The relative coordinating ability of bromide may now be included in the series of potential ligands toward cobalt(II) in concentrated solutions.[4] This series is $H_2O > Cl^- > Br^- \sim CH_3OH \sim C_2H_5OH$.

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The Extraction of Scandium from Aqueous Sulfate Solutions by Bis(3,5,5-trimethylhexyl)ammonium Sulfate

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The complex formed in the extraction of scandium from aqueous sulfate solutions by bis(3,5,5-trimethylhexyl)ammonium sulfate dissolved in chloroform has been isolated from the organic phase and has been found to have the stoichiometric formula $(R_2NH_2)_4ScOH(SO_4)_3$ where R is 3,5,5-trimethylhexyl. This complex has been shown to be monomeric whereas the amine sulfate salt conforms to a monomer–dimer equilibrium over the concentration ranges studied. Equilibrium studies have been carried out and are in agreement with the suggested stoichiometry for the complex providing that the monomer–dimer equilibrium of the amine sulfate in chloroform is taken into account.

Introduction

Bis(3,5,5-trimethylhexyl)amine and mono(3,5,5-trimethylhexyl)amine have been used in studies of the extraction of iron(III) from aqueous sulfate solutions.[1–3] The complexes isolated from the organic phase were found to have the stoichiometries $(R_2NH_2)_2FeOH(SO_4)_2$ and $(R_3NH)_2FeOH(SO_4)_2$, respectively, where R is 3,5,5-trimethylhexyl. These complexes are considered to be formed by the reaction of the amine sulfate with the species $FeOHSO_4$ and $(FeOHSO_4)_2$ from the aqueous phase.

Since scandium(III) also tends to form partially hydrolyzed species[4] in aqueous solutions it was considered that the extraction of scandium by bis(3,5,5-trimethylhexyl)amine from aqueous sulfate solutions might occur by a process similar to that of iron(III) by reaction of the amine sulfate with species such as $ScOHSO_4$ and $(ScOHSO_4)_2$ from the aqueous phase. This has, in fact, been found to be the case, except that the stoichiometric formula of the scandium complex contains two amine sulfate molecules for each scandium ion and not one as found for iron(III).

Experimental Section

Preparations.—Bis(3,5,5-trimethylhexyl)ammonium sulfate was prepared as described previously[5] and was recrystallized from acetone as white needles. On standing in air the compound absorbed 0.5 mol of water; mp 200–201°. *Anal.* Calcd for $C_{36}H_{80}N_2SO_4 \cdot 0.5H_2O$: C, 66.9; H, 12.6; N, 4.36; S, 4.96; O, 11.1. Found: C, 66.8; H, 12.4; N, 4.39; S, 4.87; O, 11.4.

The scandium complex with bis(3,5,5-trimethylhexyl)ammonium sulfate was prepared by shaking a 0.05 *M* solution of the amine sulfate in chloroform with successive, equal volumes of a 1.0 *M* aqueous scandium(III) sulfate solution at pH 2.3 until no more scandium could be extracted. The organic phase was separated and filtered and the solvent was evaporated under reduced pressure. A white waxy solid was obtained. *Anal.* Calcd for $[(C_9H_{19})_2NH_2]_4ScOH(SO_4)_3$: C, 60.4; H, 11.4; N, 3.9; S, 6.7; Sc, 3.1. Found: C, 59.9; H, 11.0; N, 3.6; S, 7.0; Sc, 3.1. This compound absorbed 1 mol of water on exposure to air.

Using the above procedure extract residues were prepared for aqueous scandium solutions with pH values in the range 0.85–2.7. The optimum pH value (2.3) for preparing the pure scandium complex was obtained by this means. The solids isolated from the organic phase in each case were analyzed for scandium, amine, and sulfate content.

Analyses.—Scandium was determined colorimetrically using a standard technique with chrome Azurol S[6] or by atomic absorption spectrophotometry[7] (error ±1%).

The amine content was determined as described previously,[1] and sulfate was calculated from the microanalytical figures for sulfur.

Scandium sulfate was prepared using scandium oxide obtained from the South Australian Department of Mines (spectroscopic analysis showed a Sc_2O_3 purity of 99.5%).

