

## EFFECT OF NITRIC ACID AND URANIUM ON THE EXTRACTION OF HYDROFLUORIC ACID BY PRIMARY AMINES

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The extraction of hydrofluoric and nitric acids into Primene-JMT solutions in benzene was studied in dependence on the acid concentration in the aqueous phase. The effect of nitric acid and of uranium on the extraction of hydrofluoric acid was studied in HF-HNO<sub>3</sub> and HF-UO<sub>2</sub>F<sub>2</sub> systems. The literature data on the extraction of hydrofluoric acid with tertiary amines were compared with the data obtained on the extraction of hydrofluoric acid with primary amines and those concerning the extraction of nitric acid with tertiary and primary amines were compared with the data obtained in the present paper. The distribution of uranyl fluoride was studied for varying concentrations of uranium in the aqueous and the amine in the organic phase.

Long-chain primary aliphatic amines can be utilized for selective extraction of strong mineral acids from acidic solutions of mineral salts, *e.g.* for extraction of nitric acid from uranyl nitrate solutions in nitric acid<sup>1</sup>. Simultaneously, part of the nitrate ions belonging stoichiometrically to the uranyl cations is also extracted from the aqueous solution in addition to free nitric acid, so that solutions of basic uranyl nitrates can be obtained from acidic solutions of uranyl nitrate after extraction with primary amines.

The difference in the ion-pair stability, (alkylammonium cation-mineral acid anion) and (alkylammonium cation-anionic metal complex), is greatest for primary alkylammonium cations; it is impossible to separate mineral acids selectively from mineral salt solutions by extraction with secondary or tertiary aliphatic amines.

In the present paper, the possibility of using extraction with primary amines for separation of hydrofluoric acid from aqueous solutions containing uranyl fluoride in addition to free hydrofluoric acid and the possibility of preferential extraction of hydrofluoric acid from solutions containing uranyl fluoride, hydrofluoric acid and nitric acid, thus converting the fluoride system into a nitrate one, were studied. Analogy with tertiary amine extraction systems was used as the basis for the present work; in these systems a ratio of HF : amine > 3 was achieved in the organic phase during the extraction of hydrofluoric acid, while the maximum value of this ratio for nitric acid ( $\approx 2$ ) is attained only during its extraction with high concentrations of the acid in the aqueous phase.

The literature data on the extraction of HF (refs<sup>2-6</sup>), HF and HNO<sub>3</sub> (refs<sup>7-12</sup>) and HF-UO<sub>2</sub>F<sub>2</sub> (refs<sup>13-15</sup>) deal mostly with tertiary amines. Extraction of nitric acid with primary amines was described in refs<sup>16-19</sup>. No literature data are available on the extraction of HF or HF-UO<sub>2</sub>F<sub>2</sub> with primary amines.

## EXPERIMENTAL

### Chemicals and Solutions

Primene-JMT (Rohm & Haas, Philadelphia, Pa., USA) is a mixture of branched primary amines with  $C_{18-22}$ , with a molecular weight of 269—325 (neutralization equivalent, 315 g/equiv.), a b.p. of 265—305°C and a density of 0.840 kg/dm<sup>3</sup> at 25°C. It was mostly used in the form of a benzene solution. The other chemicals were of *p.a.* purity and hydrofluoric acid (38%) was chemically pure.

The initial solution used in the study of the influence of uranium was the so-called hydrolyzate (MAPE, Mydlovary), which is a solution obtained by hydrolysis of uranium(VI) fluoride; it contained 0.711 mol U/l and 4.65 mol HF/l and was diluted for measuring purposes. Some solutions were prepared from pulverized  $UO_2F_2 \cdot 2 H_2O$ . All solutions were stored in polyethylene vessels.

### Analytical Methods and Instruments

The overall concentrations of hydrofluoric and nitric acids (*i.e.* free plus bound) were determined in both phases by titration with a sodium hydroxide standard solution using phenolphthalein (the organic phase was titrated after adding acetone). In solutions containing both acids, the overall acidity was determined using the above procedure and the overall concentration of hydrofluoric acid was then determined by determining the fluoride ion concentration by potentiometric titration with thorium(IV) nitrate using the fluoride ion-selective electrode<sup>20</sup>. The thorium(IV) nitrate solution was standardized with sodium fluoride<sup>20,21</sup>.

The Crytur fluoride-selective electrode type 09—17 (Monokrystal, Turnov) was stored either in a 0.1M-NaF solution or was kept dry and soaked before use. A saturated calomel reference electrode, suitably modified for application in fluoride media, was employed.

