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INFLUENCE OF TEMPERATURE ON EXTRACTION

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ABSTRACT

The literature data related to the influence of temperature on extraction are very often controversial. It appeared advisable to undertake an investigation of such an influence in systems containing diisopropyl ether (IPE), because of their ability to form three coexisting liquid phases.

In the extraction system H_2O-HCl-$FeCl_3$-IPE, the volume changes and the metal distribution depending on temperature (ranging from 13 to 40°C) and the initial concentration of hydrochloric acid (5 to 11 M) were examined. The formation of the third phase (heavy organic phase) is of special interest in the separation processes because a very high concentration of metal can be expected. The complexity of such a multicomponent and multiphase system makes a phenomenological approach more appropriate than a thermodynamic one.

In the three-phase system an increase in temperature increases the distribution ratio of iron(III) whereas in the two-phase system, the distribution ratio decreases. The extraction factors based on phase volume and distribution ratio were calculated. Phase transformations occur in a narrow temperature range. A decrease of the initial acid concentration and an increase in temperature contribute to an increase in the number of equilibrated phases. Choice of the appropriate temperature in similar systems offers new possibilities in the application of extraction in separation procedures.

INTRODUCTION

It will be very difficult to presume the specific effect of temperature on extraction when halo-metallic complex acid extracts into a carbon-bonded oxygen-donor solvent (e.g., ether). Besides, complexity of the extraction mechanism (formation of a hydrosolvated halo-metallic complex acid of changeable composition) also confirms the lack and controversy of available data.

In the literature there are data on the negative influence of temperature on extraction (1-3), and some authors (4,5) consider that an increase in temperature most frequently leads to a decrease of distribution ratio. There are also experimental data that suggest a negligible influence of temperature on extraction (6,7) or enhancement of extraction by a change in temperature. Enhancement was found in the ternary system consisting of water-hydrochloric acid-antimony(V) chloride-diisopropyl ether, which was investigated in the temperature range of 10 to 30.5°C (8). Existing data on the three-phase system point out the important role of temperature (9,10). Results of the investigations of systems with diisopropyl ether (IPE) used as a solvent indicate that temperature change can cause phase transformations occurring in a relatively narrow range and close to room temperature (11,12).

The existing data show that no general conclusions can be drawn and that only experimental evidence on the specific system can give a proper picture of the temperature dependence.

In this article results of an investigation of the system H_2O-HCl-$FeCl_3$-IPE in the temperature range of 13 to 40°C will be presented. The extraction systems containing IPE are interesting because of their ability to form three coexisting liquid phases (i.e., organic phase under particular conditions separates into two phases — the light and the heavy organic phase). Formation of the third phase is of special interest for separation processes because a very high concentration of metal can be expected. By selecting proper conditions it is relatively easy to reach the formation of a third phase and by changing definite parameters to obtain its disappearance.

MATERIALS

Diisopropyl ether, Fluka or Merck, C.P. was purified, distilled, and dried. Purification was achieved by successive treatments with ferrous sulfate (saturated solution), potassium permanganate (0.5% solution), sodium hydroxide (0.5% solution), and distilled water. Purified diisopropyl ether was distilled, and the middle fraction (b.p. 66.8 to 67.8°C at 744 mm Hg) was collected. After drying by calcium chloride, the diisopropyl ether contained 0.85 mg H_2O/ml.

The other chemicals used were: hydrochloric acid, Merck, p.a. and ferric chloride hexahydrate, Hopkins and Williams, p.a.

METHODS

The systems were prepared in 25 and 50-ml separation funnels having a calibrated stem and/or in 15-ml graduated cuvettes selected from a large group in order to assure accurate volume calibrations. After vigorous shaking, predetermined components were placed in a water bath with a thermostat held by an automatic control at any desired temperature. Each time the shaking was repeated in the same manner, at 15-min intervals for 1 hr. Volumes of equilibrated phases were determined before sampling. Sampling using pipettes thermally controlled at the extraction temperature was carried out directly (from cuvettes) or after removal of the separated phases from the funnel. All data obtained are the results of two or more repeated experiments depending on the degree of reproducibility.

Methods of Analysis

The metal content in the aqueous phase and in pretreated samples of organic phases was determined by UV absorption measurements or complexometric titration (for larger quantities of iron). Absorbance was measured at 335 nm. The complexometric titration was carried out using Titriplex III and 2-oxi-5-sulfobenzoic acid (13).

