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The Effect of Water on the Distribution of Uranyl 8-Quinolinol Chelate between Nitromethane and 1-Decanol

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Summary

An equation of the form $y = ABe^{cx^n}$ describes the effect of associated water on the distribution ratio of this nonaqueous extraction. It was also determined that there are 9.6 ± 1.5 molecules of water associated per molecule of the chelate when extracted from water into nitromethane or 1-decanol.

INTRODUCTION

It was the purpose of this study to determine the number of water molecules associated with the $UO_2(Ox)_2(HOx)$ chelate when extracted from water into 1-decanol and nitromethane. It was further desired to determine what effect water would have on the partitioning of this same chelate between these two immiscible organic solvents. Finally it was desired to see if an equation could be developed whereby it would be possible to predict the concentration of the chelate in either of the organic solvents if the amount of water present is known.

Nitromethane and 1-decanol were chosen as the two solvents to be used in this study, as a considerable number of chelates (*1,3*) have been shown to have molecules of water associated with them when extracted into these two solvents. Therefore it was desired to ascertain if it would also exhibit this phenomena when extracted into these two solvents. The use of two immiscible organic solvents reduces the background water to such a low concentration that the effects of water can be determined.

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EXPERIMENTAL

Bis(8-quinolinolo)dioxouranium(VI) 8-Quinolinol. $UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$ (molecular weight 703.54) was prepared by the method of Moeller and Wilkins (*6*).

Nitromethane. Practical-grade Matheson Coleman and Bell nitromethane was used in the extraction studies. Eastman White Label nitromethane was used in the 1-decanol–nitromethane distribution studies.

1-Decanol. Reagent-grade Fisher 1-decanol was vacuum distilled prior to use to remove any peroxides present (*5*).

0.01 *M* Uranyl Nitrate Solution. An 0.01 *M* uranyl nitrate solution was prepared by dissolving 5.0218 g of Fisher Certified Reagent $UO_2(NO_3)_2\cdot 6H_2O$ in water containing 1 ml of concentrated nitric acid and diluting to 1 liter.

EQUIPMENT

Visible Spectrophotometer. A Beckman Model DB Spectrophotometer was used for all spectrophotometric data in the visible region using matched 1-cm silica cells.

pH Meter. A Beckman Zeromatic pH meter was used for all pH measurements.

Gas Chromatograph. A Micro Tek model 2500 R gas chromatograph utilizing the thermal conductivity detector was used for all measurements.

Syringe. A Hamilton 10-μl syringe equipped with a Chaney adaptor was used for all samples injected into the gas chromatograph.

PROCEDURE

Column Preparation

A packing of 20% Carbowax 20 M on 30–60 mesh Chromsorb T was prepared by dissolving the Carbowax 20 M in methylene chloride, adding the Chromsorb T and evaporating off the solvent slowly under a stream of nitrogen. This packing was treated as described by Kirkland (*4*). This was packed into a 3 ft by ¼ in. o.d. copper tubing while vibrating the column. The resulting column was coiled and preconditioned overnight with helium carrier gas at 200°C.

Gas Chromatography Studies

The chelates were prepared by weighing out a stoichiometric quantity of the ligand and dissolving it in 25 ml of 1-decanol or nitromethane in 60-ml separatory funnels. Aqueous solutions of UO_2^{2+} were prepared and the pH was adjusted to the desired value using either dilute HNO_3 or NaOH. This aqueous solution was then added to the separatory funnel containing the ligand in the desired organic solvent. The funnel was vigorously inverted 200 times to allow adequate mixing of the two phases for maximum color development in the organic phase. The phases were allowed to separate by standing at ambient temperature (25 ± 1°C) for 1 hr. The organic layer was then withdrawn and centrifuged for 3 min at 2000 rpm to separate any emulsified water droplets. Five-microliter samples of this were then injected into the gas chromatograph where the water was quantitatively stripped from the chelate using the injection port pyrolysis technique described by Gaede (2).

RESULTS AND DISCUSSION

Before it was possible to determine the number of water molecules associated with $UO_2(Ox)_2(HOx)$, it was necessary to determine the optimum pH to be used for both 1-decanol and nitromethane as the extracting solvents.

A search of the literature showed that spectrophotometry was the most commonly employed technique for determining the concentration of $UO_2(Ox)_2(HOx)$ when extracted from water into chloroform. No values of molar absorptivity could be found for this chelate in either nitromethane or 1-decanol.

Values of molar absorptivity were determined by preparing a solution of known concentration in both nitromethane and 1-decanol solvents.

