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Monooctyl- α -anilinobenzylphosphonic Acid as Reagent for Extraction and Separation of Bismuth(III) and Lead(II)

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Monooctyl- α -anilinobenzylphosphonic acid was used as extractive reagent for the separation of bismuth(III) and lead(II). The optimal pH value for bismuth(III) extraction was 1.75, whereas lead(II) was quantitatively extracted at pH 5. The separation factor for the two investigated metal ions at pH 1.75 was 140. On the basis of extractive experimental data, the stoichiometry of the extraction mechanisms was presumed. The described method is simple and rapid and can be proposed for the separation of bismuth(III) from lead(II).

INTRODUCTION

Nowadays, attention is directed to the trace analysis of metal ions, since the consciousness of their toxicity and environmental pollution rises with every newly discovered chemical, its biological property and function. Lead is certainly one of the most frequently investigated metals from that standpoint. According to statistics, children living in urban environments run the risk of lead poisoning through the air they breathe, as well as through water and food they take.¹

Metal ions lead(II) and bismuth(III) are a very interesting pair of elements also from the radiochemical point of view. Bismuth-210 with a relatively short half-life (5.01 days) is known to be one of the lead-210 daughters in forming the stable lead-206 isotope. For example, the two isotopes have gained importance as tracers in geochemical sample, natural waters and atmospheric sample research. The methods of separation of bismuth from lead are typically precipitation, ion exchange, electrodeposition or solvent extraction.^{2,3}

The development of new effective methods and/or reagents for quick separation of these metal ions is still of considerable chemical interest. In this paper monooctyl- α -anilinobenzylphosphonic acid, already known as a good extractive reagent for some metal ions, was used for the extraction and separation of bismuth(III) and lead(II).^{4,5,6}

EXPERIMENTAL

Original metal ion solutions were aqueous solutions of hydrated lead(II) and bismuth(III) nitrates. Bismuth(III) nitrate solution ($c = 0.1 \text{ mol dm}^{-3}$) was standardized both by complexometric EDTA titration⁷ and gravimetrically by cupferon.⁸ Lead(II) nitrate solution ($c = 0.1 \text{ mol dm}^{-3}$) was standardized by gravimetric analysis with potassium chromate.⁸ Experimental solutions were obtained by dilution of the stock solutions, and their concentration was controlled by plasma spectrometric measurement included in every experimental series.

Monoctyl- α -anilino benzylphosphonic acid is one of previously prepared and characterized anilino phosphonic acids.^{9,10,11} Standard solutions of the reagent were prepared by weighing the desired amounts of the compound and dissolving them in chloroform.

All other chemicals, including nitric acid and chloroform, were of *p.a.* purity grade. Deionized water was used throughout the experiments.

Distribution ratios were obtained by plasma spectrometric measurements (ICP AES) of the non-extracted metal ions residues in the aqueous phase after equilibration. Although the equilibrium was achieved in approximately 5 minutes, the separation of phases was undertaken after strong shaking of solutions for 15 minutes. Aqueous solutions were acidified with nitric acid

