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Further Studies on the Role of Adduct Formation in the Extraction of Nickel with 8-Quinolinols in the Presence of Pyridine and Its Analogues

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Pyridine and its methyl analogues (2-methyl, 2,4-dimethyl, 2,4,6-trimethyl) were found to enhance the extraction of nickel into chloroform with 8-quinolinol and its 2-methyl, 4-methyl, 5-chloro, and 5-nitro analogues. From a quantitative evaluation of extraction equilibrium data, the adduct formation constants of what proved to be 1:2 chelate–nitrogen base adducts are determined. The results are consistent with Lewis acid–base concepts. The special role of steric factors is discussed.

Introduction

Much work has been done in the formation equilibria of simple metal chelates, and the role of such factors as ligand basicity, metal ion (Lewis) acidity, and steric factors have been reasonably well described. Relatively little is known, however, about the factors affecting the reaction of neutral, coordinatively unsaturated chelates with adducting ligands, which may be either the chelating agent itself or another base such as pyridine, TBP, etc., viz.

$$M^{n+} + (n + a)HL \rightleftarrows ML_n\cdot aHL + nH^+$$

$$M^{n+} + nHL + aB \rightleftarrows ML_n\cdot aB + nH^+$$

Adduct formation is of great importance in the solvent extraction of many metal ions.

In earlier studies with 8-quinolinolatonickel (NiQ_2), an adduct $NiQ_2\cdot HQ$ was found in which the neutral 8-quinolinol acted as a monodentate ligand involving its nitrogen atom.[1,2] Although the 4-methyl-8-quinolinol behaved similarly, the 2-methyl analogue did not form an adduct but only a simple 1:2 chelate with nickel. This behavior, analogous to that observed with zinc and 8-quinolinols,[3,4] is indicative of the adverse effect of the steric influence of the 2-methyl substituent on adduct, as well as simple chelate, formation.

This communication represents an extension of our work to the examination of electronic as well as steric influences on adduct formation with nickel chelates of 8-quinolinols and various pyridines.

Experimental Section

Apparatus. A Kahn-type shaking machine in which 10-mL centrifuge tubes with stoppers could be accommodated was used to equilibrate the solutions at ambient temperature.

Radioactivity was counted on a NaI (Tl) detector connected to a scintillation spectrometer, supplied by ECIL (India).

AR grade 8-quinolinol (Merck), 2-methyl-8-quinolinol (Fluka), 5-chloro-8-quinolinol (Aldrich), and 5-nitro-8-quinolinol (K & K) were recrystallized from absolute alcohol. 4-Methyl-8-quinolinol was synthesized from *o*-aminophenol and methyl vinyl ketone as described earlier. The crude product was purified by vacuum distillation followed by two recrystallizations from absolute alcohol. The melting point of the purified product was 140–142 °C (lit. mp 141 °C). Pyridine, 2,4,6-collidine (trimethylpyridine) (BDH AnalaR), and 2-picoline (2-methylpyridine) and 2,4-lutidine (2,4-dimethylpyridine) (Fluka AG) were purified by distillation after drying over potassium hydroxide.

Nickel-65 ($t_{1/2}$ = 2.56 h) was obtained by irradiating ~0.1 mg of enriched nickel-64 in a pneumatic rabbit facility at CIRUS, Trombay. The irradiated target was dissolved in hydrochloric acid. The final strength of the nickel tracer solution used was $\leq 10^{-6}$ M.

A potassium hydrogen phthalate–sodium hydroxide buffer solution at pH 5 was prepared and the ionic strength was maintained constant at 0.25 by sodium perchlorate.

Five milliliters of a buffered ^{65}Ni solution at 0.25 ionic strength and 5 mL of the reagent solutions in chloroform (8-quinolinol + varying amounts of heterocyclic base) were equilibrated by shaking for 30 min. The mixtures were then centrifuged, and equal volumes of both phases were pipetted out and counted at constant geometry.

