The complexes formed by Ni(II) are compared with those formed by other cations, at the same conditions.

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Thermodynamics of the Protonation of Some Cryptands in Water and Methanol

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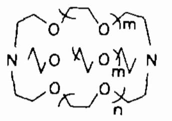
We report the results of thermochemical studies in water and anhydrous methanol of some cryptands, L = [2.2.2], [2.2.1], and [2.1.1], of general formula represented below:



m = 0, n = 1 : [2.1.1]
m = 1, n = 0 : [2.2.1]
m = n = 1 : [2.2.2]

Protonation constants K_1 and K_2, relative to the following equilibria:

$$L + H^+ \rightleftharpoons HL^+; K_1, \Delta H_1$$

$$HL^+ + H^+ \rightleftharpoons H_2L^{2+}; K_2, \Delta H_2$$

have been determined by pH-metry at 25 °C, with $I = 0.1$ or 5×10^{-2} M (Et_4NClO_4). The values of ΔH_1 and ΔH_2 have been determined from calorimetric measurements in both solvents. Corresponding ΔG and ΔS values have been calculated.

Results are discussed in terms of conformational changes of the mono- and biprotonated cryptands in the different solvent water and methanol.

Thermodynamics and Kinetics of Some Acid Base Reactions in Benzonitrile and Acetonitrile

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The proton transfer between an acid and a base involves a change of the total amount of charges in the reacting system:

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + BH^+ \qquad (1)$$

or a transfer of charge:

$$AH^+ + B \rightleftharpoons A + BH^+ \qquad (1')$$

Therefore the equilibria and the reaction mechanisms of acid base reactions depend strongly on the ability of the solvent to stabilize ions and to participate in the proton transfer process.

We have studied the reactions between five-substituted phenols (AH) and acridine orange (B) in benzonitrile and between 4-nitrobenzoic acid and 4-nitrophenol and B in acetonitrile. In these systems, free cations are formed according to eqn. (1) and the anions are stabilized by hydrogen bonding to additional phenol in a second step (homoconjugation):

$$A^- + AH \rightleftharpoons AHA^- \qquad (2)$$

Thermodynamic data were evaluated from spectrometric titrations of acridine orange base with the acids and of Bu_4N-salts of the phenols with phenol solutions at 10–50 °C. Proton transfer rates were obtained by temperature jump relaxation measurements in solutions containing 0.1 M of the inert salt Bu_4NPF_6. The sample solutions for the kinetic runs were prepared under nitrogen in an all glass apparatus and were filled into the measuring cell without opening the system to the atmosphere.

The equilibrium (1) does not depend much on the solvent, if AH = 4-nitrophenol, whereas the formation constant of AHA^- increases from $K_2 = (4.6 \pm 0.5) \cdot 10^3$ in acetonitrile to $K_2 = (2.5 \pm 0.2) \cdot 10^4$ in benzonitrile at 25 °C. This has the remarkable consequence that in benzonitrile in spite of its lower polarity more ions are formed than in acetonitrile with the same concentrations of reactants.

In acetonitrile the rates of proton transfer between 4-nitrobenzoic acid and B are $k_1 = 7.2 \cdot 10^8$ and $k_{-1} = 1.8 \cdot 10^8$ (M^{-1} s^{-1}) at 25 °C. The rates are significantly slower than those calculated for a diffusion controlled process. Similar observations had previously been made with other proton transfer reactions in acetonitrile [1].