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The Extraction of Uranium(VI) from Sulphuric Acid Solutions by Di-*n*-octylamine

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The partition of uranium(VI) between sulphuric acid solutions and solutions of di-*n*-octylamine (DOA) in benzene has been investigated at different concentrations of sulphuric acid, solvent and aqueous uranium, and at different temperatures. The acidity and the water content of the organic phase, and the effect of the organic solvent on the extraction have also been examined. An infrared spectral study has been made of the organic solutions. The mechanism of the extraction of uranium from sulphuric acid solutions by DOA is discussed on the basis of the results obtained, and a composition is proposed for the complex formed in this extraction system.

The extraction of uranium(VI) from sulphuric acid solutions by high molecular-weight amines in organic solvents has been investigated by many researchers.[1] The present author has also studied these extraction systems,[2] and this paper constitutes the work extended to the extraction with di-*n*-octylamine (DOA).

Experimental

Reagents. The DOA (the Kao Soap Co., Ltd.) was of a high purity and was used without further purification. It was diluted with various organic solvents, but was not pre-equilibrated with sulphuric acid solutions. The other chemicals were of analytical reagent grade. The uranyl sulphate solution was prepared by dissolving the uranyl sulphate tri hydrate in sulphuric acid of selected concentration, and its concentration is generally indicated in g/*l* for UO_2SO_4.

Extraction and Analytical Procedures. Equal volumes (20 m*l*) of DOA solution and uranyl sulphate solution were shaken for 10 min in 50 m*l* stoppered conical flasks in a water bath thermostatted at the required temperature (preliminary experiments showed that equilibration is established in 10 min). After the separation of the aqueous and organic phases by centrifugation, uranium in the organic phase was back-extracted with 1 N hydrochloric acid, and then the partition coefficient (the ratio of the equilibrium concentration of uranium in the organic phase to that in the aqueous phase) was determined. Uranium was determined gravimetrically: precipitated as ammonium diuranate and ignited to U_3O_8. The water content of the organic solution was determined by the Karl Fischer titration method.

Infrared Spectral Measurement. The infrared spectra were measured by a Shimadzu Model IR-27C recording spectrophotometer equipped with sodium chloride prisms. The spectra of organic extracts were determined with benzene as reference liquid, in a matched pair cell of fixed path length 0.1 mm, with thallium halide window.

Results and Discussion

Dependence on Acid Concentration and Extraction in Presence of Sodium Sulphate.

The extraction of uranyl sulphate solutions (5 g/*l*) containing sulphuric acid at various concentrations

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[1] *E. g.* C. F. Coleman, K. B. Brown, J. G. Moore and K. A. A. Allen, Proc. 2nd United Nationes Int. Conf. Peaceful Uses of Atomic Energe, Geneva, 1958, Vol. 28, p. 278, United Nations, New York (1958); C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. Eng. Chem.*, **50**, 1756, (1958); C. F. Coleman, *Atomic Energy Review*, **2**, (No. 2), 3 (1963); C. Deptuła and S. Minc, *J. Inorg. Nucl. Chem.*, **29**, 221 (1967).

[2] T. Sato, a) *J. Appl. Chem.*, **12**, 130 (1962); b) *J. Inorg. Nucl. Chem.*, **24**, 1267 (1962); **25**, 441 (1963); c) *ibid.*, **26**, 171, 181 (1964).

