Liquid-Liquid Extraction of Transition Metal Ions with *N*-Phenyl-*N'*-(2-butylthiophenyl)thiourea

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N-Phenyl-*N'*-(2-butylthiophenyl)thiourea (PBT, HL) was synthesized by the reaction of 2-butylthioaniline with phenylisothiocyanate and was studied for extracting Cu(II), Zn(II), Co(II), Cd(II), Ni(II), Hg(II) and Pd(II) from aqueous solution. Pd(II), Hg(II) and Cu(II) were readily extracted into chlorobenzene at low pH. Though the extraction of Co(II) and Zn(II) from an acidic solution was not complete, extraction from an alkaline aqueous solution containing potassium oxalate was quantitative. The composition of the complexes, Cu(II)-PBT and Cd(II)-PBT, formed in the organic phase, was found to be ML_2 by studying the pH dependence and the metal-PBT mole ratio dependence of metal extraction. The synergistic effect of 4-benzylpyridine and trioctylphosphine oxide in the metal extraction was small. PBT is suited for separating Cu(II) from a mixture of conventional metal ions other than Pd(II) and Hg(II).

Keywords Liquid-liquid extraction, *N*-phenyl-*N'*-(2-butylthiophenyl)thiourea, metal(II) ions

It has been known that thiourea forms coordination compounds with numerous heavy metals in an acidic solution. Thiourea reacts with bismuth(III) and lead(II) to give yellow coloration, which is used for the colorimetric determination of these metals. Furthermore, the reagent has been widely used in the separation of platinum-group metals.^{1,2} Phenyl derivatives, which have found increasing use in recent years³⁻⁶, form extractable complexes which extend the possibilities of using these reagents for the separation, determination and pre-concentration of the platinum-group metals.

In the present study, we lipophilized thiourea by introducing both phenyl- and 2-butylthiophenyl-group in *N*- and *N'*-position of thiourea to give a thiourea-type reagent *N*-phenyl-*N'*-(2-butylthiophenyl)thiourea for solvent extraction of heavy metal ions. For extracting "soft" metal ions the thioether group in 2-butylthiophenyl moiety is also expected to serve as an auxiliary donor group for metal complexation. The extraction of Cu(II), Zn(II), Co(II), Cd(II), Ni(II), Hg(II) and Pd(II) into chlorobenzene was studied by using PBT alone or by using PBT in conjunction with 4-benzylpyridine or trioctylphosphine oxide. The separation of Co(II) from Ni(II) was investigated.

N-Phenyl-*N'*-(2-butylthiophenyl)thiourea (PBT)

Experimental

Reagent

PBT was synthesized according to the following procedure. Two point seven grams (2.0×10^{-2} mol) of phenylisothiocyanate was placed in a three-necked flask, and 2.7 g (1.4×10^{-2} mol) of 2-butylthioaniline in 25 ml benzene was added under a nitrogen atmosphere. This mixture was stirred at 40°C for 4 h and then allowed to stand at room temperature for twelve hours. The white crystals formed were collected by filtration, digested in a small volume of warm benzene, cooled, and filtered. The product was finally washed with cold benzene. Yield 1.6 g (35%). mp 120–121°C. Found: C, 64.17; H, 6.38; N, 8.91%. Calcd for $C_{17}H_{20}N_2S_2$: C, 64.52; H, 6.38; N, 8.91%. ¹H-NMR (CDCl₃) δ 0.86 (3H, t, -CH₃, *J*=7.5 Hz), 1.33 (2H, m, -CH₂-CH₂-CH₃), 1.42 (2H, m, -CH₂-CH₂-CH₂-), 2.66 (2H, t, -S-CH₂-, *J*=7.5 Hz), 7.10–7.50 (9H, m, Ar-H), 7.90–8.40 (2H, m, -HN-CS-NH-). ¹³C-NMR δ 13.59 (-CH₃), 21.81 (-CH₂-CH₂-CH₃), 31.21 (-CH₂-CH₂-CH₂-), 34.61 (-S-CH₂-), 124.80–138.18 (Ar-C), 179.36 (-HN-(C=S)-NH-). PBT can be stored in a desiccator for more than 3–4 years without any appreciable decomposition. PBT is also quite stable in organic solutions. It can be recovered unchanged from an organic solution after metal extraction by stripping with 3 M hydrochloric acid.

Aqueous solutions containing metal ions were prepared by an appropriate dilution of standard metal

solutions for atomic absorption spectrophotometry. Demineralized (ion-exchanged) water was further distilled and used throughout the present extraction study. Other chemicals were of analytical reagent grade and used without further purification.

