

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Complexation Ion-Exchange Electrochromatography of 52 Metal Ions on Stannic Arsenate Papers

M. Qureshi^a; S. D. Sharma^b

^a CHEMISTRY SECTION Z.H. ENGINEERING COLLEGE, ALIGARH MUSLIM UNIVERSITY

ALIGARH, INDIA ^b CHEMISTRY DEPARTMENT HINDU COLLEGE, MORADABAD, (U.P.), INDIA

To cite this Article Qureshi, M. and Sharma, S. D. (1978) 'Complexation Ion-Exchange Electrochromatography of 52 Metal Ions on Stannic Arsenate Papers', *Separation Science and Technology*, 13: 8, 723 — 734

To link to this Article: DOI: 10.1080/01496397808057122

URL: <http://dx.doi.org/10.1080/01496397808057122>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Complexation Ion-Exchange Electrochromatography of 52 Metal Ions on Stannic Arsenate Papers

M. QURESHI

CHEMISTRY SECTION
Z.H. ENGINEERING COLLEGE
ALIGARH MUSLIM UNIVERSITY
ALIGARH, INDIA

S. D. SHARMA

CHEMISTRY DEPARTMENT
HINDU COLLEGE
MORADABAD (U.P.), INDIA

Abstract

The complexation effect of tartaric, citric, and oxalic acids on the electrophoretic migrations of cations has been studied. The mechanism of migration is explained in terms of precipitation, ion exchange, and adsorption phenomena.

INTRODUCTION

Electrochromatography is a rather nonselective process, especially when the background electrolyte is a noncomplexing substance, e.g., HNO_3 or HClO_4 . In such a case the separations achieved are not spectacular (1-4). It is therefore usual to combine electrochromatography with complexation or ion exchange. In the former case, solutions of complexing acids such as lactic, tartaric, citric, and oxalic acids are used as eluants (1, 3, 8), and in the later case metal ions are spotted on papers impregnated with ion-exchange materials before electrophoresis. (1-7). Both these modifications result in enhanced selectivity and lead to interesting separations.

As far as we are aware, very few attempts have been made to combine

complexation and ion exchange with electrochromatography (1, 3). In this article we wish to show that the combination of these three processes leads to excellent separation possibilities.

Stannic arsenate was used to impregnate the papers owing to its high chemical stability and good ion-exchange capacity (9, 10). Stannic arsenate belongs to the zirconium-phosphate-type of exchange materials. These substances show high selectivity at low pH and they decompose at high pH. Hence weak acids were chosen as background electrolytes to prevent the hydrolysis of the exchange material. The complexing acids chosen were oxalic, tartaric, and citric. These choices enabled us to study the effect of the OH group on the cation movement. The OH group has excellent co-ordinating properties owing to its high dipole moment and the availability of its lone pair of electrons for coordination. As a result, some very difficult separations have been achieved. The results are summarized in this report.

EXPERIMENTAL

Apparatus

Electrochromatography was performed on 46.5 × 2.40 cm. Whatman No. 1 and stannic arsenate paper strips with a horizontal strip apparatus (Toshniwal, Ltd. India).

Reagents and Chemicals

Chemicals and solvents used were B.D.H. analytical grade reagents.

Preparation of Ion-Exchange Papers

Stannic arsenate papers were prepared as in our previous publication (11).

Preparation of Cation Solutions and Detectors

These were prepared and used as described earlier (11). The test solutions were generally 0.1 *M* in the metal nitrate or chloride. Conventional spot test reagents were used for detection purposes.

Procedure

As described previously (1). In all cases electrochromatography was continued for 6 hr at a constant potential difference of 100 V. The current was 4.40 mA. There was no significant heating during electrophoresis.

RESULTS

The electrochromatographic behavior of 52 metal ions on stannic arsenate papers has been studied using 0.5 M citric acid, 0.5 M tartaric acid, and 0.5 M oxalic acid solutions as background electrolytes. The movement of the center of the zone was measured in centimeters. A positive sign indicates movement of the ion toward the cathode, i.e., positively charged species, and a negative sign indicates movement toward the anode, i.e., a negatively charged species. The binary and ternary separations achieved experimentally are given in Table 1. The possible separations of one cation from numerous metal ions are given in Table 2.

