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The thermodynamics of synergistic extraction of bismuth by 2-ethylhexyl phenylphosphonic acid and micelles of dinonyl naphthalene sulfonic acid

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Abstract

Synergism using the title metal extracting agents has been observed for bismuth. Thermodynamic parameters of the extraction process were determined by the temperature coefficient of extractability. The extraction of bismuth from $HClO_4$ by dinonyl naphthalene sulfonic acid (HDNNS) and the mixed ligand system are entropy controlled, whereas the process is enthalpy controlled when 2-ethylhexyl phenylphosphonic acid (HEHΦP) is the extractant. These results shed further light on the mechanism of the synergy by the combined extractants. Published by Elsevier Science B.V.

Keywords: Bismuth; Extraction; Micelle; Thermodynamics; Synergism

1. Introduction

Organo-phosphorus and sulfonic acids as individual metal ion extractants have been of interest for some time and such interest is quite strong at present. Past works have shown that when liquid ion exchangers form micelles, the metal ion causes the liquid to undergo electrostriction [1]. Micellar binding to an ion with a high charge to radius ratio therefore results in a phase of lower entropy. Some liquid ion exchangers such as phosphonates show much less tendency to aggregate, and as a result solution entropies are higher. The thermodynamics of ion exchange from aqueous media are such that liquids that produce solutions of ions at higher entropy show much wider ranges in free energies of extraction [2,3].

In the extraction of some lanthanides, it was shown that extraction by HEHΦP is favored by both a negative enthalpy change ($-\Delta H$) and a positive entropy change ($+\Delta S$) of the process as atomic number increases; in contrast, the entropy change opposed and out-weighed the effect of enthalpy in extractions with HDNNS [2]. The ΔS of the ion exchange process is the sum of the entropy change of hydration of the gaseous ion and the entropy change of complexation of the gaseous ion. The former is dependent on the metal ion, becoming smaller as charge density (Z/r) increases. The ΔS of complexation is affected more in the micellar extraction than for the extraction by the phosphonate dimer as the cation's charge/radius ratio increases. Other entropy contributions (to the ion exchange process) due to variations of structural order of the organic phase, solvation of both the free ligand and complex and deprotonation of the ligand are usually small, and can be ignored.

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Elemental bismuth or the mineral bismuthite (Bi_2S_3) is commonly found in lead and copper minerals. The presence of bismuth in copper and lead ores adversely affects their metallurgical recovery. Bismuth is a "green" heavy metal that is being used to replace environmentally unfavorable metals. A selective method of separating these metals continues to receive considerable attention. HDNNS forms inverted micelles in liquid–liquid extraction systems. The micelles have been shown to solubilize organophosphorus compounds like HEHΦP. Both HEHΦP and HDNNS are metal ion extractants. The former has greater selectivity for large polyvalent ions. The combination of these two ligands has been shown to demonstrate better extraction for bismuth over copper and lead than the individual ligands [4]. This synergistic approach represents an effective way of exploiting the high selectivity of HEHΦP for polyvalent ions of large radius, like bismuth.

It was proposed that the hydrophilic environment within the HDNNS micelles can favor the solvation (solubilization) of a metal ion–phosphonate complex [5]. A knowledge of the sign and magnitude of the enthalpy change and entropy change of the extraction process will add to our understanding of the nature of the bonding in the mixed ligand system and the ion exchange reactions. The author is not aware of any previous report(s) of thermodynamic data for the extraction of bismuth using this dual solvent system.

2. Experimental

2.1. Materials

The source and purification of dinonyl naphthalene sulfonic acid; the synthesis of HEHΦP and the preparation of metal perchlorates were as reported earlier [6]. All other chemicals and reagents were used without further purification.

2.2. Procedure

The aqueous phase contained perchloric acid and 10^{-5}–10^{-4} M metal ion concentration, and the organic phase contained 10^{-2} M ligand in ligroine, separately or of each in the mixed system. Five ml of the two phases were contacted in a home-made thermostated cell in the temperature range 15–75±0.5°C. The cell was fabricated in a glass blowing shop from six 10 ml glass vials enclosed in a chamber with inlet and outlet ports for water circulation. A 10 min temperature equilibrium period was allowed after the phases were placed in the vial. This was followed by 15 min of magnetic stirring, more than sufficient for equilibrium to be reached [5]. The procedure for the determination of distribution ratio, *D*, was similar to that reported earlier [6]. Triplicate extractions were performed at each temperature setting, and duplicate analyses were performed on the separated aqueous phase. Bismuth was determined as reported previously [5].

