Separation of Co (II) and Li (I) using Saponified P507/*n*-Hexanol/*n*-Heptane Salting-Out Agent Free Microemulsion

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ABSTRACT

Saponified 2-ethylhexylphosphoric acid mono-2-ethylhexyl ester (P507)/ /n-hexanol/n-heptane salting out agent free microemulsion is found to be a promising efficient system for separating Co (II) and Li (I). In this microemulsion system, the volume ratio of saponified P507, n-hexanol and n-heptane is 1:6:14. The concentration of the external aqueous Co (II) and Li (I) was 100 and 40 mg/L, respectively. The optimum condition is assured as follows: water bath temperature of 298.15 K, vibration time for 7 min, molar ratio of P507 and NaOH 1.5:1, volume ratio of aqueous phase and microemulsion 8. Under the optimum condition, the extraction yield of cobalt and lithium is 99.1% and 14.4%, respectively. The average reverse extraction yield of colbat is 97.2% when 1.0 mol/L HCl is used as reverse extraction experiments on the organic phase. The organic phase after stripping can be reused. The results show that: the saponified P507 microemulsion system is not only thermodynamic stability, but also has a broad application prospect in the extraction and separation of Co (II) and Li (I) with strong selectivity and high efficiency. Density functional theory (DFT) based calculations have been carried out on the structures and relative binding energies of Co (II) and Li (I) with the surfactant sponified P507 in n-heptane and water solution, respectively. The calculated results suggest that the different interaction between the ions with surfactant saponified P507 is responsible for the preferential complexation of saponified P507 to Co (II) and Li (I) ions. The combined experimental and theoretical studies help us to understand the superior complexation behavior of Co (II) over Li (I) within saponified P507/n-hexanol/n-heptane microemulsion.

Keywords: Extraction and separation; Co (II); Li (I); Saponified P507; Microemulsion system
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INTRODUCTION

With the increasing demand of lithium ion batteries in the mobile phones, battery cars, and electric vehicles, the consumption of metals, such as cobalt and lithium, is increasing year by year. Simultaneously, tens of billions of spent lithium ion batteries are discarded in the world, every year, according to incomplete statistics. If the spent lithium ion batteries cannot be properly handled, it not only will bring great harm to the environment, but also cause huge waste of resources. Worldwide attention is being diverted to recover these metals from secondary resources. Solvent extraction is the most used process in the conventional separation of cobalt, zinc, copper, nickel, and other metals.[1-8] There are some extractants used in the solvent extraction of cobalt: di(2-ethylhexyl) phosphoric acid (P204), P507, Cyanex 923, tributyl phosphate and triotylamine, and Cyanex 272. The extraction yield of cobalt is higher under proper conditions. However, the process of reverse extraction is often complex because of the higher consumption of organic solvents and extractants. Therefore, reducing the amount of organic solvents and extraction agents is one of the main problems.

For microemulsions, which usually formed spontaneously by two immiscible liquids, a surfactant, and occasionally a short-chained alcohol as a cosurfactant, the nanometer-sized spherical or bicontinuous structure induces its advantage of larger oil-water ratio surface area and rapid mass transfer velocity, as well as the reduces the consumption of organic solvent and extraction agents. Microemulsions have been developed as

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solvent media for extraction and separation of metal ions, such as cobalt and nickel,[9-11] platinum and palladium,[12] gold,[13] lanthanides (III),[14] uranium (VI)[15] and europium.[16] To our knowledge, there is little attention paid to the extraction and separation of cobalt and lithium by microemulsion media besides the recently reported by Lee group[17] that cobalt and lithium was separated with cyanex 272 using hollow fiber supported liquid membrane. In a recent report,[18] sulphuric acid leaching followed by solid-liquid separation and solvent extraction is used to recover cobalt from spent lithium ion batteries.

Here, a salting out agent free microemulsion was prepared and investigated for the extraction and separation of cobalt and lithium. In the microemulsion system, saponified P507 functioned extractant and surfactant. The saponified P507/*n*-hexanol/*n*-heptane extraction system was found to be a promising efficient system for separating Co (II) and Li (I). A DFT based calculations combined experimental studies help to understand the superior complexation behavior of Co (II) over Li (I) within saponified P507/*n*-hexanol/*n*-heptane microemulsion.

