Separation of Metals on Sulfonated Diphenyl Phosphonate–Formaldehyde Resin in HCl–Organic Solvent Systems

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Synopsis. The distribution coefficients of several metal ions have been measured on sulfonated diphenyl phosphonate–formaldehyde resin in HCl–water miscible organic solvent solutions. Differences in the distribution coefficients are large enough to develop multicomponent separations. Particularly in HCl–propanone systems the separation of a complex mixture, Cd(II)–Zn(II)–Pb(II)–Cu(II)–Co(II)–Mn(II)–Mg(II), can be carried out chromatographically by sequential elution.

In a previous paper,[1] a report was given on the cation exchange behavior of metal ions on sulfonated diphenyl phosphonate–formaldehyde resin (abbreviated to DFS resin) in an aqueous HCl system.

The numerous studies to improve the cation exchange separation of metal ion by addition of a water miscible organic solvent have been reported. Fritz and Rettig[2] studied the separation of metal ions using Dowex 50W-X8 resin by elution with 0.10—1.0 mol dm^{-3} HCl–60—92 vol% propanone systems. Strelow *et al.*[3] presented a procedure for the separation of metal ions using Bio-Rad AG 50W-X8 resin by elution with 0.20—1.0 mol dm^{-3} HCl–30—90 vol% propanone systems. However, the separation of Pb(II) has not been achieved. Kawazu *et al.*[4] performed the separation of Pb(II) from bivalent metal ions by elution with 1.2—1.4 mol dm^{-3} HCl–90 vol% 2 propanol system using Amberyst 15 cation exchanger.

We have selected ethanol, propanone and acetonitrile as water miscible organic solvent and examined the separation of several metal ions. In the HCl–propanone systems seven elements could be separated successfully from each other, the separation of Pb(II) being achieved. In the HCl–acetonitrile and –ethanol systems, neither Zn(II)–Pb(II) or Co(II)–Mn(II) could be separated. In both systems Pb(II) could be separated from bivalent metal ions except Zn(II).

Experimental

The DFS resin was prepared as described previously.[1] 1 cm^3 of sample solution containing 5 mg of metal as nitrate was used. The concentration of organic solvent is expressed in volume percentage and that of HCl in molarity. Procedures for the separation of metal ion mixtures are shown in Figs. 2—4. Metal ions were determined by atomic adsorption spectrometry and are given in mmol/25 cm^3.

TABLE 1. DISTRIBUTION COEFFICIENT IN HCl–ORGANIC SOLVENT MEDIA

Metal	Concentration of acid/mol dm^{-3}															
	0.10				0.20				0.30				0.40			
	Concentration of solvent/vol%															
	20	40	60	80	20	40	60	80	20	40	60	80	20	40	60	80
Propanone																
Cd(II)	300	160	20	0	35	5	0	0	20	0	0	0				
Zn(II)	420	380	150	20	190	130	10	0	60	0	0	0				
Pb(II)	670	630	180	40	200	140	30	0	80	0	0	0				
Mn(II)					190	250	280	330	200	250	270	290	50	70	100	150
Mg(II)					150	400	410	480	80	170	240	300	50	80	150	210
Cu(II)					300	330	470	1470	170	180	230	180	60	50	40	20
Acetonitrile																
Cd(II)	250	200	25	0	40	10	0	0	20	0	0	0				
Zn(II)	700	620	160	10	200	180	5	0	50	0	0	0				
Pb(II)	650	530	200	25	240	150	25	0	80	30	0	0				
Mn(II)					250	300	350	410	180	250	300	380	60	80	100	160
Mg(II)					320	330	710	930	100	280	280	460	40	80	140	190
Cu(II)					150	190	250	330	120	190	230	190	50	40	30	10
Ethanol																
Cd(II)	110	100	60	5	70	20	5	0	20	0	0	0				
Zn(II)	390	310	200	110	210	180	150	0	50	0	0	0				
Pb(II)	780	690	230	110	200	190	150	10	40	10	0	0				
Mn(II)					240	330	480	700	210	220	290	460	20	30	330	400
Mg(II)					500	600	650	730	420	520	550	630	30	50	430	600
Cu(II)					260	280	290	200	300	290	140	120	60	60	50	10

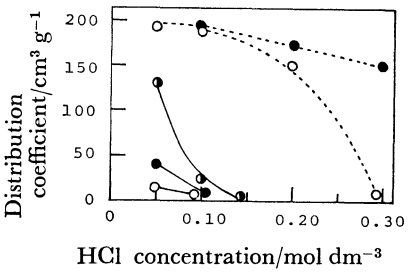

Fig. 1. Distribution coefficients as a function of acid concentration in 95 vol% organic solvent.
——: Propanone, ----: ethanol, ○: Cu(II), ●: Co(II), ◑: Mn(II).

