[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY[1]]

The Uranyl Sulfate Complexes from Tri-*n*-octylamine Extraction Equilibria

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The extraction of uranium from acidic sulfate aqueous systems by benzene solutions of tri-*n*-octylamine sulfate has been measured under various conditions of uranium loading, acid activity, sulfate ion concentration and amine concentration. An equation for the reaction between the amine sulfate–bisulfate mixture and the uranium is proposed which is consistent with the results. Under conditions of constant acid activity, amine concentration and low uranium loading, the distributions observed at varying aqueous sulfate levels are shown to lead to estimates of the formation constants for the aqueous uranium mono- and disulfate complexes which are in reasonably good agreement with those reported by Ahrland. The present evidence suggests only very low or negligible proportions of the trisulfate complex at sulfate molarities below one.

I. Introduction

The high molecular weight amines in organic diluents have been shown to extract a wide variety of substances from aqueous solutions. The first use of amines for separations was reported by Smith and Page, who also suggested the use of such reagents as anion exchangers.[2] A number of analytical separations have been based on amine extractions of various metal ions.[3] For several years an intensive study of the amines as extractants for uranium from acidic sulfate solutions has been underway at this Laboratory.[4] 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.[5]

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 phase) of from four to six 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 present investigation was undertaken with the object of further elucidating the equilibria involved in these reactions. 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 already have been examined in some detail.[6] As in the previous studies, benzene has been used throughout as the organic diluent. The present treatment is in general accord with that described by McDowell for uranium extraction by di-*n*-decylamine sulfate.[7]

II. Experimental

Materials and Apparatus.—The tri-*n*-octylamine[8] used in this work has been described previously.[6] 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 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 ± 0.1° thermostat. Five minutes shaking was found sufficient for the attainment of equilibrium under widely varying extraction conditions. The data reported below are based on shaking times of 15 minutes or more.

Procedures and Analyses.—The techniques used in running the equilibrations were similar to those described in the acid work.[6] 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 were calculated from the constants reported previously.[6] 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 then carefully evaporated 20–30%, a known amount of uranyl sulfate solution was added, and the solution was made back up to the given volume with water. A portion of this solution was then shaken with the corresponding pre-equilibrated organic phase 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 in the previous papers.[6] Most of the aqueous uranium concentrations were measured by potentiometric titration, using an automatic method which has been described elsewhere.[9] 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 resorted to. 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 *ca.*

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[1] Operated for the U.S.A.E.C. by Union Carbide Nuclear Company.

[2] E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.* (*London*), **67**, 48 (1949).

[3] G. W. Leddicotte and F. L. Moore, THIS JOURNAL, **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).

[4] K. B. Brown, C. F. Coleman, D. J. Crouse and A. D. Ryon, "Progress Report on Raw Materials," ORNL-2268, April 26, 1957; 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.

[5] 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, February 27, 1957; R. A. Foos, *Mining Eng.*, **8**, 893 (1956); "Uranium—Field for Organics," *Chem. Eng. News*, **34**, 2590 (1956).

[6] K. A. Allen, *J. Phys. Chem.*, **60**, 239 (1956); **60**, 943 (1956).

[7] W. J. McDowell and C. F. Baes, Jr., to be published.

[8] 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.

[9] K. A. Allen, *Anal. Chem.*, **28**, 1144 (1956).

±5 to ±25% for coefficients from *ca.* 100 to 4000. Organic uranium concentrations were calculated from material balances. The extraction coefficient $E = [U]_{org}/[U]_{aq}$.

