Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Cation Exchange Characteristics of Some Metal Ions in Nitric Acid-Ammonium Acetate Medium

Ashok Mahan[a]; Animesh K. Ghose[a]; Arun K. Dey[a]
[a] CHEMICAL LABORATORIES UNIVERSITY OF ALLAHABAD, ALLAHABAD, INDIA

To cite this Article Mahan, Ashok , Ghose, Animesh K. and Dey, Arun K.(1971) 'Cation Exchange Characteristics of Some Metal Ions in Nitric Acid-Ammonium Acetate Medium', Separation Science and Technology, 6: 6, 781 — 789
To link to this Article: DOI: 10.1080/01496397108066951
URL: http://dx.doi.org/10.1080/01496397108066951

SEPARATION SCIENCE, 6(6), pp. 781–789, December, 1971

Cation Exchange Characteristics of Some Metal Ions in Nitric Acid–Ammonium Acetate Medium

ASHOK MAHAN, ANIMESH K. GHOSE, and ARUN K. DEY*

CHEMICAL LABORATORIES
UNIVERSITY OF ALLAHABAD
ALLAHABAD, INDIA

Summary

Cation exchange equilibrium distribution coefficients (Λ) with Amberlite IR-120 have been determined for 20 metal ions in media consisting of mixtures of 0.1 *M* HNO_3 and varying concentrations, viz., 0.01, 0.05, 0.25, and 1.2 *M*, of ammonium acetate. The metal concentrations were so chosen that the ratio of total amount of cation to total resin capacity = 0.4, sufficient to ensure exchange. The values of separation factors of various metal ion pairs have also been evaluated, and separation possibilities for ions in a number of binary and ternary mixtures have been proposed.

A wide variety of anions have been used as eluting agents for the separation of metal ions on ion exchange resins. Acetate ion, although utilized to some extent in both anion and cation exchange, has mostly been studied empirically (*1*). Some workers reported anion exchange studies in buffered aqueous solutions of acetic acid and in acetic acid–organic solvent media (*2*, *3*). In view of the fact that no cation exchange selectivity characteristic scales for cations in acetate medium are available in the literature, an investigation of the ion exchange characterization of a large number of cations in ammonium acetate–nitric acid mixtures has been undertaken. The studies include the effect for 20 cations in mixtures of four different concentrations of ammonium

---

* To whom all correspondence should be addressed.

acetate and 0.1 *M* nitric acid as media. The results and the possibilities of the separations of the ions are discussed.

EXPERIMENTAL

Ion Exchange Resin

Amberlite IR-120 (16–50 mesh, 8–10% of cross-linking) in hydrogen form (B.D.H., Analytical Grade) was pretreated in a column with 0.02 *M* EDTA solution (pH = 8–10), and then with 2 *M* HCl and 2 *M* $HClO_4$. The final washing was done with water until neutral to litmus. The resin, air-dried by suction on a sintered bed, was stored, and the capacity and the moisture content were determined by usual methods. These were 2.56 milliequivalents (meq) and ca. 44%/g of resin, respectively.

Metal Solutions

Stock solutions (0.1–0.5 *M*) of the various metal nitrates were prepared in 0.1 *M* HNO_3 from oxides or nitrates. The samples were either of B.D.H. AnalaR or Johnson Matthey & Co. make and the prepared solutions were subsequently standardized.

Ammonium Acetate Solution

An aqueous solution of 6.0 *M* ammonium acetate (B.D.H. AnalaR) was prepared and was standardized by the indirect determination of ammonia.

Buffer Solutions

For EDTA titrations the buffer solutions of pH = 10 (NH_4Cl/ammonia) and of pH = 5 (NaOAc/HCl) were used. Other desired pH ranges were obtained by maintaining the pH of the solution by the addition of suitable quantities of acid or alkali and with the help of an L & N pH-meter. pH indicator papers (B.D.H.) were also employed in some cases during titrations, as and when necessary.