Molecular weight measurements were obtained in chloroform solution using a Hewlett-Packard vapor pressure osmometer, Model 302.

Equilibrium Studies.—Equilibrium studies were carried out at 25.0° using equal volumes of aqueous and organic solutions and an equilibration time of 30 min. After separation and filtration the aqueous phases were analyzed for scandium as above and the scandium concentrations in the organic phases were determined by difference. Stock amine sulfate solutions in chloroform were prepared either by using the pure salt or by using the amine and equilibrating the solution with an equivalent amount of aqueous sulfuric acid. These solutions were diluted to give concentrations with respect to the total amine content of 0.02–1.00 *M*. These organic solutions were then preequilibrated with aqueous solutions of the same composition as those used in the

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[1] R. W. Cattrall and B. O. West, *J. Inorg. Nucl. Chem.*, **28**, 3035 (1966).

[2] R. W. Cattrall and B. O. West, *ibid.*, **29**, 1145 (1967).

[3] R. W. Cattrall and K. I. Peverill, *ibid.*, in press.

[4] J. Aveston, *J. Chem. Soc., A*, 1599 (1966).

[5] R. W. Cattrall and B. O. West, *Aust. J. Chem.*, **20**, 669 (1967).

[6] R. Ishida and N. Hasegawa, *Bull. Chem. Soc. Jap.*, **40**, 1153 (1967).

[7] O. H. Kriege and G. G. Welcher, *Talanta*, **15**, 781 (1968).

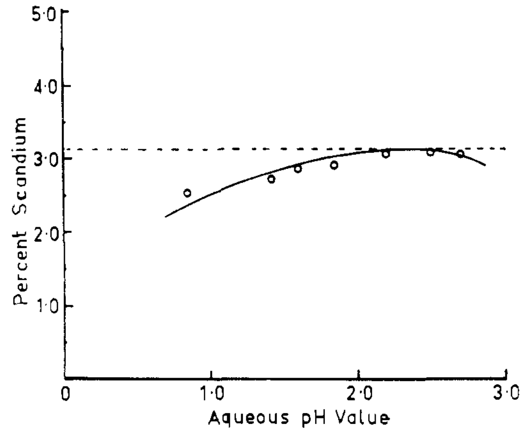

Figure 1.—The scandium contents of the organic extract residues.

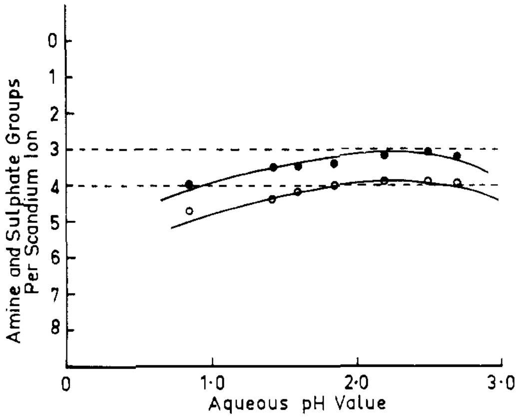

Figure 2.—The numbers of amine and sulfate groups per scandium ion for the organic extract residues.

scandium extraction experiments except that they did not contain scandium. This ensured that the only change in the organic phase during the actual scandium extraction experiments was the distribution of scandium. After equilibration the concentration of stoichiometric uncomplexed amine sulfate in the organic phase was determined using the method of Cattrall and West.[2]

Aqueous scandium solutions containing a constant molar strength of 0.5 *M* total sulfate were prepared by dissolving weighed amounts of scandium sulfate and sodium sulfate in water and adding measured volumes of a standard sulfuric acid solution. The actual compositions of the aqueous solutions are shown in Table I. The pH values were recorded but it should be pointed out that these are not particularly meaningful in solutions of such high ionic strength; however it is convenient to refer to them.

All aqueous and organic phases were preequilibrated with chloroform or water prior to the extraction experiments to prevent volume changes.

