

TABLE I
CALCULATED "INDUCTIVE" SUBSTITUENT CONSTANTS AND
RELATED P=N STRETCHING VIBRATIONS OF $X_3P_3N_3$

X	σ_I	$\nu_{P=N}, \text{cm}^{-1}$
CH ₃	-0.05	1180
C ₆ H ₅	0.10	1190
C ₆ F ₅	0.23 ^a	1200
CF ₃	0.30	1205

^a Determined from plot of σ_I vs. $\nu_{P=N}$.

The infrared absorption spectra of the bis(pentafluorophenyl)phosphonitriles display a strong band at 1200 cm^{-1} in the case of the trimer and broad medium bands in the same region for the amorphous material.

It is interesting to note the comparison of the "inductive" substituent constants¹⁷ on the P_3N_3 nucleus with their respective P=N absorptions.¹⁸ These data are listed in Table I.

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Synergistic Effect of Tri-*n*-octylamine on the Solvent Extraction of Americium by Thenoyltrifluoroacetone¹

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The synergistic effect of tri-*n*-octylamine (R_3N) on the solvent extraction of americium by thenoyltrifluoroacetone (HT) is shown to arise from organic phase reactions $AmT_3 + R_3NHCl = AmT_3R_3NHCl$, $AmT_3 + R_3NHT = AmT_3R_3NHT$, and $AmT_3 + R_3NHClHT = AmT_3R_3NHClHT$, where T^- represents the enolate ion of HT. It was ascertained that the formation constants for each of these reactions are the same. The formation constants were measured in benzene as $\log K_s = 5.03 \pm 0.20$. The formation constant for the addition reaction $AmT_3 + HT = AmT_3HT$ was measured as $\log K_{Am,HT} = 0.75 \pm 0.05$. Reasons are presented which lead to the conclusion that in the products of synergism each of the amine species is attached directly to the americium. The synergistic effect was studied for values of pH which were varied from 1.1 to 5.7.

Introduction

The synergistic effect of tri-*n*-octylamine (TNOA) on the solvent extraction of thorium by thenoyltrifluoroacetone (TTA) has already been studied.² Throughout this paper R_3N represents TNOA and T^- the enolate ion of TTA. Only R_3NHCl was found to cause a synergistic effect. Since TTA coordinately saturates the thorium it is difficult to understand how the bond is formed between the ThT_4 and the R_3NHCl . Americium(III) was selected for this work in order to study the nature of the synergistic effect exerted by TNOA on an element which is possibly coordinately unsaturated by TTA. The object of this investigation was, therefore, to determine which species of the amine can cause the synergistic effect, the values of the equilibrium constants involved, and the nature of the species formed.

Experimental Section

The source and purification of TTA and TNOA have previously been described.³ Americium (Am^{241}) was obtained from Oak Ridge National Laboratory. It was found to be free of γ -emitting contaminants in the energy range of 0 to 1.5 Mev. All

other chemicals used were of reagent grade. The stock lithium chloride solutions were filtered prior to use.

In all experiments, the aqueous phase consisted of 2 *M* LiCl except for one series which was 0.01 *M* in chloride. The organic diluent was benzene. The distribution experiments were performed with equal volumes. The activity of the americium in the aqueous phase prior to contact was $\sim 5 \times 10^4$ counts min^{-1} ml^{-1} .

A titration technique was adopted in which, for a given experiment, the TTA and TNOA concentrations were maintained constant in the organic phase and the pH of the aqueous phase was increased by the addition of alkali. The experiments were conducted in a stoppered cylindrical glass vessel which accommodated a glass electrode, a buret with an elongated tip, and a glass "dip" tube employed for taking aliquots from the aqueous (lower) phase. Aliquots from the organic phase were taken directly through a hole in the stopper. The phases were mixed by employing a magnetic stirrer. After equilibration (~ 10 min) the solutions were allowed to separate, and 2-ml aliquots taken from both phases were γ counted in a "well-type" scintillation counter. Then another addition of alkali was made. The volume of the organic phase was kept equal to the aqueous by the addition of a corresponding amount of the original organic solution. Equilibrium was ascertained by contacting for longer periods of time and by performing a reverse titration.