The difference in the results of the determination of hydrofluoric acid by titration with sodium hydroxide and with thorium(IV) nitrate is less than 1% rel. The determination of fluoride by titration with thorium(IV) nitrate is not disturbed by the presence of nitric acid or uranium. The concentration of free hydrofluoric acid in solutions containing uranium was determined by titration with sodium hydroxide, subtracting the consumption corresponding to hydrolysis of the uranium, the value of which, determined empirically, corresponds to 2.5 mol of hydroxide per mol of uranium present in the solution.

The uranium concentration was determined oxidimetrically (by titration with vanadate)<sup>22</sup>. The end-point was indicated using a sodium diphenylamine sulphonate in concentrated sulphuric acid. In our experience, the method can be used for uranyl fluoride solutions with an overall uranium concentration above  $10^{-3} M$ .

The pH in hydrofluoric acid solutions was measured with a quinhydrone electrode in connection with a saturated calomel electrode, using compensation pH-meters PHK-1 (Mikrotechna, Prague) and PHM-22 (Radiometer, Copenhagen, Denmark).

The amine concentrations in the solutions were determined by titrations with a  $HClO_4$  standard solution in acetic acid, using the crystal violet indicator<sup>23</sup>.

### Procedure

During the extractions, equal volumes of the two phases (5 or 10 ml) were shaken for an average of 10 minutes in polyethylene bottles. If glass was used, it was pretreated according to ref.<sup>20</sup>. It was found from the measured time-dependence of the extraction that 5 minutes were sufficient for equilibration.

## RESULTS AND DISCUSSION

*Extraction of Hydrofluoric Acid*

Extraction of hydrofluoric acid by benzene alone was followed and it has been found that the acid is not extracted into benzene within the concentration range, 0.05M to 5.1M-HF.

The distribution of hydrofluoric acid between the organic and the aqueous phase in dependence on the original acid concentration in the aqueous phase for three different concentrations of Primene-JMT (B) can be seen in Fig. 1, where the value,  $Z = [\text{HF}]_{\text{org}}/c_{\text{B,org}}$ , is given as a function of  $c_{\text{HF,aq}}$ .\*

At low HF concentrations, an emulsion is formed in the aqueous phase that makes phase separation and the analytical determination more difficult.

With increasing initial HF concentration in the aqueous phase, its equilibrium concentration in the organic phase also increases; it further increases with increasing amine concentrations in the organic phase. The distribution ratio of hydrofluoric

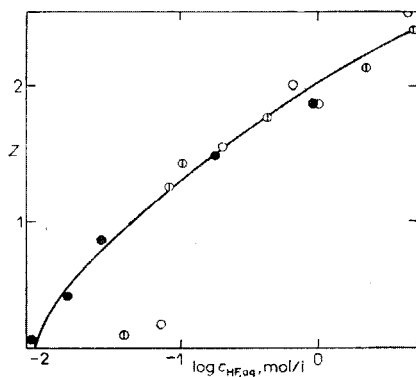


FIG. 1

Dependence of the Degree of Extraction of Hydrofluoric Acid into Primene-JMT Solution in Benzene on its Initial Concentration in the Aqueous Phase

$Z = [\text{HF}]_{\text{org}}/c_{\text{B,org}}$ ;  $c_{\text{B,org}}$ : ● 0.0230M; ○ 0.101M; ○ 0.477M.

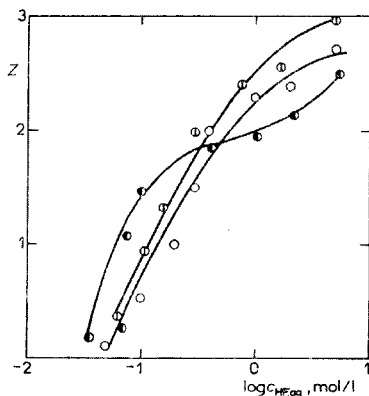


FIG. 2

Dependence of the Extraction of Hydrofluoric Acid into Various Amines on the Initial HF Concentration in the Aqueous Phase

$Z = [\text{HF}]_{\text{org}}/c_{\text{B,org}}$ ; ● 0.101M-Primene-JMT in benzene (our data); ○ 0.1M-tridodecylamine in benzene<sup>14</sup>; ○ 0.1M-tri-n-octylamine in toluene<sup>3</sup>.

