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Transference of Water to the Nitrobenzene Phase for the Extraction of Tris(1,10-phenanthroline)iron (II) and Tris(2,2′-bipyridine)iron(II) Chelate Salts

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The amount of water transferred to the nitrobenzene phase was determined 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. For both chelate systems the smaller the anion, the greater the amount of water transported, very similar results being obtained for a common anion. The results were discussed in relation to water of crystallization, extractability and temperature effect.

During the course of studies on the solvent extraction mechanism of tris(1,10-phenanthroline)iron(II) and tris(2,2′-bipyridine)iron(II) chelate ion pairs, our attention was drawn to the problem of how ion pairs are hydrated. We showed[1)] that a small amount of water in nitrobenzene greatly affects the heats of solution of the chelate salts.

In order to investigate the role of water in solvent extraction, the amount of water transported by the ion pairs was determined. Similar studies were carried out by varying chelate cations.[2)] However, no effects of anions were observed. We observed a very clear trend depending on the counter anions. Similar results were obtained between both chelate salts with a common counter anion. A part of the work has been reported.[3)]

Experimental

Materials. Crystals of $Fe(phen)_3(ClO_4)_2$, $Fe(phen)_3(SCN)_2$, $Fe(phen)_3I_2$, $Fe(phen)_3Br_2$, $Fe(bipy)_3(ClO_4)_2$, $Fe(bipy)_3(SCN)_2$, $Fe(bipy)_3I_2$, and $Fe(bipy)_3Br_2$ were prepared as follows. In 400 ml of water, 0.01 mol of Mohr's salt and 0.03 mol of 1,10-phenanthroline or 2,2′-bipyridine were dissolved. To the resulting dark red solution was added 30 ml of saturated solution of sodium salt of a corresponding anion and the solution was condensed to an appropriate volume on a water bath at about 80 °C. The solution was cooled to room temperature and the crystalline precipitate was separated by filtration. Crystals thus obtained were recrystallized twice from water and air-dried. The purity was confirmed by analysis at the Center for Chemical Analysis of Kyoto University. The analytical results are shown in Table 1.

Nitrobenzene of analytical reagent grade was successively washed with sulfuric acid, sodium hydroxide and distilled water, and was then distilled under reduced pressure.

Apparatus. A Karl Fischer automatic titrator, MK-SS of Kyoto Electronics Co., Ltd. was used for determination of the water content. The concentration of the chelate salts was determined with a spectrophotometer, Hitachi 139.

Procedure. In a glass bottle, 100 ml of nitrobenzene was mixed with 50 ml of water for 4 days under stirring with a magnetic stirrer at 25 ± 0.1 °C and the water content in nitrobenzene was occasionally checked by Karl Fischer titration. It was found that stirring for 24 hr was sufficient for the water content in nitrobenzene to become constant. A certain amount of a chelate salt was then added to this mixed solvent and the solution was stirred for 3 hr. Distribution of the chelate salt between water and nitrobenzene was found to be complete after 10 min stirring from measurement of the absorbance of both phases (510 nm for aqueous phase and 516 nm for organic phase). For an aliquot of the nitrobenzene extract, the water content was determined by titration. The concentration of the chelate salt was determined from the absorbance at 516 nm with the aid of a calibration curve prepared beforehand.

Results and Discussion

The water content at 25 °C was plotted against the concentration of $Fe(phen)_3I_2$ as in Fig. 1. The lines

TABLE 1. RESULTS OF ANALYSIS OF $FeL_3X_2 \cdot nH_2O$

X	L	$n^{a)}$	C % Calcd	C % Found	H % Calcd	H % Found	N % Calcd	N % Found
ClO_4	phen	1	53.16	53.94	3.23	3.26	10.33	10.59
	bipy	0	49.82	49.69	3.34	3.38	11.62	11.63
SCN	phen	2	60.95	61.17	3.78	3.96	14.97	14.90
	bipy	3	55.33	55.06	4.35	4.37	16.13	16.03
I	phen	2	48.78	48.73	3.18	3.16	9.48	9.76
	bipy	5	41.50	41.70	3.95	3.95	9.68	9.64
Br	phen	6	50.02	49.55	4.21	4.16	9.73	9.70
	bipy	5	46.54	46.22	4.43	4.56	10.85	10.85

a) Round numbers were allotted so that experimental values of elements most closely fit the calculated ones.

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1) Y. Yamamoto and T. Tarumoto, *Anal. Lett.*, **3**, 537 (1970).

2) S. Burchett and C. E. Meloan, *Separ. Sci.*, **3**, 119 (1968); D. R. Gere and C. E. Meloan, *ibid.*, **3**, 298 (1968).

