

Column Chromatographic Separation of Cations by Anion Exchange Chromatography using PAR as Complexing Agent^ψ

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The anion-exchange behaviour of a number of metal-4-(2-pyridylazo)resorcinal (PAR) complexes on Dowex-1-XB (Cl⁻-form) in ethanolic medium has been studied. The distribution coefficients were determined by batch technique for predicting the conditions for the possible separations on column. The effect of pH and different organic solvents on the distribution coefficients has also been studied. The column chromatographic separations achieved were quantitative. The distribution coefficients, column elution behaviour of metal complexes and the results of separation of synthetic mixtures along with elution curves are presented.

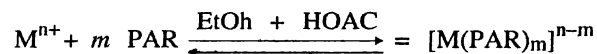
Ion exchange chromatography has proven means of separating metal ions. Korkisch *et al.*^{1,2} reported that efficiency of the ion exchange system can be enhanced to a greater extent by using mixed organic solvents with mineral acids. Furthermore, the use of chelating agents gives high sensitivity, selectivity for better separations³.

4-(2-Pyridylazo)resorcinol (PAR) is very sensitive and selective reagent used widely in many analytical techniques⁴. PAR has been used as pre- or post-column chelating agent in hplc^{2,5}. Noffsinger and Denielson⁵ studied retention characteristics of some metals as their PAR chelates on C₁₈ and amino columns. Whereas use of PAR as chelating agent reported with ion exchange membrane⁷, chelating exchangers with PAR as functional group were prepared and used for metal ion separations⁸. In spite of this wide applicability of PAR, its use as chelating agent prior to the column using synthetic organic ion exchangers has not held attention. Keeping this in view we have taken a systematic study with PAR as chelating agent in the separation of metal ions on synthetic ion exchangers in mixed organic solvents. Here we report the anion exchange chromatographic study employing Dowex 1-X B(Cl⁻-

form; 20-50 mesh) in 80% (v/v) ethanol with varying concentrations (0.10-1.00 mol dm⁻³) of acetic acid media.

Results and Discussion

The separation of metal ions in the presence of PAR and acetic acid depends predominantly on the nature of the complex formed,



The decrease in K_d values of some metal ions may be due to the formation of cationic or neutral complexes. PAR forms stable coloured complexes with all the metal ions under study. The added acetic acid (i) may serve as second solvent and complexing agent and (ii) will lead to lowering of dielectric constant of the medium which in turn results in an increase in attractive forces between ions of unlike charges thereby favouring association or complex formation.

Effect of [acetic acid] on the distribution coefficients : Mn^{II}, Mg^{II} and Ag^I show no sorption in any concentration of acetic acid (Table 1). This may be due to their formation of cationic complexes

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or neutral complexes because the stability constants with PAR are higher in their 1 : 1 metal to PAR ratio rather than 1 : 2. Higher stability constants for Cu^{II}- and Ni^{II}-PAR complexes in 1 : 2 ratio, lessens the tendency of acetate ion to complete with PAR. The same behaviour was found for La^{III} complexes except at 1.00 mol dm⁻³ concentration where La^{III} complex gets precipitated. These metal ions can be separated from moderately and strongly sorbed metal complexes. For Co^{III} complexes there is no change in K_d values in any concentration of acetic acid suggesting non-formation of anionic complexes.

TABLE 1—DISTRIBUTION COEFFICIENTS (K_d) VALUES OF 1 : 2 METAL-PAR COMPLEXES IN VARYING (0.10–1.00 mol dm⁻³) ACETIC ACID AT FIXED (80%, v/v) ETHANOL

Metal ion	Concn. of acetic acid (mol dm ⁻³)					
	0.00	0.10	0.40	0.60	0.80	1.00
Mg ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Al ^{III}	30.6	30.6	18.9	18.0	18.0	16.3
Cr ^{III}	64.8	64.8	42.3	42.3	40.0	50.0
Mn ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fe ^{III}	40.3	40.3	26.2	18.3	18.3	18.3
Co ^{III}	2.7	2.7	2.7	2.7	2.7	2.7
Ni ^{II}	3.5	<1.0	<1.0	<1.0	<1.0	<1.0
Cu ^{II}	<1.0	<1.0	<1.0	<1.0	4.1	4.1
Zn ^{II}	<1.0	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Y ^{III}	3.2	1.8	1.8	1.8	1.8	P
Ag ^I	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cd ^{II}	P	1274.7	1274.7	1274.7	1274.7	1274.7
La ^{III}	11.8	<1.0	<1.0	<1.0	<1.0	P
Hg ^{II}	22.8	29.3	13.4	11.3	2.0	<1.0
Pb ^{II}	293.3	210.0	168.3	138.5	107.0	107.0
Bi ^{III}	111.0	144.5	167.6	167.6	172.9	211.6
Th ^{IV}	4.8	3.4	3.4	3.4	2.1	<1.0
UO ₂ ^{II}	P	4.9	16.1	34.8	>10 ³	>10 ³

P = Precipitated.

