

formed from  $M(\text{acac})_3$  can be rationalized, although the results could be complicated by structural rearrangement (*e.g.*, to square-planar or tetrahedral ions). It is perhaps worth noting for  $\text{Al}(\text{acac})_3$  in which little or no  $\pi$  interaction between metal and ligand is expected that the appearance potential of  $\text{Al}(\text{acac})_2^+$  is only 1.1 V higher than that of  $\text{Al}(\text{acac})_3^+$ .

There are several additional pieces of evidence which suggest that the nature of the ligand has a far greater effect than the metal on the appearance potentials of the metal chelates. First, the metal trifluoroacetylacetonates<sup>15</sup> have appearance potentials about 1 V higher and the hexafluoroacetylacetonates about 2 V higher than

(15) G. M. Bancroft, C. Reichert, and J. B. Westmore, submitted for publication.

the corresponding acetylacetonates.<sup>15</sup> Second, in a series of 3-substituted acetylacetonates of chromium<sup>15</sup> the difference in appearance potential between the  $\text{NO}_2^-$  and the Br-substituted chelate is about 0.5 V.

Our experimental results, therefore, do not agree with Barnum's simple theoretical calculations. Owing to lack of a large body of experimental data, knowledge of the ionization process in inorganic complexes is very limited and we are pursuing further research on these and related compounds. It is hoped that these results will stimulate more theoretical work on these compounds.

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ROCKY FLATS DIVISION, GOLDEN, COLORADO 80401

## Sulfamate Complexes of Plutonium(IV)<sup>1</sup>

By J. M. CLEVELAND

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Spectrophotometric studies indicate that plutonium(IV) is complexed by sulfamate ion but give no evidence of sulfamate complexes of plutonium(III) and plutonyl(VI). From the influence of sulfamate concentration on the plutonium(IV) spectrum, the stability constant of the monosulfamate complex of plutonium(IV) was calculated to be  $1.3 \pm 0.4$  at 23°. Spectra of solutions containing predominantly the monosulfamate complex were changed significantly by the addition of sulfamic acid, indicating the formation of a mixed sulfamate-sulfamic acid complex of plutonium(IV), or the interaction of sulfamic acid with sulfamate ion thereby decreasing the concentration of the monosulfamate complex. The latter reaction was verified by determining the solubility of sulfamic acid in ammonium sulfamate and ammonium nitrate solutions, but the extent of interaction ( $K = 0.3$ ) was insufficient to account fully for the spectral changes observed. Hence it is concluded that mixed sulfamate-sulfamic acid complexes of plutonium(IV) are formed in solutions containing appreciable concentrations of sulfamate ion and sulfamic acid.

Sulfamic acid is an acid of moderate strength, with an ionization constant of 0.10 at 25°. An early suggestion<sup>2</sup> that sulfamic acid exists in the solid form as the zwitterion is supported by X-ray crystallographic data and by the relatively high melting point of the solid.<sup>4</sup> Despite a previous statement to the contrary,<sup>3</sup> there is evidence from the entropy of ionization<sup>5</sup> and non-aqueous solvent studies<sup>6</sup> that the acid also exists in solution as the zwitterion.

Sulfamic acid solution has found practical application as a solvent for plutonium metal,<sup>7</sup> but there has been very little investigation of the chemistry of plutonium in sulfamate solution. This paper describes spectrophotometric studies of plutonium complexes in

aqueous sulfamate media. These data suggest an interaction between sulfamic acid and sulfamate ion, and this interaction was investigated by determining the solubility of sulfamic acid in ammonium sulfamate and ammonium nitrate solutions of various concentrations.

### Experimental Section

The plutonium(III) solutions used in this study were prepared by dissolution of plutonium metal in 5–6 *M* perchloric acid. Plutonium(IV) was prepared by oxidation of plutonium(III) with ozone, and plutonyl(VI) was made by fuming a perchloric acid solution of plutonium(III). In each case the presence of only the desired oxidation state of plutonium in appreciable concentration was verified spectrophotometrically.