3. Results and discussions

The extraction equations are as follows: for the mixed solvent system

$$\mathrm{BiY^{2+}} + \overline{1.5(\mathrm{HX})_2} + \overline{0.5(\mathrm{HD})_6} \rightleftharpoons \overline{(\mathrm{BiYX_3H_4D_3})} + 2\mathrm{H^+} \qquad (1)$$

for the phosphonate solvent system, and

$$\mathrm{Bi^{3+}} + \overline{3(\mathrm{HX})_2} \rightleftharpoons \overline{\mathrm{Bi(H_3X_6)}} + 3\mathrm{H^+} \qquad (2)$$

for the sulfonate solvent system

$$\mathrm{Bi^{3+}} + \overline{(\mathrm{HD})_6} \rightleftharpoons \overline{\mathrm{Bi(H_3D_6)}} + 3\mathrm{H^+} \qquad (3)$$

where HX is HEHΦP, HD is HDNNS and species with overline are in the organic phase, otherwise the aqueous phase is implied. Eq. (1) and the aggregation number of the sulfonate micelle were reported previously [5], and $(HX)_2$ is the phosphonate dimer [7]. The hydrolysis of bismuth in 1 M $HClO_4$ in unlikely [8,9], suggesting the existence of $BiClO_4^{2+}$ [10]. The identity of BiY^{2+} is the subject of an on-going investigation, and that work will appear elsewhere. Various workers have reported the stoichiometries for the individual extractants shown in Eqs. (2) and (3) e.g. [1–6,11–15].

It is possible that temperature affects the aggregation numbers of both the reactant and product species. This will be evidenced by differences in the slope of plots of log *D* versus log [extractant] at different temperatures. If this is the case, using the temperature coefficient method to obtain enthalpy changes will not

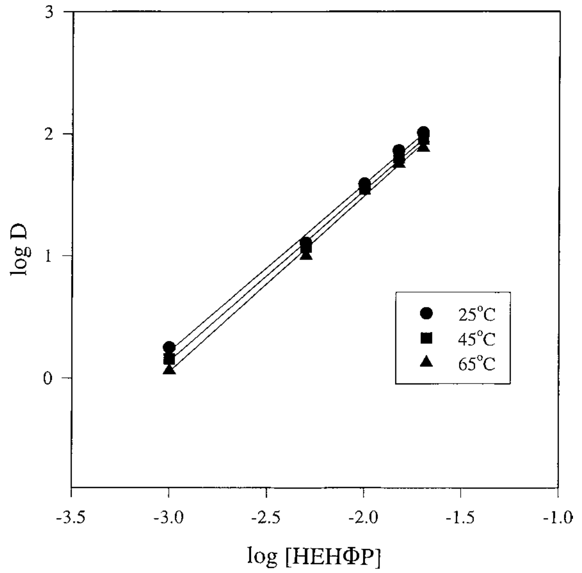

Fig. 1. Dependence of the extraction of bismuth from aqueous 1 M $HClO_4$ on the concentration of HEHΦP mixed with 0.01 M HDNNS in ligroine, at different temperatures.

