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# Chelate Extractions Involving Three Liquid Phases: Role of Water

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# Chelate Extractions Involving Three Liquid Phases: Role of Water

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## Summary

An experimental technique has been developed to determine the effect of solvent polarity on the removal of associated water molecules from metal chelates during extraction. It was found that tris(4,7-diphenyl-1,10-phenanthroline)iron(II) perchlorate had two spheres of water associated with it—one that could be displaced by organic solvent and one that could not.

## INTRODUCTION

Previous work involving water adducts associated with metal chelates and how the water effected the extraction process was performed between water and an immiscible organic solvent (*4,6,8*). Such measurements provided the number of water molecules that were associated with a metal chelate in the organic phase after the extraction took place. While the total number of water molecules was known, the relative strength of the water–chelate bond was not known, nor was it known whether the amount of water associated with the chelate was in reality part of the water normally associated with the solvent. By going to a ternary system (three pairs of mutally immiscible liquids; Fig. 1) and determining the *X*, *Y*, and *Z* values, some conclusions could be drawn.

Referring to Fig. 1, if a chelate is extracted by all three systems and *X*, *Y*, and *Z* are the same, then the water associated with the

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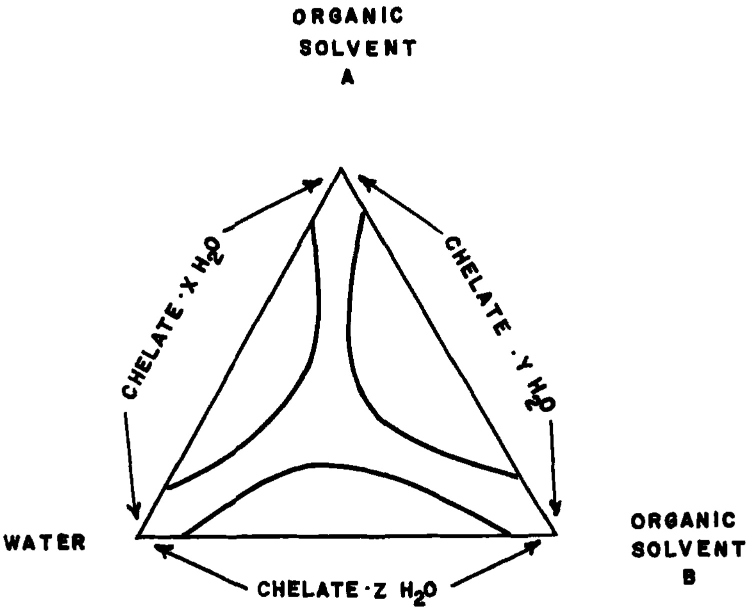

**FIG. 1.** The schematic diagram of the distribution of the water–chelate complex in the system. Water–organic solvent A–organic solvent B.

extracted chelate must be firmly bonded, so much so that an organic molecule cannot displace it. If $X$, $Y$, and $Z$ are different, then the water must be only loosely bonded to the chelate and part of it is being replaced by organic solvent molecules due to the different solvent polarities. A comparison of $X$ and $Z$ gives some idea of the effect, but $Y$ is more valuable because it is done in a system that is essentially free of water and the competition between the solvent and the chelate for the water present is more pronounced.

## EXPERIMENTAL

**Chemicals, Apparatus, and Procedures.** All chemicals, equipment, and procedures are described in previous work by the authors (*4–6,8*).

## RESULTS AND DISCUSSION

There are few descriptions in the chemical literature of immiscible solvent systems consisting of three mutually immiscible components and, in particular, systems wherein one of the components was water (3,8,9). Most analogous systems which have been described did not bond themselves to practical extractive separations (7).

The situation existing for the extraction of chelates requires that a nonaqueous solvent system must not only show a favorable partition of the chelate between the two phases, but also be favorable toward initial formation of the chelate over a practical concentration range. Such a system must also be mutually immiscible with water both individually and as a three-component–three-phase liquid system. With such severe restrictions, it was not suprising that there was no direct description of such a system in the literature.

Three systems have been found that will extract a chelate in the desired manner: water/1-decanol/nitromethane, water/1-decanol/nitroethane, and water/1-decanol/adiponitrile. The chelate chosen was tris(4,7-diphenyl-1,10-phenonthroline)iron(II) perchlorate.

