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Selective extraction of Co(II) in the presence of Mn(II), Ni(II) and Cu(II) using salting-out phase separation method

Ahsan Habib*, Md. Wahiduzzaman, Harun-Or Rashid, Anarul Islam, Farhana Khanom Ferdoushi and A M Shafiqul Alam

Faculty of Science, Department of Chemistry, University of Dhaka, Dhaka 1000

Abstract

Extraction of Co(II) in the presence of Mn(II), Ni(II) and Cu(II) has been studied using the mixture of 2-propanol with water upon the addition of $CaCl_2$ in the concentration range of 3.0 – 5.0 mol dm^{-3} (M). Co(II) was extracted selectively to the extent of 80% into the 2-propanol phase at 5.0 M $CaCl_2$. The percent of extraction of other transition metal ions, for example Mn(II), Ni(II) and Cu(II) was much lower than that of Co(II), but they were stripped in the aqueous phase upon addition of $CaCl_2$. Therefore, selective extraction of Co(II) from these metal ions was attained by using the mixture of water and 2-propanol. Co(II) was extracted as $CoCl_4^{2-}$ from the aqueous phase into the 2-propanol phase through the formation of ion pair, Ca^{2+} - $CoCl_4^{2-}$. A mechanism is proposed to explain the extraction.

Introduction

The solvent extraction is one of the most popular methods used for separation of metal ions from industrial and waste solutions, which are frequently required in hydrometallurgical processing. The separation of cobalt from copper, nickel and manganese is of major interest, and a number of works have been conducted on the solvent extraction in the hydrometallurgical field [1]. Some raw materials such as oxide, sulfide, wastes, dusts etc are the major source for production of cobalt. Hydrometallurgical methods of dissolution of such material using hydrochloric acid result in solution containing cobalt along with some impurities. Moreover, cobalt readily form alloys with other metals such as chromium, nickel, copper and tungsten which have special properties used for cutting tools [2] as drill bits for high-speed machine. Cobalt is recovered from the alloys through treatment with acids in order to dissolve cobalt. Therefore, simple and selective separation of cobalt from other metal ions in acidic solutions has been interested to hydrometallurgists. Extraction of cobalt(II) have been carried out by using several complexing agents. For example, cobalt(II) can be separated from nickel(II) by using pyridinecarboxylate esters [3], di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid (PC88A) and bis(2,4,4 trimethylpentyl) phosphonic acid (Cyanex 272) [4-7], 1-(2- thiazolylazo)-2-naphthol (TAN) [8], polyoxyethylene nonyl phenyl ether with 10 ethylene oxide units (PONE10) and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (EHPNA) [9]. Other complexation reactions between metals and ligands have been used to extract Co(II) by using PC88A [10], sodium di(2-ethylhexyl) phosphate (D_2ENa) and tributyl phosphate (TBP) into cyclohexane and n-dodecane [11,12], NPhenyl- N’-(2-butylthiophenyl)thiourea (PBT) into chlorobenzene [13]. Cobalt(II) has also been extracted as ion-pair complexes together with other transition metal ions by using N,N’-bis(2-pyridylmethylidene)-1,2-diiminoethane(BPIE), N,N’-bis[1-(2-pyridyl)ethylidene]-1,2-diiminoethane (BPEE) and N,N’-bis(2-pyridylmethylidene)- trans-1,2-diiminocyclohexane (BPIC) into nitrobenzene [14], N,N’-bis(2-hydroxyphenylmethyl)-N,N’-bis(2-pyridylmethyl)-1,2 ethanediamine (BBPEN) into chloroform [15], N,N-dibutyl-N’-benzoylthiourea (DBBT) into paraffin [16], mixture of four trialkyl phosphine oxides (cyanex 923) into toluene [17], and trioctylphosphine oxide (TOPO) into chloroform [18]. A range of pH (4 to 10) is usually maintained for the extraction of cobalt. Since the extraction ratio of cobalt(II) is not enough high in acidic medium (pH < 2)

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*Corresponding Author: mahabibbit@yahoo.com

that cobalt(II) can be separated by one step extraction, some extraction stages have been carried out to extract cobalt(II) completely.

