comparable with each other, (*iv*) when data for the same system, studied by different authors, are referred to the same standard state and temperature and then compared, the logK values usually differ for one, two and more unities.

As a part of a program of a systematic study of the thermodynamic and kinetic aspects of the reversible oxygen addition to Co(II) complexes and the successive irreversible oxidation to Co(III) species, we report here the results of a study on the system Co(II)–*en*–O_2 in aqueous solution at 25 °C (KCl 1 *M*). Other studies concerning the Co(II)–*tetren*–O_2 and Co(II)–*cyclam*–O_2 systems have been undertaken together with the Paoletti and Micheloni of the Florence University and the results obtained will be successively reported.

The thermodynamic and kinetic aspects of the reaction between Co(*en*)$_2^{++}$ complex and oxygen have been very carefully studied by Miller *et al.* [3], Nakon *et al.* [4], Powell *et al.* [5] and Zehnder *et al.* [6]. Nakon and Powell agree about the formation of a μ-peroxo-μ-hydroxo complex, but the stability constant calculated from data of Nakon ($K = 10^{6.4}$ M^{-1}) differs by three orders of magnitude in respect to that of Powell ($K = 10^{10.8}$ M^{-1}). Miller and Zehnder agree that after the fast reaction of the oxygenation a slow process follows, but they do not agree as to what this process is. Finally the enthalpy data obtained from Powell by calorimetry, are criticizable for the way they have been calculated.

By comparing the enthalpy changes measured by means of a liquid flow differential micro calorimeter and an isoperibolic calorimeter, we have been able to give a more complete picture of the mechanism of the oxygenation reaction, with respect to that given by Miller and Zehnder, by identifying as a relatively slow step the passage from the μ-peroxo to the μ-peroxo-μ-hydroxo complex. For both these products of the oxygenation, the enthalpy and the free energy changes associated to their formation have been determined. The former by a proper analysis of the calorimetric curves collected in a large range of pH and *en*/Co(II) ratios, the latter by recording at the same time the variations of both the hydrogen and the molecular oxygen concentration when known quantities of Co(II) are added to aqueous solutions of *en* differing in pH and amount of this ligand.

References

1 G. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976).
2 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev., 79,* 139 (1979).
3 F. Miller, J. Simplicio and R. G. Wilkins, *J. Am. Chem. Soc., 91,* 1962 (1969).
4 R. Nakon and A. E. Martell, *J. Inorg. Nucl. Chem., 34,* 1365 (1972).
5 H. K. J. Powell and G. H. Nancollas, *J. Am. Chem. Soc., 94,* 2664 (1972).
6 M. Zehnder, H. Mäkce and S. Fallab, *Helv. Chim. Acta, 58,* 2306 (1975).

Investigation on Complexation of Ni(II) with Sulphonated Azo-dyes

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The coordination reactions between Ni(II) and two water–soluble azo-dyes containing respectively the heterocyclic rings tetrazole and thiazole are described. The investigation was performed in 0.1 *M* $NaClO_4$ aqueous solution, at T = 25.0 °C, with the spectrophotometric method. For each solution, characterized by a constant value of the metal-ion and ligand concentration, the acidity was varied with small additions of concentrated $HClO_4$ or NaOH over the –log range 2–6, and for each –log value, the spectra were recorded. The functions A *vs.* –log were analyzed with the graphical method described by Sommer [1], so that molar absorbances, compositions and stability constants of each complex could be determined.

The following results have been obtained:

Ligand		
1,8-dihydroxy-naphthalen-2-thiazolato-3,6-disulphonic acid (TAAC) [2]	$Ni + HL \rightleftarrows NiHL$	$\log K_f = 2.41 \pm 0.03$
	$2Ni + L \rightleftarrows Ni_2L$	$\log K_f = 11.06 \pm 0.06$
1,8-dihydroxy-naphthalen-2-tetrazolato-3,6-disulphonic acid (T-azo-C) [3]	$Ni + HL \rightleftarrows NiHL$	$\log K_f = 7.86 \pm 0.03$

The molar compositions have been confirmed with Job's method [4].

Some other data on the coordination of Ni(II) with a sulphonated azo-dye in aqueous solution have been previously published [5], and the present work extends the research to other ligands of the same kind.

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

References

1 V. Kuban, L. Sommer and T. Havel, *Collect. Czech. Chem. Commun.*, *40*, 604 (1975).
2 C. Riolo Bertoglio, T. Soldi Fulle, G. Gallotti, M. Pesavento and G. Spini, *Gazz. Chim. It.*, *105*, 221 (1975).
3 M. Pesavento, C. Riolo Bertoglio, T. Soldi Fulle and G. Cervio, in press.
4 P. Job, *Ann. Chim., France*, *9*, 113 (1928).
5 T. Soldi Fulle, C. Riolo Bertoglio, G. Gallotti and M. Pesavento, *Gazz. Chim. It.*, *107*, 347 (1977).

Thermodynamics of the Protonation of Some Cryptands in Water and Methanol

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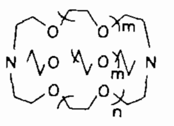
We report the results of thermochemical studies in water and anhydrous methanol of some cryptands, L = [2.2.2], [2.2.1], and [2.1.1], of general formula represented below:



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].