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TRANSFERENCE OF WATER TO THE NITROBENZENE PHASE FOR THE EXTRACTION OF TRIS(1,10-PHENANTHROLINE)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) with halide and pseudohalide anions. The results were consistent with the number of water of crystallization of these salts.

Tris(1,10-phenanthroline)iron(II) chelate cation forms ion pairs with a number of anions and is well extracted to nitrobenzene. The physico-chemical aspects of this extraction system as well as the application of this fact to the spectrophotometric determination of anions have been studied by the authors. In a previous work,[1)] it was shown that a small amount of water in nitrobenzene (or vice-versa) greatly affects the heats of solution of these chelate salts.

In order to further investigate the role of water in the solvent extraction, the amount of water transported by the chelate salts was determined. The same kind of works have been carried out by Meloan and others[2)] by varying chelate cations. However, according to their data, effects of anion were not observed. In the present work, a quite clear trend was observed depending on the counter anions.

Experimental

Crystals of tris(1,10-phenanthroline)iron(II) perchlorate, thiocyanate, iodide and bromide were prepared and the purity was checked by analysis.

To a mixture of water and nitrobenzene kept at 25°C, a certain amount of the chelate salt was added. The mixture was then stirred until the extraction equilibrium was attained. For an aliquot of the nitrobenzene layer, water content was measured by means of Karl Fischer method with an automatic titrator, MK-SS of Kyoto Electronics Co., Ltd. and the concentration of the chelate salt was determined with a spectrophotometer, Hitachi 139 from the absorbance of the chelate cation at 516 nm.

Results and Discussion

As an example of the results, the water content was plotted against the concentration of $Fe(phen)_3 \cdot I_2$ in the nitrobenzene phase, in Fig. 1. The line was drawn according to the calculation of the method of least squares.

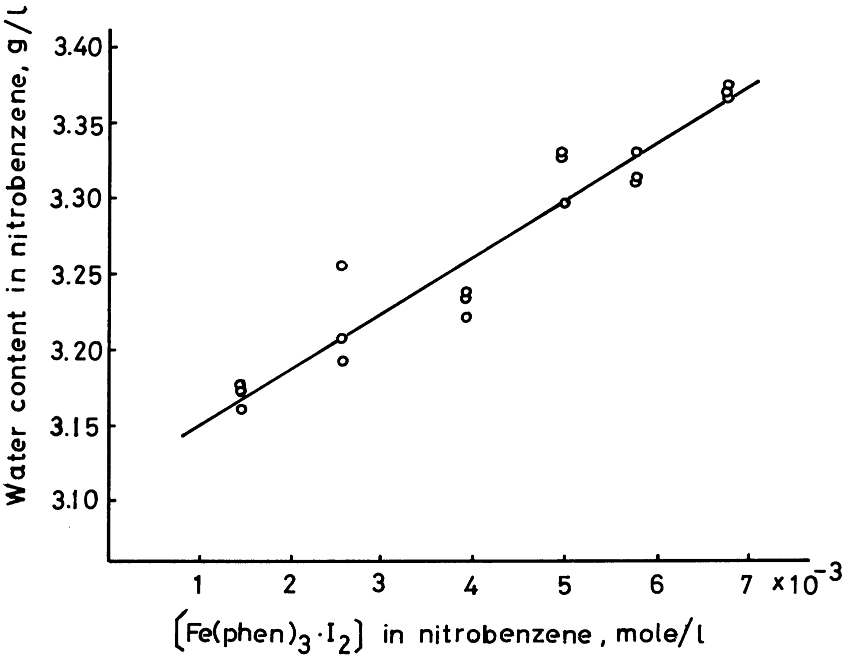

Figure 1. Water content vs the chelate salt concentration

The water content increases linearly as the chelate salt concentration increases. This trend is the same for all other chelate salts tested. The concentration range tested was: for perchlorate 1.784×10^{-2} to 5.218×10^{-2}, for thiocyanate 0.894×10^{-3} to 7.409×10^{-3}, for iodide 1.499×10^{-3} to 6.819×10^{-3} and for bromide 1.434×10^{-4} to 2.430×10^{-4} mole /litre in the nitrobenzene phase. For chloride, no clear change of water content was observed because its distribution ratio is extremely low and therefore the chelate concentration in the aqueous phase inevitably became very high for an effective extraction so that the water in the nitrobenzene phase may have been transferred back to the aqueous phase.

The number of water molecule transported by the chelate salts was calculated from the slope of the plots and the results are shown in Table 1. The results were also compared with the number of water of crystallization obtained from TGA measurements and elemental analyses.

Table 1. Water transferred and water of crystallization with $Fe(phen)_3 \cdot X_2$ (in mole/mole of the chelate salt)

X	water transferred	water of crystallization by TGA	by analysis*
ClO_4	0.64 ± 0.04	~ 1	1
SCN	1.9 ± 0.1	1.5	2
I	2.1 ± 0.2	2.0	2
Br	5.5 ± 0.8	5.9	6

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

As is obviously seen from the Table, there is a very strong consistency between the number of transported water and that of water of crystallization. A work is under way on the transference of nitrobenzene for the reverse process.

References

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

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

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