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Zbigniew Gregorowicz[a]; Wojciech Bakowski[a]
[a] DEPARTMENT OF ANALYTICAL AND GENERAL CHEMISTRY, SILESIAN TECHNICAL UNIVERSITY, GLIWICE, POLAND

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The Influence of the Dehydration Effect upon the Extraction of Tris(bathophenanthroline) Iron(II) Perchlorate in a Medium Containing Tris(bathophenanthroline) Iron(II) Sulfate

ZBIGNIEW GREGOROWICZ and WOJCIECH BĄKOWSKI

DEPARTMENT OF ANALYTICAL AND GENERAL CHEMISTRY
SILESIAN TECHNICAL UNIVERSITY
GLIWICE, POLAND

Abstract

Investigations have been carried out concerning the dehydration effect brought about by the presence of ethanol, methanol, dioxane, and acetone in the aqueous phase during the extraction of the ion pairs of tris(4,7-diphenyl-1,10-phenanthroline) iron(II) with a perchlorate and a sulfate anion in the nitrobenzene–cyclohexane system. The particulary effective influence of ethanol has been shown. It has been found that the dehydration effect increases the extraction ratio more in the case of the perchlorate anion, which leads to a greater selectivity of extraction.

INTRODUCTION

The use of a complex cation of bathophenanthroline with Fe(II) (bathoferroine) for the extraction-spectrophotometric method to determine anions is relatively rare in comparison to the proper complex of 1,10-phenanthroline. The reason for this is in the very low selectivity of extraction anions (*1*), whether one uses polar or nonpolar solvents for extraction. Up to the present, elaborate determinations imposed complicated procedure by using physical parameters, mainly low temperatures. One example is the investigations by Yamamoto and co-workers (*2*).

Some light has been cast upon the reason of low selectivity of these extractions by the investigations of Gere and Meloan (*3*, *4*) and Burchett and Meloan (*5*), who have proved that the number of water molecules associated with the ion pairs of the tris(bathophenanthroline) iron(II) cation and which are transferred in the course of extraction to the polar solvents which are being used as the organic phase is surprisingly large and does not depend on either the anion or the solvent. On the other hand, it is well known that less polar solvents, which have not been investigated by these authors, are more hydrophobic, so that they may repel strongly hydrated ion-associated compound molecules.

It is probable that the energetic differences connected with the differentiated degree of anion association would be insignificant in both cases in comparison with the effects brought about by solvation, which might account for the small differentiation of the extraction coefficients for different anions.

It is the aim of our investigations to examine the influence of the addition of ethanol, methanol, dioxane, and acetone to the aqueous phase on the selectivity of the extraction of ion pairs of bathoferroine in a chosen nitrobenzene–cyclohexane system. It is well known that such oxygen compounds can change the solvation equilibrium that might result in the dehydration effect of the ion-associated compound (*6*).

EXPERIMENTAL

Apparatus

Spectrophotometer Unicam SP–1700 provided with 1 cm long glass cells.

Titration assembly for titrating with K. Fischer's reagent, with a device for reading off the end of titration at the dead point (*7*).

Reagents

All the used reagents were of analytical grade.

Nitrobenzene and *cyclohexane* were additionally purified by distillation.

Dioxane was purified from peroxides before each use by means of the Vogel method (*9*).

Bathophenanthroline was produced by PPH Polskie Odczynniki Chemiczne.

Ferrous sulfate was purified by means of a threefold crystallization from water and precipitation with ethanol.

K. Fischer's reagent was prepared according to the literature (*8*).

The fundamental bathophenanthroline solutions were a 0.03 *M* solution of bathophenanthroline in ethanol, a 0.018 *M* solution of bathophenanthroline in methanol, and a 0.010 *M* solution of bathophenanthroline in dioxane.

PROCEDURE

Preparation of the Complex. (a) In a 100-ml measuring flask, 10 ml of the fundamental solution of bathophenanthroline was placed in either ethanol, methanol, or dioxane, and 10 ml of $FeSO_4$ solution of a three times smaller mole concentration was added.

After 10 min, 20 ml of $10^{-4}M$ ascorbic acid solution was added, and the measuring flask was filled to the scale mark with such an amount of water and ethanol, methanol, or dioxane that the final solution would be of the desired percentage by volume.

Dilution of the complex was accomplished with a phase identical in composition, though not containing the same complex.

(b) Because of the low solubility of bathophenanthroline in acetone, in all the tests involving this solvent the complex in the solid state was added to the aqueous phase. It had been obtained by mixing 10 ml of the fundamental solution of bathophenanthroline in ethanol with 2 ml of 0.05 *M* solution of $FeSO_4$ and evaporating the solvents in vacuum at room temperature.

