ASIAN JOURNAL OF CHEMISTRY

Separation of Cobalt and Nickel from Concentrated HCl Solutions by Winsor II Microemulsion System with N235 as Carrier

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The selective extraction of cobalt from concentrated HCl solutions by Winsor II microemulsion system using tertiary amine N235 as carrier was studied. In the hexadecyl trimethyl ammonium chloride (HDTAC)/*n*-pentanol/n-heptane/HCl/N235 system, HDTAC was used as a cationic surfactant to form microemulsion in *n*-heptane, *n*-pentanol was injected in the microemulsion as a cosurfactant and N235 was a typical extractant in the system. The microemulsion system without N235 showed poor extractability and stability. However, by adding N235, the extraction yield (E %) of cobalt can be almost 92 %, that of nickel was always very low. The influence of different parameters such as surfactant concentration, extractant concentration, hydrochloric acid concentration of the feed solutions, cosurfactant concentration as well as temperature on the extraction yield (E %) were investigated. The results showed 92 % of cobalt was extraced by microemulsion, while the extraction yield of nickel was very low which made the separation of cobalt and nickle possible.

Key Words: Microemulsion, Extraction, N235, Cobalt, Nickel.

INTRODUCTION

Cobalt and nickel usually appear together in ores, batteries and leach residues, the similar physical and chemical properties of these metals and the high purity degree required in their applications have led to the development of a remarkable amount of research work on cobalt-nickel separation. Both of cobalt and nickel exist as divalent hexahydrated ions in dilute aqueous solutions. However, small differences in chemical behaviour do exist such as the rate of water exchange of cobalt ion is much higher than for nickel, thus complex formation often proceeds much more readily with divalent cobalt than with nickel[1]. Generally, cobalt is preferentially removed with a suitable extractant, leaving nickel behind. The separation of cobalt and nickel has been studied extensively and early studies have led to the development of many treatment technologies, including chemical precipitation[2], ion exchange[3], flotation[4], solvent extraction[5-8], supported liquid membranes[9-10] and emulsion liquid membranes (ELM)[11-14]. The utilization of microemulsified systems in metallic cations extraction has been a good alternative. Compared with conventional solvent extraction and many other techniques, microemulsion extraction systems were more profitable because of the unique properties as separation medium, such as the nanometer sized spherical or bicontinuous structure, the rapid coalescence and resepa-

ration dynamics of the structure and the enhanced solubilization capacity.

Microemulsions are thermodynamically stable mixtures of water, oil and surfactant, occasionally including alcohol as cosurfactant. There are three possibilities for the type of phases depending on the compositions temperature and salinity. Two-phase systems, called Winsor I and Winsor II, correspond to an oil-in-water microemulsion coexisting with an oil phase and a water-in-oil microemulsion coexisting with excess water, respectively. A Winsor III system forms when the surfactant is concentrated in a middle phase, which coexists with oil and water[15]. In a Winsor type II system, the microemulsion consists of an aqueous pool surrounded by surfactant in the oil membrane, in equilibrium with excess aqueous phase. Various types of metallic ions can be extracted by this type of microemulsion and trapped in the inner aqueous phase microemulsion, such as copper[16], lanthanides[17], gallium[18], chromium and other metals[19-23]. The extraction of metal ions by water-in-oil microemulsion systems often effectively accelerates the extraction as well as improves the extractatability because of the enormous rise of the micro-interfacial surface area and the spontaneous formation of microemulsion globules. The globules can transport metal ions from the aqueous phase to the organic phase. In our previous studies[24-28], Winsor II

microemulsions with different surfactants were found to effectively extract of uranium, samarium, cobalt and germanium.

