A STUDY OF THE WATER ASSOCIATED WITH EXTRACTED METAL CHELATES

by

DENNIS ROGER GERE

B. S., Iowa State University
of Science and Technology, 1960

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1962

TABLE OF CONTENTS

INTRODUCTION 1

METHOD 5

EXPERIMENTAL 6

MATERIALS 9

Dry Methanol 9

Karl Fischer Reagent 10

Standard Water-Methanol Solution 11

0.0100 M Dioxouranium(VI) Solution 12

Chloroform 12

Water 12

Pyridinium Iodide 13

1-Decanol 13

Nitrobenzene 13

Standard Iron Solution 13

Standard Copper Solutions 14

0.01 M 1,10-phenanthroline 14

0.01 M 4,7-diphenyl-1,10-phenanthroline 14

Hydroxylammonium Chloride, 10 Per Cent Aqueous Solution . 14

Sodium Acetate Buffer 15

APPARATUS 15

Beckman Model DB Spectrophotometer 15

KF-3 Aquameter 15

KF-3 Detection Circuit 25

Volumetric Glassware 26

Sargent Oscillometer 28

pH Meter 28

RESULTS AND DISCUSSION 28

Bis (8-quinolinol) dioxouranium(VI) Extracted into Chloroform 28

Extraction of Tris (4,7-diphenyl-1,10-phenanthroline) Iron(II) Chelate 36

Extraction of Tris (1,10-phenanthroline) Iron(II) Perchlorate into Nitrobenzene 52

Extraction of Bis (1,10-phenanthroline) Copper(I) Perchlorate into Nitrobenzene 53

Extraction of Bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) Copper(I) Perchlorate into Chloroform. 55

Dielectric Constant Measurement 58

CONCLUSIONS 61

FUTURE PROJECTS 63

ACKNOWLEDGMENT 65

LITERATURE CITED 66

INTRODUCTION

It is common knowledge that the increasing complexity of chemical research and chemical industry is causing analytical chemists to deal with more complex separation and identification schemes.

Until recently, solvent extraction was one of the least used separation techniques. The advent of chelate chemistry to the family of coordination compounds has served to expand solvent extraction into ever-widening usage.

When faced with devising a new extraction separation scheme, one is presented with the problem of deciding what solvent would most advantageously extract the species of interest.

Very little theory exists in the area of the extraction of metal chelates into immiscible solvents. Several empirical rules exist in different areas, but few have general application. It is well recognized (7) that the relative solubilities of the compounds in the respective solvents have little bearing upon the distribution of the species between the two solvents at the liquid junction. This may be due to the fact that when comparing relative solubilities of the species in the solvents, the actual species which is extracted has not been fully identified. Perhaps the nature of solvation of the chelates in their respective solvents determines to a large extent where the species will reside when confronted with two differing solvents.

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 various alcohols. 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 ± 2 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 (9) 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 (10).

It was felt that the work on extracted chelates should be extended to see if the association of water molecules was present only in alcohol solvents or only with neutral chelate extractions as opposed to ion association chelate extractions.

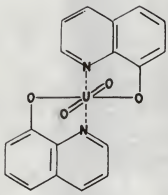
The purpose of the present investigation, therefore, was to determine to what extent, if any, the solvent, ligand, anion, and central metal ion play in the associated waters of chelate extraction.

The first phase of this investigation concerned the extraction of bis (8-quinolinol) dioxouranium(VI) from aqueous solution into chloroform, a solvent with different properties compared to 1-decanol, the solvent used primarily by Meloan and Brandt.

This particular chelate is considered a metal complex similar to the benzohydroxamic acid chelates in that 8-quinolinol loses a proton when reacted with the dioxouranium(VI) ion, such as:

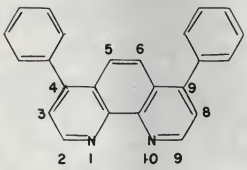
$$UO_2^{++} + 2\ C_9H_7ON \longrightarrow UO_2(C_9H_6ON)_2 + 2H^+$$

The structure of such a chelate would be:

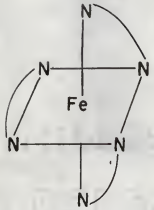


The second phase concerned the extraction of tris (4,7-diphenyl-1,10-phenanthroline) iron(II) cation chelate into the solvents, 1-decanol, chloroform and nitrobenzene. This chelate system differs from the previously mentioned systems in that the ligand coordinates through the unpaired electrons on heterocyclic nitrogen atoms with retention of the same charge of the uncomplexed metal ion on the formed chelate. Thus the mechanism of extraction falls under the arbitrary classification of an ion-association extraction.

The structure of 4,7-diphenyl-1,10-phenanthroline is:



This type of ligand forms a 3:1 chelate with iron(II) which has the following octahedral configuration:



This system enabled the change of anions while maintaining the chelate cation intact throughout a series of analogous extraction measurement experiments.

The third phase of the investigation concerned the extraction of the tris (1,10-phenanthroline) iron(II) perchlorate into nitrobenzene. This represented a change in the ligand while maintaining the anion, central metal ion and solvent constant from the previous phase of the investigation.

The final phase of the investigation concerned the extraction of the bis (1,10-phenanthroline) copper(I) perchlorate into nitrobenzene which represented a change in the central metal ion with retention of the ligand, solvent and anion of the previous phase of the investigation.

METHOD

The method used throughout the entire investigation was essentially that of Meloan and Brandt (4) with suitable variations when necessary. The Karl Fischer Reagent technique as described by Meyers, Metzler and Swift (6) was used to measure the amount of water present in the organic solvents. A Beckman KF-3 Aquameter was used for the automatic titration of the water using the dead stop endpoint detection system. The KF-3 Aquameter permitted the method to be free of human error inherent in color judging, eliminated distinquishing between true and false endpoints, and permitted titration of colored solutions.

The amount of water in the organic solvent was determined with the aqueous phase containing all components except the chelate itself. This comprised the blank determination. Solutions were then made up containing varying concentrations of the

chelate in the organic phase. The amount of water was determined in the organic phase of each of the concentrations. The number of moles of water present in a given volume of organic phase was plotted against the number of moles of chelate present in the same given volume of organic phase. The concentration of chelate present was determined spectrophotometrically.

A least squares determination was then applied to the data to obtain the slope of the straight line into which the data developed. This slope yielded the mole ratio of water molecules to chelate molecules in the organic phase. The intercept of the straight line gave the solubility of water in the organic solvent at zero concentration of chelate.

EXPERIMENTAL

For the extraction of bis (8-quinolinol) dioxouranium(VI) into chloroform, the following procedure was followed:

To make up the concentration desired, a known amount of 0.0100 M dioxouranium(VI) nitrate was pipeted into a beaker containing a magnetic stirring bar. The beaker was then placed over a magnetic rotor to provide agitation to the solution. A given volume of water was added to the beaker followed by 0.1 N sodium hydroxide added dropwise until the pH was 8.8 ± 0.1 pH units as checked by a Beckman Model H pH meter. The resulting solution was then diluted to exactly 150 ml. and transferred to a 500 ml. separatory funnel. Exactly 150 ml. of 0.033 M 8-quinolinol in chloroform solution was added to the funnel. The funnel was

shaken 100 times and placed in a constant temperature bath at 25.0°C ± 0.1°C for exactly fifteen minutes.

The funnel was then withdrawn from the water bath and the excess water was wiped off from the funnel. The delivery tube was rinsed with dry acetone and the excess acetone was evaporated with a stream of dry air. This minimized the formation of emulsions which were due to water retained from the water bath.

Four 30 ml. samples were then transferred to centrifuge tubes and centrifuged at 2000 RPM for 60 seconds. This served to remove any emulsified water. Care had to be taken not to continue the centrifugation any longer than 60 seconds as heating of the samples resulted, which drastically decreased the solubility of water in the chloroform. It was found that no appreciable temperature change occurred in the first 90 seconds, and that the emulsified water was removed in about 30 to 45 seconds. Thus 60 seconds was deemed the optimum time of centrifugation.

A 25.00 ml. sample was then pipeted from a 30 ml. centrifuge tube and immediately transferred to the reaction beaker of the KF-3 Aquameter for titration with standard Karl Fischer Reagent. Because the Aquameter was equipped with 10 ml. burets, and the aliquot oftentimes required more than 10 ml. of titrant, additional titrant was initially added from an auxillary reservoir of Karl Fischer Reagent by means of a pipet.

While the first and succeeding samples were being titrated, the remaining centrifuge tubes were placed in the 25.0°C water

bath to maintain temperature equilibrium.

The amount of dioxouranium(VI) nitrate added was adjusted such that the chelate concentration was in the range of 10^{-6} to 10^{-5} moles of dioxouranium(VI) per 25.00 ml. of chloroform. Usually a series of 10 concentrations was used in each experiment providing 40 individual titrations or 40 raw values for each least squares determination.

Basically the same sampling and titration arrangement was used for the last phases of this investigation as with the bis (8-quinolinol dioxouranium(VI) system. However, formation of the chelate and addition of reagents was somewhat different for the cation-type chelate systems.