Results and Discussion

As has been previously shown,[4] the stoichiometry (a) and equilibrium constant (K_{AD}) of adduct formation in the organic phase

$$ML_n(o) + aB(o) \xrightleftharpoons{K_{AD}} ML_n\cdot aB(o)$$

can be obtained from a log–log plot of the distribution ratio of the metal ion, D, vs. the concentration of the adducting ligand, B, under extraction conditions of constant pH and organic-phase chelating agent concentration. Such a plot will consist primarily of two linear portions: the first at zero slope, reflecting the extraction of the simple chelate at very low $[B]_0$

$$\log D = \log K_{ex} + n \log [HQ]_0 + n\text{pH} \tag{a}$$

and the second at high $[B]_0$, where the adduct extraction predominates

$$\log D = \log K_{ex} + n \log [HQ]_0 + n \log K_{AD} + a \log [B]_0 \tag{b}$$

Table I. Adduct Formation Constants for Various Pyridine Adducts of the Nickel 8-Quinolinates in Chloroform

		log K_{AD}				
base	pK[a, b]	8-quinolinol	2-methyl-8-quinolinol	4-methyl-8-quinolinol	5-chloro-8-quinolinol	5-nitro-8-quinolinol
pyridine	5.20	3.12	2.70	2.76	4.50	5.14
2-picoline	5.90	2.25	1.90	2.04	3.10	4.34
2,4-lutidine	6.72	2.50	2.24	2.36	3.56	4.84
2,4,6-collidine	7.50	2.92	2.55	2.80	4.25	4.60

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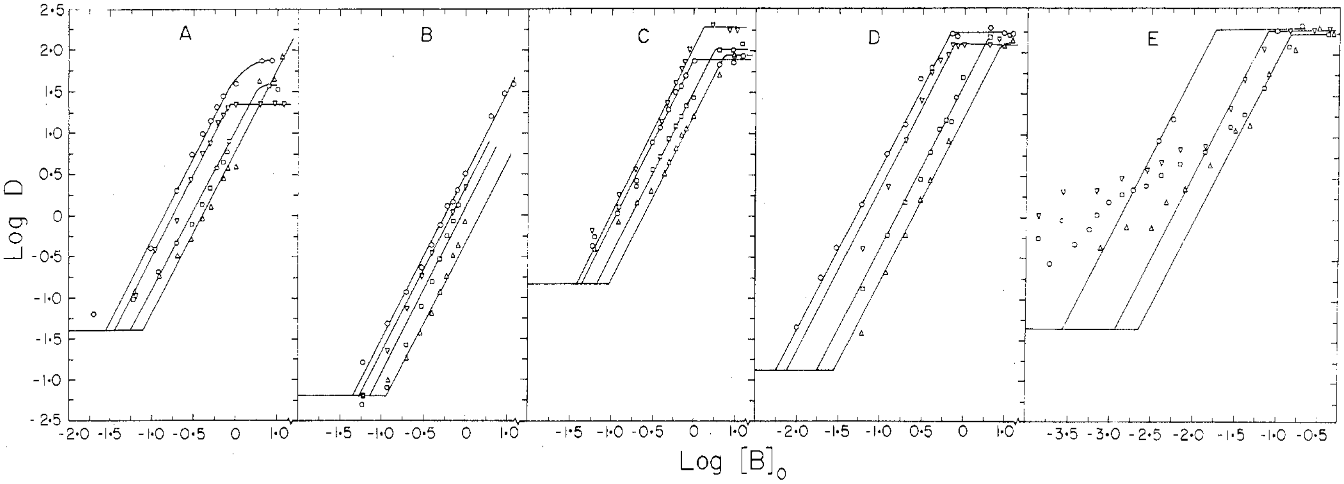

Figure 1. Distribution of pyridine adducts of nickel 8-quinolinates between chloroform and water (pH 5.0): ○, pyridine; ▽, 2,4,6-collidine; □, 2,4-lutidine; △, 2-picoline; A, $[8\text{-HQ}]_0 = 1.031 \times 10^{-3}$ M; B, $[2\text{-Me-8-HQ}]_0 = 2.226 \times 10^{-2}$ M; C, $[4\text{-Me-8-HQ}]_0 = 1.01 \times 10^{-3}$ M; D, $[5\text{-Cl-8-HQ}]_0 = 1.015 \times 10^{-3}$ M; E, $[5\text{-NO}_2\text{-8-HQ}]_0 = 1.54 \times 10^{-4}$ M.