III. Results and Discussion

A. The 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 the first section of Table I.

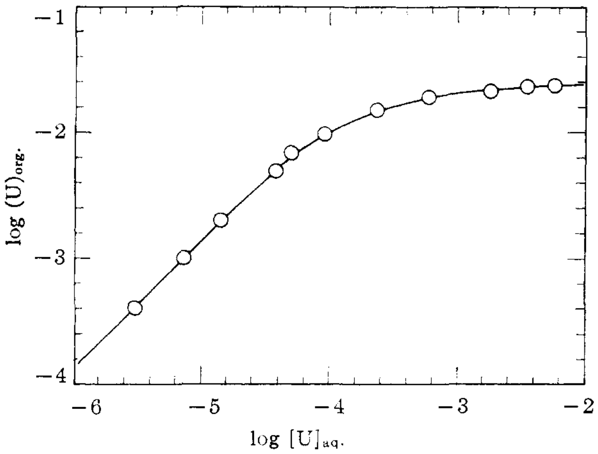

Fig. 1.—Typical uranium extraction isotherm: 0.01 *M* TOA in C_6H_6, initial (no U) $[H_2SO_4]_{aq} = 0.308$, $[H_2SO_4]_{org} = 0.0830$.

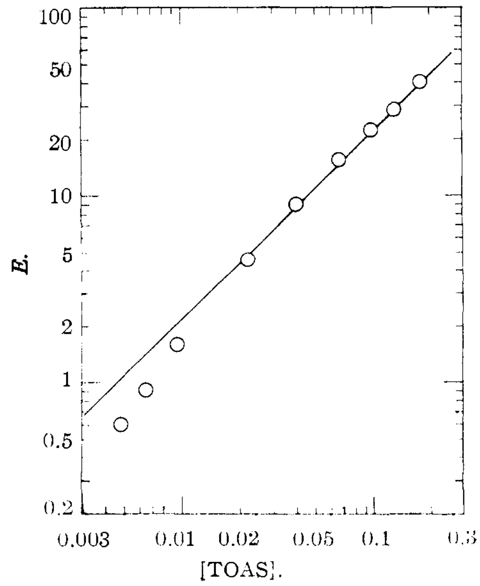

Fig. 2.—Extraction coefficient *vs.* amine molarity; $[H_2SO_4]_{aq} = 0.76$, $[\Sigma R]/[\Sigma U] = 100$.

The apparent regular increase of these n values with acidity is not considered significant, since the high acid curves show a comparatively gradual assymptotic approach to a saturation value.

TABLE I

VALUES OF n OBTAINED UNDER VARIOUS CONDITIONS AND BY DIFFERENT METHODS

A. Loading and isotherm values, H_2SO_4–H_2O, 0.1 *M* TOA system

$[H_2SO_4]_a$	$[H_2SO_4]_{org}$	$n_{loading}$	$n_{isotherm}$
0.0257	0.0485	4.1	4.3
.0713	.0570	4.2	4.5
.168	.0635	4.3	4.2
.308	.0830	4.7	4.6
.456	.0876	5.1	5.0
.763	.0926	5.2	4.5

B. Acid transfer values, from $n = 2\Delta[H_2SO_4]/x\Delta[UO_2SO_4]$

$[H_2SO_4]_{aq}$	$[Na_2SO_4]_{aq}$	$[H_2SO_4]_{org}$	[TOA]	n
0.0713	0.0	0.0570	0.100	4.6
.168	.0	.0635	.100	4.1
.308	.0	.0830	.100	4.7
.102	.400	.0576	.100	4.3
.202	.300	.0648	.100	4.4
.405	.100	.0731	.100	3.9
.200	.300	.0367	.050	4.8
.200	.300	.1497	.200	4.6

Figure 2 shows the dependence of E on total amine concentration at constant acid activity and constant low loading (100 equivalents of amine per mole of total uranium taken). On such a plot, if the amine sulfate were monomeric, one would expect a slope of two or more, to correspond with a combining ratio of 4–5 amines per uranium. It was found in the acid work,[6] however, that the activities of the amine sulfate and bisulfate species could be represented by their respective equivalent fractions.[10] 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, 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. The quantity log ($[\Sigma R] - n[U]_{org}$) is plotted *vs.* log E for these regions using $n_1 = 4$ and $n_2 = 5$ in Fig. 3. 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. Such n values, estimated from Fig. 3 and from similar plots at other acid levels, are shown alongside the loading numbers in Table I, where it is seen that they correspond roughly with the aver-

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[10] The acid extraction behavior was interpreted in ref. 6 in terms of a hypothesized aggregation of the amine sulfate-bisulfate species at concentrations greater than 0.02 *M*. Reliable physico-chemical measurements (light scattering and isopiestic results—to be published) 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 four to forty—TOAS is 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.