Electrochromatographic behavior of cations was also studied on Whatman No. 1 papers in all the three background electrolytes for comparison with impregnated papers. Some useful separations were achieved on plain papers as well (Table 3).

DISCUSSION

In order to bring out the more interesting features of these studies, migrations have been plotted vs atomic numbers (Figs. 1-3). These curves will be discussed one by one.

The citric acid curve (Fig. 1) is a beautiful periodic curve with alkali

TABLE 1
Separations Actually Achieved on Stannic Arsenate by Electrochromatography

| Background electrolyte | Separations actually achieved |
|------------------------|--|
| 0.5 M Citric acid | $\text{Te}^{4+}(-2.0)-\text{Pt}^{4+}(-5.0)$ $\text{W}^{6+}(-3.6)-\text{Ti}^{4+}(0.0)$ or $\text{VO}^{2+}(-0.4)$ $\text{Fe}^{3+}(-1.1)-\text{Co}^{2+}(+6.8)-\text{Ni}^{2+}(+2.7)$ or $\text{Mn}^{2+}(+2.5)$ $\text{Fe}^{3+}(-1.0)-\text{Mn}^{2+}(+2.7)-\text{Pt}^{4+}(-5.2)$ $\text{K}^{+}(+15.0)-\text{Ti}^{4+}(0.0)-\text{Mo}^{6+}(-2.8)$ $\text{Be}^{2+}(+3.6)-\text{Mg}^{2+}(-1.7)-\text{Sr}^{2+}(+7.3)$ |
| 0.5 M Tartaric acid | $\text{Ca}^{2+}(-1.0)-\text{Be}^{2+}(+4.0)$ or $\text{Mg}^{2+}(+4.9)$ or $\text{Sr}^{2+}(+6.5)$ $\text{Sn}^{2+}(-0.9)-\text{Mo}^{6+}(-4.0)$ $\text{Ni}^{2+}(+5.0)-\text{Ag}^{+}(+1.0)$ or $\text{Hg}^{2+}(+0.7)$ or $\text{Te}^{4+}(-1.8)$ or $\text{Pt}^{4+}(-2.0)$ or $\text{Au}^{3+}(-3.0)$ or $\text{Pd}^{2+}(-3.6)$ |
| 0.5 M Oxalic acid | $\text{Pd}^{2+}(-5.0)-\text{Hg}^{2+}(+1.0)$ $\text{VO}^{2+}(+7.6)-\text{Th}^{4+}(0.0)$ or $\text{Mo}^{6+}(-1.0)$ or $\text{UO}_2^{2+}(-2.1)$ $\text{Ti}^{+}(+11.7)-\text{Zn}^{2+}(0.0)$ or $\text{Ni}^{2+}(0.0)$ $\text{Fe}^{3+}(+12.0)-\text{Fe}^{2+}(0.0)$ or $\text{Cu}^{2+}(0.0)$ or $\text{Al}^{3+}(-2.0)$ $\text{Ti}^{4+}(+0.2)-\text{VO}^{2+}(+7.9)-\text{K}^{+}(+11.8)$ or $\text{Fe}^{3+}(+12.7)$ |

TABLE 2
Some Possible Separations of One Cation from Numerous Metal Ions by
Electrochromatography