The slope of this latter plot gives the number of adduct ligand molecules, a, involved in the adduct formation. The value of the adduct formation constant is obtained from the intersection of lines (a) and (b):

$$\log K_{AD} = -a \log [B]_0$$

In all the systems examined here, of the series of substituted 8-quinolinol chelates of nickel with various pyridines, the slopes of the plots have a limiting value of 2, indicating an adduct formula of $NiQ_2{\cdot}2B$. Since nickel 8-quinolinol chelates isolated from an aqueous phase are shown, via thermogravimetry, to have the formula $NiQ_2{\cdot}2H_2O$, the role of the adducting ligand in increasing extractability of nickel is seen to result from replacement of water by a ligand that is more compatible with the organic solvent.

The values of adduct formation constants of the pyridine adducts of the nickel 8-quinolinol chelates, shown in Table I, decrease in the order pyridine > 2,4,6-collidine > 2,4-lutidine > 2-picoline. Methyl substitution of pyridine increases the basicity of the nitrogen atom, but in either the 2- or 6-position, substitution can adversely affect metal complexation by steric hindrance. Thus, pyridine is expected to form more stable adducts than 2-picoline. The addition of a second methyl group in the 4-position, as expected, will result in an increase in K_{AD} but not enough to entirely offset the adverse steric influence of the 2-methyl group. The only surprise in the adduct stability sequence is the position of the collidine, whose additional sterically hindering methyl group seems not to have affected its adducting ability.

Comparing the K_{AD} values of a particular base with the series of chelating agents it may be seen that, aside from 2-methyl-8-quinolinol, they increased with decreasing basicity and, accordingly, decreasing nickel chelate stability. Thus, as with the corresponding zinc complexes,[4] the smaller the "residual Lewis acidity" (reflected in the greater chelate stability), the lower the adduct formation constant. In the case of the 2-methyl-8-quinolinol chelates, adverse steric influences override the simpler relationship describing the other systems.

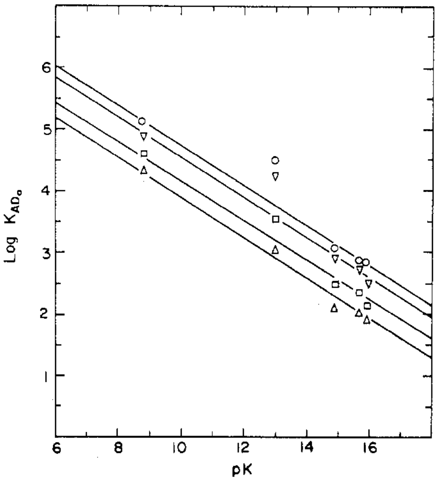

Figure 2. Correlation between adduct formation constants of nickel–pyridine adducts and the basicities of the chelating agents: ○, pyridine; ▽, 2,4,6-collidine; □, 2,4-lutidine; △, 2-picoline.

From the present study it is, thus, concluded that pyridine bases form diadducts with nickel 8-quinolinolates. Since X-ray diffraction studies[5,6] of the 8-quinolinate chelate dihydrate show that these complexes possess a trans-coplanar arrangement with the two water molecules located at axial positions, the formation of a pyridine diadduct of nickel 8-quinolinate would just involve the replacement of the axial water molecules by the pyridine molecules. This study confirms the earlier findings,[7] based on magnetic measurements, which suggest an octahedral complex containing two molecules of pyridine at its apices.

