

Anion Exchange Separation of Some Metal Ions in Aqueous Acetone-Acetic Acid Media

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The anion exchange characteristics of eight metal ions in aqueous-acetone-acetic acid media using Dowex 21-K in chloride form have been reported. The values of distribution coefficients have been evaluated. The synthetic binary and ternary mixtures were separated at suitable elution conditions.

CARBOXYLIC acid media have shown great potential for the separation of metal ions¹⁻⁶. The distribution of metal ions between an anion exchange resin and anhydrous or partially non-aqueous solvents has only recently been studied. Anion exchange distribution studies with 15 metal ions using sodium nitrite in aqueous and aqueous methanolic solutions were carried out by Bhatnagar and Jain⁷.

Since acetone is the most effective solvent⁸, a detailed study of adsorption characteristics of eight metal ions, Co(II), Ni(II), Zn(II), Mn(II), Mg(II), Ca(II), Cu(II) and Cd(II), have been investigated in aqueous acetone-acetic acid media. The distribution coefficients of these metal ions at different percentages of acetone are determined. The data has been used to develop methods of separation of binary and ternary mixtures of the metal ions.

Experimental

Ion exchange resin : An anion exchange resin, Dowex-21 K (20-50 mesh) in chloride form was used for all anion exchange distribution studies. The air dried resin (~25°) had a capacity of 3.6 meq/g and a moisture content of ~20%.

Metal ion solutions : The metal salt solutions were prepared by dissolving their chlorides (B.D.H., A.R. grade) in distilled water to give 0.05 M solutions in aqueous medium. The Co(II), Ni(II), Zn(II), Mn(II), Mg(II), Ca(II) and Cd(II) contents of the solution were estimated titrimetrically with disodium EDTA using appropriate metal indicator⁹. Cu(II) was estimated by iodometric method⁹.

Acetone-water-acetic acid mixtures : The mixtures were prepared so that the amount of acetone and water was expressed as percentage by volume and the acetic acid concentration as molarity.

Determination of distribution coefficient : The distribution studies were performed in glass stoppered Corning Erlenmeyer flasks (250 ml) with exactly 1 g of the resin and 50 ml of the solution, containing the same quantity of the metal ion (0.05 M) for

aqueous and different aqueous acetone-acetic acid media. Batches were equilibrated by shaking for 24 hr. Each solution was then analysed for the metal ion. The weight distribution coefficients (K_D) were calculated from the relation

$$K_D = \frac{\text{meq. metal per g dry resin}}{\text{meq. metal per ml solution}}$$

The results are tabulated in Table 1.

TABLE 1—ANION EXCHANGE DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE-ACETIC ACID (3 M) MEDIA ON DOWEX 21-K (Cl⁻)

Ion	Acetone concentration % (v/v)				
	0	20	40	60	80
Co(II)	52	56	56	56	1215
Ni(II)	N.A.	3	5	7	24
Zn(II)	18	45	94	421	4698
Mn(II)	N.A.	N.A.	8	10	13
Mg(II)	N.A.	N.A.	N.A.	N.A.	N.A.
Ca(II)	51	51	44	36	23
Cu(II)	3	15	15	21	44
Cd(II)	72	120	198	513	1080

N.A. = No Adsorption.

Separation of mixtures : Pyrex glass chromatography columns of 50 ml capacity were used. The column was packed by a slurry of 20 g soaked resin. The feed (10 ml) was prepared by mixing standard solutions of metal ions. It was then passed through the resin bed. The metal ions were eluted by eluting agents as shown in Tables 2-3. The rate of flow was adjusted to 1.0 ml/min. The metal ions were determined in 10 ml effluent fractions.

Results and Discussion

Measurements of the batch distribution coefficients (K_D) offers a systematic method of selecting elution conditions. To separate two metals, the elution conditions are selected in such a manner that one of the metals has a high distribution coefficient and will thus be strongly retained by the column. The distribution coefficient of the other metal should

be low so that the metal ion may be eluted with small volume of eluting agent.

The distribution coefficients (Table 1) of Zn(II) and Cd(II) increase with increasing acetone concentrations. This trend is in accordance with the fact that the presence of a less polar solvent mixed with water enhances the extent of complex formation^{8,10-13}.

