



Retention behaviour of some heavy metal ions on cation exchange papers based on cerium (IV)

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ABSTRACT

The retention behaviour of some heavy metal ions have been studied on papers impregnated with Cerium (IV) based cation exchanger in aqueous HCl and mixed solvent systems containing dimethyl sulphoxide (DMSO). A variety of separations have been achieved and the Alberti equation, in the modified form $-n \log a_K^+ = R_M^+$ constants (a_K^+ = activity of K^+) have been verified. The effect of the concentration of impregnating reagents on these papers have been determined and compared with other papers. The effect of composition of impregnated papers on R_f values of metal ions has also been examined in different solvent systems. The separation of Zn^{2+} from Hg^{2+} , Pb^{2+} from UO_2^{2+} , Pb^{2+} from Cd^{2+} and ternary separation of Pb^{2+} , Bi^{3+} and Hg^{2+} ; and Pb^{2+} , Bi^{3+} from UO_2^{2+} are of special interest.

Keywords: Ion exchange Separation, Cerium (IV) antimonate, Paper chromatography, ion separation.

INTRODUCTION

Synthetic inorganic ion exchangers (SIIE) have growing interest in field of separation science [1-3]. A number of studies have been made for their preparations and applications to the simple binary and ternary separations [4-15]. The planar chromatography is an important tool to achieve selective, analytically difficult, environmentally important separations. The selectivity in planar chromatography can be further increased, when SIIE is used as stationary phase or as impregnates in planar chromatography for metal ions.

The Cerium (IV) antimonate has been found to exhibit good ion exchange properties which give us impetus to extend our studies on retention behaviour of heavy metal ion on Cerium (IV) antimonate papers. Aqueous HCl systems and mixed solvent systems containing dimethyl sulphoxide (DMSO) have been employed to chromatograph some heavy metal ions and the results have been compared with those of similar studies on Sn (IV) and Ti (IV) antimonate papers. The effect of concentration of impregnating reagents on papers impregnated with Cerium (IV) antimonate has been determined and comparison has been made with other cation exchange papers.

The modified Alberti equation [16].

$$-n \log a_K^+ = R_M^+ \text{ constant}$$

Where n is the charge on the metal ion, a_K^+ is the activity of K^+ ion and $R_M = \log (1/R_f - 1)$ has also been verified for Cerium (IV) antimonate papers. Additionally the effect of composition of impregnated papers on R_f values of metal ions has also been studied in different solvent systems.

This paper reports the retention behaviour of some heavy metal ions on Cerium (IV) based cation exchange papers in pure and mixed solvent systems containing DMSO. Several analytically important separation have achieved such as $Zn^{2+} - Hg^{2+}$, $Pb^{2+} - UO_2^{2+}$, $Pb^{2+} - Cd^{2+}$ and ternary separation of $Pb^{2+} - Bi^{3+} - Hg^{2+}$ and $Pb^{2+} - Bi^{3+} - UO_2^{2+}$ in

different solvent systems. The Alberti equation $-\log a_k^+ = R_M^+$ for cation exchange papers have been verified. The effect of the composition of the impregnated papers plays an important role on the migration behaviour of metal ions in a variety of solvent systems.

MATERIALS AND METHODS

Apparatus

Whatman No. 1 paper 15 x 3 cm strips impregnated with Ce (IV) antimonate were developed in 20 x 5 cm glass jars.

Preparation of Cerium (IV) antimonate impregnated papers

15 x 3cm paper strips were dipped in 0.025 M $SbCl_5$ in 4 M HCl, dried for 15 minutes at room temperature and then again dipped in aqueous 0.025 M Ceric ammonium sulphate. The excess reagent was allowed to drain and the strips were left to dry on filter paper. The dried impregnated strips were washed with conductivity water twice to remove excess reagents and finally dried at room temperature.

To prepare the papers in the K^+ form, these papers were dipped in a solution of KNO_3 of 0.01, 0.05, 0.1 and 0.5 M concentration after depositing Cerium (IV) antimonate. Thereafter, they were washed with conductivity water twice and finally dried at room temperature.