The procedure followed for the formation of these chelates was essentially that of Diehl and Smith (1,2) 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.

The ligand was either dissolved in water or in the case of low solubility, prepared in ethanol-water solutions. In some instances the ethanol changed the experimental conditions in that it increased the solubility of water in certain organic solvents. If this condition arose, the ligand was prepared as a solution using the extracting solvent as the ligand solvent. Alternately, the ligand was added to the aqueous phase as a solid. In the latter two cases, each chelate sample was analyzed

spectrophotometrically.

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 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 of the chelate solutions had been prepared and titrated. There was not strict adherence to this technique, 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 procedure followed was the preparation of reagents. The usual method followed 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.

MATERIALS

Dry Methanol: Reagent grade methanol was dried by distillation with a 6-foot, 3/4 inch diameter, glass-bead-packed

fractionating column. The undistilled methanol had an average water content of 0.20% by weight and the average distillate had less than 0.01% water by weight. When the water content of the distillate rose above 0.02% by weight, it was either discarded or redistilled. When the water content was greater than 0.02%, the optimum water equivalent of the Karl Fischer Reagent could not be achieved.

Karl Fischer Reagent: Four liters of stabilized Karl Fischer Reagent were prepared by dissolving 170 g. of resublimed iodine in 1100 ml. of reagent grade pyridine. 2600 ml. of previously dried methanol were added with constant stirring. The iodine was much more soluble in pyridine than in methanol, thus it was necessary to add the pyridine first. The resulting mixture was cooled in an ice bath. 50 ml. of liquid sulfur dioxide were carefully added. The sulfur dioxide was trapped out in an ice-salt bath from a tank of sulfur dioxide gas. About 280 g. of purified pyridinium iodide were added as a stabilizer. The entire solution was placed in a dark bottle and shaken periodically during the next 48 hours. At the end of this time, a relatively stable solution of Karl Fischer Reagent was ready for standardization. The water equivalence would nominally be 1.70 mg. H_2O per ml. of solution. This solution decomposed at a rate of about 0.015 mg. water per ml. per 24 hours. Without the stabilizer added, the solution decomposed at a rate of about 0.04 mg. water per ml. per 24 hours.

TABLE 1

Comparison of Stability of Karl Fischer Reagent

Sample	Number of days	Original Value	Final Value	Mg. H_2O/Ml. KFR/Day
		Pydridinium Iodide Added		
1	4	2.108	2.024	0.022
2	6	2.376	2.255	0.011
3	6	2.615	2.421	0.019
4	18	2.956	2.483	0.025
5	21	2.196	2.006	0.010
		Without Pydridinium Iodide Added		
6	17	2.797	2.099	0.041
7	14	1.691	1.185	0.036

Standard Water-Methanol Solution: The distilled methanol was titrated with the unstandardized Karl Fischer Reagent. Exactly 1.700 g. of de-ionized water was weighed by difference and transferred to a 1.000 liter volumetric flask. The flask was then filled to the mark with dry methanol and shaken 100 times. The resulting water-methanol solution was again titrated with the unstandardized Karl Fischer Reagent. The difference in the amount of Karl Fischer Reagent per given volume between the dry methanol and the water-methanol solution yields the amount of Karl Fischer Reagent required for the weighed amount of water added to the flask. The water equivalent of the Karl Fischer Reagent, and then, the standard water-methanol solution, could be calculated.

The water equivalent of the water-methanol solution maintained a constant value in a closed system for at least one month. For instance, standardization of a water-methanol solution yielded a value of 2.526 mg. of water per ml. of solution. 37 days later, this solution was titrated with a fresh Karl Fischer Reagent solution which in turn was titrated with a newly standardized water-methanol solution. Using the new water-methanol as the reference solution, the water equivalent of the 37-day old water-methanol solution was found to be 2.544 mg. of water per ml. of solution.

This increase of 0.018 mg. of water per ml. of solution was not surprising, in that some of the methanol was continuously evaporating out through the drying tube connected to the reservoir. This effectively increased the amount of water present relative to the amount of methanol present. However, the amount of increase was insignificant considering the 37 day period of time.

0.0100 M Dioxouranium(VI) Solution: Dioxouranium(VI) nitrate dihydrate was prepared from the hexahydrate by desiccation over concentrated sulfuric acid for several days. The number of waters of hydration was then checked by titration of weighed amounts of the solid with Karl Fischer Reagent. The aqueous solution was then prepared by weight.

Chloroform: The chloroform was distilled before using.

Water: Ion-free water was prepared by running distilled water through a column of mixed-bed strong ion exchange resins, previously treated to insure water with a specific resistance

greater than 10^6 ohms per cm., as described by Samuelson (8).

Pyridinium Iodide: A mixture of 200 ml. of pyridine and 800 ml. of ether were cooled in an ice bath. 150 ml. of 47% A.C.S. grade hydriodic acid was very carefully added with constant stirring. At first a white precipitate formed, but redissolved as more acid was added. When the addition was complete, the ether layer was removed and the water layer was evaporated to near dryness. The yellow-white precipitate was then filtered on a Buchner funnel and washed with ether. The resulting material was dried in a vacuum desiccator for 48 hours. The pyridinium iodide should have been white in color, but was sometimes discolored due to some free iodine. The free iodine does not affect the Karl Fischer Reagent. Further washing and desiccation insures a pure white product.

1-Decanol: This alcohol, as with all of the other alcohols, was distilled in an all glass still just prior to use to remove peroxides which destroy the chelate (4).

Nitrobenzene: Reagent grade nitrobenzene was used without any further treatment. An infrared spectrum of the nitrobenzene was obtained with a Perkin-Elmer Model 237 Spectrophotometer. When compared to a standard spectrum, no impurity bands were found.

Standard Iron Solution: A 0.0100 M iron solution was prepared by weighing out 0.5585 g. of 99.9% iron wire and transferring to a 500 ml. conical flask. 5 ml. of concentrated acid (dependent upon the anion desired) and 30 ml. of de-ionized

water were added. Gentle heat was applied to dissolve the wire and the solution was allowed to cool. The solution was then transferred to a 1000 ml. volumetric flask and diluted to the mark with de-ionized water.

Standard Copper Solutions: These were prepared in the same manner as the iron solutions using 100.0% Cu wire and weighing appropriate amounts.

0.01 M 1,10-phenanthroline: $C_{12}H_8N_2 \cdot H_2O$, mol. wt.: 198.2. This reagent was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio, as were 4,7-diphenyl-1,10-phenanthroline and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. A 0.01 M solution of 1,10-phenanthroline was prepared by dissolving 0.1982 g. of the monohydrate in hot water and diluting to 100 ml.

0.01 M 4,7-diphenyl-1,10-phenanthroline: $C_{24}H_{16}N_2$, mol. wt.: 332.41. A 0.01 M solution of this compound was prepared by dissolving the compound in 50 ml. of absolute ethanol and diluting the solution with 50 ml. of H_2O. Alternately, 1-decanol was used as the solvent.

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline: $C_{26}H_{20}N_2$, mol. wt.: 360.3. This solution was prepared using absolute ethanol as the solvent, or alternately used, adding the ligand as a solid.

Hydroxylammonium Chloride, 10 Per Cent Aqueous Solution: 10.0 g. of reagent grade hydroxylammonium chloride was dissolved in 100 ml. of water. The solution was then placed in a 125 ml. conical separatory funnel and 1 ml. of 0.01 M 4,7-diphenyl-1,10-

phenanthroline was added. 10 ml. of chloroform was added and the funnel shaken. Allowing time for the phases to separate, the lower red chloroform layer was drawn off. The red color was due to formation of the iron(II) chelate. The iron was present as an impurity in the hydroxylammonium chloride. The procedure was repeated until the chloroform layer was colorless, usually, one extraction was all that was necessary to render the reagent iron-free.

Sodium Acetate Buffer: A 10% aqueous solution was prepared by dissolving 10 grams of the trihydrate in 100 ml. of water. This solution was rendered iron-free and copper-free by the process used for hydroxylammonium chloride.

APPARATUS

Beckman Model DB Spectrophotometer: All spectrophotometric data was obtained on a Beckman Model DB recording spectrophotometer equipped with matched 1.00 cm. silica cells.

KF-3 Aquameter: The Karl Fischer Reagent titrations were carried out on a Beckman Model KF-3 Aquameter.

The reaction vessel of the Aquameter (See Figure 1) consisted of a tall form 300 ml. beaker (H) fitted with a silicone rubber lid (G). The lid had six holes in it. Two small holes (A,B) permitted buret tips to be inserted. Through a third hole (C) there was placed a glass tube encasing two platinum electrodes. A fourth hole (D) accommodated an air inlet tube from a calcium sulfate scrubbing tower. Through a fifth hole (E) there was

placed a siphon tube for emptying the vessel. A sixth hole (F) provided a place for a removable stopper.