| Ions | Background electrolyte | Interfering ions | Impregnating material |
|---|------------------------|--|-----------------------|
| K^+ or Rb^+ or Cs^+ (+15.0) from 49 cations | 0.5 M Citric acid | None | Stannic arsenate |
| Tl^+ or Co^{2+} (+7.0) from 48 cations | 0.5 M Citric acid | Sr^{2+} , Zn^{2+} | Stannic arsenate |
| Sr^{2+} (+8.0) from 49 cations | 0.5 M Citric acid | Tl^+ , Co^{2+} | Stannic arsenate |
| Nb^{5+} (-5.4) from 50 cations | 0.5 M Tartaric acid | Mo^{6+} | Stannic arsenate |
| VO^{2+} (+8.0) from 51 cations | 0.5 M Oxalic acid | None | Stannic arsenate |
| Fe^{3+} or Tl^+ (+12.5) from 49 cations | 0.5 M Oxalic acid | K^+ , Rb^+ , Cs^+ | Stannic arsenate |
| Ni^{2+} or Be^{2+} (+8.5) from 48 cations | 0.5 M Citric acid | Co^{2+} , Cd^{2+} | None |
| Ba^{2+} (+11.6) from 48 cations | 0.5 M Citric acid | Zn^{2+} , Mn^{2+} | None |
| Mg^{2+} (+16.5) from 50 cations | 0.5 M Citric acid | Ca^{2+} | None |
| Cd^{2+} (+9.5) from 46 cations | 0.5 M Citric acid | Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Be^{2+} | None |
| Pb^{2+} (+5.8) from 51 cations | 0.5 M Citric acid | None | None |
| Mn^{2+} or Zn^{2+} (+10.5) from 48 cations | 0.5 M Citric acid | Co^{2+} , Cd^{2+} | None |
| Mo^{6+} or W^{6+} (-3.8) from 49 cations | 0.5 M Citric acid | Nb^{5+} | None |
| Fe^{2+} (+10.0) from 49 cations | 0.5 M Tartaric acid | Mn^{2+} , Sr^{2+} | None |
| Ba^{2+} or Sr^{2+} (+17.0) from 50 cations | 0.5 M Oxalic acid | None | None |
| Pt^{4+} (-7.5) from 51 cations | 0.5 M Oxalic acid | None | None |
| Pd^{2+} or Mo^{6+} (-6.0) from 48 cations | 0.5 M Oxalic acid | Fe^{3+} , Nb^{5+} | None |

TABLE 3
Separations Actually Achieved on Whatman No. 1 Papers by Electrochromatography

| Background electrolyte | Separations actually achieved |
|------------------------|--|
| 0.5 M Citric acid | $\text{Cd}^{2+}(+9.7)-\text{Sb}^{3+}(-0.6)$ or $\text{Cu}^{2+}(+3.7)$ $\text{UO}_2^{2+}(+1.8)-\text{Mo}^{6+}(-3.0)$ or $\text{Pb}^{2+}(+5.2)$ $\text{Al}^{3+}(+2.2)-\text{Zn}^{2+}(+7.3)$ $\text{Ag}^{+}(+1.5)-\text{Pb}^{2+}(+6.3)$ $\text{Co}^{2+}(+9.6)-\text{Fe}^{3+}(-2.0)$ or $\text{Cu}^{2+}(+4.0)$ $\text{La}^{3+}(+3.0)-\text{Se}^{4+}(-1.0)$ $\text{Mn}^{2+}(+10.0)-\text{Fe}^{3+}(-2.0)$ or $\text{Cr}^{3+}(0.0)$ $\text{Cr}^{3+}(0.0)-\text{Zn}^{2+}(+8.8)$ or $\text{Mo}^{6+}(-3.2)$ $\text{Tl}^{+}(+17.6)-\text{Bi}^{3+}(0.0)$ $\text{Al}^{3+}(+2.2)-\text{Be}^{2+}(+7.8)-\text{Fe}^{3+}(-1.6)$ $\text{Cu}^{2+}(+4.4)-\text{Ni}^{2+}(+8.9)-\text{Fe}^{3+}(-1.6)$ or $\text{Tl}^{+}(+17.9)$ |
| 0.5 M Tartaric acid | $\text{Cd}^{2+}(+8.1)-\text{Bi}^{3+}(+1.0)$ or $\text{Te}^{4+}(-1.0)$ or $\text{Pd}^{2+}(-1.3)$ $\text{Ca}^{2+}(+3.2)-\text{Ba}^{2+}(+8.5)$ $\text{Mn}^{2+}(+8.3)-\text{Ni}^{2+}(+4.6)$ or $\text{Pt}^{4+}(-2.0)$ $\text{Se}^{4+}(-1.0)-\text{Ni}^{2+}(+5.1)$ $\text{Tl}^{+}(+14.6)-\text{Cd}^{2+}(+8.1)-\text{Hg}^{2+}(0.0)$ or $\text{Ag}^{+}(+1.8)$ |
| 0.5 M Oxalic acid | $\text{Au}^{3+}(-1.0)-\text{Pd}^{2+}(-5.7)$ or $\text{Pt}^{4+}(-7.0)$ $\text{Ag}^{+}(+0.6)-\text{Pd}^{2+}(-5.3)$ or $\text{Pt}^{4+}(-7.2)$ $\text{Cu}^{2+}(0.0)-\text{Pd}^{2+}(-5.8)$ or $\text{Pt}^{4+}(-7.0)$ $\text{Cr}^{3+}(-4.0)-\text{Co}^{2+}(+0.8)$ $\text{Pt}^{4+}(-7.1)-\text{Se}^{4+}(-1.1)$ or $\text{Ir}^{3+}(0.0)$ $\text{Pd}^{2+}(-5.8)-\text{Pb}^{2+}(0.0)$ or $\text{Te}^{4+}(+2.1)$ $\text{Mo}^{6+}(-5.7)-\text{W}^{6+}(-0.8)$ $\text{Ti}^{4+}(-5.2)-\text{Th}^{4+}(0.0)$ $\text{Al}^{3+}(-2.7)-\text{Ba}^{2+}(+15.8)$ $\text{La}^{3+}(+2.4)-\text{Sr}^{2+}(+16.0)$ |

