

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

Cy. 4

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0361321 2

ORNL-2709
Technology-Raw Materials

URANIUM EXTRACTION BY
TRI-n-OCTYLAMINE SULFATE

K. A. Allen



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document, send in name with document and the library will arrange a loan.

Printed in USA. Price \$0.75. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-2709

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section C

URANIUM EXTRACTION BY TRI-n-OCTYLAMINE SULFATE

Kenneth A. Allen

DATE ISSUED
MAY 21 1953

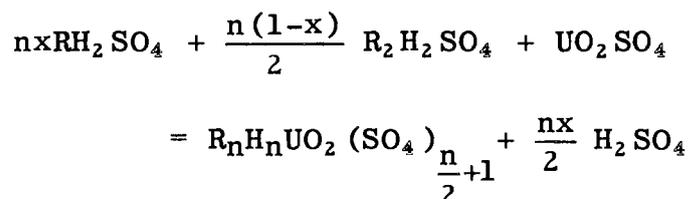
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION



3 4456 0361321 2

ABSTRACT

The extraction of uranium from acidic sulfate aqueous systems by benzene solutions of tri-*n*-octylamine sulfate was studied under various conditions of uranium loading, acid activity, sulfate ion concentration, and amine concentration. The data are consistent with the reaction



where $R = (C_8H_{17})_3N$, $x = [RH_2SO_4] / ([RH_2SO_4] + 2[R_2H_2SO_4])$, and n is the number of equivalents of amine per mole of uranium in the complex. Under conditions of constant acid activity, amine concentration, and low uranium loading, the distributions observed at varying aqueous sulfate levels lead to the following estimates of the formation quotients for the aqueous complexes UO_2SO_4 (K_1) and $UO_2(SO_4)_2^-$ (K_2) at unit ionic strength:

$$K_1 = 34(17-135), K_2 = 200(100-760), K_2/K_1 = 6.0 \pm 1.0$$

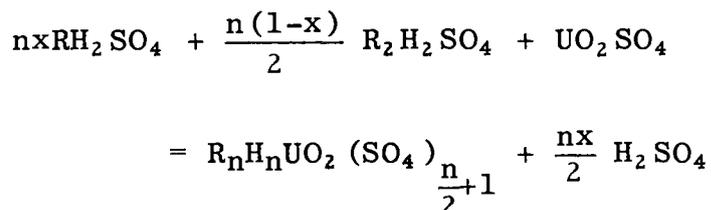
(The parenthesized ranges are based on 90% confidence interval statistics.) These K values are in reasonably good agreement with those reported by Ahrlund. The present evidence suggests only very low or negligible proportions of the trisulfate complex at sulfate molarities below 1.

CONTENTS

	Page
1.0 Summary	4
2.0 Introduction	5
3.0 Experimental	6
4.0 Results and Discussion	7
4.1 Organic Species; Acid Transfer	7
4.2 Effects of Aqueous Complexes	12
5.0 References	22

1.0 SUMMARY

The extraction of uranium from acidic sulfate solutions by benzene solutions of tri- \bar{n} -octylamine sulfate (TOAS) is rapid and strong at 25°C. The measured extraction equilibria are consistent with the reaction



where $R = (C_8 H_{17})_3 N$, $x = [R H_2 S O_4] / ([R H_2 S O_4] + 2 [R_2 H_2 S O_4])$, and n is the number of equivalents of amine per mole of uranium in the complex. A value between 4 and 5 for n over a range of acid, sulfate, and amine concentrations is consistently indicated by the limiting uranium loading attainable, analysis of the extraction isotherm at intermediate loadings, and the ratio of acid released to uranium extracted at known initial values of x . The consistency between these different measurements also indicates that bisulfate is not included in the uranium-sulfate-amine complex, and that at a given aqueous acid activity the bisulfate/total sulfate ratio x in the uncomplexed portion of amine salt is unaffected by the presence of extracted uranium.

At constant aqueous composition and constant low uranium loading, the uranium extraction coefficient $E = [U]_{org} / [U]_{aq}$, is directly proportional to the total amine concentration over a considerable range, at least 0.02 to 0.2 M. This behavior may be interpreted as indicating that the significant organic uranium activity is proportional to the ratio $[U]_{org} / [uncomplexed TOAS]$ or to the uranium equivalent fraction based on uncomplexed amine salt.

At constant aqueous acid activity, constant total amine concentration, and low loading, uranium distribution at varying aqueous sulfate levels leads to estimates of the constants for the formation of the aqueous mono- and disulfate complexes, $U O_2 S O_4$ and $U O_2 (S O_4)_2^-$. Based on approximate ionic strength corrections from the Debye-Hückel limiting law, the values obtained for zero ionic strength are

$$K_{a1} = \left(\frac{[U O_2 S O_4]}{[U O_2^{++}][S O_4^{--}]} \right)_{\mu=0} = 580 \quad (300-2300)$$

$$K_{a2} = \left(\frac{[\text{UO}_2(\text{SO}_4)_2^-]}{[\text{UO}_2^{++}][\text{SO}_4^-]^2} \right)_{\mu=0} = 3450 \quad (1900-13000)$$

and $K_{a2}/K_{a1} = K_2/K_1 = 6 \pm 1$, where the numbers in parentheses represent the high and low values consistent with the data provided the ratio K_2/K_1 is within the range given. These numbers are in good agreement with corresponding constants evaluated by Ahrland at unit ionic strength when the same limiting-law adjustments are applied in order to obtain comparisons at $\mu = 0$. Ahrland's potentiometric results suggested a formation constant K_3 for the trisulfate complex of 2500 ± 1000 ; his spectrophotometric results did not yield a value of K_3 , the latter data indicating only a much lower value than the former. The highest value of K_3 consistent with the present extraction data is ~ 125 ; it is suggested that the weight of evidence indicates only low if not negligible fractions of the trisulfate species at sulfate molarities less than 1.

2.0 INTRODUCTION

The present investigation was undertaken with the object of further elucidating the equilibria involved in the extraction of various substances from aqueous solutions by the high-molecular-weight amines in organic diluents. Tri-*n*-octylamine is typical of the good tertiary extractants, and the equilibria between this compound, as well as di-*n*-decylamine, and sulfuric acid have already been examined in some detail.¹ As in previous studies, benzene has been used throughout as the organic diluent. Most of the results have already appeared in the open literature;² however, this report presents important material (Table 2, Figs. 6 and 8, and a much clearer presentation of the mathematics leading to the evaluation of the uranium sulfate complex formation constants) that was not included in the journal article. The present treatment is in general accord with that described by McDowell for uranium extraction by di-*n*-decylamine sulfate.³

The first use of amines for separations was reported by Smith and Page, who also suggested the use of such reagents as anion exchangers.⁴ A number of analytical separations have been based on amine extractions of various metal ions.⁵ For several years an intensive study of the amines as extractants for uranium from acidic sulfate solutions has been underway at this laboratory.⁶ The primary objective of this effort has been the development of reagents capable of forming the bases of competitive processes for the purification of industrial uranium liquors arising from the sulfuric acid leaching of

ores. The resulting Amex processes have been described in recent papers.⁷

In the course of this development program a wealth of evidence relating to the extraction of uranium from acidic sulfate solutions by a large number of organonitrogen compounds has been accumulated. It has been shown that, while individual uranium extraction coefficients may vary widely, and while marked diluent effects may obtain, in several respects the amines behave quite similarly. Thus, loading numbers (equivalents of amine per mole of uranium in the saturated organic) of 4 to 6 have been obtained for a wide variety of amines. It has been shown that extraction power dependence on amine concentration is approximately linear. The uranium extraction coefficients show a marked inverse dependence on sulfuric acid activity, and a less marked inverse dependence on total sulfate concentration.

