Synthesis, Ion-Exchange Properties, and Analytical Applications of Anilinium Zirconium(IV) Phosphate

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A new inorganic ion exchanger, anilinium zirconium(IV) phosphate (AZP), has been prepared under varying conditions. The effects of mixing ratio of reagents and the pH of the mixture on the ion-exchange properties of the material have been studied. The detailed studies, such as ion-exchange capacity, chemical and thermal stabilities, chemical composition, pH titration, and IR analysis were made. Distribution coefficients of metal ions have been studied in water, nitric acid, 1,4-dioxane, aqueous ammonium nitrate, thiourea-nitric acid, and thiourea-hydrochloric acid media. Some analytically important separations of metal ions have been achieved on the small columns of AZP.

Synthesis of new inorganic ion exchangers is always of interest because of their versatility in separation science. Their analytical importance is now firmly established due to high selectivity, thermal stability and resistivity to radiations. The inorganic ion exchangers based on zirconium have been studied. Hasegawa et al.[1] have used cyclohexylammonium form of α-zirconium phosphate in nickel(II) ion-exchange. Kobayashi[2] has synthesized γ-$NH_4ZrH(PO_4)_2$ and investigated ion-exchange properties of γ-$Zr(HPO_4)_2 \cdot 2H_2O$. Hahn and Klein[3] introduced organic amine ions in place of potassium ions in potassium cobalt(II) hexacyanoferrate(II) and found that the amine compounds have excellent exchange properties for ^{137}Cs. Ammonium tin(II) hexacyanoferrate(II),[4] ammonium tin(IV) hexacyanoferrate(II),[5] anilinium tin(IV) phosphate,[6] tin(IV) diethanolamine,[7] and iron(III) diethanolamine[8] have been prepared and reported for the selective separation of metal ions.

To develop a new inorganic ion exchanger, we have synthesized anilinium zirconium(IV) phosphate (AZP) by mixing $ZrCl_2O \cdot 8H_2O$ and $(C_6H_5NH_3)_2HPO_4$. Ion exchange characteristics and analytical applications of the new ion-exchange material were investigated.

Experimental

Reagents. Zirconium(IV) dichloride oxide octahydrate (CDH, India), aniline, and orthophosphoric acid (Ranbaxy, India) were used. All other reagents were of analytical grade.

Apparatus. Perkin Elmer model 552 for spectrophotometry, Systronic digital pH meter for pH measurements and Perkin Elmer model 599 B Spectrophotometer for IR studies, were used. An electric rotary shaking machine IEC-56 was used for shaking.

Synthesis of the Exchanger. An excess of aniline (ca. 5 cm^3) was added dropwise to 10 cm^3 of 1 mol dm^{-3} orthophosphoric acid solution with constant stirring to prepare dianilinium hydrogen phosphate $(C_6H_5NH_3)_2HPO_4$. Then dianilinium hydrogenphosphate was dissolved in hot demineralized water (DMW) and diluted to 200 cm^3. This solution was added to 0.1 mol dm^{-3} zirconium(IV) dichloride oxide octahydrate solution with constant stirring, as outlined in Table 1. The pH of the sample solution in each case was adjusted by adding hydrochloric acid solution dropwise. After 24 h the product was filtered, washed with DMW and finally with 25% ethanolic DMW to remove the excess of aniline, and dried at 60 °C. The material broke into small particles when immersed in DMW. The product was ground and sieved to 60—100 mesh and was then treated with 1 mol dm^{-3} nitric acid for 24 h with occasional shaking and renewal of the acid. The excess of the acid was removed after several washings with DMW. Finally, the exchanger (AZP) were obtained by drying the product at 60 °C.

Table 1. Synthesis and Properties of Anilinium Zirconium(IV) Phosphate (AZP)[a]

Sample No.	Volume[b]	pH	Ion-exchange capacity for K^+	Yield
	cm^3		mequiv g^{-1}	g
AZP_1	50	1	1.87	1.22
AZP_2	100	1	1.56	2.36
AZP_3	200	1	1.42	3.48
AZP_4	50	2	1.48	1.21
AZP_5	50	3	1.36	1.17

a) Appearance of precipitate was white gelatinous and appearance of beads after drying at 60 °C, was white. b) Volume of 0.1 mol dm^{-3} zirconium(IV) dichloride oxide solution mixed with 200 cm^3 of 5×10^{-2} mol dm^{-3} $(C_6H_5NH_3)_2HPO_4$ solution.