Test solutions and detection reagents

Test solutions of the various metal ions were generally prepared by dissolving 0.1 M nitrates or chlorides of corresponding metals in deionised water or in the corresponding 0.1M acids. Conventional spot test reagents were used for detection purposes. These were prepared and used as described earlier [17].

PROCEDURE

(i) Chromatography

One or two spots of the test solutions were placed on the paper with a thin glass capillary and the paper was conditioned for 15 minutes over the solvent system vapours. The solvent was allowed to ascend 11 cm in all cases. After detecting the spots, the R_f values were measured.

(ii) Solvent systems

Chromatography was performed on Cerium (IV) antimonate papers with the following solvent systems:

- (1) DMSO (Pure)
- (2) DMSO + 0.1 M HCl (8:2, 6:4, 4:6, 2:8)

The same solvent systems were also used for plain whatman No. 1 papers for comparison.

The Cerium and antimony deposited on papers were determined in each case by the procedure described earlier [18, 19].

(iii) Composition of cation exchange papers

For the determination of chemical composition of the material loaded on the paper, the strips were dissolved in a mixture of perchloric acid, nitric acid and sulphuric acid (3:1:4) and the solution was evaporated to dryness. The residue was dissolved in 4 M HCl and the solution was diluted to 250 ml.

Antimony was precipitated as sulphide in presence of oxalic acid. Antimony sulphide was dissolved in concentrated HCl with addition of crystals of potassium chlorate and antimony was determined volumetrically [18]. Cerium in filtrate was determined spectrophotometrically [19].

RESULTS AND DISCUSSION

The results for the composition of Cerium (IV) antimonate papers prepared by using various concentrations of the reagents are summarised in **Table 1**.

On the basis of the difference in R_f values, a large number of separations are possible. **Table-2** summarises some of the separation achieved on Cerium (IV) antimonate papers.

Table-1: Composition of Cerium (IV) antimonate papers prepared by varying concentration of reagents

S. No.	Concentration of reagents		Sb : Ce	Sb/Ce
	SbCl ₅	(NH ₄) ₂ SO ₄ ·Ce(SO ₄) ₂		
	(M)	(M)		
1	0.025	0.025	0.16:0.15	1.10
2	0.05	0.050	0.13:0.14	0.93
3	0.075	0.075	0.16:0.56	0.30
4	0.100	0.100	0.13:0.78	0.23
5	0.025	0.050	0.14:0.23	0.60
6	0.025	0.075	0.16:0.31	0.51
7	0.025	0.010	0.16:1.10	0.15

The utility of cerium (IV) antimonate as a versatile inorganic ion-exchanger has already been established [20] for column operations. The planar chromatographic behaviour has been scarcely studied; therefore, this is a successful attempt to explore the ion-exchange potential of Cerium (IV) antimonate in paper chromatography. The results of these studies are divided into three parts:

(a) Composition of Cerium (IV) antimonite papers :

It is observed that Sb/Ce ratio decreases almost linearly with the increase of concentration of the impregnating reagents whether both the solution of antimony penta chloride and ceric ammonium sulphate are of the same concentration. If the concentration of ceric ammonium sulphate is increased, keeping the antimony penta chloride concentration constant. This is because the papers are first dipped in antimony penta chloride solution which is uniformly absorbed by the paper. When these antimony impregnated strips are dipped in ceric ammonium sulphate solution, the Cerium (IV) antimonate is precipitated. The rate of precipitation depends upon the concentration of Ceric ammonium sulphate solution and the Ce/Sb ratio should increase with the increase of concentration of Ceric ammonium sulphate solution and the Sb/Ce ratio is actually found to decrease with the increase of concentration of Ceric ammonium sulphate solution. In this respect Cerium (IV) antimonate papers also behave like other impregnated papers (13-15).