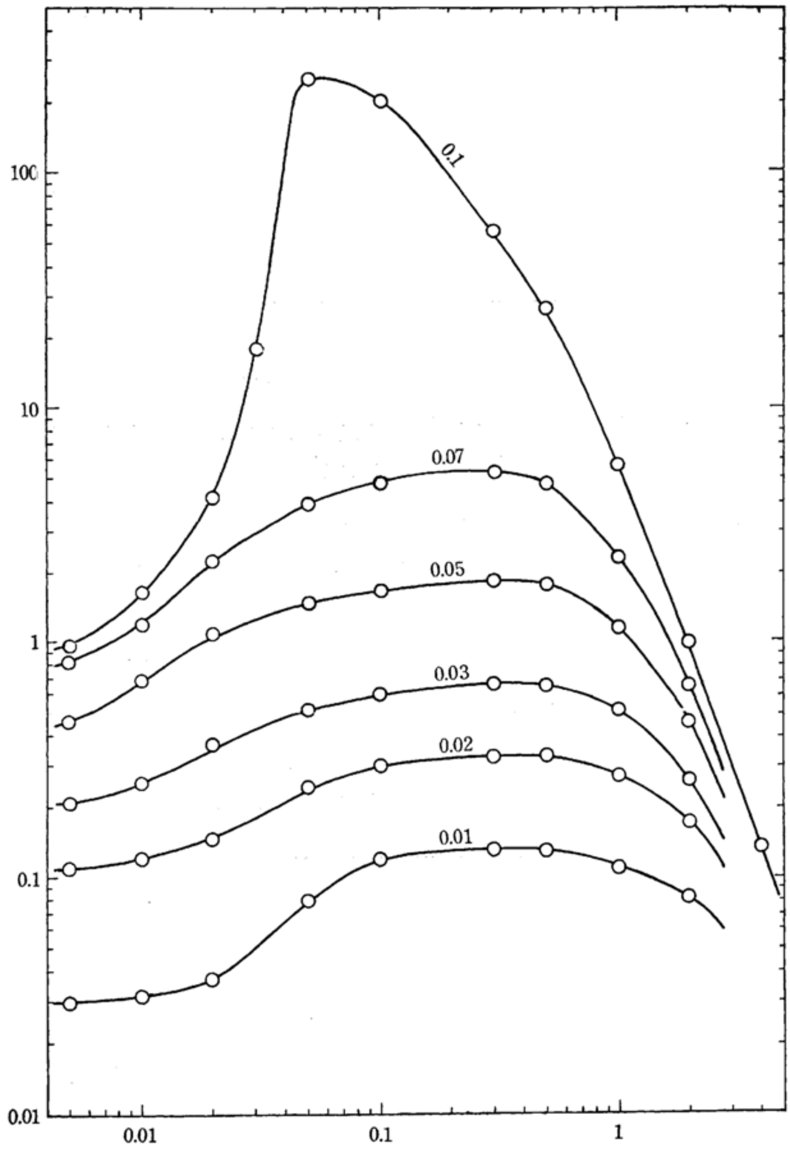

Fig. 1. Extraction of uranium(VI) from sulphuric acid solutions by solutions of DOA in benzene. numerals on curves are DOA concentrations, M.

with solutions of DOA in benzene at 20°C gave the results shown in Fig. 1.

The maximum partition coefficient appears at 0.05 M initial aqueous sulphuric acid concentration for the extraction with 0.1 M DOA and becomes indeterminate for the extraction below 0.07 M DOA, but the shape of the extraction curve resembles the forms of the curves with other amines.2) It is thus postulated that at low aqueous acidities the increase in the partition coefficient arises from the formation of DOA-uranyl sulphate complex; at higher aqueous acidities the decrease in the partition coefficient is attributed either to competition between uranium and sulphuric acid for association with the amine or to the formation of less readily extractable complexes. This interpretation is confirmed with the result in Fig. 2, illustrating the data for the extraction of uranyl sulphate solutions (5 g/l) containing sulphuric acid and sodium sulphate with 0.1 M DOA in benzene at 20°C. This shows that when the sulphuric acid in the aqueous phase is partly replaced by sodium sulphate, the decrease in the partition coefficient is checked because of the removal of competition for uranium between sulphuric acid and the amine. The gradual decrease in the partition coefficient with

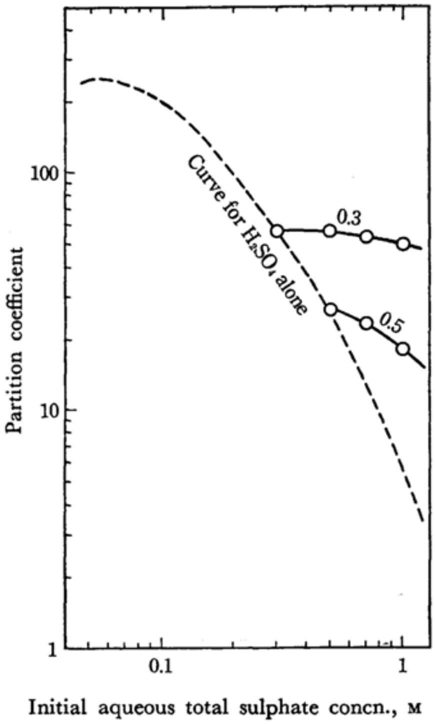

Fig. 2. Extraction of uranium(VI) from sulphuric acid solutions containing sodium sulphate by 0.1 M DOA in benzene.
(Numerals on curves are initial aqueous sulphuric acid concentrations, M).