Reagent grade sulfamic acid was used without further purification. The limited solubility and dissociation of sulfamic acid required the use of ammonium sulfamate to obtain the sulfamate concentrations necessary for this study. Since commercially available ammonium sulfamate was found to contain sulfate, this salt was prepared by the room-temperature evaporation of a sulfamic acid solution neutralized with ammonium hydroxide.

When necessary, lithium perchlorate was used to maintain constant ionic strength. This salt, obtained from G. Frederick Smith Chemical Co., was recrystallized four times before use.

Solubility measurements were made by sealing an excess of

(1) Work performed for the U. S. Atomic Energy Commission under Contract AT(29-1)-1106.

(2) (a) E. G. Taylor, R. P. Desch, and A. J. Catotti, *J. Am. Chem. Soc.*, **73**, 74 (1951); (b) E. J. King and G. W. King, *ibid.*, **74**, 1212 (1952).

(3) P. Baumgarten, *Ber.*, **62**, 820 (1929).

(4) F. A. Kanda and A. J. King, *J. Am. Chem. Soc.*, **73**, 2315 (1951).

(5) H. P. Hopkins, Jr., C. H. Wu, and L. G. Hepler, *J. Phys. Chem.*, **69**, 2244 (1965).

(6) R. A. Hovermate and P. G. Sears, *ibid.*, **60**, 1579 (1956).

(7) W. J. Jenkins, *J. Inorg. Nucl. Chem.*, **25**, 463 (1963).

sulfamic acid, along with solutions with the desired concentration of ammonium sulfamate or ammonium nitrate, in glass bottles and immersing in a constant-temperature bath at  $25 \pm 0.1^\circ$  for 16 hr. During this period the contents of the bottles were agitated continuously by magnetic stirring. At the end of this period the undissolved solid was allowed to settle for 1 hr, still at constant temperature, after which aliquots of solution were titrated with standard base to determine their sulfamic acid concentrations. The bottles were resealed and the solutions stirred for an additional 4 hr to ensure that equilibrium solubility had been attained. In every case the sulfamic acid concentration after the second stirring period was within 0.02 *M* of the value obtained after the first stirring period, from which it was concluded that equilibrium solubility had been achieved.

All spectra were determined at  $23 \pm 3^\circ$  on a Cary Model 14 recording spectrophotometer. Because of the low acidity in some of the plutonium(IV) solutions there was as much as 50% disproportionation of plutonium(IV) to plutonyl(VI) and plutonium(III). To correct for this decrease in the plutonium(IV) concentration, which was occurring during the run, the plutonyl(VI) was monitored at  $831 \text{ m}\mu$  ( $a = 550^8$ ) and the plutonium(III) at  $600 \text{ m}\mu$  ( $a = 38^8$ ). From these absorbances the concentrations of the species were calculated and subtracted from the total plutonium concentration to obtain the plutonium(IV) concentrations. These values were then used to calculate the plutonium(IV) molar absorptivities reported in the spectra.

### Results

The spectra of plutonium(III) and plutonyl(VI) in 2 *M* perchloric acid in the 400–1200- $\text{m}\mu$  wavelength range are not changed appreciably by the presence of sulfamate ion up to a stoichiometric concentration of 4 *M*, and these systems were not investigated further. It would be premature to conclude that no plutonium(III) complexes were formed however, since—as in the plutonium(III)–chloride system<sup>9</sup>—the spectrum in this wavelength range is not necessarily influenced by complex formation. The apparent absence of plutonyl(VI) complexes is consistent with polarographic and spectrophotometric evidence that uranyl(VI) is not complexed by sulfamate ion.<sup>10</sup>

The spectra of plutonium(IV) in the 400–500- $\text{m}\mu$  range at various sulfamate concentrations and approximately constant sulfamic acid concentration are shown in Figure 1. With increasing sulfamate concentration there is a steady decrease in the aquoplutonium(IV) absorption peak at  $470 \text{ m}\mu$  and an increase in a new, broad peak at  $455 \text{ m}\mu$ , indicating sulfamate complexing. There are isosbestic points at 466 and  $483 \text{ m}\mu$  up to a sulfamate ion concentration of about 1 *M*, indicating the presence of only two spectrophotometrically distinguishable species—presumably the aquoplutonium(IV) ion and the monosulfamate complex—in this concentration range. Above a sulfamate concentration of 1 *M* the  $455\text{-m}\mu$  peak continues to increase, but the spectra no longer pass through the isosbestic points, suggesting that more than two species are present at these concentrations.

