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Distribution Studies of Zinc and Copper Salicylates with Tris(2-ethylhexyl)phosphate

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ABSTRACT

Tris(2-ethylhexyl)phosphate is proposed as an extractant for the solvent extraction of zinc and copper salicylate. The optimum extraction conditions are established by studying the various experimental parameters such as pH, sodium salicylate concentration, tris(2-ethylhexyl)phosphate concentration, equilibration period, and various diluents. The probable extracted species as ascertained by log D–log C plots is $Zn(HSal)_2 2T2EHP$ and $Cu(HSal)_2 2T2EHP$. The method permits mutual separation of zinc and copper and can be used for separation and determination of zinc and copper in environmental and pharmaceutical samples.

INTRODUCTION

Zinc and copper are important elements in various biological and enzymatic reactions. They also form desired constituents of various alloys and pharmaceutical preparations. Heavier concentrations of zinc and copper in the environment, however, can severly effect aquatic as well as human life. Chronic copper poisoning causes gastrointestinal catarrh and hemochromatosis. Similarly, overexposure to zinc results in poisonous effects. In view of this, separation and determination of zinc and copper is of great importance.

A literature survey reveals that very few extractants such as tributylphosphate (1, 2), trioctylphosphine oxide (3, 4), tri-*n*-butoxyethylphos-

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phate (5), (carboxy 2-ethyl)diphenyl phosphine oxide (6), triphenylphosphine oxide (7), and bis(2-ethylhexyl)hydrogen phosphate (8) have been used for the liquid–liquid extraction of zinc(II). Extractants such as tributylphosphate (9), methylisobutyl ketone (10–12), mesityl oxide (13, 14), and trioctyl phosphine oxide (15) have been studied for the extraction of copper(II) from different complexing media. However, these methods have limitations such as the use of salting-out agents (1, 4), a longer extraction period (3, 5), preequilibration of the organic phase (5), incomplete extraction (6), and control of the critical temperature (9).

This communication reports the extraction of zinc(II) and copper(II) from salicylate solution into tris(2-ethylhexyl)phosphate. The method permits mutual separation of zinc(II) and copper(II) and has been successfully applied for the extraction and determination of zinc and copper in various pharmaceutical samples. The proposed method is simple, precise, rapid, and free from the limitations described earlier.

EXPERIMENTAL

Apparatus

A Shimadzu UV-VIS 160A spectrophotometer, a Varian techron AAS 6, and a Control Dynamics digital pH meter with a combined glass electrode were used for absorbance and pH measurements.

Reagents and Chemicals

Stock solutions of zinc(II) and copper(II) were prepared by dissolving 2.2 g $ZnSO_4 \cdot 7H_2O$ and 0.98 g $CuSO_4 \cdot 5H_2O$ in 250 mL of doubly distilled water containing 2 mL sulfuric acid. The solutions were standardized by known methods (16) and finally diluted to obtain working solutions. A 0.1% m/v ethanolic solution of 1-(2-pyridylazo)-2-naphthol (PAN) and 0.1% m/v aqueous solution of 4-(2-pyridylazo)-resorcinol (PAR) were used for spectrophotometric determination of zinc and copper, respectively. Tris(2-ethylhexyl)phosphate (T2EHP) (Fluka) dissolved in toluene was used for extraction without further purification. All other chemicals used were of analytical reagent grade.

General Extraction Procedure

Microgram amounts of zinc/copper were extracted from a 25-mL aliquot solution using the optimum extraction conditions given in Table 1.

Zinc was determined spectrophotometrically in the organic (T2EHP) phase. To the organic phase containing zinc, add 5 mL buffer (pH 5.8), 1 mL of 0.1% ethanolic solution of 1-(2-pyridylazo)2-naphthol (PAN), and

TABLE 1
Optimum Extraction Conditions for Zinc(II) and Copper(II)

