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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Extractive Recovery of Gallium(III) from Acid Sulfate Solutions with Primary Amines

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Abstract—Liquid extraction of Ga(III) ions with technical-grade aliphatic amines from sulfate media at a temperature of 20 ± 5°C was studied. The composition of the complex being extracted was determined and the equation of the reaction of Ga(III) extraction with primary amines was derived. The equilibrium constant of the reaction of gallium(III) extraction from acid sulfate solutions was found.

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Gallium(III) is a typical scattered element and its concentration in raw materials and technological industrial products from which gallium compounds are recovered is low. Therefore, a key task of the gallium (III) technology is its primary recovery and concentration. A successful solution of this problem should be promoted by wide introduction of extractive and sorption processes previously employed for recovery, concentration, and purification of numerous rare and nonferrous metals [1–4] into the chemical technology of gallium(III). Despite that the number of studies devoted to extraction of gallium(III) is sufficient, they are mostly concerned with its recovery from alkaline media [5] and chloride solutions [6]. Information about extraction of gallium(III) from neutral and acid sulfate solutions is rather scarce. The possibility of using aliphatic amines for extraction of gallium(III) was described in [1, 2, 6–10]. Gallium(III) is recovered from acid chloride solutions via the reaction of $GaCl_4^-$ anions with the ammonium cation:

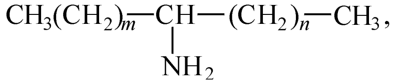
$$RNH_{3\,org}^{+} + GaCl_{4\,aq}^{-} \rightarrow RNH_3GaCl_{4\,org}.$$

The possibility of gallium(III) recovery from sulfate solutions with primary, secondary, and tertiary alkylamines in chloroform was first described by Shevchuk [10]. It was shown that gallium(III) can exist in the organic phase as acido complexes $[Ga(SO_4)_2^-$, $Ga(SO_4)_3^{3-}$, $Ga(SO_4)_4^{5-}]$ and chloroform solutions of di-*n*-ionylamine and tri-*n*-octylamine hardly extract gallium(III) at all from acid sulfate solutions.

This communication reports on a study of the extraction of gallium(III) ions from sulfate solutions with technical-grade primary aliphatic amines.

EXPERIMENTAL

We carried out the study with the use of technical-grade mixture of primary aliphatic amines (ANPO) produced from liquid paraffins of general formula



$$CH_3(CH_2)_m{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}(CH_2)_n{-}CH_3,$$

where $m + n$ = 10 to 16 carbon atoms, manufactured by Deneprodzerzhinsk chemical combine; bp = 240–345°C, extractive agent density 0.899 g cm^{-3}, refractive index 1.51, average molecular mass 185 g mol^{-1}. Burning kerosene served as a diluent.

Our preliminary experiments demonstrated that a 5-min mixing with aqueous and organic phases by shaking is sufficient for equilibrium to be attained. The complete phase stratification is achieved in 1–3 min. The phase ratio was $V_o : V_w = 1 : 2$ in all the experiments. The content of gallium(III) in the aqueous and organic phases was found by photocolorimetry [11], and the concentration of sulfate ions in equilibrium organic phases, by gravimetry, in the form of $BaSO_4$.

We prepared the starting aqueous Ga-containing solutions [Ga(III) = 7.2 × 10^{-4} M] from $Ga_2(SO_4)_3 \cdot 18H_2O$ produced using the method described in [11].

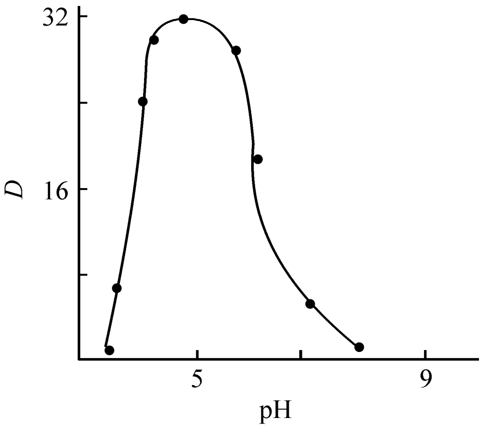


Fig. 1. Effect of the acidity of the aqueous phase on the extraction of gallium(III) ions with a 0.5 M solution of ANPO in kerosene. $c_{Ga} = 7.2 \times 10^{-4}$ M; the same for Fig. 3. (*D*) Gallium(III) distribution coefficient.