The author is indebted to G. N. Case for technical assistance, and to W. J. McDowell, C. F. Baes, Jr., and C. F. Coleman for helpful discussions throughout the work.

3.0 EXPERIMENTAL

Material and Apparatus. The tri-*n*-octylamine* used in this work has been described previously.¹ Standard uranyl sulfate solutions were prepared by the usual methods from black oxide (U_3O_8) equivalent to National Bureau of Standards material. The other reagents used were of the standard reagent grade furnished by the large chemical supply houses.

Equilibrations were carried out in separatory funnels agitated by a motor-driven assembly in a $25.0 \pm 0.1^\circ C$ thermostat. Five minutes' shaking was sufficient for the attainment of equilibrium under widely varying extraction conditions. The data reported below are based on shaking times of 15 min or more.

Procedures and Analyses. The techniques used in running the equilibrations were similar to those described in the acid work.¹ Known quantities of sulfuric acid, sodium sulfate, uranyl sulfate, and water were shaken with freshly prepared benzene solutions of TOA of known titer. In most cases the organic phase was not pre-equilibrated with a uranium-free aqueous solution; the quantities of acid necessary for the desired final aqueous and organic concentrations

*Hereinafter tri-*n*-octylamine will be referred to as TOA, the sulfate-bisulfate mixture as TOAS, and the amine molecule $(C_8H_{17})_3N$ as R.

were calculated from the constants reported previously.¹ In some of the acid transfer runs, where more accuracy was required, a quantity of amine solution was shaken with a uranium-free sulfuric acid—sodium sulfate solution. A given volume of the resulting aqueous phase was carefully evaporated 20-30%, a known amount of uranyl sulfate solution added, and the solution made back up to the given volume with water. A portion of this solution was then shaken with the corresponding pre-equilibrated organic at the previous phase ratio. Careful titrations of the aqueous phase before and after the uranium equilibration thus measured the acidity changes due only to the given uranium transfers.

The procedures for determining free amine and organic sulfate were described previously.¹ Most of the aqueous uranium concentrations were measured by potentiometric titration, using an automatic method.⁸ In many cases it was necessary to evaporate as much as 10-20 ml of aqueous raffinate down to 0.5 ml in order to obtain reliable titrations. Where this was not possible, as in the case of the high sodium sulfate runs, fluorimetric analysis was used. The reliability limits of the extraction coefficients from all the methods used may thus be considered to vary roughly as the magnitude of the coefficients themselves, i.e., from $\sim \pm 5$ to $\pm 25\%$ for coefficients from ~ 100 to 4000. Organic uranium concentrations were calculated from material balances. The extraction coefficient E is equal to $[U]_{org}/[U]_{aq}$.

4.0 RESULTS AND DISCUSSION

4.1 Organic Species; Acid Transfer

A typical isotherm for the extraction of uranium by 0.1 M TOA in C_6H_6 from sulfuric acid in water is shown in Fig. 1. Extraction isotherms at other acid and total sulfate levels have been similar to the one shown, the only important difference being the derived extraction coefficient (a translation of the curve to left or right, to give higher or lower E values, respectively). The linearity and unit slope of these curves at the lower uranium levels suggest that the organic complex is monomeric with respect to uranium, since the aqueous uranium is known to be monomeric in this range of acidities. Loading numbers (equivalents of amine per mole of organic uranium) calculated from the points at high uranium levels are shown in Table 1. The apparent regular increase of these n values with acidity is not considered significant, since the high acid curves show a comparatively gradual asymptotic approach to a saturation value.

Figure 2 shows the dependence of E on total amine concentration at constant acid activity and constant low loading

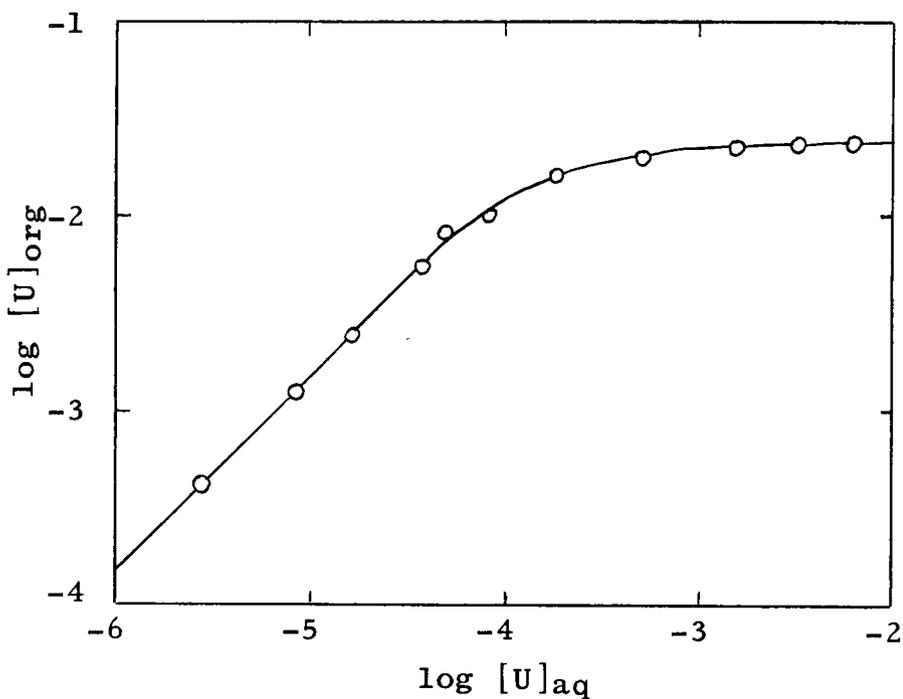


Fig. 1. Typical uranium extraction isotherm; 0.1 M TOA in C_6H_6 , initial (no U) $[H_2SO_4]_{aq} = 0.308$, $[H_2SO_4]_{org} = 0.0830$.

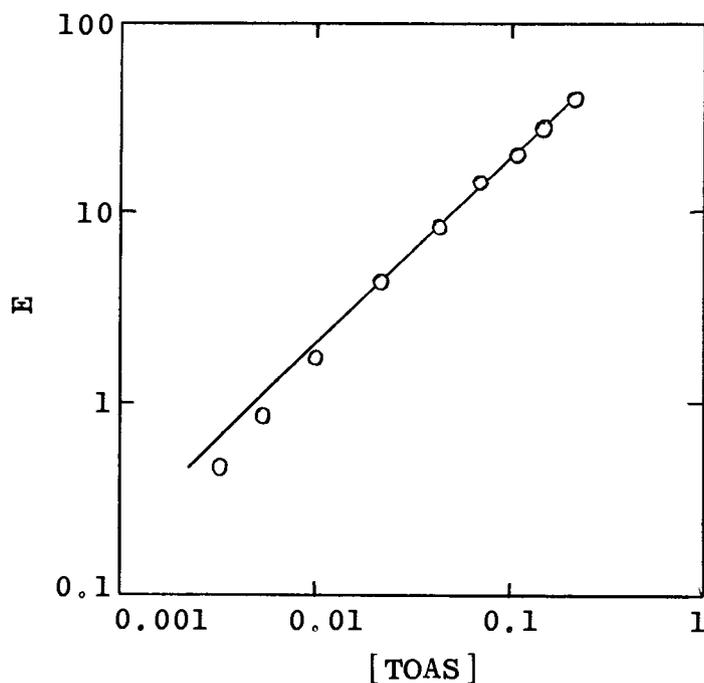


Fig. 2. Extraction coefficient vs. amine molarity; $[H_2SO_4]_{aq} = 0.76$, $[\Sigma R]/[\Sigma U] = 100$.