Metal ion	Aqueous phase salicylate (M)	pH	Organic phase	Extraction period (s)	Stripping solution	Determination procedure
Zn(II) (1–20 μg)	5×10^{-1}	5.4–5.9	50% T2EHP (5 mL)	90	—	Spectrophotometrically with PAN (7)
Zn(II) (1–5 mg)	5×10^{-1}	5.4–5.9	50% T2EHP (2 × 5 mL)	90	2 × 5 mL water	Complexometrically (16)
Cu(II) (10–50 μg)	2.5×10^{-3}	3.9–4.1	60% T2EHP (2 × 5 mL)	30	2 × 5 mL 0.1 M HNO_3	Spectrophotometrically with PAR (17)
Cu(II) (1–5 mg)	2.5×10^{-3}	3.9–4.1	60% T2EHP (2 × 5 mL)	30	2 × 5 mL 0.1 M HNO_3	Complexometrically (16)

shake for 60 seconds and dilute to 10 mL with toluene. The absorbance of the orange red Zn–PAN complex was measured at 555 nm against a reagent blank prepared analogously (7).

Copper from the organic (T2EHP) phase was stripped with 0.1 M HNO_3 and determined spectrophotometrically as described. To the aqueous phase add 10 mL buffer (pH 2), 1 mL of 0.1% aqueous solution of 4-(2-pyridylazo)resorcinol and dilute to 25 mL with distilled water. The absorbance of the Cu–PAR complex was measured at 540 nm against a reagent blank prepared analogously (17). Milligram amounts of zinc and copper were stripped with water and 0.1 M HNO_3, respectively, and determined titrimetrically (16).

RESULTS AND DISCUSSION

Effect of pH, Sodium Salicylate Concentration, and Tris(2-ethylhexyl)phosphate Concentration

The extraction of zinc(II) and copper(II) were performed at various pH values (1.5–10.0), sodium salicylate concentrations (2.5×10^{-4} to 7×10^{-1} M), and tris(2-ethylhexyl)phosphate concentrations (10–70%) (using toluene as the diluent). The extraction of zinc(II) was found to be quantitative at pH 5.4–5.9 from 5×10^{-1} M sodium salicylate solution with 50% T2EHP (dissolved in toluene). For copper(II) the extraction was quantitative at pH 3.9–4.1 from 2.5×10^{-3} M salicylate solution with 60% T2EHP (dissolved in toluene) (Figs. 1 and 2).

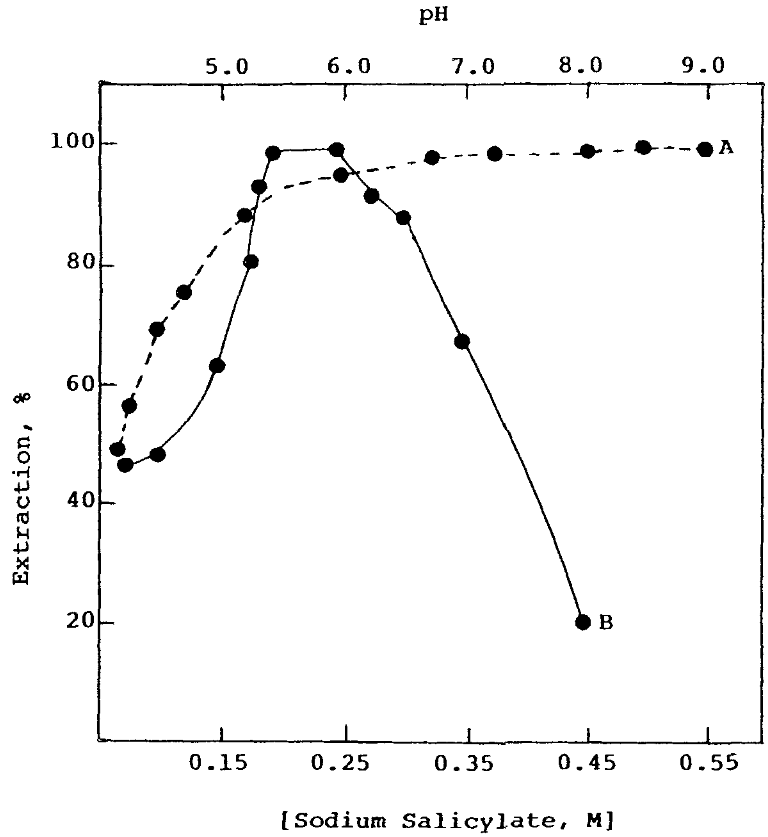

FIG. 1 (A) Extraction behavior of zinc(II) as a function of sodium salicylate concentration at 5.6 pH and 50% T2EHP. (B) Extraction behavior of zinc(II) as a function of pH at 5 × 10^{-1} M sodium salicylate and 50% T2EHP.