The free TTA concentration was kept constant by accounting for the amount consumed in reaction with the amine. The constants involved and the method employed have been described.² Although the form of the bound TTA was changed when varying the hydrogen ion concentration, the over-all excess needed remained relatively constant. The amount of

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. Newman and P. Klotz, *J. Phys. Chem.*, **67**, 205 (1963).

(3) L. Newman and P. Klotz, *ibid.*, **65**, 796 (1961).

TNOA and TTA consumed by reaction with the americium was negligible. An initial equilibrium between the TNOA, TTA, and HCl was established by precontacting the organic solutions with an aqueous phase representing the initial conditions but excluding americium.

The course of the titration was followed with a Radiometer Model 4 pH meter in conjunction with the Radiometer combined electrode. The glass electrode was calibrated from the known concentration of acid in the original solution. The electrode drift was found to be insignificant and measurements were reproducible to better than 0.005 pH unit. The titration vessel was also used for the experiments where the TTA or TNOA were varied. The concentration was changed by adding given amounts of concentrated organic stock solutions. A corresponding volume of aqueous solution was added containing enough acid or base to compensate for any slight changes in potential.

Characteristics of the TTA Extraction

In order to elucidate the nature of the synergistic effect of TNOA on the solvent extraction of americium by TTA properly, it is first necessary to determine the parameters of the TTA extraction. The extraction of americium by R_3N is negligible, $D < 10^{-4}$, for all conditions employed in this paper.

The extraction of americium by TTA should be governed by the equilibrium

$$K_{Am} = \frac{(AmT_3)(H^+)^3}{(Am^{3+})(HT)^3} \quad (1)$$

where HT stands for TTA. In this and all subsequent equations, the charged species are in the aqueous phase and uncharged species in the benzene phase. As is sometimes the case with TTA extractions⁴ an additional compound can be formed so that an additional equilibrium has to be considered.

$$K_{Am,HT} = \frac{(AmT_3HT)}{(AmT_3)(HT)} \quad (2)$$

The ionic strength was maintained at 2 with lithium chloride, and it is therefore necessary to account for complexation by chloride ion. The free americium ion concentration is

$$(Am^{3+}) = \frac{(Am)_a}{\sum_0^N \beta_{n,Cl}(Cl^-)^n} \quad (3)$$

where $(Am)_a$ is the analytical concentration of americium in the aqueous phase at equilibrium. The chloride formation constants are defined as

$$\beta_{n,Cl} = \frac{(AmCl_n)^{3-n}}{(Am^{3+})(Cl^-)^n} \quad (4)$$

where n takes on the values of 0 to N and $\beta_{0,Cl}$ is defined as unity.

The distribution coefficient is defined as

$$D = \frac{\sum \text{americium species in the organic phase}}{\sum \text{americium species in the aqueous phase}} \quad (5)$$

so that for the extraction of americium by TTA we have

$$D_0 = \frac{AmT_3 + AmT_3HT}{(Am^{3+}) \sum_0^N \beta_{n,Cl}(Cl^-)^n} \quad (6)$$

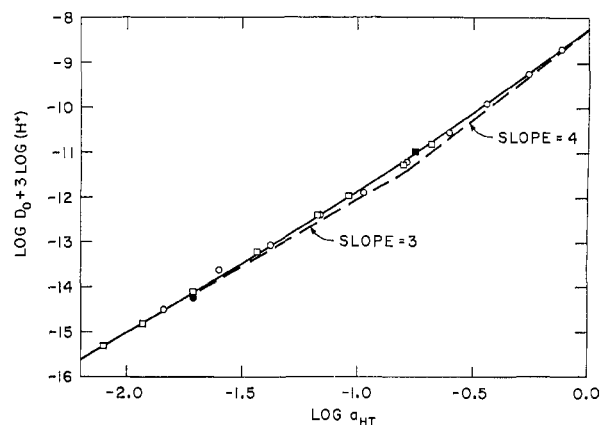


Figure 1.—The distribution of americium as a function of TTA: □, pH 4.00; ○, pH 3.70; ■, average calculated from Figure 3; ●, average calculated from Figure 4.