The purpose of the present work is to investigate the possibility of cobalt and nickel separation from concentrated HCl solutions by a new Winsor II system. N235 was used as extractant (Fig. 1). On the basis of present experiments, it is found that adding N235 into the microemulsion system had some advantages: When the microemulsion without N235 used to extract cobalt, *n*-pentanol must be more than 80 %, or the microemulsion was easily emulsified in the extraction procedure, and the extraction yield (E %) of cobalt was low. The extractability and stability of the microemulsion was increased after adding N235. It is well established that Co^{2+} cations complex readily with chloride ions to form complex anions in aqueous solutions, while Ni^{2+} has little affinity with chloride ions. It is cobalt complex anions that are responsible for electrostatic attraction with hexadecyl trimethyl ammonium chloride and ion exchange with chloride in acidulated N235 and, hence, extraction into the organic phase, leaving nickel behind.
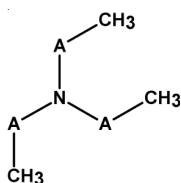
Fig. 1. Structure of N235 (A= C_nH_{2n}, n = 8/9/10)

EXPERIMENTAL

Vibrator (Yancheng Science Instrument Factory, Jiangsu Province), with a vibration frequency of 275 ± 5 min^{-1} and a temperature controlling precision of ± 1 K. UV grating spectrophotometer 754 type (Shanghai Precision & Scientific Instrument Co. Ltd).

The chemicals used in the experiments were all analytical grade except N235. Cobalt chloride hexahydrate (Sinopharm Chemical Reagent Co. Ltd.), nickel chloride hexahydrate (Sinopharm Chemical Reagent Co.,Ltd.), hydrochloric acid (Shandong Laiyang Reagent Factory), *n*-pentanol (Beijing Yili Reagent Factory), *n*-heptane (Tianjin Damao Reagent Factory). Hexadecyl trimethyl ammonium chloride (CTAC) (Tianjin Fuchen Reagent Factory), N235 (average molecular weight is 349, Chinese Academy of Sciences), 1-nitroso-2-naphthol-3,6-disulphonic acid disodium salt (Shanghai San Aisi Reagent Factory), dimethyl glyoxime (Shanghai Reagent Factory).

Preparation of microemulsion and feed solutions: N235 was acidified by 3.0 mol/L hydrochloric acid first, which swiched to N235 hydrochloride (R_3NHCl). The microemulsion phase was prepared by injecting CTAC, 0.5 mol/L hydrochloric acid solutions, *n*-pentanol and/or N235 in *n*-heptane. The resulting mixtures formed microemulsions spontaneously whenever the composition was adequate. The feed solutions were prepared using predetermined amounts Co(II) chloride hexahydrate, Ni(II) chloride hexahydrate, distilled and deionized water and fuming HCl in order to obtain solutions at different acidic molarities.

Experimental methods: In the following studies, unless otherwise stated, the experiments were generally performed at 298 ± 1 K. The initial cobalt and nickel concentration was

0.1 g/L. The volume ratio of aqueous phase to microemulsion was expressed as R (R = 1). The extraction yield was expressed as E %, which was calculated using eqn. (1):

$$E\% = \frac{(m_0 - m_t)}{m_0} \times 100\% \tag{1}$$

where, m_0 and m_t were the total amount of Co(II) (or Ni(II) ions in the feed solutions at t = 0 and t = t, respectively. The feed solution was mixed with the microemulsion in 10 mL glass container and shaken 10 min in the vibrator, which was sufficient for equilibrium. The mixture was kept still until the two phase separated completely. The UV-visible spectroscopic method was used to determine the concentrations of cobalt and nickel in aqueous solutions[29] and the concentrations in microemulsion were calculated by mass balance.

RESULTS AND DISCUSSION

Microemulsion without N235 extraction of Co(II) and Ni(II): The organic phase without N235 showed poor extractability of cobalt and nickel and the microemulsion was easily emusified in the extraction procedure. By adding pentanol (≥ 80 %), the stability of microemulsion system was enhanced, but the extractability was still poor.