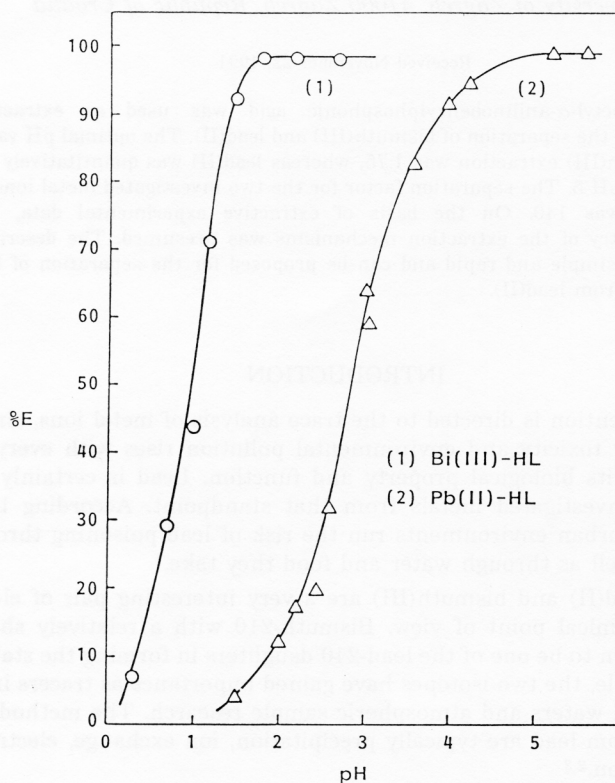


Figure 1. Dependence of the extraction of Bi(III) and Pb(II) on the initial acidity of the aqueous phase. $c_M = 1 \times 10^{-4} \text{ mol dm}^{-3}$; $c_{HL} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; (1) Bi(III)-HL system; (2) Pb(II)-HL system.

before extraction. All experiments were carried out at room temperature which was about 296 K. Reproducibility of the results indicates that a small change in room temperature does not effect extraction data.

RESULTS AND DISCUSSION

The chloroform solution of monoocetyl- α -anilinobenzylphosphonic acid (HL) was used as extractive reagent which enabled quick and simple separation of bismuth(III) and lead(II) from their nitrate solution.

Dependence of the extraction of investigated metal ions with HL on initial acidity is shown in Figure 1. In the pH range 0–4, there was no change in the acidity of the aqueous phase before and after the extraction. After pH 4, an increase was observed of the acidity of the aqueous layer after equilibration, as compared to the initial acidity. These values are beyond the range of experimental data depicted in Figure 2. The optimal pH values of bismuth(III) extraction was 1.75 with minimum lead(II) extraction, whereas quantitative lead(II) extraction was achieved with initially less acidic solutions

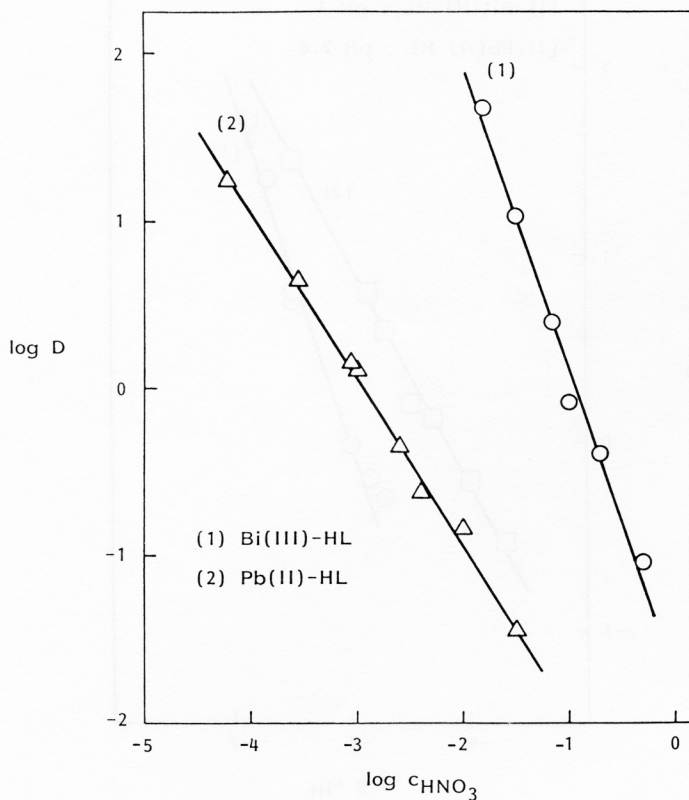


Figure 2. Distribution coefficients of Bi(III) and Pb(II) as functions of the initial acidity of the aqueous phase. $c_M = 1 \times 10^{-4} \text{ mol dm}^{-3}$; $c_{HL} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; (1) Bi(III)-HL system; (2) Pb(II)-HL system.

(pH 5), the pH values being sufficiently apart to enable reasonably good conditions for metal ion separation. The potassium nitrate, which was added to maintain a constant ionic strength in aqueous solutions, did not significantly effect the optimal extraction pH range. The linear relationship and the negative slopes of the logarithmic distribution coefficient values vs. nitric acid concentration (Figure 2) indicate that a different number of protons was released during the reaction with phosphonic acid extractant depending on the system components. During the extraction of lead(II), one proton was released whereas bismuth(III) extraction required transfer of two protons into the aqueous phase.

