On the Ion-exchange of Uranium

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With respect to the behavior of the uranium ion towards the ion-exchange resins, three investigations have thus far been reported: the elution of the uranium ions which have been adsorbed on cation-exchangers by the aid of oxalic acid[1]; the separation of UO_2^{+2} and NpO_2^{+} with nitric acid[2]; and the adsorption of uranium ions on anion-exchangers in hydrochloric acid solution[3]. Now, the authors have studied the behavior of the uranium ion towards ion-exchangers on the basis of the distribution coefficient in solutions which contain acetate, sulfate, sulfuric acid, carbonate, and hydroxylamine, respectively. Solutions which contain oxalic acid or hydrochloric acid were also studied. Thus we have obtained some knowledge which will be useful in the separation of the uranium ion. And on this basis, we attempted the separations of uranium from thorium, iron (III), and neodymium.

In addition, we made some studies of uranyl nitrate solutions which either contained or did not contain the sulfate; and from its adsorbability we tried to get some information about the state of the uranyl ion in the solutions.

I. Method of Determination of Uranium

The uranium ion was determined colorimetrically with sodium carbonate and hydrogen peroxide[4]. Five millilitres of 10% sodium carbonate solution and 2 ml. of 3% hydrogen peroxide solution were added to a neutral sample solution, and the total volume of the solution was made 25 ml. Then, the uranium ion was determined by means of a Hitachi-photoelectric colorimeter and Tôshiba-filter VC-1. The calibration curve obtained is shown in Fig. 1. Sample solutions which were not neutral were treated similarly after being neutralized. Sample solutions which contained oxalic acid were evaporated to dryness; the residue was heated to volatilize and destroy oxalic acid, and dissolved in hydrochloric acid. Then, after volatilizing excess hydrchloric acid on a water-bath, the aqueous solutions were treated as above.

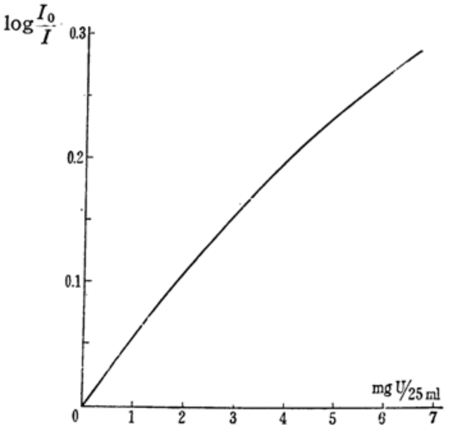

Fig. 1. Calibration curve of $Na_2CO_3.H_2O_2$ method.

II. Measurements of the Distribution Coefficient K_d

To a solution which contained a known amount of the uranyl ion and of known volume, was added a known amount of the ion-exchange resin. After the exchange-equilibrium was attained, the uranyl ions in the solution phase were determined colorimetrically, and the distribution coefficient was calculated as follows:

$$K_d = \frac{[UO_2R]}{[UO_2]_s} \quad (\text{ml./g.}),$$

where $[UO_2R]$ represents the amount of UO_2 in 1 g. of the resin, and $[UO_2]_s$, that in 1 ml. of the solution.

Most of the experiments were carried out by adding 0.2–1 g. of the resin to 25 ml. of a solution which contains 5–20 mg. of uranium. The exchange-equilibrium was attained in several hours in the case of a cation-exchanger, and in 15–20 hr. in the case of an anion-exchanger. The solutions were frequently stirred during these periods. In calculating the value of K_d, reduction in the volume of solutions due to absorption of water by the resins was neglected.

The following ion-exchangers were used. Cation-exchangers: Dowex 50, X-4; Dowex 50 (commercial). Anion-exchangers: Dowex 1, X-8.

III. Adsorption on Cation-exchange Resins

A) Uranyl Nitrate Solution.—It is reported[5] that in uranyl nitrate solutions $UO_2(NO_3)^{+}$ ions are present when the concentration is high, while

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[1] D. Dolar, Z. Draganic, *Rec. trav. inst. recherches structure matière* **2**, 7783 (1953); Zd. Dizdar, *Rec. trav. inst. recherches structure matière* **2**, 85 (1953).