Phase separation of homogeneous mixed solvents has been performed by addition of salts or changing temperature to organic solvents. For example, phase separation occurs by organic salt of (NH4)2SO4 added to a polyethylene glycol [19], or induced temperature raised to 30 ºC in diethylether-water system [20]. Tabata et al. [21] reported that phase separation of homogeneous mixtures of 2-propanol and water is occurred upon the addition of sodium chloride. It was found that different charged species of metal ions were formed at high concentration of Cl^- in aqueous solution. This led to selective extraction of specific chemical species such as $AuCl4^-$ and $TlCl4^-$ as their ion-pair complexes with Na^+ into the 2-propanol phase [21-24].

In the present study, we have investigated the phase separation that occurred by the addition of CaCl2 to the mixtures of 2-propanol and water. We have utilized the phase separation processes for selective extraction of cobalt(II) in the presence of manganese(II), nickel and copper(II) into 2-propanol phase without using any other extracting reagents. The extraction mechanism will be described.

Experimental

Reagents and apparatus

2-propanol (99.97%), chloride salts of cobalt(II), nickel(II), manganese(II) and copper(II) were purchased from E Merck, India; Sodium chloride, calcium chloride and EDTA were purchased from BDH, England; Silver nitrate was purchased from E Merck, Germany. Sodium chloride, calcium chloride and EDTA were dried in an electric oven for 2 hours at 105 ºC before use. Aqueous solutions of $CaCl_2$ and NaCl were prepared by taking requisite amount of the respective salt in separate volumetric flask. Concentration of the prepared $CaCl_2$ and NaCl were measured by EDTA titration and Volhard's method [25], respectively.

1000 mg/L (ppm) stock solution of each metal salt was prepared separately in 100 mL volumetric flask. A number of 15 mL graduated centrifuge tubes were taken and poured required volume of each metal solution in such a way that the final concentration of each metal ion was 200 ppm in the aqueous phase. The acid concentration ($[H^+]$) in each tube was adjusted at 0.10 M by dilute HCl. A range of concentration of $CaCl_2$ (3.0 to 5.0 M) and NaCl (3.0 to 4.40 M) was maintained by adding concentrated aqueous solution of the salts in the aqueous phase. In case of higher concentration, solid salts were added directly in the aqueous phase and dissolved. The volume of the aqueous layer was adjusted to 5 mL by adding deionized water. Then 5 mL of 2-propanol was added in each tube. Then the mixtures were shaken vigorously for about 10 minutes and left for 3 hrs to reach a complete equilibrium. The solutions were then centrifuged (Model YJ03—043-4000; Cycles: 50 C/ S) for 10 minutes. After that the aqueous and organic phases 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 metal ions distributed between the two phases were determined by atomic absorption spectrometry (AAS) (Model AA-680, Japan). The distribution coefficient and extraction percent were calculated from the concentrations determined. The separation factor ($\beta = D1 / D2$) between the two metals was calculated as the ratio of the distribution ratios of the two metals $D1$ and $D2$. Deionized water was used through out the experiments. All experiments were carried out at room temperature.

Determination of the concentration of Co(II), Ni(II), Cu(II) and Mn(II) by AAS.

2, 4, 6, 8 and 10 ppm standard solution of Cu(II) was prepared in 100 mL volumetric flask by diluting respectively 0.2, 0.4, 0.6, 0.8 and 1.0 mL of 1000 ppm stock solution. Similarly, the standard solutions for other metal ions were prepared. About 3 mL of aqueous phase was taken from each centrifuge tube and poured in a series of 25 mL volumetric flask and then diluted by addition of deionized water. Further dilution was done when necessary. First of all, AAS was run using the 3/4 standard solution for each metal ion and then run for unknown samples which are prepared from the aqueous phase. The percent of extraction was calculated by subtracting the measured concentration from the initial concentration 200 ppm by considering the dilution factor.

