Extraction of Iron (III) with Acetonitrile by Salting - out Phase Separation Technique

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Abstract

Extraction of iron (III) has been studied using the mixture of acetonitrile with water upon the addition of electrolytes, NaCl and CaCl$_2$. The extraction of iron also varied with the different concentration of hydrochloric acid. Upon the addition of NaCl, the phase separation was attained within the concentration range 2.0-4.0M. Iron (III) was extracted to the extent of 98.20% into the acetonitrile phase at 4.0M of NaCl and 0.1M of HCl. Again the phase separation was attained by the addition of CaCl$_2$ within the concentration range 0.5-2.0M. About 98.15% iron (III) was extracted into the acetonitrile phase within this system. Iron (III) was extracted from the aqueous phase into acetonitrile through the formation of ion pair.

I. Introduction

Traditional solvent extraction is one of the most useful techniques that are being used for selective removal and recovery of metal ions from aqueous solutions and it is largely applied in the purification processes in numerous chemical and metallurgical industries [1-3].

Phase separation of homogeneous mixed solvents can be achieved by addition of salts or application of changing temperatures to organic solvents. For example, phase separation occurs by addition of $(NH_4)_2SO_4$ to polyethylene glycol [4], or by raising the temperature to 30°C in the diethyl ether-water system[5]. The salt-induced phase separation between acetonitrile and aqueous solution was observed by addition of a variety of inorganic and organic electrolytes[6]. When inorganic salt is added to a mixture of water with organic solvent, phase separation occurs. This phenomenon is referred to as salting-out phase separation and can be explained by the following mechanism: Electrolytes are hydrated but the organic solvent molecules are hard to be hydrated. Thus, the solubility of organic solvent molecular decreases in the aqueous solution[7].

The solvent extraction technique for the recovery of Iron(III) from chloride solutions has received a strong attention from researchers. Several studies have shown that in case of conventional solvent extraction technique for the recovery of iron, various types of extractants such as basic extractants (like amines), solvating extractants (such as neutral organophosphorus compounds) and other extractants containing S as the donor atom are used[8]. Solvent extraction of iron (III) from aqueous hydrochloric acid solutions using D$_2$EHPA, PC-88A, cyanex-272 and their mixtures has been reported by Sandhibigraha et al.[9]. BB Misra and SR Mohanty have worked on the solvent extraction of iron(III) from hydrochloric acid solution by sulphoxides and their mixtures[10]. Calix(6)arene carboxylate derivative was used for solvent extraction separation of iron(III) by R. M. Khandwe and S. M. Khopkar[11].

A. Nasu et al. focused their work on solvent extraction of iron (II) and iron (III) as anionic thiocyanate complexes with tetrabutylammonium ions into chloroform solvent[12].

Beata Pośpiech, Władysław Walkowiak and Michał J. Woźniak used TBP (Tetrabutyl Phosphate) for the solvent extraction of iron (III) [13].

In the present study, the simple phase separation process for extraction of iron (III) without using any extracting reagents was utilized. First, the phase separation that occurs by the addition of NaCl and CaCl$_2$ to the mixture of acetonitrile and water was invested and then this phase separation process for the extraction of iron (III) was used. The probable mechanism was also suggested.

II. Materials and Methods

Acetonitrile, NaCl, CaCl$_2$, FeCl$_3$ and HCl were procured from the E. Mark, Germany and Aldrich chemical company, lnc., USA. Deionized water was used throughout the experiment. All experiments were carried out at room temperature. The volume of aqueous phase was measured using volume calibrated graduated centrifuge tube. The concentration of metal ion in the aqueous phase was determined by Shimadzu UV-visible spectrophotometer (Model UV-160A, Japan). All the mixtures were centrifuged using a centrifuge machine (No. 10028, Japan, R.P.M.-4000).

1000 mg/L (ppm) stock solution of FeCl$_3$ was prepared in 100ml volumetric flask.

A number of 15mL volume calibrated graduated tubes were taken and required volume of FeCl$_3$ solution was poured in such a way that the final concentration of Fe^{3+}ion was 200 ppm in aqueous phase. The acid concentration in each tube was adjusted to 0.10 M by dilute HCl. A range of concentration of NaCl (2.0-4.0M) and CaCl$_2$ (0.5-2.0M) was maintained by adding required amount of solid NaCl and CaCl$_2$ in aqueous phase and dissolved. The volume of aqueous layer was adjusted to 5mL by adding deionized water. Then 5mL of acetonitrile was added in each tube and the mixtures were vigorously shaken for 15 minutes and left for 3 hours to reach complete equilibrium. The solutions were then centrifuged and allowed to stand for 15 minutes.

