Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Spigarelli, J. and Meloan, C. E.(1972) 'Distribution Studies of Metal-8-quinolinol Chelates in a Nonaqueous System', Separation Science and Technology, 7: 1, 85 — 95
To link to this Article: DOI: 10.1080/00372367208058973
URL: http://dx.doi.org/10.1080/00372367208058973

SEPARATION SCIENCE, 7(1), pp. 85–95, 1972

Distribution Studies of Metal-8-quinolinol Chelates in a Nonaqueous System

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Summary

This investigation was concerned with the determination of the influence of water on the distribution of several metal-8-quinolinol chelates between nitromethane and 1-decanol. These observations were utilized to describe the general equilibria involved in the extraction processes.

The distribution ratios (nitromethane/1-decanol) of bis(8-quinolinolo)-dioxouranium(VI)-8-quinolinol, bis(8-quinolinolo)dioxouranium(VI), tris-(8-quinolinolo)iron(III), and bis(8-quinolinolo)zinc(II) in dry solvents were determined by visible and atomic absorption spectrophotometry to be 0.95, 0.92, 1.90 and 0.11, respectively. The extraction into the 1-decanol phase increased with the number of unfilled coordination sites of the metal, indicating that the extractions were proceeding by solvation of the metal chelates.

The influence of water was attributed primarily to hydrolysis of the chelates in nitromethane, and the magnitude of this effect was correlated to the respective metal chelate formation constants. The chelates were found to be resistant to hydrolysis in 1-decanol.

INTRODUCTION

It is well established that certain metal chelates are accompanied by associated water molecules when extracted into an organic solvent

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(*1–3*). The purpose of this study was to determine directly and quantitatively the effect of water on the extraction of metal chelate complexes. In order to quantitatively study the role of associated water in the extraction process, a nonaqueous system was utilized which consisted of two immiscible organic solvents, nitromethane and 1-decanol, to which water could be added in carefully controlled quantities. The approach used was to dissolve a previously prepared solid neutral complex in either 1-decanol or nitromethane, and to study the effect of varying amounts of water on the distribution of the complex.

Previous work had shown that the distribution of bis(8-quinolinolo)-dioxouranium(IV)-8-quinilinol, $UO_2(Ox)_2(HO_x)$, between nitromethane and 1-decanol was dependent upon the amount of water present in the system. An empirical equation was developed to describe this effect. This complex was reported to be associated with 5 to 10 molecules of water when UO_2^{2+} was extracted from water into various organic solvents (*4, 5*). The effect on the distribution of the complex was attributed to solvation of the chelate by these water molecules.

In the present study the validity of the solvation hypothesis for the change in the distribution of $UO_2(Ox)_2HO_x$ was investigated. The results show that the complex undergoes partial dissociation in both organic solvents and is subject to hydrolytic decomposition in nitromethane and does not form a definite hydrated species.

The distribution ratios between nitromethane and 1-decanol were determined for bis(8-quinolinolo)dioxouranium(VI), $UO_2(Ox)_2$; tris(8-quinolinolo)iron(III), $Fe(Ox)_3$; and bis(8-quinolinolo)zinc(II), $Zn(Ox)_2$. Variation in the water concentrations of the solvents also affected the distribution ratios of these complexes. The effects of water on the distribution ratios of the four complexes is discussed in terms of solvation, available metal coordination sites, and susceptibility to hydrolysis of each of the complexes.

EXPERIMENTAL

Chemicals

The preparation of the zinc, iron, and two uranyl complexes has been previously described (*6–8*). The purity of the complexes was verified by DTA and CHN analysis. Decanol and nitromethane were purified by methods described elsewhere (*9, 10*).

Apparatus and Materials

UV-Visible Spectrophotometer. All spectrophotometric data were obtained with a Beckman Model DB recording spectrophotometer equipped with matched 1 cm silica cells.

Atomic Absorption Spectrophotometer. A Jarrell-Ash model 82-360 Ebert-mounted 0.5 m grating monochrometer equipped with Jarrell-Ash electronics, including a 90 H2 mechanical chopper, ac amplifier, Sargent Model S-72150 recorder, and a 1P28 photomultiplier detector were used. The sampling system was a Beckman large bore turbulent flow burner. The spectral source was a Westinghouse Model WL 22811 zinc hollow-cathode.

Gas Chromatograph. A Micro Tek 2500R chromatograph equipped with a thermal conductivity detector was used for chromatographic measurements. A Sargent SR (1 mV) recorder and Disc Instruments, Inc., integrator were used to record the chromatograms and measure peak areas. Injections were made with a 10 μl Hamilton syringe equipped with a Chaney adapter.

