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Anion-Exchange Behaviour of Some Divalent Metal Ions in Nitric Acid-Organic Solvent on Amberlite IRA-410

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The adsorbability of the bivalent metals Zn(II), Mg(II), Co(II), Ni(II), Cd(II) and Cu(II) on the strong base anion exchange resin Amberlite IRA–410 in nitrate form, from mitric acid-organic solution media were investigated. The determination of the distribution coefficients was carried out in 0.05 M–2.5 M HNO_3 solution containing 0, 40, 60 and 90% (vol/vol) organic solvents. The effect of concentration of organic solvents as well as acidity on the distribution coefficient values show the importance of such media as complexing agents. Distribution coefficients were a function of both the volume percentage of organic solvents and of the nitric acid concentration. Adsorption measurements were made at constant temperature using a batch technique and employing complexometric titration and spectrophotometric analysis.

INTRODUCTION

Earlier, the influence of the organic solvent on the anion exchange behaviour of the elements from aqueous-solution has been investigated by several authors[1-5].

The most frequently reported type of behaviour is a large increase of the adsorbability with decreasing water content. Greater is this effect, the less water is present in the solvent mixtures.

In some cases, the distribution is only slightly affected by small quantities of water present in the media, as was found by Kennedy and Davies[6], for the sorption of Co(II) in acetone media. However, in a number of other systems, the percentage of organic solvents markedly increases the sorbability. Such a maximum was observed for Sc(II) and Mn(II) in HCl-ethanol[7], and for lanthanide ions in HNO_3-ethanol or HNO_3-iso-propanol[8,9].

Ion-exchange distribution of tri- and divalent metal ions has been investigated to aqueous-nitric acid-methanolic media on Dowex 1×4 exchanger; increasing the concentration of methanol leads to increased complex formation and changes in K_d-values[3]. Adscription on the adsorption behaviour of some divalent metal ions towards strongly basic anion exchanger in nitrite-methanolic solution and possible separation in such media was reported[10].

The present paper deals with the investigation of the adsorbability of the divalent metals Zn(II), Mg(II), Ni(II), Co(II), Cd(II) and Cu(II) ions on the strong base anion exchange resin Amberlite IRA–410 (420–595) in nitrate form. Some separation possibilities are discussed on the basis of the distribution data.

EXPERIMENTAL

Reagents: The resin used was the strong base anion exchanger Amberlite IRA–410 (420–595 mesh) in the nitrate form, 4.25 mequiv/g dry resin, analytical reagent quality (Rohm & Hass Co, Philadelphia, Pa.).

The salt solutions used were prepared form their nitrate form to give 0.005M solution in aqueous and aqueous-organic media. Absolute organic solvents, and HNO_3 BDH (AnalaR) were used.

The concentrations of Zn(II), Co(II), Ni(II), Mg(II), Cd(II) and Cu(II) ions were determined titrimetrically with EDTA–disodium salt, using a suitable indicator and buffer[11–14]. While in case of separation procedure (Beckman Model B spectropootometer type) 1 cm cell was used.

Determination of K_d: The distribution studied were carried out in a glass-stoppered flask 100 ml, and 0.005 M metal ion solution 50 ml in aqueous and aqueous-organic HNO_3 media. Batches were equilibrated by shaking for 24 hrs. All the experiment were carried out at 25°C ± 0.1°C. Each system was analysed for the metal ions. The distribution coefficients (K_d) values were calculated from the relation(1–3)

$$K_d = \frac{\text{mequiv. metal/g of resin}}{\text{mequiv. metal/ml of solution}}$$

The column separation technique was carried out, the same as pointed by several authors[15–16].

RESULTS AND DISCUSSION

The effect of organic solvents on the distribution coefficients of metal ions in presence of Amberlite IRA–410 anion exchanger. The solutions prepared contain the metal nitrate, nitric acid of variable concentrations and varying proportions of organic solvent and water. The organic solvents used are isopropanol, ethanol, methanol and acetone.

The first series of experiments includes the determination and evaluation of K_d values for the studied metal ions Zn(II), Cd(II), Ni(II), Co(II), Mg(II) and Cu(II) at concentration of 0.005 M, in presence of different concentrations of HNO_3 at 25°C in aqueous media.