Cd^{II} complex which gets precipitated in aqueous ethanol medium, attains higher but constant K_d values in the concentrations from 0.1 to 1.0 mol dm⁻³, showing that the complex formation is completed at lower concentration itself. Whereas in UO₂^{II}, K_d value increases with the increase in acidity suggesting the formation of anionic complex. This sharp increase in sorption is due to increased tendency to shed the water from coordination sphere of UO₂^{II}-PAR complex to accommodate acetate ion. Zn^{II} shows maximum sorption in all concentrations of acetic acid, suggesting that its complexes are fully formed

at lower concentration of acetic acid. Pb^{II}, Cr^{III}, Al^{III}, Hg^{II}, Fe^{III} and Th^{IV} show decrease in their K_d values with the concentration of acid, suggesting ternary separation possibility involving unsorbed complexes and strongly sorbed metal complexes of PAR.

Effect of pH on distribution coefficients : Interestingly in this study, Ag^I which has low sorption at pH 3.5–6.5, attains maximum sorption at pH 9.5 (Table 2). This may be due to its increasing tendency to form stable acetate complex at higher pH even in the presence of PAR. As expected Th^{IV}, Bi^{III}, Pb^{II}, Cr^{III} and Al^{III} get precipitated at pH 6.5 and above, whereas in other cases except Ag^I, only UO₂^{II}, Pb^{II} and Bi^{III} show maximum to moderate sorption leaving possibility of few ternary and quaternary separations.

TABLE 2—DISTRIBUTION COEFFICIENTS (K_d) OF 1 : 2 METAL-PAR COMPLEXES IN 80% ETHANOL AT DIFFERENT pH (3.5–9.5)

Metal ion	pH				
	3.5	4.5	6.5	8.5	9.5
Mg ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0
Al ^{III}	26.4	18.8	12.0	P	P
Cr ^{III}	27.0	47.2	P	P	P
Mn ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0
Fe ^{III}	24.4	33.2	<1.0	10.8	19.0
Co ^{III}	2.7	P	12.1	2.7	7.3
Ni ^{II}	<1.0	P	P	<1.0	7.4
Cu ^{II}	<1.0	1.5	2.8	<1.0	7.0
Zn ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0
Y ^{III}	2.5	1.1	1.1	<1.0	P
Ag ^I	<1.0	<1.0	15.5	62.6	>10 ³
Cd ^{II}	P	P	P	61.2	18.4
La ^{III}	3.2	2.5	2.5	11.3	P
Hg ^{II}	5.0	<1.0	2.0	14.6	9.3
Pb ^{II}	210.0	13.2	13.2	P	P
Bi ^{III}	80.0	104.4	P	P	P
Th ^{IV}	4.1	7.2	P	P	P
UO ₂ ^{II}	>10 ³	>10 ³	10.0	2.7	P

P = Precipitated.

Effect of organic solvents : The results of the effect of different organic solvents on the distribution coefficients of ethanolic medium are shown in Table 3. DMF, DMSO and THF unlike other solvents, are competing with solid anion exchanger in exchanging the charged complexes as liquid ion exchanger, as described by Korkisch⁹, thereby extract-

ing the metal complexes. The effective change in K_d values in different solvents may be due to the change in dielectric constants and dipole moments¹⁰.

TABLE 3—DISTRIBUTION COEFFICIENTS (K_d) OF 1 : 2 METAL-PAR COMPLEXES IN DIFFERENT ORGANIC SOLVENTS AT FIXED (1.00 mol dm⁻³) ACID CONCENTRATION

Metal ion	Organic solvent 80% (v/v)					
	Ethanol	Methanol	DMSO	DMF	THF	Acetone
Mg ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Al ^{III}	16.3	<1.0	<1.0	<1.0	28.2	4.7
Cr ^{III}	50.0	11.4	85.2	50.0	140.0	35.8
Mn ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fe ^{III}	18.3	7.7	2.5	12.4	156.7	21.7
Co ^{III}	2.7	4.9	3.4	<1.0	<1.0	14.2
Ni ^{II}	<1.0	4.2	<1.0	<1.0	<1.0	<1.0
Cu ^{II}	4.1	4.1	<1.0	<1.0	<1.0	1.5
Zn ^{II}	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³	>10 ³
Y ^{III}	P	<1.0	<1.0	<1.0	<1.0	<1.0
Ag ^I	<1.0	<1.0	<1.0	P	<1.0	<1.0
Cd ^{III}	1247.7	1274.7	57.4	222.9	29.2	222.9
La ^{III}	P	<1.0	<1.0	<1.0	<1.0	<1.0
Hg ^{II}	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pb ^{II}	107.0	85.0	116.2	43.3	98.9	138.5
Bi ^{III}	211.6	306.0	<1.0	P	>10 ³	113.7
Th ^{IV}	<1.0	<1.0	29.0	39.2	21.2	<1.0
UO ₂ ^{II}	>10 ³	>10 ³	>10 ³	P	>10 ³	>10 ³

P = Precipitated.