Table-2: Separation achieved on Cerium (IV) antimonate papers

Solvent system	Metal ion separations (R _f)
DMSO (pure)	Hg ²⁺ (0.52) – UO ₂ ²⁺ (0.80)
	Tb ³⁺ (0.41) – UO ₂ ²⁺ (0.80)
	Mo ⁶⁺ (0.0) – Hg ²⁺ (0.52) – Zn ²⁺ (0.99)
DMSO + 0.1 M HCl (8:2)	Cd ²⁺ (0.59) – Pb ²⁺ (0.82)
	Nd ³⁺ (0.47) – Pt ⁴⁺ (0.70)
DMSO + 0.1 M HCl (6:4)	Pr ³⁺ (0.59) – Dy ³⁺ (0.84)
	Se ⁴⁺ (0.54) – Hg ²⁺ (0.85)
DMSO + 0.1 M HCl (4:6)	Pr ³⁺ (0.59) – Cu ²⁺ (0.91)
	Pr ³⁺ (0.59) – Th ⁴⁺ (0.91)
	Pr ³⁺ (0.59) – Co ³⁺ (0.92)
	Se ⁴⁺ (0.46) – Ni ²⁺ (0.87)
DMSO + 0.1 M HCl (2:8)	Mo ⁶⁺ (0.58) – Fe ³⁺ (0.91)
	Ho ³⁺ (0.39) – Pd ²⁺ (0.91)
	Dy ³⁺ (0.39) – UO ₂ ²⁺ (0.90)
DMSO + 0.1 M HCl (2:8)	Se ⁴⁺ (0.58) – Hg ²⁺ (0.84)
	Pb ²⁺ (0.14) – UO ₂ ²⁺ (0.84)
	Bi ³⁺ (0.28) – Nd ³⁺ (0.78)
	Bi ³⁺ (0.28) – Se ³⁺ (0.58) – VO ²⁺ (0.90)
	Pb ²⁺ (0.14) – Bi ³⁺ (0.28) – Hg ²⁺ (0.84)

It is obvious from Table-1 the Sb/Ce ratio is a maximum at 0.025 M concentration of both the impregnating reagents. The ion-exchange capacity of the exchanger has also been found to be optimum under these conditions [20] and so the papers for chromatographic work were prepared by taking the concentration of both Cerium and antimony solution as 0.025 M.

(b) Verification of modified Alberti equation

Lederer [21] gave an equation: $n.pH = R_M^+$ constant for chromatographic papers in aqueous solvents for cations which was modified by Alberti [16] as $-n \log a_K^+ = R_M^+$ constant for impregnated papers provided the papers are converted into K⁺ form instead of their usual H⁺ form. This equation has so far been tested for Ti (IV) arsenate papers [14] and also for tin (IV) and titanium (IV) antimonates papers [13] in earlier communications. Now we have verified and tested this equation for Cerium (IV) antimonate papers and found it valid for Ti⁺, Hg⁺, Cu²⁺ and Cd²⁺ as is obvious from Fig.1. Thus Cerium (IV) antimonate papers also resemble with other ion-exchange papers in this respect.

