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Phase Volume Changes in Multicomponent Extraction Systems Containing Diisopropyl Ether*

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Changes in liquid phase volumes were examined in the following extraction systems containing diisopropyl ether (IPE):

A) $H_2O — HCl — IPE — C_6H_6$
B) $H_2O — HCl — IPE — CH_3(CH_2)_xOH$ $(x = 0 — 4)$
C) $H_2O — HCl — FeCl_3 — IPE$
D) $H_2O — HCl — AuCl_3 — IPE$
E) $H_2O — HCl — FeCl_3 — IPE — C_6H_6$
F) $H_2O — HCl — AuCl_3 — IPE — C_6H_6$
G) $H_2O — HCl — FeCl_3 — IPE — CH_3(CH_2)_4OH$

There are appreciable changes in the phase volumes and the influence of composition and temperature on these changes is very pronounced. Benzene was used as the inert diluent and pentyl alcohol was the active component of the mixed solvent. In all the above mentioned systems, except systems A and B, the third phase (heavy organic phase) was observed at room temperature. The addition of alcohols to some systems suppresses the formation of the third phase.

INTRODUCTION

In the course of a study on the extraction of inorganic ions by solvents containing diisopropyl ether (IPE)$^{1-6}$, it appeared advisable to undertake a detailed investigation of phase volume changes based on the initial composition and concentration of the components with special attention to temperature dependence. In preceding publications concerning the results of an investigation of phase composition as dependent on the initial concentration of hydrochloric acid and metal (iron(III) and gold(III)), the initial composition of the organic solvent and temperature were presented. The extensiveness of the results obtained and the number of the systems investigated make it possible to present separately in this article the results of volume changes under very different conditions. Changes of phase volumes are indicated in the literature. Appreciable changes in phase volumes is one of the outstanding features of extraction systems where aqueous electrolyte solutions are equilibrated with polar oxygen-containing extractants[7]. Extraction systems containing IPE are interesting

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due to their ability to form three coexisting liquid phases, i. e., the organic phase under particular conditions separates into two phases — the light and heavy organic phases. The appearance of a third phase was observed in many of the extraction systems. From the standpoint of the extraction of metal complexes, the most important are those using ethers, alkylamines or neutral phosphorus esters as the extracting agents. The formation of the third phase is of special interest for the separation processes because one can expect a very high concentration of metal. Because multicomponent multiphase systems are very complex and exhibit less than ideal behaviour, a phenomenological approach is preferable to a thermodynamic one.

Earlier investigation of the system H_2O — HCl — $FeCl_3$ — IPE included the analytical determination of the equilibrate composition of phases at various initial concentrations of hydrochloric acid (2.5—10.3 mol/dm^3 and iron(III) chloride (0.05—2.95 mol/dm^3). This makes it possible to draw orthogonal projections of the points representing the composition of the phases in a tetrahedral model and to find the molar ratios of the components in both the organic phases. The third phase does not have a constant composition and it depends on the initial composition of the system[1,2].

In the system H_2O — HCl — $AuCl_3$ — IPE the influence of the initial concentration of hydrochloric acid (7.7—11.8 mol/dm^3) was investigated. The third phase in that system is resistant on the addition of water.[3]

The formation of the third phase was observed in the systems H_2O — — HCl — $FeCl_3$ — IPE — C_6H_6 and H_2O — HCl — $AuCl_3$ — IPE — C_6H_6. In both of systems the concentrations of metal, water and hydrochloric acid in equilibrate organic phases were determined. The investigated ranges of the initial concentration were 0.08—0.41 mol/dm^3 of iron(III), 0.14 and 0.09 mol/dm^3 of gold(III) and 7.6—11.8 mol/dm^3 HCl. Results strongly indicate the enhancement of gold(III) extraction at 3 mol/dm^3 initial IPE concentration.[3,4]

The investigation of extraction in system H_2O — HCl — $FeCl_3$ — IPE — — $CH_3(CH_2)_4OH$ was carried out in the initial concentration ranges 0.03—0.28 mol/dm^3 of iron(III), 5.0—10.1 mol/dm^3 HCl and 0—100 percent of *n*-pentyl alcohol. The third phase was observed at 10 percent of *n*-pentyl alcohol in a mixed solvent and 8 mol/dm^3 initial concentration of hydrochloric acid. Results indicate that the use of a mixture of *n*-pentyl alcohol and IPE gives better extraction of iron(III) at lower initial concentration of hydrochloric acid (5—7 mol/dm^3) than pure IPE.[5,6]

By the selection of the proper conditions, it is relatively easy to obtain the conditions for the formation of the third phase or the disappearance of one or two of the phases. Small additions of solvents or acid or a very little change in temperature cause a jump in the volume ratio and/or intensive transfer among coexisting phases. This presents many favorable possibilities for the application of extraction in analytical chemistry as well as in technology.

EXPERIMENTAL

Materials

Isopropyl ether, Fluka or Merck, C. P. was purified, distilled and dried before use. Purification was achieved with successive treatments by ferrous sulfate (satur. solution), potassium permanganate (0.5% solution), sodium hydroxide (0.5% solution) and distilled water. Purified isopropyl ether was distilled and the middle fraction (b. p. 66.8—67.8 °C at 744 mmHg*) collected. After drying by calcium chloride the isopropyl ether contained 0.85 mg H_2O/ml.

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* mmHg = 133,322 Pa

Other chemicals used were: benzene, Merck, p. a. (0.03% water max.), *n*-alcohols $CH_3(CH_2)_xOH$, x = 0 — 4, Merck, p. a. (0.2% water max.), hydrochloric acid, Merck, p. a., ferric chloride hexahydrate, Hopkins & Williams, p. a., auric chloride tetrahydrate, Merck (48% Au min.) or metallic gold, refined, 99.9%.