Table 1. Values of n under Various
Conditions as Obtained by Different Methods

H₂SO₄-H₂O, TOA system

[H ₂ SO ₄] _{aq}	[Na ₂ SO ₄] _{aq}	[H ₂ SO ₄] _{org}	[TOA]	n		Acid Transfer
				Loading	Isotherm	
0.0257	0.0	0.0485	0.100	4.1	4.3	
0.0713	0.0	0.0570	0.100	4.2	4.5	4.6
0.168	0.0	0.0635	0.100	4.3	4.2	4.1
0.308	0.0	0.0830	0.100	4.7	4.6	4.7
0.456	0.0	0.0876	0.100	5.1	5.0	
0.763	0.0	0.0926	0.100	5.2	4.5	
0.102	0.400	0.0576	0.100			4.3
0.202	0.300	0.0648	0.100			4.4
0.405	0.100	0.0731	0.100			3.9
0.200	0.300	0.0367	0.050			4.8
0.200	0.300	0.1497	0.200			4.6

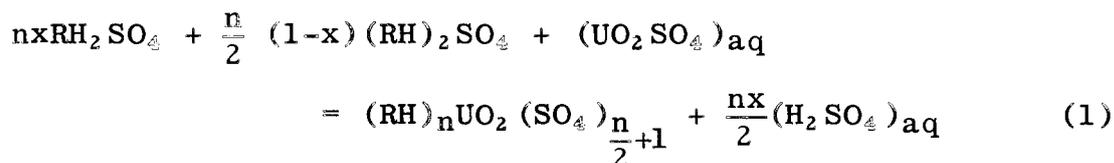
(100 equivalents of amine per mole of total uranium taken). On such a plot, if the amine sulfate was monomeric, a slope of 2 or more would be expected to correspond with a combining ratio of 4-5 amines per uranium. It was found in the acid work,¹ however, that the activities of the amine sulfate and bisulfate species could be represented by their respective equivalent fractions.* The behavior represented in Fig. 2 may thus be interpreted as indicating that the significant organic uranium activity is proportional to the ratio between the organic uranium concentration and that of the TOAS; i.e., a given aqueous uranium activity results in a given fraction, $x_U = [U]_{org}/[TOAS]$, of organic uranium per mole of amine, which is independent of the quantity of diluent (benzene) present.

The assumption that x_U should be based on the uncomplexed fraction of TOAS permits resolution of the intermediate part of the isotherm of Fig. 1. Values of $[U]_{org}$ are read from the

*The acid extraction behavior was interpreted in reference 1 by hypothesizing an aggregation of the amine sulfate-bisulfate species at concentrations greater than 0.02 M. Reliable physicochemical measurements⁹ have since shown that the normal sulfate of TOA is monomeric and that the bisulfate is dimeric in benzene (several other amine sulfates have shown aggregation numbers of from 4 to 40, TOAS being apparently an exception). Thus, the use here of equivalent or mole fractions is merely a convenient empirical description of the activity behavior of the organic uranium.

curved portion of the isotherm, the quantity $[\Sigma R] - n[U]_{org}$ is calculated, and the corresponding extraction coefficient, $[U]_{org}/[U]_{aq}$, is evaluated. Figure 3 is a log-log plot of $([\Sigma R] - n[U]_{org})$ vs. E for n values of 4 and 5. Here it is seen that the resulting uncomplexed amine molarities diverge from a line of unit slope in opposite directions, suggesting intermediate values of n. The n values estimated from Fig. 3 and from similar plots at other acid levels (Table 1) correspond roughly with the average obtained from the loading values. Similar behavior has been shown by a number of other amines.¹⁰

Accepting tentatively the hypothesis that a certain average number of equivalents, n, of normal amine sulfate are combined with each mole of uranium in the complex, an equation can be written for the reaction of the organic sulfate-bisulfate species with a neutral uranyl sulfate molecule:



where x is the equivalent fraction of bisulfate present in the uncomplexed TOAS, i.e., $x = [RH_2SO_4]/([RH_2SO_4] + 2[R_2H_2SO_4])$.

Equation 1 contains the implicit assumption that the uranium-bearing complex involves no amine bisulfate. It is generally recognized that the aqueous uranyl sulfate complexes do not involve the bisulfate ion, even at high sulfuric acid concentrations, and, while this does not preclude the presence of bisulfate in the organic complex of interest here, it does provide some basis for the analogous representation shown. On this basis, eq. 1 predicts the transfer of $nx/2$ moles of sulfuric acid to the aqueous phase per mole of uranium absorbed into the organic. Thus, the quantity $nx/2$ can be calculated from measurements of the aqueous acidity changes accompanying the sorption of known quantities of uranium. On the basis of the additional assumption that x depends only on the acid activity, independent of the presence of the uranium-bearing complex, and can therefore be calculated from the constants given in reference 1, estimates of n can be obtained from these values of $nx/2$. Under various conditions of acidity, aqueous sulfate, and amine concentration, the numbers obtained (Table 1) are in good agreement with those estimated from loading data and isotherm analysis.

The n values plotted in Fig. 4 were calculated from similar data obtained at constant acid activity and amine concentration, but with widely varying quantities of uranium. It is apparent here, within the progressively wider limits of

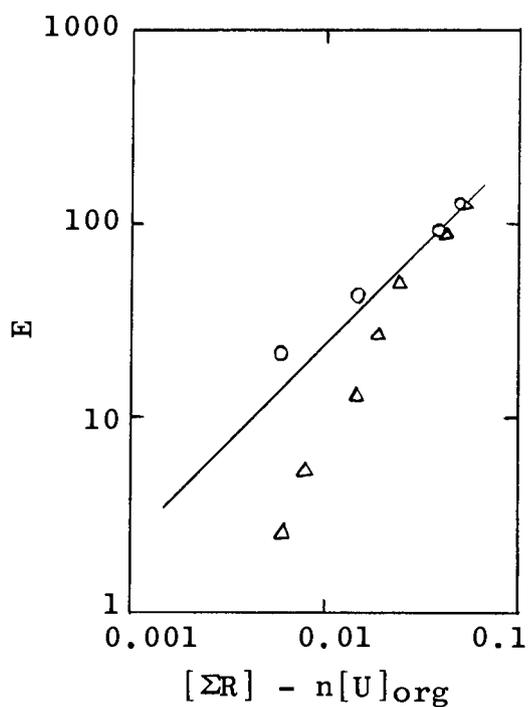


Fig. 3. Values of E vs. uncomplexed amine molarity for $n = 4$ (Δ) and $n = 5$ (O), (data of Fig. 1).