Recently, Patel et al.[8] isolated various solid pyridine adducts of nickel 8-quinolinate, and they too observed magnetic moment values of 3.2 μ_B for these adducts suggesting octahedral symmetry. They did not succeed in isolating an adduct with 2-picoline, however, which was attributed to steric hindrance.

On the basis of this discussion, it is concluded that the diadducts formed by pyridines with nickel 8-quinolinates are hexacoordinated, giving rise to an octahedral structure. It is quite probable, in the extraction system, that nickel(II) might have formed a pentacoordinated monoadduct of pyridine with 8-quinaldine (2-methyl analogue) as observed earlier in the spectrophotometric study of nickel chelates. But since the six-coordinate structure is more stable and favorable than the pentacoordinate structure, particularly, in the weak ligand field of pyridine, nickel(II) achieves hexacoordination in the course of extraction. All these findings show that adduct formation, in general, increases the hydrophobic character of the metal chelates and enhances the extraction of a metal ion.

Registry No. $NiQ_2 \cdot 2$(pyridine), 66700-88-7; $NiQ_2 \cdot 2$(2-picoline), 66632-51-7; $NiQ_2 \cdot 2$(2,4-lutidine), 66674-75-7; $NiQ_2 \cdot 2$(2,4,6-collidine), 66632-50-6; Ni(2-methyl-Q)$_2 \cdot 2$(pyridine), 66632-49-3; Ni(2-methyl-Q)$_2 \cdot 2$(2-picoline), 66632-48-2; Ni(2-methyl-Q)$_2 \cdot 2$(2,4-lutidine), 66632-64-2; Ni(2-methyl-Q)$_2 \cdot 2$(2,4,6-collidine), 66632-63-1; Ni(4-methyl-Q)$_2 \cdot 2$(pyridine), 66632-62-0; Ni(4-methyl-Q)$_2 \cdot 2$(2-picoline), 66632-61-9; Ni(4-methyl-Q)$_2 \cdot 2$(2,4-lutidine), 66632-60-8; Ni(4-methyl-Q)$_2 \cdot 2$(2,4,6-collidine), 66632-59-5; Ni(5-chloro-Q)$_2 \cdot 2$(pyridine), 66632-58-4; Ni(5-chloro-Q)$_2 \cdot 2$(2-picoline), 66632-57-3; Ni(5-chloro-Q)$_2 \cdot 2$(2,4-lutidine), 66632-56-2; Ni(5-chloro-Q)$_2 \cdot 2$(2,4,6-collidine), 66632-55-1; Ni(5-nitro-Q)$_2 \cdot 2$(pyridine), 66632-71-1; Ni(5-nitro-Q)$_2 \cdot 2$(2-picoline), 66632-70-0; Ni(5-nitro-Q)$_2 \cdot 2$(2,4-picoline), 66632-69-7; Ni(5-nitro-Q)$_2 \cdot 2$(2,4,6-collidine), 66632-68-6.

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Kinetic Parameters for the Reactions of U(III) with $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5OH_2^{3+}$, and $Ru(en)_3^{3+}$ in Trifluoromethanesulfonate Media