3) Y. Yamamoto, T. Tarumoto, and T. Tarui, *Chem. Lett.*, **1972**, 459.

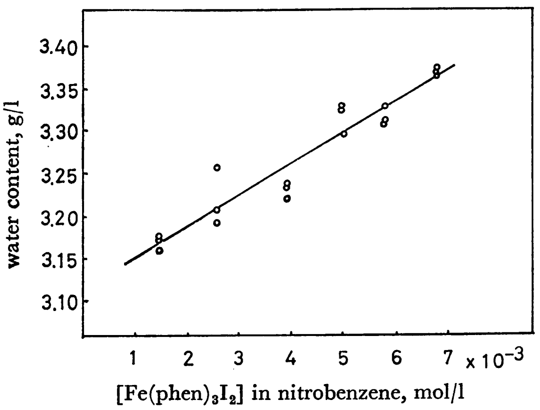

Fig. 1. Water content *vs.* the concentration of the chelate salt in nitrobenzene, 25 °C.

were drawn by means of the least-squares method. The water content increases linearly as the chelate salt concentration increases. This holds for all the other chelate salts. The concentration ranges tested were: (1) phenanthroline series, for perchlorate 1.8—5.2$\times 10^{-2}$, for thiocyanate 0.89—7.4$\times 10^{-3}$, for iodide 1.5—6.8$\times 10^{-3}$ and for bromide 1.4—2.4$\times 10^{-4}$ mol/l, (2) bipyridine series for perchlorate 3.6$\times 10^{-3}$—3.8$\times 10^{-2}$, for thiocyanate 7.2$\times 10^{-4}$—6.0$\times 10^{-3}$ for iodide 1.4—6.8$\times 10^{-3}$ and for bromide 7.2$\times 10^{-5}$—4.8$\times 10^{-4}$ mol/l in the nitrobenzene phase.

The water content in nitrobenzene in the absence of chelate salts was 2.57 g/kg and the cross sections of the plots, water content *vs.* chelate salt concentration agreed with this within experimental error. Thus the number of water molecules transported by the chelate salts was calculated from the slope of the plots. The results are shown in Table 2 where they are also compared with the number of water of crystallization obtained from TGA measurements and elemental analyses.

Very similar results were obtained for the two series. Bipyridine-bromide salt shows a somewhat lower value than that of the corresponding phenanthroline salt because the concentration of Fe(bipy)$_3$Br$_2$ in the aqueous phase is much higher than that of Fe(phen)$_3$Br$_2$. For the phenanthroline series, there is a consistency between the number of transported water and that of water of crystallization. Also for the bipyridine series similar results were obtained between the transferred water and the water of crystallization except for iodide. The consistency for the former series might be fortuitous, there being no reason why the crystalline state should be similar to the ions in solution. However, it can be concluded that water is transported exclusively by the anions and the chelate cations take no part in the transference. The chlorides did not offer any useful information because of their extremely low extractability.

TABLE 2. WATER TRANSFERRED AND THE WATER OF CRYSTALLIZATION WITH FeL$_3$X$_2$ (IN mol/mol OF THE CHELATE SALT)

L	X	Temp (°C)	Water transferred	Water of crystallization	
				TGA	Analysis
phen	ClO$_4$	25	0.64±0.04	1	1
		20	0.56±0.02		
	SCN	25	1.9 ±0.1	1.5	2
		20	1.9 ±0.1		
	I	25	2.1 ±0.2	2	2
		20	1.6 ±0.1		
	Br	25	5.5 ±0.8	6	6
		20	—		
bipy	ClO$_4$	25	0.72±0.02	0	0
		20	0.58±0.01		
	I	25	2.1 ±0.2	5	5
		20	1.6 ±0.1		
	Br	25	3.6 ±1.9	5	5
		20	—		

Temperature effect was also studied by carrying out the same procedure at 20 °C. Lower values were obtained as shown in Table 2. The solubility of water in nitrobenzene was also found to decrease as the temperature is lowered (2.57 g/kg at 25 °C and 2.16 g/kg at 20 °C). This suggests that the water transported by the chelate salts is in equilibrium with the dissolved water in nitrobenzene.

The ability of the anions to carry water into the nitrobenzene phase seems to be related to the tendency of their hydration; the smaller the anions, the greater the amount of water transported. This may cause the lower extractability of the ion pairs with smaller counter anions.[4] However, it is difficult to conclude from our results whether the transferred water in nitrobenzene exists hydrated to the anions or it is dispersed in the organic phase.

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4) Y. Yamamoto, T. Tarumoto, and E. Iwamoto, *ibid.*, **1972**, 255.