The reaction vessel was placed on a platform (See Figure 4) which was the top part of the chassis (A) of the instrument. There was an electrically-driven magnetic rotor directly beneath the reaction vessel to provide a driving force for the stirring bar. A central pole (E) attached to the back of the chassis supported the two ten ml. burets (D), of the automatic zeroing-type described previously by Nelcan (5). A four liter reservoir of Karl Fischer Reagent force fed the one buret using a float-valve aspirator bulb for pressure. Upon release of the pressure, the buret would automatically level the meniscus at 0.00 ml. A similar reservoir fed the standard water-methanol solution to the other buret.

Rather than the conventional buret tips, the burets were equipped with male ball joints. One of the ball joints was clipped into a female socket joint which proceeded down to a conventional buret tip inserted in the reaction vessel cover. The other male ball joint was inserted into a female socket joint. Below the socket joint, there was an auxillary delivery valve. (See Figure 2) This provided the automatic on-off titration. The valve had a silicone rubber diaphragm (B) which shut off the flow of liquid when pressed by an actuating lever arm (C).

The actuator arm was engaged by a relay which obtained a signal from the two platinum electrodes in the reaction vessel.

EXPLANATION OF FIGURE 1

A - Buret inlet

B - Buret inlet

C - Platinum electrode - tube inlet

D - Air inlet

E - Sample outlet

F - Removable stopper inlet

G - Silicone rubber lid

H - 300 ml. tall form beaker

I - Teflon-covered stirring bar

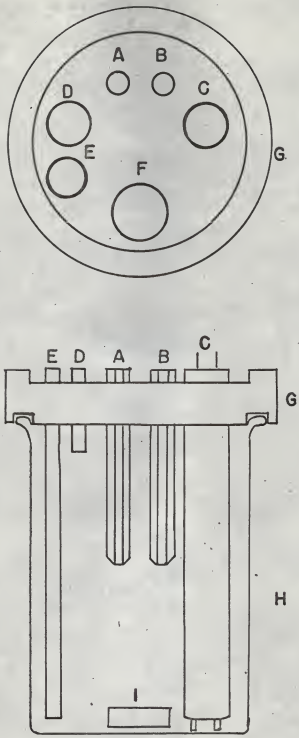


FIGURE 1 REACTION VESSEL

EXPLANATION OF FIGURE 2

A - Rubber "O" ring

B - Silicone rubber diaphragm

C - Accuator arm

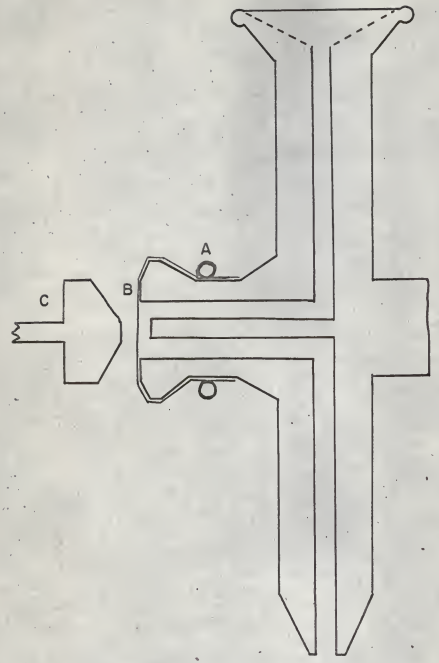


FIGURE 2 AUXILIARY DELIVERY VALVE

EXPLANATION OF FIGURE 3

A - Condenser
B - Platinum electrodes
C - Initial relay
D - Secondary power relay
E - Delivery valve relay
F - "Titrate" indicator light
G - "Standby" indicator light
H - "Read" indicator light
I - Magnetic stirring motor
J - Timer
K - Microammeter
L - "Polarizer" resistor
M - "Sensitivity" resistor
N - Variable resistor
O - Potentiometer
P - Resistor
Q - Resistor
R - Full-wave rectifier
S - "On-off" switch
T - Buret switch
U - "Titrate" switch
V - Auxillary circuit switch
W - Auxillary circuit switch
X - Transformer

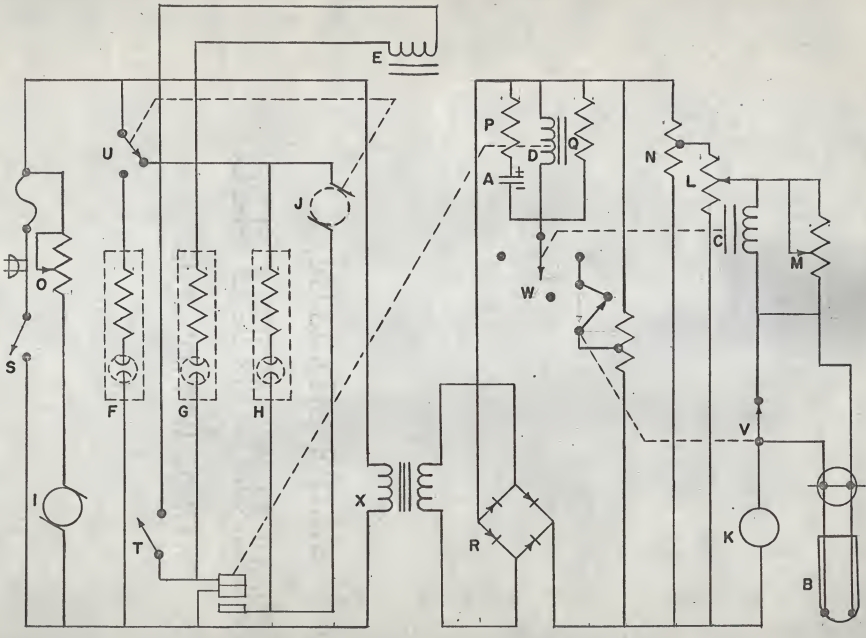


FIGURE 3 SCHEMATIC DIAGRAM OF AQUAMETER

EXPLANATION OF FIGURE 4

A - Chassis

B - 300 ml. tall form beaker

C - Auxillary delivery valve

D - 10 ml. burets

E - Central support pole

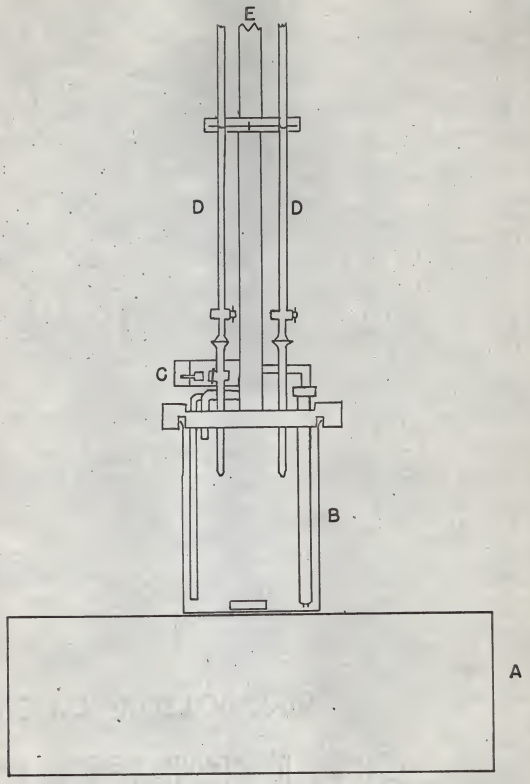


FIGURE 4 KF-3 AQUAMETER

The endpoint detection system was essentially the deadstop endpoint technique (12). A small voltage was impressed across the two platinum electrodes. When titrating a water-containing solution with Karl Fischer Reagent, one electrode had an excess of iodide ion and no free iodine present before the endpoint. One of the platinum electrodes was polarized and no current flowed through the circuit. After the endpoint had been reached, both iodide and iodine were present, neither electrode was polarized, and a current flowed through the circuit.

The current flow opened or closed the relay attached to the lever arm pushing against the delivery valve diaphragm. A timer was included in the circuit to distinguish between localized and permanent endpoints.

KF-3 Detection Circuit: (See Figure 3) 115 volt a.c. was used as the power supply. This furnished power for the magnetic rotor (I), the timer device (J) and through a step-down transformer (X) (115 v. primary coil, 16 v. secondary coil) and a rectifier (R), the power for the detection system.

The 16 volt d.c. passed through a variable resistor, (L) called the polarizer control, to apply given increments of voltage across the electrodes (B) in the solution. A 0-50 microammeter (K) was used as a measure of the current being passed in the reaction vessel. Another variable resistor (M) called the sensitivity control permitted adjustment of the solution current required to close an initial relay (C). As the titration proceeded, the current through the initial relay increased and

finally closed the contacts.

These contacts completed a circuit allowing a secondary power relay (D) to close. A circuit (P,A,Q) around the power relay prevented accidental tripping of the initial relay contacts due to jarring, from disturbing the circuit operation.

The contacts on the secondary relay stopped the titration by closing the delivery valve relay (E) actuating the lever arm into the delivery valve diaphragm and also started a preset timer (J). If the contacts on the primary relay were opened by an increase in solution resistance before the preset timer had completed its timing period, the titration continued. If the timer completed its cycle, the titration was considered complete and the circuit reset itself. Indicating lights showed the progress of the titration in three signals: titrate (F), standby (G), and read (H).

