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Ketone Extraction of Mixed Chloride-Bisulfate Complexes of Aluminum

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NOTE

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Summary

The partition ratio D of Al(III) between aqueous chloride/bisulfate solutions of constant ionic strength (5.0) and methyl ethylketone (MEK) or methyl isobutyl ketone (MIBK) was investigated radiometrically as a function of the chloride/bisulfate ratio and aqueous acidity. With MIBK, the plot of D vs chloride/bisulfate showed a maximum. Results may be explained by assuming the extraction of the following species: $\mathrm{KtH^+ \cdot AlCl_4^-}$, $\mathrm{KtH^+ \cdot AlCl_2(HSO_4)_2^-}$ and $\mathrm{KtH^+ \cdot Al(HSO_4)_4^-}$, where $\mathrm{KtH^+}$ represents a solvated hydrogen ion. Formation constants for these complexes were calculated.

INTRODUCTION

Unlike other trivalent metals, which form halometallic acids that can easily be extracted into oxygen- or nitrogen-containing organic solvents, aluminum is not readily extractable from hydrochloric acid solutions. Distribution ratios reported in the literature (*1–5*) vary between 0 (below limit of detection) and 10^{-3}. This has been used (*2, 6*) for the separation of gallium from aluminum.

Recent investigation of Ga(III) extraction by ketones from mixed hydrochloric–sulfuric solutions (*7*) showed a pronounced synergistic effect, which can be attributed to the extraction of mixed chloride–bisulfate complexes. The present work was aimed at investigating the existence of a similar effect for Al(III).

EXPERIMENTAL

The organic phase consisted of analytical pure methyl ethyl ketone (Baker) or methyl isobutyl ketone (Matheson). The aqueous phase consisted of mixtures, in varying proportions, of ammonium chloride, ammonium sulfate, hydrochloric acid, and sulfuric acid. In all experiments, the following conditions were fulfilled:

(a). All sulfate was kept in bisulfate form, with the pH always below 0.2 and in most experiments negative.

(b). Aqueous acidity never exceeded 2 *M* in order to minimize ketone solubility in the aqueous phase (*8*).

(c). The total ionic strength was kept constant at 5.0.

The aqueous solutions all contained 10^{-4} *M* of labelled Al(III) obtained from the IRR-reactor (^{28}Al, 2.3 min γ 1.78 Mev), by which the distribution ratio *D* could be measured in a γ-spectrometer.

Equilibration time between the aqueous and organic phases was 2 min. Preliminary experiments having shown this to be sufficient to reach equilibrium.

RESULTS

Figures 1 and 2 show the variation of the partition ratio *D* with total aqueous chloride/sulfate concentration for various aqueous acidities, the organic phase consisting of MEK and MIBK, respectively. In the latter case, it can be seen that there is a pronounced maximum at 2–3 *M* chloride.

DISCUSSION

The experiments were carried out under conditions (constant ionic strength, all bulk electrolyte in the form of monovalent ions) that do not warrant divergences between experiments due to nonideality of the aqueous solutions. This was shown also by pH determinations (*8*) of the various solutions, in all of which the activity coefficient for hydrogen ion was found to be 1.3 ± 0.1. Also, any significant mutual solubility of the two phases was prevented (*8*) by the high electrolyte content of the aqueous phase. Therefore, no corrections because of either nonideality or volume changes are needed.

The linear dependence of *D* on aqueous acidity, found throughout all experiments, shows the extracted species to be an ion pair of the

