Extraction of Iron(III) from Aqueous Thiocyanate Solutions by Tri-*n*-octylamine

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It is well known that iron(III) ions form a red-colored thiocyanate complex capable of being extracted with amines,[1-3] but there is little information available on the iron(III) species in the organic phase. Ziegler *et al.* reported that the iron(III) species extracted by tri-*n*-butylamine dissolved in amyl acetate is the hexathiocyanate complex of iron(III).[1] In our experiment, we found that the iron(III) species extracted by tri-*n*-octylamine dissolved in various dilutents is present in the form of the pentathiocyanate complex of iron(III).

Experimental

All the reagents used in the present study were of an analytical grade and were purified if necessary. Thiocyanic acid was prepared from ammonium thiocyanate by the ion exchange method, using a hydrogen-form cation exchange resin.[4,5] Tri-*n*-octylamine was converted to the thiocyanate form by equilibrating an amine solution (0.1 or 0.2 M) in an appropriate diluent with a 0.25 N thiocyanic acid solution. Then, the organic phase was separated and diluted to cover the concentration range studied. The amine concentration was accurately determined by measuring the concentration of thiocyanate radicals in the tri-*n*-octylammonium thiocyanate solution (0.1 or 0.2 M) by the Volhard method after back-extracting the thiocyanate ion with a 0.1 N sodium hydroxide solution. A stock solution of iron(III) thiocyanate was prepared from iron(III) hydroxide and a thiocyanic acid solution (0.1 or 0.25 N). The solutions described above were prepared daily before use.

The diluents and their dielectric constants were as follows; *n*-hexane (1.9), cyclohexane (2.0), xylene, toluene (2.4), benzene (2.3), carbon tetrachloride (2.2) and chloroform (5.0). The xylene used in the present investigation was a mixture of three isomers; therefore, the dielectric constant is not given above.

For all operations, 25 m*l* each of a tri-*n*-octylammonium thiocyanate solution and an iron(III) thiocyanate solution were mixed together and equilibrated at room temperature. The iron(III) concentration in an aliquot of the aqueous phase was determined spectrophotometrically with 1, 10-phenanthroline. The amounts of iron(III) in the organic phase were calculated by material balances.

Results and Discussion

The effects of the amine concentration on the distribution ratio of iron(III) between the two phases, $q=\sum(\text{Fe})_o/\sum(\text{Fe})_w$, were examined at fixed concentrations of iron(III) and thiocyanic acid. These results are shown in Fig. 1.

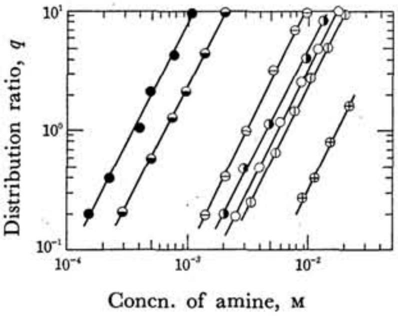

Fig. 1. Distribution of iron(III) as a function of amine concentrations -●- *n*-hexane (initial concn. of Fe(III), and aqueous HNCS concn., 5.55×10^{-5} M, 0.106 N) -◒- cyclohexane (4.45×10^{-5}, 0.0999), -⊖- xylene (4.74×10^{-5}, 0.102), 0.102), -◑- toluene (7.02×10^{-5}, 0.0971), -○- carbon tetrachloride (4.79×10^{-5}, 0.101), -⦶- benzene (3.25×10^{-5}, 0.0928), -⊕- chloroform (1.57×10^{-4}, 0.237).

If the activity coefficient of each species in both phases is kept essentially unchanged throughout the experiments and if the hydrolysis of iron(III) is negligible, then the distribution ratio, q, may be expressed by Eq. (1);

$$q=\sum(\text{Fe})_o/[\text{Fe}^{3+}](1+\sum_{n=1}^{6}\beta_n[\text{NCS}^-]^n) \qquad (1)$$

where n is the number of ligands associated with the ferric ion in each aqueous species and where β_n denotes their respective cumulative formation constants. As is generally the case for the amine extraction process,[6] the following two different mechansisms may be postulated to explain the extraction behavior of iron(III):

(a) The extraction of a neutral iron(III)

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[1] M. Ziegler, O. Glemser and N. Petri, *Z. Anal. Chem.*, **154**, 81 (1957).