An auxilliary circuit was provided to enable a "back-titration" technique. Data obtained by this investigation (See Tables 2,3) indicated, however, that much less precision could be obtained through use of this technique. This opinion was apparently shared by the manufacturers of this instrument as they provided no instructions for this technique in the original instrument manual and special instructions had to be obtained from the factory.

Volumetric Glassware: All of the pipets and burets were calibrated by weighing the amount of water delivered and applying any necessary corrections.

TABLE 2

Standard Deviation Calculation for Back-Titration of Karl Fischer Reagent with Water-Methanol Solution

Titration no.	Ml. KFR/ml. CH_3OH	d	d^2
1	1.266	0.090	0.0081
2	1.388	0.031	0.0961
3	1.388	0.031	0.0961
4	1.348	0.009	0.0081
5	1.378	0.021	0.0441
6	1.335	0.022	0.0484
7	1.400	0.043	0.1849
8	1.338	0.019	0.0361
9	1.400	0.043	0.1849
10	1.325	0.032	0.1024
n = 10	13.566	0.341	0.8092

Standard deviation = ± 0.090

TABLE 3

Standard Deviation Calculation for Forward-Titration of Karl Fischer Reagent with Water-Methanol Solution

Titration no.	Ml. KFR/ml. CH_3OH	d	d^2
1	0.957	0.026	0.00676
2	0.978	0.005	0.00025
3	0.976	0.007	0.00049
4	0.988	0.005	0.00025
5	0.981	0.002	0.00004
6	0.992	0.009	0.00081
7	0.980	0.003	0.00009
8	1.002	0.017	0.00289
9	0.989	0.006	0.00036
10	0.989	0.006	0.00036
n = 10	9.830	0.086	0.01230

Standard deviation = ± 0.035

Sargent Oscillometer: All dielectric constant measurements were made on a Sargent Chemical Oscillometer Model V using water, methanol, chloroform and nitrobenzene as the calibration standards.

pH Meter: All pH measurements were made on a Beckman Model H pH meter using commercial buffer solution for calibrations.

RESULTS AND DISCUSSION

Bis (8-quinolinol) dioxouranium(VI) Extracted into Chloroform: The results of a typical experiment for this extraction system appear in Table 4 where the value X corresponds to the moles of uranium(VI) present per 25.00 ml. of chloroform extractant times 10^5. The value Y corresponds to the number of moles of water per 25.00 ml. of chloroform extractant times 10^5. Table 4 shows the calculation of the slope of the straight line obtained from the raw values. The intercept of this straight line is also calculated in Table 4. This value corresponds to the solubility of water in the chloroform blank.

The value obtained from Table 4 indicates 5.2 moles of water associated with each mole of uranium(VI) in the extracted phase. Two independent experiments (See Tables 5 and 6) yielded values of 3.5 and 7.2 moles of water associated per mole of uranium(VI). The mean of these values would then be 5.3 ± 1.8 moles of water per mole of uranium(VI). Earlier work by Meloan and Brandt (5) suggested that the number of molecules of water associated with neutral chelates after extraction could be even multiples of the

TABLE 4

Least Squares Determination of the Number of Water Molecules Associated with Bis (8-quinolinol) dioxouranium(VI) Trial 1

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	191	0.0	0.0000
2	0.00	186	0.0	0.0000
3	0.00	192	0.0	0.0000
4	0.00	189	0.0	0.0000
5	0.00	193	0.0	0.0000
6	0.00	193	0.0	0.0000
7	0.00	192	0.0	0.0000
8	0.00	186	0.0	0.0000
9	0.17	191	32.5	0.0289
10	0.17	206	35.0	0.0289
11	0.17	193	32.8	0.0289
12	0.17	192	32.6	0.0289
13	0.29	191	55.4	0.0841
14	0.29	190	55.1	0.0841
15	0.29	204	59.1	0.0841
16	0.29	186	53.9	0.0841
17	0.40	221	88.4	0.1600
18	0.40	193	77.2	0.1600
19	0.40	193	77.2	0.1600
20	0.40	186	75.2	0.1600
21	0.57	191	108.9	0.3249
22	0.57	191	108.9	0.3249
23	0.57	188	101.7	0.3249
24	0.57	194	110.6	0.3249
n = 24	5.72	4632	1104.5	2.3916

$$\text{Slope} = \frac{\left[(n)\,\Sigma\,(X)(Y)\right] - \left[\Sigma\,(X)\,\Sigma\,(Y)\right]}{\left[(n)\,\Sigma\,(X^2)\right] - \left[\Sigma\,(X)\right]^2} = 5.2$$

$$\text{Intercept} = \frac{\left[\Sigma\,(X)^2\,\Sigma\,(Y)\right] - \left[\Sigma(X)\,\Sigma(X)(Y)\right]}{\left[(n)\,\Sigma\,(X)^2\right] - \left[\Sigma(X)\right]^2} = 192$$

TABLE 5

Least Squares Determination of the Number of Water Molecules Associated with Bis (8-quinolinol) dioxouranium(VI) Trial 2

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	187	0.0	0.0000
2	0.00	180	0.0	0.0000
3	0.00	180	0.0	0.0000
4	0.00	192	0.0	0.0000
5	0.00	184	0.0	0.0000
6	0.00	183	0.0	0.0000
7	0.00	178	0.0	0.0000
8	0.11	193	21.2	0.0121
9	0.11	186	20.5	0.0121
10	0.11	179	19.7	0.0121
11	0.23	181	41.6	0.0529
12	0.23	187	43.0	0.0529
13	0.23	186	42.7	0.0529
14	0.23	191	43.9	0.0529
15	0.34	192	65.3	0.1156
16	0.34	192	65.3	0.1156
17	0.34	180	61.2	0.1156
18	0.46	190	87.4	0.2116
19	0.46	191	87.9	0.2116
20	0.46	189	86.9	0.2116
21	0.46	189	86.9	0.2116
22	0.57	183	104.3	0.3249
23	0.57	187	106.6	0.3249
24	0.57	196	111.7	0.3249
25	0.57	190	111.7	0.3249
n = 25	6.39	4666	1207.8	2.7407

Slope = 7.2

TABLE 6

Least Squares Determination of the Number of Water Molecules Associated with Bis (8-quinolinol) dioxouranium(VI) Trial 3

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	200	0.0	0.0000
2	0.00	189	0.0	0.0000
3	0.00	191	0.0	0.0000
4	0.00	196	0.0	0.0000
5	0.00	189	0.0	0.0000
6	0.00	189	0.0	0.0000
7	0.00	197	0.0	0.0000
8	0.29	198	57.4	0.0841
9	0.29	185	53.6	0.0841
10	0.29	195	56.5	0.0841
11	0.29	189	54.8	0.0841
12	0.29	207	60.0	0.0841
13	0.29	192	55.7	0.0841
14	0.29	196	56.8	0.0841
15	0.40	193	77.2	0.1600
16	0.40	196	78.4	0.1600
17	0.40	196	78.4	0.1600
18	0.40	208	83.2	0.1600
19	0.40	190	76.0	0.1600
20	0.40	188	75.2	0.1600
21	0.40	197	78.8	0.1600
n = 21	4.83	4081	942.0	1.7087

Slope = 3.5

ionic charge of the central metal ion. The results obtained in the first phase of this investigation at first appeared to be a contradiction of this hypothesis, that is, until it was observed in the literature (10) that this chelate has the general formula $(UO_2)_3(C_9H_6ON)_6 \cdot C_9H_7ON$. If it is rationalized that there be 3 water molecules per charge on the central metal ion species, dioxouranium(VI), the species represented by the general formula would have 18 molecules of water. The experimental evidence in this investigation, however, gives a value of 15.9 molecules of water. This suggests that the "extra" protonated 8-quinolinol has displaced 2 or 3 molecules of water from one of the coordinating positions.

Neither the dioxouranium(VI) ion nor the 8-quinolinol compound reacted with the Karl Fischer Reagent (4).

It was noted that the chelate apparently dissociated after a certain number of hours. This was confirmed through spectrophotometric analysis of the chelate solutions with respect to time. An aqueous dioxouranium(VI) nitrate solution was observed to undergo some sort of hydrolysis also after a period of several hours standing. This was accompanied by a drop in the pH value indicating a hydrolysis mechanism. This may be directly related to the chelate instability as well.

Because of the chelate breakdown with time, the half-life of the water-chelate association could not be followed. Apparently, the water was there as long as the chelate was present, but the amount of water present in the chloroform returned to the

blank solubility after the chelate had dissociated.

All of these extraction studies were carried out at 25.0°C. The temperature was a critical factor as was already mentioned with respect to the process of centrifuging.

