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DEPENDENCE OF DISTRIBUTION RATIO ON THE ANIONIC RADII FOR THE SOLVENT EXTRACTION OF PHENANTHROLINE AND BIPYRIDINE IRON(II) ION PAIRS

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Distribution ratio was measured for the extraction of ion pairs of tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridine)iron(II) with halide and pseudohalide anions. Nitrobenzene and dichloroethane were used as solvents. It was found that the larger the anion, the greater is the distribution ratio of the ion pair.

Tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridine)iron(II) chelate cations are well extracted into some organic solvents with certain anions. This fact has been extensively utilized for the spectrophotometric determination of a number of anions by the authors.1) During the course of our work, it became evident that easily extractable anions are spherical and large in size. Large anions like perchlorate are thought to be less hydrated and more strongly solvated by organic solvents while smaller anions such as chloride are thought to be strongly hydrated, showing much less extractability. It was now possible, in the present work, to establish an inverse relationship between anionic radii and the logarithm of the distribution ratios.

Experimental

A glass tube with cocks at both ends, 2.5 cm in diameter and 60 cc in volume, was used as a separatory funnel. An incubater, Taiyo Model M-1 with 200 strokes/min of shaking frequency was used as a temperature-controlled shaker. A spectrophotometer, Hitachi Model 139 with 10 mm glass cells was used for the measurement of absorbance.

Nitrobenzene and dichloroethane were used as extracting solvents. These were mutually saturated with distilled water before extraction.

Crystals of tris(1,10-phenanthroline)iron(II) and tris(2,2'-bipyridine)iron(II) perchlorate, thiocyanate, iodide, bromide and chloride were prepared and purified by recrystallization, the purity of which was checked by analysis. These are expressed as $Fe(phen)_3X_2$ and $Fe(bip)_3X_2$, respectively. These species show unvaried extractability over the pH range of 2 to 9. Extraction was carried out at pH 5.3 with a phosphate buffer solution.

To 15 ml of the aqueous solution of these salts, 15 ml of a solvent was added and extraction was carried out for 10 min under various temperatures ranging from 7° to 50°C. In every case, extra phenanthroline or bipyridine was added to either the aqueous or the organic phase to prevent possible dissociation of the chelates at high temperatures. Concentration was determined by spectrophotometry at absorption maximum of each spectrum: For $Fe(phen)_3X_2$, at 510 mμ in water and 516 mμ in nitrobenzene, for $Fe(bip)_3X_2$, at 522 mμ in water and 527 mμ in the organic phases. The absorption maxima remained at the same wavelength regardless of the counter anions tested.

Results and Discussion

The distribution ratio of the chelate cations, D in this extraction system is expressed as

$$D = \frac{[FeL_3X_2]_o + [FeL_3X^+]_o + [FeL_3{}^{2+}]_o}{[FeL_3X_2]_w + [FeL_3X^+]_w + [FeL_3{}^{2+}]_w} \qquad L;\ \text{1,10-phenanthroline or 2,2'-bipyridine}$$

In Table 1, D for all cases tested are shown. Nitrobenzene was the only effective solvent for the phenanthroline series while dichloroethane as well as nitrobenzene can be used for the bipyridine system. It is clear that the oder of extractability is: $ClO_4 > SCN > I > Br > Cl$. It is very interesting to note that the extractability of the chelate salts was controlled by the size of the counter anions. Lower extractability of $Fe(bip)_3X_2$ may be due to the smaller size of the cation. The plot, log D vs the reciprocal radii of anions, gave straight lines. This fact is quite understandable in view of Born's free energy formula of solvation. Thiocyanate, however, is largely deviated, as shown in Fig. 1. This deviation may be caused by the use of an erroneous value of its radius.

Perchlorate, thiocyanate and iodide, which were well extracted, showed increasing D values as the temperature was lowered. An opposite trend was observed for chloride which was hardly extractable while for bromide, temperature dependence can not be observed.