Apparatus

A Shimadzu AA-620 atomic adsorption spectrophotometer equipped with hollow cathode lamps (Hamamatsu Photonics Co.) was used for the determination of metal ion concentration in aqueous solution. TOA HM-208 pH meter and Yamato SA-31 shaker were used.

Extraction procedure

Ten milliliters of aqueous solution containing 8.0×10^{-5} M ($1 \text{ M} = 1 \text{ mol/dm}^3$) metal salt, 0.1 M potassium nitrate and pH buffering agents (Good buffers or ammonium buffer, 0.01 M) were shaken vigorously with 10 ml of chlorobenzene solution containing 1.6×10^{-2} M (in the case of extraction of Cd(II), 0.8×10^{-2} M) PBT in a 50 ml glass-stoppered centrifuge tube on a mechanical shaker. As the need arose, 4×10^{-4} M potassium oxalate was added to the aqueous solutions as a water-soluble complexing agent in order to prevent any hydrolysis of metal ions. The shaking time for each metal ion was as follows: Pd, Cu, 30 min; Zn, Cd, 60 min; Co, 90 min; Ni, 270 min. The shaking time for each metal ion was sufficient to attain equilibrium in the present extraction study. The extraction of Hg(II) was performed as follows. Equal volumes (20 ml) of 2.0×10^{-5} M PBT in chlorobenzene and of aqueous solution containing 1.0×10^{-7} M Hg(II) were shaken for 30 min. After phase separation, the metal ion concentrations in aqueous solutions were determined by atomic absorption spectrophotometry and the pH values of the aqueous solution were measured. The amount of metal ions extracted into the organic phase was taken as the difference between the amount initially added and that determined after equilibrium in the aqueous phase. The amount of metal ions extracted in the organic phase was further confirmed by back-extracted experiments using 3 M hydrochloric acid as a stripping solution.

Results and Discussion

The extraction of divalent metal ions by PBT in chlorobenzene is shown in Fig. 1. In the acidic pH range under which metal ions are not hydrolyzed, Hg(II), Cu(II), Cd(II) and Pd(II) were quantitatively extracted into chlorobenzene; the other metal ions were not. That Hg(II) and Pd(II) were quantitatively extracted into chlorobenzene at a fairly low pH suggests that PBT has a strong affinity to "soft metals".

The extraction of metal ion (M^{n+}) with PBT (HL) may be represented by the following equation:

Fig. 1 Extraction of metal(II) ions with PBT. Aqueous solution before equilibration: 8.0×10^{-5} M M(II), 1.0×10^{-7} M Hg(II), 0.1 M KNO₃ (pH buffer: 0.01 M). Organic solution before equilibration: 1.6×10^{-2} M PBT, chlorobenzene (2.0×10^{-5} M PBT was used for extraction of Hg(II)). $\square$, Pd; $\circ$, Hg; $\bullet$, Cu; $\blacktriangle$, Cd; $\circ$, Zn; $\triangle$, Ni; $\square$, Co.

The extraction constant, K_{ex} , is defined as

$$K_{\text{ex}} = [\text{ML}_n]_{\text{o}} [\text{H}^+]_{\text{w}}^n / [\text{HL}]_{\text{o}}^n [\text{M}^{n+}]_{\text{w}}, \quad (2)$$

where subscripts o and w indicate the organic and aqueous phases, respectively. When only the ML_n complex is formed and extracted, the distribution ratio, D , which can be experimentally determined, is expressed in terms of K_{ex} , $[\text{H}^+]$ and $[\text{HL}]_{\text{o}}$:

$$\begin{aligned} \log D &= \log ([\text{ML}_n]_{\text{o}} / [\text{M}^{n+}]_{\text{w}}) \\ &= \log K_{\text{ex}} + n \log [\text{HL}]_{\text{o}} + n \text{pH}. \end{aligned} \quad (3)$$

Metal ions were extracted with an excess molar amount of PBT, and the metal distribution ratio was determined as a function of pH. A plot of $\log D$ against pH gave a straight line, the slope of which was calculated by a least-square method. The slopes (n) and extraction constants ($\log K_{\text{ex}}$) were as follows: 2.1, -1.6 (Cu); 1.9, -12.8 (Zn); 1.9, -18.8 (Cd). These results indicate that the combining ratio of metal and PBT is 1:2.

The composition of the complexes, Cu(II)-PBT and Cd(II)-PBT formed in organic phase, was further studied by the standard mole ratio and continuous variation methods as applied to a two-phase extraction system. Two phases of equal volumes were brought into equilibrium according to the extraction procedures described above. The metal-ion concentration in the aqueous phase was determined by atomic absorption spectrophotometry in the usual manner. The absorbance due to atomic copper was plotted as a function of

Fig. 2 Molar ratio study of Cu(II)-PBT complex. 1.6×10^{-4} M PBT (pH 5.5 (Good buffer)); wavelength, 325 nm. The equal volumes of organic and aqueous solutions were used.