Procedure

The systems were prepared in 25 ml and 50 ml separation funnels having a calibrated stem and/or in 15 ml graduated cuvettes which were selected from a large group in order to assure accurate volume calibrations. After vigorous shaking of the predetermined components they were placed in a water bath with a thermostat held by automatic control at 20.0 ± 0.05 °C or any desired temperature. Each time the shaking was repeated in the same manner, at fifteen-minute intervals for one hour.

The initial concentrations of metal or acid in the aqueous phase or the initial concentrations of IPE and composition in the organic phase were varied. All obtained data are the results of two or more repeated experiments dependent on the degree of reproducibility.

The initial volume ratio of the organic phase to the aqueous phase volume (r_i) was 1.0 or 1.2. The volumes of coexisting phases are expressed by volume fractions, i. e., by the ratio of the equilibrate phase volume and of the equilibrate total volume of the heterogeneous system.

RESULTS AND DISCUSSION

The investigations of the phase volume changes of a certain system by changing the initial concentrations of the constituents make possible the estimation of its effects on the transfer of components from one phase to another. In the system: $HCl — H_2O — IPE — C_6H_6$ (Figure 1) the volume change indicates

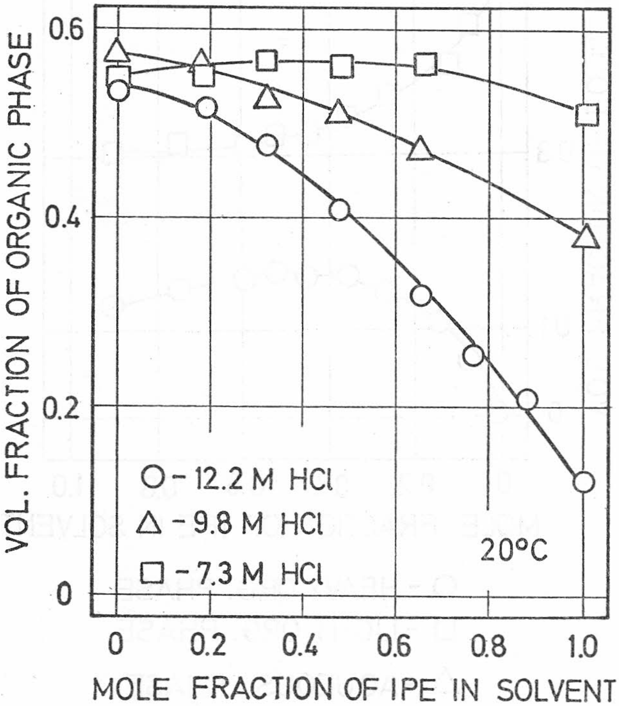


Figure 1. Volume fraction of the organic phase vs. IPE concentration in the organic solvent. System: $HCl—H_2O—IPE—C_6H_6$.

the transfer of IPE from the organic to the aqueous phase due to the solvation of acid, and as consequence of the insufficiency of water at a higher acid concentration (approximately > 7 mol/dm^3 HCl). Namely, an increase of the IPE concentration in an organic solvent increases the volume of the aqueous phase at the expense of the organic phase. It means that the quantity of IPE in the aqueous phase depends upon the concentration of IPE in a mixed solvent, and upon the concentration of acid, of course[4].

Explanation of the volume changes becomes more difficult when, due to the addition of iron(III) chloride in the system, a third phase (heavy organic phase) is formed. The heavy organic phase is most probably composed of a hydrosolvate of tetrachloroferrat(III) acid which is very slightly soluble in both phases (the aqueous and light organic phase), as it shows previous results[3]. In Figure 2. volume changes are shown in such a system: H_2O — HCl — $FeCl_3$ — —IPE — C_6H_6, when the initial concentrations of iron(III) and hydrochloric acid were 0.14 mol/dm^3 and 9.3 mol/dm^3 respectively. The shape of the curves is the result of water and hydrochloric acid removed from the aqueous phase due to the formation of hydrosolvate on the one side and IPE transfer from

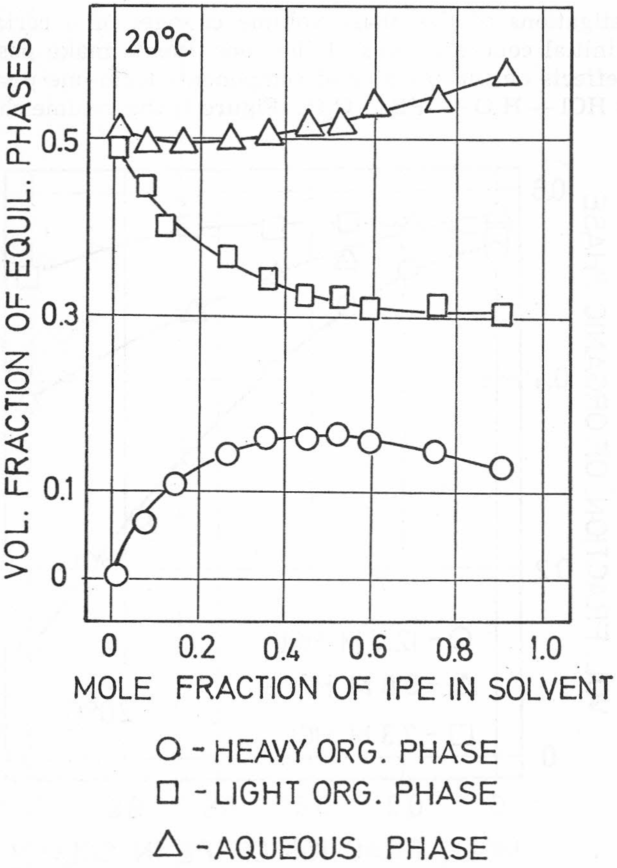


Figure 2. Volume fraction of phases vs. IPE concentration in the organic solvent. System: $FeCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{Fe} = 0.14$ mol/dm^3, $c^i_{HCl} = 9.3$ mol/dm^3, $r_i = 1.0$.