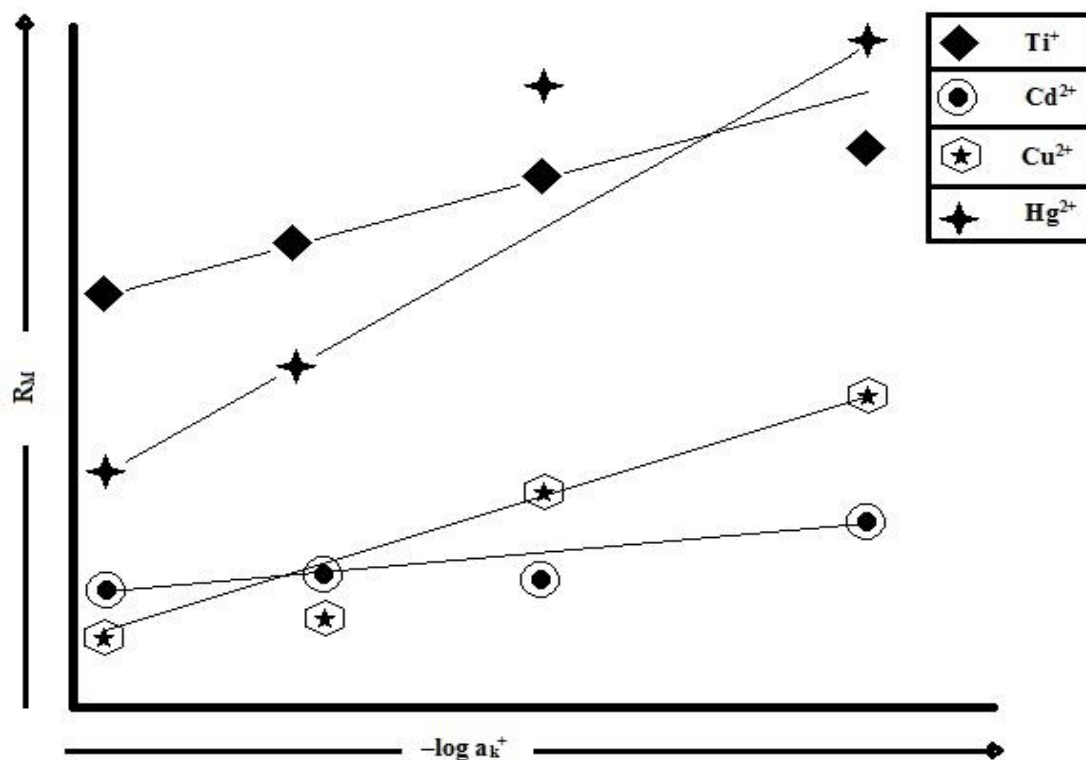


Fig-1: R_M vs $-\log a_k^+$ on Ce(IV) antimonate papers

When the R_f values of various cations were determined on impregnated papers of different compositions as given in **Table-1**, except in a few cases, the R_f values generally decreased in a linear manner with the increase of Sb/Ce ratio in different solvent system. This may be attributed to higher exchange at high Sb/Ce ratio on Cerium (IV) antimonite papers. The results are omitted for the sake of brevity.

(c) Separation of metal ions

A close examination of **Table-2** reveals that the Cerium (IV) antimonite papers have high potential for a number of metal ion separations. On the basis of results obtained in our earlier investigations [17], we have used aqueous HCl system and mixed solvent systems containing DMSO, while DMSO-HCl systems are useful to effect a large number of important and difficult separations, aqueous HCl systems predict the ion exchange potential of Ce (IV) antimonite papers. A plot of R_i ($= R_f$ on plain papers $- R_f$ on antimonite papers) against pH of aqueous HCl systems (Fig-2) indicate that the R_i values generally decrease with the increase of pH for most of the metal ions which means that there is low ion-exchange at high pH. However, in case of some ions such as Al^{3+} , Rb^{3+} , Y^{3+} , Pr^{3+} , Ho^{3+} a reversal behaviour is observed. Some binary and ternary separations of specific interest are as follows: $Zn^{2+} - Hg^{2+}$; $Cd^{2+} - Pb^{2+}$; $Pb^{2+} - UO_2^{2+}$; $Pr^{3+} - Dy^{3+}$; $Pb^{2+} - Bi^{3+} - Hg^{2+}$ and $Pb^{2+} - Bi^{3+} - UO_2^{2+}$ in different solvent systems.