Results given in Table (1) show that at 0.1 M HNO_3 the K_d values for the studied metal ions are zero; with further increase in HNO_3 concentration, the K_d values increase in general. Such trend indicates an increase in the tendency of complex formation at higher concentration of the nitric acid.

TABLE 1

K_d VALUES OF STUDIED METAL IONS IN AQUEOUS-NITRATE MEDIA ON AMBERLITE IRA-410 ANION EXCHANGE RESIN 0.005 M METAL ION

Metal ions	Nitric acid; M						
	0.1	0.5	1.0	1.5	2.0	2.5	3.0
Zn(II)	0.0	0.0	2.1	4.66	7.66	12.33	45.20
Mg(II)	0.0	0.0	0.0	9.33	55.80	66.90	98.50
Cd(II)	0.0	0.0	0.0	2.50	8.99	14.67	65.25
Cu(II)	0.0	2.33	4.00	15.40	65.30	75.32	126.20
Co(II)	0.0	0.0	0.0	6.50	25.23	33.50	73.30
Ni(II)	0.0	1.62	2.2	7.85	54.30	65.45	78.55

However, the differences in the values of K_d for the studied ions are not so great to affect possible effective separations in aqueous media at any of the studied concentrations of nitric acid.

In continuation to the systematic survey of the Amberlite IRA-410 anion exchanger behaviour, with the divalent metal ions under investigation, its adsorption characterisitics in nitric acid-organic solvent solution were determined. The results of the experiments, summarized in Tables 2-6, illustrate the obtained values of distribution coefficient for Zn(II),

TABLE 2

K_d VALUES OF STUDIED METAL ION IN AQUEOUS-ORGANIC SOLVENTS-0.05M HNO_3-0.005M METAL IONS ON AMBERLITE IRA-410 ANION EXCHANGE RESIN (NO_3 FORM)

Organic solvents % (vol/vol)	Metal ions					
	Zn(II)	Mg(II)	Cd(II)	Ni(II)	Cu(II)	Co(II)
Isopropanol						
60	4.32	6.20	3.52	0.0	6.82	0.00
90	12.36	15.25	7.62	9.51	19.50	8.55
Ethanol						
60	0.0	0.0	2.16	0.00	2.80	0.0
90	3.25	22.75	8.11	18.21	30.82	13.51
Methanol						
60	0.0	0.0	2.17	0.0	3.52	0.0
90	12.35	18.35	9.36	0.0	22.66	2.16
Acetone						
60	0.0	0.0	3.56	0.00	0.00	0.00
90	5.91	15.26	6.99	5.99	8.82	4.33

Mg(II), Cd(II), Co(II), Ni(II) and Cu(II) using variable acid concentrations and different proportions of isopropanol, methanol, ethanol and acetone.

At nitric acid molarity of 0.1M, Zn(II) is sparingly adsorbed at 60% (vol/vol)-acetone and higher, whereas Co(II) and Cu(II) are adsorbed at all acetone proportions, while Ni(II) is adsorbed only at 90%-acetone. Mg(II) and Ca(II) are adsorbed at 60% (vol/vol)-acetone and higher, where K_d values sharply increase at 90% (vol/vol)-acetone (Table 3).

TABLE 3

VALUES OF STUDIED METAL IONS IN AQUEOUS-ORGANIC SOLVENTS-0.1M HNO_3-0.005M METAL IONS ON AMBERLITE IRA-410 ANION EXCHANGE RESIN (NO_3^- FORM)

Organic solvents, % (vol/vol)	Metal ions					
	Zn(II)	Mg(II)	Cd(II)	Ni(II)	Cu(II)	Co(II)
Isopropanol						
40	0.0	0.0	0.0	2.33	28.22	6.82
60	6.85	35.35	0.71	15.34	68.92	40.13
90	14.22	58.82	26.55	38.17	145.64	65.82
Ethanol						
40	0.00	0.00	0.00	2.11	15.34	7.77
60	3.11	0.00	5.10	9.55	45.66	95.22
90	9.85	60.82	25.22	45.81	157.68	113.82
Methanol						
40	0.00	0.00	0.00	0.00	28.22	3.82
60	0.00	0.00	2.85	0.00	170.54	65.22
90	18.77	70.25	13.35	2.11	220.92	85.95
Acetone						
40	0.00	0.00	0.00	0.00	12.92	3.27
60	1.46	7.22	4.85	0.00	45.66	14.33
90	12.54	38.21	22.22	25.33	135.55	57.68