TABLE 7

Effect of Centrifuge-Time on the Solubility of Water in Chloroform

Sample	Centrifuge-Time (minutes)	Temperature	Mg. H_2O per 25.00 ml. of chloroform
1	1	25.0	36.53
2	1	25.0	34.97
3	1	25.0	35.16
4	1	25.0	34.68
5	1.5	25.0	35.92
6	1.5	25.0	36.51
7	1.5	25.0	36.04
8	1.5	25.0	36.21
9	3	27.5	31.22
10	3	27.5	28.83
11	3	27.5	29.32
12	3	27.5	31.54

It was observed repeatedly that the extraction was 57% complete after a single extraction. Although the literature (7) suggested several methods for improving the per cent extraction, such as multiple stage extractions, increased ligand concentration and varying pH values, it was found that these improvements entailed much greater experimental error rather than less, for the purpose of this experiment.

The per cent extraction (See Table 8) was calculated by making up an aqueous solution of known concentration and meas-

uring the chloroform layer spectrophotometrically. A Beer's Law calculation was applied using the molar absorptivity given in the literature (7).

TABLE 8

Determination of Per Cent Extraction of Bis (8-quinolinol) dioxouranium(VI) Spectrophotometrically

Sample	Concentration in Aqueous Phase Originally	Absorbance of Chloroform Extract	Concentration Found	Per Cent Extraction
1	0.0	0.000	0	
2	1.0×10^{-6}	0.142	0.57×10^{-6}	57
3	4.0×10^{-6}	0.605	2.30×10^{-6}	57
4	10.0×10^{-6}	1.450	5.70×10^{-6}	57
			Average =	57%

The effect of pH in the aqueous phase on the number of molecules of water associated was not investigated as the extraction system had a rather narrow optimum pH range of 8.0 to 9.0. However, the effect of solubility of water in the chloroform layer as a function of pH was investigated and found to be negligible over the range of pH of the extraction. The results in Table 9 indicate a slight increase in the solubility of water in chloroform with increase of pH in the aqueous layer. However inasmuch as the pH of the experiment was maintained at 8.8 ± 0.1 units, the effect is essentially negligible. The ionic strength was maintained at a constant value 1.0×10^{-3} over all of the pH range by addition of sodium perchlorate to the aqueous phase.

TABLE 9

Effect of pH on Solubility of Water in Chloroform

pH	Mg. water dissolved per 25.00 ml. of chloroform*
11.0	33.92
9.0	34.10
8.0	33.18
7.0	32.92
5.0	31.84
3.0	32.11

* Each value is the average of four titrations

TABLE 10

Effect of Ionic Strength on Solubility of Water in Chloroform

Ionic strength	Mg. of water dissolved per 25.00 ml. of chloroform*
0.001	30.63
0.005	31.00
0.010	30.67
0.050	29.62
0.100	29.80
1.000	28.42
5.000	25.40

* Each value is the average of four titrations

The effect of ionic strength in the aqueous phase on the solubility of water in chloroform was deemed negligible through experiments analogous to the pH-effect experiments. Solutions of known ionic strength were prepared by dissolving solid sodium perchlorate in de-ionized water. Table 10 shows the results of these experiments.

It was apparent from this data that below an ionic strength of 0.010, there was no effect on the solubility of water in chloroform. At values of ionic strength greater than 0.010, the effect was small below an ionic strength of 1.000.

It was significant that the ionic strength was always somewhat less than 0.010 for the bis (8-quinolinol) dioxouranium(VI) extractions and varied by no more than a factor of 10.

Extraction of Tris (4,7-diphenyl-1,10-phenanthroline) Iron (II) Chelate: Knowing that "neutral" chelates, extracted into alcohols and organic solvents such as chloroform, carried waters of association along with it, it was felt that ion-association chelate systems should be looked into to see if these phenomena was also present there.

It was felt that the "ferroin" chelate systems would present a good starting point because the chemistry of the entire family of chelates had been so well worked out previously. Another factor considered in this choice was the fact that the chelates extracted quite well. Some of the distribution ratios are as high as 3600 (1). In addition, it was known that this chelate was extractable into at least three different solvents, namely,

1-decanol, chloroform and nitrobenzene.

The sulfate anion was a purely random choice for the first trials. It was found that the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) sulfate ion-association chelate extracted into chloroform along with 56.0 ± 4.0 molecules of water. Table 11 gives the data used for the calculation of the slope of the plot of chelate concentration vs water concentration by the least squares method. The value of X in the table corresponds to the moles of iron(II) chelate present per 25.00 ml. of chloroform times 10^5. The value of Y corresponds to the number of moles of water found per 25.00 ml. of chloroform times 10^5.

It was of interest that much greater concentrations of chelate were used here than with the bis (8-quinolinol) dioxouranium(VI) system. The concentration was so great in fact that in some of the more concentrated solutions, the chelate precipitated out of aqueous solutions. This, however had no effect on the results. As soon as the organic solvent was added and shaking of the separatory funnel commenced, the solid precipitate dissolved in the organic solvent. It was observed that this was essentially an instantaneous dissolution in that the aqueous phase was completely clear and colorless by the fifth inversion.

As a matter of comparison, it ordinarily took between forty and fifty inversions for maximum color development in the chloroform layer during the bis (8-quinolinol dioxouranium(VI) extractions.

TABLE 11

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) sulfate Extracted into Chloroform

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	168	0.0	0.0000
2	0.00	176	0.0	0.0000
3	0.00	172	0.0	0.0000
4	0.00	174	0.0	0.0000
5	0.16	185	29.6	0.0256
6	0.16	184	29.4	0.0256
7	0.16	185	29.6	0.0256
8	0.16	174	27.8	0.0256
9	0.41	198	81.2	0.1681
10	0.41	200	82.0	0.1681
11	0.41	188	77.1	0.1681
12	0.41	177	72.6	0.1681
13	0.82	207	169.7	0.6724
14	0.82	225	184.5	0.6724
15	0.82	233	191.1	0.6724
n = 15	5.56	3063	1152.9	3.4644

Slope = 56.0

TABLE 12

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate Extracted into Chloroform

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	188	0	0.00
2	0.00	184	0	0.00
3	0.00	180	0	0.00
4	0.00	176	0	0.00
5	0.00	181	0	0.00
6	0.00	176	0	0.00
7	0.00	174	0	0.00
8	0.00	176	0	0.00
9	0.50	194	97	0.25
10	0.50	196	98	0.25
11	0.50	195	97	0.25
12	0.50	203	102	0.25
13	1.25	227	284	1.56
14	1.25	221	277	1.56
15	1.25	231	289	1.56
16	1.25	225	282	1.56
17	1.25	256	320	1.56
18	1.25	261	327	1.56
19	1.25	244	305	1.56
20	1.25	244	305	1.56
21	2.50	328	820	6.25
22	2.50	319	798	6.25
23	2.50	322	805	6.25
24	2.50	314	785	6.25
n = 24	22.0	5415	5991	38.48

Slope = 56.0

TABLE 13

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chloride Extracted into Chloroform

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	188	0	0.00
2	0.00	184	0	0.00
3	0.00	180	0	0.00
4	0.00	176	0	0.00
5	0.00	181	0	0.00
6	0.00	176	0	0.00
7	0.00	174	0	0.00
8	0.00	176	0	0.00
9	0.50	198	99	0.25
10	0.50	204	102	0.25
11	0.50	200	100	0.25
12	0.50	199	100	0.25
13	2.50	339	848	6.25
14	2.50	333	834	6.25
15	2.50	321	802	6.25
16	2.50	326	815	6.25
n = 16	12.00	2555	3700	26.00

Slope = 60.7

The concentration of chelate in the organic phase in most instances was assumed to be the theoretical amount of chelate formed from addition of stoichiometric amounts of metal and ligand standard solutions. It is known (1) that the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chelates have large formation constants and a distribution ratio of 3600. The large distribution ratio predicts a completely quantitative extraction with one stage or theoretical plate. The large molar absorptivity of this chelate provided visual proof that the theoretical predictions were correct.

In cases of doubt, such as when the extraction solvent served as the ligand solvent, and when the ligand was added as a solid, the concentrations were obtained by measuring the absorbance of a 1:10 aliquot of the organic phase and using a Beer's Law calculation based on published values of the molar absorptivity. This technique was applied in known and suspected cases of addition of excess ligand or metal ion solutions also.

It was observed that neither the sodium acetate buffer, hydroxylammonium chloride, excess iron(II) solution, excess 4,7-diphenyl-1,10-phenanthroline, nor ethanol affected the water dissolved in the chloroform. This included the ligand which was completely extracted itself when uncomplexed. It is conceivable that the ligand could carry over one molecule of water in that some of the phenanthrolines are obtained commercially as the monohydrate. However, even if a one-fold excess were accidently added and extracted, this would not have added an appreciable

error. There was no experimental evidence that the monohydrate was extracted however.

The previously mentioned techniques such as centrifuge-time and water-bath-equilibrium-time techniques were followed here as well. It was noted that the chelate was stable for a considerable length of time (1,2).

The tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate and the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chloride were prepared and extracted into chloroform. The numbers of water molecules associated with each molecules of chelate were 56.0 ± 4.0 and 60.7 ± 4.0 respectively (See Tables 12 and 13). The mean value for the three anion-associated chelates would then be 57.6 ± 2.1. Because the average deviations among a group of titrations at the same concentration for a given anion present was of higher value (approximately 4.0), one could safely say that a change of anion had no appreciable effect on the number of water molecules associated with each chelate. This was at first surprising, considering that two of the anions were monovalent and one of them was divalent. The next experimental results bear out this observation.