[2] G. Johansson, Sv. Kem. Tid., **65**, 79 (1953).

[3] K.A. Kraus. Private communication.

[4] E. B. Sandell, "Colorimetric Determination of Traces of Metals" 1950, 2nd Ed., p. 601.

[5] "Mukikagaku Zensho (Handbook of Inorganic Chemistry)," 251 (1953), Maruzen Co., Ltd., Tokyo.

in dilute solutions the salt dissociates to the second stage. Our experimental results on the cation exchange in uranyl nitrate solutions confirmed this fact.

The exchange equilibriums were studied by a batch method by adding a solution of $UO_2(NO_3)_2$ and $NaNO_3$ (in molar ratio, UO_2^{+2} : Na^+ = 1 : 1.18) to Dowex 50, X-4 (NaR-form resin). The concentration range studied was 0.36 N-0.05 N. The results are plotted in Fig. 2.

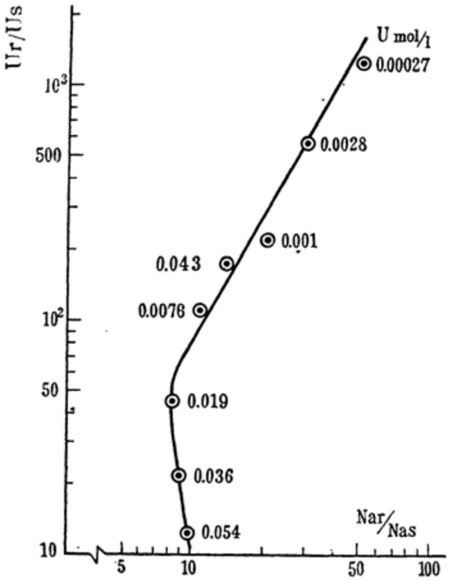
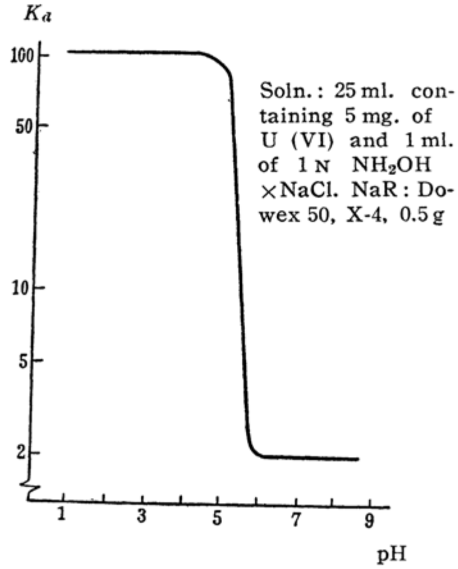


Fig. 2. Equilibrium curve of $UO_2(NO_3)_2$ in solutions.

In Fig. 2, in the concentration range where UO_2^{+2} is less than 0.007 mol./l. after equilibrium has been attained, the slope of the curve $\log\frac{[UO_2R]}{[UO_2]_s}$ vs. $\log\frac{[NaR]}{[Na]_s}$ is shown to be 2, which means that the salt is dissociated to the state of UO_2^{+2}. In the concentration range above 0.019 mol. UO_2/l., however, there can be seen no such relation; hence it is taken that the dissociation does not advance to the second stage.

In the following experiments, only the dilute uranyl solutions were dealt with; so there was no trouble with respect to the problem of dissociation of the uranyl salt. Uranyl ions may be considered to be adsorbed as di-positive ions when passed through the cation-exchanger layers.

B) Reduction of Adsorbability in Oxalic Acid, Acetate, Sulfate, Carbonate, or Hydroxylamine Solution.—The distribution coefficients in oxalic acid, acetate, or sulfate solutions are given in Table I. The adsorbability of the uranyl ion was found to decrease so considerably in the presence of acetate as well as oxalic acid that acetate solution may be utilized as an eluent for the uranyl ion. In the carbonate solution uranyl ions are not adsorbed at all. Hydroxylamine has been used for the separation of the uranyl and beryllium ions[6]. The relation between the distribution coefficient and pH in the hydroxylamine solution is given in Fig. 3.