The effect of increasing nitric acid concentration on the values of metal distribution coefficient is clear, where K_d values increase as the acid concentration increases i.e. sorbability increases with increasing acid concentration. It can be concluded from the obtained results that the effects are different from metal to metal, depending may be on the dominant nitrato-complex species in the conditions concerned. Such an effect generally means that nitrate competes more effectively for ion exchange sites as the nitric acid concentration increases (Tables 4–6).

The over-all nitric acid molarity ranges only from 0.05 to 2.5M. It is probable that the increase of organic solvent concentration makes the

TABLE 4

K_d VALUES OF STUDIED METAL IONS IN AQUEOUS-ORGANIC SOLVENTS—0.5M HNO_3-0.005M METAL IONS ON AMBERLITE IRA-410 ANION EXCHANGE RESIN (NO_3^--FORM)

Organic solvents, % (vol/vol)	Metal ions					
	Zn(II)	Mg(II)	Cd(II)	Ni(II)	Cu(II)	Co(II)
Isopropanol						
40	6.59	0.00	0.95	18.40	63.88	40.11
60	27.81	44.23	23.28	65.34	125.87	75.25
90	33.52	95.82	70.02	112.00	245.50	160.20
Ethanol						
40	15.33	0.00	3.50	25.30	55.20	38.31
60	27.81	0.00	18.58	62.56	133.60	95.20
90	35.50	82.13	30.40	95.20	200.00	125.30
Methanol						
40	8.34	0.00	0.00	15.19	70.92	8.21
60	27.81	0.00	3.56	33.75	240.55	65.26
90	45.35	10.25	25.322	65.33	366.50	112.50
Acetone						
40	0.00	0.00	0.00	15.9	70.52	8.21
60	6.80	15.25	4.85	25.33	110.50	60.25
90	12.92	70.30	25.72	65.35	185.865	110.51

TABLE 5

K_d VALUES OF STUDIED METAL IONS IN AQUEOUS-ORGANIC SOLVENTS-1.0M HNO_3-0.005M METAL IONS ON AMBERLITE IRA-410 ANION EXCHANGE RESIN (NO_3^- FORM)

Organic solvents, % (vol/vol)	Metal ions					
	Zn(II)	Mg(II)	Cd(II)	Ni(II)	Cu(II)	Co(II)
Isopropanol						
40	19.40	39.45	28.79	85.25	112.20	65.20
60	32.10	73.922	45.20	125.30	266.80	115.20
90	72.90	136.446	85.80	200.00	335.21	174.30
Ethanol						
40	18.50	45.67	16.50	60.00	85.32	15.25
60	45.30	96.85	38.50	110.50	*155.50*	*115.25*
90	65.20	112.82	55.66	155.30	255.30	200.00
Methanol						
40	35.50	45.67	0.00	60.20	126.50	65.50
60	57.50	110.24	28.50	67.60	320.20	85.35
90	65.20	155.225	75.20	120.20	385.20	238.21
Acetone						
40	11.80	19.50	2.82	33.50	70.25	37.50
60	20.20	75·20	30.77	60.30	144.50	85.20
90	20.20	120.80	55.22	115.20	192.22	170.00

TABLE 6

K_d VALUES OF STUDIED METAL IONS IN AQUEOUS ORGANIC SOLVENTS-2.5M HNO_3-0.005M METAL IONS ON AMBERLITE IRA-410 ANION EXCHANGE RESIN (NO_3^- FORM)