TABLE I

[Scandium], *M*	[Sodium sulfate], *M*	[Sulfuric acid], *M*	pH	Curve no. in Figures 5–7
0.0001	0.310	0.190	1.00	7
0.001	0.310	0.190	1.00	6
0.001	0.400	0.100	1.46	5
0.001	0.450	0.050	1.82	3
0.001	0.490	0.010	2.50	1
0.010	0.465	0.020	2.15	2
0.100	0.304	0.050	1.38	4

Results and Discussion

The Empirical Formula of the Scandium Complex.—It has been shown[1-3] that the equilibration of an amine solution in an organic solvent with an aqueous sulfuric acid solution yields an equilibrium mixture of the normal amine sulfate salt and the amine bisulfate and that the amount of amine bisulfate decreases with increase in the aqueous pH. At a certain pH value the amount of amine bisulfate present in the organic phase is negligible and at higher pH values than this a mixture of amine sulfate and free amine is obtained. The aqueous pH value at which the amount of amine bisulfate salt present in the organic phase is negligible has previously been determined for bis(3,5,5-trimethylhexyl)amine solutions in chloroform and found to be 2.3.[1,2,8] It has also been shown previously that it is the amine sulfate salt which will complex to a metal ion from the aqueous phase.[1-3]

Figure 1 shows the percentages of scandium in the organic extract residues prepared using aqueous scandium solutions of different pH values for solutions of the amine salts in chloroform. It can be seen that the percentages of scandium in the residues increase with an increase in aqueous pH up to a maximum of 3.2% at about pH 2.3, the region where the amount of the amine bisulfate salt in the organic phase is negligible.

A similar effect is noted in Figure 2 where the number of amine groups and sulfate groups per scandium ion in the organic extract residues decrease to a minimum of 4 and 3, respectively, at a pH value of about 2.3.

These results suggest that the pure scandium complex can be prepared using an aqueous pH value of 2.3 as was found for the extraction of iron(III).[1] Microanalysis of the complex isolated from the organic phase using an aqueous scandium solution at pH 2.3 agrees with the empirical formula $(R_2NH_2)_4ScOH(SO_4)_3$ where R is 3,5,5-trimethylhexyl. This formula requires a scandium content of 3.1% which agrees with the value shown in Figure 1, and it also contains four amine groups and three sulfate groups per scandium ion as found in Figure 2.

The complex can be considered to be formed by the reaction of two amine sulfate molecules with the species $ScOHSO_4$ from the aqueous phase. The dimeric species $(ScOHSO_4)_2$ may also be involved and this could react with four amine sulfate molecules to give the same stoichiometry.

This complex is interesting because in the case of iron(III) it has been shown that only one amine sulfate molecule is attached to each iron(III) species.[1,3]

It should be pointed out that, using the first hydrolysis constant for scandium obtained by Aveston,[4] a 1.0 *M* scandium solution at pH 2.0 would contain about 10^{-3} *M* $ScOH^{+2}$ which is considerable. The important factor, of course, in the extraction is the magnitude of the equilibrium constant between the organic and the aqueous phase.

A molecular weight study of the complex has been carried out in chloroform solution and it has been ob-

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[8] R. W. Cattrall, Ph.D. Thesis, Adelaide University, 1964.