increasing the sulphate concentration may be explained as being due to the formation of the inextractable species $UO_2(SO_4)_2^{2-}$, since the species UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ exist in the aqueous uranyl sulphate solution containing sulphate ion.[3]

Dependence on Uranium and DOA Concentrations. The variation in the uranium concentration of organic phase with the initial aqueous uranium concentration at 0.05 M aqueous acidity was examined with 0.1 M DOA in benzene at 20°C. The result in Fig. 3 shows that the uranium concentration of organic phase approaches a limiting value (~0.025 M) with increasing the initial aqueous uranium concentration, indicating that four amine molecules are associated with each uranium ion. This is supported by the dependence of the partition coefficient on the DOA concentration at higher aqueous acidities. In the extraction of uranyl sulphate solutions (5 g/*l*) containing sulphuric acid with the solutions of DOA in benzene at 20°C, log-log plots of E_a° *vs.* (C_A-4C_U), in which E_a° is the partition coefficient, C_A the total DOA concentration and C_U the uranium concentration of organic phase, gave straight lines whose slopes are 2.0, 1.5 and 1.0 at 0.5, 1.0 and 2.1 M sulphuric acid concentrations respectively. At low aqueous acidities, on the other hand, it is considered that the value of the association number is apparently not always four, but approaches four in 0.05 M initial aqueous sulphuric acid as the aqueous acidity is increased.

Extraction of Sulphuric Acid. The acidity and water content of the organic phase from the extraction of uranyl sulphate solutions (5 g/*l*) containing sulphuric acid at various concentrations with 0.1 M DOA in benzene at 20°C are shown in Figs. 4 and 5, compared with the data for the similar extraction of sulphuric acid solutions alone. In the extraction of sulphuric acid from

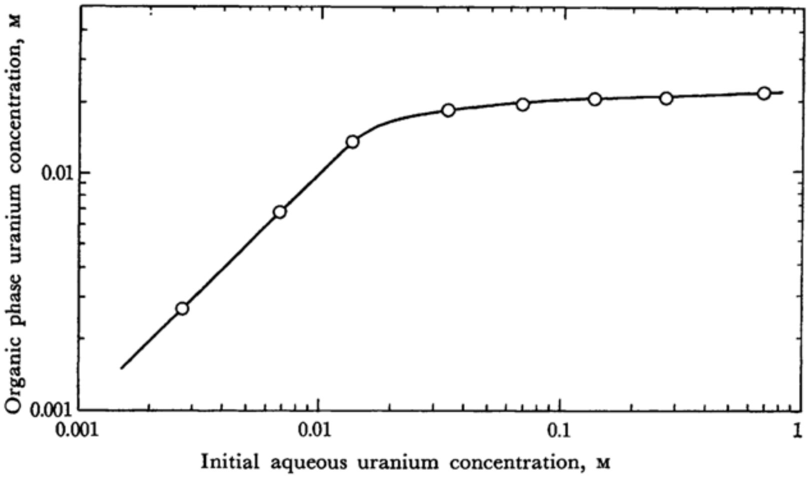

Fig. 3. Variation in uranium concentration of organic phase with initial aqueous uranium concentration in the extraction of uranium(VI) from 0.05 M sulphuric acid solution by 0.1 M DOA in benzene.

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3) W. J. McDowell and C. F. Bases, *J. Phys. Chem.*, **62**, 777 (1958).

