Asian Journal of Chemistry Vol. 10, No. 3 (1998), 409–414

Anion Exchange Separation Factor Studies of Transition Metal Ions in Sodium Nitrite Water-Acetone Medium

R.P. BHATNAGAR*, ARCHANA BHARDWAJ† and S.D. BHARDWAJ‡
School of Studies in Chemistry
Jiwaji University, Gwalior, India

Anion exchange separation of transition metal ions has been studied in aqueous sodium nitrite and aqueous acetone sodium nitrite media using Dowex-1 × 8 in nitrate form. The useful separations performed are Zn(II) Hg(II); Cd(II)-Hg(II), Mn(II)-Hg(II); Ni(II)-Hg(II); Co(II)-Hg(II), Cu(II)-Hg(II) Ag(I)-Hg(II) and Mn(II)-Cd(II). The use of acetone as a water miscible less polar medium is found to increase the distribution values in most of the cases.

INTRODUCTION

The use of complex forming media for evolving separation procedures for metal ions is common practice in ion exchange chromatography. Some recent reviews presented by Strelow[1] and Marcus[2] and the books[3, 4] for separation of metal ions have shown the utility of such complex forming reagents extensively. Very few inorganic salts have been used for such studies. Ammonium thiocyanate[5–7] has been made in quite a few anion exchange studies for separation of metal ions. The use of sodium nitrite has been done recently by Bhatnagar and co-workers[8–13] as a new complexing eluant for a number of cation-exchange chromatographic separations.

The present investigation is aimed to carry out separation of transition metal ions using sodium nitrite. The inorganic complexing agents can be decomposed by boiling with little nitric acid to give metal nitrates in soluion.

EXPERIMENTAL

0.2 N stock solution of each metal ion was prepared from their analytical grade nitrates in double distilled water. Sodium nitrite (B.D.H., AnalaR) was used to prepare the complexing media, both in water and aqueous acetone media. AnalaR quality acetone (B.D.H.) was used in all elution and separation studies.

Disodium E.D.T.A. (ethylene di-amine tetraacetic acid) (0.025 N) was prepared from its analytical grade sample. Titrations were carried out at proper pH, using suitable indicators [such as pyrocatechol violet for Cd(II), 1-(2-pyridyl azo)-2-naphthol for Cu(II) and salicylic acid solution for Fe(III)].

†Kamala Raja Girls (Autonomous) College, Gwalior-474 009, India.
‡Cancer Hospital and Research Institute, Gwalior-474 009, India.

The Resin and Resin Column

A strongly basic exchanger Dowex 1 × 8 in nitrate form, was used for metal ion exchange studies in nitrite media. It was 60–100 mesh size. The air-dried resin (*ca.* 20°C) had an exchange capacity of 2.1 meg/q. Its moisture content was *ca.* 5.0%. The resin column was of 10 × 1.0 cm size of corning glass provided with a perforated disc at the lower end.

Eluting Agent

Ammonium nitrate solutions of 10, 15, and 20% (v/v) were prepared as their aqueous-acetone solution in 30 and 40% acetone as solvent. These eluants were used for Hg(II) eution studies. Sodium nitrate solution of 2.5, 5.0, 10, 15 and 20% (v/v) were prepared in 10, 20, 30 and 40% (v/v) aqueous acetone for elution.

Separation studies for Hg(II) from other transition metal ions

All separation studies were carried out using 10.0 × 1.0 cm column of Dowex-1 × 8 in nitrate form. Every time a total influent volume of 20 mL (10 mL each of the two metal ions tried for separation) was used. The complexing agent sodium nitrite was added to it so as to make nitrite ion concentration as 1.5 N in the total solution. After keeping it for about 1 h as such, sorption step was carried out at a flow rate of 2 mL per minute. Elution of metal ions such as nickel, cobalt and manganese was first carried out with 2.5% (v/v) sodium nitrate in 30% (v/v) aqueous acetone. For other metals as zinc, silver and copper elution of the first component was done by 5% (v/v) sodium nitrate in 30% (v/v) aqueous acetone solution. Elution of cadmium was done with 5% (w/v) sodium nitrate prepared in 10% (v/v) aqueous acetone media. Every fraction of 10 mL collected was tested by drop reaction for the presence of metal ion in it. If they did not contain any contamination of the second component metal ion, then all the fractions were estimated titremetrically first destroying nitrite.

The column was washed with distilled water and made free from the eluant used previously. Another eluant, a 20% (w/v) ammonium nitrate solution in 40% (v/v) aqueous acetone, was then used for eluting Hg(II). This eluant facilitated quick elution of mercury from the column. As usual, 10 mL fractions were collected and estimated after nitrite decomposition for Hg(II) and separation of Hg(II) from Zn(II) Cd(II), Mn(II), Ni(II), Co(II) and Ag(I) in binary combination.

