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The Solvent Extraction of Uranium(VI) from Carbonate Solutions[1]

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The solvent extraction of uranium(VI) from carbonate solutions has been obtained by means of the formation of a complex salt with 8-quinolinol and a quaternary ammonium ion. The extraction is based upon the novel uranyl chelate $UO_2(C_9H_6ON)^-_3$, formed with 8-quinolinol. The structure of this uranyl chelate has been discussed previously.[2] The distribution ratios D^0_a increase as the pH is varied from 10 to 12.5.

Introduction

Considerable work has been carried out in this Laboratory on the carbonate chemistry of uranium and the related recovery of uranium from carbonate leach solutions. In the course of an investigation of methods for the recovery of uranium from carbonate solutions, a novel solvent extraction system was developed.[3]

This system consists of forming, with various complexing agents, a singly charged anion containing uranium and then extracting this anion into a suitable organic solvent with a singly charged organic cation. Complexing agents that have been shown to give substantial uranium extraction by this method are benzoin 2-oxime, cupferron, hydroxylamine, peroxide, pyrogallol and 8-quinolinol. Considering efficiency, stability and cost, 8-quinolinol appeared to be the best complexing agent, and its use was studied in more detail.

Experimental

Reagents.—The 8-quinolinol was Eastman Kodak white label grade and the Arquad 2C was used as supplied by Armour. Arquad 2C is described as a 75% solution in isopropyl alcohol of dimethyldialkylammonium chloride where the two alkyl groups vary between 8 and 18 carbon atoms, averaging about 16.

Procedure.—A given volume of an aqueous phase at the desired pH containing the desired concentrations of uranium(VI), bicarbonate, and/or carbonate was shaken vigorously in a separatory funnel with the desired volume of an organic phase (MIBK) containing the desired concentrations of 8-quinolinol and Arquad 2C. The phases were allowed to separate after which the lower phase (aqueous) was drawn off, and both phases were sampled for uranium analysis. The analysis was performed by the fluorometric method.

Discussion

The process consisted of the formation of the uranyl tri-8-quinolinolate ion[2] ($UO_2Ox_3^-$) at high pH and the subsequent extraction of this ion with a tetraalkylammonium cation. High molecular weight quaternary ammonium cations were most effective. Thus, Arquad 2C, $(R_2N(CH_3)_2Cl$, where R averages about a 16 carbon chain), is more effective than Arquad 18, $(RN(CH_3)_3Cl)$, which is much better than tetraethylammonium chloride; guanidine is least effective. This effect is expected because the increased organic character of the cation would increase the solubility of the uranyl salt in the organic phase. The quantitative data reported are those obtained with Arquad 2C.

Several organic solvents for this uranium compound were studied, including diisobutyl ketone, methyl isobutyl ketone (MIBK), amyl alcohol, butyl alcohol, ethyl ether, chloroform, benzene and kerosene. All, except kerosene, gave some extraction. MIBK appears to be the most effective.

The effect of concentration on the distribution coefficient, D^0_a, in the system R_4NCl and HOx in MIBK; $UO_2(CO_3)_3^{-4}$ in carbonate–bicarbonate solutions can be explained qualitatively by the equilibrium

$$R_4NCl_{(o)} + 3HOx_{(o)} + UO_2(CO_3)_3{}^{-4}{}_{(a)} = R_4NUO_2(Ox)_{3(o)} + 3HCO_3^- + Cl^-$$

where R_4NCl represents Arquad 2C and HOx represents 8-quinolinol.

The equilibrium constant and the distribution coefficient for the above equation, neglecting activity coefficients, are

$$K = \frac{[R_4NUO_2Ox_3][HCO_3^-]^3[Cl^-]}{[UO_2(CO_3)_3{}^{-4}][HOx]^3[R_4NCl]} = D^0_a\frac{[HCO_3^-]^3[Cl^-]}{[HOx]^3[R_4NCl]}$$

In agreement with these expressions, it is found experimentally that D^0_a increases with HOx (see Table I) and R_4NCl concentration (to an optimum value, see Table II) and that it decreases with increasing total carbonate concentration (see Table III).