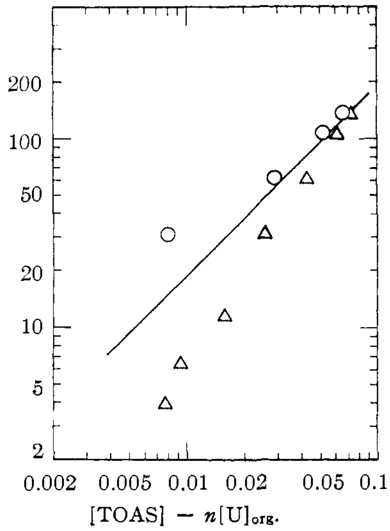

Fig. 3.—Uncomplexed amine molarity *vs.* E for △, n_1 = 4, and ○, n_2 = 5, data of Fig. 1.

age obtained from the saturation values. Similar behavior has been shown by a number of other amines.[4]

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 as

$$nx\mathrm{RH_2SO_4} + \frac{n}{2}(1 - x)(\mathrm{RH})_2\mathrm{SO_4} + (\mathrm{UO_2SO_4})_{aq} = (\mathrm{RH})_n\mathrm{UO_2(SO_4)}_{n/2+1} + \frac{nx}{2}(\mathrm{H_2SO_4})_{aq} \quad (1)$$

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

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,[11] 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, reaction 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 6, estimates of n can be obtained from these values of $nx/2$. Such n values are given in the second part of Table I, where it is apparent that under the various conditions of acidity, aqueous sulfate and amine concentration shown, the numbers obtained are in good agreement with those estimated from loading data and isotherm analysis.

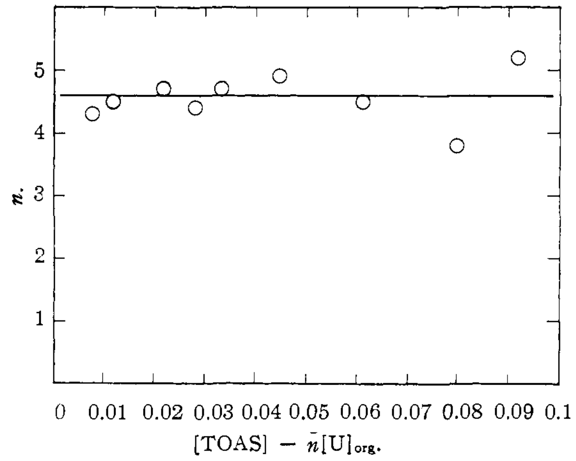

Fig. 4.—Values of n from acid transfer *vs.* uncomplexed amine molarity; $\bar{n}$ taken = 4.6.

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 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.

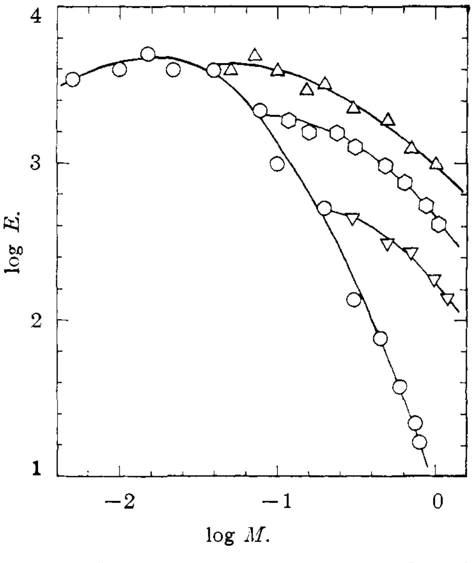

Fig. 5.—Log E *vs.* log M: ○, $\mathrm{H_2SO_4}$; △, $\mathrm{H_2SO_4}$ + $\mathrm{Na_2SO_4}$ at constant $a_{\mathrm{H_2SO_4}} = 3.5 \times 10^{-6}$; ○, $a_{\mathrm{H_2SO_4}} = 4.7 \times 10^{-5}$; ▽, $a_{\mathrm{H_2SO_4}} = 3.0 \times 10^{-4}$.