Separation studies for Cd(II) and Mn(II)

Mn(II) ion had low K_D in aqueous and non-aqueous media while Cd(II) had higher K_D value. This gave a suitable conditions for their separation from each other. 20 mL of influent volume was poured over a resin bed of 10.0 × 1.0 cm. Elution was carried out with 1.0% (w/v) sodium nitrate in 10% (v/v) aqueous—acetone solution. Mn(II) comes out as first component in the first nine fractions of 10 mL each. After this Cd(II) was eluted with 5% (w/v) sodium nitrate solution in 30% (v/v) aqueous acetone from 12th fraction onwards up to 24th fraction. All the fractions were estimated titrimetrically after nitrite decomposition.

RESULTS AND DISCUSSION

Results of these separation studies have been provided first as comparative K_D values to calculate and report separation factors. Tables 1–7 summarise this data to show that practically all ions from transition metals are separate from mercury(II) which gives a strong metal nitrite complex. The separation factors have been obtained showing the best solvent and nitrite ion concentrations for planning separations of Hg(II) in binary combination with other ions.

Table-1 gives K_D values for metal ions in presence of varying quantities of sodium nitrite in aqueous solution. An increase in nitrite concentration (0.1 to 1.5 N) increased the K_D values of all metal ions investigated. The values at 1.0 or 1.5 N sodium nitrite concentration can be used to provide the following decreasing common transition metal ion uptake sequence in nitrite media:

Hg(II) > Cd(II) > Ag(I) > Cu(II) > Zn(II) > Fe(II) > Cd(II) > Mn(II) > Ni(II).

TABLE-1
ANION EXCHANGE DISTRIBUTION CO-EFFICIENTS IN AQUEOUS NITRITE MEDIA ON DOWEX-1 × 8 (NO_3^-)

S. No.	Ion	Sodium nitrite concentration					
		0.1-N	0.2-N	0.5-N	0.7-N	1.0-N	1.5-N
1.	Ag^+	3.9	13.5	21.2	31.3	35.6	40.3
2.	Cu^{2+}	14.3	16.0	21.2	25.0	25.0	29.0
3.	Zn^{2+}	5.3	9.6	11.1	14.3	21.0	31.3
4.	Cd^{2+}	3.9	6.6	9.6	16.0	29.0	42.8
5.	Hg^{2+}	31.3	42.8	40.3	77.7	81.8	86.0
6.	Fe^{3+}	16.0	17.6	12.4	17.6	23.1	ppt
7.	Co^{2+}	3.9	8.1	11.1	14.3	16.0	25.0
8.	Ni^{2+}	2.9	8.1	13.5	17.6	19.4	19.4
9.	Mn^{2+}	3.9	5.3	6.6	11.1	14.3	23.1

Separation factors for different pairs of ions in 1.5 N sodium nitrite media (Both aqueous and mixed solvent system).

TABLE-2
SEPARATION FACTORS VALUES IN AQUEOUS MEDIA

S. No.	Pair of ions		K_{D_1}	K_{D_2}	Separation factors
	I	II			
1.	Hg—	Ag	86.05	40.31	2.13
2.	Hg—	Cu	86.05	29.03	2.96
3.	Hg—	Cd	86.05	42.86	2.00
4.	Hg—	Mn	86.05	23.10	3.73
5.	Hg—	Ni	86.05	19.41	4.43
6.	Hg—	Co	85.05	25.00	3.44
7.	Hg—	Zn	86.05	31.26	2.75

TABLE-3
SEPARATION FACTORS IN 10% (v/v) AQUEOUS ACETONE MEDIA

S. No.	Pair of ions I II	K_{D_1}	K_{D_2}	Separation factors
1.	Hg—Ag	77.77	46.00	1.69
2.	Hg—Cu	77.77	52.51	1.48
3.	Hg—Cd	77.77	31.26	2.49
4.	Hg—Mn	77.77	23.10	3.37
5.	Hg—Ni	77.77	14.32	5.43
6.	Hg—Co	77.77	29.03	2.68
7.	Hg—Zn	77.77	16.00	4.86

TABLE-4
SEPARATION FACTOR IN 20% (v/v) AQUEOUS ACETONE MEDIA

S. No.	Pair of ions I II	K_{D_1}	K_{D_2}	Separation factors
1.	Hg—Ag	81.81	42.86	1.91
2.	Hg—Cu	81.81	48.75	1.68
3.	Hg—Cd	81.81	46.00	1.78
4.	Hg—Mn	81.81	17.64	4.64
5.	Hg—Ni	81.81	13.54	6.04
6.	Hg—Co	81.81	25.00	3.27
7.	Hg—Zn	81.81	23.10	3.54

TABLE-5
SEPARATION FACTORS IN 30% (v/v) AQUEOUS ACETONE MEDIA

S. No.	Pair of ions I II	K_{D_1}	K_{D_2}	Separation factors
1.	Hg—Ag	86.05	31.26	2.75
2.	Hg—Cu	86.05	75.44	1.14
3.	Hg—Cd	86.05	60.00	1.43
4.	Hg—Mn	86.05	21.21	4.06
5.	Hg—Ni	86.05	23.10	3.73
6.	Hg—Co	86.05	23.10	3.73
7.	Hg—Zn	86.05	21.21	4.06