TABLE I

EFFECT OF HOx CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF URANIUM

Two volumes of 0.01 M $UO_2(NO_3)_2$, 0.92 M Na_2CO_3, 0.04 M NaOH, 0.02 M R_4NCl were mixed with one volume of MIBK containing varying concentrations of HOx. The phases were then separated and analyzed for uranium.

HOx concn., M	Uranium concn., M Organic phase	Aqueous phase	D^0_a
0.100	0.0172	0.00158	10.9
.060	.0144	.00268	5.4
.040	.0098	.00474	2.1
.020	.0054	.00754	0.72

TABLE II

EFFECT OF R_4NCl CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF URANIUM

Two volumes of 0.01 M $UO_2(NO_3)_2$, 0.95 M Na_2CO_3, 0.04 M NaOH were mixed with one volume of 0.06 M HOx in MIBK containing varying concentrations of R_4NCl. The phases were then separated and analyzed for uranium.

R_4NCl concn., M	Uranium concn., M Organic phase	Aqueous phase	D^0_a
0.080	0.0131	0.00352	3.7
.040	.0136	.00325	4.2
.020	.0100	.00488	2.1
.010	.0084	.00572	1.5

The chloride effect is small but in the indicated direction. With the other factors held constant, a lower amount of uranium in the system will result in higher distribution coefficients since there will be a higher concentration of free R_4NCl and HOx re-

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[1] The work reported here was carried out under Contract AT(49-6)-923 for the Atomic Energy Commission.

[2] P. Noble and E. P. Bullwinkel, THIS JOURNAL, **79**, 2955 (1957).

[3] W. E. Clifford, P. Noble, Jr., and E. P. Bullwinkel, RMO 2623.

TABLE III

EFFECT OF TOTAL CO_2 CONCENTRATION ON THE DISTRIBUTION COEFFICIENT OF URANIUM

Ten volumes of 0.01 *M* $UO_2(NO_3)_2$ containing varying concentrations of Na_2CO_3 and $NaHCO_3$ were mixed with one volume[a] of 0.03 *M* HOx, 0.1 *M* R_4NCl in MIBK. The phases were then separated and analyzed for uranium.

Na_2CO_3 concn., *M*	$NaHCO_3$ concn., *M*	D°_{a}
0.475	0.475	7.4
.25	0.25	25.2
.95	...	23.3
.50	...	58.0

[a] Final organic phase volumes were about 25% less than the starting volume.

maining at equilibrium. This effect has been demonstrated. It is also evident from the equilibrium expressions that the upper limit of uranium solubility in the organic phase is fixed by the initial 8-quinolinol and R_4NCl concentration. Therefore, the distribution coefficient will not remain constant in a multi-stage extraction but will be lowest in the first stage and increase in subsequent stages.

Experiments also have shown that with the *amounts* of all reagents held constant, decreasing the organic volume results not only in a higher distribution coefficient but also in a higher ratio of total uranium in the organic phase to total uranium in the aqueous phase (see Table IV).

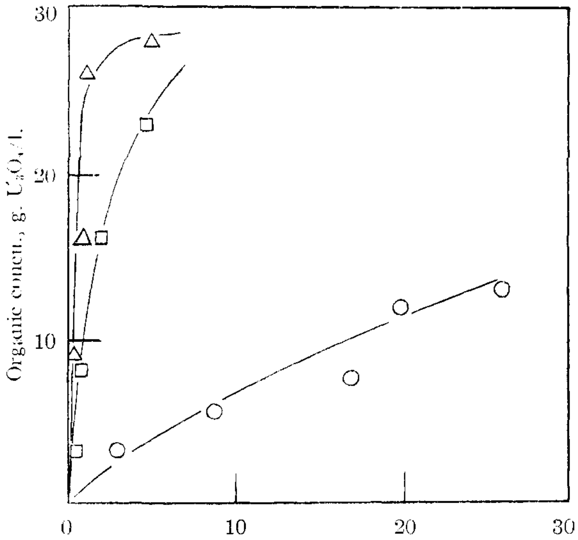

Fig. 1.—Distribution of uranium between carbonate solution and 8-quinolinol–Arquad 2C; phase ratio, aqueous to organic = 10:1; extractant, 0.3 *M* HOx and 0.1 *M* Arquad 2C in MIBK: ○, 1 *M* $NaHCO_3$; □, 1 *M* Na_2CO_3, *p*H 11.5; △, 1 *M* Na_2CO_3, *p*H 12.6.

