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

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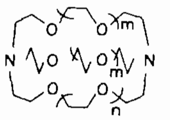
Thermodynamics of the Protonation of Some Cryptands in Water and Methanol

B. SPIESS, F. ARNAUD-NEU and M. J. SCHWING-WEILL
Laboratoire de Chimie Physique (ERA No 166 au C.N.R.S.) E.N.S.C.S., 1, rue Blaise Pascal, 67000 Strasbourg, France

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

R. SÜTTINGER and F. STROHBUSCH*
Institute of Physical Chemistry, University of Freiburg, D-78 Freiburg, F.R.G.

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

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

or a transfer of charge:

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

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):

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

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].

In benzonitrile the proton transfer rates in reaction (1) are correlated with the equilibrium constants. The fastest observed rates are diffusion controlled. Consequences of the kinetic results for the interpretation of properties of the two solvents will be discussed.

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Complex $[NHN]^+$ Formation in Aprotic Media

ZENON PAWLAK
Institute of Chemistry, University of Gdańsk, Gdańsk, Poland

The proton transfer and tautomeric equilibria $[NHN]^+$ heterocomplexes in aprotic solution are considerably more complicated than those in the gas phase. A clear correlation in different solvents between acidity of $[NH]^+$, and formation constant $K^f_{[NHN]^+}$ N-bases is not established. The same holds for the relationships with the basicity of the proton acceptor N-base. The systems studied in the present work involve the interaction of pyridinium $[PyH]^+$, and imidazolium $[ImH]^+$ cation with N-bases, where $pK_a^{H_2O}$ N-bases ranges from 11 to –1. Three terms run through the investigations: (*1*) to establish the molecularity and formation constants $K_{[NHN]^+}$ homo-, and heterocomplexes in acetone and acetonitrile, (*2*) to estimate proton transfer constants K_{PT} for heterocomplexes where proton transfer occur and (*3*) to determine the acidity of protonated N-bases in acetone and acetonitrile media.

A general scheme for the formation of complexes may thus be written as

$$PyH^+ + B \xrightleftharpoons{K} Py\cdots{}^+HB$$

$$PyH^+ + B \xrightleftharpoons{K_{PT}} Py + BH^+ \xrightleftharpoons{K_f} Py\cdots{}^+HB$$

where K is overall equilibrium constant, K_{PT}, and K_f are the proton transfer (PT) and formation equilibrium constants.

The value of K and K_{PT} was derived from the following relationships

$$K = C_BR^2 - R(C_{PyH^+} + C_B) + C_{PyH^+}/R(C_B - C_{PyH^+})^2$$

where: C_B, and C_{PyH^+} = base and acid concentration

$$R = a_{H^+}\cdot f_{C_B=C_{PyH^+}}/a_{H^+_{C_B=C_{PyH^+}}}\cdot f$$

$$K_{PT} = Ka^{acetone}_{[PyH^+]}/Ka^{acetone}_{[BH^+]}$$

Hence values of K_f, the equilibrium constant for the formation of hydrogen bonding complexes, can be found, since $K_f = K/K_{PT}$. In the case where K_{PT} equals unity (for homocomplexes), the overall equilibrium constant value K is equal to the equilibrium constant formation value $K = K_f$.

Heterobinuclear Complexes of L-Carnosine with Cu(II) and Cd(II) in Aqueous Solution

PIER GIUSEPPE DANIELE, PAOLA AMICO and GIORGIO OSTACOLI
Istituto di Analisi Chimica Strumentale, Università di Torino, Turin, Italy

The complex formation in aqueous solution between metal ions and peptides has been widely studied in recent years. Both binary (metal ion–peptide) and ternary (generally with an aminoacid as second ligand) systems have been investigated.

In previous papers [1–3] the formation was evidenced, of heterobinuclear complexes of polyfunctional ligands, such as L-histidine or citric acid (with Cu(II), Ni(II), Zn(II) and Cd(II)) and glutathionate (with Zn(II), Ca(II) and La(III)). Owing to these results too, we thought to investigate the formation of heteronuclear species in solution of the dipeptide L-carnosine (car, β-alanil-L-histidine).

The study was performed at t = 37 ± 0.1 °C and $I_c = 0.15$ mol dm^{-3} by potentiometric measurements of hydrogen ion concentration with glass electrode, in the presence of Cu(II) and Cd(II) ions.

First the stability constants were determined for the binary systems Cu(II)–car and Cd(II)–car. Concerning Cu(II) complexes a disagreement was noticed in the literature, as to the species present in solution [4, 5]: our data show a fairly good agreement with those reported by Perrin *et al.* [4]. The most important species in solution is $[Cu_2(car)_2H_{-2}]$, in which the amide hydrogen was very probaly displaced.

The stability constants for the Cd(II)–car system have not yet been reported. Our measurements evidenced the presence in solution of the species $[Cd(car)H]$, $[Cd(car)]^+$ and $[Cd(car)_2]$.

When considering the ternary Cu(II)–Cd(II)–car system the calculation of titration curves in agreement with the experimental data is possible only if we suppose that species other than binary com-