Chromatographic Columns. For the determination of the distribution of water between nitromethane and decanol a 6 ft by $\frac{1}{4}$ in. stainless steel tube packed with 60/80 mesh Poropak Q, Waters Assoc., Inc. Framingham, Massachusetts was used.

PROCEDURE

Extraction and Analysis of Complexes

Bis(8-quinolinolo)dioxouranium(IV)-8-quinolinol and Bis(8-quinolinolo)dioxouranium(IV). The procedure for the extraction and determination of the uranium complexes was more rigorous than those for the zinc and iron complexes because of the influence of water on the absorptivities of the uranium compounds. With the exception of a few slight modifications, the procedures for the self-adduct and "normal" uranium chelates were the same. The following procedure was used for the extraction of $UO_2(Ox)_2HOx$ into nitromethane. The appropriate amount of water was weighed in a capped polyethylene centrifuge tube and 10 ml of nitromethane added by means of a pipet. Dissolution of the water was aided by a vortex mixer. Ten milliliters of decanol containing $2.00 \times 10^{-4} UO_2(Ox)_2HOx$ were pipetted into the tube and the extraction carried out on a Burrell Wrist-Action shaker for 1 min (300 inversions).

The phases were allowed to equilibrate for 1 min and centrifuged for 30 sec (2000 rpm) to remove emulsions. A 5-ml aliquot of each phase was transferred to separate test tubes where the water concentration of the nitromethane phase was adjusted to 20 mg/ml. The absorbance of the nitromethane phase at 380 nm was measured exactly 5 min after the adjustment of the water concentration. Water concentration did not affect the absorptivity of the chelate at 375 nm in 1-decanol. Therefore the time of absorbance measurement of this phase was not critical.

Tris(8-quinolinolo)iron(III). The absorptivity of $Fe(Ox)_3$ in nitromethane at 460 nm was slightly affected by water. Therefore the standards and samples were adjusted to a constant water concentration following the extraction and prior to measuring absorbance. The effect was immediate so that the time of measurement was not critical. The extraction procedure was similar to that of the uranium complexes.

Bis(8-quinolinolo)zinc(II). The extraction procedure was similar to those previously described except that no water adjustment of the nitromethane phase was necessary because an atomic absorption method of analysis was developed.

A 5-ml aliquot of the nitromethane phase was transferred into a 25-ml test tube following extraction, equilibration, and centrifugation. The 1-decanol saturated nitromethane phase was analyzed directly by atomic absorption. An analysis curve was prepared from dilutions of a stock solution of $Zn(Ox)_2$. It was important that the sample and solvent test tubes be stoppered at all times because nitromethane vapor absorbs the 2138A line, causing erratic results. A small diameter Teflon hose was attached to the bottom of the large bore Beckman Burner and immersed in the solution to be analyzed through a small notch cut in the rubber stopper, thereby allowing the sample to be introduced and eliminating nitromethane vapor from the system. The instrument was adjusted to zero absorption with 1-decanol saturated nitromethane. Because of the higher boiling point and viscosity of 1-decanol, the system was flushed with ethanol following each sample introduction to prevent accumulation of 1-decanol in the system, especially in the Teflon hose. The sampling sequence was: blank–sample–ethanol.

Complimentary analysis of the 1-decanol phase by atomic absorption was not possible because of its high viscosity; it was analyzed spectrophotometrically at 385 nm.

Distribution of water. The distribution ratio of water between nitromethane and 1-decanol was determined at six different water concentrations by analysis of the nitromethane phase. The concentration in

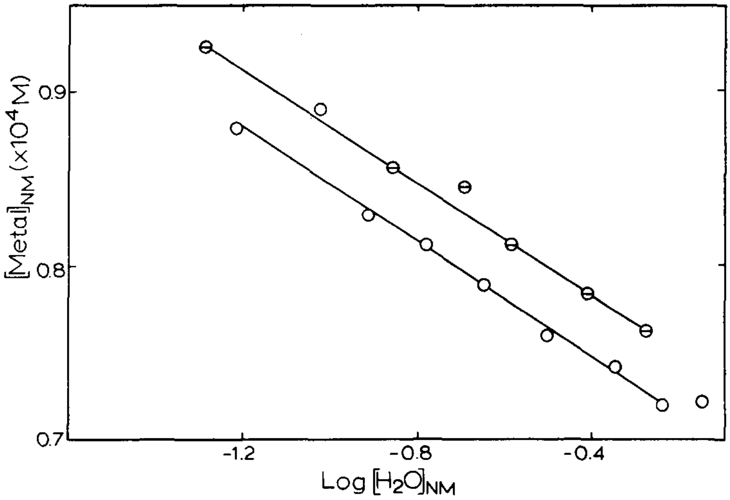

FIG. 1. Plot of uranium concentration in nitromethane as a function of log[H_2O]: (○) $UO_2(Ox)_2HO_x$, and (⊖) $UO_2(Ox)_2$.