Having decided that the anion had little or no effect on the number of water associated with the chelate extracted into chloroform, it was decided to extract the various anion-substituted chelates into other solvents.

The next choice of solvent system was nitrobenzene. The values for the sulfate, chloride and perchlorate chelates were

52.8 ± 3.0, 58.5 ± 4.0, 56.0 ± 3.0 and 54.0 ± 3.0 molecules of water per molecule of chelate (See Tables 14, 15, 16 and 17). The last value represented a repeat of the perchlorate chelate experiment. These values gave a mean value of 55.7 ± 1.9. It was significant that the average deviation was less than the experiments in chloroform. The blank solubility of water in nitrobenzene was approximately three times the value in chloroform. This meant that either a large amount of Karl Fischer Reagent must be added via the pipet or a smaller aliquot of organic solvent must be taken for titration. Because of the inherent difficulties of preparing and standardizing Karl Fischer Reagent, a smaller aliquot was taken and the corresponding smaller amount of Karl Fischer Reagent. 10.00 ml. aliquots were used for titration of nitrobenzene samples. It was observed that much better precision was obtained with the titrations of the nitrobenzene blank solutions than the chloroform blanks. A possible explanation for this might have been the greater presence of emulsified water in chloroform than in nitrobenzene. The two phases appeared to settle apart much more rapidly in nitrobenzene than in chloroform. This could possibly have been due to relative differences in specific gravity (1,203, 1.489), dielectric constant (35.0, 5.0) or interfacial tension. Although the effect was interesting and useful for this investigation, the cause was not pursued any further in this investigation.

The next extraction solvent chosen for the tris (4,7-diphenyl-1,10-phenanthroline iron(II) chelates was 1-decanol, the

TABLE 14

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) sulfate Extracted into Nitrobenzene

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	166	0.0	0.00
2	0.00	166	0.0	0.00
3	0.00	168	0.0	0.00
4	0.00	167	0.0	0.00
5	0.00	163	0.0	0.00
6	0.20	180	36.0	0.04
7	0.20	180	36.0	0.04
8	0.20	178	35.8	0.04
9	0.20	173	34.6	0.04
10	0.50	190	95.0	0.25
11	0.50	196	98.0	0.25
12	0.50	198	99.0	0.25
13	1.00	213	213.0	1.00
14	1.00	211	211.0	1.00
15	1.00	220	220.0	1.00
16	1.00	230	230.0	1.00
n = 16	6.30	2999	1308.4	4.91

Slope = 52.8

TABLE 15

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chloride Extracted into Nitrobenzene

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	165	0	0.00
2	0.0	166	0	0.00
3	0.0	160	0	0.00
4	0.0	166	0	0.00
5	0.0	164	0	0.00
6	0.0	164	0	0.00
7	0.0	165	0	0.00
8	0.0	163	0	0.00
9	0.2	175	35	0.04
10	0.2	191	38	0.04
11	0.2	187	37	0.04
12	0.2	169	34	0.04
13	0.5	186	93	0.25
14	0.5	181	91	0.25
15	0.5	176	88	0.25
16	0.5	178	89	0.25
17	1.0	233	233	1.00
18	1.0	226	226	1.00
19	1.0	225	225	1.00
20	1.0	223	223	1.00
n = 20	6.80	3664	1412	5.16

Slope = 58.5

TABLE 16

Least Squares Determination of the Number of Water Molecules Associated With
Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate
Extracted into Nitrobenzene Trial 1

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	165	0	0.00
2	0.0	166	0	0.00
3	0.0	160	0	0.00
4	0.0	166	0	0.00
5	0.0	164	0	0.00
6	0.0	164	0	0.00
7	0.0	165	0	0.00
8	0.0	163	0	0.00
9	0.2	175	35	0.04
10	0.2	191	38	0.04
11	0.2	187	37	0.04
12	0.2	169	34	0.04
13	0.5	186	93	0.25
14	0.5	181	91	0.25
15	0.5	176	88	0.25
16	0.5	178	89	0.25
n = 16	2.80	2756	505	1.16

Slope = 56.0

TABLE 17

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate Extracted into Nitrobenzene Trial 2

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	166	0.0	0.000
2	0.0	166	0.0	0.000
3	0.0	164	0.0	0.000
4	0.0	167	0.0	0.000
5	0.0	166	0.0	0.000
6	0.0	166	0.0	0.000
7	0.0	166	0.0	0.000
8	0.26	183	47.6	0.068
9	0.26	174	45.2	0.068
10	0.26	178	46.3	0.068
11	0.26	177	46.0	0.068
n = 11	1.04	1873	185.1	0.272

Slope = 54.0

original solvent used by Meloan and Brandt.

The values in 1-decanol for the sulfate, chloride, and perchlorate chelate were 60.0 ± 3.5, 48.1 ± 3.0 and 68.2 ± 3.0 (See Tables 18, 19, 20) respectively for an average value 58.7 ± 7.1 molecules of water associated with each molecule of chelate.

The much poorer precision achieved in this solvent was not at all surprising considering that the solubility of water in the solvent blank was some forty times that in chloroform. A 5 ml. aliquot of 1-decanol took nominally 75.00 ml. of Karl Fischer Reagent compared to a nominal 12 ml. of Karl Fischer Reagent required for a 25.00 ml. aliquot of chloroform. Thus even the blank values would be expected to have a poorer precision in 1-decanol.

In the previously used extraction solvents prior to the 1-decanol experiments it was observed that the ethanol used as the ligand solvent had no effect on the number of molecules of water associated with the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chelate. However, preliminary experiments indicated unbelievably high results such as 350 molecules of associated water. Suspicions centered upon the ethanol being added to the aqueous phase. Addition of increments of ethanol to blank solutions gave corresponding increases in the solubility of water in the decanol (See Table 21). Dielectric constant measurements confirmed the fact that at least a certain amount of ethanol was being extracted into the 1-decanol. Considering that water and ethanol are miscible it is not at all surprising that the water

TABLE 18

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline iron(II) sulfate Extracted into 1-Decanol

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	844	0	0.0000
2	0.00	831	0	0.0000
3	0.00	845	0	0.0000
4	0.00	836	0	0.0000
5	0.00	837	0	0.0000
6	0.00	852	0	0.0000
7	0.00	836	0	0.0000
8	0.25	857	214	0.0625
9	0.25	856	214	0.0625
10	0.25	853	212	0.0625
11	0.25	855	214	0.0625
n = 11	1.00	9302	855	0.2500

Slope = 60.0

TABLE 19

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chloride Extracted into 1-Decanol

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.000	831	0	0.0000
2	0.000	836	0	0.0000
3	0.000	837	0	0.0000
4	0.000	852	0	0.0000
5	0.000	836	0	0.0000
6	0.000	845	0	0.0000
7	0.000	844	0	0.0000
8	0.068	849	58	0.0049
9	0.068	849	58	0.0049
10	0.068	842	56	0.0049
11	0.163	852	139	0.0266
12	0.163	853	137	0.0266
13	0.163	853	139	0.0266
n = 13	0.692	10979	591	0.0945

Slope = 68.2

TABLE 20

Least Squares Determination of the Number of Water Molecules Associated With Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate Extracted into 1-Decanol

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	831	0.0	0.0000
2	0.00	836	0.0	0.0000
3	0.00	837	0.0	0.0000
4	0.00	852	0.0	0.0000
5	0.10	857	85.7	0.0100
6	0.10	850	85.0	0.0100
7	0.10	857	85.7	0.0100
8	0.25	848	212.0	0.0625
9	0.25	847	212.0	0.0625
10	0.25	855	214.0	0.0625
n = 10	1.05	8470	894.4	0.2175
			Slope = 48.1	

TABLE 21

Effect of Ethanol on the Solubility of Water in 1-Decanol

Sample	% Ethanol by Volume	Mg. H_2O/5.0 ml.	Dielectric Constant
1	0.0	144	6.5
2	0.0	152	6.5
3	0.0	148	6.5
4	0.0	152	6.5
5	16.6	188	12.5
6	16.6	185	12.5
7	16.6	185	12.5
8	16.6	185	12.5

solubility should increase considerably in a 1-decanol-ethanol solvent pair.

This difficulty was obviated by simply adding the ligand as a solid, a technique described earlier in this paper.

Table 22 summarizes the results obtained in the ten separate extraction measurement experiments of tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chelate. It became evident at this point that neither the anion nor the extraction solvent had an effect on the number of molecules of water associated with this chelate.

Extraction of Tris (1,10-phenanthroline) Iron(II) Perchlorate into Nitrobenzene: Having determined the effect of change of solvent and anion, the next phase of the investigation concerned the change of ligand maintaining the rest of the conditions constant from the previous phase. The parent homolog of the 4,7-diphenyl-1,10-phenanthroline, 1,10-phenanthroline was chosen as the ligand to use. This ligand was soluble in hot water solution such that no ethanol was introduced into the solution.