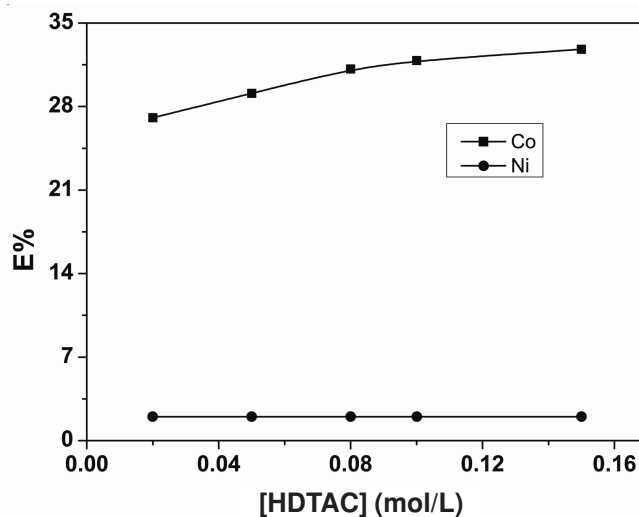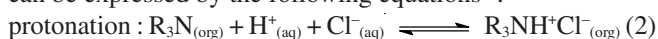Fig. 2. Effect of HDTAC concentration on the extraction yield (E%) of Co(II) and Ni(II); Oil phase: $C_{n\text{-pentanol}}$ = 80 %; inner aqueous is 0.5 mol/L HCl solution. Feed solution: $C_{Co(II)}$ = 0.1 g/L, $C_{Ni(II)}$ = 0.1 g/L; CHCl = 10 mol/L

When the *n*-pentanol concentration was 80.0 %, the effect of the HDTAC concentration on the cobalt and nickel extraction was studied. As seen in Fig. 2, the extractability of Co(II) was reinforced with HDTAC concentration increasing. In strong acidic leach solution, cobalt cations formed $CoCl_4^{2-}$ complex with Cl^- anions[30]. Because of the electrostatic attraction between cationic surfactant HDTAC and $CoCl_4^{2-}$, Co(II) was extracted by this type of microemulsion and trapped in the inner aqueous phase. While the microemulsion showed poor extractability of nickel. The reason is that Ni^{2+} has little affinity with Cl^- and Ni^{2+} are still cations in the HCl solutions, so the electrostatic effect between nickel and the polar head of HDTAC is poor which makes the nickel extraction yield (E %) very low.

Microemulsion with acidulated N235 extraction of Co(II) and Ni(II): By adding acidulated N235, the microemulsion was greatly stabilized and extremely enhanced extractability. The amount of pentanol (≥ 30 %) injected in the microemulsion was greatly decreased without the system emulsified. A further study is necessary for a complete understanding.

Effect of the extractant concentration on Co(II) and Ni(II) extraction: The extractant concentration plays a significant role in extraction of cobalt. The effect of concentration of R_3NHCl on extraction percentage of cobalt and nickel was studied. As seen in Fig. 3, with increasing the concentration of extractant in the microemulsion from 4 to 24 %, the extraction yield (E %) of cobalt increased rapidly, then it increased slowly. But that of nickel was always very low and changed very little. The reason for this difference is the tendency for Ni(II) to retain its hexa-coordination in high concentrations of Cl$^-$ and, unlike Co(II), does not form tetrahedral anionic chlorocomplexes[31].

The Co(II) that form complex anions with Cl$^-$ in HCl solutions are extracted by R_3NHCl. Both experimental results and theoretical consideration identified $CoCl_4^{2-}$ anions as the most favourable species for ion exchange with Cl$^-$ in protonated R_3NHCl[32]. The reaction between cobalt, HCl and N235, can be expressed by the following equations[33]:

protonation : $R_3N_{(org)} + H^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons R_3NH^+Cl^-_{(org)}$ (2)
exchange : $2R_3NH^+Cl^-_{(org)} + CoCl_4^{2-}_{(aq)} \rightleftharpoons (R_3NH)_2CoCl_4$
$_{(org)} + 2Cl^-_{(aq)}$ (3)