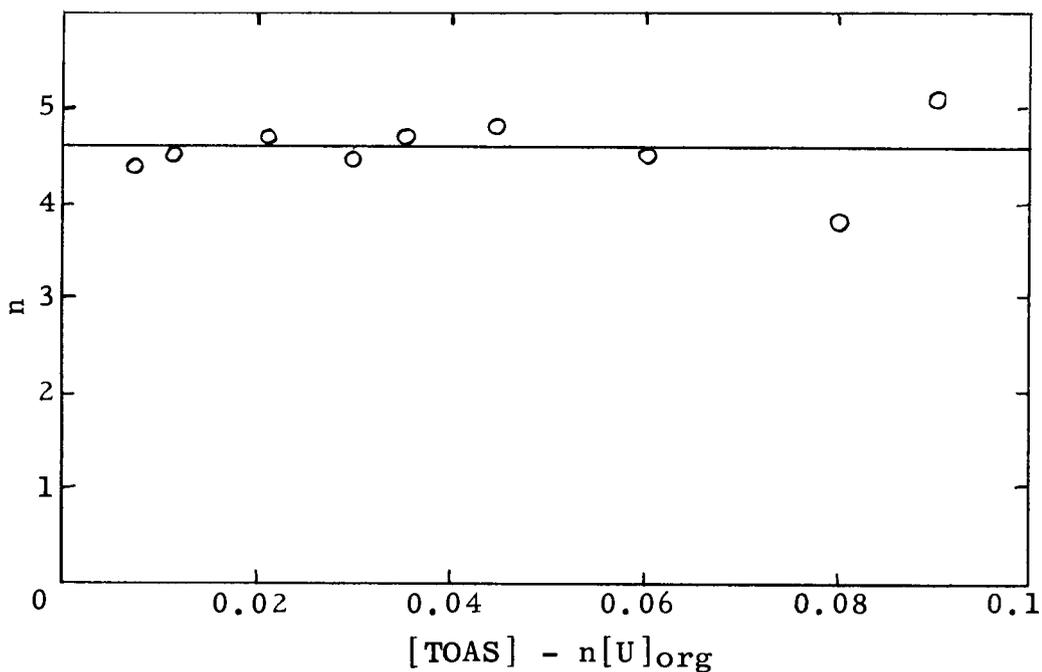


Fig. 4. Values of n obtained from acid transfer vs. uncomplexed amine molarity; the line indicates $n_{avg.} = 4.6$.

error imposed by the smaller acidity changes accompanying the lower uranium transfers, that the constancy of x assumed in making the calculations leads to reasonably constant values of n . Thus, while the possibilities have not been eliminated that the presence of some bisulfate in the complex is compensated for by changes in x and/or n , or that both x and n change in an equally compensating way, the simplest interpretation is that x is indeed independent of the presence of the uranium complex and that n is constant within the ranges of the variables examined.

4.2 Effects of Aqueous Complexes

On the basis of eq. 1 an equilibrium constant for the extraction of uranyl sulfate by the amine sulfate-bisulfate species can be written

$$K = \frac{[R_n H_n U O_2 (SO_4)_{\frac{n}{2}+1}]_O [H_2 SO_4]_a^{nx/2}}{[UO_2 SO_4]_a [RH_2 SO_4]_O^{nx} [R_2 H_2 SO_4]_O^{n(1-x)/2}} G_r \quad (2)$$

where, following Kraus and Nelson,¹¹ the symbol G_r is used for the appropriate activity coefficient ratio. It was found in the acid work¹ that the activities of the amine sulfate and bisulfate species could be represented, at least for the purpose of evaluating a concentration-independent constant for sulfate-bisulfate exchange in this system, by their respective equivalent fractions:

$$x_{RH_2 SO_4} = \frac{[RH_2 SO_4]}{[RH_2 SO_4] + 2[R_2 H_2 SO_4]} \quad (3)$$

$$x_{R_2 H_2 SO_4} = \frac{2[R_2 H_2 SO_4]}{[RH_2 SO_4] + 2[R_2 H_2 SO_4]}$$

Evidence presented in the preceding section suggests an analogous representation for the activity of the uranium-bearing complex:

$$x_U = \frac{n[R_n U]}{[\Sigma R] - n[R_n U]} \quad (4)$$

where $R_n H_n U O_2 (SO_4)_{\frac{n}{2}+1}$ is abbreviated $R_n U$. Writing a_U for the aqueous uranium activity and $a_{H_2 SO_4}$ for the sulfuric acid activity, eq. 1 can be written

$$K = \frac{x_U a_{H_2SO_4}^{nx/2}}{a_U x_{RH_2SO_4}^{nx} x_{R_2H_2SO_4}^{n(1-x)/2}} \quad (5)$$

Equations 1, 2, and 5 suggest that uranium extraction should show a marked inverse dependence on acid activity. This is known to be the case (see Fig. 5).

Equation 5 involves rather unwieldy power dependences; moreover, it is probable that these dependences may be anomalous, as was observed in the sulfate-bisulfate equilibria.¹ It is apparent that in attempting to resolve the effects of aqueous uranyl sulfate complexing on this equilibrium the superimposed effects of sulfuric acid activity and amine sulfate-bisulfate exchange should be kept as small as possible. Thus, at constant acid activity, constant total amine concentration, and constant low loading (the latter conditions making it possible to ignore loading effects and write $a_{Uorg} \propto [U]_{org}$), eq. 5 can be written

$$K' = \frac{[U]_{org}}{a_U} = \frac{E}{a_U / [\Sigma U]_{aq}} \quad (6)$$

which is the expected form of the distribution relation, showing that the quotient of the extraction coefficient and the ratio between the appropriate aqueous uranium activity and the total aqueous uranium concentration should be constant.

In Table 2 are presented uranium extraction data obtained at three acid activity levels, where the total aqueous sulfate concentration was varied at each level. Loading was kept at 20 amines per uranium in these runs, and, while it would be desirable to have results at still lower loadings, practical limitations were imposed by the extremely low equilibrium aqueous uranium concentrations that had to be measured. However, while some interference may have been introduced by the tying up of as much as one-fourth of the amine present as uranium-bearing complex, it is felt that the comparative results are reasonably indicative of the E vs. M relations* that hold under more nearly ideal conditions.

The sulfuric acid concentrations necessary for the maintenance of constant activity within each series were calculated from the amine-acid constants of reference 1, together

*The acid activity $a_{H_2SO_4} = 4\gamma_{\pm}^3 m^2M$, where $m = [H_2SO_4]_{aq}$ and $M = [H_2SO_4]_{aq} + [Na_2SO_4]_{aq}$.

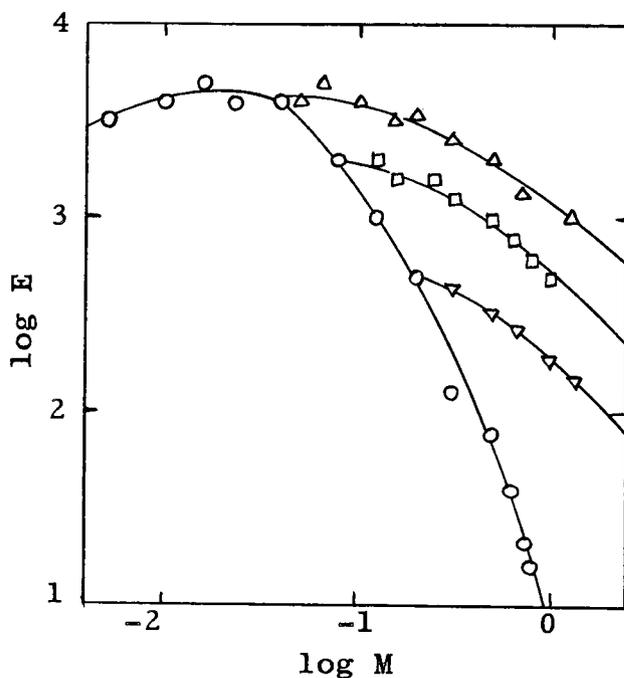


Fig. 5. Log E vs. log M; O, H_2SO_4 ; Δ , $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$ at constant $a_{\text{H}_2\text{SO}_4} = 3.5 \times 10^{-6}$; \square , $a_{\text{H}_2\text{SO}_4} = 4.7 \times 10^{-5}$; ∇ , $a_{\text{H}_2\text{SO}_4} = 3.0 \times 10^{-4}$.