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After that the aqueous and organic phase were allowed to stand for few minutes. The volume of the aqueous and organic phase in each tube was measured from the scale of the graduated tubes. The concentrations of Fe^{3+} distributed between the two phases were determined spectrophotometrically by UV-visible spectrophotometer.

The distribution coefficient and percentage of extraction were calculated from the iron(III) concentration.

Determination of the concentration of Iron(III) by UV-visible spectrophotometer.

The content of Fe^{3+} in aqueous phase was determined using a complexing reagent 1, 10-phenanthroline.

0.1, 0.5, 1.0, 1.5, 2.0 and 5.0 ppm standard solution of Fe^{3+} were prepared in 100ml volumetric flask by diluting respectively 0.1, 0.5, 1.0, 2.0 and 5.0 mL of 100ppm stock solution. 1mL of 10% hydroxylamine hydrochloride, 1,10-phenanthroline and 8 mL of sodium acetate were added to each standard solution. Then the absorbance of each mixture was taken by UV-visible spectrophotometer at 510nm.

About 2.0mL of aqueous phase from each centrifuged tube was taken and poured in a series of 50ml volumetric flask and then mixtures were prepared similar to the standard solution. The absorbances of each solution were taken by the spectrophotometer. The percent of extraction was calculated by subtracting the measured concentration from the initial concentration (200ppm) by considering the dilution factor.

III. Results and Discussion

Effect of electrolytes and their concentration on the extraction of iron(III)

Figure 1 shows the dependence of the percentage of extraction of iron(III) on the initial sodium chloride concentration in aqueous solution. The extraction percentage rises with the increase of concentration of sodium chloride. About 98.20% Fe (III) was extracted at 4.0M of NaCl.

However, figure 2 shows that the extraction percent of Fe(III) increases with increasing calcium chloride concentration in aqueous solution. Iron(III) was extracted to the extent of 96.07% into the organic phase at 2.0M of $CaCl_2$. Both sodium and calcium ion play significant roles for the high extractability of Fe(III) in the organic solution. $CaCl_2$ and NaCl play three important roles in the present system: (1) phase separation from the mixed aqueous solution of acetonitrile, (2) the formation of chloro complex with iron(III) and (3) they act as counter ion for the formation ion pair e.g. Na^+-$[FeCl_4]^-$.
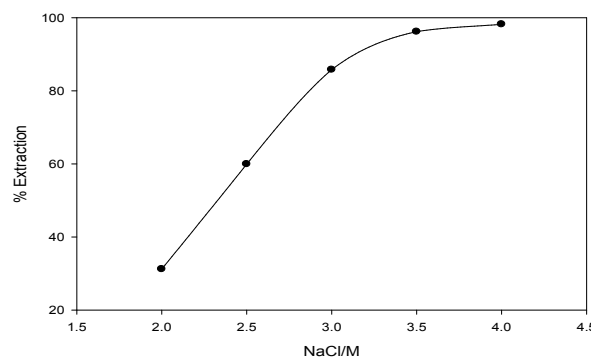

Fig. 1. Effect of sodium chloride in the extraction of Fe(III) from 1:1 (v/v) mixture of acetonitrile and aqueous solution at different concentrations of NaCl when the concentration of HCl was adjusted at 0.1M.
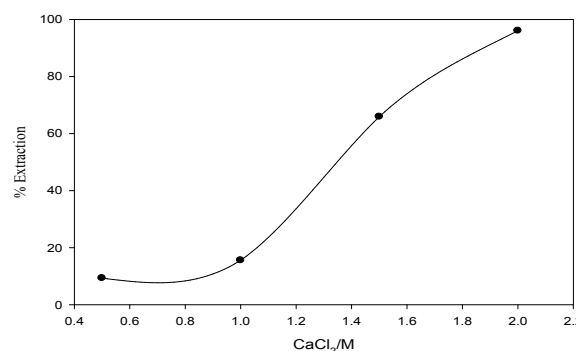

Fig. 2. Effect of calcium chloride in the extraction of Fe(III) from 1:1 (v/v) mixture of acetonitrile and aqueous solution at different concentrations of $CaCl_2$ when the concentration of HCl was adjusted at 0.1M.

Effect of acid on the extraction of iron (III)

Table 1 shows percentage of extraction of Fe (III) as a function of concentration of hydrochloric acid at constant concentration of NaCl (4.0M). Fe(III) was extracted to the extent of about 98.20% into acetonitrile at 0.1M HCl. The percentage of extraction increased up to 0.1M HCl and then decreased. Again table 2 expresses the extraction percentage of Fe(III) as a function of concentration of HCl at constant concentration of $CaCl_2$ (2.0M). About 98.15% Fe(III) was extracted at 0.15M of HCl.