The binary complex $(R_3NH)_2CoCl_4$, which formed on the external aqueous/organic interface diffused to the inner organic/aqueous interface and Co(II) was easily trapped in the internal aqueous phase of low hydrochloric acid concentration (0.5 mol/L)[32].
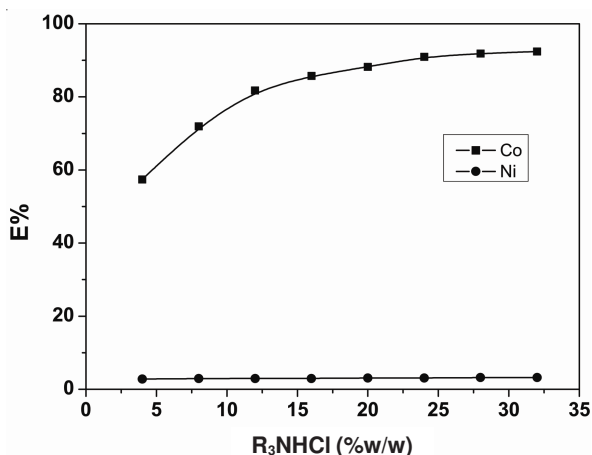

Fig. 3. Effect of extractant concentration on the extraction yield (E %) of Co(II) and Ni(II); Oil phase: HDTAC = 2.0 %, CR_3NHCl = 4.0 - 32.0 %, C_n - pentanol = 30.0 %; inner aqueous is 0.5 mol/L HCl solution. Feed solution: $C_{Co(II)}$ = 0.1 g/L, $C_{Ni(II)}$ = 0.1 g/L, C_{HCl_3} = 10 mol/L

Effect of *n*-pentanol concentration on Co(II) and Ni(II) extraction: The cosurfactant is a non-ionic molecule that combines with surfactant to neutralize the repulsive effect among the surfactant polar heads. Most of microemlsions need cosurfactant to form micellars. The effect of *n*-pentanol concentration on the cobalt and nickel extraction yield (E %)

was investigated. The results were shown in Fig. 4. As *n*-pentanol concentration increased, the cobalt extraction yield (E %) reduced. The limited solubility of amines or the metal-ligand complexes in organic diluents leads to the formation of third phase. Long chain alcohol can effectively restrain the third phase. However, the interaction between *n*-pentanol and R_3NHCl makes some of extractants lose their activity. A third phase appeared when the n-pentanol concentration was less than 30 %. The *n*-pentanol in this extraction system is not only as cosurfactant but also as static modifier, which restrains the third phase.
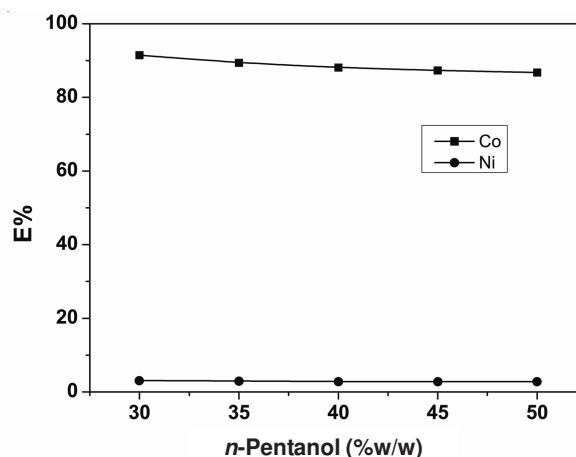

Fig. 4. Effect of *n*-pentanol concentration on the extraction yield (E %) of Co(II) and Ni(II); Oil phase: HDTAC = 2.0 %, CR_3NHCl = 24.0 %, C_n-pentanol =30.0 - 50.0 %; inner aqueous is 0.5 mol/L HCl solution. Feed solution: $C_{Co(II)}$ = 0.1 g/L, $C_{Ni(II)}$ = 0.1 g/L, C_{HCl_3} = 10 mol/L

Effect of HCl concentration on Co(II) and Ni(II) extraction: Since cobalt was extracted in the form of complex with Cl$^-$, the role of presence of HCl in the transportation phenomena was examined by experiments with adding acidic molarity values. In the Fig. 5, it could be noted that the extraction yield (E %) of cobalt increased greatly as the HCl concentration ranged from 7 to 10 mol/L and kept invariable as the acidity grew higher than 10 mol/L. The complete extraction of cobalt is due to the rapid formation of anionic $CoCl_4^{2-}$ with increasing acidic molarity values. The microemulsion systems were found to be stable at all concentrations of HCl studied.