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[3] M. W. Desai and T. K. S. Murthy, *Analyst*, **88**, 322 (1963).

[4] M. Fujimoto, *Bunseki Kagaku, (Japan Analyst)* **2**, 360 (1953).

[5] M. Fujimoto, This Bulletin, **26**, 353 (1953).

[6] Y. Marcus, *Chem. Revs.*, **63**, 139 (1963).

thiocyanate complex, which then forms a further complex with tri-*n*-octylammonium thiocyanate.

(b) An anion exchange of the thiocyanate ion for an anionic iron(III) thiocyanate complex already formed in the aqueous phase.

As for mechanism (a), the extracted species should be $Fe(NCS)_3$,[7] which associates with various numbers of tri-*n*-octylammonium thiocyanate to form an ion pair; Eq. (2) may then be written;

$$m\mathrm{R_3NH^+NCS^-} + \mathrm{Fe(NCS)_3} \rightleftharpoons (\mathrm{R_3NH})_m\mathrm{Fe(NCS)}_{3+m} \quad m = 1,\ 2,\ 3 \qquad (2)$$

where $R_3NH^+NCS^-$ refers to the tri-*n*-octylammonium thiocyanate. The equilibrium constant, K_m, is given by;

$$K_m = [(\mathrm{R_3NH})_m\mathrm{Fe(NCS)}_{3+m}]/[\mathrm{R_3NH^+NCS^-}]^m[\mathrm{Fe(NCS)_3}] \qquad (3)$$

Provided that the predominant iron(III) species in the organic phase is $(R_3NH)_jFe(NCS)_{3+j}$, where j is a fixed number of m, then, the distribution ratio, q, may be expressed in terms of K_j:

$$q = \beta_3 K_j[\mathrm{NCS^-}]^3[\mathrm{R_3NH^+NCS^-}]^j/\left(1 + \sum_{n=1}^{6}\beta_n[\mathrm{NCS^-}]^n\right) \qquad (4)$$

From the differentiation of the logarithmic form of Eq. (4) with respect to $\log[R_3NH^+NCS^-]$, Eq. (5) is obtained:

$$(\partial \log q/\partial \log[\mathrm{R_3NH^+NCS^-}])_{\mathrm{NCS}} = j$$

$$\text{or} \quad \log q = j \log[\mathrm{R_3NH^+NCS^-}] + C \qquad (5)$$

Equation (5) shows that, if the ligand concentration is kept constant, a linear relationship exists between $\log q$ and $\log[R_3NH^+NCS^-]$; the slope gives the number of amine molecules combined with the iron(III) thiocyanate complex in the organic phase. For mechanism (b), a similar relationship is derived between $\log q$ and $\log[R_3NH^+NCS^-]$, and the slope has the same meaning as j.

In Fig. 1, a log-log plot of q to $[R_3NH^+NCS^-]$ yields straight lines whose slopes are nearly 2. This means that the species of iron(III) thiocyanate with an amine-iron(III) ratio of "two-to-one" is predominant in the organic phase; hence, the complete formula is bis(tri-*n*-octylammonium)-pentathiocyanatoferrate(III).

In Eq. (5), $[R_3NH^+NCS^-]$ denotes the equilibrium concentration, but in the present paper the total concentration of amine is considered to be nearly equal to the $[R_3NH^+NCS^-]$ since the total iron(III) concentration is very small compared with the total amine concentration. The same applies to the equilibrium concentrations of the thiocyanate ion.

The effects of diluents on the extractability of iron(III) are also shown in Fig. 1. The extractability of iron(III) is roughly correlated with the dielectric constant of diluents; that is, the smaller the value of the dielectric constant, the larger the extractability.

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[7] Aquo groups were omitted for the sake of simplicity.