EXPERIMENTAL SECTION

Apparatus and reagents

Before and after extraction and separation, the concentration of Co (II) and Li (I) in the aqueous phase was determined by an atomic absorption spectrophotometer (TAS-986, Spectrometer instrument Corp., Ltd, Beijing, China). The operational conditions were as follows: lamp current, 2.0 mA; slit width, 0.4 nm; height of the flask, 5.0 mm; flow yield of burning gas, 1.4 L/min. The linear equation of Co (II) concentration was Abs=0.0536c+0.0594, R=0.9990. The linear equation of Li (I) concentration was Abs=0.29929c+0.00525, R=0.9998. All the linear ranges were 0-2.0 mg/L. Then the concentrations of metals in the organic phase were calculated by mass balances. Shaking table (Jintan Science Instrument Factory, Jiangsu Province), with a vibration frequency of 275 ± 5 min^{-1} and temperature controlling precision of ± 1 K.

P507 was from Fengxing Chemical Reagent Jiangxi Corp. (Jiangxi, China) and used without any further purification. *N*-heptane and *n*-hexanol (both A.R.) are from Fuchen Chemical Reagent Tianjin Corp. (Tianjin, China). Standard solution of cobalt and lithium were from National Center for the analysis and testing of nonferrous metals and electronic materials. Distilled water was used to prepare the aqueous solutions in all experiments. The feed solutions were prepared by dissolving metal chlorides in distilled water. LiCl, $CoCl_2 \cdot 6H_2O$, HCl, and NaOH were from Hengxing Chemical Reagent Tianjin Corp. (Tianjin, China). All other chemicals used in this experimental were of analytical or regent grade.

Saponification and Microemulsion preparation

P507 was saponified by 1.0 mol/L NaOH solution, in which the molar ratio of P507 : NaOH = 0.5, 1, 1.5, 2, 2.5, and 3, respectively. In detail, firstly, amount of P507 was added in 1.0 mol/L NaOH solution. Then the mixture was shook for 30 min at 313 ± 1 K in the shaking table. A required amount of saponified P507 was added into the mixture of *n*-hexanol and *n*-heptane according to the volume ratio of saponified P507:*n*-hexanol:*n*-heptane is 1:6:14. The mixture was ultrasonicated for 20 min at 298.15 K. The transparent saponified P507/*n*-hexanol/*n*-heptane salting out agent free microemulsion was obtained when the above mixture was equilibrated for 24 hours.

Extraction/stripping procedure

The microemulsion and the aqueous solution containing Co (II) or Li (I) metal ions were added to a conical flask with plug (the volume ratio of the aqueous phase to the microemulsion was $R_{w:m} = 8$) and then equilibrated mechanically in an shaking table for 7 min. Afterward, the microemulsion phase and the aqueous phase were separated by standing for 2 h at room temperature, although two-phase separation can be accomplished at room temperature for 10 min. Then, the concentration of the metal ions in the aqueous phase was measured by an atomic absorption spectrophotometer (TAS-986); those in the organic phase were calculated by the mass balance of the metal ions before and after the extraction.

Computational details

Structural optimizations and frequency calculations for all atoms except to Co were carried out using the hybrid B3LYP method[19] with the basis set of 6-311G(d,p). To easy the computational cost, Lanl2dz basis set was employed for Co. All calculations were performed with Gaussian 03 package. The binding energies were corrected for solvent effects and evaluated by taking into consideration of the free energy corrections.