Absorbance and pH Measurements and Equilibration of the Systems

A Unicam SP 500 spectrophotometer and a Leeds and Northrup pH-indicator were employed for the absorbance and pH measurements, respectively. A wrist-motion Microid flask shaker (Griffin & George) was used for shaking. Solutions were shaken in glass stoppered 100 ml Pyrex flasks.

DISTRIBUTION STUDIES

Determination of Distribution Coefficients

The batch equilibration method was employed; weighed amounts of the air-dried resin (1.000 g each) were added to the mixture solution containing the metal ion, the acid (HNO_3), and ammonium acetate, and shaken for 2 hr (it was ascertained previously that this time was adequate to attain equilibrium). The resin was filtered and the metal ion determined in an aliquot of the filtrate. At lower concentration of the ions where titrimetry was not possible, a spectrophotometric procedure was used with suitable chromogenic reagents. The distribution coefficients were calculated using the relation

$$\text{distribution coefficient} = \frac{\text{meq of the metal ion/g of resin}}{\text{meq of the metal ion/ml of solution}}$$

The experiments were performed at a metal concentration ratio of total amount of cation to total resin capacity ≈ 0.4, using 0.1 M HNO_3 with varying ammonium acetate concentrations, i.e., 0.01, 0.05, 0.25, and 1.2 M, and at a room temperature of $30 \pm 2°$. The total volume of aqueous phase was 50 ml. The results obtained are given in Table 1. All experiments were carried out in duplicate and average values taken.

RESULTS AND DISCUSSION

Accumulative experimental errors in Table 1 are estimated to be less than about 2–5% of the results for coefficients between 10 and 500, but are higher for very high or very low coefficients. The main sources of the errors are inhomogeneity of the resin, water content of the resin (the dry resin is a strong desiccant), and analytical errors. Generally, distribution coefficient values determined at relatively higher resin loadings, as in these experiments, provide more practical results than at tracer concentrations, because the errors due to secondary effects such as sorption by the walls of the vessels are not significant.

TABLE 1

Values of Distribution Coefficients (Λ) in NH_4OAc–0.1 M HNO_3[a]

	Distribution coefficients			
Cation	(a)	(b)	(c)	(d)
Mg(II)	334.5	292.9	65.3	3.1
Al(III)	4140.6	4284.4	658.7	0.9
Ca(II)	664.3	559.8	116.7	7.9
Sc(III)	2659.6	2778.9	13.4	0.1
Fe(III)	686.3	1246.0	27.5	18.6
Mn(II)	442.5	391.0	73.1	4.7
Co(II)	400.0	361.4	65.2	0.2
Ni(II)	626.6	568.6	77.4	4.7
Cu(II)	481.9	404.6	20.6	1.0
Zn(II)	413.0	366.7	55.0	0.5
Ga(III)	3750.0	2482.8	ppt	140.0
Y(III)	4225.2	2150.7	165.1	0.1
Ag(I)	76.8	71.6	26.8	5.7
Ba(II)	1600.7	1511.5	369.4	25.4
La(III)	2583.9	4841.6	306.7	0.9
Ce(IV)	994.0	994.0	385.0	0.2
Hg(II)	1.2	1.4	2.9	3.6
Pb(II)	2033.3	1512.5	30.6	1.0
Bi(III)	5778.3	11383.3	ppt	ppt
Th(IV)	12736.0	6375.0	31.1	0.8

[a] Over-all concentrations of ammonium acetate (M): (a) = 0.01; (b) = 0.05; (c) = 0.25; (d) = 1.2.

Figures 1 and 2 illustrate the separation possibilities, in which the logarithms of the distribution coefficients are plotted against the concentrations of ammonium acetate. Significant separations are of Hg(II) and Ga(III) from other cations, and hence the plots of log Λ against NH_4OAc concentrations of these two cations have been shown in both figures. To avoid the overlapping of the plots, two groups of appropriate cations have been made: (a) Mg(II), Al(III), Ca(II), Ni(II) Cu(II), Zn(II), La(III), Ce (IV), and Pb (II); and (b) Sc(III), Mn(II), Fe (III), Co(II), Y(III), Ag(I), Ba(II), Bi(III), and Th (IV), and are shown separately.