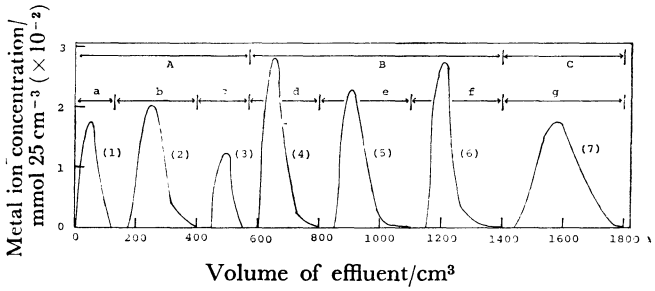

Fig. 2. Elution curves for a seven-component mixture in HCl–propanone system.
Propanone(vol%); A: 60, B: 95, C: 20, HCl(mol dm⁻³); a: 0.10, b: 0.14, c: 0.20, d: 0.025, e: 0.05, f: 0.10, g: 0.40,
(1): Cd(II), (2): Zn(II), (3): Pb(II), (4): Cu(II), (5): Co(II), (6): Mn(II), (7): Mg(II), yield of metal ion: over 99.0 wt%, column: 8ϕ×250 mm, flow rate: 2.5 cm³/min

Results and Discussion

Distribution Coefficient. The distribution coefficients of metal ions were measured in HCl–organic solvent media in the acid concentration range 0.10—0.40 mol dm⁻³ and solvent concentration range 20—80 vol% (Table 1). The coefficients of Cd(II), Zn(II), and Pb(II) decreased in the HCl concentration range 0.10—0.30 mol dm⁻³ with increase in solvent concentration. The coefficient of Cu(II) in 0.40 mol dm⁻³ HCl decreased with increase in solvent concentration. The coefficients of Mn(II) and Mg(II) gave the lowest value in 20 vol% organic solvent at 0.40 mol dm⁻³ HCl. The coefficients of Co(II), Ni(II), and Ca(II) were higher than under the conditions given in Table 1.

For the organic solvent concentration of 95 vol%, the coefficients of Cd(II), Zn(II), and Pb(II) were nearly 0 in 0.025 mol dm⁻³ HCl. On the other hand, in the HCl–propanone and –acetonitrile systems the coefficients of Cu(II), Co(II), and Mn(II) decreased sharply from 0.025 to 1.0 mol dm⁻³ HCl. In the HCl–ethanol system only the adsorption of Cu(II) decreased significantly from 0.10 to 0.30 mol dm⁻³ HCl. The results for Cu(II), Co(II), and Mn(II) in propanone and ethanol systems are given in Fig. 1.

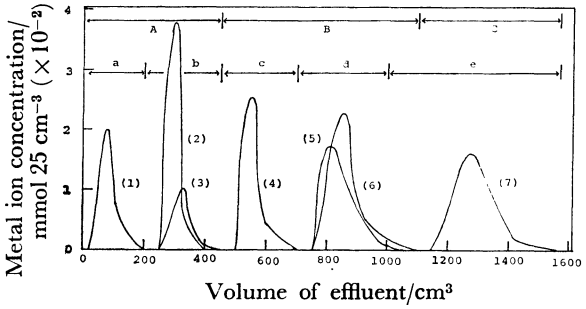

Fig. 3. Elution curves for a seven-component mixture in HCl–acetonitrile system.
Acetonitrile(vol%); A: 60, B: 95, C: 20, HCl(mol dm⁻³); a: 0.10, b: 0.20, c: 0.05, d: 0.10, e: 0.40, (1): Cd(II), (2): Zn(II), (3): Pb(II), (4): Cu(II), (5): Co(II), (6): Mn(II), (7): Mg(II), yield of metal ion: over 99.0 wt%, column: 8ϕ×250 mm., flow rate: 2.5 cm³/min.

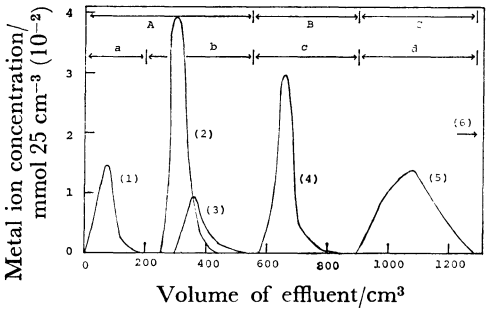

Fig. 4. Elution curves for a seven-component mixture in HCl–ethanol system.
Ethanol(vol%); A: 80, B: 95, C: 20, HCl(mol dm⁻³); a: 0.10, b: 0.20, c: 0.30, d: 0.40, (1): Cd(II), (2): Zn(II), (3): Pb(II), (4): Cu(II), (5): Mg(II), (6): Co(II) and Mn(II), yield of metal ion: over 99.0 wt%, column: 8ϕ×250 mm, flow rate: 2.5 cm³/min.

Separation of Mixtures. Based on the relevant distribution coefficients, several procedures for the separation of Cd(II)–Zn(II)–Pb(II)–Cu(II)–Co(II)–Mn(II)–Mg(II) were developed. Cd(II)–Zn(II)–Pb(II) were stripped consecutively by elution with 0.10—0.20 mol dm⁻³ HCl–60—80 vol% organic solvent systems, then Cu(II)–Co(II)–Mn(II) with 0.025—0.30 mol dm⁻³ 95 vol%, and Mg(II) with 0.40 mol dm⁻³ —20 vol%. The elution curves with HCl–propanone, –acetonitrile, and –ethanol systems are shown in Figs. 2, 3, and 4, respectively.

References

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