Upon substitution of eq 1-4 we obtain

$$D_0 = K^0_{Am}(HT)^3(H^+)^{-3}[1 + K_{Am,HT}(HT)] \quad (7)$$

where

$$K^0_{Am} = K_{Am} \left[\sum_0^N \beta_{n,Cl}(Cl^-)^n \right]^{-1} \quad (8)$$

It was thought that the best way to analyze this system was to make use of the method of normalized equations for determining coefficients in polynomials proposed by Sillén.⁵ Accordingly, eq 7 was rearranged to

$$D_0(H^+)^3 = K^0_{Am}(HT)^3 + K^0_{Am}K_{Am,HT}(HT)^4 \quad (9)$$

The form of eq 9 was chosen so that data at different pH values could be incorporated into a single plot.

If we define an auxiliary variable, V , as

$$\log V = \log (HT) + \log K_{Am,HT} \quad (10)$$

then by substitution into eq 9 and rearranging we obtain

$$\log (V^3 + V^4) = \log D_0 + 3 \log (H^+) + 3 \log K_{Am,HT} - \log K^0_{Am} \quad (11)$$

The normalized curve was constructed by plotting $\log (V^3 + V^4)$ vs. $\log V$ for values of V from $10^{-2.5}$ to $10^{1.5}$. This curve could then be compared to the data plotted as $\log D_0 + 3 \log (H^+)$ vs. $\log (HT)$. The constants are obtained by measuring the translation in the ordinate, which is equal to $3 \log K_{Am,HT} - \log K^0_{Am}$, and from the translation in the abscissa, $\log K_{Am,HT}$.

In order to test eq 9, we obtained distribution data as a function of the concentration of TTA, maintaining the pH relatively constant but measuring it at each point. Two sets of data were obtained, one at a pH of ~ 3.70 and the other at 4.00. The data can be found plotted in Figure 1. Since a constant ionic strength of 2 was maintained, the activity coefficient of H^+ is approximately unity but nonetheless was assumed to be constant and is incorporated into the value of K^0_{Am} . Activity corrections were made for HT according to the article by King and Reas.⁶ The plot initially has a third-power dependency on TTA and then gradually

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(5) L. G. Sillén, *Acta Chem. Scand.*, **10**, 186 (1956).

(6) E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, **73**, 1806 (1951).

approaches a fourth power as the TTA concentration is increased. Consequently, it was necessary to include the addition reaction postulated in eq 2. With the aid of a light box, the normalized curve was superimposed on the data until a "best fit" was obtained. From the translation in both axes the constants were calculated as

$$\log K^0_{Am} = -9.05 \pm 0.05 (2 M \text{ LiCl})$$

and

$$\log K_{Am,HT} = 0.75 \pm 0.05$$

The value of $\log K_{Am,HT}$ indicates a reaction about as extensive as found for uranium ($\log K_{U,HT} = 0.55$). The errors inherent in the measurements did not allow us to obtain a fit better than 0.05 log unit. The theoretical curve (full drawn) in its "fitted" position along with the two asymptotes is presented in Figure 1. The significance of the two filled points will be described in a later section.

Theory for the Synergistic Effect

The tertiary octyl amine, R_3N , is known to react with hydrochloric acid to form R_3NHCl and with TTA to form R_3NHT and when both are present to form $R_3NHClHT$. The equilibrium constants have been measured^{3,7} under conditions suitable for this study as

$$K_{Cl} = \frac{(R_3NHCl)}{(R_3N)(H^+)(Cl^-)} = 1.3 \times 10^4 \quad (12)$$

$$K_T = \frac{(R_3NHT)}{(R_3N)(HT)} = 1.4 \times 10^3 \quad (13)$$

$$K_{Cl,T} = \frac{(R_3NHClHT)}{(R_3N)(H^+)(Cl^-)(HT)} = 2.1 \times 10^5 \quad (14)$$

If we consider that each of these amine species can add on to AmT_3 just as HT does then we introduce the following, as the possible equilibria accounting for the synergism.