Effect of Equilibration Time

Variation in equilibration time from 10 to 180 seconds showed that shaking periods of 90 and 30 seconds were sufficient for quantitative extraction of zinc(II) and copper(II), respectively. Prolonged extraction had no adverse effect.

Choice of Diluents

The suitability of various diluents such as toluene, xylene, benzene, chloroform, and carbon tetrachloride was studied. It was observed that

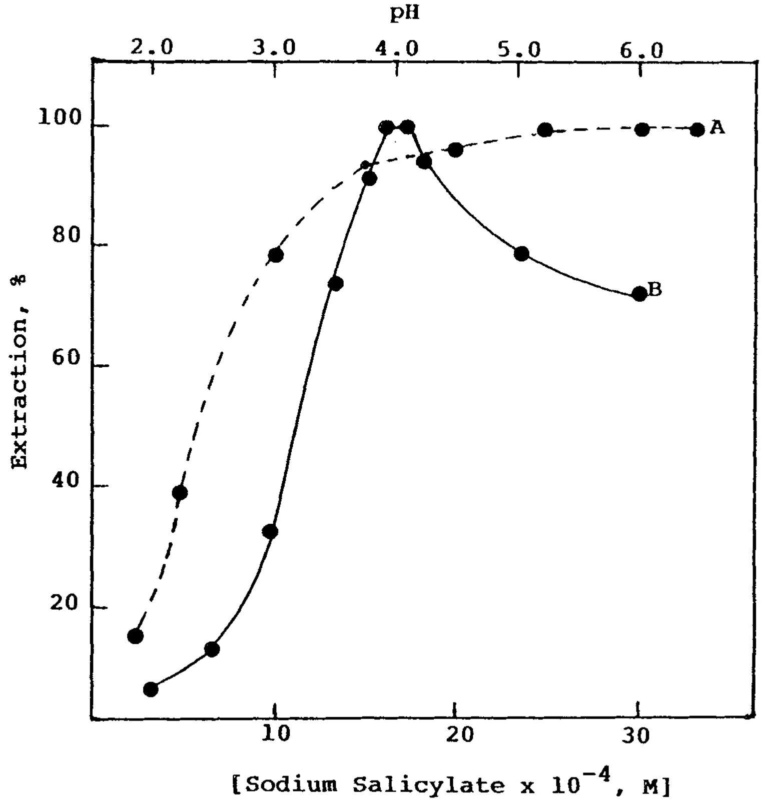

FIG. 2 (A) Extraction behavior of copper(II) as a function of sodium salicylate concentration at 4.0 pH and 60% T2EHP. (B) Extraction behavior of copper(II) as a function of pH at 2.5×10^{-3} M sodium salicylate and 60% T2EHP.

T2EHP dissolved in toluene or xylene gave quantitative extraction for both zinc and copper. The extraction with benzene, chloroform, and carbon tetrachloride as diluents was 93.62, 84.66, and 90.71% respectively for zinc and 94.48, 89.65, and 85.51% respectively for copper. Toluene was used for further studies as it gave better phase separation.

Nature of Extracted Species

An attempt was made to ascertain the nature of the extracted species using log *D*–log *C* plots. A plot of the log of distribution ratio versus log of salicylate concentration (at a fixed pH and a fixed T2EHP concentration) gave slopes of 1.9 and 1.92 for zinc and copper, respectively (Figs. 3 and 4). Similarly a plot of the log of distribution ratio versus the log of T2EHP concentration (at a fixed pH and a fixed sodium salicylate concentration) gave a slope of 2.1 and 1.94 for zinc and copper, respec-

