The Synergistic Effect of Organophosphorus and Dithiocarbamate Ligands on Metal Extraction in Supercritical CO_2

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Received April 6, 2004

The bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex-272) and sodium diethyl- dithiocarbamate (NaDDC) ligands were used to extract of metal ions (Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) in supercritical CO_2. Experiments showed a strong synergistic effect and better extraction efficiency if the two ligands were used together. In-situ UV-visible observation indicates that NaDDC in the water/supercritical CO_2 started to decompose slowly. The synergistic effect seems to come from the deprotonation of the organophosphorus ligand by amines from the decomposed NaDDC. The enhancing role of amines was confirmed using the mixture of Cyanex-272 and diethylamine(DEA) in the metal extraction.

Key Words : Supercritical, Carbon dioxide, Metal extraction, Synergistic effect, Amine

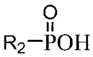
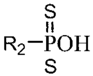
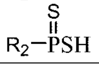
Introduction

Solvent extraction of metallic ions is a technically important and also well-established process that is used in the chemical and hydrometallurgical industries.[1] Solvent extraction techniques use the chelation of metallic ions dissolved in liquid solution with organic ligands. Conventional solvent-extraction technique needs large amount of organic solvents and often creates environmental problems.[2] More environment-friendly technology is needed nowadays, and there have been increasing attentions to extract metal ions by supercritical fluid extraction. CO_2 becomes one of the most notable alternative organic solvents due to its nonflammable, nontoxic, nonpolluting, and relatively inexpensive properties with its moderate critical point (73.8 bar, 31.06 °C). Many works have been reported in metal extraction under the supercritical CO_2 ($scCO_2$) solvent.[3-12]

Synergistic effects of mixed ligands on metal extraction are very interesting and also important from the scientific as well as engineering viewpoints. Few experiments show the synergistic effects of mixed ligands on the extraction of metal ions such as lanthanides (Ln) under $scCO_2$ solvent[5,7] as well as conventional solvents.[13] The mixture of tributylphosphine (TBP) and 2-thenoyltrifluoroacetone (TTA) extractant is superior to TBP or TTA alone in the extraction of lanthanide ions under $scCO_2$ solvent.[5,7] The main reason for this synergistic effect is not clearly known. However, TBP as an additive extractant seems to do an important role in the formation of metal complexes, presumably replacing the coordinated water molecules by forming adducts with the $Ln(TTA)_3$ complexes which become more stable in $scCO_2$[7]. A more general explanation can be the effect of the additive as a base that can enhance the formation of metal complexes in the organic phase,[4] which results in a synergistic effect.

To see the synergistic effect of ligands, we selected two ligands – Cyanex-272 and NaDDC (sodium diethyldithiocarbamate) for the metal extraction in $scCO_2$. Cyanex-272 is a commercially available extractant along with its series, Cyanex-301 and Cyanex-302. The structural formulas and physical properties or the Cyanex series are given in Table 1. That is, the organophosphorus compounds containing the phosphoryl group (P=O) have been widely used as analytical extractants since the 1940s. Especially, Smart and coauthors measured the metal extracting abilities of these three extractants, and found that Cyanex-301 and Cyanex-302 extracted metal ions much better than Cyanex-272 in the $scCO_2$ solvent.[10] The pH of water contacted with high-pressure CO_2 (70-200 bar, 25-70 °C) is about 2.8-2.95 based on the calculation[14] and the measurement.[15] Cyanex-272 is

Table 1. The physical properties of Cyanex series

Extractant	Structural Formula[a]	pKa in H_2O	Density (kg m^{-1})	Viscosity (kg m^{-1} s^{-1})	Molar Mass (g mol^{-1})	Aqueous Solubility (mg L^{-1})
Cyanex 272	 $R_2{-}\overset{O}{\overset{\parallel}{P}}OH$	6.37	910	14.2	290	38
Cyanex 302	 $R_2{-}\overset{S}{\overset{\parallel}{P}}OH$	5.63	930	19.5	306	3
Cyanex 301	 $R_2{-}\overset{S}{\overset{\parallel}{P}}SH$	2.61	950	7.8	322	7

[a]R represents the 2,4,4-trimethylpentyl group.

known to be less effective as a metal extractant in this low pH environment compared with other Cyanex series.