$$K_{Am,Cl} = \frac{(AmT_3R_3NHCl)}{(AmT_3)(R_3NHCl)} \quad (15)$$

$$K_{Am,T} = \frac{(AmT_3R_3NHT)}{(AmT_3)(R_3NHT)} \quad (16)$$

$$K_{Am,Cl,T} = \frac{(AmT_3R_3NHClHT)}{(AmT_3)(R_3NHClHT)} \quad (17)$$

The concentration of the free amine, R_3N , is always so low that its analogous reaction, if it occurs, could not be measured. The distribution coefficient then becomes

$$D = \frac{AmT_3 + AmT_3HT + AmT_3R_3NHCl + AmT_3R_3NHT + AmT_3R_3NHClHT}{(Am^{3+}) \sum_0^N \beta_{n,Cl}(Cl^-)^n} \quad (18)$$

By substitution we obtain

$$D = D_0 + K^0_{Am} \left[\frac{K_{Am,Cl}K_{Cl}(Cl^-)(H^+) + K_{Am,T}K_T(HT) + K_{Am,Cl,T}K_{Cl,T}(Cl^-)(H^+)(HT)}{K_{Cl}(Cl^-)(H^+) + K_T(HT) + K_{Cl,T}(Cl^-)(H^+)(HT)} \right] \times \frac{(HT)^3}{(H^+)^3} (R_3N)_T \quad (19)$$

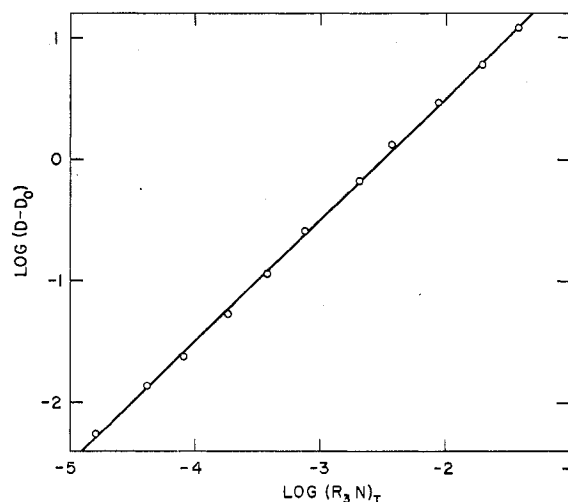


Figure 2.—Demonstration of the first power dependency of synergism on amine concentration at 0.1 *M* TTA and 2.0 *M* chloride.

where the concentration of the amine in all forms is

$$(R_3N)_T = (R_3NHCl) + (R_3NHT) + (R_3NHClHT) \quad (20)$$

If any of the species postulated are not involved in the synergistic effect than it is only necessary to delete the corresponding term from the numerator within the brackets of eq 19.

The first test of these assumptions was to conduct a distribution experiment at constant TTA concentration (0.1 *M*) and at constant pH (3.17) but with varying amine concentration ($\sim 10^{-5}$ to $\sim 10^{-1}$ *M*). The first point in the distribution was obtained in the absence of amine to give us a value of $\log D_0 = -2.22$. The data are plotted in Figure 2 as $\log(D - D_0)$ vs. $\log(R_3N)_T$. Under these conditions eq 19 predicts a straight line with a slope of 1. A line with this slope was drawn through the points and found to give excellent agreement. Therefore when the amine concentration is changed over almost four orders of magnitude it appears that in the organic phase we only need consider species which involve one amine per americium. It now remained to ascertain which, if any, of the assumed species cause the synergistic effect.

Test of the Theory

The first and most detailed family of curves was obtained at 0.2 *M* TTA for 0, 10^{-4} , 10^{-3} , and 10^{-2} *M* TNOA and for values of pH between 2 and 5. The results are presented in Figure 3 as $\log D$ vs. $-\log(H^+)$. It is important to know just how well we are testing for the effect of each of the amine species. Consequently as a guide, the fraction of amine in each form was calculated at representative values of pH. This information appears in Table I for this experiment and for all others which were performed.