From the spectra the wavelength of maximum absorbance was found to be 385 μ in the nitromethane and 375 μ in the 1-decanol. By the use of Beer's law, values of molar absorptivity determined at these two wavelengths were found to be 3270 and 3120 liters/mole/cm in nitromethane and 1-decanol, respectively.

A study of the effect of pH on the extraction was performed to determine the optimum pH of the aqueous solution to obtain maximum extraction. Figure 1 shows the results of the percent extraction as a function of the pH of the aqueous phase. It can be seen that

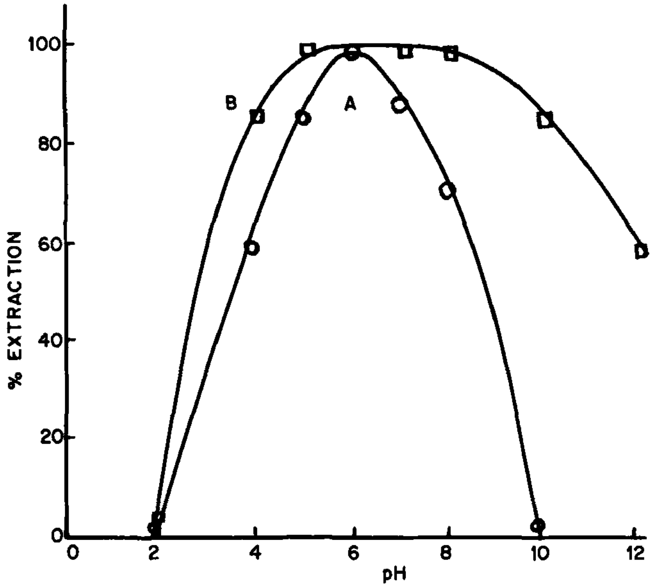

FIG. 1. Plot of extraction efficiency as a function of pH. A, 1-Decanol; B, nitromethane.

1-decanol has a narrow pH range where quantitative extraction occurs centering around pH 6 and that nitromethane quantitatively extracts the chelate over the pH range of 5 to 8. As it was desired to keep as many of the experimental parameters as possible constant for both solvents, pH 6 ± 0.1 was chosen as the optimum pH for this study.

It was decided to determine the number of water molecules associated with the $UO_2(Ox)_2(HOx)$ chelate utilizing the direct gas chromatography method developed by Gaede (2) in this laboratory. Gaede has shown the gas chromatography method to have several advantages over the previously used Karl Fischer titration method and to yield results which are as good as those obtained by the earlier method.

When the chelate was extracted into 1-decanol, a slow decomposition of the chelate was observed to occur. As a precautionary measure the solutions were injected into the gas chromatograph in order of decreasing chelate concentration to minimize any error which would be due to decomposition of the chelate.

One of the limiting factors in the use of these two solvents for the extraction of this chelate is that of the solubility of the chelate. It was observed that the chelate concentration must be kept below 5×10^{-3} *M* in 1-decanol and 4×10^{-3} *M* in nitromethane to prevent precipitation of the chelate. This had no bearing on the results but merely limits the range of chelate concentrations which could be employed.

The gas chromatograms obtained in this study look much like those reported by Gaede (2) and thus are not reported here.

Table 1 lists the results obtained for the number of water molecules associated with the $UO_2(Ox)_2(HOx)$ chelate when extracted into 1-decanol. This shows that the chelate has 9.6 ± 1.8 molecules of water associated with each molecule of the chelate. Table 2 shows that the $UO_2(Ox)_2(HOx)$ chelate has 9.6 ± 1.5 molecules of water associated with each molecule of the chelate when extracted into nitromethane.

The question arose as to whether water will cause a change in the partitioning of $UO_2(Ox)_2(HOx)$ between the immiscible solvents 1-decanol and nitromethane. If it does, can an equation be developed which can be used to predict the chelate concentration in one of the phases as a function of the amount of water present?