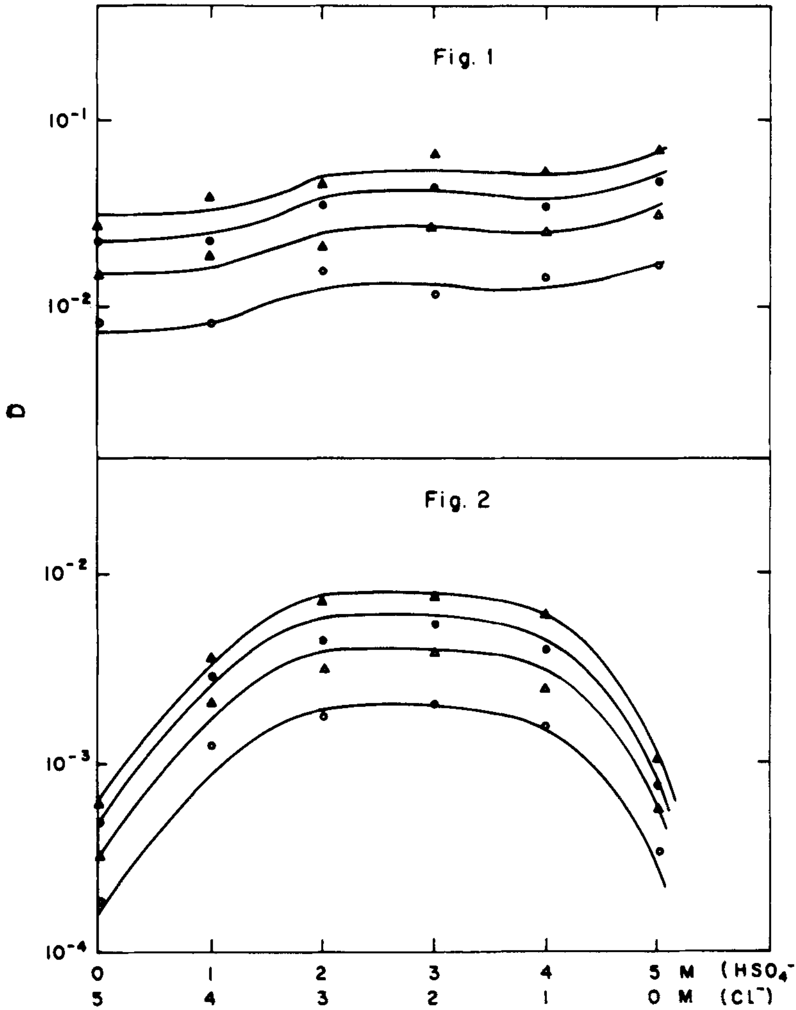

FIG. 1. Partition ratio of Al(III) between aqueous chloride-bisulfate solutions (total ionic strength = 5.0) and methyl ethyl ketone as a function of chloride/bisulfate concentrations, for aqueous acidity 2.0 M (▲), 1.5 M (●), 1.0 M (△), and 0.5 M (○).

FIG. 2. As in Fig. 1 but with methyl ethyl ketone replaced by methyl isobutyl ketone.

form $KtH^+ \cdot AlX_4^-$ where X may represent both chloride and bisulfate. [For our purpose, the exact structure of KtH^+, ketonium ion, or solvated hydronium ion (*9*), is irrelevant.]

As in any two-ligand system where the sum of concentrations of both ligands is kept constant, it can easily be shown that, if no mixed chloride–bisulfate complex were extracted, the plot of D vs chloride/bisulfate concentration should show a minimum. The absence of such a minimum and, even more, the presence of a maximum in the extraction with MIBK show that at least one mixed chloride–bisulfate complex is extracted, and the position of the maximum suggests equal participation of chloride and bisulfate in the mixed complex, i.e., $KtH^+ \cdot AlCl_2(HSO_4)_2^-$. The accuracy of the data does not, however, allow us to decide whether additional mixed complexes are formed.

The stepwise complexation of Al^{3+} by either chloride or bisulfate in the aqueous phase has not been considered in the preceding treatment. We have been unable to find any quantitative data on such complexation in the literature. Curve-fitting methods, applied to our experiments, allow us only to find an average value for

$$K_n(\mathrm{Cl}) = \frac{(\mathrm{AlCl}_n^{3-n})}{(\mathrm{AlCl}_{n-1}^{4-n})(\mathrm{Cl}^-)}, \qquad \log K_n(\mathrm{Cl}) = 0.8 \pm 0.2$$

and

$$K_n(\mathrm{HSO_4}) = \frac{(\mathrm{Al(HSO_4)}_n^{3-n})}{(\mathrm{Al(HSO_4)}_{n-1}^{4-n})(\mathrm{HSO_4^-})}, \qquad \log K_n(\mathrm{HSO_4}) = -0.75 \pm 0.2$$

By the same curve-fitting methods, the values of Table 1 are found for

$$K_{40} = \frac{(\mathrm{KtH^+ \cdot AlCl_4^-})_{\mathrm{or}}}{(\mathrm{Al^{3+}})(\mathrm{Cl^{-4}})}$$

$$K_{22} = \frac{(\mathrm{KtH^+ \cdot AlCl_2(HSO_4)_2^-})_{\mathrm{or}}}{(\mathrm{Al_3^+})(\mathrm{Cl^-})^2(\mathrm{HSO_4^-})^2}$$

and

$$K_{04} = \frac{(\mathrm{KtH^+ \cdot Al(HSO_4)_4^-})_{\mathrm{or}}}{(\mathrm{Al^{3+}})(\mathrm{HSO_4^-})^4}$$

TABLE 1

	$\log K_{40}$	$\log K_{22}$	$\log K_{04}$
MEK	-4.7 ± 0.1	-3.4 ± 0.1	-4.4 ± 0.1
MIBK	-6.4 ± 0.1	-4.2 ± 0.2	-6.2 ± 0.1

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