RESULTS AND DISCUSSION

Influence of volume ratio of microemulsion and aqueous phase

Figure 1 showed the effect of $R_{w/m}$ (the volume ratio of the aqueous phase to the microemulsion) on the extraction yield of Co (II) and Li (I) at some condition. On the whole, with the increase of $R_{w/m}$, the extraction

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yield of Co (II) and Li (I) all decreased. The extraction yield of Co (II) decreased slowly (R from 4 to 8) and then remarkably decreased after reaching the maximum value. Taking into account the economic benefits, we believe that R=8 was the right. Here，the extraction yield of Li (I) was 15.4%．
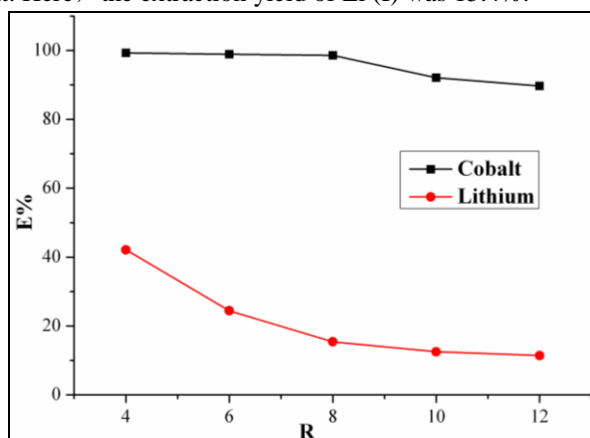

Figure 1: Effect of $R_{w/m}$ (the volume ratio of the aqueous phase to the microemulsion) on the extraction yield (E%) of Co (II) and Li (I). (298.15 K, shaking time: 7 min, molar ratio of P507 and NaOH: 1.5:1, the volume ratio of saponified P507, n-hexanol and n-heptane: 1:6:14, Co (II): 100.0 mg/L, Li (I): 40.0 mg/L)

Effect of phase contact time

The extraction behavior of Co (II) /Li (I) by P507/*n*-hexanol/*n*-heptane extraction system has been measured at different phase contact time from 1 to 9 min, at the temperature 298.15 K, molar ratio of P507 and NaOH: 1.5:1, $R_{w/m}$: 8, the volume ratio of saponified P507, *n*-hexanol and *n*-heptane: 1:6:14, Co (II): 100.0 mg/L, Li (I): 40.0 mg/L. As shown in Figure 2, the percentage extraction of cobalt was increased with increase in contact time up to 7 min. Then the extraction is independent of the contact time. Thus, the equilibrium time for this system was 7 min and the extraction yield (*E%*) of Co (II) was 99.9%．
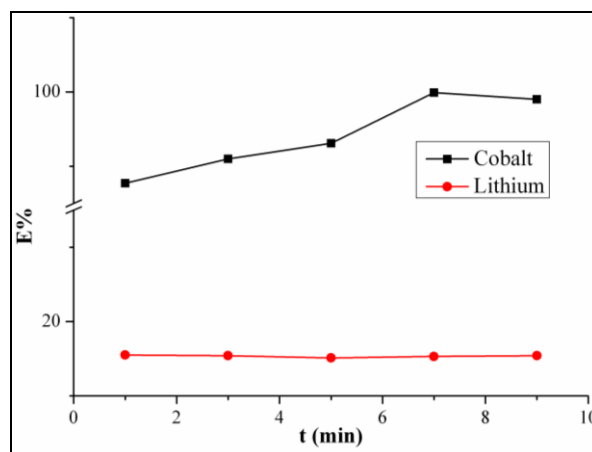

Figure 2: Effect of contact time on the extraction yield (E%) of Co (II) and Li (I). (298.15 K, molar ratio of P507 and NaOH: 1.5:1, $R_{w/m}$: 8, the volume ratio of saponified P507, n-hexanol and n-heptane: 1:6:14, Co (II): 100.0 mg/L, Li (I): 40.0 mg/L)