Organic solvents, % (vol/vol)	Metal ions					
	Zn(II)	Mg(II)	Cd(II)	Ni(II)	Cu(II)	Co(II)
Isopropanol						
40	33.50	85.32	54.05	95.92	300.82	110.20
60	55.22	110.30	65.52	163.44	350.64	190.52
90	85.50	185.59	98.90	240.30	465.32	260.33
Ethanol						
40	38.52	80.66	49.35	85.25	125.44	95.250
60	45.51	112.32	66.22	125.35	190.35	170.55
90	81.41	136.41	90.56	178.52	275.32	260.30
Methanol						
40	42.82	75.82	58.51	80.20	126.51	75.32
60	57.53	125.24	71.35	130.81	380.16	220.16
90	90.399	155.56	112.82	165.50	410.32	246.51
Acetone						
40	33.82	74.82	55.800	80.92	130.22	42.51
60	50.81	80.82	64.46	129.11	165.85	135.62
90	72.39	120.52	80.52	148.92	200.32	175.22

formation of nitrato complexes easier, even at low nitric acid concentrations, because the organic solvent lowers the dielectric constant of the medium, thereby increasing the attraction between ions, therefore, ion association and complex formation are favoured[17].

It is probable that organic solvents in general make it easier to strip coordinated water from a metal cation and from a metal nitrate complex. The metal nitrate complexes formed may be taken up by the anion exchange resin. This may occur by simple ion exchange of the anionic metal nitrate complex or a neutral metal nitrate complex may invade the resin and form an anionic complex inside the resin by reaction with additional nitrate ion[18].

Due to the increase in the values of K_d with the percentage of organic solvent and acid molarity above 0.5M, possible separations from aqueous-organic media cannot be judged.

Upon the batch distribution coefficients determined in the present work, conditions for separation are easily predicted. An eluent is chosen so that the distribution coefficient of the major constituent is approximately zero and that of the minor constituent is quite large, preferably several hundred. Under these conditions the minor constituent should remain on the column and be separated quantitatively from the major sample component. For example Mg(II) has K_d zero at 60% (vol/vol)-ethanol, and could be separate from Co(II), Ni(II) from Cu(II) at 60% (vol/vol)-methanol–0.1M HNO_3.

Upon further increasing nitric acid up to 0.5M the results show the possibility of separating Mg(II) from Ni(II) or from Cu(II) and from Co(II) in aqueous-isopropanol medium. In aqueous ethanol medium 60% (vol/vol) it is possible to separate Mg(II) from Ni(II) or from Cu(II) or from Co(II). In aqueous-methanol medium 40% (vol/vol) it is possible to separate Mg(II) or Cd(II) from Cu(II). In acetone-aqueous media 40% (vol/vol), it is possible to separate Cd(II) from Cu(II). The increase in the values of K_d with increasing the concentration of nitric acid probably indicate complex formation which leads to the uptake of complexed metal ions on the resin.

Separation of Ni(II) from Cu(II)

The resin was packed in a glass column (1.2 cm dia. × 30 cm) and washed with 100 ml aqueous methanolic solution, 60% (vol/vol)–0.1M HNO_3. Two ml of Ni(II) solution equiv. to 10 mg Ni are mixed with two ml of Cu(II) ion solution to give 10 mg Cu with 1.0 ml of .5M HNO_3 and 45 ml methanol are added. The mixture having total acidity of 0.1M, then passes through the column at a flow rate of 0.3 ml/min. A total amount of 190 ml of the first eluting solution 0.1M nitric acid–60% (vol/vol)-methanol is passed through the column at the same flow rate as mentioned above. This quantitatively elutes out Ni(II). Cu(II) is next eluted with 0.1M nitric acid solution. 220 ml. of this eluent are required for complete elution of Cu(II). The concentrations of nickel and copper in solution are determined spectrophotometrically.

Separation of Magnesium from Cobalt in Binary System

The same procedure was used for the separation of Mg(II) from Co(II) (Table 7). The resin column was first washed with aqueous–60% (vol/vol)-solution–0.1M HNO_3 (50 ml); two ml of $Mg(NO_3)_2$ solution was mixed with $Co(NO_3)_2$ solution at flow rate of 0.3 ml/min. A total volume of 120 ml of the first eluting solution (0.1M HNO_3–60%-(vol/vol) ethanol-aqueous solution) sufficiently elutes out Mg(II). Co(II) is next separated with aqueous 1.0M HNO_3 solution. 160 ml is required for complete elution of Co(II). The concentrations of the elements are determined with help of Beckman Model B spectrophotometer type. The procedure is also valid for separation of zinc from copper except for the volume of the solution and also the media used because in this case the media is

60% (vol/vol)-isopropanol-aqueous–0.1M HNO_3 solution.