\* The initial concentration (in  $\text{mol l}^{-1}$ ) of substance B is termed  $c_{\text{B}}$ , the equilibrium concentration is termed  $[\text{B}]$ ; subscripts aq and org refer to the aqueous and the organic phase, respectively.

acid depends linearly on the amine concentration in the organic phase, as is evident from the  $D_{\text{HF}}$  values for two equilibrium HF concentrations (0.2M and 1.0M), obtained by interpolation from experimental curves:

$c_{\text{B,org}}$ (mol l <sup>-1</sup> ):	0.0230	0.101	0.477
$D_{\text{HF}}$ (0.2M-HF):	0.170	0.850	3.80
$D_{\text{HF}}$ (1.0M-HF):	0.045	0.200	0.99

The concentration ratio,  $Z$ , attains virtually identical values for various  $c_{\text{B}}$  values at the same values of  $c_{\text{HF,aq}}$ ; the maximum ratio in the studied range equalled 2.6 mol HF per mol of amine in the organic phase. This relatively high ratio seems to be advantageous for removal of hydrofluoric acid from aqueous solutions.

Comparison of our data for primary amines with some literature data for tertiary amines is given in Fig. 2. The curves for tertiary amines were transferred from refs<sup>3,8,14</sup> and their shape is therefore not entirely accurate. However, it is obvious that the results for the extraction of hydrofluoric acid with primary amines do not differ much from those with tertiary amines.

#### Extraction of Nitric Acid

Nitric acid is not extracted into benzene when its concentration is lower than 6M (refs<sup>24,25</sup>). The distribution of the acid between the aqueous phase and an amine-benzene solution is depicted in Fig. 3, in which the concentration ratio for nitric acid and the amine in the organic phase,  $Z = [\text{HNO}_3]_{\text{org}}/c_{\text{B,org}}$ , is plotted against the initial acid concentration in the aqueous phase for a 0.101M solution of Primene-JMT in benzene. For the sake of comparison, the data for the extraction of nitric acid with tertiary amines<sup>8,16</sup> and with Primene in benzene<sup>16</sup> are also given.

With increasing acid concentration in the aqueous phase its fraction extracted into the organic phase increases up to a value somewhat higher than that corresponding to one equivalent, and then remains virtually constant in the studied range. The maximum value of  $Z$  attained equalled 1.1 for an initial nitric acid concentration of 2.18M. The nitric acid concentration extracted over the stoichiometric ratio,  $Z = 1$ , is linearly dependent on  $[\text{HNO}_3]_{\text{aq}}$  and the value of empirical coefficient  $\alpha$ , introduced in refs<sup>16,19</sup>

$$\alpha = [\text{HNO}_3 \text{ excess}]_{\text{org}}/c_{\text{B,org}}[\text{HNO}_3]_{\text{aq}}$$

is 0.05–0.12.

In Fig. 3 are also given the  $Z$  values for the extraction with tertiary amines, taken from refs<sup>8,16</sup>. It is evident that tertiary amines extract a higher excess of nitric acid than primary amines (the  $\alpha$  values is 0.16–0.18, see ref.<sup>19</sup>).

### Effect of Nitric Acid on the Extraction of Hydrofluoric Acid

The effect of nitric acid was studied for variable hydrofluoric acid concentration and for two different concentrations of nitric acid. The nitric acid concentration was selected so that the  $\text{HNO}_3$ : amine ratio was either smaller or greater than unity ( $0.0276\text{M-HNO}_3$  and  $0.114\text{M-HNO}_3$ , respectively).

The resultant extraction of hydrofluoric acid for the two cases is shown in Fig. 4, in which the equilibrium hydrofluoric acid concentrations in the organic phase are plotted against the initial HF concentrations in the aqueous phase. The extraction of hydrofluoric acid alone, in the absence of nitric acid, is also illustrated here for the sake of comparison.

It can be seen from Fig. 4 that nitric acid decreases the extraction of HF in proportion to its concentration; this is especially apparent with the higher nitric acid concentration ( $0.114\text{M}$ ), which causes a decrease in the amount of HF in the organic phase by almost one order. Only in the region of lower nitric acid concentrations does the shape of the curve indicate that hydrofluoric acid is extracted better under these conditions than in the absence of  $\text{HNO}_3$ ; this is apparently due to the facts that nitric acid suppresses emulsion formation, the phase separation improves

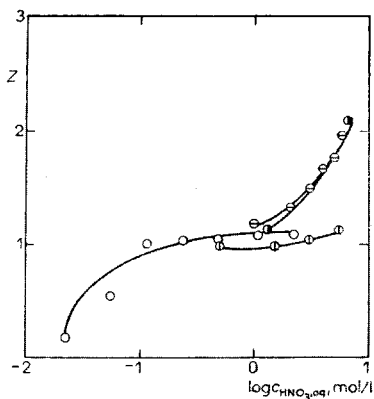


FIG. 3

Dependence of the Extraction of Nitric Acid into Various Amines on the Initial  $\text{HNO}_3$  Concentration in the Aqueous Phase

$Z = [\text{HNO}_3]_{\text{org}}/c_{\text{B,org}}$ ; ○ 0.101M-Primene-JMT in benzene (our data); ⊕ 0.16M-Primene-JMT in benzene<sup>16</sup>; ● 0.1M-tri-n-octylamine in xylene (a mixture of isomers)<sup>8</sup>; ⊗ 0.16M-trilaurylamine in benzene<sup>16</sup>.