Soln.: 25 ml. containing 5 mg. of U (VI) and 1 ml. of 1 N NH_2OH ×NaCl. NaR: Dowex 50, X-4, 0.5 g

Fig. 3. Distribution coefficient curve in hyrdoxylamine solution.

TABLE I

DISTRIBUTION COEFFICIENTS OF THE URANYL IONS ON THE CATION EXCHANGER IN OXALIC ACID, ACETATE, AND SULFATE SOLUTIONS

(a)	$(COOH)_2$	$[(COOH)_2]$ %	0.05	0.2	1	2	4		
	—HR	Kd	72	25	5.7	5.6	0.5		
(b)	$CH_3\cdot COONa$	[AcO] N	0	0.016	0.032	0.056	0.08	0.096	0.16
	—NaR	Kd	119	28	13	5.7	4.3	2.5	0.5
(c)	Na_2SO_4	$[SO_4]$ N	0	0.04	0.10	0.14	0.20	0.24	0.3
	—NaR	Kd	98	37	24	21	15	13	10

Solution: 25 ml.

(a) HR: Dowex 50 (commerical) 0.5 g.; 10.8 mg. U/25 ml.

(b) NaR: Dowex 50, X-4 0.5 g.; 5.4 mg. U/25 ml. CH_3COONa-$NaNO_3$ mixed soln.: conc. of the sodium ion = 0.16 N

(c) NaR: Dowex 50, X-4 0.5 g.; 5.4 mg. U/25 ml. Na_2SO_4-$NaNO_3$ mixed soln.: conc. of the sodium ion = 0.30 N

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[6] P.H. M-P Brinton, R. B. Ellestad, *J. Am. Chem. Soc.*, **45**, 395 (1923).

C) Change of Adsorbability with the Addition of Alcohol.—In the cation-exchange in an alcoholic solution, alkali metals are known to increase their adsorbabilities. In uranyl nitrate-HR form resin system, too, an increase in adsorbability was found to be produced by the addition of methyl alcohol (Fig. 4). This fact may be utilized to catch the uranyl ion which is relatively weak in adsorbability as a di-positive ion.

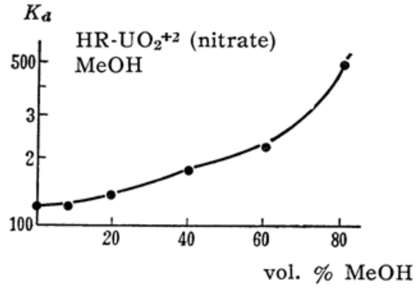

Fig. 4. Effect of alcohol.
Soln.: 25 ml. of 0.18N HNO_3, containing 20 mg. of U(VI).
HR: Dowex 50, X−4, 0.2g.

IV. Adsorption on Anion-exchange Resins

A) Adsorption in Hydrochloric Acid Solutions.—With regard to the ion-exchange of the uranyl ion in hydrochloric acid solutions, Diamond, Street, and Seaborg studied its cation-exchange[7], and Kraus studied the anion-exchange[3]. In Table II are shown our results on the adsorbability into the anion-exchanger in hydrochloric acid solutions of various concentrations. These results are found to be in agreement with those of Kraus.

B) Adsorption in Sulfuric Acid and Sulfate Solutions.—Absorption of the uranyl ion on the anion-exchanger in sulfuric acid and ammonium sulfate solutions is presented in Table II in terms of their distribution coefficients. Generally, stronger adsorption occurs in the latter solutions than in the former. This may be due to the insufficient formation of the complex anions, owing to the presence of HSO_4^- ion, in sulfuric acid solutions. In both cases adsorbability decrease as the concentration of the solution increases.

C) Adsorption in Carbonate Solutions.—In sodium carbonate solution uranyl dissolves in excess of the reagent, and the complex anion formed has a strong tendency to be adsorbed. The distribution coefficient is shown in Table II. This tendency may be used to concentrate uranium (VI) which has been extracted with excess of sodium carbonate.