Ion Exchange Capacity. The ion-exchange capacity of various samples of AZP was determined by the column method (Table 1). One gram exchanger was taken in the column of 7.2 mm (i.d.). The H^+ ions were eluted by percolating 1 mol dm^{-3} potassium chloride solution through the column. The feed was passed until its pH became equal to that of the effluent. The hydrogen ions so eluted were titrated against standardized 0.1 mol dm^{-3} NaOH.

Chemical Analysis. The well-powdered exchanger, AZP_1 (0.5 g) was fused with a 1 : 1 mixture of potassium carbonate and sodium carbonate. The fused mixture was extracted with hot water, the undissolved portion was ignited and weighed as ZrO_2.[9] The diphosphorus pentoxide present in the dissolved portion was precipitated as ammonium molybdophosphate, filtered and determined gravimetrically.[10] To determine the content of aniline, another 0.5 g sample of the exchanger was introduced into a Kjeldahl digestion flask. After digestion, 25 cm^3 potassium

hydroxide solution (50%) was added dropwise. The amine distilled into 50 cm^3 boric acid solution (1%) was titrated with 0.1 mol dm^{-3} HCl using a mixed indicator (Bromocresol Green and Methyl Red).[11]

IR Spectra. IR spectrum of sample AZP_1 was obtained by KBr disc method.

Chemical Stability. A two hundred milligram of the material (AZP_1) was shaken with 20 cm^3 of the various solutions at 30±2 °C for 6 h. Amounts of zirconium, phosphorus and aniline released into the solution were determined spectrophotometrically with Alizarin Red S,[12] molybdovanadophosphoric acid,[13] and iron(III) nitrate,[14] respectively.

pH Titration. Topp and Pepper's[15] method was used for pH titrations using NaOH-NaCl system. A two hundred milligram samples of dry exchanger (AZP_1) were shaken with 20 cm^3 portions of 0.1 mol dm^{-3} (NaCl+NaOH) cationic solution at 30±1 °C. The concentration ratio of NaCl/NaOH was varied from 0.096 mol dm^{-3}/0.004 mol dm^{-3} to 0.004 mol dm^{-3}/0.096 mol dm^{-3}. After equilibrium (6 h), the pH values of the supernatant solution of each flask was recorded and plotted against the meq of OH^- added per 0.2 g of dry exchanger.

Batch Equilibrium. The relative affinities of the exchanger, for 21 metal ions were studied by batch equilibrium[16] on the AZP_1 beads in aqueous media of different systems. A quarter gram of the exchanger (60—100 mesh) was equilibrated with 25 cm^3 cation solutions (4×10^{-3} mol dm^{-3}) at 30±1 °C for 6 h in 100 cm^3 Pyrex conical flask. Then exchanger was allowed to settle for 1 h, a 5 cm^3 aliquot of the supernatant liquid was carefully withdrawn with a pipette. The amounts of Ag^+, Au^{3+}, Cr^{6+}, Pt^{4+}, Ru^{3+}, and Mo^{6+} were determined spectrophotometrically,[17] the rest of the metal ions were determined by EDTA titrations. The distribution coefficients (K_d values) were calculated from the following equation

$$K_d(cm^3\,g^{-1}) = \frac{\text{Amount of metal ion in exchanger phase per gram}}{\text{Amount of metal ion in solution phase per } cm^3}.$$

Column Separations. Quantitative separations of some important metal ions of analytical utility were achieved on the columns of AZP_1. Two grams of the exchanger (60—100 mesh) was taken into a glass column of i.d. of 3.9 mm. The column was first washed with about 20 cm^3 DMW and then the mixture of metal ions having concentration 0.644 to 1.044 mg 10 cm^{-3} was introduced into the column and allowed to be adsorbed. The metal ions were then eluted separately using suitable eluting reagents and determined by EDTA titrations except Ag^+, Au^{3+}, Cr^{6+}, Pt^{4+}, Ru^{3+}, and Mo^{6+} which were determined spectrophotometrically. The flow rate was maintained about 0.2 $cm^3\,min^{-1}$ throughout the elution process.