In most of the cases sorption of the metal ion decreases with increasing ammonium acetate concentration. The media studied here are considered as buffer solutions, so the availability of acetate ions depends upon the pH of the solution or on the dissociation of the acetic acid formed by the interaction between nitric acid and ammonium acetate. Along with this, the exchange equilibria are also affected by the exchange affinities of hydrogen and ammonium ions present in the systems.

At lower ammonium acetate concentrations, i.e., 0.01 and 0.05 *M*, exchange equilibria are mostly affected by the pH of the solution because the free available acetate ion concentration is small. When the concentration of free hydrogen ions is decreased by the formation of acetic acid (due to its low degree of dissociation), in the case of most of the cations, the higher distribution coefficient values are obtained in

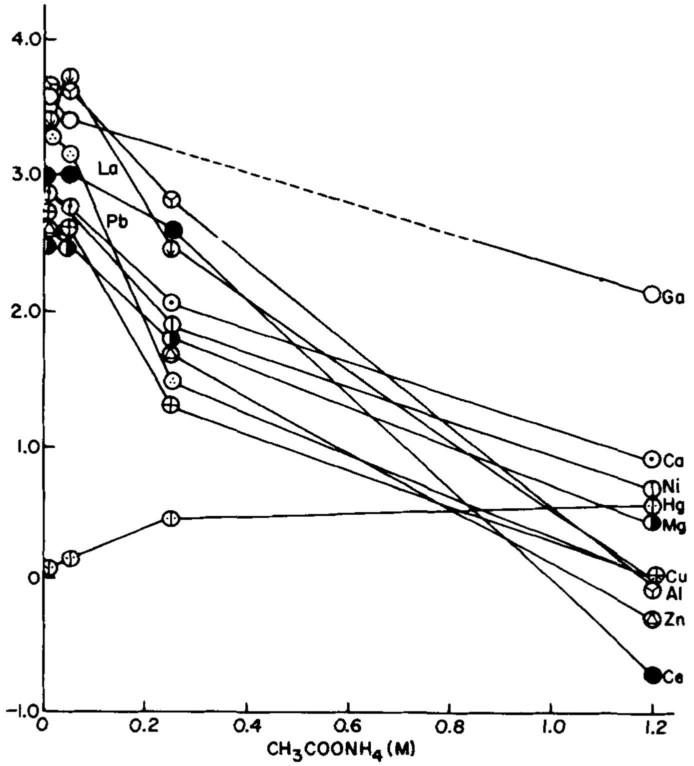

FIG. 1. Variation of log A with concentration of CH_3COONH_4. (Over-all acidity, 0.1 *M* HNO_3.)