An anion-exchanger was saturated with 0.2 N sodium carbonate solution and uranium (VI) solution (2 mg./ml.), then washed with dilute sodium carbonate solution. The result of measurement of the exchange capacity for the exchanger (Dowex I, X-8) showed that one mol. of uranium (VI) corresponded to 5.9 equiva lents. As one mol. of uranium corresponds to 6 equivalents, the complex anion supposed is $[UO_2(CO_3)_4]^{-6}$. The relatively small capacity is disadvantageous in concentrating and recovering uranium by this procedure.

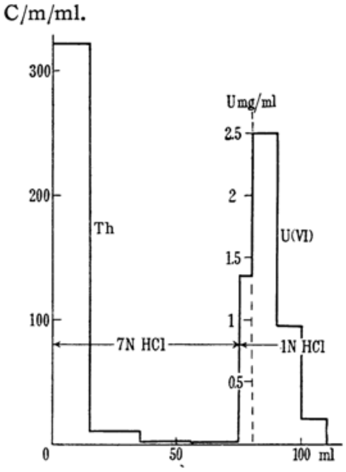

Fig. 5a. Separation from Th-234.

TABLE II

DISTRIBUTION COEFFICIENTS OF THE URANYL IONS ON ANION-EXCHANGERS IN HYDROCHLORIC ACID, SULFATE, SULFURIC ACID, AND CARBONATE SOLUTIONS

(a)	HCl-RCl	[HCl] N	2.4	3.6	4.8	6	7.2	11.5
		Kd	13	45	150	216	394	445
(b)	$(NH_4)_2SO_4$	$[(NH_4)_2SO_4]$ N	0.05	0.21	0.5	1.0	1.5	2
	—RSO_4	Kd	3000	1110	632	347	322	169
(c)	H_2SO_4	$[H_2SO_4]$ N	0.025	0.12	0.47	1.2	2.5	
	—RSO_4	Kd	590	356	69	2.6	0	
(d)	Na_2CO_3	$[Na_2CO_3]$ N	0.24	0.48	0.96	1.28	1.6	
	—RCO_3	Kd	3250	1230	394	261	192	

Anion exchanger: Dowex 1, X-8,
Solution: 25 ml.
(a) RCl: 0.5 g., Solution: U 20 mg.
(b) RSO_4: 0.2 g., Solution: U 10 mg.
(c) RSO_4: 0.2 g., Solution: U 10 mg.
(d) RCO_3; 0.2 g., Solution: U 11 mg.

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[7] R.M. Diamond, K. Street Jr., G.T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

V. Separations

A) Separation from Thorium.—Separation from thorium-234 was tried utilizing the adsorbability of U (VI) in hydrochloric acid solution. Dowex 50, X-8 resin was used. The elution curve is given in Fig. 5a. First, thorium was eluted with 8 N hydrochloric acid; and then U (VI), adsorbed on the exchanger, was eluted with 1 N hydrochloric acid.

The adsorption curve of the radiations of uranium here obtained was measured by means of a Lauritsen electroscope and aluminum absorbers. The results are plotted in Fig. 6.

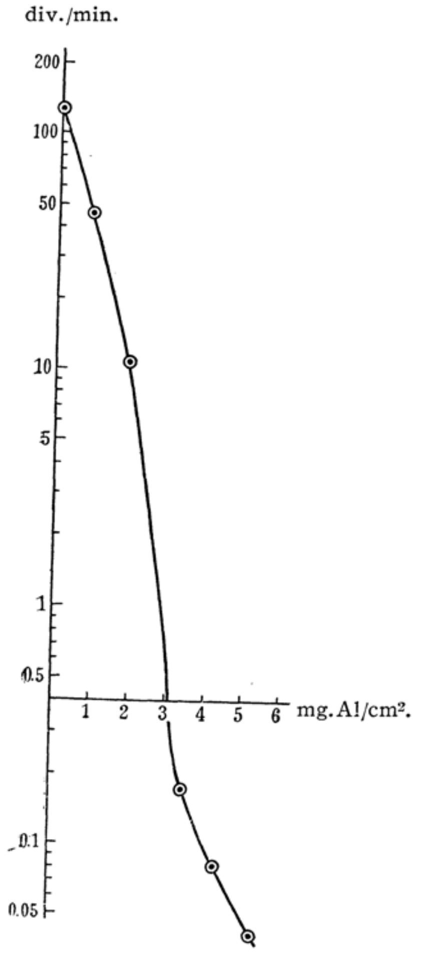

Fig. 6. Absorption curve of U-fraction.