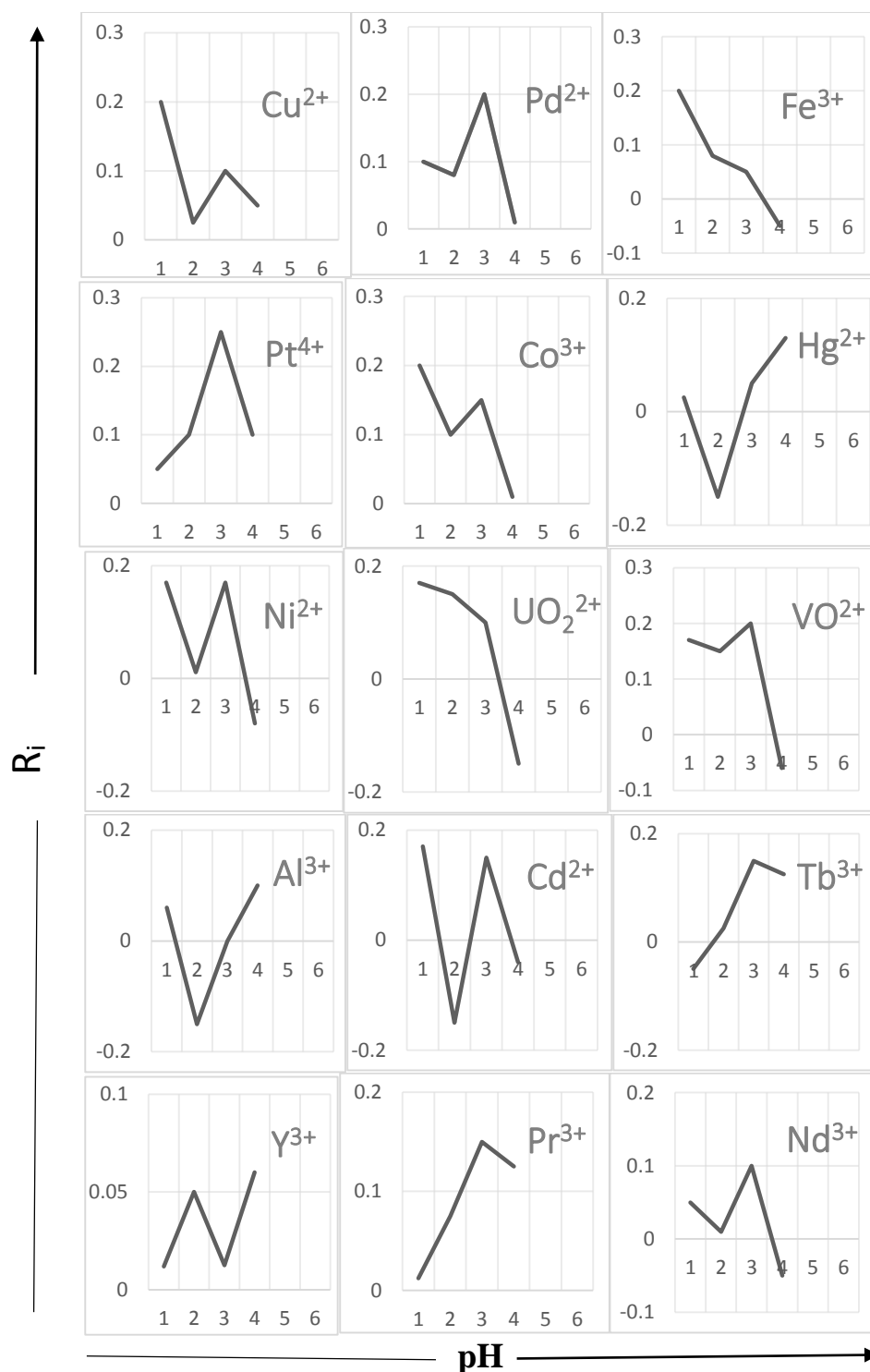


Fig-2: R_i vs pH of aqueous systems.

Hence, the exchanger Ce (IV) antimonate is more effective at low pH for most of the metals. R_M and $\log R_f$ values are also found to be linearly dependent on pH for most of the metal ions.

CONCLUSION

The cerium (IV) antimonate papers have been used to achieve some important separations like $Zn^{2+} - Hg^{2+}$, $Pb^{2+} - UO_2^{2+}$, $Pb^{2+} - Cd^{2+}$, $Pb^{2+} - Bi^{3+} - Hg^{2+}$ and Alberti Equation have been verified which gives the linear relationship in R_m values and $\log a_k$, where a_k is the activity coefficient of K^+ ions.

Acknowledgement

The authors are thankful to Uttar Pradesh Council of Science and Technology, Lucknow, (UP) India for financial support.

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