Under optimal pH conditions, the maximum extraction was achieved with a ten-fold excess of reagent. By varying the reagent concentrations at a constant pH value at less than 50% extraction, experimental data were obtained for determining the $\log D$ vs. $\log c_{HL}$ relationship (Figure 3). Positive slopes indicate the number of reagent molecules bound per metal ion in the extracted species. One ligand molecule bound

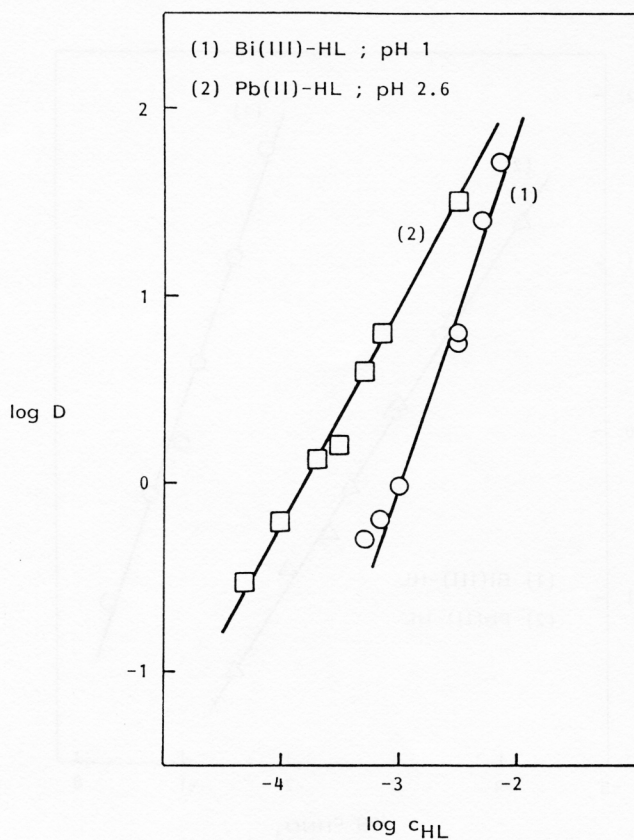
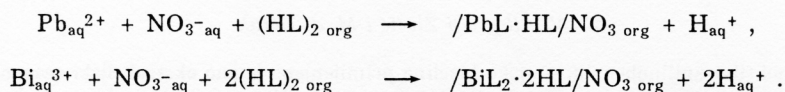


Figure 3. Distribution coefficients of Bi(III) and Pb(II) as functions of HL concentrations in the organic phase. $c_M = 1 \times 10^{-4}$ mol dm⁻³; $c_{HL} = 5 \times 10^{-5} - 1 \times 10^{-2}$ mol dm⁻³; (1) Bi(III)-HL system; (2) Pb(II)-HL system.

to the lead cation and two phosphonic acid molecules bound to the bismuth cation are in agreement with the released proton data gained for the systems with various acid concentrations. The HL fraction bound to the metal ions did not significantly effect the total HL amount so the proposed stoichiometry of the extraction was based on the initial reagent concentrations.

The extraction mechanism and the nature of complexes formed with phosphonic acids are difficult to determine without taking into account the properties and behaviour of the reagents. Formerly, the distribution and dimerization of HL in various solvents was studied.^{10,11} It was found that HL in chloroform has the highest distribution constant ($\log K_d = 1.97$) in comparison with other solvents, resulting in a high dimerization constant ($\log K_2 = 4.98$). Monoionization of dimer molecules may occur on complexation with metal ions.^{12,13} Further, the co-extraction of inorganic anions, especially nitrate, has been also confirmed in the case of different phosphonic acids.^{10,11,14} The number of the reagent molecules bound to the extracted metal complex is not always equal to the charge on the metal ion.¹⁵ Recently, mono-octyl- α -(4-carboxyanilino)-benzylphosphonic acid, a reagent related to HL, was also proposed as an extractant for the separation of bismuth(III) and lead(II).¹⁶ Its optimal extracting pH values were slightly lower than in the case of HL, a fractional number of reagent molecules bound to metal ion was obtained, and the co-extraction of nitric acid was assumed.