TABLE-6
SEPARATION FACTOR IN 40% (v/v) AQUEOUS ACETONE MEDIA

S. No.	Pair of ions I II	K_{D_1}	K_{D_2}	Separation factors
1.	Hg—Ag	110.53	48.15	2.29
2.	Hg—Cu	110.53	ppt	—
3.	Hg—Cd	110.53	63.27	1.75
4.	Hg—Mn	110.53	27.00	4.09
5.	Hg—Ni	110.53	29.03	3.81
6.	Hg—Co	110.53	35.62	3.10
7.	Hg—Zn	110.53	31.26	3.54

TABLE-7
SEPARATION FACTOR IN 50% (v/v) AQUEOUS ACETONE MEDIA

S. No.	Pair of ions I II	K_{D_1}	K_{D_2}	Separation factor
1.	Hg—Ag	150.00	50.95	2.95
2.	Hg—Cu	150.00	ppt.	—
3.	Hg—Cd	150.00	77.77	1.93
4.	Hg—Mn	150.00	ppt	—
5.	Hg—Ni	150.00	27.00	5.55
6.	Hg—Co	150.00	37.93	3.95
7.	Hg—Zn	150.00	31.26	4.80

Tables 1–7 show that in all cases the α_B^{Hg} is greater than unity. 30% (v/v) acetone solvent with 1.5 N sodium nitrite has been preferred for getting high K_D values. At the same time no precipitate was formated for other ions used for separation purpose. Similarly pairs of ions such as Ag—Mn, Cu—Ni, Cd—Co have also been selected for evaluating their separation factors under different conditions.

To obtain a favourable condition for a good separation, it is essential to get a good and high separation factor. This factor is defined as

$$\alpha_B^A = \frac{K_{D_A}}{K_{D_B}}$$

where A and B are the two ions to be considered for separation. K_{D_A} and K_{D_B} are the equilibrium distribution co-efficients of these elements. These distribution co-efficients for the more strongly absorbed element should be quite high, while that of the less strongly absorbed one should be quite low for getting a favourable α_B^A value. If this is so then only the separation becomes easy and quick. Quickness involves the kinetics of exchange and hence an idea about the rates of exchange is also required for planning separations.

A complexing nitrite media has been used to prepare exchangeable anionic

complexed metal nitrite species. If this formation is complete and species resulting from the process are stable enough to retain their anionic nature, then their absorption on the anion-exchanger (Dowex-1 × 8) is no problem. A stronger, stable, complexed species is bound to get exchanged at the top of the column and that too quite strongly. The weaker less stable complexes are supposed to follow it on the column. Release of the weaker species during elution steps will be thus quicker than that of the stabler species.

The distribution co-efficient data for all the concerned ions have been obtained under different conditions of nitrite concentration and solvent composition. These values have been used to evaluate α_B^A for the ion pairs concerned. Such factors have been given for Hg—Ag, Hg—Cu, Hg—Cd, Hg—Mn, Hg—Ni, Hg—Co and Hg—Zn pairs of ions for aqueous nitrite and solvent (acetone).

REFERENCES

1. F.W.E. Strelow, Ion-exchange and Solvent Extraction, Vol. 5, Marcel-Dekker Inc., New York, pp.132–206 (1973).
2. Y. Marcus, Ion Exchange and Solvent Extraction, Vol. 4, Marcel-Dekker Inc, New York (1973).
3. O. Samuelson, Ion Exchange Separation in Analytical Chemistry, John Wiley and Sons, New York, pp. 338–349 (1963).
4. J. Korkisch, Modern Methods for the Separation of Rarer Metal Ions, Pergamon Press, Oxford (1969).
5. J.B. Turner, R.H. Philip and R.A. Day, *Anal. Chem. Acta*, **26**, 94 (1962).
6. H. Grosse-Ruyken and H.G. Dore, *Talanta*, **12**, 73 (1965).
7. D.J. Pietrzyk and D.L. Kisser, *Anal. Chem.*, **37**, 1578 (1965).
8. R.P. Bhatnagar and R.P. Shukla, *Anal, Chem.*, **32**, 777 (1960).
9. R.P. Bhatnagar, R.C. Arora and V.J. Rao, *India, J. Chem.*, **1**, 159 (1963).
10. R.P. Bhatnagar and V.M. Pandse, *Indian J. Chem.*, **1**, 226 (1963).
11. R.P. Bhatnagar and R.C. Arora, *Indian J. Chem.*, **3**, 89 (1965).
12. _____, *Indian J. Chem.*, **2**, 206 (1964).
13. R.P. Bhatnagar and R.G. Trivedi, *J. Indian Chem. Soc.*, **42**, 53 (1965).

(*Received:* 7 June 1997; *Accepted:* 24 November 1997) AJC-1412