One can immediately observe that the data follow a third-power dependency on the hydrogen ion concentration not only in the absence of the amine but at all levels tested. The data appear to be remarkably self-consistent down to a distribution coefficient of 10^{-4} , although there appears to be a slight leveling effect at

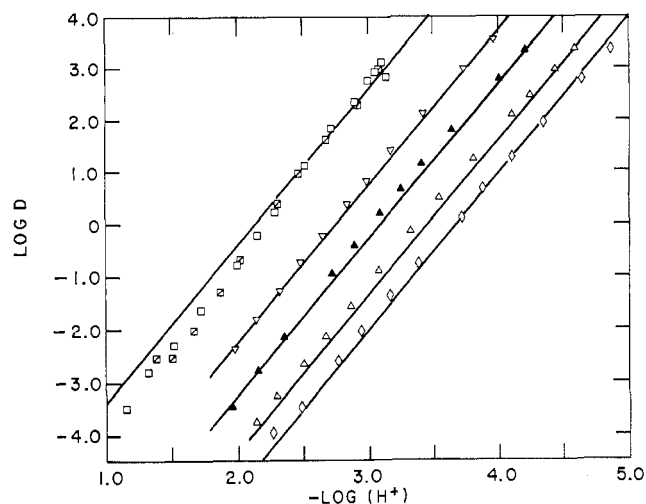


Figure 3.—Distribution data demonstrating the synergistic effect as a function of pH. At 0.2 *M* TTA and 2.0 *M* chloride: \diamond , no amine; \triangle , 10^{-4} *M* amine; \blacktriangle , 10^{-3} *M* amine; ∇ , 10^{-2} *M* amine. At 1 *M* TTA and 2.0 *M* chloride: \square , 10^{-2} *M* amine; \boxplus , repeat of 10^{-2} *M* amine.

TABLE I

GUIDE FOR THE DISTRIBUTION OF THE AMINE AT REPRESENTATIVE VALUES OF pH FOR EACH LEVEL OF TTA
Aqueous = 2.0 *M* LiCl, organic = benzene

HT, <i>M</i>	pH	Fractional distribution			
		R_3N	R_3NHCl	R_3NHT	$R_3NHClHT$
0.02	3	0.016	0.418	0.436	0.130
	4	0.032	0.083	0.859	0.026
	5	0.035	0.009	0.953	0.003
0.2	2	0.001	0.207	0.198	0.594
	3	0.003	0.074	0.710	0.213
	4	0.004	0.010	0.957	0.029
1.0	1	0.000	0.073	0.030	0.897
	2	0.000	0.058	0.235	0.707
	3	0.001	0.018	0.755	0.226
0.2 ^a	2	0.004	0.005	0.978	0.013
	3	0.004	0.001	0.994	0.001
	4	0.004	0.000	0.996	0.000
0.1	3.17	0.006	0.102	0.741	0.151

^a Ionic strength of the aqueous phase was 0.01.

distributions greater than 10^3 . This could easily be caused by "natural" errors such as mutual solubility of the phases or trace impurities which tend to depress high distributions and/or increase low values. That stable values of pH are obtained even at a pH of 5 would indicate there is a buffering action in the aqueous phase brought about by the slight solubility of the TTA and the amine.

The second family of curves was obtained at 0.02 *M* TTA and with 0, 10^{-4} , and 10^{-3} *M* TNOA. At this lower concentration of TTA no attempt was made to obtain data at 10^{-2} *M* TNOA since the extent of the reactions between TTA and TNOA would have introduced a large uncertainty concerning the maintenance of the constancy of the free TTA concentration. The data are presented in Figure 4 and show a very similar behavior to the previous set. In this case we obtained reproducible data to a pH approaching 6, which once again attests to the fact that a buffering action must be brought about by the organic reactants. The amer-