Spectra were run for solutions 4 and 9 in Figure 1 at different plutonium(IV) concentrations (in the 0.005–0.013 *M* range) to determine whether the  $455\text{-m}\mu$

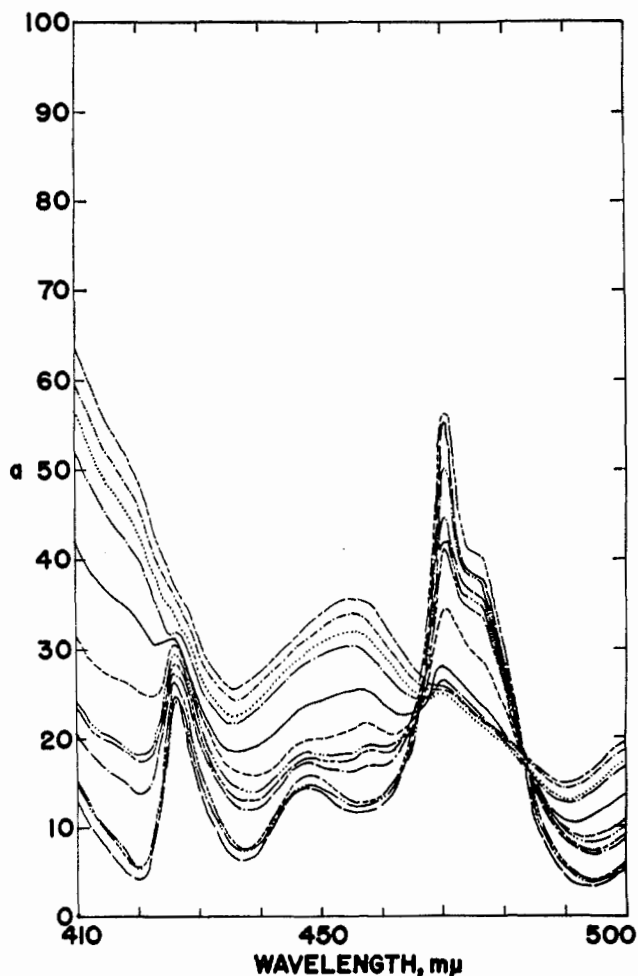
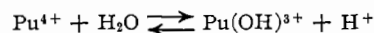


Figure 1.—Spectra of plutonium(IV) at various sulfamate ion concentrations and approximately constant sulfamic acid concentration. Total [Pu] = 0.016 *M*; *I* = 2.1 *M* (based on an assumed ionization constant of 0.2 for sulfamic acid). (Only solutions 1–5, which contain greater than 80% of the plutonium(IV) in the unhydrolyzed form, were used in the calculations.): (1) ———, 0.8 *M* HClO<sub>4</sub>, 1.3 *M* LiClO<sub>4</sub>; (2) - - - - -, 0.53 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 1.29 *M* HClO<sub>4</sub>, 0.71 *M* LiClO<sub>4</sub>; (3) ·····, 0.63 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.86 *M* HClO<sub>4</sub>, 1.04 *M* LiClO<sub>4</sub>; (4) - · - · - ·, 0.73 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.72 *M* HClO<sub>4</sub>, 1.08 *M* LiClO<sub>4</sub>; (5) - · - · - ·, 0.83 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.65 *M* HClO<sub>4</sub>, 1.05 *M* LiClO<sub>4</sub>; (6) - - - - -, 0.93 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.60 *M* HClO<sub>4</sub>, 1.00 *M* LiClO<sub>4</sub>; (7) - - - - -, 1.03 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.57 *M* HClO<sub>4</sub>, 0.93 *M* LiClO<sub>4</sub>; (8) ———, 1.23 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.54 *M* HClO<sub>4</sub>, 0.76 *M* LiClO<sub>4</sub>; (9) - · - · - ·, 1.42 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.50 *M* HClO<sub>4</sub>, 0.60 *M* LiClO<sub>4</sub>; (10) ·····, 1.63 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.50 *M* HClO<sub>4</sub>, 0.40 *M* LiClO<sub>4</sub>; (11) - · - · - ·, 1.84 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.50 *M* HClO<sub>4</sub>, 0.20 *M* LiClO<sub>4</sub>; (12) - - - - -, 2.04 *M* NH<sub>4</sub>SO<sub>3</sub>NH<sub>2</sub>, 0.50 *M* HClO<sub>4</sub>.