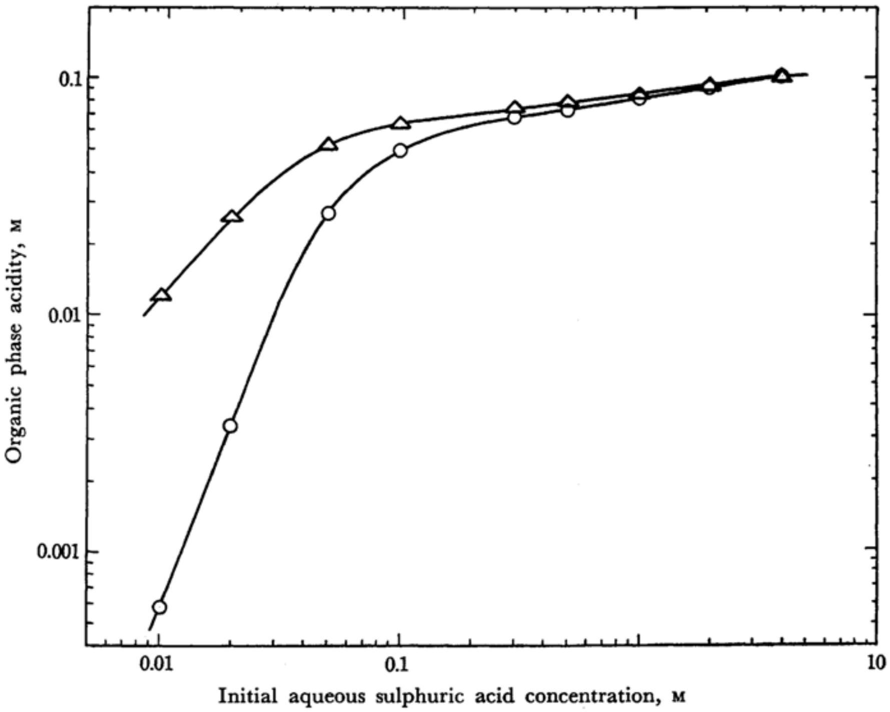

Fig. 4. Change in acidity of organic phase in the extraction of uranium(VI) from sulphuric acid solutions by 0.1 M DOA in benzene.
○ in the absence of uranium, △ in the presence of uranium).

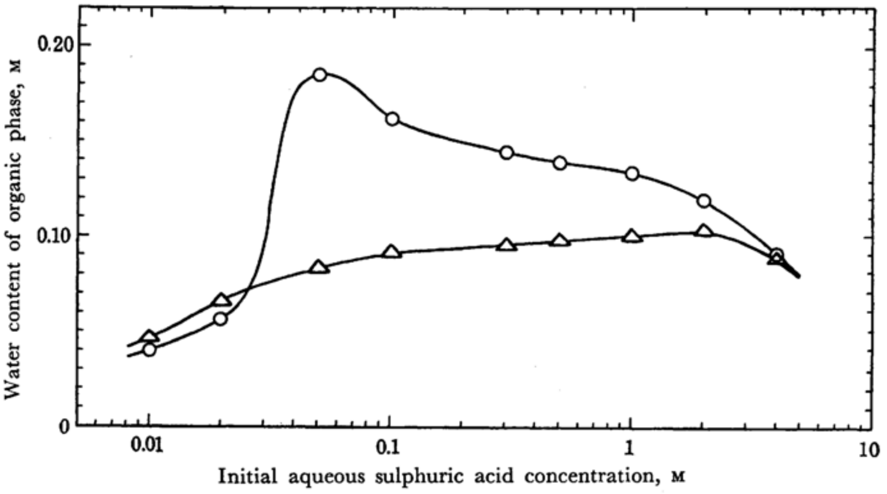

Fig. 5. Change in water content of organic phase in the extraction of uranium(VI) from sulphuric acid solutions by 0.1 M DOA in benzene
○ in the absence of uranium, △ in the presence of uranium.

aqueous solutions with solutions of DOA in benzene, the slope of log-log plots of the sulphuric acid distribution ratio *vs.* the initial DOA concentration was nearly two in 0.05 M H_2SO_4 and unity in 0.5 and 2.0 M H_2SO_4 respectively.

By analogy with the case of TOA (tri-*n*-octylamine),[4] it is considered that the equilibrium between DOA and sulphuric acid is expressed as follows: at low acidities

$$H_2SO_4(a) + 2R_2NH(o) \rightleftarrows (R_2NH_2)_2SO_4(o) \quad (1)$$

and at higher acidities

$$(R_2NH_2)_2SO_4(o) + H_2SO_4(a) \rightleftarrows 2(R_2NH_2)HSO_4(o) \quad (2)$$

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[4] T. Sato, *J. Appl. Chem.*, **15**, 10 (1965).

in which (a) and (o) denote aqueous and organic phases respectively, and R is C_8H_{17}.