These indicate that at certain concentration of acid the extraction percentage of iron(III) is maximum. It is a fact that with the increase of the concentration of HCl usually Cl^-, iron(III) chloride complexes become important with $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3(aq)$ and $FeCl_4^-$ being formed. The progressive addition of Cl^- to the Fe^{3+} ion the geometry of the complex changes[14].

Table. 1. Percentage of extraction of metal ion from aqueous phase with acetonitrile in presence of 4.0M NaCl with different concentration of HCl.

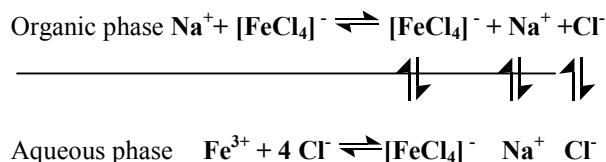| Conc. of NaCl, M	Conc. of HCl, M	Percentage extraction of Fe^{3+} in acetonitrile
4.0	0.01	96.87
	0.05	97.56
	0.10	98.20
	0.15	97.89

Table. 2. Percentage of extraction of metal ion from aqueous phase with acetonitrile in presence of 2.0M $CaCl_2$ with different concentration of HCl.

Conc. of $CaCl_2$, M	Conc. of HCl, M	Percentage extraction of Fe^{3+} in acetonitrile
2.0	0.01	90.79
	0.05	92.24
	0.10	96.07
	0.15	98.15

Mechanism of extraction of Fe(III) in acetonitrile

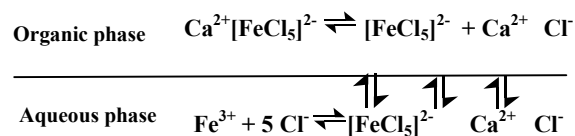The following mechanisms may be suggested for the extraction of Fe(III).

Figure 3 shows an equilibrium scheme involving Na^+, Cl^- and $[FeCl_4]^-$. The mechanism indicates that initially Fe(III) reacts with chloride ions to form $[FeCl_4]^-$ at higher concentration of NaCl. Since the organic phase contains water, Na^+ and Cl^-, $[FeCl_4]^-$ is extracted into the organic phase with Na^+ and partly ionize to $[FeCl_4]^-$ and Na^+ in the organic phase.

Organic phase $Na^+ + [FeCl_4]^- \rightleftharpoons [FeCl_4]^- + Na^+ + Cl^-$

Aqueous phase $Fe^{3+} + 4\ Cl^- \rightleftharpoons [FeCl_4]^-$ Na^+ Cl^-

Fig. 3. Reaction scheme for the extraction of iron (III) in the presence of sodium chloride.

Similarly the mechanism of the extraction of Fe (III) in the presence of $CaCl_2$ can be suggested as shown in figure 4. The figure shows that an equilibrium scheme involving Ca^{2+}, Cl^- and $[FeCl_5]^{2-}$. The mechanism indicates

NaCl and $CaCl_2$ plays the following roles in the present system: (1) phase separation from the mixed aqueous solution of acetonitrile, (2) the formation of $FeCl_4^-$ and

$[FeCl_5]^{2-}$ with Na^+ and Ca^{2+} respectively, resulting in the extraction of Iron(III) into the organic phase.

Organic phase $Ca^{2+}[FeCl_5]^{2-} \rightleftharpoons [FeCl_5]^{2-} + Ca^{2+}\ Cl^-$

Aqueous phase $Fe^{3+} + 5\ Cl^- \rightleftharpoons [FeCl_5]^{2-}$ $Ca^{2+}\ Cl^-$

Figure 4 : Reaction scheme for the extraction of Iron(III) in the presence of calcium chloride.

IV. Conclusion

Iron(III) was extracted to the extent of 98.20% into the acetonitrile at 4.0M NaCl and 0.1M HCl. On the other hand the percent of extraction of iron(III) was 98.15% at 2.0M $CaCl_2$ and 0.15M HCl. The extraction was attained by using the mixture of water and acetonitrile. Fe(III) was extracted as $FeCl_4^-$ or $[FeCl_5]^{2-}$ from the aqueous phase into the acetonitrile phase through the formation of ion pair: Na^+-$FeCl_4^-$ and Ca^{2+}-$[FeCl_5]^{2-}$.

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