ABSTRACT

Studies of Solvation and Reactivity of Mono and Dinuclear Cobalt(III) Complexes in Tetramethylurea-water Mixtures

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Transfer chemical potentials of some mononuclear and dinuclear cobalt(III) complexes were determined using solubility data for the complexes in tetramethylurea-water mixtures. Single ion transfer chemical potentials were evaluated using the TATB assumption. A qualitative estimate of the relative affinity of the complex ions for water and for tetramethylurea was made on the basis of transfer chemical potential determinations which were discussed with respect to sizes, charges, ligands and bridging groups.

Solubilities of carbonato (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo-tetradeca-4,11-diene cobalt (III) perchlorate [trans-14...Co(III)] have been determined in a series of tetramethylurea-water solvent mixtures over the temperature range 283.2 to 308.2K. Solubility maxima are independent of temperature. Enthalpies and entropies of solution exhibit compensation. Maxima in thermodynamic solution parameters correspond to maximal solvent structured effects and are therefore assignable to solvent-solvent interactions.

Free energies ($\Delta G_t°$) and entropies ($\Delta S_t°$) of transfer at 25°C of the

nonelectrolyte p-nitroaniline from water to various 1,1,3,3-tetramethylurea mixtures have been determined from solubility measurements at eight temperatures from 282.7 - 218.2K. Increasing specific solute-solvent interactions have been proposed to interpret the nature of $\Delta G_t°$-composition profiles. The enhanced structure of water in the water-rich mixed solvent has been correlated with maximum in the $\Delta S_t°$-composition profiles.

Rates of solvolysis of the complex cation *trans*-$[Co(en)_2Cl_2]^+$ have been determined in mixtures of water with tetramethylurea. Initial state-transition state analysis yielded ΔH^*, ΔS^* and ΔG^* (enthalpies, entropies and free energies of activation respectively). The solvent composition at which the maximum is found in the variation of ΔH^* and the entropy ΔS^* of activation correlates well with the maximum in the variation of the relative partial molar volume of tetramethylurea in the mixture. A free energy cycle is applied to the process initial state (C^{n+}) going to the transition state $[M^{(n+1)+\cdots Cl^-}]$ in water and in the mixture using free energies of transfer of the individual ionic species $\Delta G_t°(i)$, from water into the mixture. Values of $\Delta G_t°(i)$ are derived from the tetraphenylarsonium tetraphenylboride (TATB) extrathermodynamic assumption. Using this data, changes in solvent structures on going from water into the mixture are found to stabilize the cation in the transition state, $M^{(n+1)+}$, more than in the initial state, C^{n+}.

The kinetics of the oxidation of L-ascorbic acid by the mononuclear *cis*-diaquatetraammine cobalt(III) ion $[(NH_3)_4\ Co(H_2O)_2]^{3+}$ were studied as a function of L-ascorbic acid concentration, pH and tetramethylurea content of the solution. The kinetic data indicated an outer sphere mechanism, where (HA^-) monoprotonated

ascorbate was involved in the redox process. The presence of TMU in the cosolvent increased the rate of reaction.