Influence of temperature on the extraction

Considering the temperature was one important influencing factor in the extraction procedure, we investigated the effect of temperature on the extraction yield (*E%*) of Co (II) and Li (I) (Figure 3). Notably, an increase of the temperature (from 298.15 to 318.15 K) leaded to a decrease of cobalt and lithium extraction efficiency. This phenomenon can be explained that the extraction process is an exothermic nature and lower temperature favor the metal extraction.
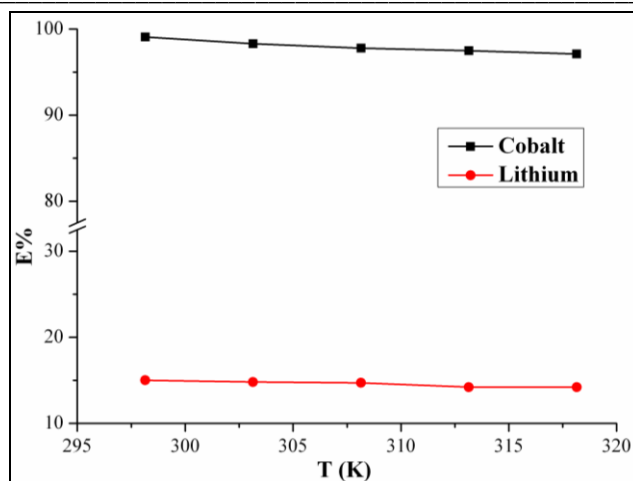
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Figure 3: Effect of temperature on the extraction yield (E%) of Co (II) and Li (I). (shaking time: 7 min, molar ratio of P507 and NaOH: 1.5:1, $R_{w/m}$: 8, the volume ratio of saponified P507, n-hexanol and n-heptane: 1:6:14, Co (II): 100.0 mg/L, Li (I): 40.0 mg/L)

Cobalt and lithium extraction and separation

This method may be used for the separation of cobalt and lithium from secondary resources, such as anode material of spent lithium ion battery.[20] To investigate the ability of saponified P507/*n*-hexanol/*n*-heptane microemulsion to extract Co(II) selectively, a mixed metal ions solutions were prepared by adding chloride metal salts in distilled water. The concentrations of Co (II) and Li (I) are 100 mg/L and 40 mg/L, respectively. Under the optimum conditions, experiments were repeated three times. The results were tabulated in table 1. Notably, under the optimum conditions, the average cobalt and lithium extraction yield (E%) is 99.1% and 14.4%, respectively, and β=654.6. Therefore, saponified P507/*n*-hexanol/*n*-heptane microemulsion was considered to be efficient, effective, and highly selective approach for the separation of Co (II) and Li (I).

Table 1: The extraction yield of Co(II) and Li(I) under the optimum conditions

Number	1	2	3
Extraction yield of Co(II)	99.7	98.6	99
Extraction yield of Li(I)	13.6	14.8	14.8

Stripping studies

It was necessary to back extract the metal from the loaded phase to the commercial extraction process. Cobalt stripping from a single stage loaded organic phase from *section 3.4* was investigated using hydrochloric acid of different concentration. The obtained results demonstrated that the equal volume of 1.0 mol/L HCl solution was better for the cobalt stripping.

Recycling capacity of saponified P507 microemulsion system

Investigation on the recycling capacity of saponified P507 microemulsion system for the extraction of cobalt (II) was carried out by first loading the microemulsion system (in which, the volume ratio of saponified P507, *n*-hexanol and *n*-heptane is 1:6:14) with an aqueous phase containing 100 mg/L cobalt (II) according to $R_{m/w}$=8. The loaded organic was stripped with 1.0 mol/L HCl solution for the back extraction of cobalt. The recovery of each step was calculated from the amount of cobalt that was extracted in the organic phase in the particular cycle. A slight change in the extraction yield and recovery was observed up to six cycles.

Theoretical results: driving force of the extraction process

The extraction of metal ions using W/O microemulsion coexisting with a water phase is often very effective to accelerate extraction and improve on extractability. Many researchers note that the electrostatic attraction between the headgroup of surfactant and metal ions is the driving force of the extraction process in the W/O microemulsion and process mechanism may be ion exchange.[21] So are for this system? To obtain direct evidence of the interaction between saponified P507 and Co (II) or Li (I), DFT calculations were employed. In this paper, we investigated the interaction between saponified P507 and Co (II), Li (I) and Na (I) by analyzing the main chemical bonds and binding energies (BEs) of complexes on saponified P507 with Co (II), Na (I), and Li (I), in water and *n*-heptane, respectively.
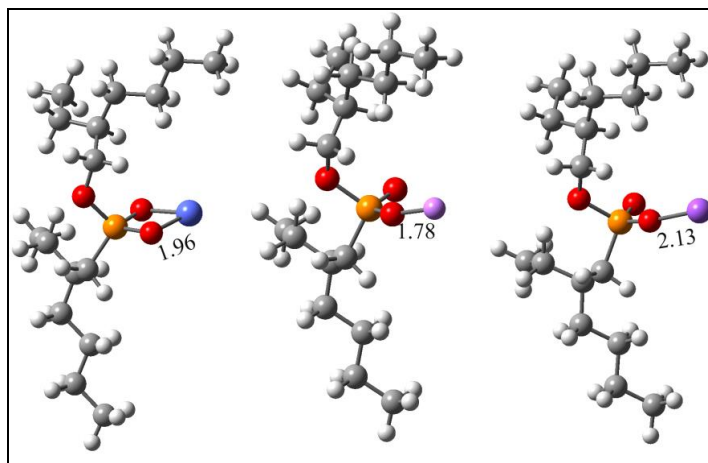
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Figure 4: Optimized structures of saponified P507 with Co (II), Li (I), and Na (I) in water.