1-decanol was determined by difference from the total amount added. Analyses were based on 5 μl injections utilizing a carbowax column.

RESULTS AND DISCUSSION

Water influenced the distribution of the zinc and both uranium complexes of 8-quinolinolo between nitromethane and 1-decanol; the distribution of the iron complex was only slightly affected. The effects of water in these systems are shown in Figs. 1 and 2 in which the final metal concentration is plotted against a function of the final water concentration for each metal–chelate system. Both concentrations are shown for the nitromethane phase. Similar results were obtained regardless of which phase contained the chelate or water initially. Both phases were analyzed in order to insure a material balance of the chelate as demonstrated for $UO_2(Ox)_2HOx$ in Fig. 3.

Although the results show the effect of water on chelate distribution in the nitromethane–1-decanol system, the influence of water cannot be attributed to hydration of a definite metal–chelate species. Solutions of both $UO_2(Ox)_2HOx$ and $UO_2(Ox)_2$ deviate from Beer's law at lower chelate concentrations. Figure 4 indicates that the self-adduct uranyl-8-

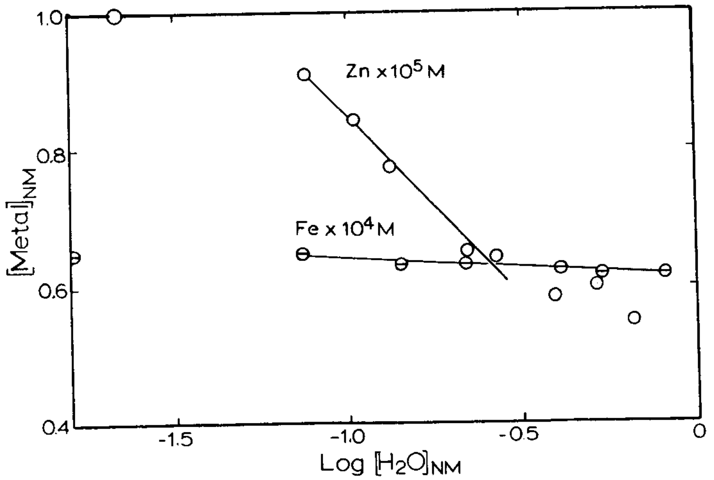

FIG. 2. Plots of zinc and iron concentrations in nitromethane as a function of log$[H_2O]$.

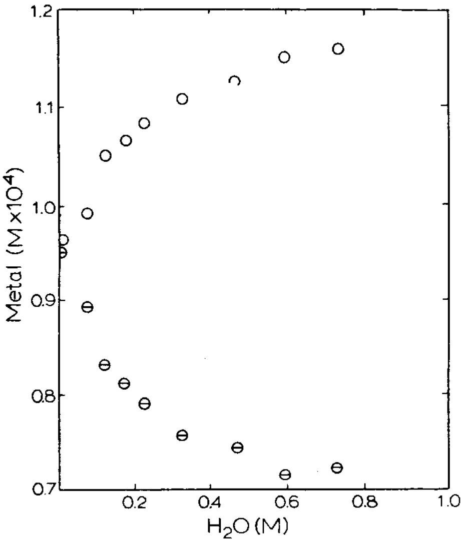

FIG. 3. Effect of H_2O on the distribution of 2.00×10^{-4} M $UO_2(Ox)_2HOx$ between nitromethane and 1-decanol. Concentration in nitromethane (⊖) and in 1-decanol (○).