In order to understand the possibility of separation, the batch experiment data of K_d values of different metal-PAR complexes were tried on column.

Ternary separations : Synthetic mixtures from Hg^{II}, Th^{IV} or Co^{III}-Fe^{III} or Al^{III}-Zn^{II} were prepared by mixing appropriate metal ion solution. The feed was added on the top of the column. After sorption, a volume of 70 cm³ for Hg^{II}, 100 cm³ for Th^{IV} and 130 cm³ for Co^{II} was enough (including 25 cm³ feed) to recover them quantitatively. Al^{III} and Fe^{III} complexes followed this with increasing the eluent to ~180 cm³, whereas Zn^{II} complex which is strongly sorbed and not eluting with excess of eluting agent, is tried with 4 mol dm⁻³ HCl for full recovery of Zn^{II}. The analytical results are shown and the chromatograms (Fig. 1).

Quaternary separations : The feed in quaternary mixtures from Mn^{II}, Mg^{II} or Ni^{II}-Fe^{III} or Cr^{III}-Bi^{III}-Zn^{II} were fed on top of the column. After sorption the column was washed with feed base

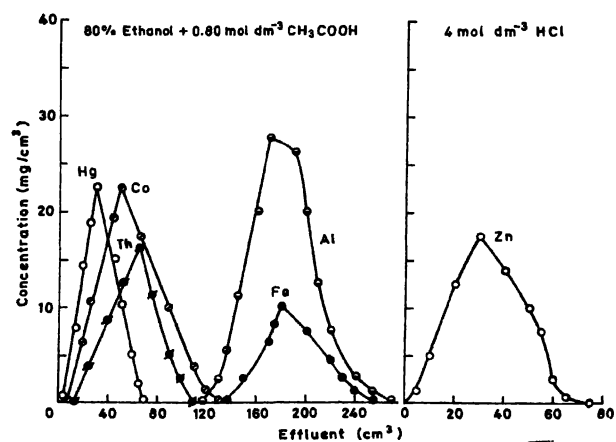


Fig. 1

solution to collect Mn^{II}, Mg^{II} or Ni^{II}. Cr^{III} or Fe^{III} were collected with the same eluent in extended elution. Bi^{III} was eluted with large excess of feed base. Whereas strongly sorbed Zn^{II} complex was eluted with 4 mol dm⁻³ HCl using 75 cm³. The effluents in both the cases were collected in 10

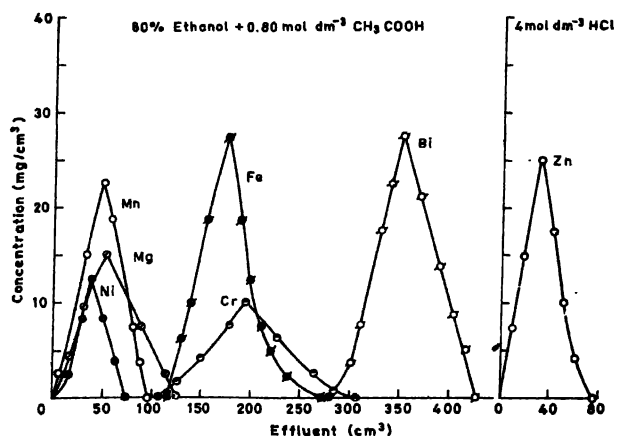


Fig. 2.

ml fractions and their metal content were determined as described. The analytical results for synthetic mixtures are shown in the chromatograms (Fig. 2).

Experimental

Stock solutions (0.10 mol cm⁻³) of all the metal ions were prepared from their nitrates or chlorides. Fe^{III}, Hg^{II} and Bi^{III} nitrates were prepared afresh adding sufficient amount of acid. All the reagents and metal salts used were of A.R. grade. The metal solutions were standardised by the usual methods.

PAR (Loba) stock solution (0.01 mol dm^{-3}) was prepared by direct weighing. In all the experiments redistilled ethanol (E. Merck) was used.

Strongly basic anion exchanger Dowex 1-X8 (Cl^- -form; 20–50 mesh) was washed with $\sim 1.0 \text{ mol dm}^{-3}$ HCl and 1.0 mol dm^{-3} NaOH solution alternatively and finally with water. It was converted to Cl^- form by treating with 2.0 mol dm^{-3} HCl, the excess acid removed by washing with water, and the resin was dried by suction. The capacity of the resin was found to be 3.10 meq/g .