B) Separation from Iron III.—Separation from iron (III) was carried out utilizing the adsorbability of U (VI) in sulfuric acid solution. The experimental conditions and the elution curve obtained are shown in Fig. 5b. A mixture of uranium (VI) and iron (III) in sulfuric acid solution was evaporated to dryness, then dissolved in 0.2 N H_2SO_4 and 0.6 N $(NH_4)_2SO_4$. Iron (III) was separated by passing RSO_4-form exchanging layer. Afterwards uranium (VI) was recovered by eluting with 2 N sulfuric acid.

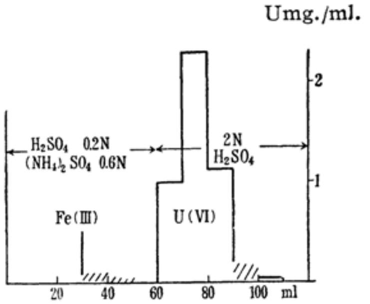

Fig. 5b. Separation from Iron (III)

C) Separation from Neodymium.—Based on the fact that neodymium is not adsorbed on an anion-exchanger in hydrochloric acid solution, the separation was carried out similarly as in the case of thorium. The same resin was used. The result is given in Fig. 5c.

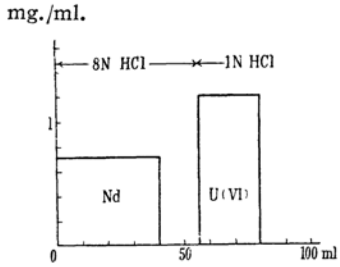

Fig. 5c. Separation from Nd.

VI. Complex Formation between Uranyl and Sulfate Ions

The state of the complex ion which is formed between uranyl and sulfate ions in solution was studied after the method suggested by J. Schu-

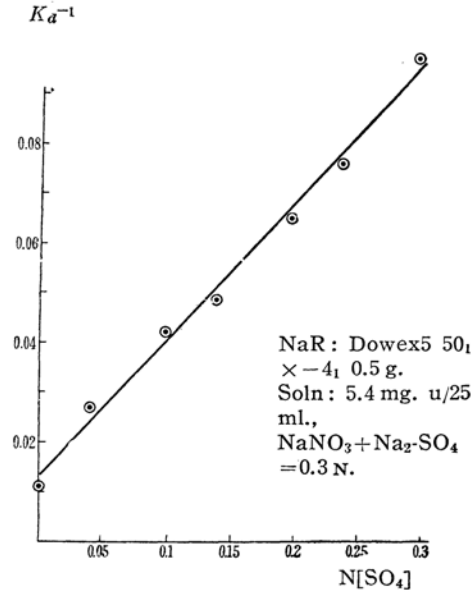

Fig. 7. The relation between K_a^{-1} and the concentration of sulfate.

bert[8], and it was found the complex present is in molar ratio UO_2^{+2}: SO_4^{-2}=1:1. A mixed solution containing sodium nitrate, sodium sulfate, and a definite amount of uranyl nitrate was added to a NaR-type resin, and the distribution coefficient was determined. The amount of uranium added was less than one-twentieth of the capacity of the ion-exchanger used. The total concentration of the $NaNO_3$-Na_2SO_4 mixed solution was 0.3 N, while the concentration of Na_2SO_4 was varied between 0 and 0.3 N. The result is given in Fig. 7.

As is seen in Fig. 7, the relation between K_d^{-1} and the concentration of sulfate ion is linear. Hence, it may be inferred that the ratio UO_2^{+2}: SO_4^{-2} is 1:1 as described above. That uranyl ions may be adsorbed on an anion-exchanger in sodium sulfate solution may be explained in terms of shifting of the equilibrium due to the formation and adsorption of the complex anion.

VII. Conclusions

From the experimetal results on the ion-exchange of uranium (VI), it was found that acetate solution is excellent for the elution in canion-exchange procedure; and that separation of uranium can be effected with sulfate solution in anion-exchange procedure.

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[8] J. Schubert, *Anal. Chem.*, 22, 1359 (1950).