and  $470\text{-m}\mu$  peaks obey the Beer–Lambert law. The absorbance of both the  $455\text{-m}\mu$  and  $470\text{-m}\mu$  peaks was proportional to the plutonium(IV) concentration within 15%, a reasonable agreement in view of the concentration uncertainties resulting from the disproportionation of plutonium(IV).

To determine whether the spectral changes observed were due to hydrolysis of plutonium(IV)



spectra were determined of solutions containing equal concentrations of plutonium(IV) but with acidities varying from 1 to 0.06 *M*, the latter acidity being com-

(8) D. Cohen, *J. Inorg. Nucl. Chem.*, **18**, 207 (1961).

(9) M. Ward and G. A. Welch, *ibid.*, **2**, 395 (1956).

(10) O. Tubertini, M. Bettoli, and G. Bertocci, *Ann. Chim. (Rome)*, **57**, 555 (1967); see *Chem. Abstr.*, **67**, 70,184 (1967).

parable to the most weakly acid solutions in Figure 1. Values of light absorption at 470 and 455  $m\mu$  as a function of acidity and plutonium(IV) concentration are (given as  $[H^+]$ ,  $[Pu(IV)]$ ,  $a_{470}$ ,  $a_{455}$ ): 1.0, 0.018, 55, 13; 0.19, 0.0018, 51, 16; 0.06, 0.0016, 34, 15. (Cell path lengths were chosen to give absorbance values in the 0.5–1.0 range for the 470- $m\mu$  peak; the resulting absorbances at 455  $m\mu$  were in the range 0.2–0.4.) The decrease in the 470- $m\mu$  peak is caused by a reduction in the plutonium(IV) concentration due to hydrolysis. This decrease, however, is not as great as that shown in the spectra in Figure 1; moreover, there is no evidence for a new peak at 455  $m\mu$  with decreasing acidity. Hence it is concluded that the significant spectral changes of Figure 1 are not caused by hydrolysis.

If the sulfamic acid concentration is increased and the sulfamate ion concentration held approximately constant, the spectrum becomes more similar to that of aquoplutonium(IV); *i.e.*, the 455- $m\mu$  peak decreases, and the 470- $m\mu$  peak increases, as shown in Figure 2. There are differences from the aquoplutonium(IV) spectrum, however, *viz.*, the diminished height of the 470- $m\mu$  peak and the appearance of a discrete secondary peak at 476  $m\mu$ . This observation may be partially due to interaction between sulfamate ion and sulfamic acid, thus lowering the free sulfamate ion concentration and thereby decreasing the concentration of the plutonium(IV) sulfamate complex. The changes may also be caused by interaction between plutonium(IV) (or its monosulfamate complex) and sulfamic acid to form a new species responsible for the 476  $m\mu$  peak. To investigate the plutonium(IV)–sulfamic acid interaction, spectra of plutonium(IV) in various concentrations of sulfamic acid were determined under conditions that suppressed its ionization to form sulfamate ion. These spectra are shown in Figure 3.

The possibility of sulfamic acid–sulfamate ion interaction was investigated by determining the solubility of sulfamic acid in ammonium sulfamate and ammonium nitrate solutions. These results are in Table I.