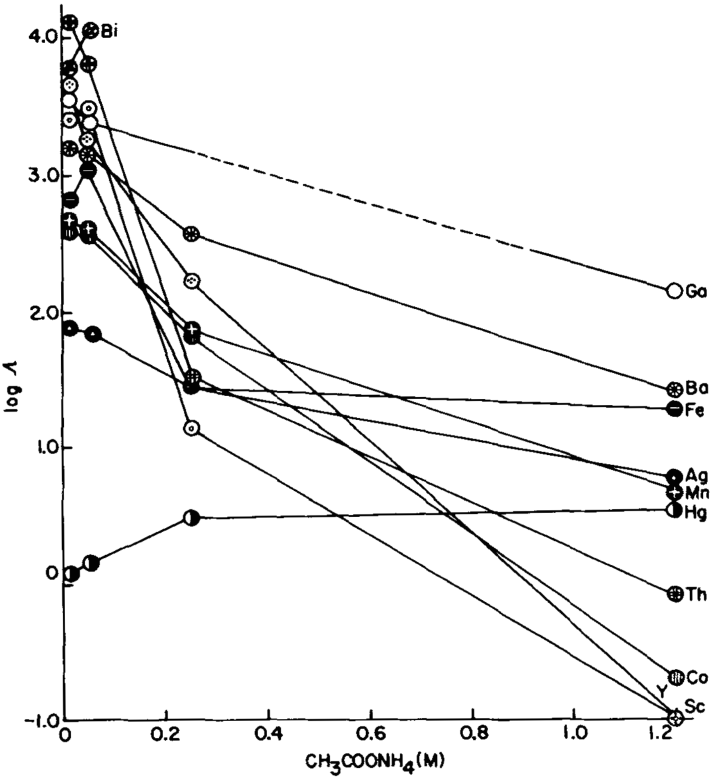

FIG. 2. Variation of log Λ with concentration of CH_3COONH_4. (Over-all acidity, 0.1 *M* HNO_3.)

such media. Ag(I) has slightly lower distribution coefficient values in these media, which is perhaps due to the higher affinities of hydrogen and ammonium ions toward the resin as compared to silver. The cations Al(III), Sc(III), Fe(III), La(III), and Bi(III) show slightly higher sorption in 0.05 *M* ammonium acetate medium than in 0.01 *M*. As in 0.05 *M* ammonium acetate solution, free acetate ions are low, and the concentration of hydrogen ions would be less than that in 0.01 *M* ammonium acetate solution. Furthermore, the higher charge on these cations is responsible also for their higher sorption in 0.05 *M* ammonium acetate. But this effect is not so pronounced in the case of other cations, as evidently their affinities toward the resin are decreased, probably by complexation with acetate. A remarkable decrease in distribution coefficient values of Hg(II) in all media are noted. This anomalous behavior may be due to the strong complexing tendency of Hg(II) with acetate and also with the ammonium ion (*4*).

The separation procedures are better illustrated in terms of separation factor, $\alpha^{\mathrm{M_I}}_{\mathrm{M_{II}}}$, a quantity which is given by the ratio of the distribution coefficient values of the two separating cations. Quantitative separations are generally possible when the values of separation factors are sufficiently large, i.e., 100 or more. The values of the separation factors in the present studies, with respect to Hg(II) for all the cations except Ag(I), and with respect to Ag(I) for Th(IV) and Bi(III), in 0.01 and 0.05 *M* ammonium acetate are given in Table 2.

In 0.25 *M* ammonium acetate solution only Al(III), Ba(II), La(III), and Ce(IV) can be separated from Hg(II), the values of the separation

TABLE 2

Separation Factors (α)

	Concentration of ammonium acetate (*M*)		
Separated cations	0.01 $\alpha_{\mathrm{Hg/Ag}}{}^{\mathrm{M}}$	0.05 $\alpha_{\mathrm{Hg/Ag}}{}^{\mathrm{M}}$	0.25 $\alpha_{\mathrm{Hg}}{}^{\mathrm{M}}$
Mg(II)-Hg(II)	278.7	209.2	—
Al(III)-Hg(II)	3450.4	3060.3	227.1
Ca(II)-Hg(II)	553.6	399.9	—
Sc(III)-Hg(II)	2216.2	1985.0	—
Mn(II)-Hg(II)	368.7	279.3	—
Fe(III)-Hg(II)	686.3	890.0	—
Co(II)-Hg(II)	333.3	258.1	—
Ni(II)-Hg(II)	522.1	406.1	—
Cu(II)-Hg(II)	401.6	289.0	—
Zn(II-Hg(II)	344.2	261.9	—
Ga(III)-Hg(II)	3124.9	1773.5	—
Y(III)-Hg(II)	3520.9	1536.2	—
Ba(II)-Hg(II)	1333.9	1079.7	127.4
La(III)-Hg(II)	2153.2	3458.3	105.8
Ce(IV)-Hg(II)	828.3	710.0	132.7
Pb(II)-Hg(II)	1694.3	1080.4	—
Bi(III)-Hg(II)	4815.0	8131.1	—
Th(IV)-Hg(II)	10612.9	4553.7	—
Th(IV)-Ag(I)	165.8	—	—
Bi(III)-Ag(I)	—	159.0	—