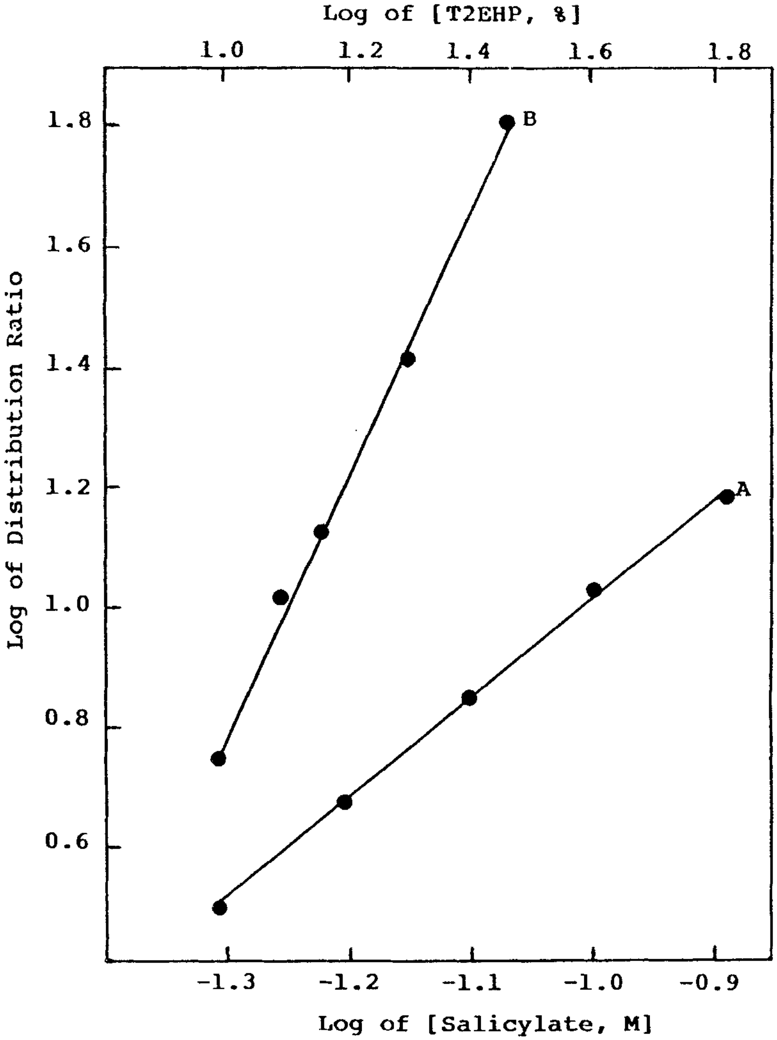

FIG. 3 Plots of log distribution ratio for zinc(II) versus (A) log of salicylate concentration (at pH 5.6 and 50% T2EHP concentration), and (B) log of T2EHP concentration (at pH 5.6 and 5×10^{-1} M sodium salicylate concentration).