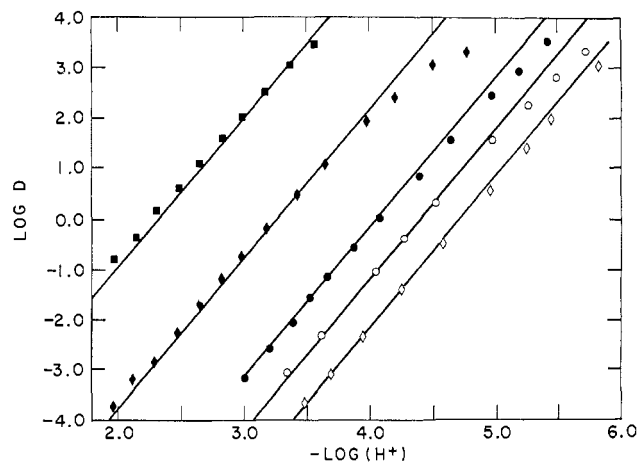


Figure 4.—Distribution data demonstrating the synergistic effect as a function of pH. At 0.02 *M* TTA and 2.0 *M* chloride: \diamond , no amine; \circ , 10^{-4} *M* amine; \bullet , 10^{-3} *M* amine. At 0.2 *M* TTA and 0.01 *M* chloride: \blacklozenge , no amine; \blacksquare , 10^{-2} *M* amine.

icium does not appear to be undergoing extensive hydrolysis even at this high pH. The presence of hydrolysis would have been demonstrated by a gradual decrease in slope from 3 to 0, indicating the formation of $Am(OH)_3$. Complexation of the americium by the 2 *M* chloride no doubt accounts for the retardation of hydrolysis.

Next, data were obtained for a TTA concentration of 1 *M* with a TNOA concentration of 10^{-2} *M*. The results of two titrations run some months apart with completely different reagents are presented in Figure 3. The good agreement demonstrates both the within experiment consistency and the between experiment reproducibility. The base line was established by taking the data point at 1 *M* TTA from the result presented in Figure 1.

Finally, data were again obtained at 0.2 *M* TTA for 0 and 10^{-2} *M* TNOA, but this time the aqueous phase was maintained with lithium chloride at an ionic strength of only 0.01. The results are shown in Figure 4. This ionic strength was selected to emphasize the effect of one species by the almost complete conversion of the amine into R_3NHT (see Table I).

An array of data has now been obtained over almost two orders of magnitude change in (HT) concentration, two orders of magnitude in $(R_3N)_T$, and almost five orders of magnitude in (H^+) . The concentrations of each of the three amine species under question have been varied so that each represents a minimum of 3% of the total amine, up to at least as high as 40%. The most striking aspect of all these data is that the amine, no matter what form it is in, always causes a synergistic effect resulting simply in a linear displacement (increase) of the distribution. Inspection of eq. 19 indicates that if any or all of the postulated species are causing the synergistic effect then not only a displacement but also a change in slope should have been anticipated with the change in pH. There is, however, one condition under which the observed effects can be rationalized. If each of the postulated species does

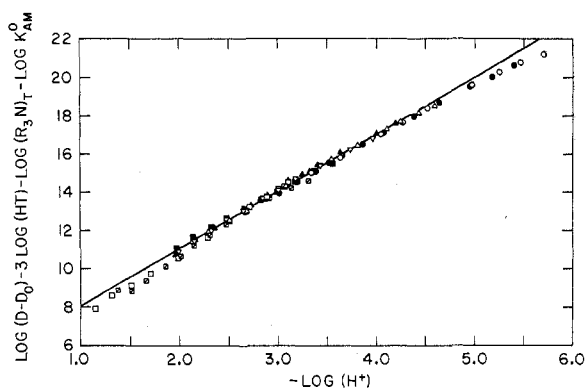


Figure 5.—Demonstration that the synergistic constants for all the species are the same. Symbols represent the equivalent points as in Figures 3 and 4.

indeed cause the synergistic effect and if the constants involved are exactly equal, then the constants $K_{Am,Cl}$, $K_{Am,T}$, and $K_{Am,Cl,T}$ can be replaced by a single constant, K_s , and eq 19 would be reduced to

$$\log \frac{(D - D_0)}{(\text{HT})^3 (\text{R}_3\text{N})_T (K^0_{Am})} = \log K_s - 3 \log (H^+) \quad (21)$$

This condition predicts that the synergistic effect should be independent of the form of the amine.