The selection of a solvent system for the three-phase extraction of a given chelate was critically dependent upon experimentally determined distribution of "free" water between the immiscible phases. In the case of a water–organic solvent two-phase system, this distribution corresponded to the solubility of water in the organic phase. In the case of an organic solvent–organic solvent two-phase system, this distribution ratio usually was close in value to the ratio of the individual solubilities of water in the organic solvents, but deviated greatly enough to require experimental measurements. A complicating factor arose from the fact that if water-saturated organic solvent A was mixed with organic solvent B containing less than a saturation amount of water, the overall system was water unsaturated.

The final concentration of water in organic solvent B was dependent upon the product of (a) the distribution ratio of water between organic solvent A and organic solvent B and (b) the sum of the original amount of water in organic solvent A (saturation amount) and the amount of water present in organic solvent B prior to equilibration (less than its corresponding saturation amount). Measurement of the individual water concentrations of organic solvent A and organic solvent B after equilibration would not allow succinct calculation of any additional amount of bound water above the amount of free water without normalization of the total amount of water in the system.

To calculate the relative difference in water content of the organic solvent B phase as a function of extracted chelate, two extraction trials were carried out (one at low chelate concentration and the other at high chelate concentration). The total amount of water in the system at a given chelate concentration was then normalized to the average value of the two trials. The symbols used in the calculation are as follows:

$X_H$ = adjusted $[H_2O]$ in nitromethane for high chelate concentration
$X_L$ = adjusted $[H_2O]$ in nitromethane for low chelate concentration
$Y_H$ = adjusted $[H_2O]$ in 1-decanol for high chelate concentration
$Y_L$ = adjusted $[H_2O]$ in 1-decanol for low chelate concentration

The calculation of the distribution ratio for water between the immiscible organic phases at high and low chelate concentrations would be as follows:

$$D_{\mathrm{H_2O},H} = \frac{X_H}{[(X_H + Y_H) + (X_L + Y_L)]/2 - X_H}$$

and

$$D_{\mathrm{H_2O},L} = \frac{X_L}{[(X_H + Y_H) + (X_L + Y_L)]/2 - X_H}$$

Once the normalized water concentrations in organic solvent B are determined, the linear dependence of the water concentration upon the concentration of chelate extracted into organic solvent B may be calculated. This linear dependence is then the stoichiometric ratio of adduct water molecules to chelate molecules.

To reduce the experimental error in measuring the concentration of water in organic solvent B, it would be preferable to reduce the background amount of water (the "free" or "unbound" water molecules) as much as possible. For example, the experimental value for the distribution ratio of water between 1-decanol and adiponitrile was

$$D_{\mathrm{H_2O}} = \frac{[\mathrm{H_2O}]\ \text{adiponitrile}}{[\mathrm{H_2O}]\ \text{1-decanol}} = 1.79$$

This system was not ideal with such a distribution ratio. Ideally, the extracting solvent would bring over the chelate and perhaps any associated water molecules, leaving behind the majority of the "background" water molecules. This would correspond to a distribution ratio of 1:0 or less with the concentration of water in the extracting solvent appearing in the numerator.

The system water/1-decanol/nitromethane was found to best approach the conditions desired. Water/1-decanol, water/nitromethane, 1-decanol/nitromethane, and water/1-decanol/nitromethane were all mutually immiscible systems. The water solubilities were 30.0 mg of water per milliliter of 1-decanol and 25.2 mg of water per milliliter of nitromethane. 1-Decanol has a dielectric constant of 6.5 and nitromethane has a dielectric constant of 35.9. The experimental distribution ratio for water between 1-decanol and nitromethane was 0.894, with the concentration of water in nitromethane appearing in the numerator.

The tris(4,7-diphenyl-1,10-phenanthroline)iron(II) perchlorate had a distribution ratio between water and 1-decanol of 3000, with the concentration of chelate in 1-decanol appearing in the numerator, and a distribution ratio of 150 between 1-decanol and nitromethane, with the concentration of chelate in nitromethane appearing in the numerator. The distribution ratio of the chelate between water and nitromethane was 200, with the concentration of chelate in nitromethane appearing in the numerator.