the light organic phase to the heavy organic phase and aqueous phase (due to the solvation of HCl and $HFeCl_4$) on the other side. It is clear that at lower concentrations of IPE an insufficiency of IPE exists in the whole system. At higher iron(III) concentration (0.28 mol/dm^3) the volume changes of the phases are more pronounced (Figure 3). The number of phases changes too, and by

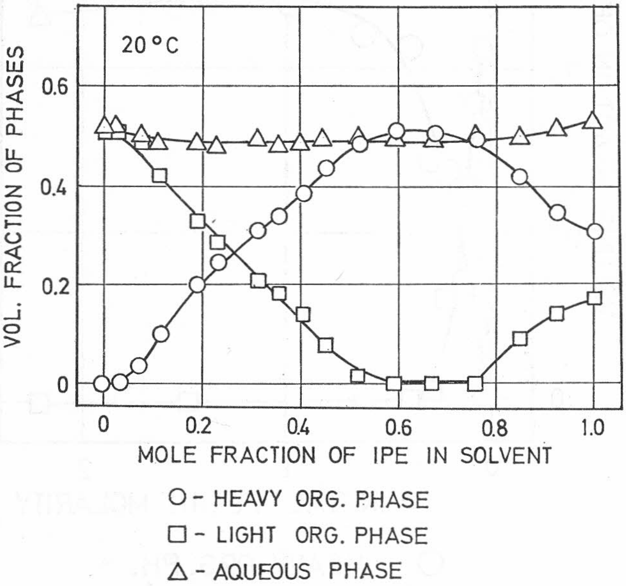


Figure 3. Volume fraction of phases vs. IPE concentration in the organic solvent. System: $FeCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{Fe} = 0.28$ mol/dm^3, $c^i_{HCl} = 7.6$ mol/dm^3, $r_i = 1.0$.

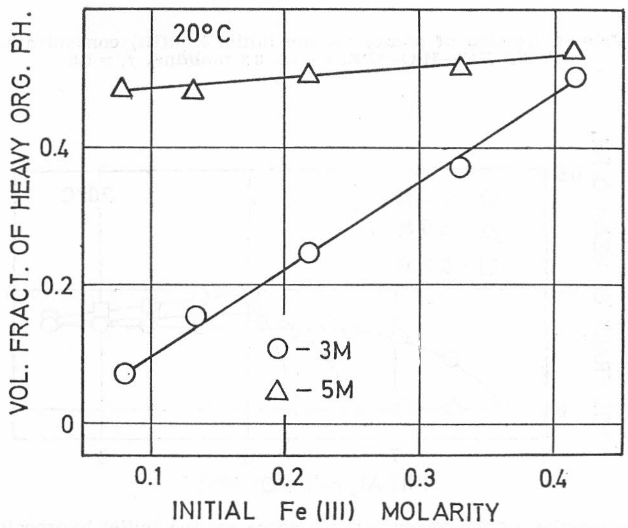


Figure 4. Volume fraction of the heavy organic phase vs. the initial iron(III) concentration. System: $FeCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{HCl} = 7.6$ mol/dm^3, $c^i_{IPE} = 3.0$ and 5.0 mol/dm^3, $r_i = 1.0$

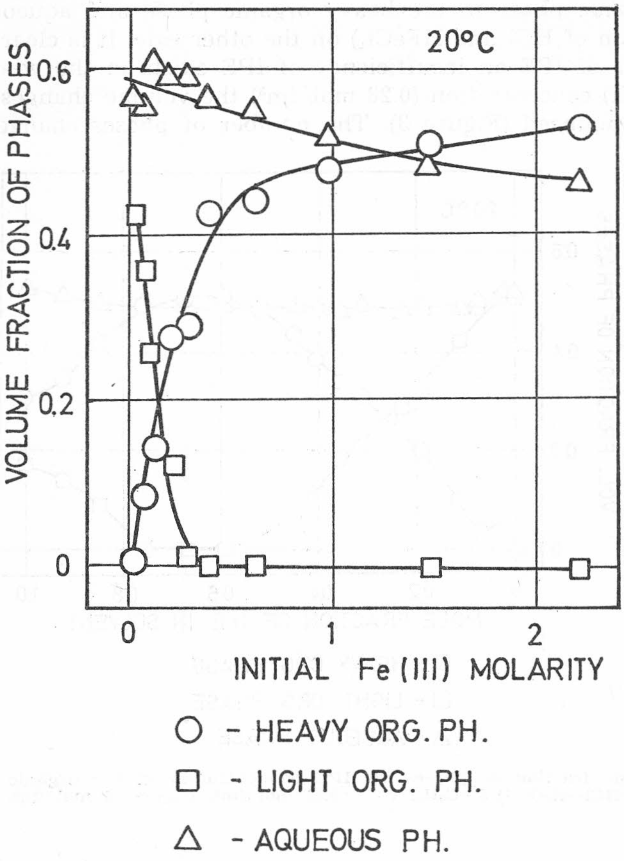


Figure. 5. Volume fraction of phases vs. the initial iron(III) concentration. System: $FeCl_3$—HCl—H_2O—IPE, $c^i_{HCl} = 8.2$ mol/dm^3, $r_i = 0.8$.