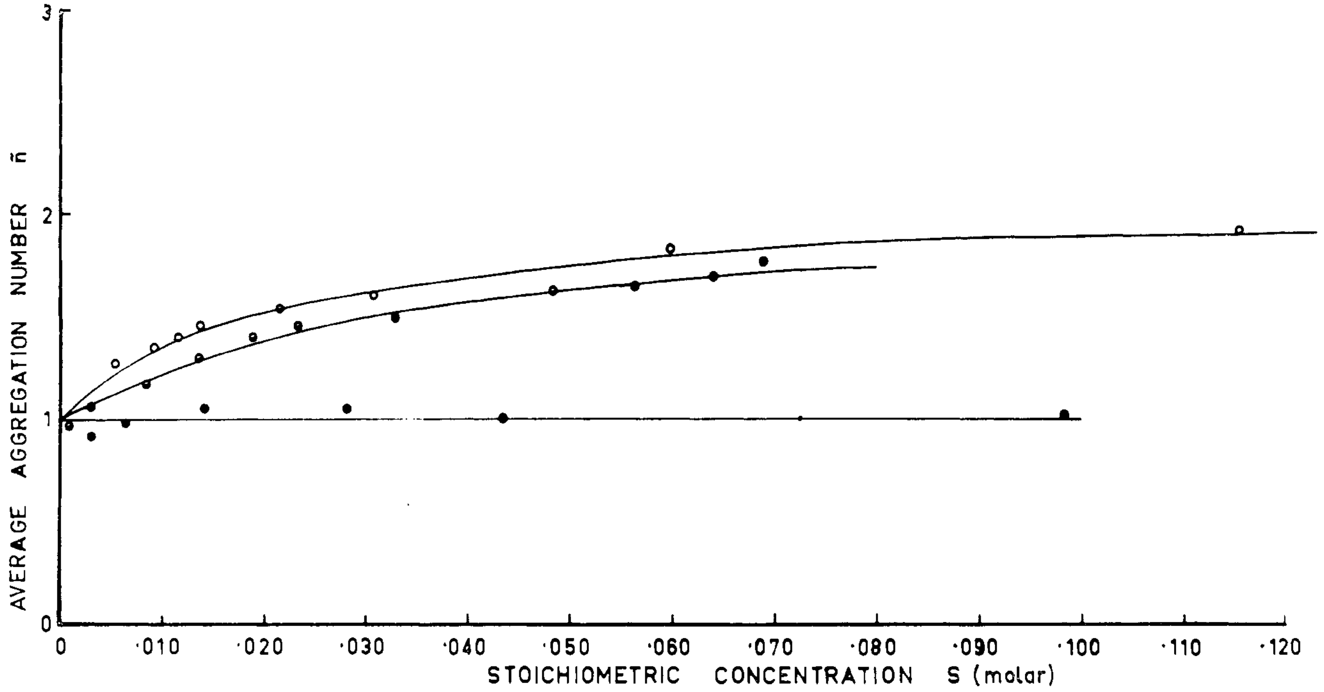

Figure 3.—Molecular weight study of bis(3,5,5-trimethylhexyl)ammonium sulfate and the scandium complex in chloroform solution: -●-●-●-, scandium complex at 37.0°; -○-○-○-, amine sulfate at 25.0°; -⊖-⊖-⊖-, amine sulfate at 37.0°.

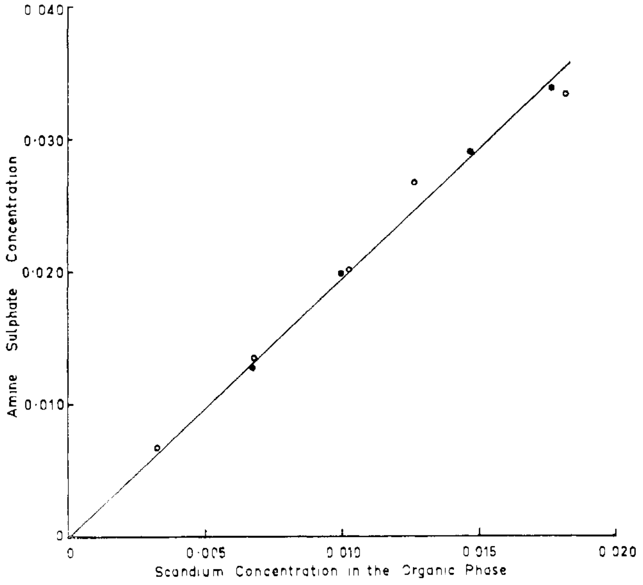

Figure 4.—"Saturation" of the organic phase with scandium: -○-○-○-, pH 1.46; -●-●-●-, pH 1.29.

served that the complex is monomeric over the concentration range of 0.003–0.10 *M* as shown in Figure 3. This is also interesting because the analogous iron(III) compounds have been shown to be associated to some extent.[1,3] The complex with 3,5,5-trimethylhexylammonium sulfate is dimeric,[3] and there is evidence for bridging hydroxyl groups in the complex. The second amine sulfate molecule in the scandium complex may occupy a coordination site on the scandium ion which could otherwise be used in forming hydroxy bridges, and this may be the reason why the scandium complex is monomeric.