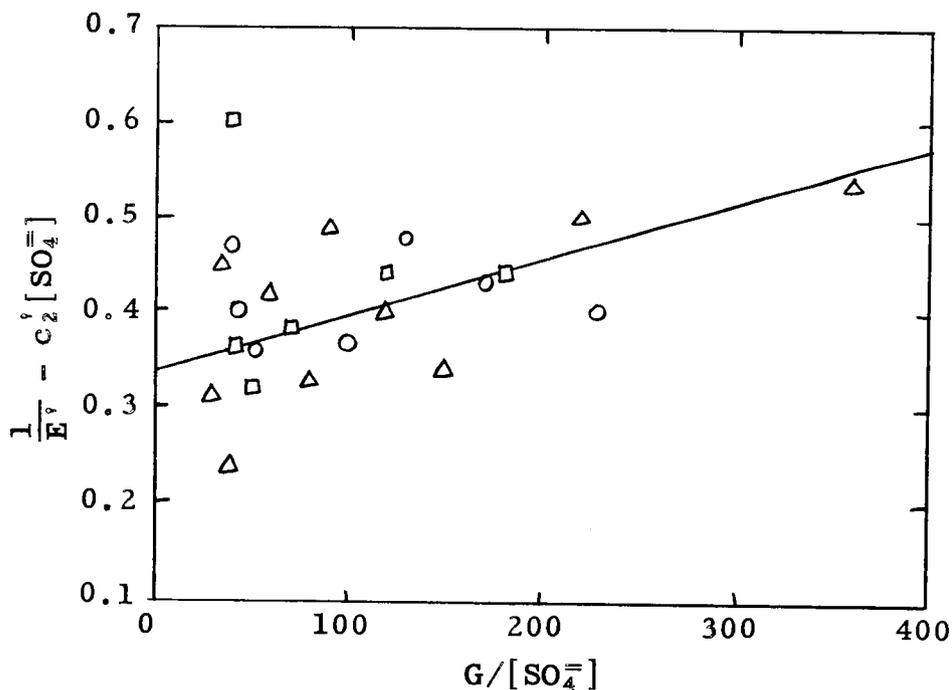


Fig. 6. $1/E' - c_2'[\text{SO}_4^-]$ vs. $G/[\text{SO}_4^-]$ for estimation of a and b; Δ , $a_{\text{H}_2\text{SO}_4} = 3.5 \times 10^{-6}$; O, $a_{\text{H}_2\text{SO}_4} = 4.7 \times 10^{-5}$; \square , $a_{\text{H}_2\text{SO}_4} = 3.0 \times 10^{-4}$.

Table 2. Uranium Extraction by 0.1 M TOA at
Constant Acid Activities

$[H_2SO_4]_{aq}$	$[Na_2SO_4]_{aq}$	$[\Sigma U]_{aq}$	$[SO_4^-]_{org}$	$[\Sigma U]_{org}$
$a_{H_2SO_4} = 3.5 \times 10^{-6}$				
0.0218	0.000	1.2×10^{-6}	0.0561	0.00500
0.0222	0.018	1.2×10^{-6}	0.0561	0.00500
0.0234	0.048	1.0×10^{-6}	0.0561	0.00500
0.0245	0.077	1.2×10^{-6}	0.0564	0.00500
0.0270	0.125	1.7×10^{-6}	0.0566	0.00500
0.0286	0.173	1.5×10^{-6}	0.0561	0.00500
0.0322	0.270	2.2×10^{-6}	0.0561	0.00500
0.0365	0.465	2.6×10^{-6}	0.0561	0.00499
0.0399	0.662	4.0×10^{-6}	0.0560	0.00499
0.0445	0.957	4.9×10^{-6}	0.0561	0.00499
$a_{H_2SO_4} = 4.7 \times 10^{-5}$				
0.0782	0.000	2.3×10^{-6}	0.0673	0.00499
0.0827	0.035	2.6×10^{-6}	0.0677	0.00499
0.0854	0.072	3.1×10^{-6}	0.0677	0.00499
0.0942	0.144	3.1×10^{-6}	0.0667	0.00499
0.1014	0.217	3.8×10^{-6}	0.0668	0.00499
0.1133	0.365	5.1×10^{-6}	0.0667	0.00499
0.1244	0.514	6.6×10^{-6}	0.0667	0.00498
0.1342	0.744	9.3×10^{-6}	0.0668	0.00498
0.1498	0.888	12.3×10^{-6}	0.0669	0.00497
$a_{H_2SO_4} = 3.0 \times 10^{-4}$				
0.204	0.000	9.4×10^{-6}	0.0739	0.00498
0.219	0.085	11.0×10^{-6}	0.0745	0.00498
0.244	0.260	16.0×10^{-6}	0.0745	0.00497
0.263	0.440	18.6×10^{-6}	0.0744	0.00496
0.294	0.710	27.3×10^{-6}	0.0748	0.00495
0.313	0.890	35.4×10^{-6}	0.0748	0.00493

with activity coefficients for the sulfuric acid—sodium sulfate system assembled and re-evaluated by Baes from existing emf data.¹² Experimental verification of the resulting activity constancy is evidenced by the column headed $[SO_4^-]_{org}$. Also, it should be pointed out that each value of $[H_2SO_4]_{aq}$, $[\Sigma U]_{aq}$, and $[SO_4^-]_{org}$ represents an average of at least two analytical determinations on each of at least two separate equilibrations at each total sulfate level shown. Values of $[SO_4^-]_{aq}$ at the m and M levels shown were calculated from the relations given by Baes.

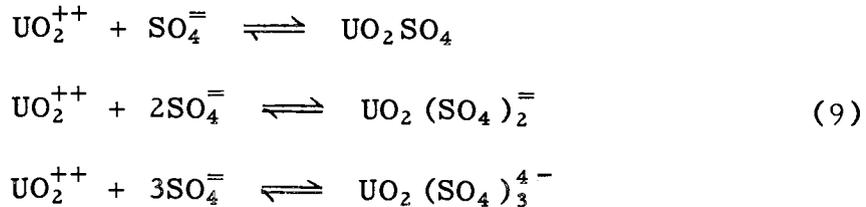
Of the several uranium species present in aqueous sulfate systems, i.e., UO_2^{++} , UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^-$, ... , one, the neutral monosulfate complex UO_2SO_4 , should show activity behavior independent of ionic strength variations in the medium. It is assumed therefore that eq. 6 can be written

$$K'' = E[\Sigma\text{U}]_{\text{aq}}/[\text{UO}_2\text{SO}_4]_{\text{aq}} \quad (7)$$

i.e., the fraction of total aqueous uranium in the form of the neutral complex should be proportional to the extraction coefficient under the conditions of constant acid activity, etc., stipulated above. Defining the fractions of the uranyl species (all molarities given in the following sections represent equilibrium aqueous concentrations) as

$$\begin{aligned} f_0 &= \frac{[\text{UO}_2^{++}]}{[\Sigma\text{U}]} & f_1 &= \frac{[\text{UO}_2\text{SO}_4]}{[\Sigma\text{U}]} \\ f_2 &= \frac{[\text{UO}_2(\text{SO}_4)_2^-]}{[\Sigma\text{U}]} & f_3 &= \frac{[\text{UO}_2(\text{SO}_4)_3^{4-}]}{[\Sigma\text{U}]} \end{aligned} \quad (8)$$

and for the reactions



and writing the concentration quotients

$$\begin{aligned} K_1 &= \frac{[\text{UO}_2\text{SO}_4]}{[\text{UO}_2^{++}][\text{SO}_4^-]} & K_2 &= \frac{[\text{UO}_2(\text{SO}_4)_2^-]}{[\text{UO}_2^{++}][\text{SO}_4^-]^2} \\ K_3 &= \frac{[\text{UO}_2(\text{SO}_4)_3^{4-}]}{[\text{UO}_2^{++}][\text{SO}_4^-]^3} \end{aligned} \quad (10)$$

it is easily shown that in systems of the kind under discussion, where $[\Sigma\text{U}] \ll [\text{SO}_4^-]$,

$$f_0 = \frac{1}{1 + K_1[\text{SO}_4^-] + K_2[\text{SO}_4^-]^2 + K_3[\text{SO}_4^-]^3}$$

$$\begin{aligned}
 f_1 &= f_0 K_1 [\text{SO}_4^-] \\
 f_2 &= f_0 K_2 [\text{SO}_4^-]^2 \\
 f_3 &= f_0 K_3 [\text{SO}_4^-]^3
 \end{aligned}
 \tag{11}$$

Higher complexes than the trisulfate will not be considered here, since even the trisulfate fraction must be very small compared to f_1 and f_2 for $[\text{SO}_4^-] < 1$ (see below).