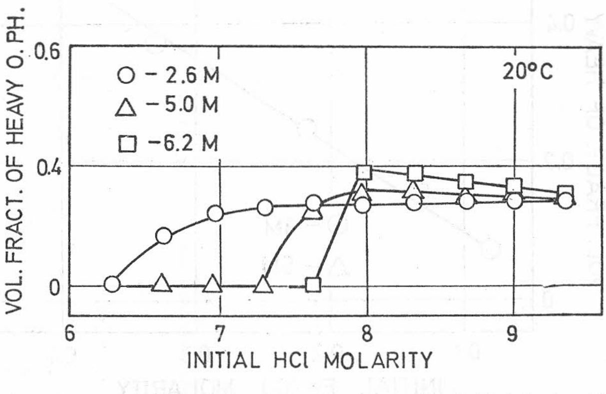


Figure 6. Volume fraction of the heavy organic phase vs. the initial hydrochloric acid concentration. System: $FeCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{Fe} = 0.14$ mol/dm^3, $c^i_{IPE} = 2.6$, 5.0 and 6.2 mol/dm^3, $r_i = 1.0$.

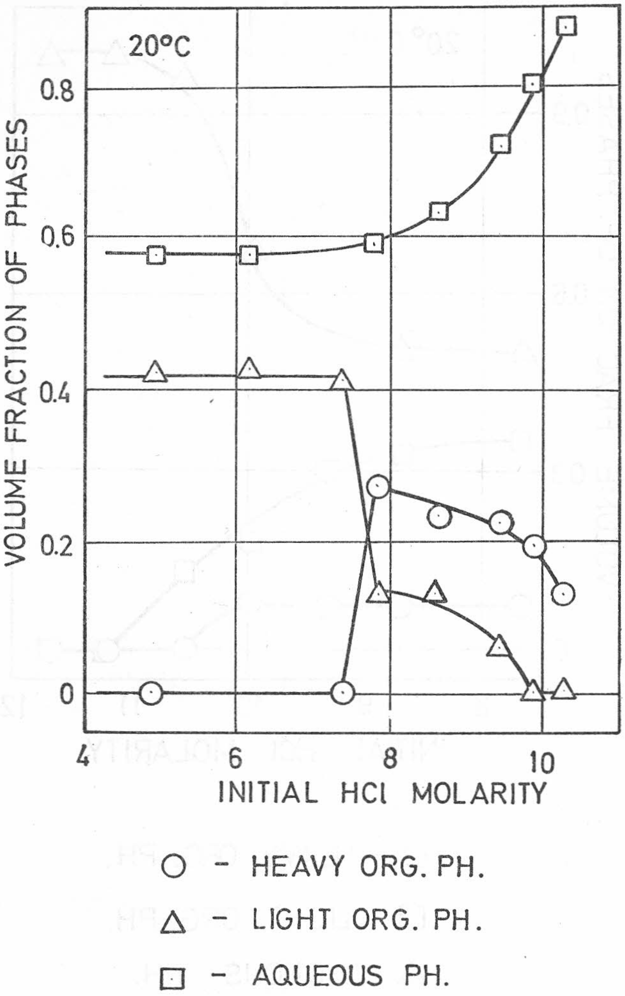


Figure 7. Volume fraction of phases vs. the initial hydrocloric acid concentration. System: FeCl—HCl—H_2O—IPE, $c^i_{Fe} = 0.20$ mol/dm^3, $r_1 = 0.8$.

IPE concentration it is possible to select a number and, of course, the equilibrate volume ratio of the coexisting phases.

The influence of the initial iron(III) concentration on phase volumes depends on the initial IPE concentration in the solvent. In Figure 4. the volume change of the heavy organic phase is shown in the case of 3 mol/dm^3 and 5 mol/dm^3 initial IPE concentration. In Figure 5. a volume change of phases in the extraction system with pure IPE (H_2O — HCl — $FeCl_3$ — IPE) is presented. When an increase of the initial metal concentration transforms a system into a two-phase one, where the only organic phase is the heavy organic phase (the light organic phase disappears) the effect becomes smaller and the increase of the heavy organic phase volume runs at the expense of the aqueous phase. An increase in the iron(III) content in the system causes a

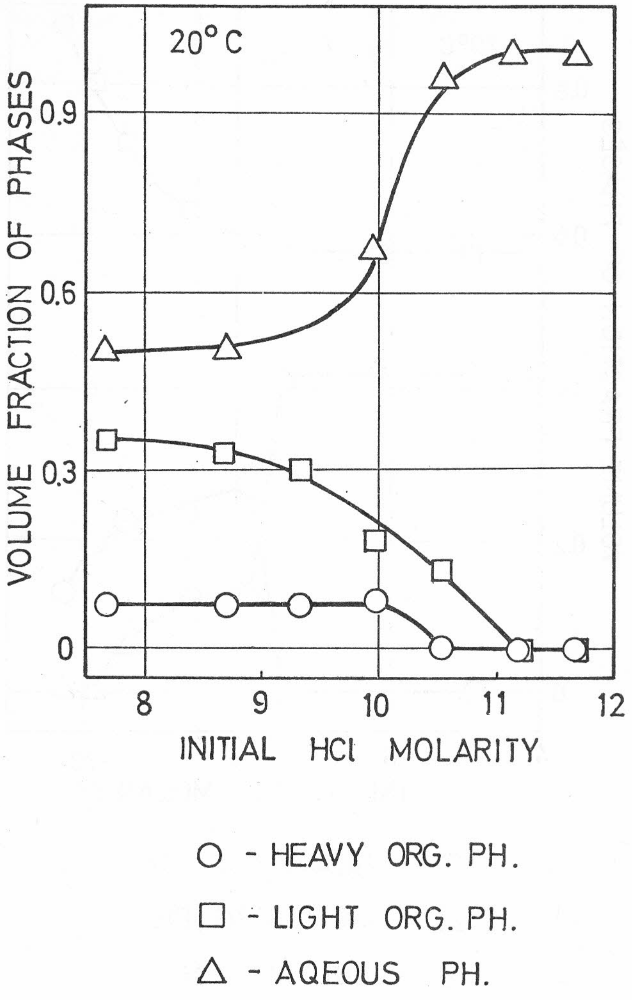


Figure 8. Volume fraction of phases vs. the initial hydrochloric acid concentration. System: $AuCl_3$—HCl—H_2O—IPE, $c^i_{Au} = 0.14$ mol/dm^3, $r_i = 1.0$.

decrease of IPE solubility in the aqueous phase (salting out effect) and it reflects on the organic phase volume, as explained in an earlier publication[3].