NaDDC is a well-known ligand to extract over 40 metal species from aqueous solutions into organic solvents.[7] However, the main problem is that NaDDC as an extractant has its poor solubility (10^{-4}~10^{-3} M) to $scCO_2$, and its instability especially in acidic solution below pH=4, decomposing to CS_2 and ammines.[15] Although each Cyanex-272 and NaDDC do not seem to be effective metal-extractants in $scCO_2$, there is a strong possibility of NaDDC working as a base, which results in a synergistic effect on metal extraction in $scCO_2$ if used with Cyanex-272. In this paper, we examined the possible synergistic effect of NaDDC and Cyanex-272, and discussed the plausible mechanism.

Experimental Section

The ligands - Cyanex-272 (bis(2,4,4-trimethylpentyl)phosphinic acid) (Cytec Industries Inc. U.S.A.), NaDDC (sodium diethyldithiocarbamate)(Alfa Aessar, USA) and diethylamine (DEA) (Aldrich, U.S.A.) - were purchased and used as received. The standard solution of atomic absorption spectroscopy (1,000 ppm) for each ion was used for specimen preparation. The extraction specimen was prepared using Whatman #2 filter paper. On the 0.6 × 4 cm^2 filter paper, 50 mL solution containing equal amount (200 ppm) of metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}) was loaded and dried. Water (30 mL) was added to the specimen just before the experiment.

The experimental setup for the measurement of metal extraction is shown in Figure 1. Liquid CO_2 from the cylinder (Air Tech., Korea, 99.95% purity) goes through the connecting tubing to the syringe pump (ISCO, model 260D, U.S.A.). The pump presses liquid CO_2 into an assigned pressure and also reads out the flow rate. The mixing cell (19 mL, NEXT Instruments, Korea) with a rotating magnetic bar dissolves a certain amount of a ligand (or a mixture of ligands) into $scCO_2$. Supercritical CO_2 fluid containing ligand reaches to the 3.5 mL extraction tube cell (Dionex, Sunnyvale, CA, U.S.A.) and extracts metal ions from the specimen inside. Both the mixing cell and the extraction cell are placed in a temperature-controlled oven.

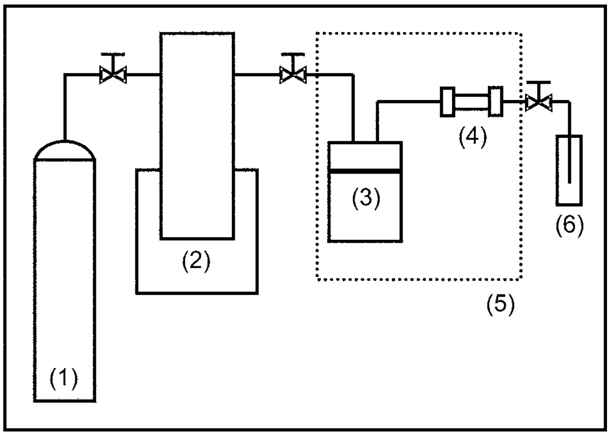


Figure 1. Schematic diagram of experiment setup. (1) liquid CO_2, (2) syringe pump, (3) mixing cell, (4) extraction tube cell, (5) constant temperature oven, (6) collecting vial.

All experiments were performed at 200 bar, 60 °C. CO_2 was filled into both the mixing and the extracting tube cells at the desired pressure and temperature by opening the inlet valve. After 20 minutes mixing, dynamic extraction was occurred by opening the exit valve. A 50 mm i.d. and 20 cm long fused-silica tubing (Dionex) was used as a pressure restrictor for exit gas. The depressurized CO_2 was bubbled through a collection vial containing chloroform. The CO_2 flow rate during dynamic extraction was about 3 mL (liquid CO_2)/min. Dynamic extraction was done for 20 minutes. After the experiment, the specimen was removed from extraction cell and treated with 10 mL of 1 M nitric acid, and was subsequently analyzed by inductively coupled plasma (ICP) method. The extraction tube cell and the outlet valve were also cleaned by nitric acid, and the amounts of metal ions in the nitric acid waste were examined as well as those in the collection vial to check the material balance of each metal ion.

To observe the reaction in $scCO_2$, a reactor having in-situ UV-visible cell port (10 mL, Hanwoul Eng, Korea) was made. Two optical fibers – one from the light source and the other to the spectrometer (Avantest DH-2000) - were connected in the middle of the reactor. The distance between the optical fibers was adjusted to optimize the Beer's law. The design and its performance was reported previously.[17-19] The reactor with UV-visible cell port was connected instead of the mixing and the extraction cells when spectroscopic measurements were needed.