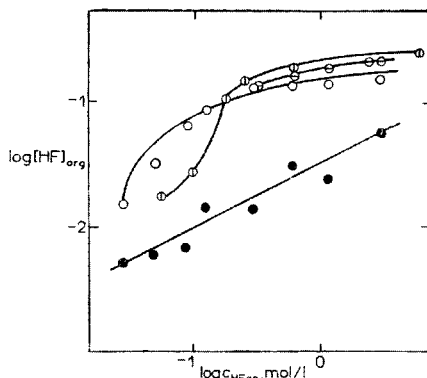


FIG. 4

The Effect of Various Initial Concentrations of Nitric Acid on the Extraction of Hydrofluoric Acid

○ 0.101M-Primene-JMT in benzene without  $\text{HNO}_3$ ; ⊕ 0.101M-Primene-JMT in benzene,  $0.0276\text{M-HNO}_3$ ; ● 0.101M-Primene-JMT in benzene,  $0.114\text{M-HNO}_3$ ; ⊗ 0.206M-Primene-JMT in benzene,  $0.114\text{M-HNO}_3$ .

and the HF activity in the aqueous phase increases. In the system with the initial concentration of 0.114M, nitric acid is extracted preferentially, up to the ratio,  $[\text{HNO}_3]_{\text{org}}/c_{\text{B,org}} = 1$ . Therefore amine nitrate is formed preferentially and hence the absolute amount of hydrofluoric acid extracted is considerably decreased.

In order to elucidate the effect of nitric acid on the extraction of hydrofluoric acid, it was assumed that the extracted nitric acid forms neutral amine nitrate with the amine in the organic phase. The extraction of hydrofluoric acid was then expressed in the  $Z' = [\text{HF}]_{\text{org}}/c'_{\text{B,org}}$  coordinates against  $[\text{HF}]_{\text{aq}}$  (Fig. 5), where  $c'_{\text{B,org}} = c_{\text{B,org}} - [\text{HNO}_3]_{\text{org}}$ . It can be seen that at lower nitric acid concentrations its effect on the extraction of hydrofluoric acid is not very pronounced. However, hydrofluoric acid is extracted even at higher nitric acid concentrations (Fig. 4), when  $c'_{\text{B,org}} \rightarrow 0$ . Therefore, mixed acid alkylammonium nitrates and fluorides are apparently formed.

Formal neutralization of the amine by nitric acid, *i.e.* at  $[\text{HNO}_3]_{\text{org}}/c_{\text{B,org}} = 1$ , thus does not prevent the extraction of hydrofluoric acid. Increased extraction of HF from a given mixture of  $\text{HNO}_3 + \text{HF}$  can then be achieved by using a higher amine concentration in the organic phase.

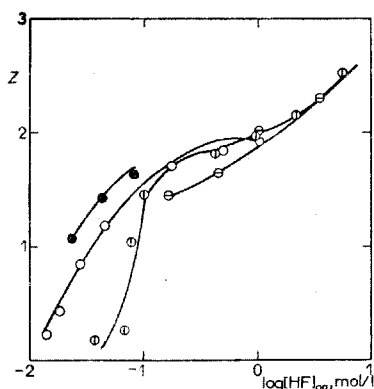


FIG. 5

The Effect of Nitric Acid on the Extraction of Hydrofluoric Acid into Primene-JMT (B) Solutions in Benzene

$Z' = [\text{HF}]_{\text{org}}/(c_{\text{B,org}} - [\text{HNO}_3]_{\text{org}})$ ; the symbols as in Fig. 4.