To determine the water concentration in either of the organic solvents, it was necessary to know the distribution ratio of water between these solvents. The distribution ratio of water between

TABLE 1

Results of Direct Gas-Chromatographic Determination of the Number of Water Molecules Associated with the $UO_2(Ox)_2(HOx)$ Chelate when Extracted into 1-Decanol

Chelate conc., *M*	Waters per chelate
1.75×10^{-3}	9.05
4.85	8.63
3.10	8.39
2.34	11.72
4.61	7.79
1.81	8.80
3.90	12.54
Avg. = 9.6 waters per chelate $\sigma = \pm 1.8$	

TABLE 2

Results of Direct Gas-Chromatographic Determination of the Number of Water Molecules Associated with the $UO_2(Ox)_2(HOx)$ Chelate when Extracted into Nitromethane

Chelate conc., M	Waters per chelate
1.36×10^{-3}	8.98
2.72	9.83
1.36	10.68
1.48	11.11
2.96	7.18
1.70	8.40
1.86	10.86
Avg. = 9.6 waters per chelate $\sigma = \pm 1.5$	

1-decanol and nitromethane has been determined to be 0.905, with the concentration of water in the nitromethane appearing in the numerator, by earlier work in this laboratory (3). This value was shown to be independent of chelate concentration and for this reason this value was used for all calculations of water concentration in this study without further experimental verification.

The effect of water on the chelate partition between the 1-decanol and nitromethane solvents was performed by examining all possible combinations of where to start the process. Table 3 shows the combinations when the chelate and water were placed initially before mixing the two solvents. This was done to ensure that in

TABLE 3

Initial Conditions for Study of the Effect of Water on the Partitioning of $UO_2(Ox)_2(HOx)$ between 1-Decanol and Nitromethane

H_2O initially in:	Chelate initially in:
1-Decanol	Nitromethane
Nitromethane	1-Decanol
1-Decanol	1-Decanol
Nitromethane	Nitromethane
1-Decanol and nitromethane	1-Decanol
1-Decanol and nitromethane	Nitromethane

fact we were observing an equilibrium situation which was not influenced by the starting conditions of the experiment.

All spectra were run only on the nitromethane solvent and calculations performed only for this solvent. It was decided to concentrate all efforts on this solvent, as the chelate concentration could be determined spectrophotometrically without any dilution of the test solutions. At high concentrations of water, the chelate concentration in the 1-decanol solvent would have been so high that a dilution of that phase would have been necessary.

Figure 2 shows the effect of water concentration on the $UO_2(Ox)_2(HOx)$ chelate concentration in the nitromethane phase. These curves were constructed from data obtained using all possible combinations of initial starting conditions. The fact that all these

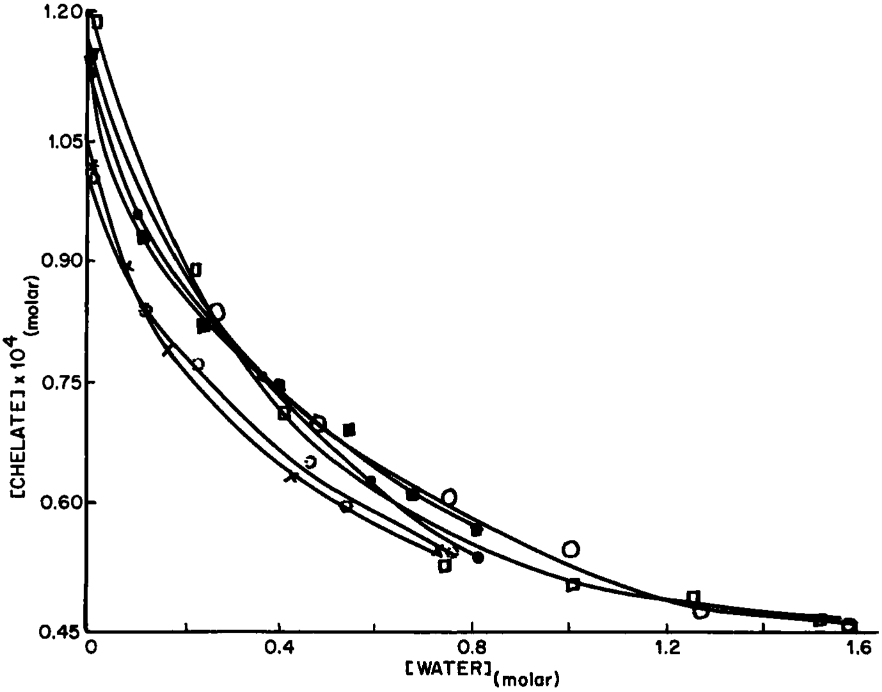

FIG. 2. Plot of $UO_2(Ox)_2(HOx)$ concentration in CH_3NO_2 as a function of H_2O concentration in CH_3NO_2. Initial conditions: ●, H_2O in 1-decanol, chelate in CH_3NO_2; X, H_2O in CH_3NO_2, chelate in 1-decanol; ○, H_2O in 1-decanol; chelate in 1-decanol; ■, H_2O in CH_3NO_2, chelate in CH_3NO_2; □, H_2O in CH_3NO_2 and 1-decanol, chelate in 1-decanol; O, H_2O in CH_3NO_2 and 1-decanol, chelate in CH_3NO_2.

curves exhibit the same general characteristic shape shows that indeed we are observing an equilibrium situation which is independent of where the water and chelate are placed initially.