factors for these cations with respect to Hg(II) are also given in Table 2. Ga(III) has a higher distribution coefficient value even in 1.2 *M* ammonium acetate. This allows its separation from Al(III), Sc(III), Co(II), Cu(II), Zn(II), Y(III), La(III), Ce(IV), Pb(II), and Th(IV). The sufficiently high distribution coefficient values of Fe(III) and Ba(II) in 1.2 *M* ammonium acetate also permit their separation from Sc(III), Co(II), Y(III), and Ce(IV). As Ga(III), Fe(III), and Ba(II) have higher distribution coefficient values in 1.2 *M* ammonium acetate, the separation factors with respect to these three cations for the other cations mentioned are given by inverse values in Table 3.

Ternary separations are also possible by column chromatography, i.e., in 0.01 or 0.05 *M* ammonium acetate solution of all other cations sorbed except Hg(II), and then by elution with 1.2 *M* ammonium acetate solution only Ga(III), Fe(III), or Ba(II) remain on the column, and the cations Al(III), Sc(III), Co(II), Cu(II), Zn(II), Y(III), La (III), Ce(IV), Pb(II), and Th(IV) will pass in the effluent. Thereafter

TABLE 3

Separation Factors (α)[a] with 1.2 *M* NH_4OAc

Separated cations	$1/\alpha_{Ga/Fe/Ba}{}^{M}$
Al(III)–Ga(III)	155.5
Sc(III)–Ga(III)	1400.0
Co(II)–Ga(III)	700.0
Cu(II)–Ga(III)	140.0
Zn(II)–Ga(III)	280.0
Y(III)–Ga(III)	1400.0
La(III)–Ga(III)	147.3
Ce(IV)–Ga(III)	700.0
Pb(II)–Ga(III)	140.0
Th(IV)–Ga(III)	175.0
Sc(III)–Fe(III)	186.0
Co(II)–Fe(III)	93.0
Y(III)–Fe(III)	186.0
Ce(IV)–Fe(III)	93.0
Sc(III)–Ba(II)	254.0
Co(II)–Ba(II)	127.0
Y(III)–Ba(II)	254.0
Ce(IV)–Ba(II)	127.0

[a] Values given here are inverse of the separation factor.

Ga(III), Fe(III), or Ba(II) can be eluted by suitable eluting agents, mostly mineral acids. The possible ternary separations are:

(a) Hg(II)–Al(III)–Ga(III)
(b) Hg(II)–Sc(III)–Ga(III), Fe(III), or Ba(II)
(c) Hg(II)–Co(II)–Ga(III), Fe(III), or Ba(II)
(d) Hg(II)–Cu(II)–Ga(III)
(e) Hg(II)–Zn(II)–Ga(III)
(f) Hg(II)–Y(III)–Ga(III), Fe(III), or Ba(II)
(g) Hg(II)–La(III)–Ga(III)
(h) Hg(II)–Ce(IV)–Ga(III), Fe(III), or Ba(II)
(i) Hg(II)–Pb(II)–Ga(III)
(j) Hg(II)–Th(IV)–Ga(III)

Acknowledgment

The work was supported by the Council of Scientific and Industrial Research, New Delhi, and financial assistance to one of the authors (A.M.) is gratefully acknowledged.

REFERENCES

1. R. Djurfelt, J. Hansen, and O. Samuelson, *Svensk Kem. Tidskr.*, *59*, 13 (1947).
2. J. Korkisch and S. Urubay, *Talanta*, *11*, 721 (1964).
3. J. P. Riley and H. P. Williams, *Mikrochim. Acta*, *1959*, 825.
4. H. W. Thomas and N. Davidson, *J. Amer. Chem. Soc.*, *86*, 4325 (1964).

Received by editor May 11, 1971