The distribution coefficients of Ni(II), Mn(II), Mg(II), Cu(II) and Ca(II) are low at all concentrations of acetic acid showing that the less stable complex or no complex formation takes place in these metal ions. The distribution coefficients of Co(II) in 0.05 M and 1 M acid at all percentages of acetone and in 2 M, 3 M acid upto 60% acetone show no measurable change and the K_D value (~54) shows approximately equal distribution of metal ion in solution and resin phases. Co(II) shows maximum K_D at 80% acetone-3 M acetic acid medium. It forms a blue coloured anionic complex. It is observed that the blue colour of the solution changes to its original pink colour on addition of water,

TABLE 2—QUANTITATIVE SEPARATION OF SYNTHETIC BINARY MIXTURES (FIRST ION IN THE MIXTURE IS ELUTED, WHILE THE SECOND ION IS RETAINED)

Mixture	Metal ion eluted	Eluting agent	m. moles taken	m. moles found
1. Mg(II) + Co(II)	Mg(II)	a	0.176	0.179
	Co(II)	b	0.244	0.244
2. Cu(II) + Co(II)	Cu(II)	a	0.248	0.247
	Co(II)	b	0.244	0.244
3. Mn(II) + Co(II)	Mn(II)	a	0.211	0.200
	Co(II)	b	0.244	0.244
4. Ca(II) + Co(II)	Ca(II)	a	0.184	0.172
	Co(II)	b	0.244	0.244
5. Ni(II) + Co(II)	Ni(II)	a	0.280	0.255
	Co(II)	b	0.244	0.244
6. Cu(II) + Cd(II)	Cu(II)	c	0.245	0.245
	Cd(II)	d	0.277	0.278
7. Mn(II) + Cd(II)	Mn(II)	c	0.211	0.200
	Cd(II)	d	0.277	0.278
8. Co(II) + Cd(II)	Co(II)	e	0.292	0.288
	Cd(II)	d	0.277	0.288
9. Ni(II) + Cd(II)	Ni(II)	e	0.280	0.255
	Cd(II)	d	0.277	0.278
10. Mg(II) + Cd(II)	Mg(II)	c	0.256	0.255
	Cd(II)	d	0.277	0.278
11. Ca(II) + Cd(II)	Ca(II)	c	0.258	0.252
	Cd(II)	d	0.277	0.278
12. Cu(II) + Zn(II)	Cu(II)	a	0.248	0.240
	Zn(II)	g	0.250	0.251
13. Co(II) + Zn(II)	Co(II)	c	0.292	0.288
	Zn(II)	g	0.296	0.282
14. Mn(II) + Zn(II)	Mn(II)	e	0.211	0.200
	Zn(II)	g	0.250	0.244
15. Ni(II) + Zn(II)	Ni(II)	e	0.280	0.255
	Zn(II)	g	0.250	0.251
16. Mg(II) + Zn(II)	Mg(II)	c	0.233	0.223
	Zn(II)	g	0.250	0.251
17. Ca(II) + Zn(II)	Ca(II)	e	0.263	0.252
	Zn(II)	g	0.250	0.244

a = 80% acetone-3 M acetic acid.
 b = distilled water.
 c = 60% acetone-0.5 M acetic acid.
 d = 5% acetone-0.1 M acetic acid.
 e = 80% acetone-0.5 M acetic acid.
 f = 60% acetone-3 M acetic acid.
 g = 20% acetone-1 M acetic acid.

TABLE 3—QUANTITATIVE SEPARATION OF THE SYNTHETIC TERNARY MIXTURES

Mixture	Metal ion eluted	Eluting agent	m. moles taken	m. moles found
1. Ni(II) + Co(II) + Zn(II)	Ni(II)	a	0.280	0.255
	Co(II)	f	0.244	0.244
	Zn(II)	g	0.250	0.251
2. Mg(II) + Co(II) + Zn(II)	Mg(II)	a	0.176	0.179
	Co(II)	f	0.244	0.244
	Zn(II)	g	0.250	0.251
3. Cu(II) + Co(II) + Zn(II)	Cu(II)	a	0.245	0.245
	Co(II)	f	0.244	0.244
	Zn(II)	g	0.250	0.251
4. Mn(II) + Co(II) + Zn(II)	Mn(II)	a	0.211	0.200
	Co(II)	f	0.244	0.244
	Zn(II)	g	0.250	0.251
5. Ca(II) + Co(II) + Zn(II)	Ca(II)	a	0.184	0.172
	Co(II)	f	0.244	0.244
	Zn(II)	g	0.250	0.251
6. Ni(II) + Co(II) + Cd(II)	Ni(II)	a	0.280	0.255
	Co(II)	f	0.244	0.244
	Cd(II)	d	0.277	0.278
7. Mg(II) + Co(II) + Cd(II)	Mg(II)	a	0.176	0.179
	Co(II)	f	0.244	0.244
	Cd(II)	d	0.277	0.278
8. Cu(II) + Co(II) + Cd(II)	Cu(II)	a	0.245	0.245
	Co(II)	f	0.244	0.244
	Cd(II)	d	0.277	0.278
9. Ca(II) + Co(II) + Cd(II)	Ca(II)	a	0.184	0.172
	Co(II)	f	0.244	0.244
	Cd(II)	d	0.277	0.278
10. Mn(II) + Co(II) + Cd(II)	Mn(II)	a	0.211	0.200
	Co(II)	f	0.244	0.244
	Cd(II)	d	0.277	0.278