Results and Discussion

The conditions of synthesis and ion-exchange capacity of AZP are shown in Table 1. The increased pH and volume of 0.1 mol dm^{-3} $ZrCl_2O\cdot8H_2O$ in the synthesis of AZP resulted in decreased ion-exchange capacity, being analogous to anilinium tin(IV) phosphate.[6] The sample AZP_1 prepared by mixing 50 cm^3 of 0.1 mol dm^{-3} $ZrCl_2O\cdot8H_2O$ solution with anilinium phosphate solution at pH 1 showed maximum ion-exchange capacity of 1.87 mequiv g^{-1} (The capacity value is for one gram of dry AZP). The ion-exchange capacity of AZP_1 is higher than that of anilinium tin(IV) phosphate[6] (1.7 mequiv g^{-1}).

The ion-exchange capacity for alkali metals and alkaline earth metals is given in Table 2. The data revealed that the ion-exchanger showed higher capacity for alkali metals than for alkaline earth metals.

In order to check the working temperature range of the ion-exchange material, the ion-exchange capacity for K^+ was determined after drying the material at various temperatures. The results showed that this exchanger could be used upto 100 °C without any loss in ion-exchange capacity; above 100 °C there was a decrease in ion-exchange capacity though the decrease

Table 2. Ion-Exchange Capacity (I.E.C.) of Anilinium Zirconium(IV) Phosphate, AZP_1 for Various Cations

Cation[a]	Equilibrium	I.E.C.
	pH	mequiv g^{-1}
Li^+	6.8	1.36
Na^+	6.8	1.68
K^+	6.8	1.87
Mg^{2+}	6.5	1.15
Ca^{2+}	6.5	1.54
Sr^{2+}	6.2	1.59
Ba^{2+}	6.2	1.70

a) Used as chloride (1 mol dm^{-3}).

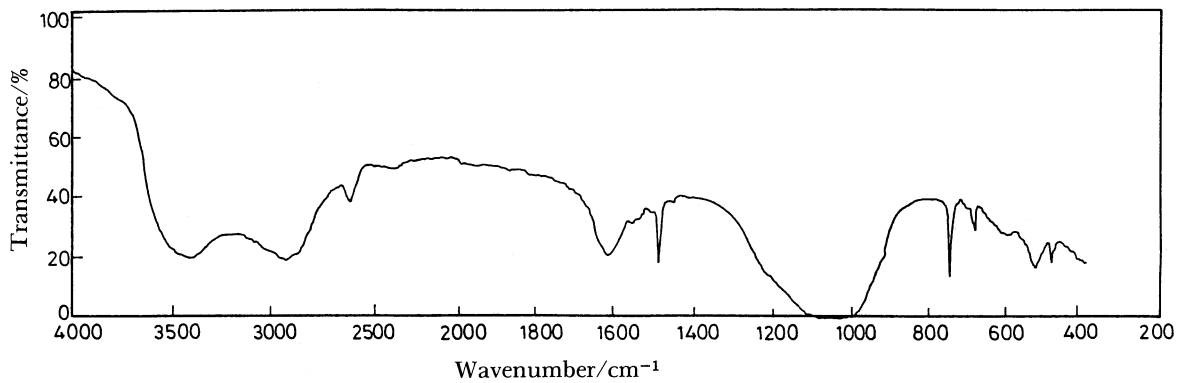

Fig. 1. IR Spectrum of anilinium zirconium(IV) phosphate, AZP_1.

was less than other anilinium exchangers.[4-6]

The data of chemical analysis of AZP_1 are as follows: Zr, 30.7% (calculated 30.6%); N, 4.5% (calculated 4.7%); P, 5.1% (calculated 5.2%).

In the IR spectrum of AZP_1 (Fig. 1) a broad but strong peak in the region 3800—3240 cm^{-1} represents N-H and O-H stretching vibrations. The peak between 1650—1580 cm^{-1} is the characteristic of N-H deformation. A strong band observed at 740 cm^{-1} is due to N-H wagging. The absorption band in the region 1250—950 cm^{-1} represents phosphate vibrations. Hence, the IR spectrum of AZP_1 was in accord with its formula proposed below.