B. Effects of Aqueous Complexes.—On the basis of reaction 1 an equilibrium constant for the extraction of uranyl sulfate by the amine sulfate–

[11] R. H. Betts and R. K. Michels, *J. Chem. Soc.*, Supp. Issue, 286, 5289 (1949).

bisulfate species can be written as

$$K = \frac{[\mathrm{R}_n\mathrm{H}_n\mathrm{UO}_2(\mathrm{SO}_4)_{n/2+1}]_o[\mathrm{H}_2\mathrm{SO}_4]_a{}^{nx/2}}{[\mathrm{UO}_2\mathrm{SO}_4]_a[\mathrm{RH}_2\mathrm{SO}_4]_o{}^{nx}[\mathrm{R}_2\mathrm{H}_2\mathrm{SO}_4]_o{}^{(n/2)(1-x)}}\, G_r \qquad (2)$$

where, following Kraus and Nelson,[12] the symbol G_r is used for the appropriate activity coefficient product. Equations 1 and 2 suggest a marked inverse dependence of uranium extraction on acid activity. This is known to be the case, and Fig. 5, in which the circles represent E values for the pure H_2SO_4 system, illustrates this effect. At constant acid activity, constant total amine concentration and constant low loading (the latter condition making it possible to ignore loading effects and write $a_{\mathrm{uorg}} \propto [\mathrm{U}]_{\mathrm{org}}$), (3) can be written

$$K' = \frac{[\mathrm{U}]_{\mathrm{org}}}{a_{\mathrm{uaq}}} = \frac{E}{a_{\mathrm{uaq}}/[\Sigma\mathrm{U}]_{\mathrm{aq}}} \qquad (3)$$

where the use of $[\mathrm{U}]_{\mathrm{org}}$ for the organic uranium activity, a_{uorg}, and of a_{uaq} for the aqueous uranium activity, allow K' to be interpreted as an equilibrium constant without the need of an indeterminate activity coefficient product.

The non-circled points in Fig. 5 show data obtained under the conditions for which equation 3 holds. Within each of the three series, the sulfuric acid activity was kept constant,[13] loading was 20 amines per uranium, and only the total aqueous sulfate concentration was varied. The acid concentrations necessary for the maintenance of constant activity within each series were calculated from the amine–acid constants of reference 6, together with activity coefficients for the sulfuric acid–sodium sulfate system assembled and re-evaluated by Baes from existing e.m.f. data.[14] In the Baes and McDowell work[7] where sulfate variation data were obtained at constant pH, corrections for acid activity variation were necessary and, while these were relatively small, the availability since that work was done of the material in reference 14 made it possible in the present case to ensure experimental acid activity constancy. That this condition did indeed hold throughout each of the three series shown in Fig. 5 was verified by careful titrations of each final organic phase for total sulfate: the maximum variation observed within any one of the three series was ±0.6%. Values of $[\mathrm{SO}_4^=]_{\mathrm{aq}}$ at the m, M levels used also were calculated from Baes' relationships.[14]

Of the several uranium species present in aqueous sulfate systems, *i.e.*, UO_2^{++}, UO_2SO_4, $UO_2(SO_4)_2^=$, . . ., one, the neutral monosulfate complex, UO_2SO_4, should exhibit activity behavior independent of ionic strength variations. It follows that (3) can be written (all molarities given below represent equilibrium aqueous concentrations)

$$\frac{[\mathrm{UO}_2\mathrm{SO}_4]}{[\Sigma\mathrm{U}]} = \frac{E}{K'} = bE \qquad (4)$$

The equilibrium constants for the formation of the mono-, di- and trisulfate complexes can be written $K_{a1} = K_1G_1$, $K_{a2} = K_2G_2$, and $K_{a3} = K_3G_3$, respectively, where the K_i are the concentration quotients and the G_i 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

$$\log K_a = \log K_m - 0.509\Delta(Z_i^2)\frac{\sqrt{\mu}}{1 + p\sqrt{\mu}} \qquad (5)$$