* a = 80% acetone-3 M acetic acid.
 b = distilled water.
 c = 60% acetone-0.5 M acetic acid.
 d = 5% acetone-0.1 M acetic acid.
 e = 80% acetone-0.5 M acetic acid.
 f = 60% acetone-3 M acetic acid.
 g = 20% acetone-1 M acetic acid.

showing the stability of the complex at 80% acetone-3 M acetic acid only. The standard solutions of the metal ions under study and Co(II) were prepared in this medium and the respective separation of mixtures were carried out. Similar to Co(II), Zn(II) and Cd(II) show maximum K_D at 80% acetone-3 M acetic acid. All these metal ions have been considered to be forming quite stable complexes. Very high values of K_D for Zn(II) are indicative of this fact. Zn(II) shows highest K_D values at all concentrations of acetic acid and at almost all percentages of acetone. Thus Zn(II) complexes were the most preferred complex species for Dowex 21-K.

Of the other metal ions, Cd(II) and Co(II) were much preferred by this resin as compared to ions such as Ca(II), Mg(II), Cu(II), Ni(II) and Mn(II). From the K_D data of the metal ions, the following selectivity sequence for the anion exchanger studied can be given :

- (1) Zn(II) > Cd(II) > Co(II) > Ca(II) > Cu(II) > Mg(II) ≈ Ni(II) ≈ Mn(II) in 0.5 M acid, 80% acetone + 2/3 M acid.
- (2) Cd(II) > Zn(II) > Co(II) > Ca(II) > Cu(II) in 1,2,3 M acid.

The results of quantitative separation of synthetic binary and ternary mixtures are presented in Tables 2 and 3. It is observed that Co(II) can be separated from Mg(II), Cu(II), Mn(II), Ca(II) and Ni(II). These metals are eluted by 80% acetone-3 *M* acetic acid, retaining Co(II) on the resin. After complete elution of these metal ions Co(II) is stripped off by distilled water. The use of distilled water for elution of Co(II) and ultimately for separation of mixtures is one of the merits of these results. Cd(II) can be separated from Cu(II), Mn(II), Co(II), Ni(II) and Mg(II). Zn(II) can be separated from Cu(II), Co(II), Mn(II), Ni(II), Mg(II) and Ca(II).

The results of the separation of the ternary mixtures (Table 3) indicate that one of Ni(II), Mg(II), Cu(II), Mn(II), Ca(II) ions is eluted first, as these are having lower distribution coefficients (Table 1) than Co(II). The distribution coefficients of Co(II) are lower than Zn(II) and Cd(II) at respective concentrations of acetone and acetic acid and hence it is eluted in preference to Zn(II) or Cd(II) by suitable eluting agent. Zn(II) or Cd(II) is eluted last from ternary mixtures.

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References

1. I. D. FRIDMAN and I. N. YUDINAZH, *Fizikhim. (Leningrad)*, 1959, **32**, 1914.
2. S. A. BROOKSBANK and G. W. LEDDICOTTE, *J. Phys. Chem.*, 1963, **57**, 819.
3. M. QURESHI and W. HUSAIN, *Talanta*, 1971, **18**, 399.
4. V. P. MEHTA and S. M. KHOPKAR, *Chromatographia*, 1978, **11**, 586.
5. M. QURESHI, K. G. VARSHNEY and R. C. KAUSHIK, *Anal. Chem.*, 1973, **45**, 2433.
6. K. SOBHANA, P. MADHAVANKUTTY and C. P. SAVARIAR, *J. Indian Chem. Soc.*, 1978, **55**, 458.
7. R. P. BHATNAGAR and N. C. JAIN, *J. Indian Chem. Soc.*, 1980, **57**, 168.
8. J. S. FRITZ and T. A. RETTIG, *Anal. Chem.*, 1962, **34**, 1562.
9. A. I. VOGEL, "A Text Book of Quantitative Inorganic Analysis", Longmans Green, London, 1961.
10. R. W. GABLE and N. P. STROBEL, *J. Phys. Chem.*, 1965, **60**, 513.
11. J. S. FRITZ and D. J. PIETRZYK, *Talanta*, 1961, **8**, 143.
12. D. J. PIETRZYK and D. L. KIZSER, *Anal. Chem.*, 1965, **37**, 233.
13. D. J. PIETRZYK and D. L. KIZSER, *Anal. Chem.*, 1965, **37**, 1978.