Further evidence has been obtained to establish the empirical formula of the complex by equilibrating solutions of various concentrations of the amine in chloroform with aqueous scandium solutions of high enough concentrations such that the amount of scandium present in the system is sufficient to react completely with all the stoichiometric amine sulfate present in the organic phase. Initially the amine solutions in chloroform were preequilibrated with aqueous solutions of various pH values without scandium being

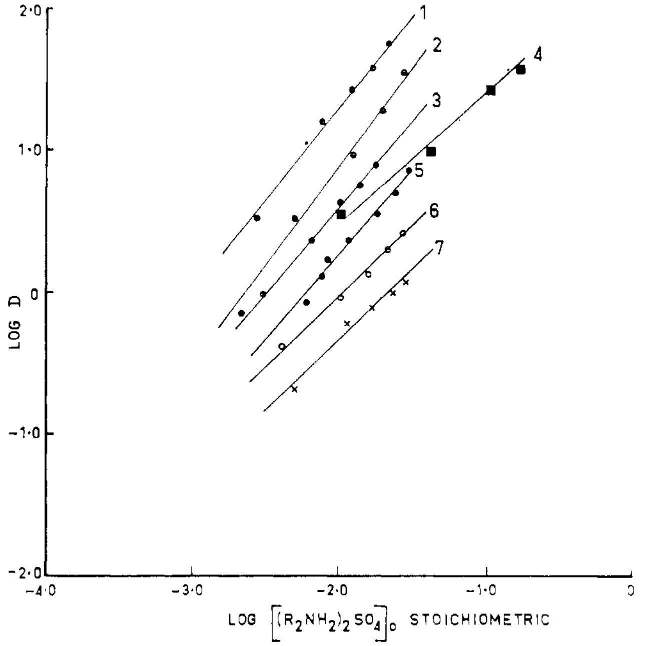

Figure 5.—Log *D vs.* the logarithm of the stoichiometric uncomplexed amine sulfate concentration: line 7 (1.0); 6 (1.0); 5 (1.2); 3, (1.2); 1 (1.3); 2 (1.4); 4 (0.9). The numbers given for the straight lines correspond to the aqueous solution conditions shown in Table I. The values in parentheses are the slopes.

present. The concentrations of the stoichiometric amine sulfate present in the organic phases were determined by the method of Cattrall and West.[2] These organic phases were then reequilibrated with aqueous solutions of identical composition except that this time they contained enough scandium to react completely with all the amine sulfate in the organic phase.

If the empirical formula suggested previously is correct, the scandium concentration in the organic phase should be exactly half the stoichiometric amine sulfate concentration. The results of this study are shown in Figure 4 for two aqueous pH values 1.29 and 1.46 and for stoichiometric amine sulfate concentrations in the region of 0.005–0.035 *M*. The slope of the straight line obtained is 2 which agrees with the suggestion that two amine sulfate molecules are complexed to each scandium ion.

Equilibrium Studies.—It should be possible to obtain supporting evidence regarding the stoichiometric formula of the extracted complex by carrying out a series of distribution studies to determine the dependence of the distribution ratio on the reagent concentration. This procedure has often been used as the basis for postulating the nature of the extracted complex. Several workers[9,10] have pointed out the dangers associated with this kind of treatment of data without obtaining additional evidence for the nature of the extracted complex, since often the stoichiometry predicted[9] by equilibrium studies has been found to be different from that determined by isolation of the complex. The system reported in this paper gives one further example of this and clearly shows that it is possible to misinterpret the equilibrium results unless factors such as the aggregation of the species present in the organic phase are considered.

Figure 5 shows log *D* plotted against the logarithm of the stoichiometric uncomplexed amine sulfate concentration for a series of aqueous scandium solutions of concentrations from 10^{-4} to 10^{-1} *M* (0.5 *M* total sulfate) and pH values from 1.00 to 2.50. The actual compositions of these solutions are given in Table I.

It should be pointed out that the initial amine concentrations in chloroform were in the range of 0.004–0.191 *M* and these solutions, of course, on equilibration with the acidic aqueous scandium solutions gave equilibrium mixtures of the scandium complex, stoichiometric uncomplexed amine sulfate, and amine bisulfate in the organic phases. Stoichiometric uncomplexed amine sulfate concentrations were determined using the method of Cattrall and West[2] and were in the range 0.0022–0.175 *M*. It can be seen from Figure 5 that straight-line plots are obtained of slope close enough to unity to perhaps lead to the conclusion that 1 mol of amine sulfate is coordinated to each scandium ion. This has been shown, in fact, to be incorrect since the preparative studies described above clearly show a stoichiometry of two amine sulfates per scandium ion.