K_a is the constant at zero ionic strength μ, where the activities are assumed to be proportional to concentrations, and K_m is the concentration quotient at a given finite ionic strength.[15] This equation has been found to give a reasonably good fit to data on U(IV) hydrolysis obtained by Kraus and Nelson.[16] Values of p of from 2.0 to 2.5 have been used for electrolyte systems similar to the present one[17]; fortunately the relative changes of K_m and μ are not markedly affected by the particular p value chosen in the range $2.2 < p < 2.4$, and 2.3 will be used here throughout. From the formation reactions for the mono-, di- and trisulfate complexes we have $\Delta(Z_i^2)_1 = -8$, $\Delta(Z_i^2)_2 = -8$, and $\Delta(Z_i^2)_3 = 0$, respectively. Thus, putting $\log G = 0.509(8)\sqrt{\mu}/(1 + 2.3\sqrt{\mu})$, it follows that $G_1 = G_2 = G$, and $G_3 = 1$. Values of μ were obtained in the usual way from the known $[\mathrm{SO}_4^=]$.

Now, from (4), since in the present systems $[\Sigma\mathrm{U}] << [\mathrm{SO}_4^=]$, we have

$$\frac{[\mathrm{UO}_2^{++}]}{[\Sigma\mathrm{U}]} = \frac{EG}{K'K_{a1}[\mathrm{SO}_4^=]} = \frac{aEG}{[\mathrm{SO}_4^=]}$$

$$\frac{[\mathrm{UO}_2(\mathrm{SO}_4)_2^=]}{[\Sigma\mathrm{U}]} = \frac{K_{a2}E[\mathrm{SO}_4^=]}{K_{a1}K'} = cE[\mathrm{SO}_4^=] \qquad (6)$$

and

$$\frac{[\mathrm{UO}_2(\mathrm{SO}_4)_3^{-4}]}{[\Sigma\mathrm{U}]} = \frac{K_{a3}EG[\mathrm{SO}_4^=]^2}{K_{a1}K'} = dEG[\mathrm{SO}_4^=]^2$$

where the constants are all now independent of ionic strength. Summing (4) and (6), the left side becomes unity; dividing through by E we obtain

$$\frac{1}{E} = \frac{aG}{[\mathrm{SO}_4^=]} + b + c[\mathrm{SO}_4^=] + dG[\mathrm{SO}_4^=]^2 \qquad (7)$$

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(12) K. A. Kraus and F. Nelson, Paper No. P/837, International Conference on the Peaceful Uses of Atomic Energy, Geneva, June 23, 1955.

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

(14) C. F. Baes, Jr., THIS JOURNAL, **79**, 5611 (1957).

(15) It is realized that (5) is at best only a good approximation. In systems which lend themselves to determinations of the concentrations of the individual species, it is sometimes possible to use expressions of the form

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

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 employ only the limiting term, accepting the probability that at the higher ionic strengths the approximation to the activity coefficient ratio G becomes poorer.

(16) K. A. Kraus and F. Nelson, THIS JOURNAL, **72**, 3901 (1950).

(17) 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 Nelson[12] and the 6 Å. used by R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941), for similar electrolytes.

Values of a, b and c were obtained by a repetitive process of plotting $1/E - c[SO_4^=]$ vs. $G/[SO_4^=]$ and $1/E - aG/[SO_4^=]$ vs. $[SO_4^=]$, with normalization of the $1/E$ values at the high and low acid activities to those at the intermediate level, allowing final plots on which all three sets of data were combined. Figure 6 shows the final plot for b and c.[18] The plot for a showed considerably more scatter, but here, since the intercept b was known from Fig. 6, greater weight could be given to the high values of $G/[SO_4^=]$, and it was possible to assign a value to a, with a rather wide range of uncertainty. Finally, the quantity $1/E - aG/[SO_4^=] - c[SO_4^=]$ was plotted against $G[SO_4^=]^2$ to obtain an estimate of d. The scatter here was worse than for a; again, however, the known intercept b allowed an estimate of an upper limit for the slope d: all of the points fell below a line for which $d = 0.02$. Back calculations using this maximum value of d showed that the resulting changes in a, b and c were negligible.