The data from all the experiments could thereby be incorporated into one graph by plotting $\log (D - D_0) - 3 \log (HT) - \log (R_3N)_T - \log K^0_{Am}$ vs. $-\log (H^+)$. If K_s is indeed a constant, then the data should coalesce into a straight line with a slope of 3 and an intercept equal to $\log K_s$.

For the 2 M lithium chloride data a value of -9.05 was used for $\log K^0_{Am}$. From the intercept of the base-line curve of the 0.01 M lithium chloride data and the previously calculated value of $K_{Am,HT}$ we were able to calculate

$$\log K^0_{Am} = -7.80 \pm 0.05 \text{ (0.01 M LiCl)}$$

A value of D_0 had to be calculated for each data point. This could have been accomplished by employing the base-line curves and of necessity was the approach used for the data obtained at 0.01 M chloride. For 2 M lithium chloride we used all our measurements rather than the base-line curves, and, consequently, the values of D_0 were calculated with the aid of eq 7 and the constants measured in that section. In order to ascertain that the base-line curves also fit this equation, values of $\log D_0 + 3 \log (H^+)$ were calculated for each point at the given TTA concentration. The averages of these values are incorporated as the filled points in Figure 1, and it can be seen that a good fit is obtained. The positions of the base lines shown in Figures 3 and 4 were calculated from eq. 7.

The resultant plot for eq 21 is shown in Figure 5. The data do indeed coalesce into one curve. A straight line with a slope of 3 was put through the data. There is a slight negative bias at both low and high values of pH. One cannot argue that the negative bias at high pH values comes about because most of the amine is in the form of R_3NHT and therefore $K_{Am,T}$ must be smaller than either $K_{Am,Cl}$ or $K_{Am,Cl,T}$. If this were

true, then the data obtained at an ionic strength of 0.01 should have also been biased low, but this was not observed. The negative bias is probably caused either by the high distribution involved and/or a slight amount of hydrolysis. In support of these arguments it is noteworthy that even in the absence of amine there is a negative bias in the distribution data.

The explanation for the negative bias at low pH values must be different. The bias probably arises from the fact that when 1 M TTA is employed the uncertainties in either the activity coefficient of TTA, the constant for the formation of AmT_3HT , or the constants describing the form of the amine are too great.

In the final calculation extreme values of pH were neglected and the position of the straight line shown in Figure 5 was obtained by averaging the values of K_s calculated for each data point between a pH of 1.9 and 4.9. The value obtained is $\log K_s = 5.03 \pm 0.20$. The positions of the theoretical curves were calculated for each set of data, and these are the curves presented in each of the figures.

A method of normalized curves suggested by Sillén⁵ was utilized to ascertain whether the constants were equal. In one plot values of $\log K_{Am,T}$ at each level of HT were obtained. The values varied between 4.98 and 5.15 with an average of 5.04, in excellent agreement with our value of 5.03. From parameters in the first plot a second plot was made where a normalized curve could be fitted at the position where $\log K_{Am,Cl}$ and $\log K_{Am,T,Cl}$ are equal to 5.03, thereby corroborating that the constant for the reaction producing synergism is independent of the form of the amine.

Discussion

Considering that eight equilibria, excluding the aqueous complexes of americium, are involved in measuring the synergistic effect, the fit obtained with solvent extraction data is remarkably good. The organic phase reaction between AmT_3 and R_3NHCl , R_3NHT , or $R_3NHClHT$ leads to the formation of AmT_3R_3NHCl , AmT_3R_3NHT , and $AmT_3R_3NHClHT$, respectively. It is quite remarkable that the formation constants for each of these reactions are identical. This is in contrast to thorium, where only the formation of ThT_4R_3NHCl could be observed. Furthermore, the formation constant for the americium reaction, $\log K_s = 5.03$, is 400 times stronger than the formation constant of the analogous thorium species, $\log K_{Th,Cl} = 2.42$.

It was previously concluded³ that the amine is bound to one of the TTA molecules in the case of a coordinately saturated species such as ThT_4 . This was supported by the existence of the reaction between R_3NHCl and HT to form $R_3NHClHT$. In contrast it is thought that the amine binds directly to the element in a coordinately unsaturated molecule such as AmT_3 . This is supported by the observations that all three amine species cause synergism, that all the formation constants are the same, and that comparable reactions between R_3NHT or $R_3NHClHT$ and HT do not exist.