This is in accordance with the assumed equilibrium. There are four organic soluble molecules on the left of the equation and only one on the right, hence, decreasing the organic volume drives the reaction to the right sufficiently that the product of uranium concentration in the organic phase times the organic volume increases even though the volume decreases.

While the given equilibrium expression is a useful concept in organizing the data, it does not explain all the observations. For example, we find that while increasing the quaternary salt-to-uranium ratio initially increases extraction, as would be expected from the equilibrium expression, when the ratio gets beyond about 2, the extraction falls off (see Table II). This can be explained by the side reaction

$$2R_4NCl + R_4NUO_2(Ox)_3 + 3CO_3^{=} = 3R_4NOx + UO_2(CO_3)_3^{-4} + 2Cl^-$$

TABLE IV

EFFECT OF ORGANIC PHASE VOLUME ON THE DISTRIBUTION COEFFICIENT OF URANIUM

Ten volumes of 0.01 *M* $UO_2(NO_3)_2$, 0.93 *M* Na_2CO_3, 0.04 *M* NaOH, 0.01 *M* R_4NCl were mixed with three volumes of 0.1 *M* HOx in MIBK plus varying amounts of pure MIBK. The phases were then separated and analyzed for uranium.

Added MIBK, volumes	Total organic volume, volumes	Uranium concn., *M* Organic phase	Uranium concn., *M* Aqueous phase	D°_{a}	% U in organic phase
0	3	0.0254	0.00289	8.8	72
2	5	.0133	.00303	4.4	69
7	10	.00504	.00480	1.1	51

It is found that there is a strong *p*H effect—the higher the *p*H the more nearly complete is the uranium extraction (see Fig. 1). This is reasonable since the oxinate concentration will increase by a larger factor than the carbonate ion concentration and so compete better for uranium, although both oxinate and carbonate concentration in the aqueous will increase with *p*H. Most of the total 8-quinolinol is in the organic phase, and a change from *p*H 10 to 11 can increase the oxinate solubility and thus concentration in the aqueous phase by a factor of ten,[4] while it can only change the carbonate concentration by a factor of roughly two (*i.e.*, from half carbonate to all carbonate).

Figure 1 gives the distribution of uranium between 0.3 *M* HOx–0.1 *M* R_4NCl in MIBK and aqueous carbonate solutions of different *p*H. It is seen that the upper limit of uranium dissolution is one mole of uranium for three moles of 8-quinolinol and one mole of Arquad. It has been found that the uranium solubility never exceeds that of the Arquad (on a mole basis) or one-third that of the 8-quinolinol, whichever is less. This clearly shows that the species extracted is $R_4NUO_2(Ox)_3$ and confirms the proposed structure of the uranyl 8-quinolinolate.[2]

It was found that vanadium can interfere seriously with uranium extraction, if conditions are not carefully controlled. Vanadium extracts very well at *p*H 8, but the extraction falls off as the *p*H is raised (especially beyond *p*H 12), presumably due to hydroxide concentration increasing more rapidly than oxinate concentration with *p*H, thus converting the vanadium species to orthovanadate. Even though extraction falls off at higher *p*H, it appears that some oxinate is still tied up with the vanadium in the aqueous phase, since it was observed that a sodium vanadium(V) quinolinolate precipitated out in countercurrent batch extraction experiments. Preliminary experiments with vanadium indicate

(4) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Second Edition, Interscience Publishers, Inc., New York, N. Y., 1950, p. 138.

that one mole of Arquad and two moles of 8-quinolinol are required per mole of vanadium (*cf.* ref. 2).

We found that solubility and entrainment losses of 8-quinolinol to the uranium barren carbonate solution could be held to negligible amounts (0.02%) by adjusting the pH to 9.7 and scrubbing once with MIBK.