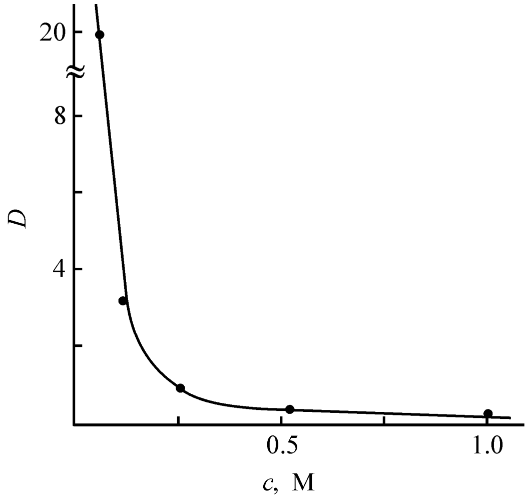


Fig. 2. Gallium(III) distribution coefficient *D* vs. H_2SO_4 concentration *c* in solution.

For this purpose, an appropriate weighed portion was dissolved under heating in water and then the solution was acidified to a required pH. IR spectra were recorded with a Specord 75-IR spectrometer in the range 400–4000 cm^{-1}.

The acidity of the aqueous phase most strongly affects the degree of gallium(III) recovery with a primary aliphatic amine (Fig. 1). It follows from the results obtained that the maximum extraction of Ga(III) ions lies in the weakly acid, nearly neutral region (pH 4–6). The maximum recovery of gallium(III), with a distribution coefficient of about 32, is observed at pH ~4.8.

In the extraction, the amine reacts with sulfuric acid in accordance with the equation $2RNH_2 + H_2SO_4 \rightarrow (RNH_3)_2SO_4$. The salt formed is distributed among the aqueous and organic phases. To study the extraction of gallium(III) from aqueous solutions, we examined the distribution of the amine salt among the aqueous and organic phases in relation to the sulfuric acid concentration. The experiments demonstrated that the ammonium salt is almost insoluble in kerosene.

Further, we studied the effect of the sulfuric acid concentration on the extraction of gallium(III) from aqueous solutions with a primary amine. It can be seen from Fig. 2 that the maximum distribution constant is observed at an H_2SO_4 concentration of 0.05 M in the starting solution. As the sulfuric acid concentration increases, the distribution coefficient of gallium(III) steeply decreases. The possible reason is that, as a result of appearance of an excess amount of sulfuric acid, H_2SO_4 is bound with ammonium ions and displaces the anion from the organic phase via competitive extraction. Ammonium sulfate is co-extracted with gallium(III) into the organic phase.

This is indicated by the results of the following experiments. The extraction was performed from a 0.05 M aqueous solution of H_2SO_4 in the absence of gallium(III), and the content of the ions in the organic phase was determined. Then, we carried out the same experiment in the presence of gallium(III). The difference between the contents of SO_4^{2-} ions in the extract was used to judge about the form of gallium being extracted, whose ions are contained in the organic phase. The experimental data are listed in the table.