TABLE 7

SEPARATION OF METAL ION MIXTURES ON AMBERLITE IRA-410 NITRATE FORM

Eluting agent	Taken, *m* moles	Found, *m* moles	Recovery
Ni(II)-Cu(II)			
Ni(II) 60% (V/V) methanol-0.1 MHNO_3	0.281848	0.2817948	99.98%
Cu(II) 0.1M HNO_3 solution	0.24024	0.239184	99.56%
Mg(II)-Co(II)			
Mg(II) 60% (V/V) ethanol-0.1M HNO_3	0.25130	0.250768	99.79%
Co(II) 1.0M HNO_3 solution	0.224185	0.223511	99.69%
Zn(II)-Cu(II)			
Zn(II) 40% (V/V) isopropanol-0.1M HNO_3	0.29009	0.28995	99.95%
Cu(II) 0.1M HNO_3 solution	0.23998	0.23998	100%
Mg(II)-Co(II)			
Mg(II) 60% (V/V) methanol-0.5M HNO_3	0.25076	0.25076	100%
Co(II) 1.0M HNO_3 solution	0.297237	0.29685	99.87%
Mg(II)-Ni(II)			
Mg(II) 60% (V/V) ethanol-0.5M HNO_3	0.2546169	0.254871	100%
Ni(II) 0.05M HNO_3 solution	0.2327178	0.232648	99.90%

Separation of Mg(II) from Co(II) or Ni(II) in Binary System

Using the above procedure, the first elution solvent required to elute Mg(II) was 60% (vol/vol)-methanol–0.5M HNO_3. Co(II) was then eluted with 1.0M HNO_3 solution, and 0.1M HNO_3 Ni(II) separately.

REFERENCES

1. J. Korkisch and I. Hazan, *Talanta*, **11**, 1175 (1964).
2. ———, *Analyt. Chem.*, **36**, 2308 (1964).
3. P. E. John and W. W. Poseph, *Analyt. Chem.*, **9**, 34 (1962).
4. A. S. Aboul-Magd, F. H. Kamal, E. A. Hassan and A. R. Ebaid, *Indian J. Chem.*, **25**, 1097 (1986).
5. A. S. Aboul-Magd, F. H. Kamal and E. A. Hassan, *J. Indian Chem. Soc.*, **65**, 535 (1988).
6. J. Kennedy and R. V. Davies, *J. Inorg. Nucl. Chem.*, **12**, 193 (1959).
7. D. H. Wilkins and G. E. Smith, *Talanta*, **32**, 138 (1970).

8. L. W. Marple, *J. Inorg. Nucl. Chem.*, **26**, 859 (1964).

9. P. Van Acker, P. De Corte and J. Hoste, *J. Inorg. Nucl. Chem.*, **37**, 2549 (1975).

10. E. A. Hasan, M. F. El-Hadi, A. S. Aboul-Magd and A. M. Barkat, *Pak. J. Sci. Ind. Res.*, **26**, 289 (1983).

11. A. I. Vogel, Text Book of Quantitative Inorganic Analysis, 3rd edn., Longman Green, London, p. 707 (1961).

12. Standard Methods for the Examination of Water and Waste Water, American Public Health Association (1965).

13. G. Schwarzenbach, Complexemetric Titrations, Methuen, London, pp. 69–95 (1957).

14. S. E. Zayan, *Quantitative Chem. Acta*, Dar El-Maaref, Cairo, **1** (1974).

15. Zhiqniew, Hubicki, Jusiak and Stainslow, *Chem. Abstr.*, **90**, 125144 (1979).

16. F. W. E. Strelow, C. R. Van Zyl and C. J. C. Bothma, *Analyt. Chem. Acta*, **45**, 81 (1969).

17. N. Yoshikuni and R. Kuroda, *Talanta*, **24**, 163 (1972).

18. J. S. Fritz and M. L. Gillette, *Talanta*, **15**, 287 (1968).

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