Determination of the Number of Water Molecules Associated with the Ion Pair Which, During the Extraction Process, Are Transferred to the Organic Phase. For each concentration of ethanol, methanol, dioxane, and acetone in the aqueous phase, a series of 8 to 16 samples were tested, each series comprising three different concentrations of $Fe(bath)_3(ClO_4)_2$ as well as a blank. In each test the pH was checked and a constant ionic strength of the aqueous phase (0.1 *M* NH_4ClO_4) was applied. All the extractions were carried out at the same temperature (21 ± 0.2°C) and in the same phase volumes. A nitrobenzene–cyclohexane system was used as the organic phase with a 1:3 ratio v/v. The time of shaking was 45 min for acetone and 15 min in the remaining cases.

When the extraction was completed, the system was left standing for 6 hours for the phases to separate. Then samples of the organic phase were taken and the total water content determined. The concentration of the complex in the organic phase was determined spectrophotometrically (at λ = 535 mm) after each titration. The straight-line parameters showing the relation between the complex and the total water concentration in the organic phase were calculated by the least squares method. The number of water molecules corresponding to one complex molecule was calculated from the slope of the plot.

Determination of the Extraction Ratio of the Ion Pairs of Bathoferroine in Dependence on the Composition of the Aqueous Phase. In each test 13 ml of the organic phase were used, each containing 6 volumes of cyclohexane and 1 volume of nitrobenzene. The complex was prepared in the same way as described above. The aqueous phase always contained 3 μmoles of $Fe(bath)_3SO_4$ and 1 μmole of NH_4ClO_4 in 13 ml. The blank did not contain NH_4ClO_4. The shaking time always amounted to 5 min, and the temperature was 21 ± 0.2°C. After the separation of the phases the organic phase was diluted to 25 ml with a fresh batch of nitrobenzene–cyclohexane mixture, after which the absorbance at λ = 535 nm was measured in relation to the solvent (in the case of acetone, in relation to the blank). The absorbance of the blanks of systems containing ethanol, methanol, and dioxane was also measured in relation to the solvent. While investigating the extraction from water alone—due to the low solubility of the complex—the system was supplemented with an ion associated compound in the form of a solid; two series of measurements were carried out, one with the complex added to the aqueous phase and the other with the complex added to the organic phase. The content of the remaining components and the procedure were identical with those described above.

RESULTS AND DISCUSSION

The results obtained by measuring the hydration number are presented in Table 1 and in Fig. 1. All the other results are presented in Figs. 2 and 3.

Due to the behavior of the $Fe(bath)_3(ClO_4)_2$, it is convenient to disccus the results obtained within the following three ranges of the ethanol, methanol, dioxane, and acetone content in the aqueous phase:

(a) From 0 to 5% in volume.
(b) From 5 to 20% in volume.
(c) Above 20% v/v.

In range "a" the decrease of the hydration number is the same for every compound investigated and does not depend on their structure or

TABLE 1

Investigated substance	Concentration of the substance in the aqueous phase	Hydration number	Average standard deviation	Number of measurements
Ethanol	0	26.4	5.5	8
	9	3.4	0.6	14
	13.5	0.6	0.3	8
	22.5	0.0	0.5	8
	40.5	0.1	0.5	8
Methanol	0	26.4	5.5	8
	9	4.0	0.5	8
	18	2.3	0.3	8
	40.5	1.0	0.1	8
Dioxane	0	26.4	5.5	8
	9	5.1	1.1	16
	14.4	9.4	5.0	8
	18	25.6	1.4	8
Acetone	0	26.4	5.5	8
	9	3.9	3.3	16
	14.4	14.0	3.4	10
	22.5	15.4	3.3	10

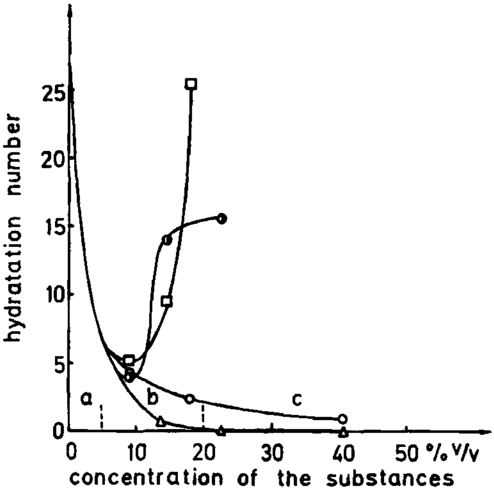

FIG. 1. Curves showing the dependence of the hydration number on the concentration of the substance investigated in the aqueous phase: (△) ethanol, (○) methanol, (□) dioxane, and (◑) acetone.