Equilibrium constants for reactions 9 may be written

$$K_{a1} = K_1 G_1 \qquad K_{a2} = K_2 G_2 \qquad K_{a3} = K_3 G_3 \tag{12}$$

where the G's are the appropriate activity coefficient ratios. It is customary to assume that such ratios remain constant at a given ionic strength, independent of medium effects. In the present systems both the ionic strengths and the media change markedly, the latter changes being from pure sulfuric acid to predominantly sodium sulfate solution. While it is realized that such medium changes probably have some effect on the G's (and therefore also on K_1 , K_2 , and K_3), in the absence of quantitative theoretical relations for their estimation they will be ignored. Ionic strength corrections, on the other hand, can be estimated on the basis of the Debye-Hückel limiting law. We write

$$\log K_a = \log K_m - 0.509 \Delta(Z_i^2) \frac{\sqrt{\mu}}{1 + p \sqrt{\mu}} \tag{13}$$

where K_a is the constant at zero ionic strength μ (at $\mu = 0$ the activities are assumed to be proportional to the concentrations), and K_m is the concentration quotient at a given finite ionic strength.* This equation has been found to give

*It is realized that eq. 13 is at best only a good approximation. In systems that lend themselves to determinations of the concentrations of the individual species, it is sometimes possible to use expressions of the form

$$\frac{d \sqrt{\mu}}{1 + a \sqrt{\mu}} + B\mu + C\mu^2 + \dots$$

which give progressively better fits to data at high ionic strengths ($\mu > 1$) as more terms are taken. The present distribution data allow no such treatment; values of the constants B, C, etc. would have to be chosen arbitrarily. Thus, it seemed preferable to use only the limiting term, accepting the probability that at the higher ionic strengths the approximation to the activity coefficient ratio becomes poorer.

reasonably good correlation with data on U(IV) hydrolysis obtained by Kraus and Nelson.¹³ Values of p of 2.0 to 2.5 have been used for electrolyte systems similar to the present one; * fortunately, the relative changes of K_m and μ are not markedly affected by the particular p value chosen in the range $2.2 \leq p \leq 2.4$, and 2.3 will be used here throughout. For reactions 9 described by K_1 , K_2 , and K_3 of eq. 10, we have, respectively,

$$\Delta(Z_i^2)_1 = -8 \quad \Delta(Z_i^2)_2 = -8 \quad \Delta(Z_i^2)_3 = 0 \quad (14)$$

If we put

$$\log G = 0.509(8) \frac{\sqrt{\mu}}{1 + 2.3 \sqrt{\mu}} \quad (15)$$

it follows from eq. 13 that $G_1 = G_2 = G$, and $G_3 = 1$. Values of μ were calculated from the relation

$$\mu = \frac{1}{2} \sum c_i Z_i^2 = M + 2[SO_4^-] \quad (16)$$

and G was then evaluated from eq. 15 for each value in Table 2.

From eqs. 7 and 8, replacing the constant K'' (independent of ionic strength) by $1/b$, we have

$$\frac{E}{f_1} = K'' = \frac{1}{b} \quad (17)$$

It follows that

$$\begin{aligned} \frac{E}{f_0} &= \frac{[U]_{org}}{[UO_2^{2+}]_{aq}} = \frac{K''K_1 a [SO_4^-]}{G} = \frac{[SO_4^-]}{aG} \\ \frac{E}{f_2} &= \frac{[U]_{org}}{[UO_2(SO_4)_2^-]_{aq}} = \frac{K''K_1 a}{K_2 a [SO_4^-]} = \frac{1}{c [SO_4^-]} \\ \frac{E}{f_3} &= \frac{[U]_{org}}{[UO_2(SO_4)_3^{4-}]_{aq}} = \frac{K''K_1 a}{K_3 G [SO_4^-]^2} = \frac{1}{dG [SO_4^-]^2} \end{aligned} \quad (18)$$

*The value 2.3 results from a mean distance of approach of 7 Å; this distance value is intermediate between the 7.5 Å used by Kraus and Nelson¹³ and the 6 Å used by Robinson and Harned for similar electrolyte systems.¹⁴

where a, b, c, and d are constants involving only K'' , $K_1 a$, $K_2 a$, and K_3 , all of which are independent of ionic strength variations. Solving eqs. 17 and 18 for the f's and adding, we obtain, on dividing through by E,

$$\frac{1}{E} = \frac{aG}{[SO_4^-]} + b + c[SO_4^-] + dg[SO_4^-]^2 \quad (19)$$

The following procedure was used in evaluating a, b, and c from the data of Table 2 (d will be considered later). For each set of data* at the acid activities 1, 2, and 3, $1/E$ was plotted against $[SO_4^-]$. From the resulting curves, each of which was fairly linear over a considerable range, tentative values of the slopes c_1 , c_2 , and c_3 were obtained. Using these slopes, $1/E - c[SO_4^-]$ was then plotted against $G/[SO_4^-]$, and tentative values of a_1 , a_2 , and a_3 were calculated. From these a values, $1/E - aG/[SO_4^-]$ was calculated and plotted against $[SO_4^-]$ for each of the three acid activities. The resulting plots showed better linearity than the initial $1/E$ vs. $[SO_4^-]$ plots, and new values of the slopes, c'_1 , c'_2 , and c'_3 , were obtained. The $1/E$ values at the low and high acid activities were then normalized to correspond with those at the intermediate activity by multiplying by c'_2/c'_1 and c'_2/c'_3 , respectively. The resulting normalized reciprocal extraction coefficients, $1/E'$, were used in calculating the quantity $1/E' - c'_2[SO_4^-]$ for all the data of Table 2. A plot of this latter quantity against $G/[SO_4^-]$ is shown in Fig. 6. From the plot of Fig. 6 a final value of a was obtained, as well as an estimate of b. The quantity $1/E' - aG/[SO_4^-]$ was then calculated; a plot of this quantity against $[SO_4^-]$ is shown in Fig. 7, from which final values of b and c were estimated visually.

The results of least-squares analysis of the data of Figs. 6 and 7 were in good agreement with the slope and intercept values obtained visually. The standard deviations of these quantities were calculated and adjusted to a 90% confidence interval by multiplication by the appropriate value of the t statistic.¹⁵ The following numbers are thus shown with the associated range of deviation within which corresponding numbers calculated from similar sets of data could be expected to fall nine times out of ten:

$$\begin{aligned} a &= 0.00058 \pm 0.00042 \\ b &= 0.335 \pm 0.033 \\ c &= 2.00 \pm 0.11 \end{aligned} \quad (20)$$

*The E values calculated from Table 2 were divided by 1000 before making these plots for more convenient numerical handling.