An increase in the initial concentration of hydrochloric acid is favourable to third phase formation, but conditions of appearance also depend on the IPE concentration in the solvent, as shown in Figure 6. In the three phase region the volumes of organic phases are practically unchanged in the wide range of initial acid concentration. In the system with pure IPE (Figure 7.) an increase of initial acid concentration is characterized by remarkable volume changes in the three phase region. Due to increased IPE transfer from the organic phases, especially the light organic phase, into the aqueous phase a volume of aqueous phase increases and a volume of organic phases decreases and finally the light organic phase disappears.

In the case of diluted IPE, relations among the volumes of phases depend on the IPE quantity, i. e., the saturation of hydrosolvate by IPE is connected with the possiblity of IPE transfer into the aqueous phase. The cited processes are followed by corresponding changes in phase characteristics i. e., concentrations of components in the equilibrate phase changes and details are given in Ref. 3. In the system: $AuCl_3$ — HCl — H_2O — IPE under particular conditions (e. g. $c^{i}_{Au} = 0.14$ mol/dm³, $c^{i}_{HCl} = 10—11 \cdot 5$ mol/dm³) a heterogeneous three-phase system transfers in a two-phase one and finally in a homogeneous one-phase system (Figure 8.). It is evident that the heavy organic phase volume depends on gold(III) quantity when the quantities of IPE and HCl are sufficient.

Investigation of volume changes in the extraction of gold(III) by diluted IPE (Figure 9.) shows that after the saturation of the hydrosolvate of metal-chloro complex acid with IPE (maximum value of heavy organic phase volume) the volume of the aqueous phase increases due to the transfer of IPE to the aqueous phase. The similarity of coexisting phases grows and leads to a reduction in the number of phases. As is shown in Figure 10, in the system with diluted IPE (3.6 mol/dm³) the third phase appears at a higher acid concentration (more than 9 mol/dm³) and attains a constant value as in the analogous system with iron(III).

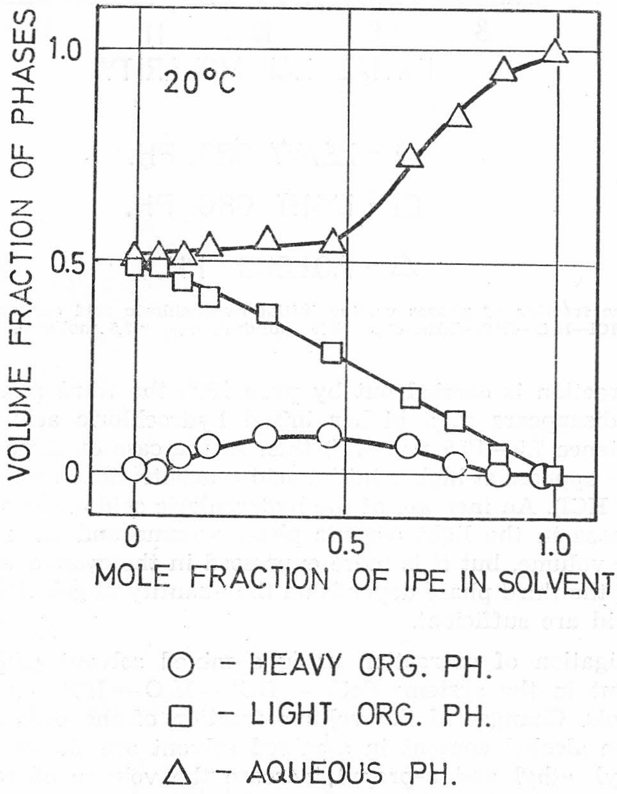


Figure 9. Volume fraction of phases vs. the IPE concentration in the organic solvent. System: $AuCl_3$—HCl—H_2O—IPE—C_6H_6, $c^{i}_{Au} = 0.09$ mol/dm³, $c^{i}_{HCl} = 11.8$ mol/dm³, $r_i = 1.0$.

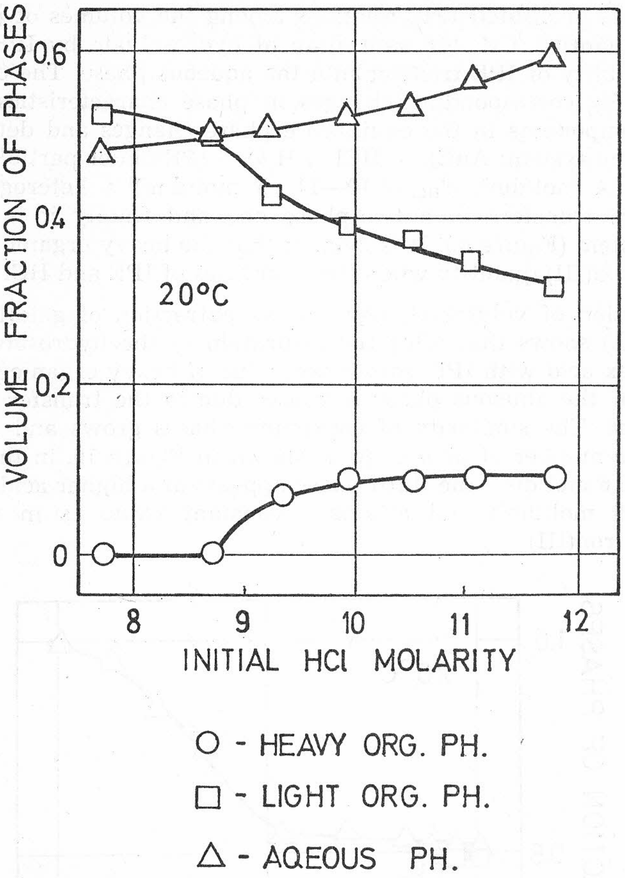


Figure 10. Volume fraction of phases vs. the initial hydrochloric acid concentration. System: $AuCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{Au} = 0.09$ mol/dm³, $c^i_{IPE} = 3.6$ mol/dm³, $r_i = 1.0$.