The perchlorate anion, and nitrobenzene were used. The sulfate and chloride analogs were not extractable into any of the common immiscible solvents and the perchlorate is extractable only into nitrobenzene (12).

The value for the extraction of tris (1,10-phenanthroline) iron(II) perchlorate extracted into nitrobenzene was 18.7 ± 2.0 molecules of water associated with each molecule of chelate extracted (See Table 23).

The concentration range covered exactly that of the previous phase of this investigation.

Extraction of Bis (1,10-phenanthroline) Copper(I) Perchlorate into Nitrobenzene: The next step was to change the central metal ion retaining all other factors constant. The copper(I) ion was chosen as it formed a tetrahedral sp^3 complex with the phenanthrolines as opposed to an octahedral d^2sp^3 complex of iron(II) with similar ligands. This implied of course that the copper chelate would be a 1:2, metal to ligand chelate as opposed to a 1:3 ratio in the iron(II) derivatives.

TABLE 22

Summary of Results of the Extraction of Tris (4,7-diphenyl-1,10-phenanthroline) iron(II) chelates

Experiment	Anion	Solvent	Waters Associated
1	sulfate	chloroform	56.0
2	chloride	chloroform	60.7
3	perchlorate	chloroform	56.0
4	sulfate	nitrobenzene	52.8
5	chloride	nitrobenzene	58.5
6	perchlorate	nitrobenzene	56.0
7	perchlorate	nitrobenzene	54.0
8	sulfate	1-decanol	60.0
9	chloride	1-decanol	68.2
10	perchlorate	1-decanol	48.1
		Mean value =	57.0 ± 3.8

The experiment was carried out just as in previous phases of this investigation.

The value for the extraction of bis (1,10-phenanthroline)

TABLE 23

Least Squares Determination of the Number of Water Molecules Associated With Tris (1,10-phenanthroline) iron(II) perchlorate Extracted into Nitrobenzene

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	168	0.0	0.00
2	0.0	169	0.0	0.00
3	0.0	166	0.0	0.00
4	0.0	167	0.0	0.00
5	0.2	168	33.6	0.04
6	0.2	172	34.4	0.04
7	0.2	170	34.0	0.04
8	0.2	171	34.2	0.04
9	0.5	172	86.0	0.25
10	0.5	176	88.0	0.25
11	0.5	175	87.5	0.25
12	0.5	183	92.5	0.25
13	1.0	186	186.0	1.00
14	1.0	191	191.0	1.00
15	1.0	188	188.0	1.00
16	1.0	187	187.0	1.00
n = 16	6.8	2809	1241.0	5.16

Slope = 18.7

copper(I) perchlorate extracted into nitrobenzene was 14.0 ± 2.0 molecules of water associated with each molecule of chelate extracted (See Table 24).

Extraction of Bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) Copper(I) Perchlorate into Chloroform: Two separate experiments were then run with the same conditions prevailing as were present in the preceding phase of this experiment except that a tetra-substituted phenanthroline was used as the ligand and chloroform was used as the solvent.

Both attempts yielded 0.0 ± 1.0 molecules of water associated with each molecule of chelate extracted (See Tables 25 and 26).

In one of these experiments (Table 25), the ligand was added as an ethanol solution. Exactly the same amount of ethanol was added to each concentration and to the blank. Although the blank solution water solubility increased, the amount of water present did not increase in increasing chelate concentration.

The second experiment (Table 26) had no ethanol present and the ligand was added to the aqueous phase as a solid.

Two possible explanations were advanced for these results. First of all, there is the possibility that the chelate has no associated water molecules in the organic solvent. Secondly, there is the possibility that the associated water molecules if present were somehow bound so tightly to the chelate that they could not react with the Karl Fischer Reagent in the normal manner.

TABLE 24

Least Squares Determination of the Number of Water Molecules Associated With Bis (1,10-phenanthroline) copper(I) perchlorate Extracted into Nitrobenzene

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.00	156	0.0	0.0000
2	0.00	152	0.0	0.0000
3	0.00	157	0.0	0.0000
4	0.00	154	0.0	0.0000
5	0.00	158	0.0	0.0000
6	0.00	155	0.0	0.0000
7	0.00	150	0.0	0.0000
8	0.00	152	0.0	0.0000
9	0.41	159	65.1	0.1681
10	0.41	156	64.0	0.1681
11	0.41	163	66.8	0.1681
12	0.41	163	66.8	0.1681
13	0.47	161	75.7	0.2209
14	0.47	161	75.7	0.2209
15	0.47	160	75.2	0.2209
n = 15	3.05	2357	489.3	1.3351

Slope = 14.0

TABLE 25

Least Squares Determination of the Number of Water Molecules Associated With
Bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline copper(I)
Extracted into Nitrobenzene Trial 1*

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	222	0	0.0
2	0.0	222	0	0.0
3	0.0	224	0	0.0
4	0.0	222	0	0.0
5	1.0	223	223	1.0
6	1.0	210	210	1.0
7	1.0	232	232	1.0
8	1.0	222	222	1.0
n = 8	4.0	1777	887	4.0
			Slope = 0	

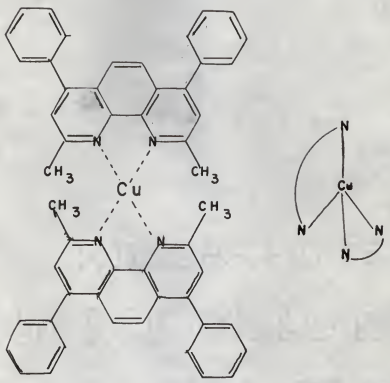
* Ethanol was used as the ligand solvent, therefore the same amount of ethanol was added to the blank.

TABLE 26

Least Squares Determination of the Number of Water Molecules Associated With
Bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline copper(I)
Extracted into Nitrobenzene Trial 2

Sample	X	Y	(X)(Y)	$(X)^2$
1	0.0	166	0	0.0
2	0.0	166	0	0.0
3	0.0	164	0	0.0
4	0.0	167	0	0.0
5	1.0	166	166	1.0
6	1.0	166	166	1.0
7	1.0	166	166	1.0
8	1.0	166	166	1.0
n = 8	4.0	1327	664	4.0
			Slope = 0	

The structure of bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) copper(I) is:



These studies could not be pursued any further at the present time due to a lack of reagent available.

Dielectric Constant Measurement: A calibration chart was prepared by plotting instrument readings of the Sargent Chemical Oscillometer vs dielectric constant values for certain known compounds. The calibration dielectric constant values were obtained from Morrison and Freisers book (7).

Using the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate extraction as a basis of comparison, the dielectric constants of several solvents which extracted the chelate were

obtained and also the dielectric constants of two solvents which failed to extract this chelate to any measurable extent. Table 27 shows the results obtained.

The results in Table 27 themselves were not too surprising, for it was well known that the higher the dielectric constant, the better a polar compound would dissolve. However, it was observed that the solubility of water in amylene was 18 X 10^{-5} moles of water per 10.00 ml. of amylene.

Now if the tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate would have been dissolved to the extent of 10^{-3} M (a concentration obtained easily in the other solvents), it would have been expected to carry over 56 X 10^{-5} moles of water with it. This was some three times the solubility limit. This assumed that the 56 X 10^{-5} moles of water would have been evenly distributed throughout the 10.00 ml. In reality it probably would have been concentrated about the chelate, explaining why even one-third of this amount of chelate failed to dissolve.

The dielectric constant was measured for various other solutions (See Table 28). It was noted that equilibrating these solvents with water did not measurably increase the dielectric constant value. In fact, in 1-decanol the value decreased slightly. This was probably due to the dipole-dipole interaction of the water and alcohol lowering the polarity of the solvent somewhat.

The dissolution of a ligand itself did not change the dielectric constant appreciably. However, extraction of 10^{-3} M

TABLE 27

Dielectric Constants of Organic Solvents

Solvent	Dielectric Constant	H_2O in Solvent*	Does Extract
Nitrobenzene	35.0	3.0	Yes
Methyl-phenyl	17.0	20.0	Yes
Methyl-hexyl ketone	10.0	12.0	Yes
1-decanol	6.5	30.0	Yes
Chloroform	5.0	1.2	Yes
Amylene	2.2	0.3	No
2,2,4-trimethylpentane	1.8	0.2	No

* Solubility in terms of mg. of water per ml. of solvent.

TABLE 28

Dielectric Constant Measurements

Solvent	Dielectric Constant	Solute
Air	1	None
Water	78	None
Nitrobenzene	35	None
Nitrobenzene	35	Water
Nitrobenzene	42.5	Water, Fe-Chelate
Nitrobenzene	43.5	Water, Cu-Chelate
Chloroform	5.0	None
Chloroform	5.0	Water
Chloroform	5.0	Ligand
Chloroform	5.5	Water, UO_2-Chelate
1-Decanol	7.0	None
1-Decanol	6.5	Water
1-Decanol	12.5	Ethanol

tris (1,10-phenanthroline) iron(II) perchlorate into nitrobenzene increased the dielectric constant value by 6 units. Roughly the same increase was found for the same concentrations of tris (4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate in nitrobenzene and bis (1,10-phenanthroline) copper(I) perchlorate in nitrobenzene.