TABLE I  
SOLUBILITY OF SULFAMIC ACID IN AMMONIUM NITRATE AND AMMONIUM SULFAMATE SOLUTIONS AT  $25.0 \pm 0.1^\circ$

$[NH_4NO_3], M$	Sulfamic acid solubility, $M$	$[NH_4SO_3NH_2], M$	Sulfamic acid solubility, $M$
0	2.15	0	2.15
0.09	2.16	0.09	2.14
0.27	2.20	0.27	2.12
0.91	2.33	0.91	2.12
1.35	2.37	1.35	2.12
1.80	2.43	1.80	2.16

### Discussion

The spectra in Figure 1 show a significant change with increasing sulfamate concentration, indicating the formation of one or more sulfamate complexes of plutonium(IV). The failure of spectra 7–12 to pass through the isosbestic points at 466 and 483  $m\mu$  may be due either to the presence of a second sulfamate complex

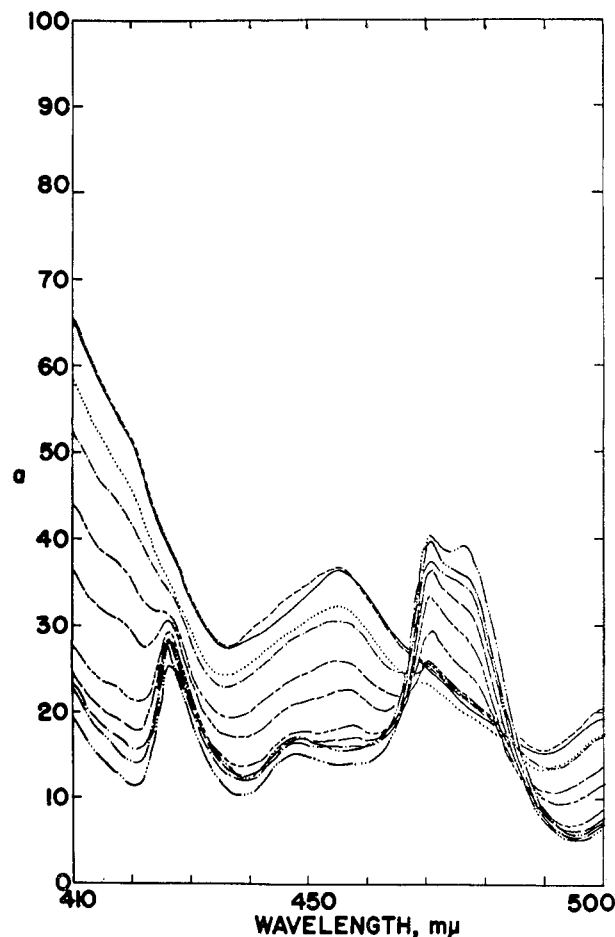


Figure 2.—Spectra of plutonium(IV) at various sulfamic acid concentrations and approximately constant sulfamate ion concentration. Total  $[Pu] = 0.016 M$ ;  $I = 2.1 M$  (based on an assumed ionization constant of 0.2 for sulfamic acid). (Only solutions 8–11 contain greater than 80% of the plutonium(IV) in the unhydrolyzed form): (1) —, 1.1  $M NH_4SO_3NH_2$ , 0.12  $M HClO_4$ , 0.98  $M LiClO_4$ ; (2) ---, 1.2  $M NH_4SO_3NH_2$ , 0.24  $M HClO_4$ , 0.86  $M LiClO_4$ ; (3) ····, 1.3  $M NH_4SO_3NH_2$ , 0.36  $M HClO_4$ , 0.74  $M LiClO_4$ ; (4) —·—, 1.4  $M NH_4SO_3NH_2$ , 0.48  $M HClO_4$ , 0.62  $M LiClO_4$ ; (5) —·—, 1.5  $M NH_4SO_3NH_2$ , 0.60  $M HClO_4$ , 0.50  $M LiClO_4$ ; (6) —·—, 1.6  $M NH_4SO_3NH_2$ , 0.72  $M HClO_4$ , 0.38  $M LiClO_4$ ; (7) —·—, 1.8  $M NH_4SO_3NH_2$ , 0.96  $M HClO_4$ , 0.14  $M LiClO_4$ ; (8) —·—, 1.76  $M NH_4SO_3NH_2$ , 0.24  $M HSO_3NH_2$ , 0.96  $M HClO_4$ , 0.14  $M LiClO_4$ ; (9) —·—, 1.72  $M NH_4SO_3NH_2$ , 0.48  $M HSO_3NH_2$ , 0.96  $M HClO_4$ , 0.14  $M LiClO_4$ ; (10) —·—, 1.68  $M NH_4SO_3NH_2$ , 0.72  $M HSO_3NH_2$ , 0.96  $M HClO_4$ , 0.14  $M LiClO_4$ ; (11) —·—, 1.64  $M NH_4SO_3NH_2$ , 0.96  $M HSO_3NH_2$ , 0.96  $M HClO_4$ , 0.14  $M LiClO_4$ .