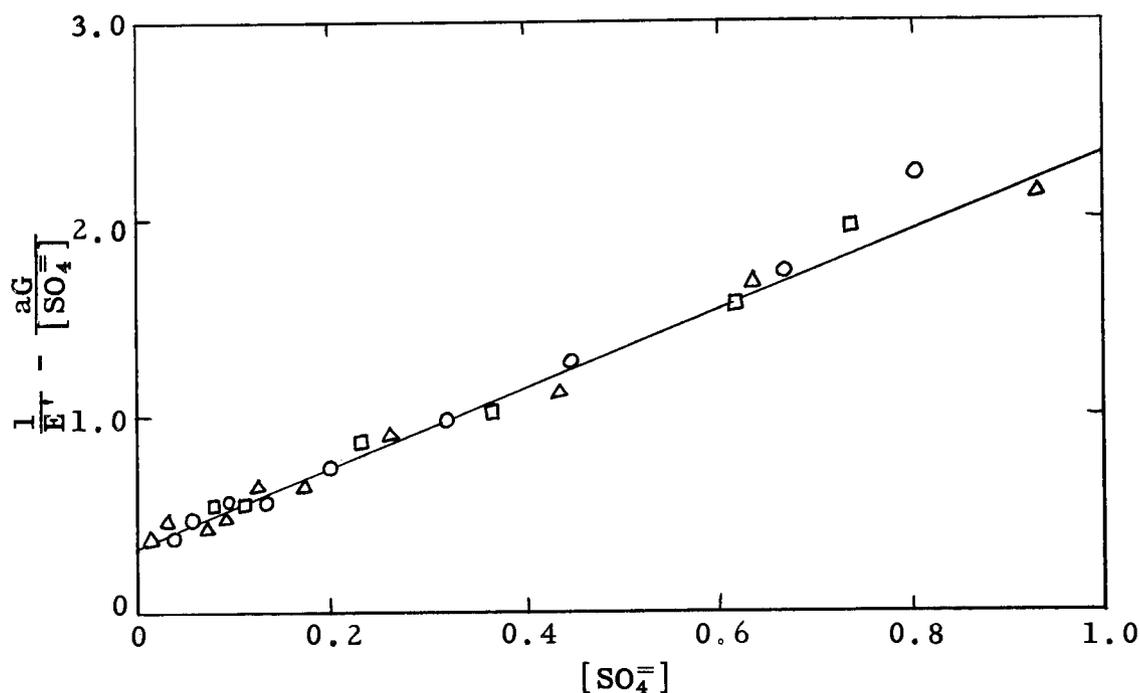


Fig. 7. $1/E' - aG/[SO_4^=]$ vs. $[SO_4^=]$ for final values of b and c ; Δ , $a_{H_2SO_4} = 3.5 \times 10^{-6}$; O , $a_{H_2SO_4} = 4.7 \times 10^{-5}$; \square , $a_{H_2SO_4} = 3.0 \times 10^{-4}$.

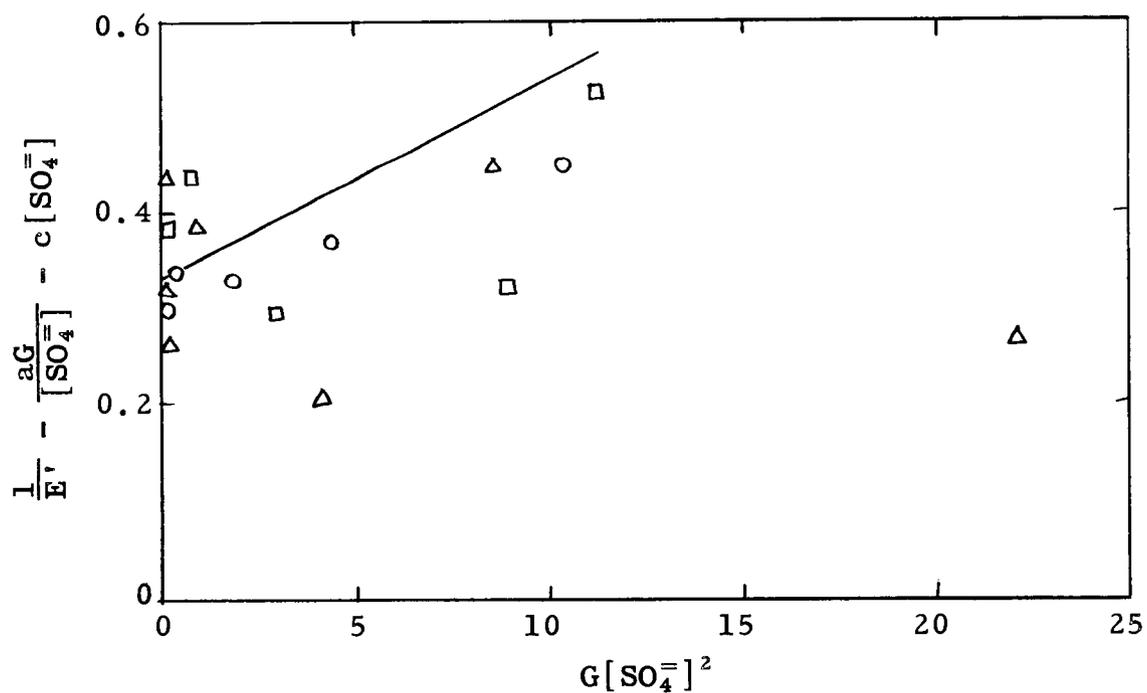


Fig. 8. $1/E' - aG/[SO_4^=] - c[SO_4^=]$ vs. $G[SO_4^=]^2$ for estimate of upper limit of d ; Δ , $a_{H_2SO_4} = 3.5 \times 10^{-6}$; O , $a_{H_2SO_4} = 4.7 \times 10^{-5}$; \square , $a_{H_2SO_4} = 3.0 \times 10^{-4}$. The line shown was drawn with intercept $b = 0.335$ and slope $d = 0.02$.

Figure 8 shows a plot of $\frac{1}{E} - \frac{aG}{[\text{SO}_4^-]} - c[\text{SO}_4^-]$ against $G[\text{SO}_4^-]^2$. It is apparent on this plot that there is little or no justification for attempting to assign a value to the slope d . On the other hand, from the general appearance of the plot it may be estimated reasonably that d cannot be greater than ~ 0.02 for the present data. Back calculations using this maximum value of d showed that the resulting changes in a , b , and c were negligible.

From eqs. 12 through 18

$$\begin{aligned} K_{a1} &= b/a & K_{a2} &= c/a \\ K_{a3} &= K_3 = \frac{d}{a} & \frac{K_{a2}}{K_{a1}} &= \frac{K_2}{K_1} = \frac{c}{b} \end{aligned} \quad (21)$$

In Table 3 the values of K_{a1} , K_{a2} , etc., calculated from eqs. 12, 20, and 21 are presented together with corresponding values of these constants obtained by Ahrland,¹⁶ although the values obtained here and those given by Ahrland are not strictly comparable. In the first place, Ahrland's measurements were made in aqueous systems containing uranyl perchlorate, sodium sulfate, sodium perchlorate, sodium acetate, and acetic acid, maintained throughout at unit ionic strength. As in the present work, no allowance for medium effects was possible. The present data yield directly only the K_{a1} , K_{a2} , and K_3 values at $\mu = 0$; the numbers given for $\mu = 1$ are estimates based on eq. 13. The same limiting-law adjustments were applied to Ahrland's values in order to obtain comparisons at $\mu = 0$. In the second place, Ahrland's measurements were made at 20°C, while the present data were obtained at 25°C. With some knowledge of the appropriate heats of reaction this temperature difference might be corrected for; however, in view of the spreads shown in Table 3, which for the present data are inclusive in all cases of Ahrland's ranges, it is doubtful that such corrections would result in any significant differences in the correspondences shown. In the light of these considerations, it is felt that the agreements among the values given in Table 3 are good, and especially so in the case of the ratio K_2/K_1 . The situation with K_3 is less satisfactory; it is to be pointed out, however, that even here there is reasonable agreement with Ahrland's spectrophotometric results, for which he claimed greater precision in his values of K_1 and K_2 . The weight of evidence suggests low if not negligible proportions of the trisulfate complex at sulfate molarities below 1.

