Determination of Multiple Ion Association and Ion Mobilities in Aqueous Li₂SO4 and K₂SO₄ from Conductance Measurement at Temperatures from 523 K to 673 K

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The electrical conductivity of aqueous solutions of Li_2SO_4 and K_2SO_4 have been measured at 523 - 673 K at 20 - 28 MPa in dilute solutions for molalities up to $2 \cdot 10^{-2}$ mol/kg. These conductivities have been fit to the conductance equation of Turq, et al. (1995) with a consensus mixing rule and mean spherical approximation activity coefficients. In the temperature range 523 - 653 K, where dielectric constant $\varepsilon > 14$, the conductance data can be fitted by an association model. The adjustable parameters of this model are the overall dissociation constants of $MeSO_4^-$ and $Me_2SO_4^0$ associates and SO_4^{-2} limiting conductance (ion mobility) at infinite dilution. The resulting parameters for conductance data of Li_2SO_4 aqueous solutions are shown in Table, where the 95% confidence limits of the last digit are given in parenthesis.

T, K	ρ^0_{H2O}, kg m^{-3}	$\Lambda^0_{SO4=}$, Scm^{2}eq^{-1}	Log K$_{NaSO4-}$	Log K$_{Na2SO4}$
524	815	500(10)	-2.00(4)	----
576	740	681(2)	-2.60(1)	-4.16(1)
624	626	920(140)	-3.6(1)	-5.6(1)

For the 673 K state point with the lowest dielectric constant, $\varepsilon = 5$, where the Coulomb interactions are the strongest, more complex models are needed. Good fits to the data were found for multi-ion association models. In the case of K_2SO_4 aqueous electrolyte solutions the ion associates $K_3(SO_4)_2-$ and $K_4(SO_4)_2$ are necessary to fit the conductance data. In the case of Li_2SO_4 solutions it is necessary to assume the existence of ion associates of higher order. Reasonable fits were found for $Li_{2n}(SO4)_n$ models where n was in the range of 3 to 5.

Recent Progress in Predicting Free Energy of Aqueous Solutes at High Temperatures

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Semi-Empirical Methods

New semi-empirical methods of predicting free energies of aqueous solutes that improve upon the revised HKF model embodied in the Supercrit 92 software will be briefly reviewed.

Simulations

Recently simulations have added a great deal to our understanding of high-temperature aqueous solutions. These simulations give quantitative information about properties of the approximate models used in the simulations. Because of the difficulty in estimating the difference between the approximate models and the real world, most of the information about the real world has been qualitative or semi-quantitative. High-level *ab initio* models are accurate enough, but simulations with these models are prohibitively expensive.

A new method, that shows great promise, is the ab initio/classical free energy perturbation (ABC/FEP) method. This method combines the free energy calculated from a classical simulation of an approximate model with the free energy of perturbing the approximate solute-solvent energies into high-level *ab initio* energies. A recent test of this method at 573 K and a water density of 0.725 g/cm^3 gave a hydration free energy for NaCl at infinite dilution of -657 kJ/mol, which is within 4 kJ/mol of the well-known experimental value. This method can also be used to predict association constants of aqueous sodium chloride at high temperatures with an accuracy of about 0.3 log units. A related method can predict the pair correlation function and the co-ordination number of the solute. Results using these methods for NaCl at eight different high-temperature state points will be discussed.