Equilibria of Liquid Phases in the Ternary System: Ferric Chloride — Water — Isopropyl Ether

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Experimental investigations of the heterogeneous system: ferric chloride-water-isopropyl ether, at 20^0 C, were carried out. From the experimental results the equilibrium compositions of the phases, tie lines in the two-liquid-phase region and the isothermal curve of the three-component system were determined.

INTRODUCTION

In the course of a study of the extraction of ferric chloride by isopropyl ether from aqueous solutions of hydrogen chloride, it appeared advisable to undertake investigations of the ternary system: ferric chloride-water-isopropyl ether in order to determine the influence of ferric chloride on the mutual solubility of isopropyl ether and water. This system is one of the lateral planes of the tetrahedral model which represents the four-component system ferric chloride-hydrochloric acid-water-isopropyl ether.

EXPERIMENTAL

Materials.

The isopropyl ether, *Fluka* c. p., was purified by treatment with saturated ferrous sulfate solution followed by sodium hydroxide solution. After washing it with water, it was distilled and the middle fraction (b. p. 66.8^0—67.8^0 C at 743.5 mmHg) was collected for further use. Isopropyl ether which is prepared in this way contained 1.63 mg. H_2O/ml. Anhydrous ferric chloride, *T. Schuchardt,* was 98 per cent pure. Other chemicals used were of analytical reagent grade.

Methods of analysis.

Iron and isopropyl ether from the aqueous phase and iron and water in the ethereal phase were determined directly. The third component in both phases was found by a difference. For the determination of iron in quantities greater than 1 millimole complexometric titration (Titriplex III with 2-oxi-5-sulfo-benzoic acid[1]) was used. For quantities less than 1 millimole the ultraviolet light absorption of samples was measured. The ethereal phase was analysed for water by the Karl Fischer titration method[2] as modified by Laurene.[3] The analysis resulted in a considerable problem, since very small quantities were present in the aqueous phase. The method which was proposed by Tuck[4] was applied to solutions containing ferric chloride. Centrifuge tubes with calibrated narrow necks were used. The height of the separated ether (over solubility) after neutralization was measured with a cathetometer. The solubility of isopropyl ether in the final solution in the tube containing approximately 12 ml. was 19.57 mg. In a number of samples quantities of ether were

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under the sensitivity limit of method. When greater quantities of iron were present, the determination was more difficult because of precipitation of iron hydroxide. The equilibrium ratio of volumes of the phases were determined in a graduated separation funnel (the accuracy was ± 0.05 ml.). Density determinations of the phases were made with 10 ml. pycnometers.

Procedure.

Systems were prepared in separation funnels. The funnels were shaken vigo-rously for 15 seconds and placed in a water bath thermostat held by automatic control at 20.0 ± 0.05° C. The shaking was repeated, always in the same manner, during one hour in intervals of fifteen minutes. The analyses of the phases were performed after one hour, i. e. when equilibria were attained.

Apparatus.

The separations were made in 25 ml. and 50 ml. separation funnels having a calibrated stem. The zero of the calibration was at the drain cock. A thermostat *Towson & Mercer,* Croydon, an apparatus for electrometric titration of water *Baird & Tatlock,* London and a spectrophotometer *Hilger* Uvispek were used.

RESULTS AND DISCUSSION

Series of compositions of coexisting phases at 20° C were determined by analytical method. The influence of ferric chloride on the mutual solubility of isopropyl ether and water is very small. These results could be expected because the principal factor effecting an increase of solubility of ether in aqueous solutions was the formation of the species Et-H$^+$ which occurs only in strong acid solutions.[5] It is well known that the percentage of extraction of ferric chloride with isopropyl ether is practically nil if the initial concentration of hydrochloric acid is less than two molar.[6]

The data obtained from the analyses are presented in the Table. The mole percentages are schematically plotted on the shortened ternary diagram in Fig. 1, and on an enlarged scale in Fig. 2.

In Figs. 1 and 2 the area above the uppermost tie line is the three-phase region, i. e. all compositions represented by points inside this region separate

TABLE I

Molarity of the Heterogeneous System: FeCl$_3$—H$_2$O-Isopropyl Ether

Initial volume ratio IPE*—H$_2$O was 1 : 1, at 20° C

FeCl$_3$ initial	Aqueous phase			Ether phase		
	FeCl$_3$	IPE*	H$_2$O	FeCl$_3$	IPE*	H$_2$O
3.45	2.71	0.10	49.74	0.046	7.02	0.34
3.10	2.67	+	49.34	0.020	7.06	0.31
2.26	2.03	+	50.60	0.001	7.06	0.21
2.15	2.00	+	50.71	0.000	7.05	0.20
1.28	1.21	+	52.53	0.000	7.08	0.22
1.00	0.97	+	52.92	0.000	7.07	0.24
0.62	0.62	+	53.67	0.000	7.08	0.25
0.43	0.42	+	54.53	0.000	7.05	0.26
0.33	0.33	+	54.66	0.000	7.06	0.26
0.18	0.18	+	54.88	0.000	7.06	0.27
0.07	0.061	+	55.11	0.000	7.07	0.26
0.02	0.020	+	55.17	0.000	7.04	0.26