Determination of the Ga^{3+}/SO_4^{2-} ratio in the extract under study

SO_4^{2-}, Ga(III)	Content, g	ν, mol
SO_4^{2-}:		
in the $Ga_2(SO_4)_3$ solution before extraction	0.0615	0.0006406
in the aqueous phase after extraction	0.009306	0.0000969
in the organic phase after extraction	0.0265	0.000276
in the organic phase after extraction from H_2SO_4	0.0156	0.0001625
in the organic phase after extraction from $Ga_2(SO_4)_3$	0.0101	0.0001052
Ga(III) in the organic phase after extraction	0.0050	0.0000717

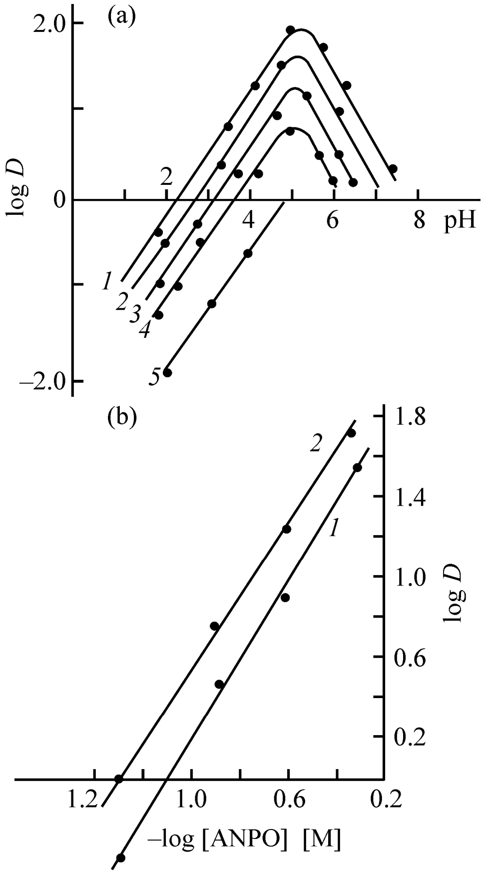


Fig. 3. Gallium(III) distribution coefficient D vs. (a) pH of the medium and (b) ANPO concentration. (a) c_{ANPO} (M): (*1*) 1, (*2*) 0.5, (*3*) 0.25, (*4*) 0.125, and (*5*) 0.05. (b) pH: (*1*) 45 and (*2*) 5.0.

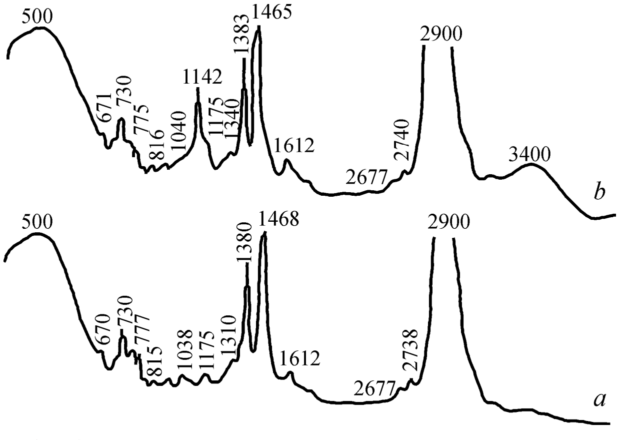


Fig. 4. IR absorption spectra. (*a*) Extractive agent and (*b*) extract.

Theoretically, it follows from the composition $Ga_2(SO_4)_3$ that 1 mg of Ga^{3+} corresponds to 2.06 mg SO_4^{2-}. The ratio experimentally found in the organic phase is 5 mg Ga^{3+} to 10.1 mg SO_4^{2-}, i.e., gallium(III) exists in the organic phase in the form of $Ga_2(SO_4)_3$.

At any of the amine concentrations studied in the organic phase, the maximum distribution coefficient corresponds to pH 4.8 (Fig. 3a).

To determine the stoichiometry of the components in the composition of the compounds being extracted, we analyzed the dependence of the distribution coefficient of gallium(III) at a constant concentration of the metal ion (0.05 g l^{-1}) and varied content of the amine in the organic solvent (Fig. 3b). In recovery of gallium (III) from weakly acid sulfate media, this dependence is represented by a straight line (Fig. 3b) with a slope approaching 2. This means that two amine molecules are associated with a single gallium(III) atom, at least within that range of amine concentrations in which the organic phase remains ideal.