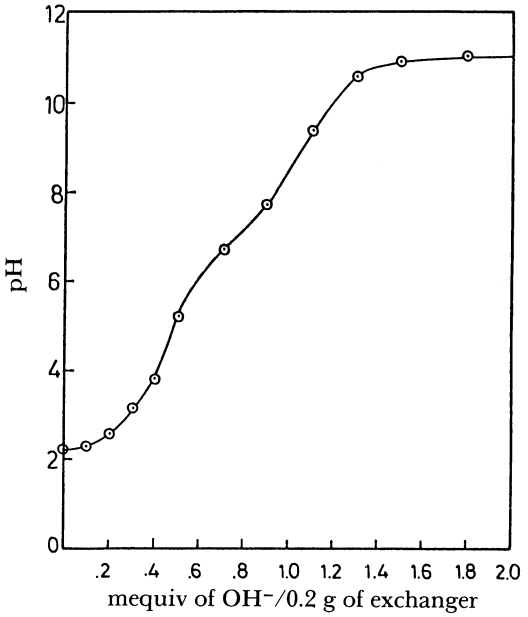

Fig. 2. pH titration curve of anilinium zirconium(IV) phosphate AZP_1.

The results of pH titration curve of AZP_1 are shown in Fig. 2. The total ion-exchange capacity is 3.8 mequiv g^{-1} calculated at the neutralization point.

On the basis of chemical analysis, water content determination (10.8%), pH titration, and IR data, the following chemical formula of AZP_1 has been assigned tentatively.

$$(ZrO_2)_2\,(C_6H_5NH_3)_2HPO_4 \cdot 3.7H_2O.$$

The results of chemical stability of AZP_1 (Table 3)

Table 3. Chemical Stability of Anilinium Zirconium(IV) Phosphate, AZP_1

Solvent	Amounts released into various solutions of 20 $cm^3\,mg^{-1}$		
	Zr	$C_6H_5NH_2$	P
Demineralized water	0.00	0.00	0.00
1,4-Dioxane	0.00	0.00	0.00
Acetone	0.00	0.00	0.00
Methanol	0.00	0.00	0.00
Nitric acid (1 mol dm^{-3})	0.04	0.05	0.02
Nitric acid (4 mol dm^{-3})	1.18	1.24	0.70
Hydrochloric acid (1 mol dm^{-3})	0.16	0.18	0.10
Hydrochloric acid (4 mol dm^{-3})	2.60	2.74	1.42
Sodium hydroxide (0.1 mol dm^{-3})	0.03	3.18	1.68

Table 4. Distribution Coefficients of Some Metal Ions on Anilinium Zirconium(IV) Phosphate, AZP_1

Metal ion	$K_d/cm^3\,g^{-1}$					
	Water	HNO_3 0.1 mol dm^{-3}	1,4-Dioxane 20%	NH_4NO_3 0.1 mol dm^{-3}	NH_4NO_3 0.5 mol dm^{-3}	NH_4NO_3 1.0 mol dm^{-3}
Zn^{2+}	41	9	62	26	14	6
Cd^{2+}	87	13	47	48	25	10
Hg^{2+}	360	167	433	325	290	231
Ba^{2+}	207	83	360	130	91	43
Sr^{2+}	63	46	69	41	29	10
Ca^{2+}	38	12	65	28	17	8
Mg^{2+}	27	7	42	5	4	2
Cu^{2+}	90	53	107	43	36	29
Fe^{3+}	67	25	100	32	25	20
Co^{2+}	155	133	34	130	101	86
Ni^{2+}	47	22	40	22	9	7
Pd^{2+}	200	88	150	87	53	41
Mn^{2+}	33	17	64	15	10	8
Pb^{2+}	400	237	633	235	126	96
Al^{3+}	146	91	3	25	14	8
Ag^{+}	267	180	267	120	69	30
Au^{3+}	3186	838	3209	1953	1327	1106
Cr^{6+}	136	51	92	47	31	18
Pt^{4+}	96	13	55	51	30	19
Ru^{3+}	178	—	198	152	101	82
Mo^{6+}	120	181	359	66	48	36

showed that the material was perfectly stable in water, 1,4-dioxane, acetone, and methanol; and considerably stable in 0.1 mol dm^{-3} NaOH and in nitric acid and hydrochloric acid up to 1 mol dm^{-3}.

Distribution coefficients of 21 metal ions in water, 0.1 mol dm^{-3} nitric acid, 20 percent 1,4-dioxane, and ammonium nitrate solutions (0.1, 0.5, and 1 mol dm^{-3}) are presented in Table 4. The cation-exchange distribution coefficients decreased with increasing in ammonium nitrate concentration from 0.1 to 1 mol dm^{-3}.