+ The actual quantity of IPE* is less than 19.57 mg.
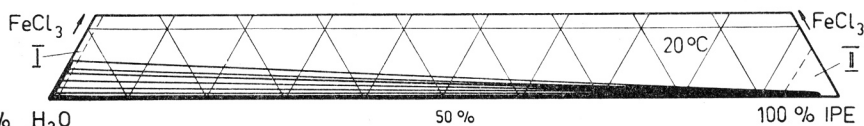* IPE = isopropyl ether

Fig. 1. Ternary system FeCl₃—H₂O — IPE in the section of triangle diagram, at 20⁰ C. Isothermal curve and tie lines of the system are plotted in molar percents.

into one solid and two liquid phases with compositions A (aqueous phase) and B (ethereal phase). The obtained composition of the aqueous phase at point A is 5.16 mol % $FeCl_3$, 0.19 mol % IPE and 94.65 mol % H_2O; and that of ethereal phase at point B is 0.64 mol % $FeCl_3$, 94.72 mol % IPE, and 4.64 mol % H_2O. The composition of the solid phase (ferric chloride and/or hydrates) was not reported in this paper because it is out of the scope of the extraction system studied. The area under the uppermost tie line is the heterogeneous region of two liquid phases, where tie lines connect the points representing the compositions of coexisting liquid phases on the isothermal curve.
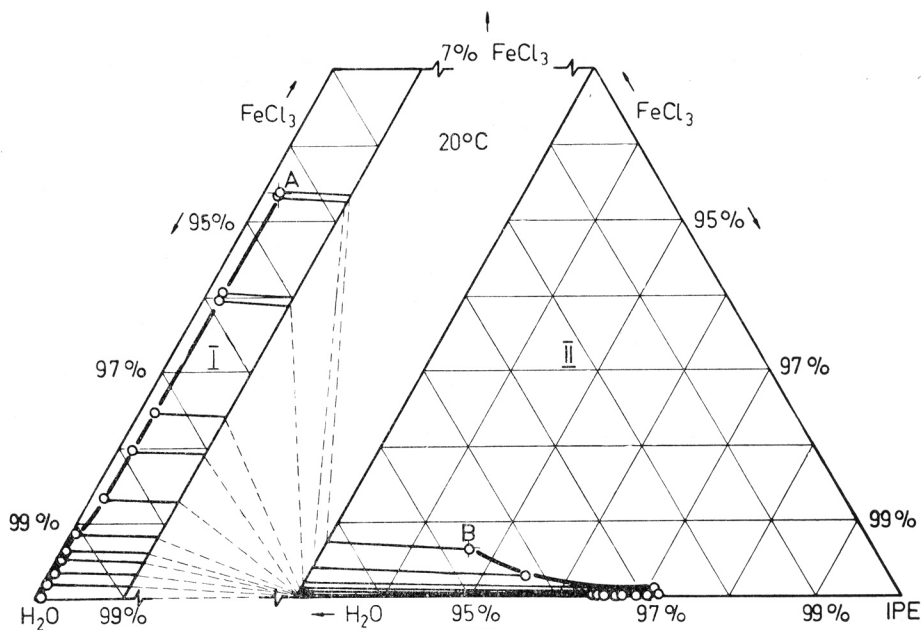

Fig. 2. Experimental points representing equilibrium of the coexisting liquid phases is shown in sections on the enlarged triangle diagram.

In Fig. 2 experimental points representing equilibrium compositions of coexistent phases in the enlarged section of the triangle diagram with corresponding tie lines are shown. On the basis of the results experimentally obtained it may be supposed that the solubility of water in the ether phase decreases markedly to a minimum at initial concentration of 2.15 M ferric chloride. It increases slowly when the initial concentration of ferric chloride is further decreased. This influence of ferric chloride on the mutual solubility of water and ether is similar to the one of hydrochloric acid in the system HCl-H_2O-iso-propyl ether.[7]

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IZVOD

Ravnoteža tekućih faza u' trokomponentnom sistemu: željezni (III) klorid-voda--izopropilni eter

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Izvršena su ispitivanja ravnoteže tekućih faza heterogenog trokomponentnog sistema: željezni (III) klorid-voda-izopropilni eter kod 20⁰ C. Na osnovu eksperimentalnih rezultata nađeni su ravnotežni sastavi faza, vezne linije u dvofaznom području i izotermna krivulja topivosti sistema.

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