On the basis of these facts, as well as from the experimental data obtained, the following extraction mechanisms for lead(II) and bismuth(III) with mono-octyl- α -anilino-benzylphosphonic acid systems could be proposed:



Nitrate ions co-extract with phosphonic acids, as well as with their metal complexes. Their presence in extraction systems may effect the reaction mechanisms. In the case of bismuth(III)-HL system, such an effect was observed. Nitrate ions are probably a part of the extracted complex species, even at low concentrations. Enhancement of the nitrate concentration by adding potassium nitrate leads to changes in the essential stoichiometry of the extraction mechanism.

The effect of lead(II) on the extraction of bismuth(III) was investigated by varying lead(II) concentrations in the system with optimal conditions for bismuth(III) extraction. The investigated concentration range $c_{\text{Pb(II)}}/c_{\text{Bi(III)}}$ was increased from 1 to 500, with a tenfold excess of reagent with respect to the initial bismuth concentration ($c_{\text{Bi}} = 1 \times 10^{-4}$ mol dm⁻³). No effect of lead was observed until the ratio $c_{\text{Pb}}/c_{\text{Bi}} = 50$, and then probably because of the consumption of the reagent. The separation factor gained as $D_{\text{Bi}}/D_{\text{Pb}}$ at pH 1.75 was approximately 140.

The proposed analytical method was shown to be simple and rapid. Mono-octyl- α -anilino-benzylphosphonic acid can be suggested as an efficacious extractive reagent, which enables good separation of bismuth(III) and lead(II) under the experimental conditions described.

REFERENCES

1. R. L. Boeckx, *Anal. Chem.* **58** (2) (1968) 1851.
2. J. S. Blais, W. D. Marshall, *Anal. Chem.* **60** (1988) 1851.
3. H. Narita, K. Harada, W. C. Burnett, S. Tsunogai, and W. J. McCabe, *Talanta* **36** (9) (1989) 925.
4. V. Jagodić and M. J. Herak, *J. Inorg. Nucl. Chem.* **33** (1971) 2641.
5. M. J. Herak and V. Jagodić, *Croat. Chem. Acta* **36** (1964) 51.
6. J. Radošević, V. Jagodić, and M. J. Herak, *J. Inorg. Nucl. Chem.* **39** (1977) 2053.
7. E. Merck, *Komplexometrische Bestimmungsmethoden mit Titriplex*, Merck, Darmstadt.
8. A. I. Vogel, *A Text-Book of Quantitative Inorganic Analysis*, Longmans, Green and Comp., London, 1945.
9. V. Jagodić, *Chem. Ber.* **93** (1960) 2308.
10. V. Jagodić and M. J. Herak, *J. Inorg. Nucl. Chem.* **32** (1970) 1323.
11. M. J. Herak and V. Jagodić, *J. Inorg. Nucl. Chem.* **35** (1973) 995.
12. D. F. Peppard, G. W. Mason, W. J. Driscoll, and R. J. Sironen, *J. Inorg. Nucl. Chem.* **7** (1958) 276.
13. C. F. Baes, Jr., R. A. Zingero, and C. F. Coleman, *J. Phys. Chem.* **62** (1958) 129.
14. K. Inoue and Y. Baba, *Solvent Extr. Ion Exch.* **5** (1987) 1031.
15. E. O. Otu and A. D. Westland, *Solvent Extr. Ion Exch.* **8** (1990) 759.
16. V. Živčić and M. J. Herak, *J. Radioanal. Nucl. Chem.* **140** (2) (1990) 409.

SAŽETAK

Monooktil- α -anilinobenzilfosfonska kiselina kao reagens za ekstrakciju i odjeljivanje bizmuta(III) od olova(II)

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Monooktil- α -anilinobenzilfosfonska kiselina primijenjena je kao ekstrakcijski reagens za odjeljivanje bizmuta(III) od olova(II). Optimalna vrijednost pH za ekstrakciju bizmuta iznosila je 1,75 dok se olovo(II) kvantitativno ekstrahiralo pri pH 5. Faktor odjeljivanja bizmuta(III) od olova(II) pri pH 1,75 iznosio je 140. Na temelju ekstrakcijskih eksperimentalnih podataka pretpostavljeni su stehiometrijski parametri ekstrakcijskih mehanizama. Opisana metoda jednostavna je i brza te se može preporučiti za međusobno odjeljivanje iona navedenih metala.