The acidity of the organic phase in the presence of uranium is higher than that in the absence of uranium, but this difference is remarkably decreased above 0.1 M initial aqueous acidity. This probably implies that the reaction of the extraction at low acidities is different from that at higher acidities. From Fig. 5 it is deduced that the hydrated amine sulphate is gradually replaced by the unhydrated amine bisulphate as the aqueous acidity is further increased, and the water content of the organic phase is diminished by the formation of the DOA - uranyl sulphate complex. Further it is inferred that the DOA not associated with uranium is present in the bisulphate form at higher aqueous acidities, and is likely to be present as the free amine form at low aqueous acidities since the concentration of the amine sulphate present as the available amine is restricted by the aqueous acidity.

Infrared Spectral Study. The organic phases from the extraction of uranyl sulphate solutions (5 and 25 g/*l*) containing sulphuric acid of various concentrations by 0.1 M DOA in benzene at 20°C were examined by infrared spectroscopy. Similar measurements were also made of the organic solutions from the extraction of sulphuric acid solutions alone. The spectra are presented in Fig. 6.

In the extraction of sulphuric acid, the following results are observed as the aqueous acidity is increased: for 0.02 M sulphuric acid, the bands of

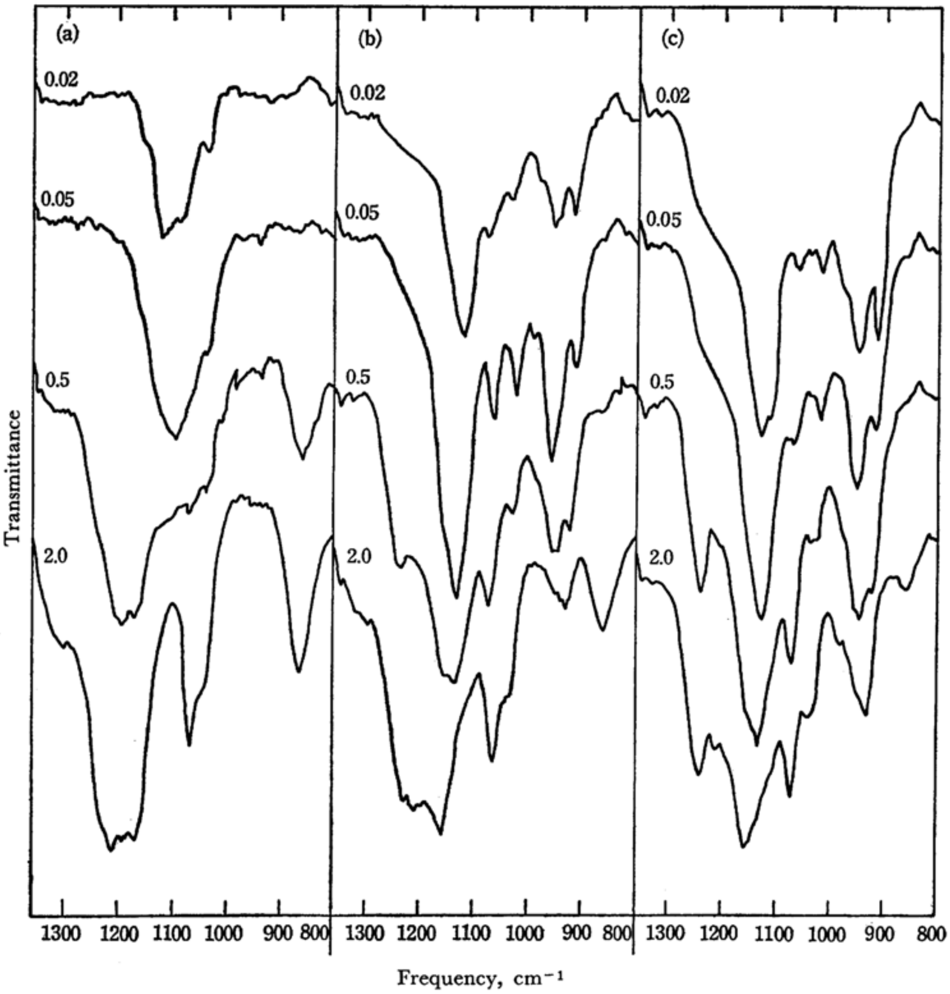


Fig. 6. Infrared spectra of the organic solutions from the extraction of uranium(VI) from sulphuric acid solutions at various concentrations by 0.1 M DOA in benzene.
Numerials on curves are sulphuric acid concentration, M.
(a) sulphuric acid solutions without uranium
(b) uranyl sulphate solutions at 5 g/*l*
(c) uranyl sulphate solutions at 25 g/*l*.

