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Solvent Extraction of Zinc(II), Indium(III), Thallium(III) & Bismuth(III) with N-*n*-Octylaniline from Hydrochloric Acid Media & Their Separation

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The solvent extraction of zinc(II), indium(III), thallium(III) and bismuth(III) from hydrochloric acid media using N-*n*-octylaniline in benzene is described. Dependence of distribution ratios on the aqueous to organic phase ratio and the use of selective strippant lead to quantitative separation of these metals from a mixture containing these metal ions. The nature of the probable extracted species has been determined.

High molecular weight amines, useful as liquid anion exchangers have found wide applications for analytical separations of many metals from different aqueous media[1-4]. However, clean cut separation of the metals has not been achieved. The aim of this investigation is to achieve separation of zinc(II), indium(III), thallium(III) and bismuth(III) ions from a mixture containing these metal ions using N-*n*-octylaniline solution in benzene. Such a separation of this group of elements is expected to be of analytical importance. N-*n*-Octylaniline is almost insoluble in the aqueous phase, there is no emulsion formation and has the potential of being prepared on a large scale.

Stock solutions of indium(III) and thallium(III) were prepared and standardized as described earlier[5,6]. Zinc(II) and bismuth(III) solutions were prepared using sulphate and nitrate salts (AR grade) respectively and standardized[7,8].

N-*n*-Octylaniline was prepared by the method of Gardlund[9] and its solutions (%, v/v) were prepared in benzene.

Acetic acid (AR) and 0.2 *M* sodium acetate (AR) were used to prepare the buffer solution of *p*H 4.5.

Extraction of Tl(III), Bi(III) and Zn(II) from their solutions

To an aliquot of solution containing the metal ion (Tl, 10 mg; or Bi, 2 mg; or Zn, 0.5 mg) enough hydrochloric acid and water (15 ml for Tl or Bi; 10 ml for Zn) were added to give the desired acid concentration (Tl, 0.5 *M*; Bi, 0.5 *M*; Zn, 2 *M*). The metal ion was extracted with 2%, 3% and 7% solutions of the reagent in benzene keeping the aqueous to organic phase ratio as 1.5:1, 1.5:1 and 1:1 for thallium, bismuth and zinc respectively. The benzene layer was separated and Tl or Bi from the organic phase was stripped with the buffer solution (2 × 45 ml for Tl and 25 ml for Bi). Zinc from the organic phase was stripped with ~0.5 *M* ammonia solution (2 × 10 ml). The metal ions were estimated in aqueous phase complexometrically[7,8,10].

The extraction of Zn(II), Tl(III) or Bi(III) by the reagent solution in benzene as a function of hydrochloric acid concentration (0.1 to 5 *M*) was investigated. Zinc(II), Tl(III) and Bi(III) could be quantitatively extracted from 1.5-3 *M*, 0.5-5 *M* and 0.5-1.5 *M* HCl with 7%, 2% and 3% reagent solutions respectively. Indium(III) was not extracted from 1 to 7 *M* HCl with 1-10% reagent solution. Extraction of Bi(III) increased upto 0.5 *M* HCl, became quantitative from 0.5-1.5 *M* HCl and thereafter the extraction was negligible at 5 *M* HCl. Per cent extractions of zinc, thallium and bismuth with 2% reagent solution were 0.00%, 100.00% and 84.10% respectively when aqueous to organic phase ratio was 1.5:1 and the acid concentration was 0.5 *M*.

Log-log plot of distribution ratio versus amine concentration at fixed acid concentration indicated a molar ratio of 1:2 for Zn (1 *M*) and 1:1 for thallium (0.1 *M*) and bismuth (0.1 *M*) with respect to amine concentration. At 4 *M* HCl concentration, the molar ratio for bismuth was 1:2. Hence, the extracted species are $[RR'NH_2^+TlCl_4^-]$, $[RR'NH_2^+BiCl_4^-]$, $[(RR'NH_2^+)_2ZnCl_4^{2-}]$ and $[(RR'NH_2^+)_2BiCl_5^{2-}]$ where, $R = C_8H_{17}$ and $R' = C_6H_5$.