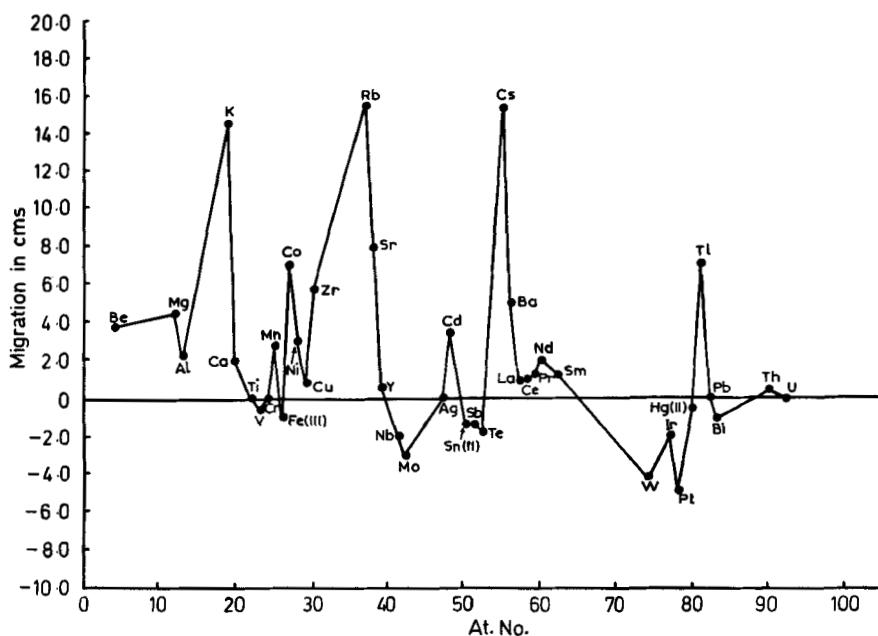


FIG. 1. Plot of migration of cations on stannic arsenate papers in 0.5 M citric acid vs atomic number.

metals occupying the maxima. Li^+ and Na^+ ions have not been studied but their migration will also be approximately the same as those of K^+ , Rb^+ , and Cs^+ . In the citric acid curve for plain papers (Fig. 4), Tl^+ also occupies the same position as Rb^+ and Cs^+ . Thallous arsenate is probably less soluble than thallous nitrate and hence there is a decrease in the migration of Tl^+ on impregnated papers as compared to plain papers. As the charge increases the migration decreases, and we have $\text{Rb}^+ > \text{Sr}^{2+} > \text{Y}^{3+} > \text{Zr}^{4+} > \text{Nb}^{5+}$ or $\text{Cs}^+ > \text{Ba}^{2+} > \text{La}^{3+} > \text{Hf}^{4+} > \text{W}^{6+}$ or $\text{Tl}^+ > \text{Pb}^{2+} > \text{Bi}^{3+} > \text{Th}^{4+}$. Bivalent ions such as Be^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} have a migration up to almost 9 cm. There are a few exceptions, i.e., Ca^{2+} , Cu^{2+} , Pb^{2+} , Pd^{2+} , Hg^{2+} , and UO_2^{2+} . These ions have much lower migration, probably because they form stronger complexes with citric acid than Be^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} . It is known that Hg^{2+} forms stronger complexes than Zn^{2+} and Cd^{2+} . On the impregnated papers the trend is the same as on plain papers except for UO_2^{2+} , Pb^{2+} ,