Results and Discussion

Figure 2 shows the result of extracting five metal ions - Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Co^{2+}. The extraction ratio of each metal ion is defined as the ratio of the extracted amount to the amount originally in the specimen. The accuracy of the extraction rate was found to be less than 10%, based on the material balance before and after the experiments. Four different extraction cases are shown in the Figure 2.

Metal ions could not be extracted at all with the $scCO_2$ solvent only. In prior to metal extraction, we checked the solubility of Cyanex 272 using a home-built variable volume cell. The solubility of Cyanex272 in supercritical CO_2 at 60 °C under different pressures was determined to be 11 g/L, 42 g/L, and 78 g/L at 150 bar, 200 bar and 250 bar, respectively. When 300 mg of Cyanex-272 was used as an extractant, less than 20% of metal ions were extracted. Since pH of $scCO_2$ fluid containing water is about 2.9 and Cyanex 272 has been known to be an effective extractant of metal ions at pH > 6,[10] it seems natural that Cyanex 272 hardly extracts the metal ions in $scCO_2$. According to Figure 2, NaDDC looks more effective as an extractant than Cyanex-272, by extracting Cu^{2+} up to 70%, and other metal ions by 20-50%. On the other hand, when both Cyanex-272 and NaDDC were used together, the mixture could extract 5 metal ions by 90% or

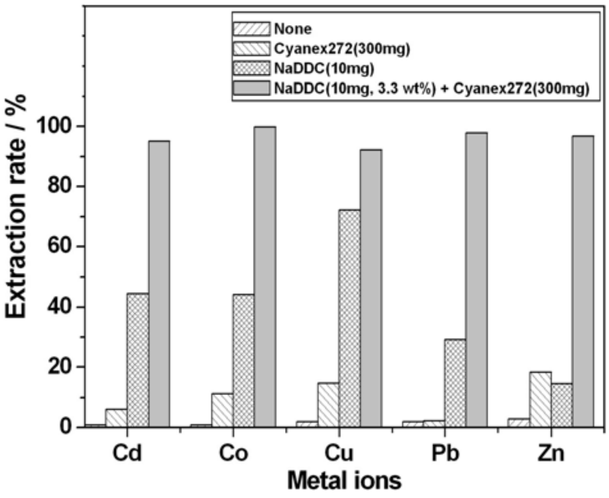


Figure 2. The extraction rate of metal ions, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}. Four different extraction cases were shown-pure CO_2, Cyanex-272, NaDDC, and the mixture of Cyanex-272 and NaDDC.

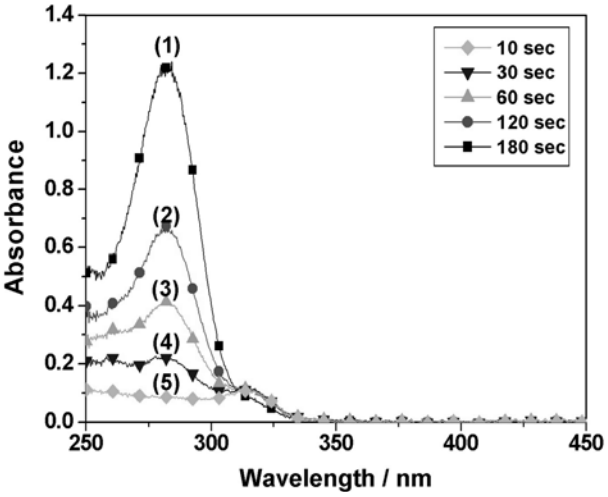


Figure 4. UV-visible spectrum of cyanex272 and NaDDC with reaction time. (1) 10 sec, (2) 30 sec, (3) 60 sec, (4) 120 sec, (5) 180 sec.

more as shown in the Figure 2. The synergistic effect of Cyanex-272 and NaDDC on the metal ion extraction is clearly shown in the Figure 2.

Since NaDDC has a limited solubility in $scCO_2$ and can be easily decomposed at $pH < 4$, the amount of NaDDC should affect the synergistic effect on the metal extraction. The amount of NaDDC was varied in the mixture with a given 300 mg of Cyanex-272. Figure 3 shows the extraction rate change as a function of the amount of NaDDC used. 1mg of NaDDC enhances the extraction of metal ions by 30-40% in the rate. The extraction was increased as the amount of NaDDC increased, and became saturated when more than 5 mg of NaDDC was used.