Table 3. Formation Constants of Uranyl Sulfate Complexes

	This Paper, TOA Extraction Data ^a	Ahrland ¹⁶	
		Potentiometric	Spectrophotometric
$\mu = 0, G = 1$			
K _{a1}	580 (300-2300)	860 ± 170	960 ± 100
K _{a2}	3450 (1900-13000)	6000 ± 2600	7700 ± 860
K ₃	(0-125)	2500 ± 1000	<<2500
K ₂ /K ₁	6.0 ± 1.0	7 (3.3-12.5)	8 (6.5-10)
$\mu = 1, G = 17.1$			
K ₁	34 (17-135)	50 ± 10	56 ± 6
K ₂	200 (100-760)	350 ± 150	450 ± 50
K ₃	(0-125)	2500 ± 1000	<<2500
K ₂ /K ₁	6.0 ± 1.0	7 (3.3-12.5)	8 (6.5-10)

^aThe numbers given in parentheses represent the low and high values obtained from eqs. 21 on substituting the corresponding values of the constants minus or plus their associated deviations shown in eqs. 20; e.g., K_{a1} (low) = (0.335 - 0.033)/(0.00058 + 0.00042), K_{a1} (high) = (0.335 + 0.033)/(0.00058 - 0.00042), etc.

5.0 REFERENCES

1. K. A. Allen, J. Phys. Chem., 60, 239(1956); *ibid.*, 60, 943(1956).
2. K. A. Allen, J. Am. Chem. Soc., 80, 4133(1958).
3. W. J. McDowell and C. F. Baes, Jr., J. Phys. Chem., 62, 777(1958).
4. E. L. Smith and J. E. Page, J. Soc. Chem. Ind. (London), 67, 48(1949).
5. G. W. Leddicotte and F. L. Moore, J. Am. Chem. Soc., 74, 1618(1952); J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, Anal. Chem., 26, 1045(1954); H. A. Mahlman, G. W. Leddicotte, and F. L. Moore, *ibid.*, 26, 1939(1954); F. L. Moore, *ibid.*, 27, 70(1955).

6. K. B. Brown, C. F. Coleman, D. J. Crouse, and A. D. Ryon, "Progress Report on Raw Materials," ORNL-2268 (Apr. 26, 1957).
7. K. B. Brown, D. J. Crouse, and C. F. Coleman, "Some New Solvent Extraction Processes for Use in the Hydrometallurgical Treatment of Uranium, Thorium, and Vanadium Ores," presented at the New Orleans Meeting of the American Institute of Mining Engineers, Feb. 27, 1957; K. B. Brown et al., Paper P/509, Proc. 2nd Internatl. Conf. on Peaceful Uses of Atomic Energy, Vol. 3, p. 472, United Nations, New York, 1958.
8. K. A. Allen, Anal. Chem., 28, 1144(1956).
9. K. A. Allen, J. Phys. Chem., 62, 1119(1958).
10. K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis, and J. G. Moore, "The Use of Amines as Extractants for Uranium from Acidic Sulfate Liquors - A Preliminary Report," AECD-4142 (May 27, 1954); J. G. Moore, K. B. Brown, and C. F. Coleman, "Further Studies of Amines as Extractants for Uranium from Acid Sulfate Solutions," AECD-4145 (June 24, 1955).
11. K. A. Kraus and F. Nelson, Paper P/837, Proc. 1st. Internatl. Conf. on Peaceful Uses of Atomic Energy, Vol. 7, p. 113, United Nations, New York, 1955.
12. C. F. Baes, Jr., J. Am. Chem. Soc., 79, 5611(1957).
13. K. A. Kraus and F. Nelson, J. Am. Chem. Soc., 72, 3901(1950).
14. R. A. Robinson and H. S. Harned, Chem. Rev. 28, 419(1941).
15. W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, 1951, pp. 42, 43, 119.
16. S. Ahrland, Acta Chem. Scand., 5, 1151(1951).



INTERNAL DISTRIBUTION

- | | | | |
|--------|---|------|--|
| 1. | C. E. Center | 69. | K. O. Johnsson |
| 2. | Biology Library | 70. | B. Weaver |
| 3. | Health Physics Library | 71. | J. C. Bresee |
| 4-5. | Central Research Library | 72. | C. A. Blake |
| 6. | Reactor Experimental
Engineering Library | 73. | J. G. Moore |
| 7-26. | Laboratory Records Department | 74. | K. A. Allen |
| 27. | Laboratory Records, ORNL R. C. | 75. | C. F. Baes |
| 28. | A. M. Weinberg | 76. | W. D. Arnold |
| 29. | L. B. Emlet (K-25) | 77. | F. L. Daley |
| 30. | J. P. Murray (Y-12) | 78. | D. E. Horner |
| 31. | J. A. Swartout | 79. | F. J. Hurst |
| 32. | E. H. Taylor | 80. | B. B. Klima |
| 33. | E. D. Shipley | 81. | R. S. Lowrie |
| 34. | M. L. Nelson | 82. | W. J. McDowell |
| 35-36. | F. L. Culler | 83. | J. M. Schmitt |
| 37. | W. H. Jordan | 84. | F. G. Seeley |
| 38. | J. B. Adams | 85. | J. S. Drury |
| 39. | J. H. Frye, Jr. | 86. | J. C. White |
| 40. | S. C. Lind | 87. | J. T. Long |
| 41. | G. I. Cathers | 88. | R. E. Leuze |
| 42. | A. Hollaender | 89. | R. A. McNees |
| 43. | F. F. Blankenship | 90. | J. T. Roberts |
| 44. | M. T. Kelley | 91. | J. R. Flanary |
| 45. | C. F. Coleman | 92. | W. Davis |
| 46. | R. S. Livingston | 93. | R. H. Rainey |
| 47. | C. P. Keim | 94. | R. G. Mansfield |
| 48. | D. J. Crouse | 95. | F. A. Kappelmann |
| 49. | C. E. Winters | 96. | E. M. Shank |
| 50. | A. D. Ryon | 97. | J. O. Blomeke |
| 51. | D. Phillips | 98. | C. D. Watson |
| 52. | W. K. Eister | 99. | W. H. Lewis |
| 53. | F. R. Bruce | 100. | E. Lamb |
| 54. | D. E. Ferguson | 101. | W. R. Grimes |
| 55. | R. B. Lindauer | 102. | P. M. Reyling |
| 56. | H. E. Goeller | 103. | S. H. Jury |
| 57. | R. A. Charpie | 104. | M. H. Lietzke |
| 58. | M. E. Whatley | 105. | R. W. Stoughton |
| 59. | M. J. Skinner | 106. | F. L. Moore |
| 60. | R. E. Blanco | 107. | K. A. Kraus |
| 61. | G. E. Boyd | 108. | M. Benedict (consultant) |
| 62. | W. E. Unger | 109. | D. L. Katz (consultant) |
| 63. | R. R. Dickison | 110. | C. E. Larson (consultant) |
| 64. | A. T. Gresky | 111. | J. H. Rushton (consultant) |
| 65. | E. D. Arnold | 112. | I. Perlman (consultant) |
| 66. | C. E. Guthrie | 113. | H. Worthington (consultant) |
| 67. | J. W. Ullmann | 114. | ORNL - Y-12 Technical Library,
Document Reference Section |
| 68. | K. B. Brown | | |

EXTERNAL DISTRIBUTION

- 115. Division of Research and Development, AEC, ORO
- 116. H. L. Hazen, Farmer's Union Bldg., Denver, Colo.
- 117. M. E. Wadsworth, University of Utah
- 118-126. E. C. Van Blarcom, Division of Raw Materials, Washington
- 127-616. Given distribution as shown in TID-4500 (14th ed.) under Technology-Raw Materials category (75 copies - OTS)