It is quite evident that the amount of water present has a pronounced influence on the partitioning of the chelate between these immiscible organic solvents. The chelate concentration in nitromethane is seen to decrease rapidly with increasing water concentration and this effect tapers off at the higher water concentrations. The complimentary effect occurs in 1-decanol in that as the water concentration increases, the chelate concentration also increases.

Now that it has been shown that water has an influence on the partitioning of $UO_2(Ox)_2(HOx)$ between 1-decanol and nitromethane, it was desired to determine if an expression could be developed which could be used to predict the final chelate concentration in nitromethane as a function of the amount of water.

The expression which was developed is for equal volumes of the two solvents used in this study.

If we allow the chelate to partition itself between the two solvents in the absence of water, an equation which expresses the final concentration of the chelate in the nitromethane phases may be written as

$$Y = AB \tag{1}$$

where Y is the final chelate concentration in nitromethane, A is the fraction partitioned into the nitromethane ($1 - A =$ fraction in 1-decanol), and B is the original chelate concentration present in

TABLE 4

Values of A (fraction partitioned into CH_3NO_2) for $UO_2(Ox)_2(HOx)$ Chelate from Fig. 2

Figure part	A
A	0.58
B	0.50
C	0.50
D	0.59
E	0.50
F	0.57
Avg. = 0.54	
$\sigma = \pm 0.04$	

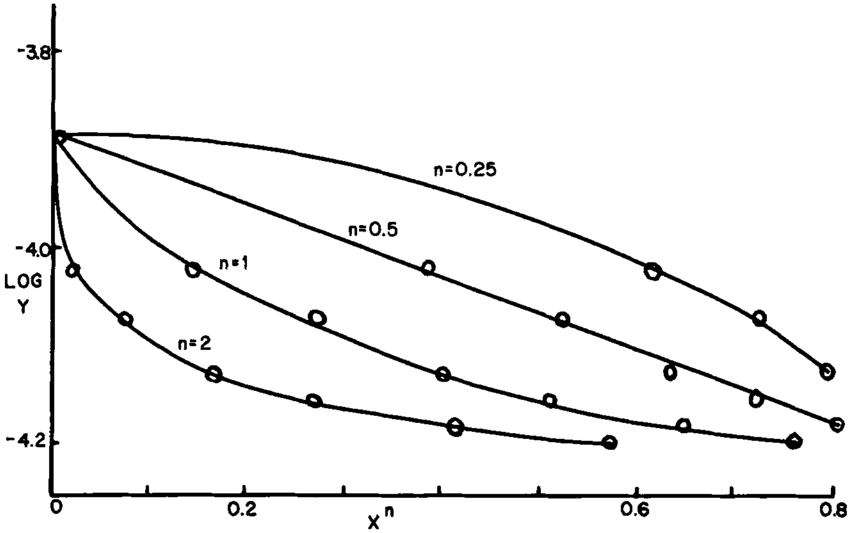

FIG. 3. Determination of value for n and c from the plot of log Y as a function of x^n.

either phase. Values of A were determined from Fig. 2 and are shown in Table 4. The average value of A was determined to be 0.54 with a standard deviation of ±0.04.

$$Y = ABe^{cx^n} \tag{2}$$

fits the curves obtained. Here x is the water concentration in CH_3NO_2 and c and n are constants. If Eq. (2) is transformed into natural logarithms, it can be arranged as

$$\ln Y = \ln AB + cx^n \tag{3}$$

This is the working form of the equation. If this equation will fit the experimental data obtained, then a plot ln Y as a function of x^n will yield a straight line whose slope is c if the right value of n is chosen. Figure 3 shows a plot of this type using average experimental data points of Fig. 2 and values of $n = 0.25$, 0.5, 1, and 2. From this figure it can be seen that a straight line results only for $n = 0.5$ and thus this was chosen as the value for n in Eq. (2) and (3). From the slope of this plot a value for c was determined. If similar plots are made using the remaining experimental data of Fig. 2 and a value for n of 0.5, they all result in straight-line plots from which values of c can be calculated. The results of these plots which were evaluated for

TABLE 5

Values Determined for *c* in Eq. (2) and (3) Using Experimental Points of Fig. 2

Figure part	*c*
A	−0.93
B	−0.71
C	−0.74
D	−0.88
E	−0.76
F	−0.57
Avg. = −0.76	
$\sigma = \pm 0.13$	

c are shown in Table 5. From this table it can be seen that *c* has an average value of −0.76 with a standard deviation of ±0.13.