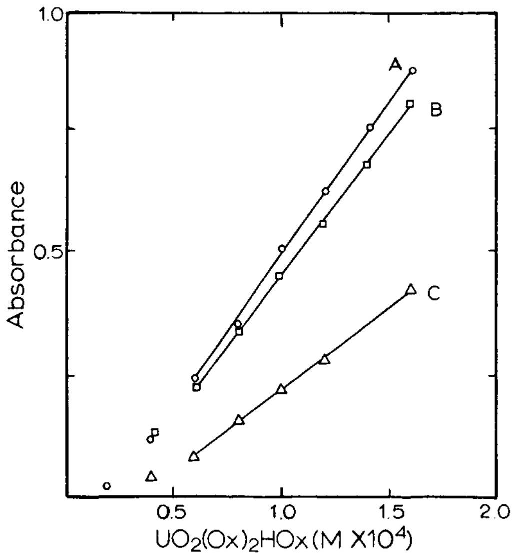

FIG. 4. Beer's law plots of $UO_2(Ox)_2HOx$: (A) in nitromethane, (B) in 1-decanol, and (C) in nitromethane measured 30 min after dissolution of 20 mg/ml water.

quinolinol complex is partially dissociated in both nitromethane and 1-decanol. Detailed studies of the absorption spectra of the 8-quinolinol chelates of uranium in chloroform and ethonol by Moeller and Ramaniah (*11*) also revealed that neither chelate rigorously adhered to Beer's law.

The absorption spectra of the 8-quinolinol chelates are similar to each other provided that ligand field effects are absent (*12*). These bands are red shifted from their position in the spectra of free 8-quinolinol and the 8-quinolinium ion. They result from the $\pi \rightarrow \pi^*$ transitions of the ligands. The intensity of absorption is an approximate measure of the number of 8-quinolinol molecules bound to the cation (*13–15*). The molar absorptivity contribution of each bound ligand to the molar absorptivity of $UO_2(O_x)_2$ was calculated to be 2.7×10^3 at 380 nm based on the assumption that a $1.00 \times 10^{-4} M$ solution of this chelate in dry nitromethane exists entirely as the 2:1 complex. An average ligand number, $\bar{n}$, per uranyl cation for a $1.00 \times 10^{-4} M$ solution of $UO_2(Ox)_2HOx$ in dry nitromethane was calculated to be 2.68, indicating the probable equilibrium species of the dissolved 3:1 complex to be

$$3UO_2(Ox)_2HOx \rightarrow 2UO_2(Ox)_2HOx + UO_2(Ox)_2 + HOx$$

This is reasonable considering the structure of the solid 3:1 complex contains a monodentate solvate ligand. The addition of 20 mg/ml of water results in a change in $\bar{n}$ from 2.0 to 1.6, 5 min after dissolution in a 1.00×10^{-4} *M* nitromethane solution of $UO_2(Ox)_2$.

The effects of the addition of various amounts of water to a 1.01×10^{-4} *M* $UO_2(Ox)_2$ solution in nitromethane are shown in Fig. 5. Decanol solutions of both chelates were not affected by the addition of water. Moeller and Ramaniah (*11*) found that ethanol solutions of these complexes were similarly resistant to hydrolysis.

The zinc and iron chelates adhered to Beer's law, which indicates each forms a single species in dry nitromethane and 1-decanol solutions. These complexes were chosen for distribution studies in order to determine the influence of water on the distribution of a coordinately saturated complex, $Fe(Ox)_3$, as compared with a complex, $Zn(Ox)_2$, with two metal coordination sites available for solvation.

$Zn(Ox)_2$ was susceptible to hydrolysis in the nitromethane phase as evidenced by the decrease in absorbance upon the addition of water to a $0.5 \times 10^{-4}M$ solution. This chelate was not hydrolyzed in 1-decanol.

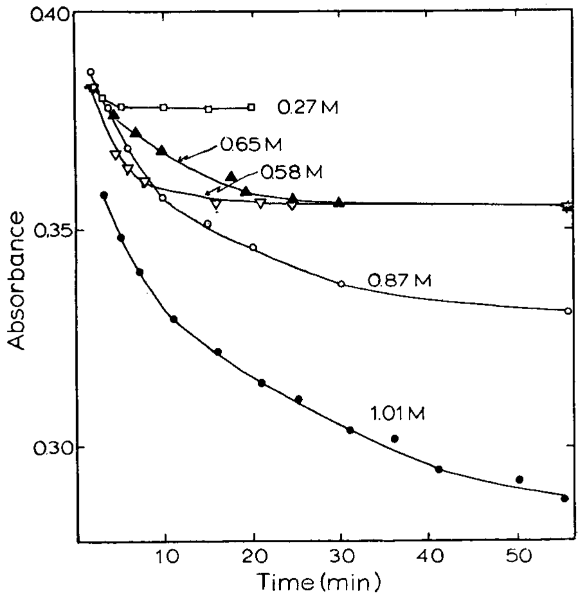

FIG. 5. Hydrolysis of 1.01×10^{-4} *M* $UO_2(Ox)_2$ in nitromethane at various water concentrations.