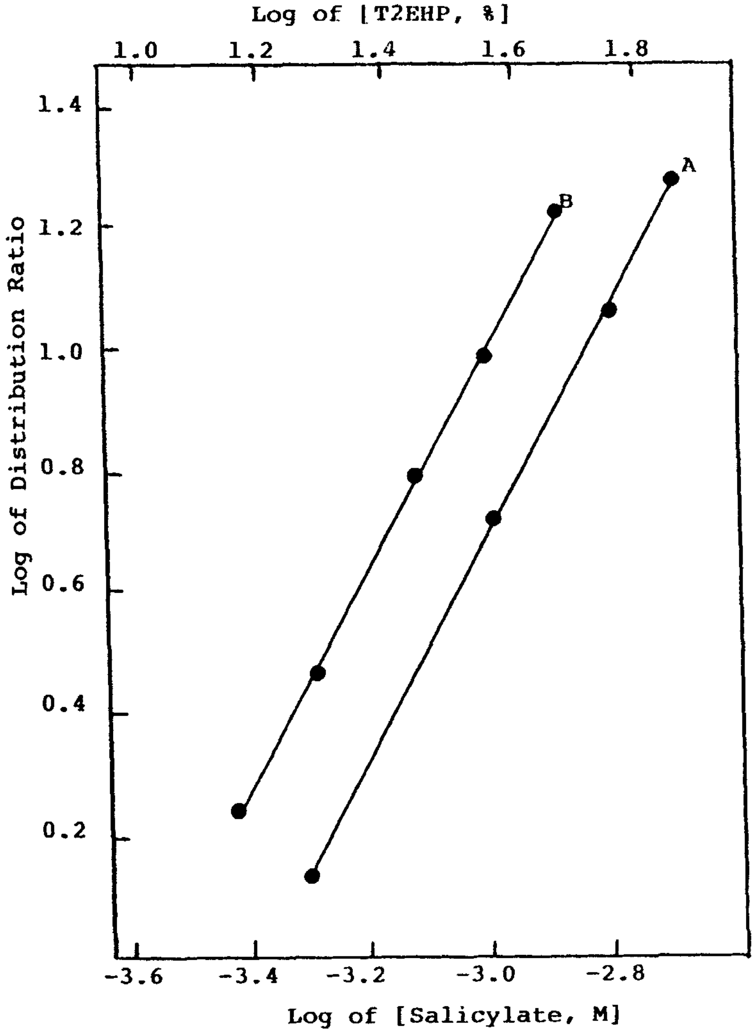

FIG. 4 Plots of log distribution ratio for copper(II) versus (A) log of salicylate concentration (at pH 4.0 and 60% T2EHP concentration), and (B) log of T2EHP concentration (at pH 4.0 and 2.5×10^{-3} M sodium salicylate concentration).

tively (Figs. 3 and 4), thus indicating a metal-to-salicylate and metal-to-T2EHP ratio of 1:2 in the extracted species. The probable extracted species will be $M(HSal)_2 2T2EHP$, where M is Zn(II) or Cu(II), $HSal^-$ is salicylate, and T2EHP is tris(2-ethylhexyl)phosphate. The extraction occurs by a solvation mechanism where T2EHP, being more basic, solvates the metal salicylate, rendering it hydrophobic.

$$M(HSal)_2{\cdot}2H_2O + 2T2EHP \rightleftharpoons M(HSal)_2 2T2EHP + 2H_2O$$

Effect of Diverse Ions

Varying amounts of foreign ions were added to a fixed amount of zinc (5 μg) and copper (30 μg) to study their interference in the extraction and spectrophotometric determination of zinc and copper by the proposed method. The tolerance limit was set at the amount required to cause a ±2% error in metal recoveries. The results showed that 200 μg each of Mg(II), Al(III), citrate, and chloride; 150 μg each of Cr(VI), iodide, and fluoride; 100 μg each of Ag(I), Ba(II), Ca(II), Fe(III), Sb(III), Se(IV), oxalate, and nitrate; 75 μg each of Sn(IV), Bi(III), Mo(VI), W(VI), and ascorbate; 50 μg each of Te(IV), Ti(IV), Zr(IV), Hf(IV), and Nb(V); and 25 μg each of Pb(II), Cu(II), and V(V) did not interfere with the extraction and determination of zinc. Similarly, 2500 μg each of Mg(II), Ag(I), Sb(III), Pt(IV), tartrate, thiourea, phosphate, chloride, bromide, iodide, nitrate, and sulfate; 1000 μg each of Pb(II), Ni(II), Zn(II), Sn(IV), Mo(VI), and thiocyanate; 500 μg each of Hg(II), Cd(II), As(III), Au(III), and Cr(VI); 250 μg each of U(VI) and Mn(II); 100 μg each of Fe(III) and Ce(IV); and 50 μg each of Bi(III) and V(V) did not interfere in the extraction and determination of copper(II). Co(II) and Mn(II) interfere seriously in the extraction of zinc while Co(II), Pd(II), and Al(III) interfere in the extraction of copper by the proposed method.

TABLE 2
Mutual Separation of Zinc(II) and Copper(II)

No.	Binary mixture (μg)	Recovery[a] (μg)	Standard deviation	Relative standard deviation (%)
1	Zn(II); 500 μg	Zn(II); 496	4.32	0.87
	Cu(II); 50 μg	Cu(II); 49.2	0.86	1.75
2	Zn(II); 500 μg	Zn(II); 497	3.64	0.73
	Cu(II); 200 μg	Cu(II); 198	2.01	1.01
3	Zn(II); 500 μg	Zn(II); 495	5.14	1.04
	Cu(II); 500 μg	Cu(II); 497	4.89	0.98

[a] Mean of triplicate analysis.