in these solutions or to the presence of an appreciable concentration of the hydrolyzed species,  $Pu(OH)^{3+}$ . A measure of the extent of hydrolysis may be obtained from the variation of the absorbance of the 470- $m\mu$   $Pu^{4+}$  peak with acidity, the plutonium(IV) concentration being held constant. With the assumption that the hydrolyzed species,  $Pu(OH)^{3+}$ , does not absorb appreciably at 470  $m\mu$ , values of

$$K_h = \frac{[Pu(OH)^{3+}][H^+]}{[Pu^{4+}]}$$

were calculated to be 0.033 and 0.011 in 0.06 and 0.19  $M$  perchloric acid, respectively. These values compare

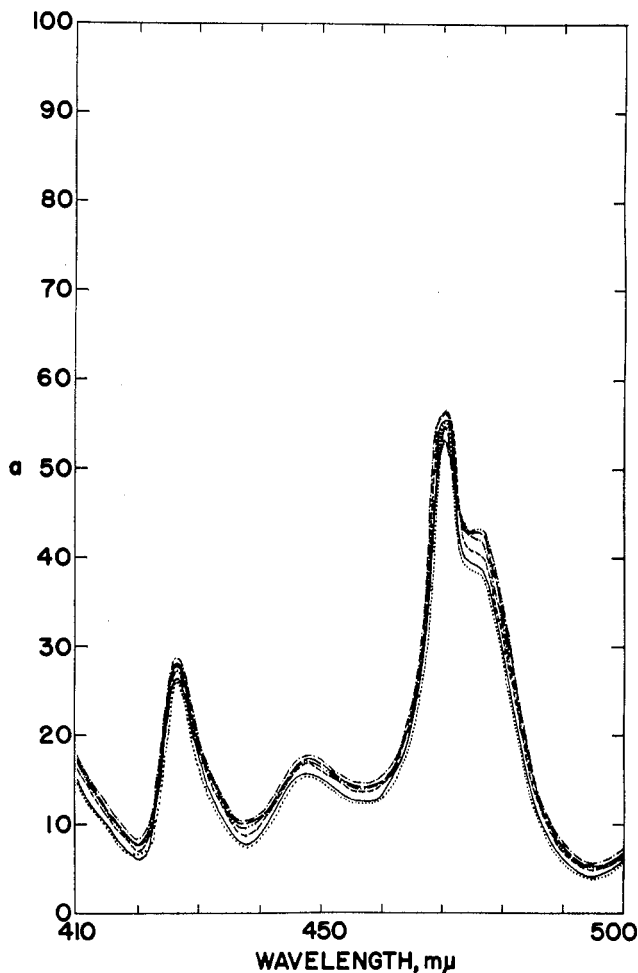


Figure 3.—Spectra of plutonium(IV) at various sulfamic acid concentrations and negligible sulfamate ion concentration. Total  $[Pu] = 0.016 M$ : (1)  $\cdots$ ,  $1.0 M HClO_4$ ; (2)  $—$ ,  $0.1 M HSO_3NH_2$ ,  $1.0 M HClO_4$ ; (3)  $---$ ,  $0.3 M HSO_3NH_2$ ,  $1.0 M HClO_4$ ; (4)  $- \cdot -$ ,  $0.6 M HSO_3NH_2$ ,  $1.0 M HClO_4$ ; (5)  $—$ ,  $1.0 M HSO_3NH_2$ ,  $1.0 M HClO_4$ ; (6)  $- \cdot - \cdot -$ ,  $1.4 M HSO_3NH_2$ ,  $1.0 M HClO_4$ .

with a  $K_b$  of 0.019 reported by Rabideau and Kline<sup>11</sup> in perchlorate solutions of ionic strength 0.5 at  $25^\circ$ , reasonable agreement in view of the assumption made in the present calculation and the differences in ionic strength.