In the case of synergism with TBP, where the magnitude of the synergistic constant was independent of the element involved, it was reasoned that the TBP must be bound to the TTA and not to the metal.⁸ Consequently, we might have predicted that the synergistic constants for thorium and americium should be equal. There is, however, a basic difference in the case of TBP, where only thorium forms a species containing one TBP per ThT₄ and all other elements investigated form species containing two molecules of synergist.⁹ Although it might be possible for an additional molecule of amine, in the form of R₃NHCl, to be attached to a TTA molecule on each of the americium products of synergism, the extent of this reaction must be very small.

We feel that the argument in the case of TBP should now be modified to the extent that one of the molecules is bound to the TTA and the second bound to the metal. In a benzene system the TBP is bound to TTA with a formation constant of 10^{4.7} and to the element

with a constant of ~10^{1.9} (derived from the values of 10^{6.6} × 10^{-4.7} in Table 1, ref. 8).

It is now reasonable that thorium, the only element which was coordinately saturated by the TTA, should be the only element which does not show evidence for the formation of a species containing two molecules of TBP. Synergism in the case of TBP is therefore governed mainly by a reaction involving binding with a TTA which is attached to a metal, whereas in the amine system the synergism is governed mainly by a reaction involving binding directly with the element which has TTA attached. It is now also reasonable that differences between elements could not be observed in the case of TBP, since the contribution from that part of the reaction is very small. This modifies the previous conclusion which implied that differences between elements could not be observed because both molecules of TBP were bound to molecules of TTA. In the amine system where synergism arises mainly from reactions involving binding with the element, it would be most interesting in future works to explore whether differences between elements can be detected.

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(9) (a) T. V. Healy, *ibid.*, **19**, 314 (1961); (b) *ibid.*, **19**, 328 (1961).

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The Kinetics of Formation of Blue Peroxychromic Acid in Aqueous Solution^{1a}

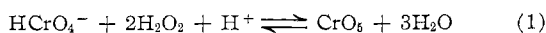
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The formation of blue peroxychromic acid, CrO₅(aq), has been investigated spectrally by the stopped-flow technique. Over a limited range of reactant concentrations, $d[\text{CrO}_5(\text{aq})]/dt = k[\text{H}^+][\text{H}_2\text{O}_2][\text{HCrO}_4^-]$, $k = 10^{7.6 \pm 0.2} \exp(-4500 \pm 200/RT)$, and at 25°, $k = 2.0 \times 10^4 M^{-2} \text{sec}^{-1}$. Two possible mechanisms are suggested, both involving protonation preequilibria.

Introduction

Blue peroxychromic acid is formed when hydrogen peroxide is added to acidified solutions of dichromate. The formula is now well established as CrO₅²⁻,³ although in aqueous solution it might better be regarded as CrO₅·H₂O.⁴ The predominant equilibrium in dilute aqueous solution is



with an equilibrium constant of 5.4×10^7 at 10° and ionic strength 0.09.³ The blue species decomposes readily and in a complex manner to chromium(III) species.^{5,6} It may be stabilized, however, by extrac-

tion into a variety of complexing organic solvents such as ether or ethyl acetate⁷ or by conversion to solid complexes of nitrogen bases, e.g., pyridine (CrO₅·py)⁸ and phenanthroline (CrO₅·phen).³

Although the formation of blue peroxychromic acid in aqueous solution has been variously described as "virtually instantaneous,"³ "immediate,"⁶ and "very rapid,"⁹ in fact, Chance¹⁰ in 1940 showed its formation to be in the flow range of study while testing his stopped-flow apparatus with spectral monitoring. He found a second-order rate constant of $1.9 \times 10^3 M^{-1} \text{sec}^{-1}$ in 0.005 M H₂SO₄ at 18°.

We have examined the formation of CrO₅(aq) in detail, and the over-all order of the reaction (not established by Chance) and the Arrhenius parameters have been obtained.

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