sulphate ion[5-7] appear at 1120—1080 and 1038 cm^{-1}, the NH_2^+ stretching vibration[8,9] which indicates the presence of hydrogen-bonding in the broad band centred at 3100 cm^{-1}, and the OH stretching and bending bands at 3560—3380 and 1635 cm^{-1} respectively; for 0.05 M sulphuric acid, the above absorption bands were more intense; for 0.5 M sulphuric acid, the absorptions due to the bisulphate ion[6,7] at 1210—1165, 1070, and 860 cm^{-1} were accompanied, whereas those of the sulphate ion become weaker; for 2.0 M sulphuric acid, the bands of the bisulphate ion show a progressive increase in intensity, and the intensities of the OH bands decrease, corresponding to the result in Fig. 5.

For the spectra in the presence of uranium, the band at 955 cm^{-1} is assigned to the asymmetric stretching frequency of the uranyl group,[10] and the bands at 1130, 1070, 1020 and 915 cm^{-1} to the vibrational frequencies of the sulphato group,[11] indicating a lower symmetry (point group C_{2v} symmetry) than the sulphate ion (point group T_d symmetry), due to covalent bonding to the uranyl ion. At the same time the absorption assigned to the NH_2^+ stretching vibration, which probably indicates the formation of the hydrogen bond in the complex, is observed at 2830 cm^{-1}. These are stronger in the extraction of uranyl sulphate solutions at 25 g/*l*, since the uranium concentration of organic phase is higher than those at 5 g/*l*. At low acidities the absorptions due to the amine-uranyl sulphate complex become stronger with increasing the aqueous acidity because of the increase in the concentration of amine sulphate formed by the extraction of acid, while at higher acidities the absorption bands due to the bisulphate ion appear in addition to the weaker bands of the amine - uranyl sulphate complex. These results closely resemble those for cyclohexyl- and benzyl-alkylamines,[2a,c] and is basically analogous to the cases of TOA and TDA (tri-*n*-dodecylamine).[2b]

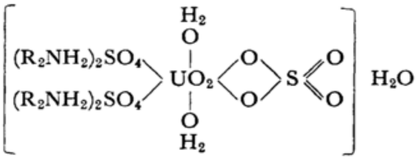
Consequently the following mechanism is proposed for the extraction of uranium(VI) from sulphuric acid solutions by DOA:
at low acidities

$$UO_2SO_4(a) + 2(R_2NH_2)_2SO_4(o) \rightleftarrows [(R_2NH_2)_2SO_4]_2UO_2SO_4(o) \quad (3)$$

and at higher acidities

$$UO_2SO_4(a) + 4(R_2NH_2)HSO_4(o) \rightleftarrows [(R_2NH_2)_2SO_4]_2UO_2SO_4(o) + 2H_2SO_4\ (a)\,. \quad (4)$$

As reported previously,[12] the TOA or TDA-uranyl sulphate complex further shows the absorption assigned to the stretching vibration of the sulphate ion. For the spectrum of the DOA - uranyl sulphate complex, this point is not distinct since the strong band due to the vibration of the sulphato group, co-ordinated to the uranyl ion, at 1130 cm^{-1} overlaps to the absorption assigned to the sulphate ion. However, the organic solution from the extraction of aqueous solution containing 250 g/*l* of uranyl sulphate in 0.05 M sulphuric acid solution with 0.1 M DOA in benzene at 20°C was found to contain uranium: sulphate : amine : water in the mole ratio 1 : 3 : 4 : 3, indicating the stoichiometry to be $(R_2NH_2)_4UO_2(SO_4)_3(OH_2)_3$, *i. e.* $[(R_2NH_2)_2SO_4]_2UO_2SO_4(OH_2)_3$. As this composition resembles the cases of TOA or TDA, it is assumed that the structure similar to the TOA or TDA - uranyl sulphate complex[12] may be given for the DOA - uranyl sulphate complex:



Dependence on Temperature. The extraction of uranyl sulphate solution (5 g/*l*) containing 0.02 and 1.0 M sulphuric acid with 0.1 M DOA in benzene at temperatures between 10 and 50°C gave the result shown in Fig. 7, where the logarithm of the partition coefficient is plotted against the reciprocal of the absolute temperature. This shows that the partition coefficient decreases with rising temperature, and accordingly the heat of reaction (change in enthalpy, kcal/mol) is 4.3 in 0.02 M H_2SO_4 and 4.5 in 1.0 M H_2SO_4.