Effect of temperature on Co(II) extraction: The effect of temperature on cobalt extraction was studied. The results obtained were shown in Fig. 6, indicated that the distribution coefficient of the Co(II) between the organic and aqueous phases (D) was decreased with the tempreture increased. This phenomenon can be explained that the extraction is an exothermic nature and lower tempreture favour the metal extraction. The enthalpic change was -15.07 kJ·mol^{-1}, which was calculated by eqn. (4)[34].

$$\left(\frac{\delta \ln D_{Co}}{\delta \frac{1}{T}} \right) = \frac{-\Delta_r H_m^{\theta}}{R} \quad (4)$$

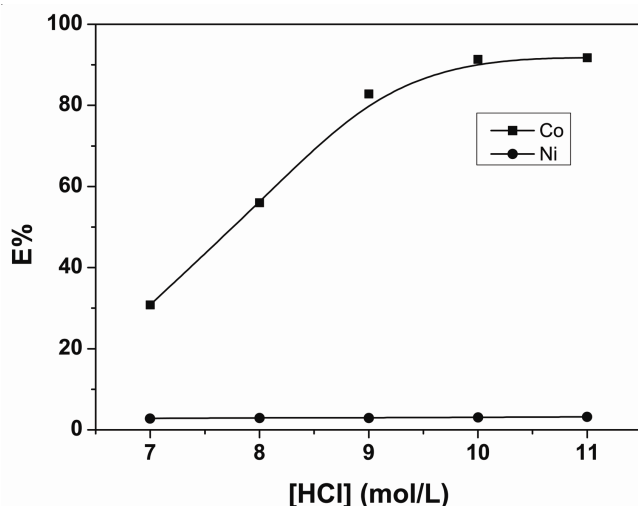where, D_{Co} refers to distribution coefficient of Co(II), T (K) is the temperature and R is the gas constant.

Fig. 5. Effect of the HCl concentration on the extraction yield (E %) of Co(II) and Ni(II); (Oil phase: HDTAC = 2.0 %, CR₃NHCl = 24.0 %, Cₙ-pentanol = 30.0 %; inner aqueous is 0.5 mol/L HCl solution. Feed solution: $C_{Co(II)}$ = 0.1 g/L, CNi(II) = 0.1 g/L, CHCl = 7-10 mol/L
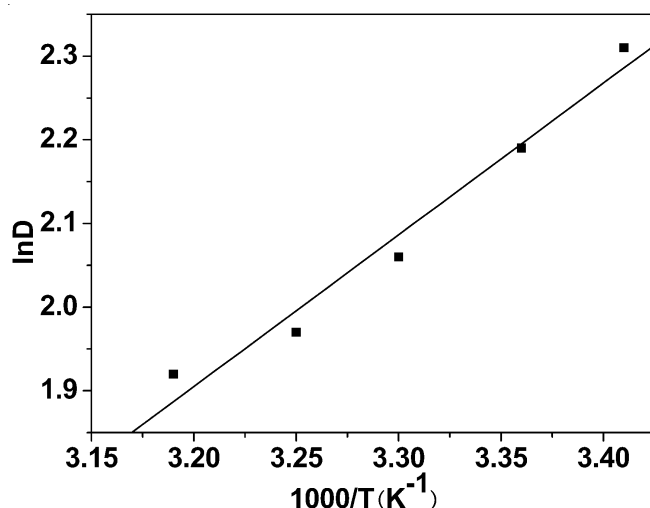