In a separatory funnel containing water/1-decanol/nitromethane (densities equal to 1.00, 0.830, and 1.131, respectively), 1-decanol formed the top layer, water the intermediate layer, and nitromethane the bottom layer. If the tris(4,7-diphenyl-1,10-phenanthroline) iron(II) perchlorate was introduced into the aqueous layer with no agitiation or mixing of the three phases, the color was seen to diffuse through both the interfaces, up into the 1-decanol layer and down into the nitromethane layer. If the separatory funnel were inverted several times, bringing about mutual contact of the three phases, the colored chelate was found residing in the bottom nitromethane phase after the three phases separated.

In this system, then, it was possible to extract the chelate from water into 1-decanol and determine the stoichiometry of the associated water molecules, follow this with an extraction of the chelate from 1-decanol into nitromethane, and again determine the stoichiometry of the associated water molecules. A comparison of the stoichiometry of the associated water molecules relative to the chelate molecule in these two steps is described schematically in Fig. 1. Obviously the experiment would be completed by extraction of the chelate directly from water into nitromethane, again followed by determination of the associated water–chelate stoichiometry.

Table 1 shows the data obtained for the extraction of tris(4,7-diphenyl-1,10-phenanthroline)iron(II) perchlorate from water into nitromethane.

A least-squares slope of 48 molecules of associated water per molecule of chelate extracted from water into nitromethane agrees with the previous results for the same system (6). Data for the other systems were obtained in the same manner.

The determination of the stoichiometry of the water molecules associated with each chelate molecule extracted from 1-decanol into nitromethane required more calculation than the experiments concerned with extraction from water into a nonaqueous organic solvent, as mentioned earlier.

The final concentration of chelate molecules in nitromethane was dependent upon the product of the amount of chelate originally formed in the aqueous phase and the distribution ratio between nitromethane and 1-decanol. The solubility of the chelate in nitro-

TABLE 1

Least-Squares Determination of the Number of Water Molecules Associated with Tris(4,7-diphenyl-1,10-phenanthroline)iron(II) Perchlorate Extracted into Nitromethane from Water

| Sample | Moles iron(II) | Moles water |
|---|---|---|
| 1 | 0.00 | 135 |
| 2 | 0.00 | 138 |
| 3 | 0.00 | 136 |
| 4 | 0.00 | 138 |
| 5 | 0.00 | 137 |
| 6 | 0.10 | 142 |
| 7 | 0.10 | 141 |
| 8 | 0.10 | 142 |
| 9 | 0.10 | 143 |
| 10 | 0.10 | 141 |
| 11 | 0.50 | 158 |
| 12 | 0.50 | 162 |
| 13 | 0.50 | 164 |
| 14 | 0.50 | 163 |
| 15 | 0.50 | 159 |

Least-squares slope = 48.7 ± 2.0

TABLE 2

Water Concentration Found in 1-Decanol/Nitromethane System Following Extraction of Tris(4,7-diphenyl-1,10-phenanthroline)iron(II) Perchlorate

| | 1-Decanol[a] | Nitromethane[a] |
|---|---|---|
| Low | 443 | 402 |
| chelate | 451 | 402 |
| concentration | 452 | 402 |
| | 448 | 403 |
| Mean | 448 | 402.4 |
| High | 437 | 397 |
| chelate | 439 | 393 |
| concentration | 433 | 396 |
| | 437 | 396 |
| Mean | 436.5 | 396 |

[a] Moles × $10^{-5}$ of water per 5.0 ml of solvent.

TABLE 3

Distribution Ratios for Water between 1-Decanol and Nitromethane at Two Chelate Concentrations

Low chelate concentration

$$D_{H_2O} = \frac{[H_2O]\ CH_3NO_2}{[H_2O]\ \text{1-decanol}} = \frac{[402]}{[448.5]} = 0.896$$

High chelate concentration

$$D_{H_2O} = \frac{[396]}{[436.5]} = 0.907$$

methane was independently found to be approximately 0.12 *M*, which was at least 100 times greater than the typical concentration in the aqueous phase (and subsequently the concentration in both the 1-decanol and the nitromethane).