Although the lack of ionization constant data for sulfamic acid in solutions of  $2.1 M$  ionic strength and the quantitative uncertainties in the spectra preclude precise calculations, it is possible to obtain an approximate value for the stability constant

$$K = \frac{[Pu(SO_3NH_2)^{3+}]}{[Pu^{4+}][^-SO_3NH_2]}$$

Calculations were based on the effect of various sulfamate ion concentrations on the intensity of the  $470\text{-m}\mu$  peak, by substituting the appropriate absorptivities and concentrations into the above equation. The following assumptions were made: (a) The monosulfamate complex is the species responsible for the spectral changes in Figure 1 and is the only complex species present in appreciable concentration. (b) The

(11) S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **64**, 680 (1960).

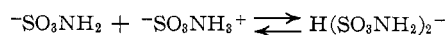
ionization constant of sulfamic acid in solutions of  $2.1 M$  ionic strength is 0.2. (This value was estimated from the variation in ionization constant of other moderately strong electrolytes with ionic strength.) (c) The  $470\text{-m}\mu$  peak obeys the Beer-Lambert Law.

To minimize uncertainties due to hydrolysis, calculations were based solely on solutions (1-5) containing greater than 80% of the plutonium(IV) in the unhydrolyzed form. In the hydrolysis calculations a value for  $K_b$  of 0.054 for plutonium(IV) at ionic strength 2.0 and at  $25^\circ$  was used.<sup>12</sup>

Since the molar absorptivity of the monosulfamate complex at  $470\text{ m}\mu$  is not known, a value must be assumed. By extrapolation of the spectra in Figure 1, two reasonable molar absorptivities—22 and 15—were chosen, and calculations were made with both values, so that a range for  $K$  could be estimated. Calculated values of  $K$  varied from 0.9 to 1.6, leading to an approximate value for  $K$  of  $1.3 \pm 0.4$  at  $23 \pm 3^\circ$ . This stability constant is comparable to those for other complexes of plutonium(IV) with univalent anions<sup>13</sup> ( $PuCl^{3+}$ ,  $K = 1.4$ ;  $Pu(NO_3)^{3+}$ ,  $K = 5.5$ , both values at  $20^\circ$ ).

Any interaction between sulfamic acid and sulfamate ion to form a new protonated dimeric species  $[H(SO_3NH_2)_2^-]$ —in a manner analogous to the interaction between carboxylic acids and their anions<sup>14</sup>—should cause an enhancement of the solubility of sulfamic acid in the presence of ammonium sulfamate. No conclusion can be drawn from a cursory examination of the data in Table I without considering the variation in the activity coefficients of hydrogen ion and sulfamate ion with ionic strength. These data are not available, so it is necessary to make the following assumptions: (a) The product of the activity coefficients of hydrogen ion and sulfamate ion in a solution of a given ionic strength is equal to the square of the activity coefficient of sodium nitrate in a solution of the same ionic strength. (The choice of an alkali metal nitrate was dictated by the availability of the necessary activity coefficient data.<sup>15</sup> Sodium nitrate was chosen because its values were intermediate between the extremes for the alkali metal nitrates.) (b) The activity coefficient of undissociated sulfamic acid is independent of ionic strength. (c) The activity coefficients of sulfamate ion and the dimeric anion hydrogen disulfamate are equal.

Calculations based on the data in Table I were made to obtain a quantitative measure of the sulfamate-sulfamic acid interaction, represented by the equation



$$K' = \frac{[H(SO_3NH_2)_2^-]}{[^-SO_3NH_2][^-SO_3NH_2]}$$

The concentration of sulfamate ion is related to that of hydrogen ion by the equilibrium

(12) S. W. Rabideau, *J. Am. Chem. Soc.*, **79**, 3675 (1957).

(13) I. Grenthe and B. Noren, *Acta Chem. Scand.*, **14**, 2216 (1960).