Extraction of 10^{-3} M concentration of bis (8-quinolinol) dioxouranium(VI) chelate into chloroform increased the dielectric constant value, at most, 0.5 units.

These results confirm the assumption that the neutral chelates are extracted as essentially non-polar species while ion-association chelates extract as a quite polar species.

Again, no work was carried out on the bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) copper(I) perchlorate chelate due to temporary lack of reagent.

CONCLUSIONS

Based upon the experimental results obtained in this investigation, it is evident that there are a certain number of molecules of water associated with the neutral chelate bis (8-quinolinol) dioxouranium(VI) extracted into chloroform. This is evidence that the phenomena is by no means present only in alcoholic solvents nor restricted to a certain family of chelate compounds.

In like manner, the ion-association chelates of the 1,10-phenanthroline family also show this phenomena. In fact, the

water is present to the extent of ten times that found associated with neutral chelates.

Changing solvent, and anion around one given metal-ligand group had no measurable effect upon the number of water molecules associated about the chelate. This would imply that there must be a bonding of some sort between the chelate and the water molecules. Another way of stating this, if the water molecules were not bound to the chelate, but simply dissolving in the solvent in addition to a prior solubility quantity because of the presence of a new species, then one would expect a different solvent or different anion to give a different stoichiometry.

Changing from the diphenyl-substituted 1,10-phenanthroline to the parent 1,10-phenanthroline ligand yielded a change from 56 to 18 molecules of water associated with each molecule of chelate.

This leads one to correlate the decrease in molecules of water associated with the chelate to a decrease in surface area of the chelates. Making the assumption that each of the chelates exists as a sphere, one calculates an effective radius of 6.3 A for the diphenyl-substituted chelate and 3.0 A for the parent chelate. This gives a ratio of approximately 4:1 for the surface area. This is qualitatively in the same general area as the ratio of water molecules associated with the chelates.

Based on similar assumptions, the surface area of the copper (I) derivative of 1,10-phenanthroline has somewhat less area due to one less ligand per metal ion. This would then explain a somewhat reduced amount of molecules of water associated with the

chelate assuming that the metal ion was not contributing an effect.

The absence of any water molecules associated with the dimethyl-, diphenyl-substituted 1,10-phenanthroline copper(I) chelate is a bit difficult to explain based upon the limited data presently available. Perhaps the four methyl groups in close proximity to the central metal ion have a good bit to do with this phenomena.

Somewhat contrary to the old adage "likes dissolve likes", it is becoming apparent that the ion-association chelates which are quite polar in nature, not only have much larger distribution coefficients, but also carry along more waters of association into the relatively non-polar organic solvents than do the neutral chelate extracting species.

FUTURE PROJECTS

There remain many more unanswered questions at this time. Although the presence of waters of association with extracted chelates is quite well established, the question of importance of their presence or absence still remains.

Before this question can be fully answered, some light must be shed upon the type and degree of bonding existing between the water and the chelates. Infrared studies on the organic solution of hydrated and non-hydrated chelates would be helpful in this respect.

The effect of waters of association upon the half-extrac-

tion might aid in understanding the importance of the presence of the water around the chelate. Radioactive tracers would be helpful in this respect.

The availability of some 100 substituted phenanthrolines and polypridyls causes one to consider the extension of chelate size relative to waters of association studies.

There are many other types of chelate systems which also should be investigated for the presence and importance of associated water molecules.

The sulfate and chloride compounds of tris (1,10-phenanthroline) iron(II) should be examined to see if it is possible to associate water molecules with them. The bis (2,4,6-tripyridyl-s-triazine) iron(II) chelate shows similar characteristics in that only the perchlorate salt will extract only into nitrobenzene.

ACKNOWLEDGMENT

The author wishes to express his appreciation to his research director, Dr. Clifton E. Meloan, for the motivation, suggestions and guidance. He has enabled this investigation to be a truly educational experience.

The author wishes to thank his many colleagues who have contributed to this undertaking. If nothing more, they endured the odors of the Karl Fischer Reagent with a minimum of complaint.

Special thanks is due to his wife, Jo, whose encouragement, understanding, and assistance in the typing of this manuscript has enabled it to be a much less formidable task than it could have been.

LITERATURE CITED

(1) Diehl, Harvey C. and Smith, G. Frederick
The Copper Reagents: Cuproine, Neocuproine, Bathocuproine. Columbus, Ohio: The G. Frederick Smith Chemical Company, 1958.

(2) Diehl, Harvey C. and Smith, G. Frederick
The Iron Reagents: Bathophenanthroline, 2,4,6-Tripyridyl-s-Triazine and Phenyl-2-Pyridyl Ketoxime. Columbus, Ohio: The G. Frederick Smith Chemical Company, 1960.

(3) Duval, C.
Inorganic Thermogravimetric Analysis. New York: Elsevier Publishing Company, 1953. 245 p.

(4) Meloan, Clifton Edward
Analytical Applications and Extraction Studies of Some Metal Chelate Compounds of Benzohydroxamic Acid. Doctoral Thesis. Purdue University. 1959.

(5) Meloan, Clifton E., and Brandt, Warren W.
J. Inorg. and Nuc. Chem. 00: 000. 1962.

(6) Meyers, R. J., Metzler, D. E., and Swift, E. H.
J. Amer. Chem. Soc. 72: 3767. 1950.

(7) Morrison, George H., and Freiser, Henry
Solvent Extraction in Analytical Chemistry. New York: John Wiley & Sons, Inc., 1957.

(8) Samuelson, Olof
Ion Exchangers in Analytical Chemistry. Third Printing. New York: John Wiley & Sons, Inc., 1956. 259 p.

(9) Swift, E. H. and Axelrod, J.
J. Amer. Chem. Soc. 62: 33. 1940.

(10) Tuck, D. G., and Diamond, Richard M.
J. Phys. Chem. 65: 193. 1961.

(11) Wilkins, D. H., and Smith, G. Frederick
Anal. Chem. Acta. 9: 538. 1953.

(12) Willard, H. H., Merritt, L. L. Jr., and Dean, J. A.
Instrumental Methods of Analysis. Third Edition. New York: D. Van Nostrand and Company, 1958. 563-565 p.

A STUDY OF THE WATER ASSOCIATED WITH EXTRACTED METAL CHELATES

by

DENNIS ROGER GERE

B. S., Iowa State University
of Science and Technology, 1960

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1962

The primary objective of this investigation has been to study the number of molecules of water associated with metal chelates extracted into immiscible solvents.

Previous work described the water associated with certain "neutral" metal chelates extracted into 1-decanol. In this investigation, a "neutral" metal chelate was extracted into another solvent, chloroform and the number of water molecules associated were determined. Then, a series of "charged" metal chelates were extracted into the solvents; chloroform, nitrobenzene, and 1-decanol. The effect of solvent, associated anion, ligand, and central metal ion, upon the number of water molecules associated, was determined.

The solvent was saturated with water and the amount of water present was determined via titration with standard Karl Fischer Reagent. A series of concentrations of the chelate was extracted from aqueous solution. The amount of water present in the immiscible solution was determined via titration with standard Karl Fischer Reagent. The number of moles of water present was plotted *vs* the number of moles of chelate present and the slope of the resultant straight line was determined. This slope represented the number of water molecules associated with each molecule of chelate extracted into the immiscible solvent.

Extraction of the "neutral" chelate bis (8-quinolinol) dioxouranium(VI) into chloroform associated with 5.3 ± 1.8 molecules of water per molecule.

The "charged" chelate, tris (4,7-diphenyl-1,10-phenanthroline) iron(II) when extracted into immiscible solvents was associated with 57.0 ± 3.8 molecules of water per molecule. The same results were obtained whether this species was extracted into chloroform, nitrobenzene or 1-decanol. Likewise no change was observed whether the associated anion was sulfate, perchlorate or chloride.

The "charged" chelate, tris (1,10-phenanthroline) iron(II) extracted into nitrobenzene was associated with 18.7 ± 2.0 molecules of water per molecule. The associated anion was perchlorate. This suggested that the ligand size was effecting the number of molecules of water associated with the chelate.

The "charged" chelate, bis (1,10-phenanthroline) copper(I) extracted into nitrobenzene was associated with 14.0 ± 2.0 molecules of water per molecule. The associated anion was perchlorate. This suggested that the central metal ion contributed an effect on the number of molecules of water associated with the chelate, at least if the configuration of the metal ion changed.

The "charged" chelate, bis (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) copper(I) extracted into chloroform was associated with 0.0 ± 1.0 molecules of water per molecule. The associated anion was perchlorate. This was not readily explained based upon the data obtained, but is possibly correlated with the 4 methyl groups surrounding the central metal ion.

Dielectric constant measurements of the solvents involved indicated a trend between the dielectric constant and the solubility of water in the solvent. There appeared to be a certain minimum dielectric constant value (and corresponding water solubility) before a solvent would extract the chelates.