As expected, the total amount of water varied significantly at the two chelate concentrations. In addition, as mentioned above, the overall distribution ratio for water between 1-decanol and nitromethane increased as a function of the increase in concentration of chelate extracted. The data obtained are shown in Tables 2 and 3. From these data, the total water content of the system at each chelate concentration was normalized to an average value as follows:

$$X_H = 396.0$$
$$Y_H = 436.5$$
$$X_L = 402.5$$
$$Y_L = 448.0$$
$$\frac{[(X_H + Y_H) + (X_L + Y_L)]}{2} = 841.5$$
$$D_{\mathrm{H_2O},H} = 0.907 = \frac{X_H}{(841.5) - X_H}$$
$$X_H = 400.3$$
$$D_{\mathrm{H_2O},L} = 0.896 = \frac{X_L}{(841.5) - X_L}$$
$$X_L = 397.8$$

From these normalized values, the linear regression of the water content as a function of chelate content was calculated as follows:

$$\begin{aligned}\text{Slope} &= \frac{X_H - X_L}{[\text{chelate}]_H - [\text{chelate}]_L} \\ &= \frac{(400.3 - 397.8)(10^{-5})}{(0.650 - 0.125)(10^{-6})} \\ &= 48.2 \text{ moles of } \mathrm{H_2O} \text{ per mole of chelate}\end{aligned}$$

Referring to Fig. 1, values for $X$, $Y$, and $Z$ have been determined to be 68.1, 48.2, and 48.7, respectively.

These results may be explained as follows: The polar water associated with a polar chelate is not removed appreciably by the 1-decanol molecule which has a low dipole moment and low dielectric constant (6.5). However, when nitromethane with a dipole moment of 3.44 (dielectric constant 35.9) is present, the polar nitromethane molecules can compete with the water molecules and remove some of them from around the chelate. Since there are still quite a few water molecules that remain, these water molecules must be rather tightly held. Recent work by Burchett (*1*) using infrared spectroscopy has shown this bond strength to be about 7.2 kcal/mole.

As suggested by Buchowski (*2*), these results indicated that the macroscopic property of dielectric constant cannot be simply correlated with the direction of partition of solute between solvents. For example, the chelate originated in water (dielectric constant 78) was extracted into 1-decanol (dielectric constant 6.5) and was further extracted from this medium into nitromethane (dielectric constant 35.9).

Along the same trend, the water solubility in the nonaqueous solvent does not necessarily give an indication of the distribution of this polar chelate, for the solvents 1-decanol and nitromethane have solubilities of 30.0 mg of water per milliliter and 25.2 mg of water per milliliter, respectively.

The distribution of "free" water between 1-decanol/nitromethane agreed quite well with the relative solubilities for water which were measured independently. The ratio of solubilities was 0.840, while the experimental distribution ratio of water extrapolated to zero chelate concentration was 0.894.

Although it was not attempted experimentally, such a distribution ratio for water along with a distribution ratio for the chelate of approximately 200 would indicate that complete separation of water and chelate could be accomplished via the Craig countercurrent distribution method or by manual serial extractions. To do this, anhydrous 1-decanol would be added to the nitromethane phase following extraction of the chelate (and its associated water molecules and the free water molecules) from water-saturated 1-decanol into nitromethane. The water present in the nitromethane would back-extract into the 1-decanol, while the chelate remained in the nitromethane layer. Assuming no complications, such as mutual solubility changing the volumes of the phases, seven serial back-extractions would reduce the water concentration of the nitromethane layer to a value less than that required for the chelate–water complex.

This sort of experiment could possibly aid in defining the relative strength of the chelate water bonds and suspected chelate–solvent interactions. A method of detecting the difference between "free water" and "associated water" would be necessary for definitive measurements. At the time of these studies no independent method was available for the concentration range for chelate necessary for optimum extraction equilibria.

Infrared spectra of the extracted chelate indicate that the skeletal bands of the chelate molecule do not shift in frequency or change in intensity as the water concentration around the chelate is changed. This indicated that the water molecules associated with the chelate are not bonded to the ligand group. For a complete discussion of the assignment of the infrared frequencies and spectra, see the work of Gere (*4*). Burchett's infrared studies (*1*) substantiated the above conclusion in that he had evidence for a metal–water bond.

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