RESULTS AND DISCUSSION

The previously indicated strong influence of temperature on the volumes of equilibrate phases (10,13) is confirmed by the results obtained. Figure 1 shows the influence of temperature on the change of equilibrate phase volumes in the system investigated: H_2O-HCl-$FeCl_3$-IPE at the constant initial aqueous concentration of

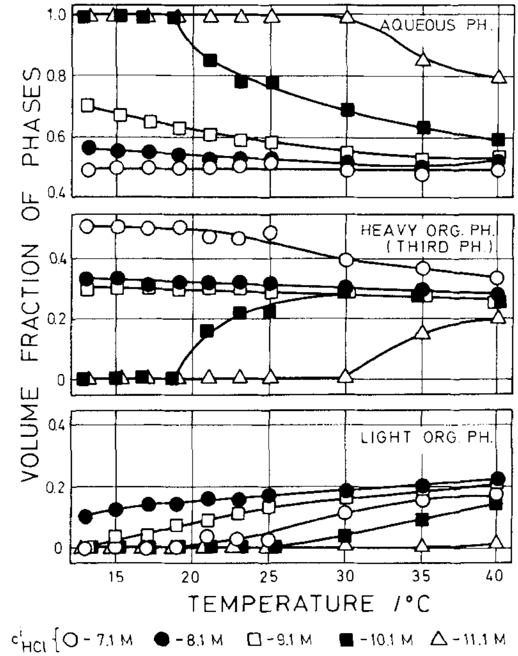

FIGURE 1. Volume fraction of phases vs temperature at different initial hydrochloric acid concentrations (7.1 to 11.1 M) (System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, r^i = 1.0.

iron(III) of 0.28 M and the initial phase ratio of 1.0. Temperature varied in the range from 13 to 40°C by steps of 2 or 5°, and the initial acid concentration varied in the range from 5.0 to 11.1 M. For purposes of clarity, curves on Fig. 1 pertaining to different phases are presented separately. Volumes of coexisting phases are expressed by volume fractions (i.e., by the ratio of the equilibrate phase volume and the equilibrate total volume of the heterogeneous system). It is evident that in the region investigated a decrease in the initial acid concentration and an increase in the temperature contribute to an increase in the number of phases. The change of volume is greatest in aqueous and heavy organic phases at 10.1 M and 11.1 M initial concentrations of hydrochloric acid. In the temperature range of 13 to 19°C, a homogeneous system (one liquid phase) is obtained. At 21°C it becomes a heterogeneous system with two coexisting liquid phases. Above 30°C, a three-liquid phase exists. The heavy organic phase appears before the light organic phase and in the two-phase region its volume increases at the expense of the aqueous-phase volume. After the appearance of the light organic phase, the volume of the heavy organic phase remains practically constant. An increase in temperature at 0.28 M initial iron(III) concentration contributes to the formation of the third-phase existance in the extended acid concentration range.

Iron(III) concentration depends only slightly on the temperature in the case of the 5.0 M initial acid concentration. At 10.1 M initial acid concentration, the homogeneous system above 19°C transfers in the two-phase system by forming a "third phase" (heavy organic phase) as the organic phase. Concentration of iron (III) in the heavy organic phase increases with temperature (Fig. 2).

Dependence of the distribution ratio vs temperature at different initial acid concentrations is given in Fig. 3. With 5.0 M initial acid concentration the distribution ratio is slightly decreased. At 7.1 M and 8.1 M the influence of temperature

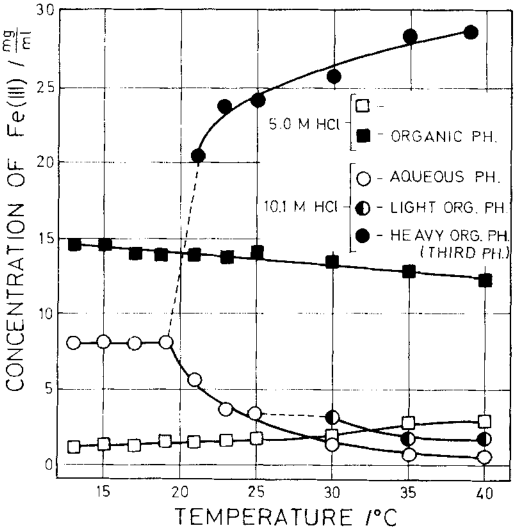

FIGURE 2. Concentration of iron(III) in the phases vs temperature at 5.0 M and 10.1 M initial concentrations of hydrochloric acid. System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, r^i = 1.0.