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The rates of the reactions between U(III) and aquopentaammineruthenium(III), hexaammineruthenium(III), and tris(ethylenediamine)ruthenium(III) are reported. In all three reactions the observed rates show a first-order dependence on each reactant. Over the acid range investigated ($[H^+]$ = 0.02–1.0 M, except for $Ru(en)_3^{3+}$ where $[H^+]$ = 0.1–1.0 M), no acid dependence is observed and over the temperature range investigated (5–40 °C), no temperature dependence is observed. The reaction parameters (rate at 25 °C in $M^{-1}\,s^{-1}$, $\Delta H^\ddagger$ in kcal/mol, $\Delta S^\ddagger$ in eu) are as follow: In 1 M HCF_3SO_3, $k = (1.11 \pm 0.33) \times 10^4$, $\Delta H^\ddagger = -0.6 \pm 1.4$, and $\Delta S^\ddagger = -38 \pm 5$ for $U^{3+} + Ru(NH_3)_5OH_2^{3+}$; $k = (1.10 \pm 0.46) \times 10^4$, $\Delta H^\ddagger = 1.0 \pm 0.7$, and $\Delta S^\ddagger = -38 \pm 2$ for $U^{3+} + Ru(NH_3)_6^{3+}$; in 0.1 M HCF_3SO_3, $k = 1.62 \pm 0.27 \times 10^5$, $\Delta H^\ddagger = -1.3 \pm 1.3$, and $\Delta S^\ddagger = -39 \pm 4$ for $U^{3+} + Ru(en)_3^{3+}$. The small enthalpies of activation are rationalized in terms of the Coulombic energy and solvent reorganization energy required to form the precursor complex. Ionic strength parameters derived from the reactions of aquopentaammineruthenium(III) and hexaammineruthenium(III) with U(III) in the range I = 0.1–2.0 M ($LiCF_3SO_3$) are of the magnitudes expected for reactions between two 3+ species. Rate constants derived from perchlorate media are similar to those from trifluoromethanesulfonate media, indicating that the two anions behave similarly even for reactions between highly charged species. Starting with the Marcus cross relation and the known electron self-exchange rate for $Ru(NH_3)_6^{3+/2+}$, the experimental results are used to calculate self-exchange rates for the other reactants. Assuming that at I = 1.0 M the electron self-exchange rate for $Ru(NH_3)_6^{3+/2+}$, is $2.1 \times 10^4\ M^{-1}\,s^{-1}$, the calculated electron self-exchange rates (in $M^{-1}\,s^{-1}$) are 5.9×10^{-5} for $U^{4+/3+}$, 3.6×10^4 for $Ru(en)_3^{3+/2+}$, and 2.9×10^3 for $Ru(NH_3)_5OH_2^{3+/2+}$. The results for the ruthenium self-exchange rates agree qualitatively with those obtained from a similar calculation using the analogous Np(III)–Ru(III) reaction rates, suggesting the applicability of the Marcus cross relation to reactions that differ in $\Delta G°$ by as much as 18 kcal/mol.

Introduction

The purpose of this work is to examine the reaction between some ruthenium(III) amines and U(III) in acidic aqueous media. The results are expected to shed light on two aspects of redox kinetics. First, they should help elucidate the nature of the reductant, U(III), which is of interest because its large reduction potential makes it a potentially useful and versatile reagent. The high charge, ionic nature, large size, and f valence electrons of this ion distinguish it from other reductants, but its reactivity patterns have not yet been broadly characterized. Second, since the reactions are outer sphere, the Marcus theory of electron transfer can be applied and the results obtained used to gain insight into the nature of both the oxidants and reductants. An example of such insight is that derived from the reactions of Np(III) with both aquopentaammineruthenium(III) and hexaammineruthenium(III), which have already been studied.[2] Applying the Marcus cross relation to the rates of these two reactions and using the known self-exchange rates of hexaammineruthenium$^{3+/2+}$ leads to a predicted value of the self-exchange rate of aquopentaammineruthenium$^{3+/2+}$, a number which is difficult to obtain directly.

The actinide ion U(III) is believed to be a well-behaved ionic species in solution. It is reversibly oxidized to the 4+ state by loss of an f electron. The 3+ state appears to undergo insignificant hydrolysis (from spectrophotometric evidence), despite the high formal charge. The 4+ state undergoes detectable hydrolysis, but in media with $[H^+] \geq 0.1$ M, the hydrolyzed forms make up only 1–2% of the total U(IV).[3] There are only a few cases of 3+ ions that can behave as reductants and in these, loss of an electron is usually accompanied by a significant structural change—such as addition