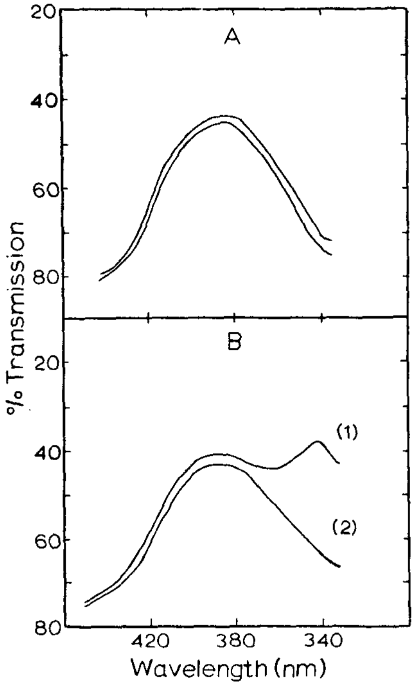

FIG. 6. Spectrophotometric analysis of 1 × 10^{-4} *M* zinc oxinate: (A) before and after the addition of 20 mg/ml H_2O in 1-decanol, (B) after into 1-decanol from nitromethane containing (1) 0.52 *M* H_2O and (2) 0.02 *M* H_2O.

Figure 6 shows the stability of $Zn(Ox)_2$ in 1-decanol and also the extraction of free 8-quinolinol (absorbance at 340 nm) from a nitromethane solutions of $Zn(Ox)_2$ containing $0.52M$ water. Observation of the free ligand in nitromethane was not possible because of the high cutoff point, 375 nm, of this solvent. $Fe(Ox)_3$ was not hydrolyzed to an appreciable extent in either solvent.

A comparison of the effects of water on the distribution of the four metal chelates studied indicate that the phenomenon is due primarily to hydrolysis of the oxinates in the nitromethane phase. The distribution of iron oxinate, which was only slightly hydrolyzed, was negligibly affected by the addition of water to the system. The importance of available coordination sites in the uranium and zinc systems and possible formation of adducts of the type $Zn(Ox)_2 \cdot 2H_2O$ is probably ancillary to a reaction of the following type:

$$Zn(Ox)_2 + H_2O \rightarrow Zn(Ox)(OH) + HO_x$$

TABLE 1

A Comparison of Water Effects on the Distribution of Metal Oxinates with Their Corresponding Formation Constants

Metal oxinate	Distribution ratio[a] in dry solvents	Slopes from Figs. 1 and 2	log K_f[b]
$Fe(OX)_3$	1.90	−0.029 ± .004	4.11
$UO_2(Ox)_2HOx$	0.98	−0.167 ± .006	−1.60
$UO_2(Ox)_2$	0.92	−0.171 ± .016	—
$Zn(Ox)_2$	0.11	−0.507 ± .049	−2.41

[a] The distribution ratio is defined as the metal concentration in nitromethane divided by the metal concentration in 1-decanol.

[b] From Ref. *12*.

The addition of water enhanced the extraction of each oxinate into 1-decanol. This is reasonable considering the formation of a partially hydrolyzed species which would have a greater affinity for 1-decanol because of hydrogen bonding.

A comparison of the magnitude of the water effect on the distribution of each complex can be obtained graphically from the slopes of the curves in Figs. 1 and 2. The enhancement of chelate distribution into 1-decanol should, if caused primarily by the hydrolysis of the metal chelate, reflect the relative stabilities of each of the oxinates. The data in the regions indicated by the solid lines in Figs. 1 and 2 were treated by means of regression analysis computer program. A comparison of the slopes of these data and the formation constants of the metal chelates is consistent with the hydrolysis hypothesis. The results are shown in Table 1.

A comparison of the distribution ratios of the four metal oxinates in dry solvents indicates a solvation mechanism of extraction and reflects the relative strengths of the solvents as Lewis bases. Nitromethane is an extremely poor electron donor; the chelates in this phase are weakly solvated. Zinc oxinate, having two unfilled coordination sites, is very susceptible to solvation by the stronger Lewis base, 1-decanol. Uranium oxinates have one or two sites available for solvation while iron oxinate is coordinately saturated and should be the least susceptible to a Lewis acid–base interaction with 1-decanol. The distribution ratios listed in Table 1 show that extraction of the metal oxinates into nitromethane follows the order:

$$Fe(Ox)_3 > UO_2(Ox)_2HOx \simeq UO_2(Ox)_2 > Zn(Ox)_2$$

Acknowledgment

The financial assistance by the National Science Foundation is greatly appreciated.

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Received by editor May 10, 1971