NaDDC is decomposed in the acidic solution (HA) into diethylamine and carbondisulfide, notified by the following reaction.[7,15]

$$(C_2H_5)_2NCS_2^- \, Na^+ + HA \longrightarrow (C_2H_5)_2NH + CS_2 + Na^+ + A^- \qquad (1)$$

We measured the UV-visible spectrum of NaDDC to conform this decomposition. NaDDC (5 mg) and small amount of water (10 μL) were put in the measurement cell (10 mL) and monitored the change of UV-visible spectrum with time. Figure 4 shows the spectrum change with reaction time. In the beginning of the reaction, a peak at about 280 nm clearly appeared due to the UV absorption of NaDDC and gradually disappeared as the decomposition proceeded.

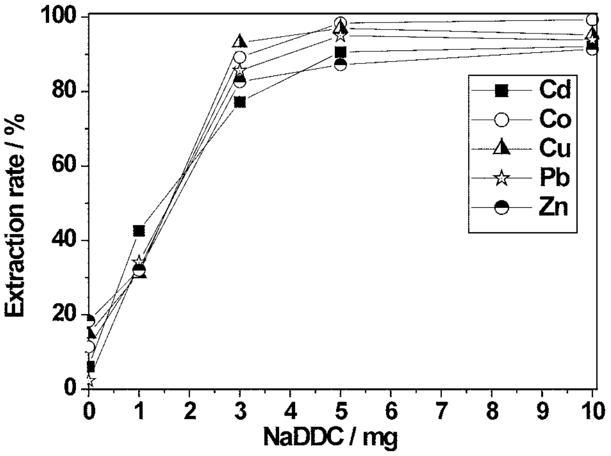


Figure 3. The dependency of metal extraction rate on the amount of NaDDC with 300 mg of Cyanex-272.

Diethylamine (DEA), a product after the dissociation of NaDDC, may be a reason for the synergistic effect of NaDDC and Cyanex-272 on metal extraction. Therefore, instead of NaDDC, we used DEA to execute the extraction in the same manner with NaDDC. As shown in Figure 5, DEA itself hardly extracted the metal ions by 5% or less, whereas the specific ions (Cu, Co, Zn) were extracted by 40-60% using NaDDC. In the presence of water, it is well known that dithiocarbamate reagent tends to decompose into diethylamine in supercritical CO_2 and its extraction effi-

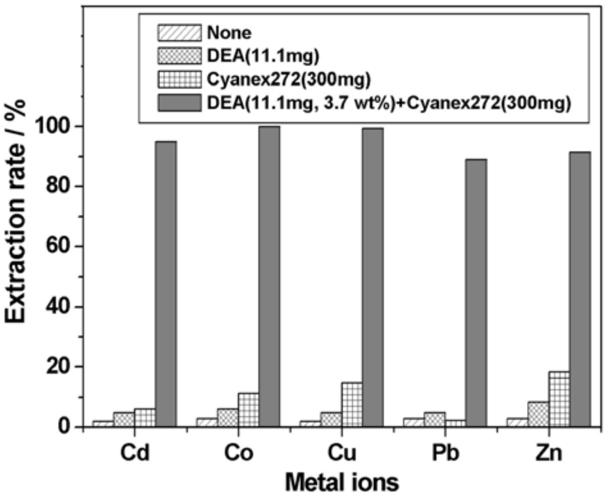


Figure 5. The extraction rate of each metal ion with DEA and Cyanex-272 as extractants. For comparison, the extraction rates by pure CO_2, DEA and Cyanex-272 were shown together.