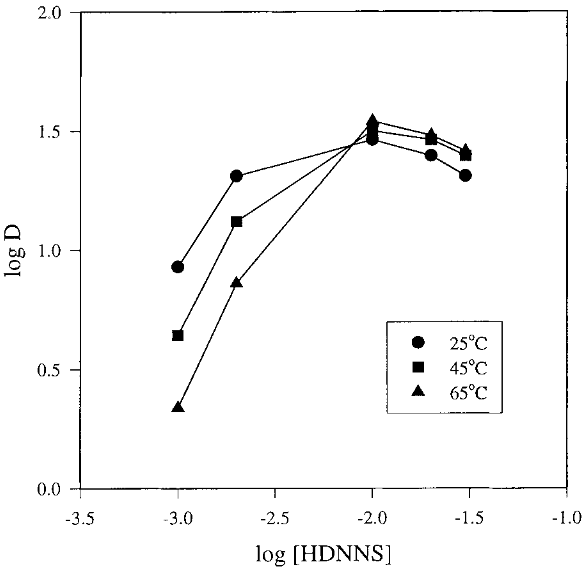

Fig. 2. Dependence of the extraction of bismuth from aqueous 1 M $HClO_4$ on the concentration of HDNNS mixed with 0.01 M HEHΦP in ligroine, at different temperatures.

be valid. A direct calorimetric measurement will be required.

To verify that such complication, i.e., change in aggregation state with temperature, does not occur in this case, extractions were performed at different temperatures as reagent concentrations were varied. The plots are shown in Figs. 1 and 2. No change is seen in the slope of the observed dependence of D on ligand concentration as temperature is varied. However, there is a reversal with concentration of HDNNS which was discussed in more detail in [5]. Briefly, it arises as a result of the presence of non-extractable bismuth complexes in the aqueous phase.

Neglecting the activity coefficients of neutral species, the thermodynamic equilibrium constant, K_e, for the mixed ligand system is:

$$K_e = \frac{[H^+]^2\overline{[(BiYX_3H_4D_3)]}}{[BiY^{2+}]\overline{[(HX)_2]}^{1.5}\,\overline{[(HD)_6]}^{0.5}}\,\frac{\gamma^2_{H^+}}{\gamma_{BiY^{2+}}}. \qquad (4)$$

It should be noted that the previous work did not reveal polynuclear bismuth complexes in the organic phase. Recognize that

$$D = \frac{\overline{[BiYX_3H_4D_3)]}}{[BiY^{2+}]}. \qquad (5)$$

At low (tracer) metal ion concentration in the aqueous phase, $[(HX)_2]$ and $[(HD)_6]$ may be replaced by their analytical concentrations, $C_{(HX)}$ and $C_{(HD)}$, respectively, and at constant ionic strength, activity coefficients are constant.

The enthalpy change (ΔH) of the extraction process was estimated from the temperature coefficient of extraction. This ΔH of extraction was obtained from the slope of the plot of the log D versus $1/T$ using the Van't Hoff equation in the form:

$$\log D = -\frac{\Delta H}{2.303\,R}\frac{1}{T} + C, \qquad (6)$$

where R is the gas constant and C is a constant. For a solution of constant ionic strength, if we assume that (i) the dependence of the aqueous activity coefficients on temperature is (as usual) negligible, (ii) only a small amount of the extracted metal-complex is present in the organic phase, (iii) the enthalpy change, ΔH, is constant in the 15–75°C temperature range (i.e., the heat capacity change is negligible), and (iv) the activity coefficient of the neutral species is ca. unity, then the enthalpy change values would be standard values, i.e., ΔH^0. Justification and problems associated with these assumptions were examined, in detail, in a previous work [3]. Various workers have

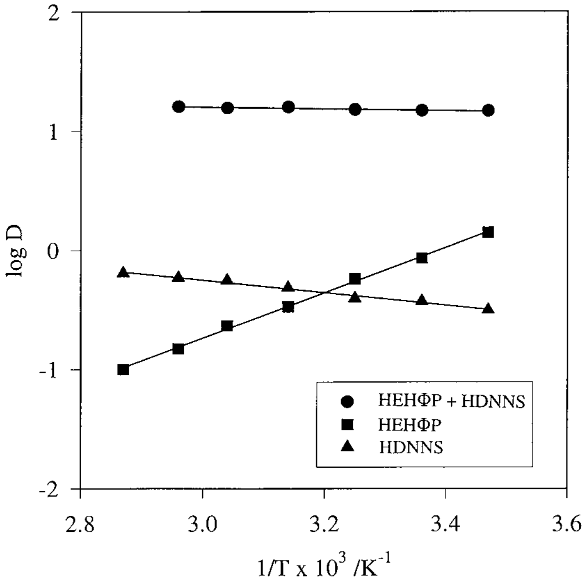

Fig. 3. Effect of temperature on the extraction of bismuth from aqueous 1.0 M $HClO_4$ into 0.01 M HEHΦP, 0.01 M HDNNS and mixture of 0.01 M HEHΦP+0.01 M HDNNS, in ligroine.

studied the thermodynamics of synergistic extraction of metals using the temperature coefficient method e.g., [16–18].