The results of least squares analyses of the data 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.[19] The following numbers are thus shown with the associated range of deviation within which corresponding numbers obtained from similar sets of data could be expected to fall nine times out of ten

$$\begin{aligned} a &= 0.00058 \pm 0.00042 \\ b &= 0.335 \pm 0.033 \\ c &= 2.00 \pm 0.11 \end{aligned} \qquad (8)$$

In Table II the values of K_{a1}, K_{a2}, etc., calculated from equations 4, 6 and 8 are presented together with corresponding values of these constants obtained by Ahrland.[20]

The constants 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 equation 5. 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°, while the present data were obtained at 25°. With some knowledge of the appropriate heats of reaction this temperature difference might be corrected for; however, in view of the spreads exhibited in Table II, 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 II 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 one.

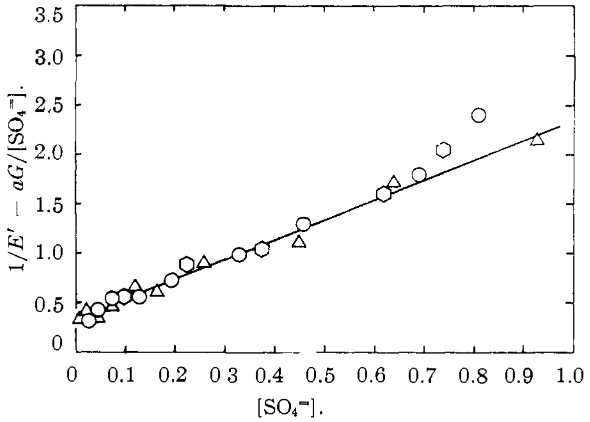

Fig. 6.—$1/E' - aG/[SO_4^=]$ vs. $[SO_4^=]$ for final values of b and c: △, $a_{H_2SO_4} = 3.5 \times 10^{-6}$; ○, $a_{H_2SO_4} = 4.7 \times 10^{-5}$; ⬡, $a_{H_2SO_4} = 3.0 \times 10^{-4}$.

TABLE II

FORMATION CONSTANTS OF THE URANYL SULFATE COMPLEXES

	This paper TOA extraction data[a]	Ahrland[20] Potentiometric	Ahrland[20] Spectrophotometric
	A. $\mu = 0, G = 1$		
K_{a1}	580 (300–2300)	860 ± 170	960 ± 100
K_{a2}	3450 (1900–13000)	6000 ± 2600	7700 ± 860
K_3	(0–125)	2500 ± 1000	$K_3 << 2500$
K_2/K_1	6.0 ± 1.0	7 (3.3–12.5)	8 (6.5–10)
	B. $\mu = 1, G = 17.1$		
K_1	34 (17–135)	50 ± 10	56 ± 6
K_2	200 (100–760)	350 ± 150	450 ± 50
K_3	(0–125)	2500 ± 1000	$K_3 << 2500$
K_2/K_1	6.0 ± 1.0	7 (3.3–12.5)	8 (6.5–10)

[a] The numbers given in parentheses represent the low and high values obtained on substituting the corresponding values of the constants minus or plus their associated deviations shown in (8); e.g., K_{a1} (low) = (0.335 − 0.033)/(0.0058 + 0.00042), K_{a1} (high) = (0.335 + 0.033)/(0.00058 − 0.00042), etc.

IV. **Acknowledgments.**—The experimental work described in this paper was done by G. N. Case of this Laboratory, and the author wishes to express appreciation for the contributions made through helpful discussions with W. J. McDowell, C. F. Baes, Jr., and C. F. Coleman.

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[18] The E values of Fig. 5 were divided by 1000 before making these plots, for more convenient numerical handling.

[19] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 42, 43, 119.

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