that have demonstrated significant electrolyte composition gradients at Ag electrodes in electrolyzed $NaNO_3$–$AgNO_3$ mixtures (C. E. Vallet, D. E. Heatherly and J. Braunstein, *Abstract #340, 2nd Int. Symp. Molten Salts, The Electrochem. Soc., Pittsburgh, Oct. 15 - 20*, p. 921). In collaboration with G. Mamantov, University of Tennessee, a cell has been designed and constructed for electrolysis–e.m.f. relaxation measurements in the cell $Na/\beta''Al_2O_3/NaCl$, $AlCl_3/Al$ to determine the importance of migrational polarization involving the beta alumina membrane.

During the remainder of 1979 and 1980 we will conduct a systematic series of electrolysis–e.m.f. relaxation measurements at LiAl electrodes in LiCl–KCl mixtures, varying alloy and electrolyte compositions and current densities in order to resolve diffusional relaxations in the alloy and in the electrolyte. Scanning electron microscopic examination of quenched electrolyzed salt samples will be tested as a means of observation of composition gradients.

ELECTROLYTE DATA EVALUATION

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The objective of this project is to collect, compile and evaluate the thermodynamic data on aqueous electrolyte solutions. This project will provide for the electrochemical community a broad data reference base on electrolyte solutions as well as critically evaluated values of osmotic and activity coefficients for these solutions. Thermodynamic equilibrium properties (ionic activities, apparent and partial molal enthalpies and heat capacities) and transport properties (conductivity, transference numbers, and diffusion coefficients) are included. This project is complementary to a continuing program sponsored by the Office of Standard Reference Data of the National Bureau of Standards.

Past accomplishments include the following:

(1) Development of a comprehensive set of computer programs for the evaluation of mean ionic activity and osmotic coefficients for aqueous electrolyte solutions [3].

(2) Application of this correlational scheme to calcium chloride [4] – both as a standard for isopiestic measurements and to demonstrate the utility of the scheme.

(3) A comprehensive literature search for sources of thermodynamic data pertinent to aqueous solutions. This search disclosed useful sources of data in the literature [2].

(4) A literature search for sources of data that can be used to calculate activity and/or osmotic coefficients for polyvalent electrolytes in water [5].

(5) Evaluation of the activity and osmotic coefficients of aqueous sulfuric acid from zero to 28 mol kg^{-1} at 25 °C [9].

(6) A literature search for sources of data that can be used to calculate relative partial molal enthalpies and apparent molal heat capacities for electrolytes in water [8].

(7) The detailed evaluation of activity and osmotic coefficients for aqueous solutions consisting of the alkaline earth metal halides [6], the bi-univalent compounds of iron, nickel, and cobalt, [10] the bi-univalent compounds of lead, copper, manganese and uranium [11], the bi-univalent compounds of zinc and cadmium [13], the alkali metal nitrites [12], and thirty-seven uni-bivalent systems [15]. In all, activity and osmotic coefficients for approximately one hundred and thirty binary electrolyte solutions have been evaluated in detail.

Future plans include:

(1) Completion of the evaluation of the activity and osmotic coefficients for the alkaline earth compounds (the non-halides).

(2) Development of a computational scheme for the evaluation of the relative apparent molal enthalpy of solutions.

(3) Complete annotated bibliography on H_2SO_4 solutions; initiate bibliography on KOH solutions.

(4) Completion of the evaluation of the activity and osmotic coefficients for aqueous electrolytes of charge type 3-1 and 1-3.

(5) Extension and further development of our computational ability to treat electrolyte solutions undergoing complex chemical behavior such as extensive ion-pairing, hydrolysis, etc.

(6) Transfer of an activity and osmotic coefficient data base to the computer data base currently operational at Lawrence Livermore Laboratory.

(7) The initiation of a comprehensive literature search for the conductivities, transference number, and diffusion constants for aqueous electrolyte solutions.

During the coming year work will be devoted to studying and developing methods suitable for correlation of electrolyte systems in which ion pairing plays a significant role and for concentrated solutions. Generalized correlation schemes for the treatment of mixed electrolyte systems must also be developed.

Recent publications

1 W. Hamer and Y. C. Wu, Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25 °C, *J. Phys. Chem. Ref. Data, 1* (1972) 1047.

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3 B. R. Staples and R. L. Nuttall, Computer programs for the evaluation of activity and osmotic coefficients, *Nat. Bur. Stand. (U.S.) Tech. Note 928,* U.S. Government Printing Office, Washington, DC, 1976.
4 B. R. Staples and R. L. Nuttall, The activity and osmotic coefficients of aqueous calcium chloride at 298.15 K, *J. Phys. Chem. Ref. Data, 6* (1977) 385.
5 R. N. Goldberg, B. R. Staples, R. L. Nuttall and R. Arbuckle, A bibliography of sources of experimental data leading to activity and osmotic coefficients for polyvalent electrolytes in aqeous solution, *Nat. Bur. Stand. (U.S.) Spec. Publ. 485,* U.S. Government Printing Office, Washington, DC., 1977.
6 R. N. Goldberg and R. L. Nuttall, Evaluated activity and osmotic coefficients for aqueous solutions: the alkaline earth metal halides, *J. Phys. Chem. Ref. Data, 7 (1978) 263.*
7 B. R. Staples, Association constants for aqueous species of alkali earth salts, *Environ. Sci. Technol., 12* (1978) 339.
8 D. Smith-Magowan and R. N. Goldberg, A bibliography of experimental data leading to thermal properties of binary aqueous electrolyte solutions, *Nat. Bur. Stand. (U.S.) Spec. Pub. 537,* U.S. Government Printing Office, Washington, DC, 1979.
9 B. R. Staples, Activity and osmotic coefficients of aqueous sulfuric acid, *J. Phys. Chem. Ref. Data,* in press.
10 R. N. Goldberg, R. L. Nuttall and B. R. Staples, Evaluated activity and osmotic coefficients for aqueous solutions of iron chloride and the bi-univalent compounds of nickel and cobalt, *J. Phys. Chem. Ref. Data,* in press.
11 R. N. Goldberg, Evaluated activity and osmotic coefficients for aqueous solutions: bi-univalent compounds of lead, copper, manganese, and uranium, *J. Phys. Chem. Ref. Data,* in press.
12 B. R. Staples, Activity and osmotic coefficients of aqueous alkali metal nitrites, *J. Phys. Chem. Ref. Data,* in press.
13 R. N. Goldberg, Evaluated activity and osmotic coefficients for aqueous solutions: bi-univalent compounds of zinc, cadmium, and ethylene bis(trimethylammonium) chloride and iodide, manuscript in review.
14 *Proc. U.S. Bur. Mines Workshop on Techniques for Measurement of Thermodynamic Properties, Aug. 1979, I and II.*