To obtain additional evidence about the extractive agent and compounds being extracted, we examined their IR spectra in the range 400–4000 cm^{-1} (Fig. 4). It can be seen in Fig. 4 that the spectra of the extractive agent generally reproduce the IR spectra of a 1 M ANPO solution in kerosene, but with certain distinctions. It was demonstrated that vibrations of the following bonds appear in both the spectra: N–H (775, 1310, 3100–3200 cm^{-1}), C–N (1380 cm^{-1}), S–O (670, 1038, 1142 cm^{-1}), and O–H (1612, 3200–3700 cm^{-1}). In contrast to the IR spectrum of the reagent, the IR spectrum of the extractive agent shows a noticeable peak at around 1142 cm^{-1}, which can be attributed to stretching vibrations of the SO_4^{2-} group. The presence of a weak band in the region of deformation vibrations of water molecules (1612 cm^{-1}) can be attributed to the hygroscopic nature of the compounds studied, which is presumably due to the possibility of formation of $AmH^+\cdots OH_2$ hydrogen bonds [12].

A broad absorption band at 3100–3700 cm^{-1}, peaked at 3400 cm^{-1} and associated with deformation vibrations of OH groups of molecular water, appears in IR spectra of the extractive agent saturated with gallium(III). The absence of narrow absorption bands in the range of stretching vibrations of OH^- (3500–3700 cm^{-1}) [13] indicates that this extract contains no hydroxy groups.

In the presence of sulfuric acid, the complexation capacity of gallium(III) is manifested to a lesser extent, compared with in weakly acid sulfate media in which the $GaSO_4^+$ complex is formed [14]. Other possible sulfate acido complexes $[Ga(SO_4)_2^-$, $Ga(SO_4)_3^{3-}$, $Ga(SO_4)_4^{5-}$ are only formed in the presence of organic solvents (acetone, *n*-propanol, dioxane) [15]. Therefore, the mechanism described in the literature [10] is unlikely and was studied for analytical purposes. We believe that gallium exists in the organic phase as $n[(RNH_3)_2SO_4] \cdot Ga_2(SO_4)_3$, as also does Fe(III) described in [2].

With account of the aforesaid, the extraction of gallium(III) from sulfuric acid solutions can be expressed by the equation

$$2Ga^{3+}_{aq} + 4(RNH_3)^{+}_{aq} + 5SO^{2-}_{4aq}$$

$$\rightleftarrows 2[(RNH_3)_2SO_4] \cdot Ga_2(SO_4)_{3org},$$

with the reaction constant

$$K_{ex} = \frac{\{2[(RNH_3)_2SO_4] \cdot Ga_2(SO_4)_3\}_{org}}{[Ga^{3+}]^2_{aq}\,[SO_4^{2-}]^5_{aq}\,[(R(NH_3)_7]^4_{aq}}.$$

Based on the data obtained for the pH range 3.5–4.9, we calculated the concentration constants of gallium extraction $\log K_{ex} = 5.82 \pm 0.88$.

The fact that the calculated values of the extraction constants are invariable confirms the validity of the equation we suggested.

Gallium(III) was quantitatively re-extracted with a 1 : 1 NH_4OH ammonia solution from the organic phase, the pH value of whose equilibrium aqueous phase was 9–10, in agreement with the available recommendation for re-extraction of gallium(III) from amines [1]. In re-extraction of gallium from the organic phase with an ammonia solution, 80–85% of gallium(III) passes to the aqueous phase in a single stage.

CONCLUSIONS

(1) Ga(III) is extracted from sulfate acid solutions with primary aliphatic amines in the form of a complex compound $2[(RNH_3)_2SO_4] \cdot Ga_2(SO_4)_3$, whose composition was determined by the extraction method and analysis of the organic phase.

(2) The maximum degree of extraction is achieved in the weakly acid region at pH 4.8–5.4. Gallium(III) is quantitatively re-extracted from the organic phase with a 1 : 1 NH_4OH solution.

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