Results and Discussion

Effect of salts and their concentration on the extraction of Co(II)

Figure 1 shows the percent extraction of Co(II) as a function of $CaCl_2$ concentration in the aqueous solution. Co(II) was extracted to the extent of about 80% into the organic phase at 5.0 M $CaCl_2$ whereas poor extraction was observed for Mn(II) (8.06%), Ni(II) (5.2%) and Cu(II) (9.2%). This indicates that calcium ion has significant role for the high percent extraction of Co(II) in the organic phase. Calcium chloride play important roles in the present study. These are as follows: (1) causes the phase separation of the mixture of aqueous and organic; (2) forms chloro-complexes with Co(II); and (3) it acts as counter ion for the formation ion pair e.g., Ca^{2+} - $CoCl_4^{2-}$ resulting migration of Co(II) ion in the organic phase. Tabata et al.[21] reported that different charged species of the metal ions may form at high concentration of Cl^- in the aqueous phase.

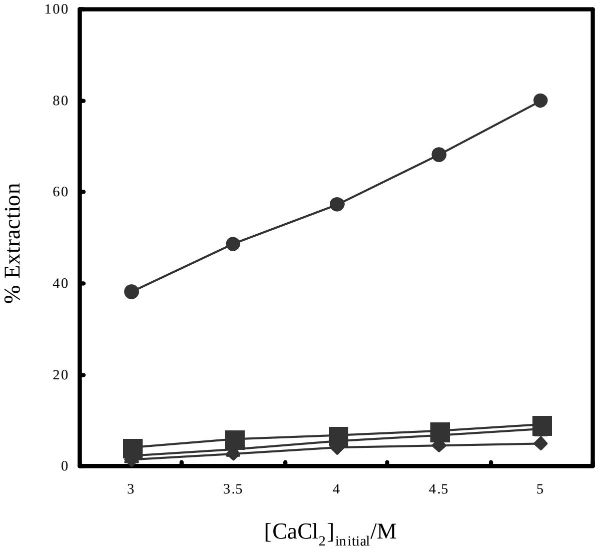

Figure 1. **Effect of initial concentrations of calcium chloride on the extraction of Co(II) (●) Mn (II) (■), Ni(II) (▲), Cu(II) (♦) from a 1:1 (vol/vol) mixture of 2-propanol and aqueous solution at different concentrations of $CaCl_2$. Concentration of H^+ was adjusted at 0.1 M. Initial concentration of each metal ion is 200 ppm.**

This may be explained by consideration of separation factor ($\beta=D_1/D_2$) of different transition metal ions where D_1 and D_2 indicate the distribution ratios of Co(II) and other metal ions, respectively. Some separation factors ($\beta=D1/D2$) for the extraction of Co(II) from the other transition metal ions and $CaCl_2$ into 2-propanol after salting out process at high concentration of $CaCl_2$ are as follows: $\beta_{(Co\text{-}Mn)} = 2.6x10^2$; $\beta_{(Co\text{-}Ni)} = 4.8x10^2$; $\beta_{(Co\text{-}Cu)} = 1.9x10^2$ and $\beta_{(Co\text{-}CaCl2)} = 6.7x10^1$ [22]. It has been reported that the pink color of Co(II) changes to blue along with shifting of absorption maximum (λ_{max}) to higher wavelength as a function of $CaCl_2$ concentration. This suggests that the structure of Co(II) changes from octahedral species ($CoCl_x(H_2O)_{6-x}$) to tetrahedral species ($CoCl_4^{2-}$) through the replacement of water molecules bound to the Co(II) by chloride ion [22, 26-30].