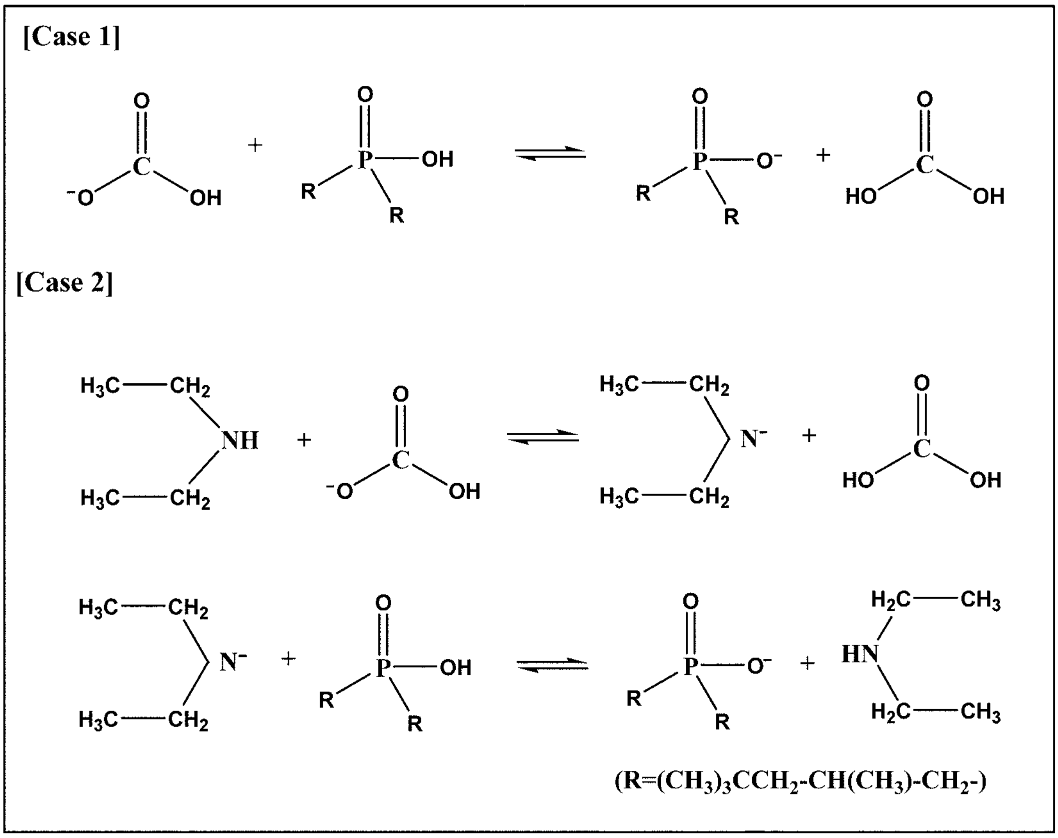


Figure 6. Possible reaction scheme during complexation by Cyanex-272. ‘Case 1’ is Cyanex-272 in $scCO_2$, and ‘Case 2’ is Cyanex-272 with DEA.

ciency is reduced.[7] However, when we used DEA together with Cyanex-272, the extraction rate rose by 90% or more for all metal ions. DEA turned out to be a key compound to make a synergy effect with Cyanex-272.

Cyanex-272 is known to extract more metal ions from the aqueous solution, when pH of the aqueous solution is higher than 6.[20,21] This fact suggests that Cyanex-272 works as a cationic exchanger,[4] its extracting efficiency strongly depends on pH. The reaction of cationic exchanger such as Cyanex-272 to form a complex with metal ions should accompany the deprotonation of Cyanex-272. It has been reported that when water is in equilibrium with CO_2 under $scCO_2$ conditions, the pH of the water is around 2.9 due to the formation and dissociation of carbonic acid.[22] Hence, the poor extracting ability of Cyanex-272 in $scCO_2$ can be explained by the fact that carbonic ion formed under $scCO_2$, is less basic than the conjugate base of Cyanex-272 resulting in negligible concentration of deprotonated Cyanex-272 in the complex formation reaction (see Figure 6, Case 1). However, when DEA is added to metal extraction reaction with Cyanex-272, DEA works as a strong base to Cyanex-272 converting Cyanex-272 to a deprotonated form (see Figure 6, Case 2), which results in an easy formation of metal complex and the enhanced extraction rate of metal ion.

The synergistic effect of NaDDC (or DEA) and Cyanex-272 is in fact originated from the role of a base. DEA(or decomposed NaDDC) makes Cyanex-272 a deprotonated form. Shadrin suggested a recipe of mixing extractants in the actinide ion extraction in $scCO_2$.[16] He found the use of HFA (hexafluoroacetylacetone) with pyridine increased the metal extraction efficiency. This phenomenon can be explained similarly, since pyridine acts as a base and increases the number of deprotonated enol form of HFA resulting in improved metal extraction efficiency.

Conclusion

Supercritical carbon dioxide extraction was applied to extract the metal ions and to reduce the secondary wastes. With Cyanex-272 and NaDDC, the strong synergistic effect has been observed in metal extraction. The used NaDDC was confirmed by the UV-visible spectrum to decompose into DEA in $scCO_2$ containing small amount of water. DEA itself, the side-product from the decomposition of NaDDC, plays a role as a base and enhances the deprotonation of Cyanex-272 in the metal complex formation reaction, which results in a strong synergistic effect. It is highly probable to have a synergistic effect when a base such as amines is added to a cationic exchanger type extractant such as Cyanex-272.

Acknowledgment. This work was financially supported by MOCIE through EIRC program and by National Research Laboratory Fund, Ministry of Science and Technology of Korea.

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