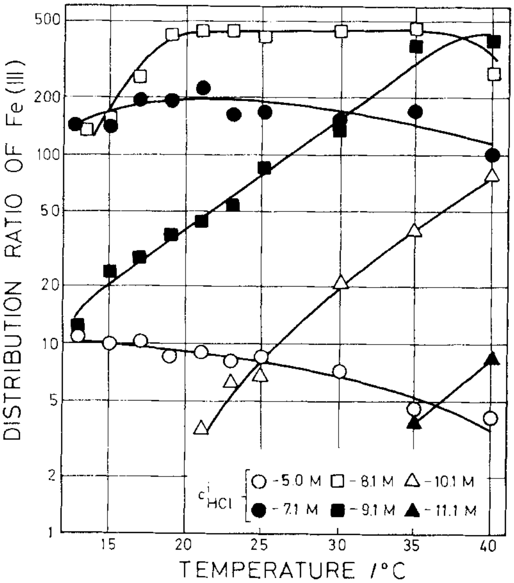

FIGURE 3. Distribution ratio of iron(III) vs temperature at different initial hydrochloric acid concentrations. System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, c^i_{HCl} = 5.0 to 11.1 M, r^i = 1.0.

is not evident in the full temperature range. At higher initial acid concentrations (between 9.1 and 10.1 M) the distribution ratio value is significantly increased. For instance, with 9.1 M the initial acid concentration distribution ratio at 35°C is a hundred times higher than at 19°C. Consideration is incomplete if the extraction is discussed on the basis of the distribution ratio for systems where the changes of phase volumes are strong. Data shown in the example presented (Fig. 4) confirm this statement. Concentration of iron(III) in the heavy organic phase increases and in the light organic phase decreases; on the contrary, the total quantity of iron(III) in the heavy organic phase decreases and in the light organic phase increases due to the change of volume ratio caused by the increase of temperature (above 25°C). The maximum value of the total quantity of Fe(III) at 25°C is

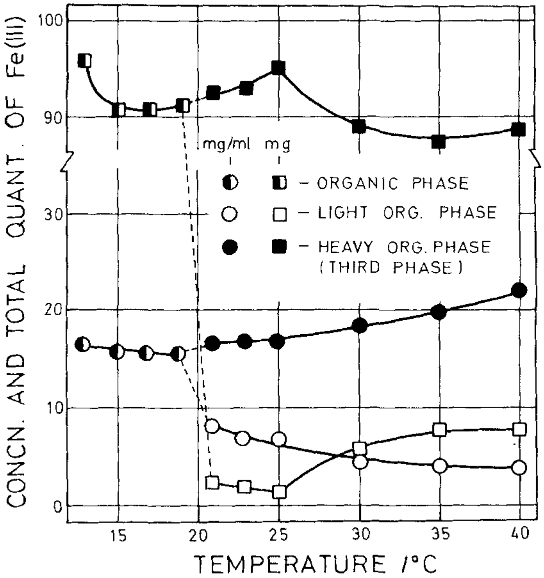

FIGURE 4. Concentration and total quantity of iron(III) in the organic phases vs temperature. System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, c^i_{HCl} = 7.1 M, r^i = 1.0.

connected with corresponding volume changes (Fig. 4). Therefore, it was necessary to complete results by obtaining extraction factors (Fig. 5) and partial extraction factors (Table 1 and Fig. 6). Figure 5 compares the extraction factors (D_m) with distribution ratios (D_c) as well as the dependence on temperature at different initial concentrations of hydrochloric acid. In the case of 5.0 M initial concentration of acid, the D_c and D_m values are approximately equal, but at 9.1 M and 10.1 M they are different. However, these changes caused by the temperature are similar. In the three-liquid-phase system distribution among any two of the coexisting phases can be expressed by partial values of D_c and D_m.

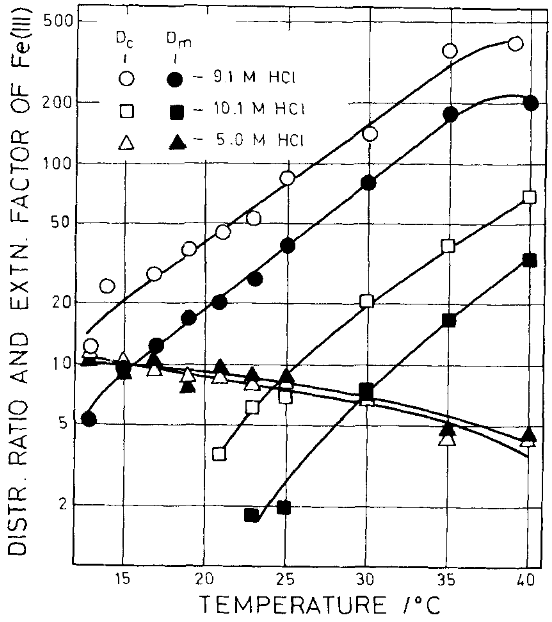

FIGURE 5. Distribution ratio and extraction factor of iron(III) vs temperature at different initial hydrochloric acid concentrations (5.0, 9.1, and 10.1 M). System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, r^i = 1.0.