Mixture of 80% (v/v) ethanol with varying concentrations ($0.10\text{--}1.00 \text{ mol dm}^{-3}$) of acetic acid and different concentrations of HCl or HNO_3 were used.

A Beckman 171 pH meter was used for pH measurements.

Procedure : The conditioned resin (Cl^- -form) (1.0 g) was put into the mixture of metal ion solution. Varying concentrations ($0.10\text{--}1.00 \text{ mol dm}^{-3}$) of acetic acid in 80% (v/v) ethanol and PAR were then added in the order (total volume was fixed to 25 cm^3) and shaken on a Microid shaker (Griffin and George) for 30 min. The resin was then filtered off and metal ion determined titrimetrically and/or spectrometrically with a Spikol-11 spectrophotometer. The aliquot of the filtrate was directly fed in to spectrophotometer without any addition of the reagent. The experiments were carried out in 1 : 2 metal to PAR ratio. The distribution coefficients (K_d) were calculated. The relative experimental error in the determination of K_d values was found between ± 2 to $\pm 5\%$.

Column chromatography : A slurry of well-washed and purified anion exchanger (in deionised water) was transferred to a column (about $65 \text{ cm} \times 0.5 \text{ cm}$ dia). The height of the resin bed was maintained at $\sim 8 \text{ cm}$ and the bed was treated with 80% (v/v) ethanol – 0.80 mol dm^{-3} acetic acid mixture. The feed (25 cm^3) was prepared by mixing measured quantities of the separable metal ions in their 1 : 2 ratio complexes with PAR in ethanol – 0.80 mol dm^{-3} acetic acid medium. This feed was passed through the column at a flow rate of $1.5 \pm 0.3 \text{ cm}^3 \text{ min}^{-1}$. The effluents were collected

in 10 cm^3 fractions and the metal content was estimated titrimetrically with EDTA and/or spectrophotometrically.

Regeneration of used resin : The resin was treated with water then kept in acidified EDTA with occasional stirring for 24 h and finally washed with water. Regeneration was done by treating the resin alternatively with 2 mol dm^{-3} HCl and 2 mol dm^{-3} NaOH followed by water-rinse in each step. The resin was finally converted to chloride-form by treating with $\sim 2 \text{ mol dm}^{-3}$ HCl.

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References

1. J. KORKISCH, P. ANTAL and F. HECHT, *J. Inorg. Nucl. Chem.*, 1960, **14**, 247, 251; G. E. JANAUR and J. KORKISCH, *J. Chromatogr.*, 1962, **8**, 510.
2. J. KORKISCH and F. TERA, *J. Inorg. Nucl. Chem.*, 1960, **15**, 177; *J. Chromatogr.*, 1962, **7**, 564.
3. J. E. DINUNZIO, R. W. YOST and E. K. HUTCHISON, *Talanta*, 1985, **32**, 803.
4. R. G. ANDERSON and G. NICKLESS, *Analyst*, 1967, **92**, 207; S. SHIBATA in "Chelates in Analytical Chemistry", eds. H. A. FLASCHKA and A. J. BARNARD, JR., Marcel Dekker, New York, 1976, Vol. 4; H. HOSHINO, T. YOTYANAGI and K. AOMURA, *Bunseki Kagaku*, 1978, **27**, 315; D. A. ROSTON, *Anal. Chem.*, 1984, **109**, 281; X. ZHANG, X. ZHU and C. LIN, *Talanta*, 1986, **33**, 838; C. BAIOCCHI, F. CANTONE, A. MARCHELTO, M. C. GENNARO, E. MENTASTI and C. SARZANINI, *Chromatographia*, 1987, **23**, 736.
5. J. B. NOFFSINGER and N. D. DENIELSON, *J. Liq. Chromatogr.*, 1986, **9**, 2165.
6. F. I. LABANOV, G. K. NURTAIEVA and E. E. ERGOZHIN, *Izv. Akad. Nauk. Kaz. SSR Ser. Khim.*, 1983, 36 (*Chem. Abstr.*, 1983, **98**, 2091740).
7. E. ECCLES and F. VERNON, *Anal. Chim. Acta*, 1973, **66**, 231; K. BRAJTER and E. DEBEK-ZLOTORZYNSKA, *Analyst*, 1988, **113**, 1571; X. MAO, F. TANG, Y. CHEN and M. ZHONG, *Huaxue Shiji*, 1986, **8**, 269 (*Chem. Abstr.*, 1987, **106**, 55520).
8. J. KORKISCH, *Nature*, 1966, **210**, 626; *Sep. Sci.*, 1966, **1**, 159.
9. Y. MARCUS and A. S. KERTES, "Ion Exchange and Solvent Extraction of Metal Complexes", Wiley-Interscience, London, 1969.