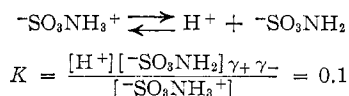
(14) D. L. Martin and F. J. C. Rossotti, *Proc. Chem. Soc.*, 60 (1959).

(15) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1950, p 563.

TABLE II  
 CONCENTRATIONS OF SPECIES AND  $K_{sp}$  CALCULATED ASSUMING  $K' = 0.3^a$ 

Electrolyte conc	NH <sub>4</sub> NO <sub>3</sub>					NH <sub>4</sub> SO <sub>3</sub> NH <sub>2</sub>				
	[H <sup>+</sup> ]	[-SO <sub>3</sub> NH <sub>2</sub> ]	[HSO <sub>3</sub> NH <sub>2</sub> ]	[H(SO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> <sup>-</sup> ]	$K_{sp}$	[H <sup>+</sup> ]	[-SO <sub>3</sub> NH <sub>2</sub> ]	[HSO <sub>3</sub> NH <sub>2</sub> ]	[H(SO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> <sup>-</sup> ]	$K_{sp}$
0	10 <sup>-7</sup>	0	0	0	0.12	10 <sup>-7</sup>	0	0	0	0.12
0.09	0.71	0.51	1.25	0.20	0.12	0.67	0.54	1.25	0.22	0.12
0.27	0.74	0.53	1.25	0.21	0.12	0.61	0.62	1.25	0.26	0.12
0.91	0.83	0.58	1.25	0.25	0.12	0.46	0.96	1.25	0.41	0.12
1.35	0.87	0.62	1.25	0.25	0.12	0.38	1.24	1.25	0.49	0.12
1.80	0.90	0.62	1.25	0.28	0.13	0.33	1.55	1.25	0.58	0.12

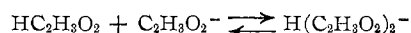
<sup>a</sup> All concentrations are given in molarity.



A method of successive approximations was employed to determine the value of  $K'$ . Various values of  $K'$  were assumed and the  $[\text{H}^+]$  necessary to satisfy them were calculated. The resulting values of  $[\text{H}^+]$  and  $[\text{-SO}_3\text{NH}_2]$  were then substituted, along with activity coefficients, into the solubility product expression

$$K_{sp} = [\text{H}^+][\text{-SO}_3\text{NH}_2]^{\gamma_+ \gamma_-}$$

As shown in Table II, essentially constant values of  $K_{sp}$  were obtained when  $K'$  was assumed to be 0.3. It is noteworthy that this value is close to the equilibrium constant of 0.46 found for the corresponding reaction with acetic acid<sup>14</sup>



Such a low value of  $K'$ , however, cannot explain the large changes in spectrum shown in Figure 2. The differences between spectrum no. 11 in Figure 2, corresponding to the highest sulfamic acid concentration, and the spectrum of aquoplutonium(IV) (spectrum no. 1 in Figure 1) also indicate that the changes observed in Figure 2 cannot be explained entirely on the basis of a lowered concentration of complex caused by sul-

famate-sulfamic acid interaction. Similarly, the spectra in Figure 3 indicate that sulfamic acid—in the absence of an appreciable sulfamate ion concentration—produces slight changes in the plutonium(IV) spectrum that suggest plutonium(IV)-sulfamic acid interaction but are not great enough to explain the large changes observed in the spectra of Figure 2. It would appear, therefore, that the changes observed in Figure 2 are primarily due not to formation of a plutonium(IV)-sulfamic acid complex, nor to the dissociation of the sulfamate complexes of plutonium(IV), but rather to the formation of a plutonium(IV) sulfamate-sulfamic acid complex—or protonated sulfamate complex—whose spectrum is more similar to that of aquoplutonium(IV) than to the spectra of the unprotonated complexes shown in Figure 1.

In summary, it appears that plutonium(IV) is complexed by sulfamate ions and also by sulfamic acid. In mixtures of sulfamate ion and sulfamic acid, a mixed complex is formed whose spectrum is more similar to that of aquoplutonium(IV) than to the spectrum of the plutonium(IV)-sulfamate species.

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