The K_d values of some metal ions in thiourea-hydrochloric acid and thiourea-nitric acid systems are given in Tables 5 and 6. Thiourea (Tu) is a neutral ligand as well as a reducing agent. It forms complexes with only a relatively small number of elements in aqueous solutions.[18] The fully coordinated complexes are cationic, and in several cases the central atom is present in an oxidation state lower than that normally encountered in solution.[18] The formation of complexes is generally associated with an increase in the distribution coefficients. This increase may occur over different range of thiourea concentration, depending on the thermodynamic stability of the complexes.[18]

The distribution coefficients for most of metal ions decreased with increasing Tu concentration. In the case of Co^{2+} the slight decrease in K_d values can probably be explained by the fact that Tu has a strong dipole which competes for exchange sites in the exchanger. In other cases, the decrease occurred after the K_d values had reached a maximum. For Hg^{2+}, Pd^{2+}, Ag^{+}, and Au^{3+} the decrease in K_d's became apparent at [Tu]$>$0.1 mol dm^{-3}, but the values remained relatively high. Therefore, these metal ions cannot be effectively eluted with aqueous mixtures of Tu and hydrochloric or nitric acid. Similar behavior on cation-exchange resins was reported by Weinert and Strelow et al.[18-20]

In general, the distribution coefficients and separation factors, $K_d(M)/K_d(M')$, for two cations M and M' for which $K_d(M)>K_d(M')$, decreased with increasing acid concentration at constant Tu concentration. It is, therefore, important to optimize the acid concentra-

Table 5. Distribution Coefficients in Solutions Containing Various Amounts of Thiourea and Nitric Acid

Metal ion	Thiourea	HNO_3/mol dm^{-3}			
	mol dm^{-3}	0.01	0.1	0.2	0.5
Ag^{+}	0.0	236	—	112	53
	0.01	295	186	146	65
	0.1	398	216	190	87
	0.2	158	100	75	28
	0.5	60	32	13	6
	1.0	46	18	8	1
Hg^{2+}	0.0	278	—	70	28
	0.01	300	202	87	39
	0.1	350	248	105	52
	0.2	310	103	67	26
	0.5	208	60	32	18
	1.0	100	29	14	4
Pb^{2+}	0.0	255	—	126	78
	0.01	267	169	143	95
	0.1	295	190	175	116
	0.2	323	246	231	182
	0.5	351	297	290	234
	1.0	408	327	304	269
Cd^{2+}	0.0	24	—	—	—
	0.01	38	18	—	—
	0.1	82	39	—	—
	0.2	103	81	—	—
	0.5	180	111	—	—
	1.0	106	62	—	—
Zn^{2+}	0.0	11	—	1	—
	0.01	13	11	3	—
	0.1	16	14	5	—
	0.2	25	19	8	—
	0.5	30	23	13	—
	1.0	39	24	16	—
Co^{2+}	0.0	187	—	102	—
	0.1	146	57	36	—
	0.2	115	48	28	—
	0.5	76	31	17	—
	1.0	48	29	9	—

Table 6. Distribution Coefficients in Solutions Containing Various Amounts of Thiourea and Hydrochloric Acid

Metal ion	Thiourea	HCl/mol dm^{-3}		
	mol dm^{-3}	0.01	0.1	0.2
Au^{3+}	0.0	—	379	131
	0.01	—	385	117
	0.1	—	397	89
	0.2	—	275	71
	0.5	—	213	60
	1.0	—	128	42
Pd^{2+}	0.0	78	57	39
	0.01	85	72	62
	0.1	70	64	57
	0.2	58	52	45
	0.5	50	40	38
	1.0	42	37	30
Pt^{4+}[a]	0.0	9	4	—
	0.01	11	5	—
	0.1	—	6	—
	0.2	7	5	—
	0.5	6	3	—
	1.0	—	—	—
Ru^{3+}	0.0	16	28	32
	0.01	20	33	45
	0.1	25	37	49
	0.2	32	49	60
	0.5	57	72	90
	1.0	83	109	130
Zn^{2+}	0.0	5	—	—
	0.01	7	—	—
	0.2	10	—	—
	0.5	14	—	—
Co^{2+}	0.0	128	92	40
	0.1	98	66	26
	0.5	42	38	14
	1.0	30	14	8

a) Oxidation state prior to reduction by Tu.