The plots of log D versus $1/T$ for the extraction are shown in Fig. 3. These plots were obtained using a linear regression program at the 95% confidence level.

Absolute values of the free energy change (ΔG^0) cannot be calculated because activity coefficients of bismuth perchlorate in perchloric acid solution are unavailable. Therefore, a shifted free energy, ΔG^*, has been defined as follows:

$$\Delta G^* = \Delta G^0 + RT\ln\frac{\gamma^{2z}_{\pm\mathrm{HClO_4}}}{\gamma^{m+n}_{\pm\mathrm{M_m(ClO_4)}_n}}. \qquad (7)$$

For an electrolyte of stoichiometry (cation)$_m$ (anion)$_n$, the mean activity coefficient, $\gamma_\pm^{m+n} = \gamma_+^m\gamma_-^n$.

$$\Delta G* = -RT\ln D\frac{[\mathrm{HClO_4}]^z}{[\mathrm{ligand}]^y}, \qquad (8)$$

(y=n and/or p, and z are the stoichiometric coefficients for HEHΦP and/or HDNNS, and H^+, respectively, in Eqs. (1)–(3)). Thus, the calculated free energy changes are less negative than the absolute free energy, by an amount equal to the second term on the right-hand side of Eq. (7). If $\gamma_\pm$ for $Bi(ClO_4)_3$ at an ionic strength μ=0.1 M is used in the place of the correct values at μ=1 M, the second term (in Eq. (7)) leads to an estimated ΔG^0 value that is 3 kJ mol^{-1} (for the mixed ligand system) or 2 kJ mol^{-1} (for the individual ligands) greater than ΔG^*. The γ values were taken from [19]. Therefore, the difference between ΔG^* and ΔG^0 is small and will not affect conclusion about other factors involved in the extraction process.

Also, a shifted entropy change is defined as follows:

$$\Delta S^* = \Delta S^0 - R\ln\frac{\gamma^z_{\mathrm{H^+}}}{\gamma_{\mathrm{M^{z+}}}} \qquad (9)$$

and calculated from

$$\Delta G^* = \Delta H^0 - T\Delta S^* \qquad (10)$$

at 25°C. These entropy changes are more positive than the standard free entropy changes, ΔS^0, by an amount equal to the second term on the right-hand side of Eq. (8). Again using γ at μ=0.1 M in place of the correct value at 1 M, ΔS^* would be more positive than ΔS^0 by 8–12 JK^{-1} mol^{-1}. This difference is presumed to be somewhat greater at μ=1 M.

The thermodynamic values are shown in Table 1. Previous works [2,3] have examined the enthalpy and entropy changes associated with the individual ligands. To summarize results of those works, extractions with HEHΦP are enthalpy controlled due to the highly ordered chelate structures formed, with the attendant strong bonding energy, between the partially dehydrated metal cation and the deprotonated ligand, and the hydration of the exchanged proton. In other words, the chelate effect is one of the features account-

Table 1
Thermodynamic parameters for the extraction of bismuth from 1 M $HClO_4$

Ligand	ΔH^0 (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔG^* (kJ mol^{-1})
HEHΦP[a]	−36.6±0.6	−9.1±2.1	−33.9±0.2
HDNNS[b]	10.1±0.6	63.8±2.1	−8.9±0.1$_9$
HEHΦP+HDNNS[c]	1.4±0.3	103.7±1.1	−29.5±0.0$_7$
Sum[d]	−26.5±0.8	54.7±3.0	−42.8±0.3

[a] 0.01 M HEHΦP.
[b] 0.01 M HDNNS.
[c] 0.01 M HEHΦP+0.01 M HDNNS.
[d] Sum of HEHΦP and HDNNS.

ing for the high selectivity exhibited by HEHΦP for large polyvalent ions.

