

NITROBENZENE SOLVATE OF TRIS(1,10-PHENANTHROLINE)IRON(II) IODIDE

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Nitrobenzene solvated tris(1,10-phenanthroline)iron(II) iodide was isolated out of nitrobenzene-saturated water. The amount of nitrobenzene was determined by spectrophotometry in the U.V. region. Other facts supporting the solvate formation are also presented.

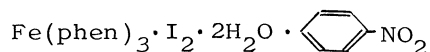
During the course of our physico-chemical study^{1)~5)} of the extraction mechanism of the solvent extraction of tris(1,10-phenanthroline)iron(II) chelate ion pairs, the problem of solvation of the ion pairs attracted our attention.

As a step to solving this problem, the crystal of tris(1,10-phenanthroline)-iron(II) iodide was isolated out of water saturated with nitrobenzene. Nitrobenzene is a unique solvent for the extraction of the ion pairs because of its high dielectric constant and dipole moment. The chelate salt thus prepared had one molecule of nitrobenzene attached to it. This was confirmed by elemental analysis, spectrophotometric determination in the U.V. region and thermal gravimetric analysis.

The method of preparation of the chelate salt was as follows. A certain amount of the crystal of tris(1,10-phenanthroline)iron(II) iodide dihydrate, $[\text{Fe}(\text{phen})_3] \cdot \text{I}_2 \cdot 2\text{H}_2\text{O}$ already prepared according to the method presented elsewhere¹⁾, was dissolved in water saturated with nitrobenzene. The salt was recrystallized after evaporation of the solution. The crystal thus obtained was air-dried and was subjected to analysis.

In Table I, the results of analysis are shown, where the values of analysis are compared with the calculated values by taking the composition of the chelate

salt as:



Quite a good agreement is observed for each element analyzed.

Table 1

	C	H	N	Fe	I
calcd.(%)	49.97	3.29	9.71	5.53	25.14
found(%)	49.95	3.28	9.73	(5.83) (ash)	24.97

It was thus found that the tris(1,10-phenanthroline)iron(II) iodide salt had one molecule of nitrobenzene and two molecules of water attached to it.

The amount of nitrobenzene was also determined to be one molecule using a calibration curve at 252 nm made by dissolving known amounts of nitrobenzene in pure cyclohexane. A certain amount of the chelate salt was dissolved in water and the solution was extracted with appropriate volume of cyclohexane. The absorption spectra was measured against a reference solution. The reference solution was prepared exactly in the same manner except that the nitrobenzene-free dihydrate salt was used instead. The spectrum of cyclohexane extract was identical to that of nitrobenzene dissolved in cyclohexane shown in Fig. 1. To confirm that the extraction of nitrobenzene is complete, the nitrobenzene-free chelate salt solution was extracted also with cyclohexane containing a known amount of nitrobenzene. The concentration of nitrobenzene in cyclohexane remained unchanged after the extraction.

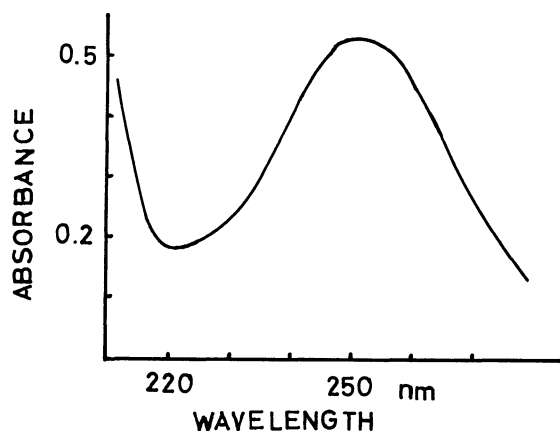


Fig. 1. Spectrum of nitrobenzene in cyclohexane, 7.2 mg/l at 25°C.

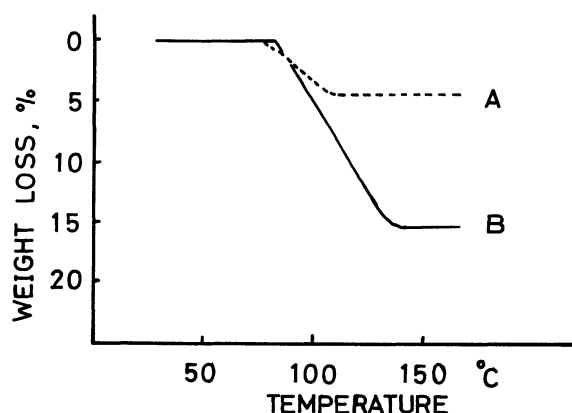


Fig. 2. TGA curve of the chelate salt. A: nitrobenzene-free. B: nitrobenzene solvated.

A TGA curve of this chelate salt is shown in Fig. 2. The curve A corresponds to the dehydration and the curve B is due to the removal of both nitrobenzene and water. The amount of nitrobenzene from the TGA data also supported the result obtained above.

It was found that the solubility⁵⁾ of the nitrobenzene-free chelate salt in water is decreased by the presence of nitrobenzene, i.e., 6.15×10^{-3} mole/kg in water and 3.29×10^{-3} mole/kg in nitrobenzene-saturated water at 25°C. This may be explained by the solvation of the chelate salt with nitrobenzene. The heat of solution of the anhydrous nitrobenzene-free salt was 5.3 kcal/mole in water and 3.5 kcal/mole in nitrobenzene-saturated water at 25°C. The decrease may also be due to the solvation with nitrobenzene. The method of measurements of heat of solution is previously presented elsewhere²⁾.

The same procedure was applied to tris(2,2'-bipyridine)iron(II) iodide but no solvated nitrobenzene was found. This was confirmed also by TGA, elemental analysis and heat of solution measurement. This difference may be that the bipyridine chelate salt, which is pentahydrate, has greater affinity to water than phenanthroline chelate salt. The fact that phenanthroline system has larger distribution ratios than bipyridine system,³⁾ can be explained by the same behavior.

It is not yet clear, from this experiment, how the nitrobenzene is solvated to the ion pair. However, it can be said that the nitrobenzene solvate plays a positive role for the extraction of the ion pair to nitrobenzene.

References

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