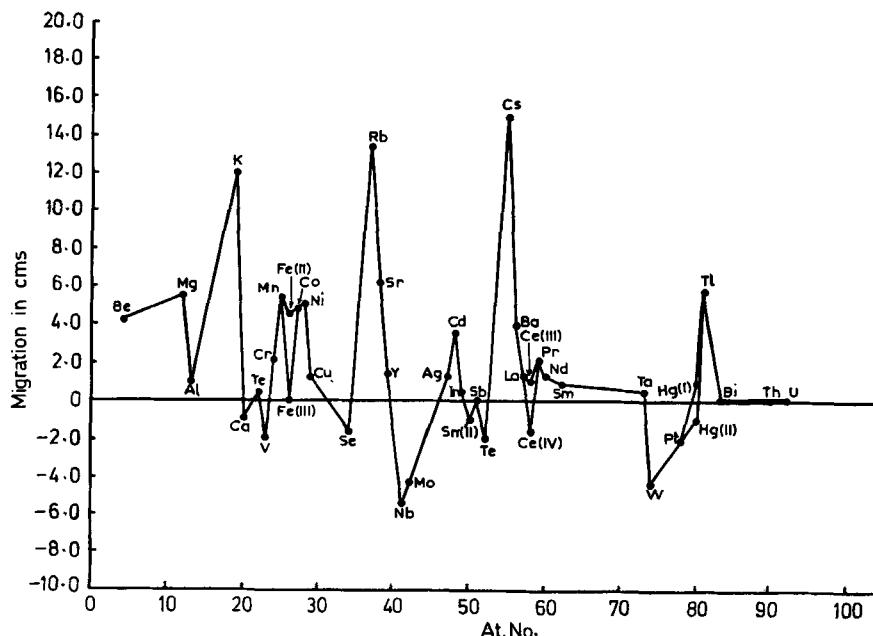


FIG. 2. Plot of migration of cations on stannic arsenate papers in 0.5 M tartaric acid vs atomic number.

Ag^+ , and Hg^{2+} . This is probably due to the fact that these ions are precipitated if sodium arsenate is added to the cation solution followed by 0.5 M citric acid.

In the case of oxalic acid (Fig. 3) most of the ions have zero mobility because oxalic acid is a good precipitating agent and it is used to precipitate Cu^{2+} in the presence of Fe^{3+} , Al^{3+} , and Mn^{2+} (12). Our observations also show that Cu^{2+} , Ni^{2+} , and Zn^{2+} have zero mobility while Fe^{3+} , Al^{3+} , and Mn^{2+} have finite mobility. Oxalic acid is also used to precipitate thorium and lanthanones from monazite (13). We also found that thorium and lanthanones have zero mobility. This background electrolyte is very suitable for the separation of K^+ , Rb^+ , Cs^+ , Fe^{3+} , VO^{2+} , Tl^+ , and Pt^{4+} from numerous metal ions. A number of ternary separations are also possible, e.g., Fe^{3+} - VO^{2+} - Tl^{4+} , Fe^{3+} - Zr^{4+} - Nb^{5+} , VO^{2+} - Zr^{4+} - Nb^{5+} , Ta^{5+} - VO^{2+} - Fe^{3+} , VO^{2+} - Th^{4+} - UO_2^{2+} , and Tl^+ - Ag^+ - Pt^{4+} . UO_2^{2+} forms anionic complexes of the type $[\text{UO}_2(\text{C}_2\text{O}_4)_2]^{2-}$ or $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$ and therefore UO_2^{2+} appears as an anion in the graph (14).