When extraction is carried out by pure IPE, the third phase appears at a lower and disappears at a higher initial hydrochloric acid concentration (range of existence 7.5—10.5 mol/dm³) than in the case of diluted IPE, where the third phase appears at higher initial acid concentrations (range of existence 9—12 mol/dm³ HCl). An increase of the hydrochloric acid concentration always causes a decrease in the light organic phase volume and an increase in the aqueous phase volume, but it is more expressed in the system with pure IPE. The volume of the third phase depends on the quantity of gold(III) if quantities of IPE and acid are sufficient.

An investigation of extraction using a mixed solvent (IPE — *n*-alcohol) was carried out in the system: $FeCl_3$ — HCl — H_2O — IPE — *n*-alcohol using C_1 — C_5 alcohols. Changes of the volume fraction of the organic phase as a function of the alcohol content in a mixed solvent are shown in Figure 11. Alcohols-methyl, ethyl and *n*-propyl increase the volume of aqueous phase, but *n*-butyl and *n*-pentyl alcohols increase the volume of organic phase. Preliminary examination of separation conditions by paper chromatography[8] and

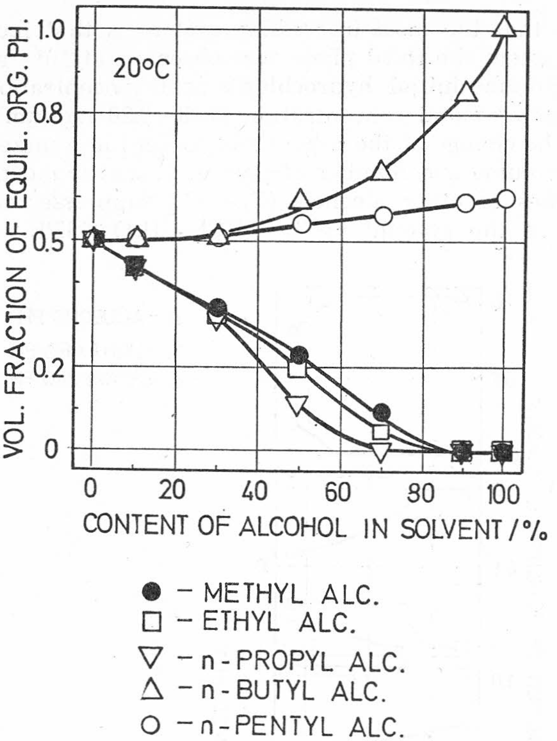


Figure 11. Volume fraction of phases vs. the alcohol content in the mixed solvent. System: HCl—H_2O—IPE- *n*-alcohol, $c_{\mathrm{iHCl}} = 5.0$ mol/dm³, $r_i = 1.0$.

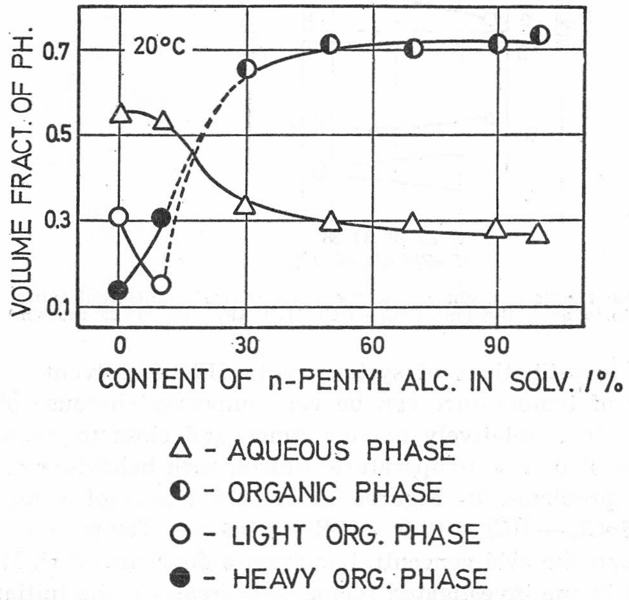


Figure 12. Volume fraction of phases vs. the content of *n*-pentyl alcohol in the mixed solvent. System: $FeCl_3$—HCl—H_2O—IPE—$CH_3/CH_2/_4OH$, $c^{i}_{\mathrm{HCl}} = 8.0$ mol/dm³, $c^{i}_{\mathrm{Fe}} = 0.15$ mol/dm³, $r_i = 1.0$.

extraction shows that the most interesting system is that including *n*-pentyl alcohol. In this system the third phase was observed at 10% alcohol in mixed solvent and 8 mol/dm^3 initial hydrochloric acid concentration in the whole investigated range of metal concentration (0.03—0.28 mol/dm^3). In Figure 12. it is shown that the change of the *n*-pentanol content in a mixed solvent causes a change in the volume and number of phases. It was found that the addition of minor quantities of other alcohols (C_1 — C_4) suppresses the formation of the third phase in the system: $FeCl_3$ — HCl — H_2O — IPE.