Fig. 6. Effect of temperature on the extraction yield (E %) of Co; (Oil phase: HDTAC = 2.0 %, CR₃NHCl = 24.0 %, Cₙ-pentanol =30.0 %; inner aqueous is 0.5 mol/L HCl solution. Feed solution: $C_{Co(II)}$ = 0.1 g/L, C_{HCl} = 10 mol/L

Separation of cobalt and nickel: The separation of cobalt and nickel was carried out through five feed mixtures. On the basis of the above experiments, separation conditions were as follows: the mass fraction of HDTAC, R₃NHCl and pentanol in the microemulsion were 2, 24 and 30 %, HCl concentration of feed solutions was 10 mol/L. Under these conditions, the extraction yields of cobalt and nickel and the separation factors for the five feed mixtures were given in Table-1. As seen from Table-1, from the feed solutions containing Co^{2+} and Ni^{2+}, cobalt in comparison with nickel was extracted preferentially with R₃NHCl. The percentages of cobalt extraction were above 91.3 % for the five feed mixtures. On the other hand, for the same feed mixtures the percentages of Ni extraction were below 6.7 %. Consequently, cobalt was selectively separated and concentrated by Winsor II microemulsion from concentrated HCl solutions. It could be also noted from Table-1 for equimolar cobalt-nickel mixtures, the separation

TABLE-1
SEPARATION FACTORS OF COBALT OVER
NICKEL AT THE OPTIMUM CONDITIONS

Feed mixture	E % (Co)	E % (Ni)	$\beta_{Co/Ni}$
0.1 g/L Co – 0.1 g/L Ni	91.4	6.7	148.0
0.3 g/L Co – 0.3 g/L Ni	92.5	5.7	204.0
0.5 g/L Co – 0.5 g/L Ni	91.3	2.7	378.2
0.1 g/L Co – 0.5 g/L Ni	93.0	5.2	242.2
0.1 g/L Co – 1.0 g/L Ni	92.1	6.7	162.3

factor of cobalt increased as the cobalt concentration in the feed solution increased. Separation factor as high as 378.2 for cobalt had been achieved. For non-equimolar feed mixtures, the separation factor of cobalt decreased as the nickel concentration increased. Similar results were observed by Osman Tutkun[35]. The difference in extractability between these two metal ions appears to be related to their ability to form chloride complexes in chloride aqueous solutions. It is well documented that cobalt complexes readily with chloride to form $CoCl_4^{2-}$ and/or $HCoCl_4^{2-}$; while nickel ions show only a marginal degree of complexation with chloride[36]. Therefore, using R₃NHCl as an extractant is favourable for the separation of Co(II) and Ni(II) in HCl solutions. The separation factor, $\beta_{Co/Ni}$, was calculated using the following eqn. (5):

$$\frac{D_{Co}}{D_{Ni}} = \frac{\left[Co(II)\right]_{org}}{\left[Co(II)\right]_{aq}} \times \frac{\left[Ni(II)\right]_{aq}}{\left[Ni(II)\right]_{org}} \qquad (5)$$

Conclusion

HDTAC/n-pentanol/n-heptane/HCl/N235 was chosen for the formation of the microemulsion. The results obtained in the present study showed that the extraction equilibrium was immediately achieved and the microemulsion system provided an attractive alternative to conventional solvent extraction methods for the separation of Co(II) from Ni(II). The system showed high selectivity for Co(II) in the presence of Ni(II). The microemulsion system without N235 showed poor extractability and the microemulsion was easily emulsified. When N235 was injected in the microemulsion, the extractability was greatly improved and the extraction yield could be almost 92 % for cobalt. Through the experiments of cobalt-nickel separation, the extraction yield of cobalt was about 92 % from various cobalt-nickel mixtures, while the extraction yield of nickel was very low. The highest separation factor of cobalt over nickel can achieve 378.2 when the feed solution containing 0.5 g/L cobalt and 0.5 g/L nickel ions.

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