Effect of Organic Solvent. Table 1 shows the results for various DOA - organic solvent systems in the extraction of uranyl sulphate solutions (5 g/*l*) containing 0.02 and 1.0 M sulphuric acid at 20°C, together with some properties of the solvent (dielectric constant and dipole moment).[13] It is

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[5] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York (1945), p. 167.

[6] F. A. Miller and C. H. Wilkins, *Analyt. Chem.*, **24**, 1253 (1952).

[7] G. E. Walrafen and D. M. Dodd, *Trans. Faraday Soc.*, **57**, 1286 (1961).

[8] E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, **13**, 261 (1959); J. Bellanato, *ibid.*, **16**, 1344 (1960).

[9] L. J. Bellamy, "Infra-red Spectra of Complex Molecules," 2nd Edn, John Wiley & Sons, Inc., New York (1958), p. 259.

[10] B. M. Gatehouse and A. E. Comybes, *J. Chem. Soc.*, **1958**, 3965; G. L. Caldow, A. B. VanCleave and R. L. Eager, *Canad. J. Chem.*, **38**, 772 (1960).

[11] K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

[12] T. Sato, *J. Inorg. Nucl. Chem.*, **26**, 2229 (1964); *Naturwissenschften*, **52**, 258 (1965).

[13] A. Weissberger, E. S. Proskauer, J. A. Riddck and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. 7, Organic Solvents," 2nd Edn, Interscience, New York (1955).

TABLE 1. EXTRACTION OF URANIUM(VI) FROM 0.02 AND 1.0 M SULPHURIC ACID SOLUTIONS BY 0.1 M DOA IN VARIOUS ORGANIC SOLUVENTS

Diluent	Dielectric constant*	Dipole moment	Partition coefficient	
			0.02 M H_2SO_4	1.0 M H_2SO_4
Carbon tetrachloride	2.238	0.00	1.32	9.96
Benzene	2.284	0	4.93	4.90
Toluene	2.379	0.39	3.50	5.43
Chloroform	4.806	1.15	3.26	3.16
Chlorobenzene	5.621	1.56	6.84	5.78
o-Dichlorobenzene	9.93	2.26	6.66	5.74
1, 2-Dichloroethane	10.36	2.06	30.4	2.38
Nitrobenzene	34.8	3.99	46.2	1.03

* All values at 25°C except for carbon tetrachloride, benzene and chloroform at 20°C.

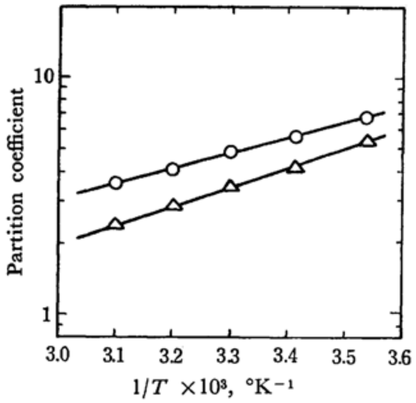

Fig. 7. Temperature-dependence of partition coefficient in the extraction of uranium(VI) from sulphuric acid solutions by 0.1 M DOA in benzene.
△ and ○ represent 0.02 and 1.0 M sulphuric acid concentration respectively.

seen that although the partition coefficient depends markedly on the nature of the diluent, no simple relationship holds between the extraction efficiency of DOA and the physical parameter of organic solvent in these systems. It is presumed, however, that at low aqueous acidity, the extraction efficiency of DOA is enhanced with the diluents which have relative a large dielectric constant such as nitrobenzene and 1, 2-dichloroethane, and contrarily, at high aqueous acidity, these solvents reduce the extraction; at high acidity, carbon tetrachloride gives high extraction efficiency, but chloroform which solvates the amine relatively strongly, presumably through hydrogen-bonding, is not always good extraction medium; halogen substituted aromatic hydrocarbon exhibits considerable good extraction. Similar effect is also observed in the extraction by TOA.[14]

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[14] T. Sato, unpublished data.