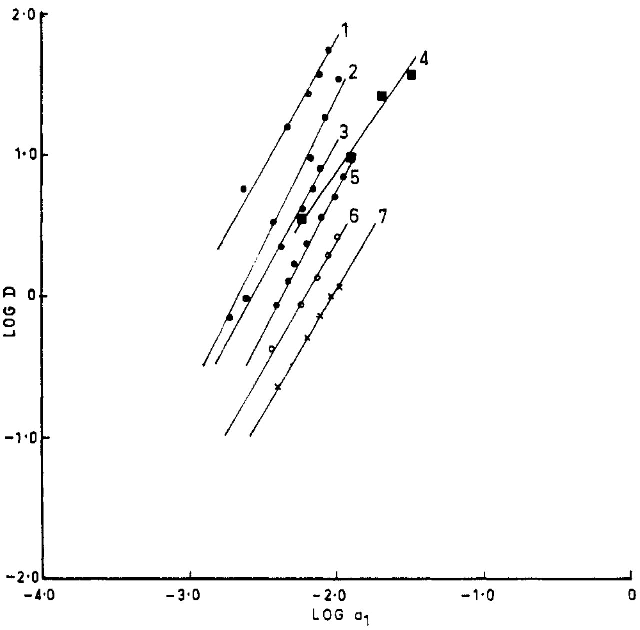

Figure 6.—Log *D* *vs.* the logarithm of the uncomplexed amine sulfate monomer concentration (a_1): line 7 (1.8); 6 (1.8); 5 (2.0); 3 (1.9); 1 (1.8); 2 (2.0); 4 (1.6).

A study of the dependence of the distribution ratio on the concentration of "uncomplexed" reagent in the organic phase gives the ratio of the number of amine groups in the extracted complex aggregate to the number of amine groups in the reagent aggregate. This follows from the normal treatment of extraction equilibria which includes the equilibrium reactions involving the aggregation of species in the organic phase. It is necessary therefore to determine the state of aggregation of both the complex and the reagent in the organic phase.

It has been shown above that the scandium–amine sulfate complex is monomeric over the concentration range studied, however, the amine sulfate salt shows a monomer–dimer equilibrium behavior over the concentration range 0.005–0.12 *M* as shown in Figure 3. A complete description of the monomer–dimer relationship for the amine sulfate salt and the bisulfate salt will be published elsewhere.

Using the method of Scibona, *et al.*,[11] concentrations of amine sulfate monomer and dimer at 25.0° have been calculated for the various stoichiometric uncomplexed amine sulfate concentrations shown in Figure 5.

In Figure 6, log *D* is plotted against the logarithm of the amine sulfate monomer concentration and it can be seen that straight lines are again obtained; however, the slopes of these lines are close to 2 as expected for the stoichiometry found for the scandium complex. It would also follow then that a plot of log *D* against the logarithm of the amine sulfate dimer concentration should give straight lines of slope 1. This is shown in

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(9) C. F. Coleman and J. W. Roddy, "Solvent Extraction Chemistry," D. Dryssen, J. O. Liljenzin, and J. Rydberg, Ed., North-Holland Publishing Co., Amsterdam, 1967, pp 362–368.

(10) C. Djordjevic, "Solvent Extraction Chemistry," D. Dryssen, J. O. Liljenzin, and J. Rydberg, Ed., North-Holland Publishing Co., Amsterdam, 1967, pp 493–498.

(11) G. Scibona, S. Basol, P. R. Danesi, and F. Orlandini, *J. Inorg. Nucl. Chem.*, **28**, 1441 (1966).