Several possible reagents for separating uranium from the organic phase were tested, including solutions of mineral acids, organic acids, acids plus uranyl precipitants, H_2S, Na_2S, $(NH_4)_2CO_3$ and $NaHCO_3$.

The use of strong acids has the complication that 8-quinolinol as well as uranium is removed from the organic phase. The most efficient extracting agent appears to be sodium bicarbonate solutions. While sodium bicarbonate does not take out the organic phase completely in a single stage, complete removal could be achieved on a countercurrent basis. On such a basis, the aqueous phase could be loaded to approximately 30 g./l. U_3O_8 (see Fig. 1). Recovery from the bicarbonate solution could then be made by usual methods.

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Kinetics of the Formation of the Ferric Thiocyanate Complex

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An apparatus for rapidly mixing two solutions has been developed and applied to a study of the kinetics of the reaction: $Fe^{+++} + SCN^- = Fe(SCN)^{++}$ in aqueous solution. The forward rate law has been determined to be $d(FeSCN^{+2})/dt = k_1(Fe^{+++})(SCN^-) + [k_2(Fe^{+++})(SCN^-)]/(H^+)$. At 25° and an ionic strength of 0.40 the values of k_1 and k_2 are 127 ± 10 M^{-1} sec.$^{-1}$ and 20.2 ± 2 sec.$^{-1}$, respectively. From the variation of the rate with temperature the following values were found: $\Delta H_1^{\ddagger} = 13.0 \pm 1.4$ kcal./mole, $\Delta S_1^{\ddagger} = -5 \pm 5$ e.u., $\Delta H_2^{\ddagger} = 20.2 \pm 1.4$ kcal./mole and $\Delta S_2^{\ddagger} = 15 \pm 5$ e.u. The entropies of activation are compared with those for analogous reaction rates and with some equilibrium entropies of complexing. The mechanisms are discussed.

Introduction

The red complexes formed between ferric and thiocyanate ions have been studied by numerous workers.[1-10] The principal species in aqueous solution at low thiocyanate concentrations is $FeSCN^{++}$ with some formation of $Fe(SCN)_2^+$. The complexes appear to form instantly upon mixing. Chance,[11] using his rapid mixing device, studied the reaction between dilute ferric alum and NH_4SCN and determined the reaction to be first order in SCN^-. Assuming the reaction to be first order in ferric ion, he found a second-order rate constant of 1.7×10^4 M^{-1} sec.$^{-1}$ at room temperature at an ionic strength of approximately 0.01. Bjerrum and Poulson[12] measured the reaction in methanol at temperatures of −75 and −100°. Extrapolating their data, and assuming the reaction to be first order in ferric and thiocyanate ions, one can calculate a rate constant of 10^5 M^{-1} sec.$^{-1}$ at 25°.

The present study was undertaken to obtain more detailed information on this reaction and to test the operation of a newly designed rapid mixing device.

In the experimental measurement of rapid reactions in solution, mixing is a problem because of the relatively high viscosity and low diffusion rates in liquids. Hartridge and Roughton[13] developed a flow mixer with spectrophotometric detection which gave essentially complete mixing in 0.4 msecond. Chance[11,14] improved their apparatus, still using a short optical path length, *i.e.*, 0.8 mm. A review of recent modifications of the short path length devices and some others not discussed here may be found in reference 15. For reactions of higher than first order the half-life may be increased by using lower concentrations. Spectrophotometric detection then requires longer path lengths. Such devices with light-path lengths of 0.5 and 10 cm. have been used by Stern and DuBois[16] and Awtrey and Connick,[17] respectively.

Significant decrease in the mixing time of the mixers with short light-path length did not seem likely. Since we wished to study fast second-order reactions primarily, attention was directed toward the development of a mixer with a long path length but with more rapid mixing than had been achieved previously. After experimenting with a number of designs[18] the device shown in Fig. 1 was developed. It consists essentially of a chamber 5.9 cm. long, with flat glass or quartz windows on the ends. A movable baffle divides the interior into two equal regions which initially contain the reactants. A coil spring mechanism serves to raise

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