Table 7. Quantitative Separations of Metal Ions on Anilinium Zirconium(IV) Phosphate (AZP_1) Columns

Sample No.	Separation	Amount fed to column	Amount found after elution	Percent of metal ions eluted	Total elution volume	Eluent used
		μg	μg	%	cm^3	
1	Co^{2+}	245	242	98.8	30	0.2 mol dm^{-3} HNO_3-0.5 mol dm^{-3} Tu
	Pb^{2+}	518	511	98.6	40	0.5 mol dm^{-3} HNO_3-0.01 mol dm^{-3} EDTA
2	Ni^{2+}	240	243	101.2	30	1.0 mol dm^{-3} NH_4NO_3
	Co^{2+}	245	242	98.8	30	0.2 mol dm^{-3} HNO_3-0.5 mol dm^{-3} Tu
3	Pt^{4+}	490	486	99.2	40	0.01 mol dm^{-3} HCl
	Pd^{2+}	270	268	99.2	30	0.1 mol dm^{-3} NH_3-0.01 mol dm^{-3} EDTA
4	Cd^{2+}	225	223	99.1	40	0.1 mol dm^{-3} HNO_3
	Ag^{+}	270	265	99.2	30	0.2 mol dm^{-3} HNO_3-0.5 mol dm^{-3} Tu
5	Pt^{4+}	490	485	99.0	40	0.01 mol dm^{-3} HCl
	Ag^{+}	270	266	98.5	30	0.2 mol dm^{-3} HNO_3-0.5 mol dm^{-3} Tu
	Au^{3+}	250	252	100.8	40	2.0 mol dm^{-3} NH_3
6	Zn^{2+}	320	320	100.0	30	0.01 mol dm^{-3} HNO_3-0.1 mol dm^{-3} Tu
	Cd^{2+}	225	222	98.7	40	0.1 mol dm^{-3} HNO_3
	Hg^{2+}	400	394	98.5	40	0.5 mol dm^{-3} HNO_3-0.5 mol dm^{-3} Tu
7	Mg^{2+}	243	243	100.0	30	0.1 mol dm^{-3} NH_4NO_3
	Ca^{2+}	401	396	98.7	40	0.1 mol dm^{-3} HNO_3
	Ba^{2+}	137	138	100.1	40	0.1 mol dm^{-3} HNO_3-1.0 mol dm^{-3} NH_4NO_3

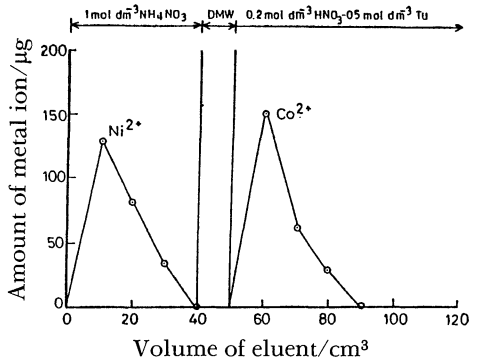

Fig. 3a. Separation of Ni^{2+}-Co^{2+}.

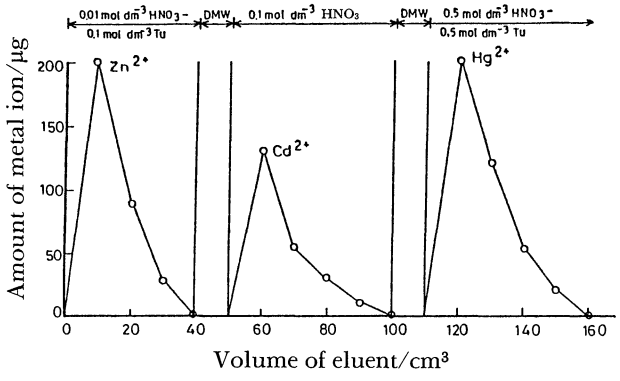

Fig. 3b. Separation of Zn^{2+}-Cd^{2+}-Hg^{2+}.

tion in order to obtain the best separation factors for a particular pair of cations, and to elute M′ with the minimum volume of eluent. The distribution coefficients tended to be lower in hydrochloric acid than in nitric acid.

On the basis of K_d values separations were tried. Those experimentally successfully achieved are reported in Table 7. The order of elution and eluents for Ni^{2+}-Co^{2+}, and Zn^{2+}-Cd^{2+}-Hg^{2+} are presented in Figs. 3a and 3b. It is interesting that no significant tailing was observed during the elution of various metal ions and only small volumes of eluents were required to give compact chromatograms.

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