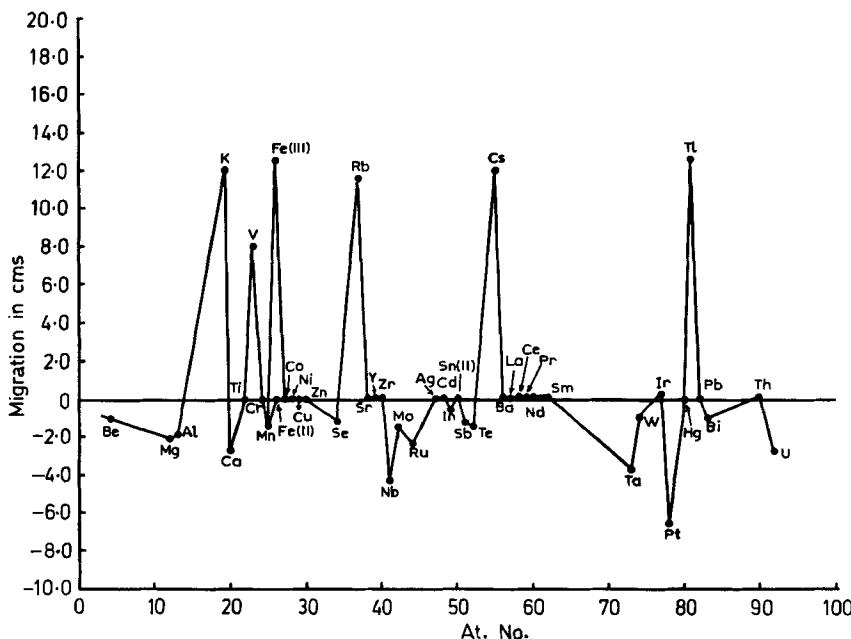


FIG. 3. Plot of migration of cations on stannic arsenate papers in 0.5 M oxalic acid vs atomic number.

The curve for tartaric acid (Fig. 2) is again of a periodic nature. The monovalent ions K^+ , Rb^+ , Cs^+ , and Tl^+ appear on the maxima. The ions appearing at minima are either anions such as selenite, tellurite, molybdates, and tungstates or ions which give rise to anions on interaction with tartaric acid, e.g., Nb^{5+} , VO^{2+} , Ca^{2+} , and Ce^{4+} . The effect of charge is easily seen in such cases as (a) $K^+ > Mg^{2+} > Al^{3+}$, (b) $Rb^+ > Sr^{2+} > Y^{3+}$, and (c) $Cs^+ > Ba^{2+} > La^{3+}$. Titanium hydroxide precipitates at pH = 0 to 2; therefore Ti^{4+} has zero mobility. According to the Irving Williams stability series (15), $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. Cu^{2+} therefore has the lowest mobility and Mn^{2+} the highest. Zn^{2+} tails and Ni^{2+} , Co^{2+} , and Fe^{2+} are very close. Cu^{2+} has a zero charge at pH = 5 and the charge becomes more and more negative as the pH increases (16). Therefore it is safe to assume that Cu^{2+} has a positive charge at pH = 1 as is apparent from Fig. 2.

This study has resulted in numerous separations of analytical importance as is apparent from Tables 1, 2, and 3. Actually a still larger