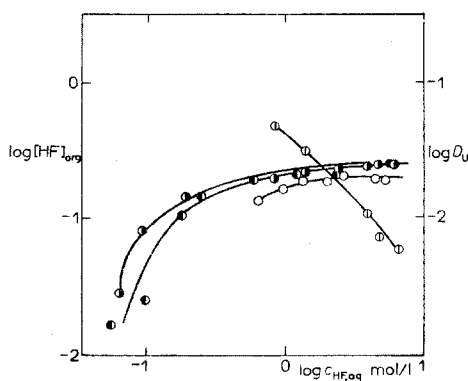


FIG. 6

Dependence of the Extraction of Hydrofluoric Acid and Uranyl Fluoride on the Initial HF Concentration

Extraction of HF into 0.101M-Primene-JMT (left-hand scale): ● without uranium; ○  $c_{\text{U,aq}} = 0.01$  mol/l; ○  $c_{\text{U,aq}} = 0.1$  mol/l. Extraction of  $\text{UO}_2\text{F}_2$  (right-hand scale): ○  $c_{\text{U,aq}} = 0.1$  mol/l.

### Uranyl Fluoride–Hydrofluoric Acid System

The distribution of hydrofluoric acid and uranium between the organic and the aqueous phase in the given system was studied in dependence on the HF concentration in the initial aqueous phase. The results are given in Fig. 6.

Similar to the extraction of the acid alone, an emulsion is formed in the aqueous phase at lower hydrofluoric acid concentrations. This unfavourably affects the precision of the determinations, especially that of uranium, and thus the distribution ratios of uranium are given only for the region of higher hydrofluoric acid concentrations. The extraction of hydrofluoric acid in the HF–UO<sub>2</sub>F<sub>2</sub> system is further complicated by precipitates formed in the aqueous phase at higher concentrations of uranium (>0.05 mol/l), which are concentrated at the interface. The precipitates are probably of the same type as the complexes of uranyl fluoride and hydrofluoric acid with some organic bases, described in ref.<sup>26–28</sup>. The formation of the precipitate can be prevented by increasing the initial concentrations of hydrofluoric acid and the amine; for example, the turbidity at the interface disappears and the phases can be analyzed in the system 4.5–5.2M-HF–0.544M solution of Primene-JMT in benzene. The precipitate formation in the region of lower hydrofluoric acid concentrations can be prevented by adding aluminium nitrate or by increasing the overall acidity with nitric acid.

From the comparison of the distribution of hydrofluoric acid in the presence of 0.01M-uranium with that of the acid alone it can be seen (Fig. 6) that the extraction recovery of hydrofluoric acid is not affected by uranium at the given concentration. However, at a concentration of 0.1M-uranium in the initial aqueous phase, a decrease in the extraction of hydrofluoric acid can be observed, apparently caused by the formation of stable, unextractable complexes of uranyl with fluoride ligands. These values were, however, determined only from the HF concentrations in the organic phase,

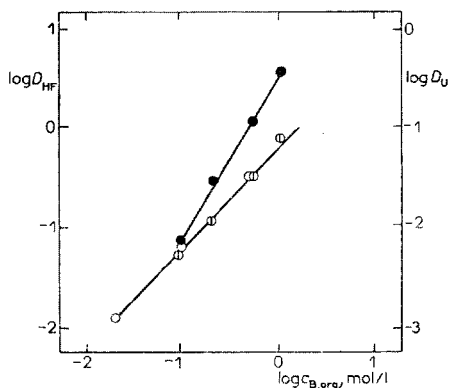


FIG. 7

Dependence of the Uranium Distribution Ratio on the Initial Primene-JMT (B) Concentration

Composition of the initial aqueous phase: 0.00998M-U, 4.765M-HF. ● Distribution of uranium; ◻ distribution of HF; ○ distribution of HF ( $c_{HF,aq} = 4.0M$ ) in the absence of uranium.

because of the presence of the precipitate in the aqueous phase. Since part of the HF is bound in the precipitate, the actual overall HF concentration in the liquid phase of the system is lower and the curve in Fig. 6, representing the extraction of HF in the presence of 0.1M-uranium, can be considered as the lower limit for the extraction of HF in this system.

The uranium distribution ratio decreases with increasing concentrations of hydrofluoric acid in the initial aqueous phase (Fig. 6). Thus hydrofluoric acid could be partially removed from solutions containing uranyl fluoride by multistage extraction with the amine. If it is assumed that curve  $D_U$  in Fig. 6 can be extrapolated to the region of lower  $c_{\text{HF}}$  (and this assumption seems to be justified in view of the  $D_U$  values, which are not given in Fig. 6 because of their poor precision), then  $D_U = 1$  is attained at  $[\text{HF}]_{\text{aq}} < 0.1\text{M}$ . However, the extraction in this HF concentration region is complicated by the formation of precipitates as has been pointed out above.

The dependence of the distribution ratios of uranium and hydrofluoric acid on the amine concentration in the organic phase is given in Fig. 7.

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