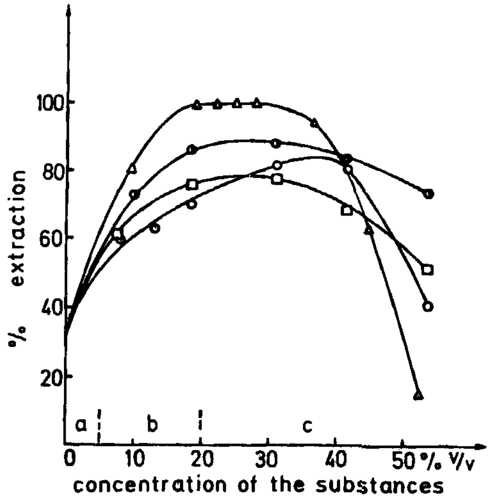

FIG. 2. Curves showing the dependence of the extraction ratio on the concentration of the substance investigated in the aqueous phase: (△) ethanol, (○) methanol, (□) dioxane, and (◑) acetone.

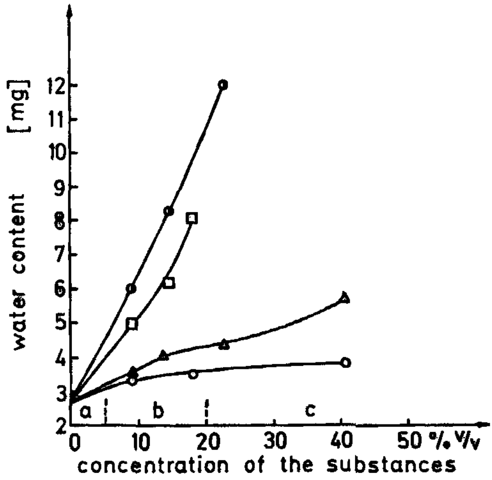

FIG. 3. The dependence of the equilibrium water content in 10 ml of the organic phase on the concentration of the substance investigated in the aqueous phase: (△) ethanol, (○) methanol, (□) dioxane, and (◑) acetone.

the dipole moment. This fact suggests that at least some of water molecules are bound with the complex cation (*7*) in such a way that they are easily accessible.

However, from the investigations of Burchett and Meloan (*10*) it is known that some part of them are bound rather strongly. Therefore it seems possible that within this range of concentrations of dehydration substances the secondary hydration shell will be broken during extraction. It is to be noted that within this range, although there is relatively great dehydration (reduction of dehydration number of about 72%), a relatively small increase in the extraction percentage takes place (~15%). This proves that the dehydrated molecules are still strongly hydrophilic.

Within the "b" range the reduction of the dehydration number depends largely on the kind of compound introduced. Methanol and ethanol pass into the organic phase in rather small quantities, causing only insignificant changes of its physicochemical properties. However, dioxane and acetone cause a great increase in hydrophilicity. This makes it possible not only for large quantities of water to pass over into the organic phase (Fig. 3) but also strongly hydrated associated molecules.

The organic phase begins to behave like a polar solvent, i.e., it ceases to play the part of the agent, and even strongly hydrated ion pair molecules can leave the aqueous phase. It is easy to understand why many authors (*3–5, 7*) have not noticed the influence of high concentrations of ethanol and methanol in the aqueous phase upon the hydration number of similar ion pairs while they were being extracted by strongly polar solvents such as the higher alcohols, nitrobenzene, and nitromethane.

Range "c" is characterized by a rapid decrease of the extraction ratio as the concentration of the compounds being investigated is increasing although (in case of ethanol and methanol) there is almost total dehydration. Based on our investigation, it is not possible to state precisely whether this phenomenon is brought about by the formation of new complex compounds with ethanol, methanol, dioxane, and acetone as one of ligands or by the increasing solubility of the ion associated compound in the aqueous phase due to the addition of these substances (all four compounds are good solvents of the ion pairs of bathoferrione). A complete explanation of this phenomenon would exceed the limits of this paper.

Generally, analysis of the data shows that the extraction ratio of the ion pair $Fe(bath)_3(ClO_4)_2$ is a function of the hydration number, and if this process is not disturbed by the miscibility of the two phases, the decrease of the number of water molecules, which together with the ion-associated compound are transferred to the organic phase, leads to an increase of the extraction ratio. The investigations of Gere and Meloan (*3*, *4*) and Burchett and Meloan (*5*) suggest that the $Fe(bath)_3^{2+}$ cation is mainly hydrated, and there is no reason to assume that this effect is not also true for the $Fe(bath)_3SO_4$ system, which has also been tested by the extraction ratio–concentration of ethanol, methanol, dioxane, and acetone.

Because this ion-associated compound was not extracted in any of the tests, irrespective of the content of the substances being investigated (with the exception of systems containing acetone) which were added to the aqueous phase, and taking into account that the ClO_4^- ion (as opposed to SO_4^{2-}) is a strongly associating anion, it is implied that in the extraction of dehydrate bathoferroine ion pairs the degree of association of the ions is one of the most decisive factors determining the extraction ratio. The increase of the extraction ratio of the ClO_4^- anion brought about by the observed dehydration effect is thus tantamount to an increase of the selectivity of extraction, as the dehydration effect does not influence the extraction of SO_4^{2-} ions. This latter conclusion may prove to be of great practical importance for the development of extraction methods of anion separation by means of a bathoferroine cation, together with the simultaneous spectrophotometric determination of these anions.

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