Table 1, Distribution Ratio*

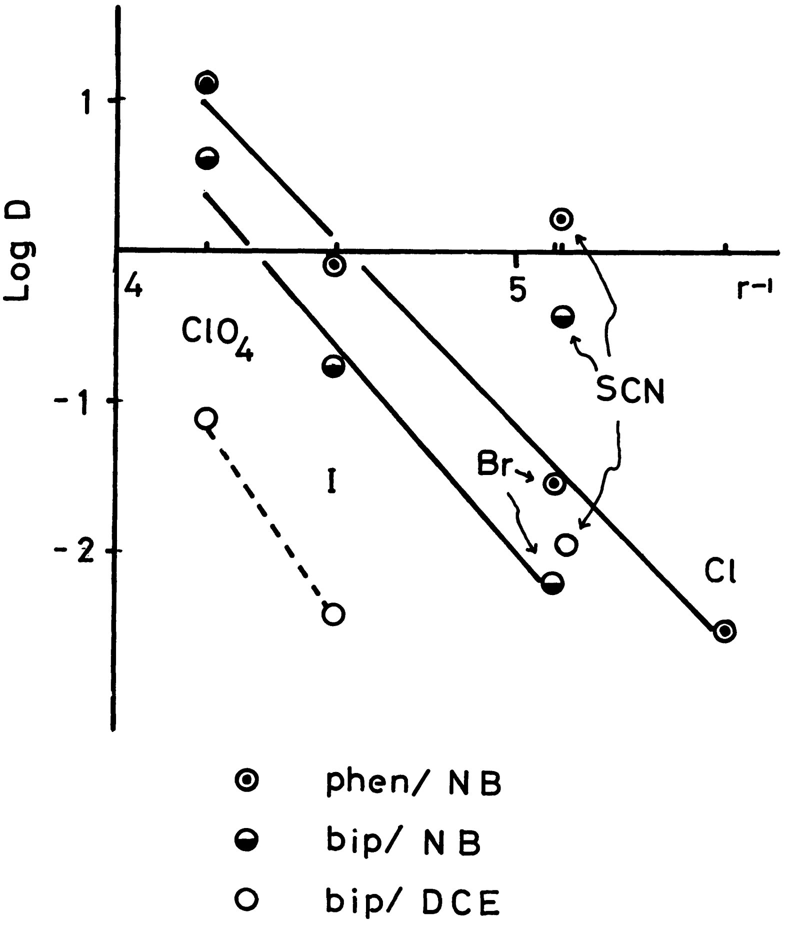
X radius Å	temp. °C	extraction system**		
		phen/NB	bip/NB	bip/DCE
		(original concentration of chelate salts in the aqueous phase)		
		(10^{-4}M)	(6×10^{-5}M)	(5×10^{-4}M)
ClO_4	15	14.9	5.37	0.128
2.36	25	13.5	4.22	0.077
	35	10.3	3.21	0.045
		(10^{-4}M)	(2.5×10^{-4}M)	(5×10^{-3}M)
SCN	15	1.98	0.45	0.014
1.95***	25	1.71	0.39	0.012
	35	1.46	0.34	0.009
		(10^{-4}M)	(3×10^{-4}M)	(3×10^{-3}M)
I	15	1.02	0.23	0.009
2.20	25	0.83	0.19	0.004
	35	0.76	0.17	0.002
		(10^{-3}M)	(2×10^{-3}M)	
Br	15	0.03	0.006	-
1.96	25	0.03	0.006	-
	35	0.03	0.006	-
		(10^{-2}M)		
Cl	15	0.002	-	-
1.81	25	0.003	-	-
	35	0.004	-	-

* with 1/15 M phosphate buffer

** NB = nitrobenzene, DCE = dichloroethane

*** cited from, K.S. Krasnov et al., Radiokhim., 4, 148 (1962)

Fig. 1. log D vs reciprocal radii of anions, at 25°C



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1) For example:

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(b) Y. Yamamoto, T. Tarumoto and Y. Hanamoto, ibid., 42, 268 (1969).

(c) Y. Yamamoto, T. Tarumoto and M. Tsubouchi, ibid., 44, 2124 (1971).

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