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Extraction of Tris(1, 10-phenanthroline) Iron(II) Perchlorate into Nitrobenzene: Role of Water

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Summary

The number of molecules of water associated with the tris(1, 10-phenanthroline) iron(II) perchlorate ion association chelate was found to be 14 ± 4 when this chelate was extracted into nitrobenzene.

Meloan and Brandt (*4*) measured the number of water molecules associated with the benzohydroxamic acid chelates of uranium(VI) and iron(III) when extracted into 1-decanol. A general relationship was established between the amount of water soluble in a given alcohol and the amount of chelate extracted into the alcohol. They found 6 ± 1 molecules of water associated with the uranium(VI) chelate and 9 ± 3 associated with the iron(III) chelate.

Although this was the first published account of the measurement of water associated with extracted chelates, Swift and Axelrod (*7*) had been interested in this idea in 1940, relative to the extraction of ferric chloride into ether from aqueous solution. This sort of information had been sought more recently in the field of inorganic extractions such as the extraction of hydrated acids described by Tuck and Diamond (*8*).

More recently, Gere and Meloan (*2*) have found 5 ± 2 molecules of water associated with the bis(8-quinolinol) dioxouranium(VI)

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chelate extracted into chloroform and 57.0 ± 8.8 molecules of water associated with the tris(4, 7-diphenyl-1, 10-phenanthroline) iron(II) chelate when either the sulfate, chloride, or perchlorate was extracted into chloroform, nitrobenzene, or 1-decanol (3).

Because of the unusually high number of water molecules associated with the latter chelate, it was felt that this should be investigated further. The tris(1, 10-phenanthroline) iron(II) system was selected because it would extract into a solvent previously used and because the perchlorate anion which is involved had been used also in the prior work, so effective comparisons could be made. However, the big change was the absence of the two phenyl groups from the ligand. The tris(4, 7-diphenyl-1, 10-phenanthroline) system is an octahedral chelate and the six phenyl groups increase the chelate volume by a significantly large amount; in fact, two layers of water could fit in the available space and account for the large water content. It was not known if these 57 molecules of water were all associated directly with the chelate or if a part of the water was actually bonded to the chelate and that the resulting compound was altering the solubility characteristics of the solvent to the extent that other water molecules would dissolve.

It was thought that if the diphenyl groups were actually acting as a "protective cage" for the water molecules then the associated water should drop if the phenyl groups were removed. This is why the phenanthroline ligand was chosen.

EXPERIMENTAL

See Ref. *4* for the experimental details.

REAGENTS

The dry methanol, the standard water solution, pyridinium iodide, and the Karl Fischer reagent were prepared as described by Meloan and Brandt (*3*).

Water. Ion-free water was prepared by running distilled water through a column of mixed-bed ion-exchange resins, previously treated to assure water with a specific resistance of greater than 10^6 ohms/cm, as described by Samuelson (*6*).

All other chemicals were reagent grade and used as received.

METHOD

The method used throughout the entire investigation was essentially that of Meloan and Brandt (*3*), with suitable variations when necessary. The Karl Fischer reagent technique as described by Meyers et al. (*5*) was used to measure the amount of water present in the organic solvents.

The procedure followed for the formation of these chelates was essentially that of Diehl and Smith (*1*) in their booklets concerning the chemistry of ferroin chelates. The chelate formation took place in the aqueous phase, and when complete, the extracting solvent was then added and the extraction proceeded as in the bis(8-quinolinol) dioxouranium(VI) method (*2*). The ligand was dissolved in hot water.

It was important to note that in each experiment a different order of concentrations was used in obtaining the raw values. That is, one time the least concentrated chelate solution was prepared and titrated first, followed by the next most concentrated solution, proceeding in the order of increasing concentrations to the final concentration. Another time the order would be completely reversed and then random selection was used.

At least two and sometimes more solution blanks were prepared and titrated with each experiment. Usually one blank would be run initially and the second blank would be run after all the chelate solutions had been prepared and titrated. This technique was not strictly adhered to, however. This was because there was usually no detectable difference between the blank solutions run at different times.

These two techniques would eliminate possible trends intentionally or unintentionally forming to induce artifacts.

Another standard procedure involved the preparation of reagents. The usual method was to prepare each reagent freshly for each experiment with the exception of the standard metal-ion solutions. This would preclude any error due to miscalculation of any concentrations.

RESULTS AND DISCUSSION

It was found that none of the reagents involved in this system reacted with the Karl Fischer reagent under the conditions em-

TABLE 1

Effect of Ionic Strength on the Solubility of Water in Nitrobenzene (ionic strength determined by calculation of reagents added)

	mg H_2O/ml nitrobenzene
0.000	2.84
0.001	2.86
0.005	2.90
0.010	2.91
0.050	2.91
0.100	2.96
1.000	2.90
5.000	2.48[a]

[a] Addition of 30 g of sodium perchlorate/50 ml of deionized H_2O changed the density of the aqueous phase so much that the H_2O and nitrobenzene phases reversed themselves.

ployed. The effects of ionic strength and pH were of no consequence since these were held to 0.001 in ionic strength and ±0.05 in pH. Tables 1 and 2 show the results of these studies. The pH data were obtained at constant ionic strength. Notice that under these conditions there is no real effect due to change in acidity. The ionic strength does affect the solubility of water into the organic phase but not so much that it cannot be easily controlled. Only with saturated aqueous solutions is there an appreciable effect.

Using perchlorate as the anion and nitrobenzene as the organic phase, the tris(1, 10-phenanthroline) iron(II) chelate was found to have 14 ± 4 molecules of water associated with it. This is an aver-

TABLE 2

Effect of pH on the Solubility of Water in Nitrobenzene

pH	mg H_2O/ml
3	3.05
5	3.08
7	3.03
9	3.02
11	3.07

age value based upon 48 individual determinations. These results are in accord with the trend postulated earlier and indicate that the removal of the six phenyl groups, that is, the removal of the "cage," did reduce the amount of water.

In all previous work (*2*,*3*,*4*) the ligand and the metal were reacted to form the chelate in the aqueous phase. Having formed the chelate in the aqueous phase, the chelate was then extracted into the organic phase.

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