To test the validity of the empirical expression developed, Eq. (2) with suitable values for the constants as discussed above was used to calculate the chelate concentration in nitromethane as a function

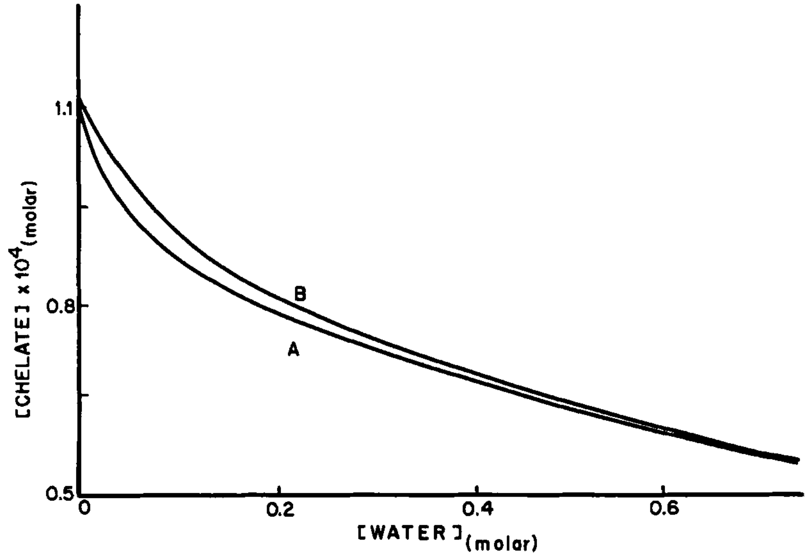

FIG. 4. Comparison of calculated and experimental curves showing $UO_2(Ox)_2(HOx)$ concentration in CH_3NO_2 as a function of H_2O concentration. A, Experimental; B, calculated.

of the amount of water present in that phase. The result is shown as curve A of Fig. 4. It was decided to draw a composite or average curve using all the experimental data of these curves. This result is shown as curve B of Fig. 4.

A comparison of curves A and B of Fig. 4 will show that the calculated curve approximates the experimental curve over the whole region. That both curves have the same general shape shows that the empirical relationship developed earlier is valid and can be used to calculate the effect that water will have on the partitioning of this chelate between 1-decanol and nitromethane. Even though the calculated and experimental curves do not coincide, they agree everywhere along the curve to within approximately 5%, and at higher water concentrations the agreement is even better. It is felt that the development of this expression is an important contribution in that until this time no method has been available whereby it was possible to calculate the effect water has on the partitioning of a metal chelate between two immiscible organic solvents.

CONCLUSIONS

Molar absorptivity values for bis(8-quinolinolo)dioxouranium(VI) 8-quinolinol in 1-decanol and nitromethane have been shown to be 3120 and 3270 liters/mole/cm, respectively. Nitromethane has been shown to quantitatively extract the chelate over the pH range of 4 to 8 and 1-decanol over a narrow range at pH 6.

Direct gas chromatography has been utilized to show that there are 9.6 ± 1.5 and 9.6 ± 1.8 molecules of water associated per molecule of the chelate when extracted from water into nitromethane and 1-decanol, respectively.

Spectrophotometric techniques have been used to show that water affects the partitioning of this chelate between the immiscible solvents 1-decanol and nitromethane. It was shown that as the concentration of water increased in the nitromethane phase, the chelate partitioned less favorably into this solvent. A complimentary effect occurred in the 1-decanol in that as the water concentration increased in this solvent, the chelate partitioned more favorably into 1-decanol. For partitioning between equal volumes of the immiscible solvents 1-decanol and nitromethane, an empirical expression of the form

$$Y = ABe^{cx^n}$$

was developed which can be used to predict the chelate concentration in nitromethane as a function of the concentration of water in that phase. In this expression Y is the final chelate concentration in nitromethane, A is the fraction partitioned into nitromethane in the absence of water, B is the original chelate concentration in either phase, x is the water concentration in nitromethane, and c and n are constants.

Acknowledgment

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