However, the chemical species of Mn(II), Ni(II) and Cu(II) are mixtures of many ionic species at high concentrations of Cl^-: $MnCl_2$ and $MnCl_3^-$; $NiCl_3^-$ and $NiCl_2^-$: $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$ [22] which resulted low extraction due to their strong hydration and the difficulty in charge neutralization by Ca^{2+}. On the other hand, Co(II) ion forms tetrahedral of $CoCl_4^{2-}$ and the coordination sites of the anionic species is fully occupied by the chloride ions. Therefore, water molecules do not bind to $CoCl_4^{2-}$ species [22]. As a result, $CoCl_4^{2-}$ is extracted as the ion pair Ca^{2+} -$CoCl_4^{2-}$ into the organic phase as compared to the other transition metal ions e.g., Mn(II), Ni(II) and Cu(II).

On the other hand, percent extraction of Co(II) is about 27% at 3.0 M NaCl concentration. The extraction is decreased not only for Co(II) but also for other metal ions with increasing of NaCl concentration as shown in Figure 2. This can be explained by considering the increasing tendency of aqueous phase as a function of NaCl concentration that explained in the following section.

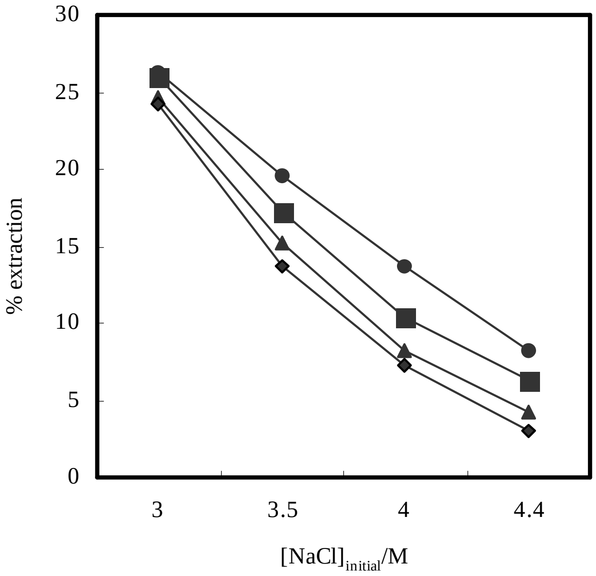

Figure 2. **Effect of initial concentrations of sodium chloride on the extraction of Co(II) (●) Mn (II) (■), Ni(II) (▲), Cu(II) (♦) from a 1:1 (vol/vol) mixture of 2-propanol and aqueous solution at different concentrations of NaCl. Concentration of H^+ was adjusted at 0.1 M. Initial concentration of each metal ion is 200 ppm.**

Effect of amount of water on the extraction of Co(II)

Table 1 and 2 show the volume change in the aqueous and organic phases with increasing concentration of $CaCl_2$ and NaCl, respectively. Table 1 shows the volume of the aqueous phase decreases with increasing of $CaCl_2$. We also observed that the percent of extraction of Co(II) increased with increasing of $CaCl_2$ concentration. Therefore, it is suggested that the extraction of Co(II) increases with increasing of water amount in the organic phase. Mixing of water with organic solvent has strong effect on changing of chemical as well as properties of solvent. The high amount of water in the organic phase enhances the polarity of 2-propanol [22] and can extract ion pairs, which is followed by dissociation in the 2-propanol phase, as observed in aqueous acetonitrile [23]. In addition, water in the 2-propanol phase enhances the formation of solvent clusters of 2-propanol molecules that preferentially solvate the ion pairs [24]. These effects increase the extraction of metal ions with increasing the amount of water in the 2-propanol phase.