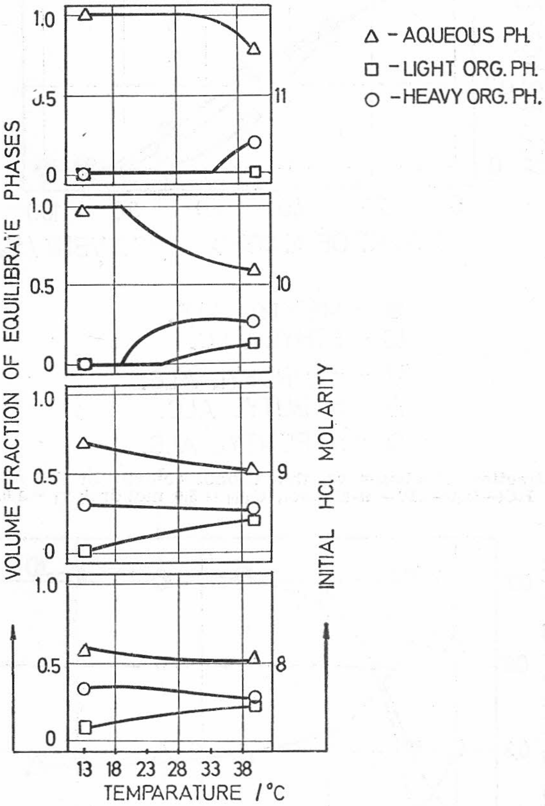


Figure 13. Volume fraction of phases vs. the temperature at different initial concentration of hydrochloric acid. System: $FeCl_3$—HCl—H_2O—IPE, c^i_{Fe} = 0.28 mol/dm^3, r_i = 1.0.

Previous investigations of systems with IPE as solvent[3,5,8] indicate that the influence of temperature can be very important because phase transformations occur in a relatively narrow range and close to room temperature. In the absence of precise temperature control, such behaviour can cause many experimental problems. In Figures 13 and 14 trends of volume changes in the system: $FeCl_3$ — HCl — H_2O — IPE are shown. Temperature ranged from 13 ° to 40 °C and the acid concentration from 8 do 11 mol/dm^3. It is possible to conclude that in the investigated region, a decrease in the initial acid concentration and an increase in the temperature contribute to an increase in number of phases. An increase in temperature, at given 0.28 mol/dm³ iron(III) concentration, contributes to the third phase existence in the extended acid concentration range.

Change in the number of phases vs. temperature for the same system and conditions is shown in Figure 15. For instance, at 10 mol/dm³ the initial acid concentration system is homogeneous till 19 °C, between 21° to 25 °C it is two-phase and at 30 °C the third liquid phase appears. Such behaviour perhaps offers some new possibilities in the separation technique.

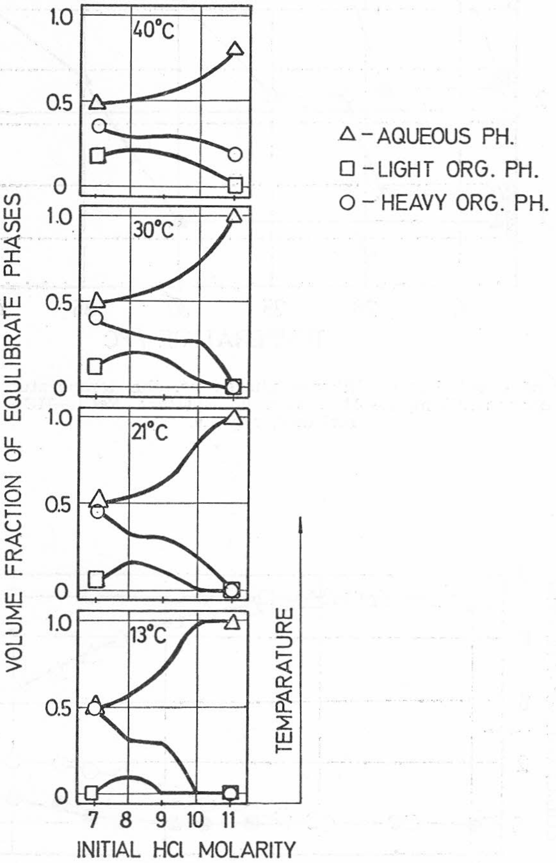


Figure 14. Volume fraction of phases vs. the initial hydrochloric acid concentration at different temperatures. System: $FeCl_3$—HCl—H_2O—IPE, c^i_{Fe} = 0.28 mol/dm³, r_i = 1.0.

The system: $AuCl_3$ — HCl — H_2O — IPE (Figure 16), behaves similarly to the above mentioned but when the system contains benzene (diluted IPE) behaviour is different (Figure 17) i. e.,an increase in temperature at given conditions (c^i_{Au} — 0.14 mol/dm³, c^i_{HCl} — 11.8 mol/dm³ and c^i_{IPE} — 3.6 mol/dm³) contributes to an increase in the number of phases. The third phase volume is unchangeable in a wide temperature range (0° — 25 °C) and at 28 °C it dissapears.

Such systems have a very complex picture, depending on temperature as well as composition, and additional studies are in progress to explain the mechanisms in the formation of different coexisting liquid phases.

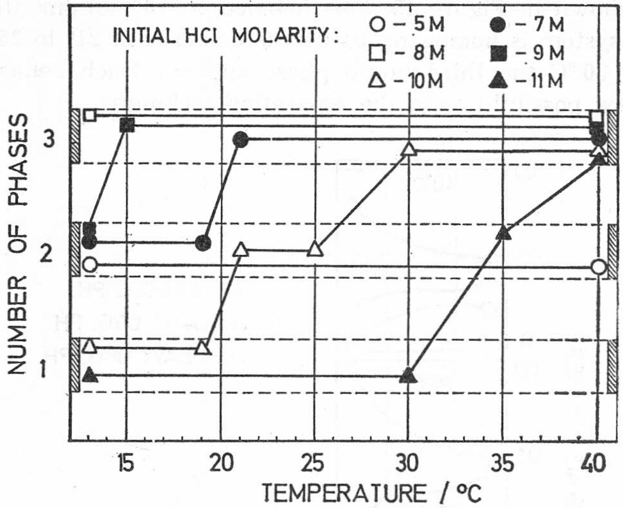
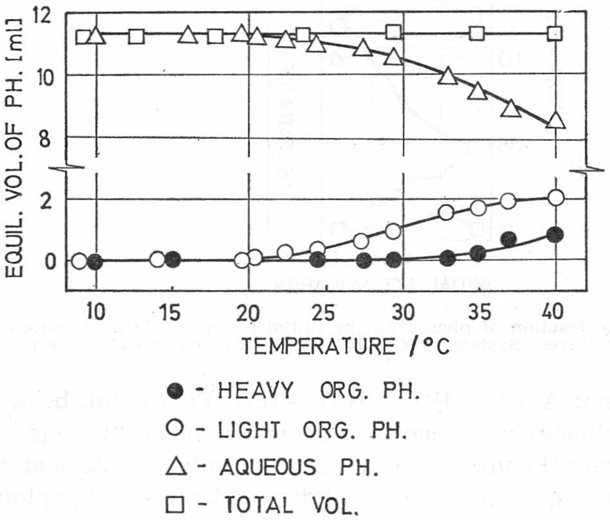