Fig. 3 Continuous variation methods for Cd(II)-PBT complex. $\text{Cd(II)} + \text{PBT} = 1.3 \times 10^{-4}$ M; pH 9.3 (Good buffer); wavelength, 229 nm. The equal volumes of organic and aqueous solution were used.

Cu(II) to PBT mole ratio (mole ratio method) or as a function of the fraction of Cu(II) to the combined concentration of Cu(II) and PBT (continuous variation method).

The results of a mole ratio study are shown for the Cu(II)-PBT extraction system in Fig. 2; they indicate that 1 mol of PBT combines with 0.55 mol of Cu(II) ion. A similar study with Cd(II)-PBT gave a ratio of 0.45. The results involving continuous variation are shown in Fig. 3 for a Cd(II)-PBT system; the combining ratio of Cd(II)/PBT in the extracted complex was 0.35/0.65. A similar result was obtained with the Cu(II) complex, giving a Cu(II)/PBT ratio of 0.31/0.69. These results, as well as those obtained in Fig. 1, prove that both metal Cu(II) and Cd(II) extraction take place according to reaction (1).

The extraction of Zn(II), Co(II) and Ni(II) was studied at a higher pH region. Figure 4 shows the extraction profiles of metal ions from an alkaline solution containing potassium oxalate. Zn(II) and

Fig. 4 Extraction of Zn(II), Co(II) and Ni(II) with PBT from alkaline aqueous solution containing potassium oxalate. Aqueous solution before equilibration: 8.0×10^{-5} M M(II), 4.0×10^{-4} M $(\text{COOK})_2$ ($\circ$, Zn; $\square$, Co; $\triangle$, Ni), 2.0×10^{-2} M $(\text{COOK})_2$ ($\bullet$, Zn; $\blacksquare$, Co), 0.1 M KNO_3 (pH buffer, 0.01 M Good buffer). Organic solution before equilibration: 1.6×10^{-2} M, chlorobenzene.

Co(II) were extracted nearly quantitatively into chlorobenzene. The extraction of Ni(II) was not complete, but increased remarkably compared with extraction from an acidic solution. The half-extraction pH of Zn(II) and Co(II) in the presence of 2.0×10^{-2} M potassium oxalate was higher than that in the absence of oxalate by about 1 pH unit. This was due to a shift in the equilibrium toward metal-oxalate complex formation in an aqueous potassium oxalate solution.

Ammonium buffer ($\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$) was used to adjust the pH of an aqueous solution in place of using Good buffer agents, and the extraction of Co(II) and Ni(II) was studied. The extraction profiles are shown in Fig. 5. Dips in the extraction curves around pH 10.6 for Co(II) and pH 11 for Ni(II) are rather anomalous. It was reproducible in repeated experiments which included a prolonged equilibration time (1–5 h shaking). Such phenomena have often been described in the literature.^{8–13}

From Fig. 1, it seems to be quite easy to separate Pd(II), Hg(II) and Cu(II), from other metal ions by selecting suitable pH conditions. On the other hand, the separation between Co(II) and Ni(II) is difficult by using the conditions given in Figs. 1 and 4. However, Fig. 5 lists the conditions for their partial separation. In fact, mixtures of Co(II) and Ni(II) each in 8.0×10^{-5} M concentration were treated with 1.6×10^{-2} M PBT in chlorobenzene at pH 11.3 in the presence of oxalate; 90% of the Co(II) and 37% of the Ni(II) were found to be extracted into chlorobenzene.

The extraction of Co(II) and Ni(II) from acidic solution is rather low. Though it is possible that PBT forms stable neutral complexes with Co(II) or Ni(II),

Fig. 5 Extraction of Co(II) and Ni(II) with PBT in case of using $\text{NH}_4\text{OH-NH}_4\text{Cl}$ as buffer agent. Aqueous solution before equilibration: 8.0×10^{-5} M M(II), 0.1 M KNO_3 (buffer, 0.01 M $\text{NH}_4\text{OH-NH}_4\text{Cl}$). Organic solution before equilibration: 1.6×10^{-2} M PBT, chlorobenzene. ●, Co; □, Ni.

the six-coordination in these metal complexes leaves some of the coordination sites occupied with water molecules which make the complexes unsuitable for extraction into organic solution. In order to study this possibility as well as to increase the extractability of Co(II) and Ni(II), the effects of 4-benzylpyridine (4-BP) and trioctylphosphine (TOPO) were studied. These neutral ligands were used in a pH range where they remain essentially unprotonated and are present in organic solution. The concentrations were 6.4×10^{-2} – 1.6×10^{-3} M for 4-BP and TOPO, while the concentration of PBT was kept constant at 1.2×10^{-2} M.