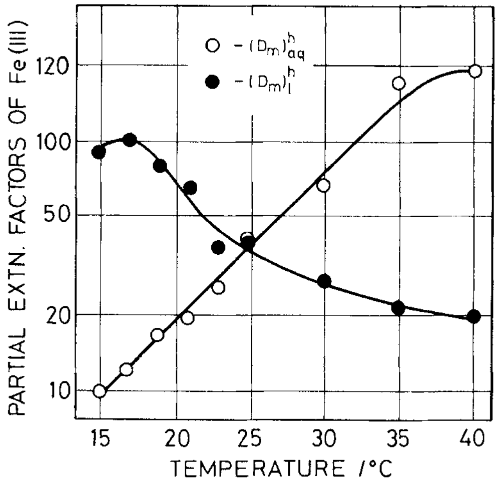

FIGURE 6. Partial extraction factors of iron(III) vs temperature. System: $FeCl_3$-HCl-H_2O-IPE, c^i_{Fe} = 0.28 M, c^i_{HCl} = 9.1 M, r^i = 1.0.

The partial extraction factor of heavy organic phase to the aqueous phase $(D_m)^h_{aq}$ and the partial extraction factor of heavy organic phase to the light organic phase $(D_m)^h_l$ change differently in intensity and the direction with the change of temperature, as is evident in Fig. 6. In Table 1 values of partial extraction factors at different initial acid concentrations (7.1 to 11.1 M) in the temperature range of 13 to 40°C are presented. It is evident that the influence of temperature on the values of the partial extraction factor strongly depends on the initial acid concentration. For instance, the observed strong temperature effect on $(D_m)^h_{aq}$ at 9.1 M initial acid concentration is not observed in the case of lower as well as higher initial acid concentration.

CONCLUSIONS

The experimental data indicate an unpredictable behavior of the investigated extraction system because the phase transformations

TABLE 1

The Influence of Temperature on Partial Extraction Factors in the System: $FeCl_3$-HCl-H_2O-IPE at Different Initial Concentrations of Hydrochloric Acid, c^i_{Fe} = 0.28 M, r^i = 1.0

Temp. (°C)	Initial HCl molarity									
	$(Dm)^H_{Aq}$					$(Dm)^H_L$				
	7.1	8.1	9.1	10.1	11.1	7.1	8.1	9.1	10.1	11.1
13	-[2]	131.7	-[2]	-[1]	-[1]	-[2]	13.5	-[2]	-[1]	-[1]
15	-[2]	144.4	21.2	-[1]	-[1]	-[2]	13.9	8.1	-[1]	-[1]
17	-[2]	234.4	26.3	-[1]	-[1]	-[2]	15.7	15.0	-[1]	-[1]
19	-[2]	397.5	35.3	-[1]	-[1]	-[2]	13.3	18.9	-[1]	-[1]
21	150.2	406.8	40.7	-[2]	-[1]	2.0	12.8	20.5	-[2]	-[1]
23	111.6	406.8	51.1	-[2]	-[1]	2.3	10.5	14.5	-[2]	-[1]
25	117.6	397.5	82.5	-[2]	-[1]	2.3	11.9	18.6	-[2]	-[1]
30	124.6	407.3	132.9	18.5	-[1]	4.1	10.4	16.7	8.3	-[1]
35	141.5	421.2	348.8	37.7	-[2]	4.7	10.8	17.5	17.2	-[2]
40	84.2	244.7	374.9	73.0	7.8	5.7	10.8	17.0	17.6	4.9

[1] - homogeneous system

[2] - two-phase system

occur in a very narrow temperature range. The decrease in the initial acid concentration and the increase in the temperature contribute to an increased number of coexisting liquid phases. In the three-phase system the distribution ratio of iron(III) is increased by an increase in temperature whereas in the two-phase system it is decreased. The choice of appropriate temperature in extraction systems of similar behavior offers new possibilities in the application of extraction to separation procedures.

SYMBOLS USED

c^{i}_{Fe}	Initial concentration of iron(III)
c^{i}_{HCl}	Initial concentration of hydrochloric acid
r^{i}	Initial volume ratio of organic phase to the aqueous phase
D_c	Distribution ratio
D_m	Extraction factor
$(D_m)^{h}_{aq}$	Partial extraction factor of heavy organic phase to the aqueous phase
$(D_m)^{h}_{l}$	Partial extraction factor of heavy organic phase to the light organic phase

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