The results show that at lower and higher acid concentrations bismuth forms anions of the types $BiCl_4^-$ and $BiCl_5^{2-}$, respectively. Formation of these anions has been reported earlier also[11].

Effect of diverse ions

A large number of cations and anions do not interfere (as shown by less than 1% deviation in analyte recovery) in the extraction and complexometric determination of zinc, thallium and bismuth by the proposed method. The few cations and anions that do interfere are listed in Table 1.

Extraction, separation and estimation of Zn(II), In(III), Tl(III) and Bi(III)

The extraction studies show that it is possible to separate zinc, indium, thallium and bismuth from a mixture containing these elements (Scheme 1). The average recoveries of zinc, indium, thallium and

Table 1—Effect of Diverse Ions on Extraction of Zinc(II) (1.0 mg), Thallium(III) (2.04 mg) and Bismuth(III) (1.0 mg)

Tolerance limit, mg	Zinc[a]	Thallium[b]	Bismuth[b]
100	Citrate, thiocyanate	Oxalate, fluoride, nitrate, sulphate	Ascorbate, oxalate, nitrate, sulphate, acetate
50	Thiourea, oxalate, acetate, ascorbate, fluoride	Tartrate, EDTA, Ca(II), Sr(II), Mg(II), Ba(II)	SCN^-, EDTA, fluoride, Ca(II), Mg(II), Sr(II), Ba(II)
10	Ga(III), In(III), Be(II), Mg(II), Ca(II), Sr(II), Ba(II)	Be(II)	Be(II)
5	Al(III), Cu(II)[c], Hg(II)[c], Mn(II), As(III), Ti(IV), Bi(III)[c], Tl(III)[c], Cr(VI)[d], W(VI)[d]	Ni(II), Zn(II), Cd(II), Mn(II), Cu(II), Pb(II), Co(II), Sn(II), Te(IV), Fe(III), Cr(III), In(III), As(III), U(VI), V(VI)[d], W(VI)[d], Ga(III), Sb(III)[d]	Cu(II), Sn(II), Zn(II), Ni(II), Mn(II), Pb(II), Ga(III), In(III), Fe(III), Sb(III)[d], Al(III), Cr(III), Te(IV), Mo(V), U(VI), W(VI)[d], V(VI)[d], Ti(IV), As(III), Co(II).
2.5	—	Al(III), Au(III), Pt(IV), Ce(IV), Rh(III), Pd(II)	Rh(III), Ce(IV), Pt(IV), Au(III), Pd(II)
	Ions not Cd(II), Pb(II) tolerated	Bi(III), ascorbate, citrate, thiourea, thiocyanate	Tl(III), thiourea, citrate

(a) 7% reagent solution; 2 *M* HCl; aqueous to organic phase ratio as 1:1
(b) 2% reagent solution; 0.5 *M* HCl; aqueous to organic phase ratio as 1.5:1.
(c) and (d) masked with thiourea and tartrate respectively.

Mixture (total volume 15 ml; 0.5 *M* in HCl)
Extraction for 1 min with 2% reagent solution (2 × 10 ml)

Aq. phase (In, Zn)
Rendered 2 *M* in HCl followed by extraction of zinc with equal volume of 7% reagent solution

- Aq. phase In(III): Estimated complexometrically[10].
- Org. phase: Zn(II) stripped with 0.5 *M* ammonia solution (2 × 10 ml) and estimated complexometrically in aq. phase[7].

Org. phase (Bi, Tl)
Scrubbed with 5 *M* HCl (2 × 10 ml)

- Aq. phase Bi(III): Estimated complexometrically[8].
- Org. phase: Tl(III) stripped with acetate buffer (2 × 45 ml) and estimated complexometrically in aq phase[10].

Scheme 1—Extraction and separation of Zn(II), In(III), Tl(III) and Bi(III) from a mixture containing Zn (0.5-1 mg) + In (1.14-5.7 mg) + Tl (1.02-2.04 mg) + Bi (0.5-1.0 mg) in 0.5 *M* HCl in a total volume of 15 ml.

bismuth are 99.50%, 99.84%, 97.32% and 100.00% respectively.

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