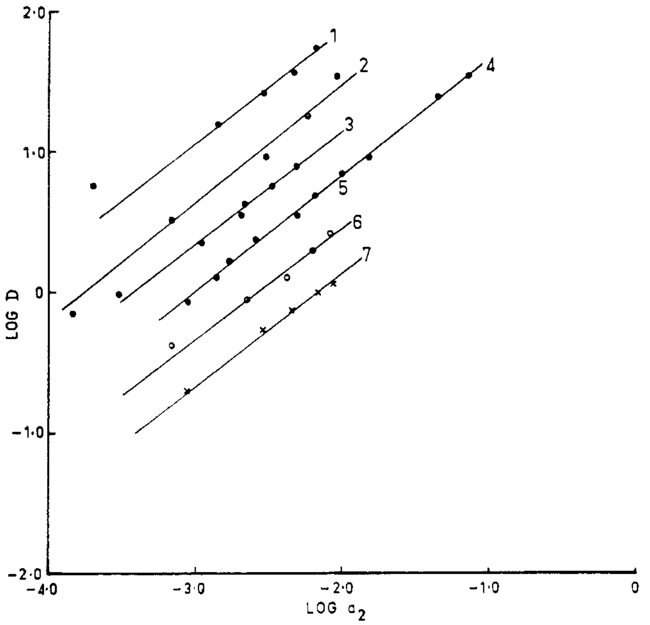

Figure 7.—Log D *vs.* the logarithm of the uncomplexed amine sulfate dimer concentration (a_2): line 7 (0.8); 6 (0.8); 5 (0.8); 3 (0.8); 1 (0.8); 2 (0.9); 4 (0.9).

Figure 7, and the straight lines obtained have, in fact, slopes close to unity.

Since it is suggested that the partially hydrolyzed scandium species $ScOHSO_4$ and $(ScOHSO_4)_2$ are involved in the extraction process the distribution ratio for scandium should be first-order dependent on the pH of the aqueous phase.[2] In Figure 8 log D values, which were obtained from Figure 5 for a stoichiometric uncomplexed amine sulfate concentration of 0.01 M, are shown plotted against pH. The straight line obtained has a slope of unity.

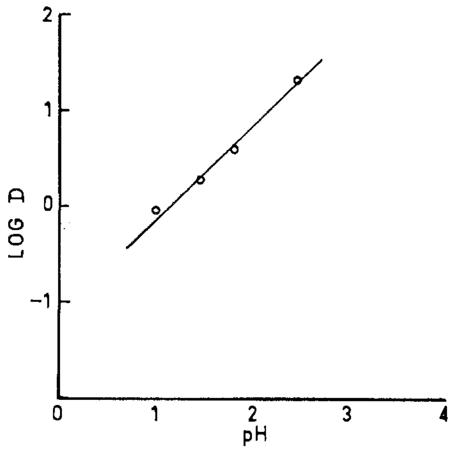

Figure 8.—Log D *vs.* pH for 0.01 M stoichiometric uncomplexed amine sulfate.

These results show that the equilibrium studies are in agreement with the stoichiometry found for the complex; however it is necessary to take into account the aggregation of the sulfate salt in chloroform.

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The Explosive Reaction between Tetrafluorohydrazine and Hydrogen

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Hydrogen and tetrafluorohydrazine have been shown to undergo an explosive chain reaction. The products vary both in type and in stoichiometry depending upon whether the ratio $H_2:N_2F_4$ is 2, 1, or 0.5. In the latter two cases different products are obtained depending upon the presence of inert gas. It is believed that the effect of the inert gas is to lower the explosion temperature. The postulated intermediate, N_2F_2, reacts in different ways depending upon the temperature and upon the relative abundance of the reactants. A weakly exothermic step is believed to predominate at the higher explosion temperature and a strongly exothermic step predominates at the lower temperature.

Introduction

Compounds containing the difluoramino group, NF_2, are powerful oxidizers and are therefore of interest to the chemist concerned with propellants and combustion processes. The present work is concerned with the explosive reaction of tetrafluorohydrazine with the simplest fuel, hydrogen, a reaction which has not been previously reported in the literature.

In our early experiments we learned that an explosive reaction can occur between tetrafluorohydrazine and hydrogen but the reaction was extremely irreproducible. Thus in a clean, dry Pyrex flask a 1:1 mixture of the gases at 30 Torr would not explode below 80°. After conditioning of the flask by several explosions, subsequent additions of the same mixture of gases would explode at 20°. By pumping and baking the flask or by washing with water and alcohol and drying thoroughly, the flask could be returned to its initial condition and the 1:1 gas mixture again required a temperature of 80° for explosion when the pressure