Figure 15. Number of coexisting equilibrate phases vs. the temperature at different initial hydrochloric acid concentrations (5—11 mol/dm³). System: $FeCl_3$—HCl—H_2O—IPE, $c^i_{Fe} = 0.28$ mol/dm³, $r_i = 1.0$.



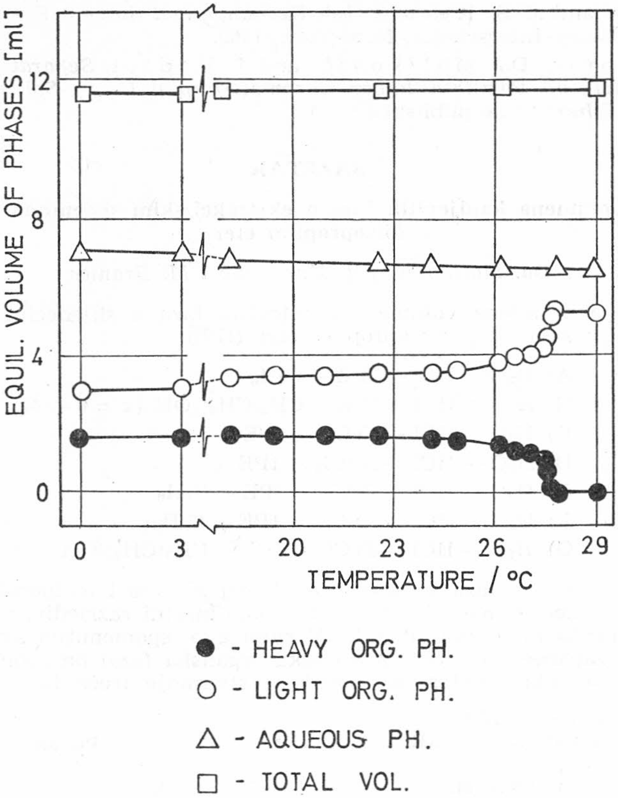


Figure 17. Phase volumes vs. the temperature. System: $AuCl_3$—HCl—H_2O—IPE—C_6H_6, $c^i_{Au} = 0.14$ mol/dm^3, $c^i_{HCl} = 11.8$ mol/dm^3, $c^i_{IPE} = 3.6$ mol/dm^3, $r_i = 1.0$.

Symbols Used

c^i_{Fe} — initial concentration of iron(III)
c^i_{Au} — initial concentration of gold(III)
c^i_{HCl} — initial concentration of hydrochloric acid
c^i_{IPE} — initial concentration of IPE
r_i — initial volume ratio of the organic phase to the aqueous phase

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REFERENCES

1. Da. Maljković, *M. Sc. Thesis,* Univ. Zagreb, 1965.
2. Da. Maljković and M. Branica, *Croat. Chem. Acta,* **38** (1966) 193.
3. Da. Maljković, *Ph. D. Thesis,* Univ. Zagreb, 1976.
4. Da. Maljković and M. Branica, *Proc. ISEC* **77,** Toronto, 1977; in print.
5. Du. Maljković, *Ph. D. Thesis,* Univ, Zagreb, 1978.
6. Da. Maljković, Du. Maljković, and M. Branica, *Proc. Advances in Separation Science,* Trieste, 1978, p. 99.

7. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes,* Wiley-Interscience, New-York, 1969.
8. Da. Maljković, Du. Maljković and J. Hedžet, *Separation of Iron (III) and Gold (III) by Partition Paper Chromatography Using Solvents Containing Diisopropyl Ether;* to be published.

SAŽETAK

Promjene volumena kapljevitih faza u ekstrakcijskim sistemima koji sadrže diizopropilni eter

Da. Maljković, Du. Maljković i M. Branica

Ispitivana je promjena volumena kapljevitih faza u slijedećim ekstrakcijskim sistemima koji su sadržavali diizopropilni eter (IPE):

A) H_2O — HCl — IPE — C_6H_6
B) H_2O — HCl — IPE — $CH_3(CH_2)_xOH$ ($x = 0 — 4$)
C) H_2O — HCl — $FeCl_3$ — IPE
D) H_2O — HCl — $AuCl_3$ — IPE
E) H_2O — HCl — $FeCl_3$ — IPE — C_6H_6
F) H_2O — HCl — $AuCl_3$ — IPE — C_6H_6
G) H_2O — HCl — $FeCl_3$ — IPE — $CH_3(CH_2)_4OH$

Promjene volumena faza su znatne a utjecaj sastava i temperature na te promjene je jako izražen. Benzen je upotrebljen kao inertni razrjeđivač a pentanol kao aktivna komponenta miješanog otapala. U svim gore spomenutim sistemima, izuzev sistema A i B, zapažena je treća faza (teška organska faza) na sobnoj temperaturi. Dodatak alkohola nekim sistemima potiskuje stvaranje treće faze.

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