The extraction profiles of metal ions with PBT in the presence of 4-BP are shown in Fig. 6. It is observed that the extraction curves shifted by only 0.2–0.5 pH unit to the lower pH side. In addition, there is not much difference among Cd(II), Co(II) and Ni(II) regarding the magnitude of the shift of extraction curves. A similar small enhancement of metal extraction was observed with TOPO, though the study was not extensive, since in some cases precipitation took place in both organic and aqueous phases when the TOPO concentration was high (6.4×10^{-2} – 1.6×10^{-2} M TOPO; Cd-PBT system). These results indicate that a synergistic reaction by 4-BP and TOPO is not important in metal extraction by PBT. The inefficient extraction of Co(II) and Ni(II) by PBT is most probably due to the softness of donor atoms in PBT when it complexes with metal ions.

PBT behaves as a monoprotic and probably bidentate ligand in metal extraction. However, it is not quite certain which atoms in PBT are involved in complexation. A deprotonation from N–H in the 2-butylthioaniline structure leads to an N^- , S^- coordinated five-membered chelate. On the other hand, an isomerization from $\text{ArNH}(\text{C}=\text{S})\text{NHR}'$ to $\text{ArN}=\text{C}(\text{SH})-$

Fig. 6 Extraction of Cd(II), Co(II) and Ni(II) with PBT. Aqueous solution before equilibration: 8.0×10^{-2} M M(II), 0.1 M KNO_3 ; organic solution before equilibration: 1.6×10^{-2} M PBT. ○, 4-benzylpyridine (6.2×10^{-2} M) present; ●, 4-benzylpyridine absent.

NHR' structures followed by deprotonation from SH would give an S^- , S-coordinated seven-membered chelate ring. In the latter case, the possibility can not be discarded that PBT serves as a monodentate, S^- -donating extractant. For such detailed discussions, it is required to know the behavior of metal extraction for a simply lipophilized thiourea derivative which lacks the thioether function in PBT. Such a study is now under way.

PBT is quite suited for extraction of soft metal ions, such as Pd(II) and Hg(II), from acidic media. It seems especially suited for the separation of Cu(II) from other conventional metal ions. It is stable and preparable in a massive scale if desired, though not so cheaply as widely-used phosphate-type or hydroxime-type industrial extractants. PBT thus seems to be a reagent of choice for separating on a moderate scale Cu(II) ions in mixtures with conventional metal ions.

References

1. E. E. Rakovskii, N. V. Shvedova and L. D. Berliner, *J. Anal. Chem., USSR*, **30**, 1492 (1975).
2. E. E. Rakovskii, N. V. Shvedova and L. D. Berliner, *J. Anal. Chem., USSR*, **29**, 1946 (1974).
3. Yu. A. Zolotov, O. M. Petrukhin, V. N. Shevchenko, V. V. Dunina and K. G. Rukhadze, *Anal. Chim. Acta*, **100**, 613 (1978).

4. A. Diamantatos and A. A. Verbeck, *Anal. Chim. Acta*, **91**, 287 (1977).
5. G. A. Vorobeve, Yu. A. Zolotov, L. A. Izosenkova, A. V. Karyakin, L. I. Pavlenko, O. M. Petrukhin, I. V. Seryakova, L. V. Simonova and V. N. Schevchenko, *J. Anal. Chem., USSR*, **29**, 425 (1974).
6. S. J. Al-Bazi and H. Freiser, *Solvent Extr. Ion Exch.*, **4**, 1121 (1986).
7. C. Mahr, *Angew. Chem.*, **50**, 412 (1937).
8. S. Ide, Y. Katayama H. Nakamura and M. Takagi, *Solvent Extr. Ion Exch.*, **5**, 835 (1987).
9. Yu. A. Zolotov and V. G. Lambrev, *Radiokhimiya*, **8**, 627 (1966).
10. I. P. Alimarin and Yu. A. Zolotov, *Talanta*, **9**, 891 (1962).
11. F. Umland and W. Hoffmann, *Z. Anlyt. Chem.*, **168**, 268 (1959).
12. Yu. A. Bankovskii, G. P. Mezharaps and A. F. Irvin'sh, *Izv. Akad. Nauk Latv. USSR*, No. 3, 323 (1962).
13. D. Betteridge, Q. Fernando and H. Freiser, *Anal. Chem.*, **3**, 294 (1963).
14. M. Tanaka, "San to Enki (Acids and Bases, in Japanese)", Shokabou, Tokyo, 1971.

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