Thermodynamics of Concentrated Electrolyte Mixtures. II. Densities and Compressibilities of Aqueous NaCl-CaCl$_2$ at 25 °C

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Densities and ultrasonic velocities of NaCl-CaCl$_2$ aqueous mixtures at 25 °C have been measured for the ionic strength range $I=0.30-20.0$. Where NaCl solubility permitted, both properties were measured over the range of compositions from pure NaCl to pure CaCl$_2$ at constant $I$. Apparent molar volumes and apparent molar compressibilities of the mixtures were calculated. The Pitzer form of the specific interaction theory is used to predict the properties of the binary mixtures from the properties of the single salt solutions. It provides a good fit over the full range of ionic strength for apparent molar volumes but a much inferior fit for compressibilities. It is also clear that in the high ionic strength range, explicit mixing parameters must be included for an excellent fit.

KEY WORDS: Densities; compressibilities; aqueous NaCl-CaCl$_2$; apparent molar volumes; apparent molar compressibilities; Pitzer theory.

1. INTRODUCTION

The recent growing interest in the properties of concentrated aqueous electrolyte mixtures has been generated in part by attempts to understand natural brines such as seawater and geothermal brines. Also, concentrated electrolytes are involved in various industrial processes, an example of which is the use of concentrated salt solutions to provide hydrostatic pressure in the drilling of oil and gas wells.

Attempts to deal with the free energies of electrolyte mixtures were made by Harned and his collaborators$^{(1)}$ and by Scatchard $et$ $al.$$^{(2)}$

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These are exhaustively described by Whitfield. Another approach, the Bronsted-Guggenheim specific interaction approach, never received extensive use. The only widely adapted approach to the volume and heat properties of electrolytes was the 'Young's rules' approach. This is clearly described by Millero who also explains the extension of the Bronsted-Guggenheim approach to such properties.

The most generally applicable approach to this problem, developed in recent years is that of Pitzer which has been summarized briefly with references to the original papers. In essence, the Pitzer approach is a specific interaction or virial approach. Single salt data are fitted to an equation containing adjustable binary and ternary interaction coefficients. These same coefficients can then be used in mixtures. However, at high mixture concentrations, additional ternary interaction coefficients may be needed. Examples of the application of the Pitzer theory to activity coefficients of mixtures have been reported by Roy et al. and by Khoo et al. The successful application to extremely concentrated and complex mixtures is exemplified by the geochemical work of Harvie and Weare.

We have embarked on an extensive program of measurements of both free energies and volume properties of binary (and ternary) mixtures up to saturation. The ternary systems of interest to us include the present aqueous NaCl-CaCl₂ system where specific interactions are fairly weak and systems such as ZnCl₂-NaCl where interactions are strong and chemically identifiable complexes exist.

2. EXPERIMENTAL

The NaCl (Fisher, ACS Certified) was dried in a vacuum oven before making up solutions by weight. CaCl₂·2H₂O (Mallinckrodt, AR Grade) was purified in solution by activated charcoal and stock solutions were prepared. The solutions were analyzed for calcium by EDTA titration and for chloride by AgNO₃ titration. All solutions were prepared using distilled water that was passed through a NANOPure (Barnstead) ion exchange apparatus.

The densities of the solutions were measured by a vibrating tube densimeter (Sodev, Model O2D), whose details are given elsewhere. The densimeter constant was obtained by calibration with NaCl solutions using the density data of Desnoyers in the concentration range up to 6 molal. Our measured densities agree with those of Desnoyers to ±8 ppm and with the density data of Vaslow for NaCl. All measurements were made with a dilution flow technique with the solution