, can be calculated. Very accurate results can be obtained by the isopiestic method, but primary vapor pressure data for standard solutions are needed. In order to obtain vapor pressures at conditions where accurate isopiestic standards are not available and to establish more accurate standards, the ORNL isopiestic apparatus was modified for simultaneous direct vapor pressure measurements and isopiestic comparisons.

There are no comprehensive solution theories derived from molecular level models and able to predict thermodynamic properties of various electrolytes as the composition changes from dilute solutions to molten salts in a wide range of temperatures. Empirical and semi-empirical models are useful for representation of experimental results, interpretation of measurements of other properties such as conductance, solubility or liquid-vapor partitioning of solutes, and for verification of theoretical predictions.

Vapor pressures for aqueous  $\text{CaCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ,  $\text{NaI}$  were measured at temperatures between 380 and 523 K in the concentration range extended to water activities below 0.2 (over 30 mol/kg for  $\text{LiCl}$ ). General equations based on the modified Pitzer ion-interaction model were used to obtain enthalpy and heat capacity surfaces, which are compared with direct calorimetric measurements.

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