As shown in Figure 4, Co (II) interacted with two O atoms of saponified P507 simultaneously, for Li (I) and Na (I) just interacted with one O atom. So we predicted that the interaction between Co (II) and saponified P507 was stronger. Table 2 tabulated the binding energies (BEs, in kcal/mol) of different complexes of Co (II), Li (I), and Na (I) with saponified P507 and Wiberg bond indices (WIBs) of M-O (M= Co, Li, and Na) in water and *n*-heptane, respectively. Notably, the calculated values WIBs of O-Co=0.34, O-Li=0.15, and O-Na=0.09 in water indicated that the interactions between the saponified P507 and Co (II), Li (I), and Na (I) are decreased. In *n*-heptane, the WIBs were 0.37, 0.26, and 0.11, respectively. Thus, the interaction between saponified P507 and Co (II) was strongest whether they were in water or in *n*-heptane. Therefore, saponified P507 system had higher selectivity and extraction yield to Co (II) in mixture aqueous of Co (II), Li (I) and Na (I). Furthermore, the highest BEs of saponified P507 and Co (II) (-226.12 kcal/mol in *n*-heptane) helped us to understand the superior complexation behavior of Co (II) over Li (I) within saponified P507/*n*-hexanol/*n*-heptane microemulsion. Among them, the interaction between Na (I) and saponified P507 were the weakest. Maybe due to this, NaCl was usually used as salt out agent in extraction systems.

Table 2: Binding energies (BEs, in kcal/mol) of different complexes of Co (II), Na (I), and Li (I) with saponified P507 in water and *n*-heptane, respectively. Bond distances (in Å) and Wiberg bond indices (WIB) of M-O (M= Co, Li, and Na) are labeled

series	BEs(kcal/mol)		bond length (Å)		WIB	
	water	*n*-heptane	water	*n*-heptane	water	*n*-heptane
S-P507Co[+]	-25.85	-226.12	1.78	1.69	0.34	0.37
S-P507Li	-17.13	-87.79	1.96	1.91	0.15	0.26
S-P507Na	-12.91	-78.73	2.13	2.29	0.09	0.11

Based upon analyses, the driving force of the extraction process in the W/O microemulsion is not limited to the electrostatic interaction between the anionic surfactant and the metal ions. Additionally, the results of the study indicated the possibility that controlling the binding energies of extractant with metal ions in different solvent leads to the effective separation.

CONCLUSIONS

A saponified P507/*n*-hexanol/*n*-heptane microemulsion system with P507 used as surfactant and extractant was investigated for selectively extraction cobalt from a mixture aqueous of Co (II) and Li (I). The results showed that the extraction equilibrium can be rapidly achieved and the separation of Co (II) and Li (I) is easily. The combined experimental and theoretical studies help us to understand the better complexation and hence extraction behavior of Co (II) over Li (I) using saponified P507/*n*-hexanol/*n*-heptane microemulsion as extraction system. Saponified P507 microemulsion system has a broad application prospect in the extraction and separation of Co (II) and Li (I) with strong selectivity and high efficiency. The present microemulsion system may be applicable to the separation of other transition metals and primary metals. Furthermore, results from theoretical calculations may provide some reliable references for the extraction and separation of metal ions by microemusion system.

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