On the other hand, extractions with HDNNS are entropy controlled owing to extensive dehydration of the metal ion as it extracts into the organic phase. Small heat effects are expected from the ion pairs formed between the anionic HDNNS micelle and the partially dehydrated metal ion. The positive value of the enthalpy change given in Table 1 (when HDNNS is the extractant) is consistent with heat effects involved in the dehydration of the metal cation being the predominant enthalpy factor.

It was postulated that micellar solubilization of HEHΦP-metal complexes was responsible for the observed synergism [5]. Therefore, the mixed ligand system should be entropy controlled. The results shown in Table 1 are consistent with strong micellar involvement in the mixed ligand system.

The small value of the enthalpy change for the mixed ligands system is indicative of weak interaction. The HDNNS and HEHΦP results are in agreement with previous works [2,3]. The slightly higher entropy changes observed in the present work may be due to the different diluents used.

4. Conclusion

Although the temperature coefficient of extraction method provides only approximate values of the enthalpy change of the extraction process in comparison to direct calorimetric method, the small concentration of metal ions (leading to small heat effects) makes its choice necessary. So far, synergism between HEHΦP and HDNNS is known essentially to be due to an organic phase effect, a change in the composition of the metal-bearing species in the organic phase in the system of two extractants.

A comparison of the sum (see Table 1) of the data obtained for individual ligands to that obtained for the mixed ligand system indicates that the enhanced extraction observed for the mixed ligand system can be attributed to favorable heat effects with HEHΦP and favorable entropy with the micellar HDNNS. The favorable enthalpy change associated with HEHΦP outweighs the opposing change with HDNNS. Entropy change effects by the micellar HDNNS outweighs opposing effects with HEHΦP. The observed synergism is attributable to cooperative effects resulting for the two ligands.

Acknowledgements

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References

[1] G.Y. Markovits, G.R. Choppin, in: J.A. Marinsky, Y. Marcus (Eds.), Ion Exchange and Solvent Extraction, vol. 3, Marcel Dekker, New York, 1973, p. 51.

[2] E.O. Otu, A.D. Westland, Solvent Extr. Ion. Exch. 9 (1991) 607.

[3] E.O. Otu, A.D. Westland, Solvent Extr. Ion. Exch. 8 (1990) 827.

[4] M.L. Rutherford, E.O. Otu, The Fourth Indiana University Undergraduate Research Conference, Indianapolis, IN, 6 November 1998.

[5] E.M. Pepe, E.O. Otu, Solvent Extr. Ion. Exch. 14 (1996) 247.

[6] E.O. Otu, A.D. Westland, Polyhedron 8 (1989) 1307.

[7] F. Peppard, J.R. Mason, G.W. Mason, J. Inorg. Nucl. Chem. 22 (1961) 285.

[8] F. Graner, L.G. Sillen, Acta Chem. Scand. 1 (1947) 63.

[9] A. Olin, Acta Chem. Scand. 11 (1957) 1445.

[10] B. Pokric, Z. Pucar, J. Inorg. Nucl. Chem. 35 (1973) 3287.

[11] D.F. Peppard, G.W. Mason, I. Hucher, J. Inorg. Nucl. Chem. 18 (1961) 245.

[12] I. Fidelis, S. Siekierski, J. Inorg. Nucl. Chem. 28 (1966) 185.

[13] R. Chiarizia, P.R. Danesi, M.A. Raieh, G. Scibona, J. Inorg. Nucl. Chem. 37 (1975) 1495.

[14] E. Högfeldt, R. Chiarizia, P.R. Danesi, V.S. Soldatov, Chem. Script. 18 (1981) 13.

[15] M.A. Raieh, N. Zakareia, H.F. Aly, J. Radioanal. Chem. 52 (1979) 285.

[16] J.N. Mathur, G.R. Choppin, Solvent Extr. Ion. Exch. 11 (1993) 1.

[17] M.M. Saeed, M. Ahmad, A. Ali, M.N. Cheema, Radiochim. Acta 57 (1992) 125.

[18] I.L. Dukov, Hydrometallurgy 44 (1997) 21.

[19] J. Kielland, J. Am. Chem. Soc. 59 (1937) 1675.