Table 1. **Volume change in the aqueous and organic phase upon addition of $CaCl_2$.**

$[CaCl_2]$ with 2-propanol. [M]	Volume of organic phase (mL)	Volume of aqueous phase (mL)
3.0	5.70	4.26
3.5	5.74	4.17
4.0	5.82	4.11
4.5	5.95	3.98
5.0	6.02	3.87

Table 2. **Volume change in the aqueous and organic phase upon addition of NaCl**

[NaCl] [M]	Volume of organic phase (mL)	Volume of aqueous phase (mL)
3.0	4.25	5.72
3.50	4.43	5.55
4.0	4.57	5.41
4.40	4.65	5.30

On the contrary, the extraction of Co(II) in the presence of 3.0 M NaCl is much lower than that for $CaCl_2$ and percent extraction decreased with increasing of NaCl concentration. The percent extraction of Co(II) is about 5 % at 4.4 M NaCl whereas that for 4.0 M $CaCl_2$ is about 60 %. Co(II) ion forms di-negative $CoCl_4^{2-}$ species at high concentration of chloride.

The high percent extraction of Co(II) in the presence of $CaCl_2$ is due to formation of stable ion pair of Ca^{2+}-$CoCl_4^{2-}$ and can easily migrate into the organic phase but Na^+ may not form stable ion pair like Ca^{2+} resulting in lower percent of extraction. In addition, the increasing trend of volume of aqueous layer suggested that migration of water molecules into the 2-propanol phase is not suitable where for efficient extraction water molecules is necessary in the organic phase. But in the case of $CaCl_2$, the volume in aqueous phase decreased with increasing of $CaCl_2$. This indicates that upon addition of $CaCl_2$, maximum water molecules migrated into the 2-propanol phase. The presence of water molecules in the organic phase changes the chemical properties of the organic molecules e.g., increased polarity etc.

Mechanism of Extraction of Cobalt(II) by 2-Propanol and water mixture in the presence of $CaCl_2$

According to the high percent extraction of Co(II) in the presence of $CaCl_2$, the following mechanism is suggested as shown in Figure 3. The figure shows an equilibrium scheme involving Ca^{2+}, Cl^- and $CoCl_4^{2-}$. The mechanism indicates that initially Co(II) reacts with chloride ions to form CoCl4 $^{2-}$ at higher concentration of CaCl2. Since the organic phase contains water, Ca^{2+} and Cl^- , CoCl4^{2-} is extracted into the organic phase with Ca^{2+} and partly ionize to CoCl4 $^{2-}$ and Ca^{2+} in the organic phase. CaCl2 plays the following roles in the present system: (1) phase separation from the mixed aqueous solution of 2-propanol, (2) the formation of CoCl4^{2-} in both aqueous and organic phases and (3) charge-neutralization of CoCl4^{2-} with $Ca^{2+,}$ resulting in the extraction of cobalt(II) into the organic phase.

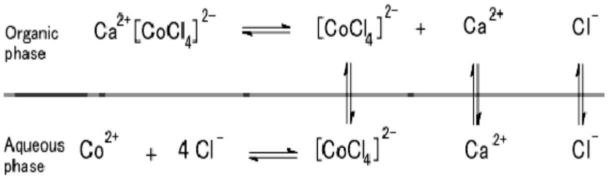

Figure 3. **Extraction scheme for the extraction of cobalt (II) in the presence of Ni(II), Mn(II) and Cu(II) where the salt was calcium chloride.**

Conclusion

Cobalt(II) was extracted selectively to the extent of 80% into the 2-propanol phase at 5.0 M $CaCl_2$. The percent of extraction of other transition metal ions, for example Mn(II), Ni(II) and Cu(II) was much lower than that of Co(II), but they were stripped in the aqueous phase upon addition of $CaCl_2$. Therefore, selective extraction of Co(II) from these metal ions was attained by using the mixture of water and 2-propanol. Moreover, the results indicated that the extraction of Co(II) enhanced with increasing concentration of water in the 2-propanol phase. Co(II) was extracted as $CoCl_4^{2-}$ from the aqueous phase into the 2-propanol phase through the formation of ion pair, Ca^{2+} - $CoCl_4^{2-}$.

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