Mutual Separation of Zinc(II) and Copper(II)

The proposed method provides mutual separation of zinc(II) and copper(II). Under the optimum extraction conditions for copper(II) at pH 4.0 from a salicylate solution of 2.5×10^{-3} mol·dm^{-3} with 60% T2EHP (dissolved in toluene), zinc(II) shows no coextraction and remains quantitatively in the aqueous phase. Zinc is subsequently determined complexometrically (16) while copper is stripped with 0.1 M HNO_3 and determined either spectrophotometrically (17) or titrimetrically (16). The recoveries were >99.0% and are reported in Table 2.

APPLICATIONS

The suitability of the proposed method was tested by applying it to the separation and determination of zinc and copper in a variety of environmental and pharmaceutical samples.

Analysis of Environmental Samples

The proposed method was applied to the separation and determination of copper in two samples of industrial wastewater collected from The Maharashtra Pollution Control Board, New Bombay. The method was also applied to the analysis of airborne particulates collected by Municipal Corporation, Air Quality Monitoring, Bombay. The particulate samples were brought into solution by treating them with 5 mL nitric acid and digesting for 15 minutes. The solution was filtered and diluted to 25 mL

TABLE 3
Determination of Copper in Environmental Samples

No.	Cu found by AAS	Cu found by proposed method[a]	Relative standard deviation (%)
		A. Wastewater	
1	90.12 ppm	88.56 ppm	0.99
2	72.29 ppm	71.36 ppm	0.74
		B. Airborne Particulates	
1	0.874 μg/m^3	0.856 μg/m^3	0.72
2	0.519 μg/m^3	0.505 μg/m^3	1.05

[a] Mean of triplicate analysis.

TABLE 4
Determination of Zinc in Pharmaceutical Samples

No.	Sample	Zn found by AAS[a]	Zn found by proposed method[a]	Relative standard deviation (%)
1	Zevit capsule (Remidex Pharma Pt. Ltd.)	22.1 mg[b]	22.0 mg[b]	1.91
2	Tineafax (Burroughs Wellcome [India] Ltd.)	2.0%	1.98%	1.25
3	Siloderm ointment (Neopharma Pvt. Ltd.)	6.0%	5.98%	1.37
4	Nycil powder (Glaxo [India] Ltd.)	12.4%	12.38%	1.55

[a] Mean of triplicate analysis.
[b] Per capsule.

with distilled water and an aliquot of the sample was taken for extraction of copper by the proposed method. The recoveries were excellent and are reported in Table 3.

Analysis of Pharmaceutical Samples

The proposed method was also applied to the separation and determination of zinc and copper in a variety of pharmaceutical samples such as

TABLE 5
Determination of Copper in Pharmaceutical Samples

No.	Sample	Cu found by AAS (mg)[a]	Cu found by proposed method (mg)[a]	Relative standard deviation (%)
1	Supradyn (Roche India)	0.860[b]	0.848[b]	1.07
2	Multivitamin Iron Minerals (Meyer Organics India)	0.254[b]	0.249[b]	1.06

[a] Mean of triplicate analysis.
[b] Per capsule.

Supradyn, Multivitamin Iron tablets, Zevit capsules, Siloderm ointment, Tineafax ointment, and Nycil powder. Tablets of Supradyn, Multivitamin Iron and Zevit capsule were each treated with perchloric acid and evaporated to dryness. The residue was treated with a minimum quantity of hydrochloric acid, filtered through filter paper, and diluted to a definite volume. Iron(III) was removed by prior extraction with mesityl oxide (18). Subsequently, an aliquot of each of the samples was taken for extraction. Siloderm ointment, Tineafax ointment (0.1 g each), and Nycil powder (50 mg) were treated with a minimum of concentrated sulfuric acid and digested for 15 minutes. The solution was treated with water, filtered, and diluted to a known volume. An aliquot of each of the samples was used for the extraction of zinc by the proposed method. The results are reported in Tables 4 and 5.

The total time required for analysis was 20 minutes.

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