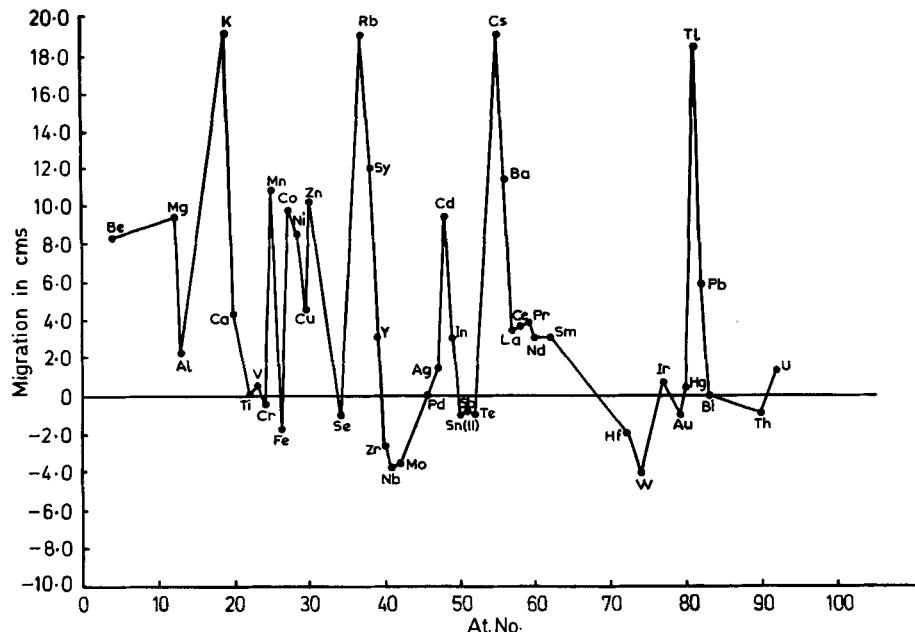


FIG. 4. Plot of migration of cations on plain papers in 0.5 M citric acid vs atomic number.

number of separations are possible. We discuss briefly only the salient features.

(1). The alkali metals K^+ , Rb^+ , and Cs^+ can be separated from numerous metal ions on either plain or impregnated papers in any one of the solvent systems studied. However, the best results are obtained on stannic arsenate papers in 0.5 M citric acid in which there is no interference at all. On plain papers using 0.5 M citric acid it is not possible to separate K^+ from Tl^+ as they are very close. However, on stannic arsenate papers even this separation is possible. Thus impregnation results in a very selective differential migration. The large mobilities of the alkali metal ions are due to their high electropositive character and low complexing ability, and they can be separated from alkaline earths easily in 0.5 M citric acid on stannic arsenate papers. It is apparent from Table 2 that K^+ has been actually separated from $Ti(IV)$ and $Mo(VI)$ in 0.5 M citric acid and from $Ti(IV)$ and VO^{2+} in 0.5 M oxalic acid.

TABLE 4
Comparison of Electrochromatographic Behavior of Some Metal Ions on
Whatman No. 1 and Stannic Arsenate Papers

| Cations | Background electrolyte | Whatman No. 1 papers | Stannic arsenate papers |
|-----------|------------------------|-------------------------|----------------------------|
| Pb^{2+} | 0.5 M Citric acid | + 5.8 | 0.0 |
| Tl^+ | 0.5 M Citric acid | +18.3 | + 7.0 |
| Ni^{2+} | 0.5 M Citric acid | + 8.5 | + 3.0 |
| Mn^{2+} | 0.5 M Citric acid | +10.8 | + 2.8 |
| Ba^{2+} | 0.5 M Citric acid | +11.6 | + 5.0 |
| Tl^+ | 0.5 M Tartaric acid | +15.5 | + 5.8 |
| Fe^{2+} | 0.5 M Tartaric acid | +10.0 | + 4.5 |
| Mg^{2+} | 0.5 M Tartaric acid | +13.0 | + 5.5 |
| Fe^{3+} | 0.5 M Oxalic acid | - 5.5 | +12.5 |
| VO^{2+} | 0.5 M Oxalic acid | - 4.5 | + 8.0 |
| Ba^{2+} | 0.5 M Oxalic acid | +17.0 | 0.0 |
| Sr^{2+} | 0.5 M Oxalic acid | +17.5 | 0.0 |

(2). In 90% of the cases the ions show a lower migration on impregnated papers compared to plain papers. This is because the arsenates of most ions are less soluble than the corresponding nitrates and chlorides. In some cases the difference is very remarkable, as shown in Table 4.

(3). Most ions move as positive species toward the cathode. Thus in 0.5 M citric acid the following ions behave as positively charged species and move toward the cathode on stannic arsenate papers in the order given below. The ions which tail have been omitted from the series to simplify the discussion. $K^+ \approx Rb^+ \approx Cs^+ (+15.0) > Tl^+ \approx Co^{2+} (+7.0) > Zn^{2+} (+5.0) > Be^{2+} (+3.8) > Cd^{2+} (+3.5) > Ni^{2+} \approx Mn^{2+} (+3.0) > Al^{3+} (+2.3) \approx Nd^{3+} (+2.0) > Sm^{3+} \approx Pr^{3+} (+1.3) > Ce^{3+} \text{ or } Ce^{4+} \text{ or } La^{3+} (+1.0) > Cu^{2+} (+0.8) \approx Y^{3+} (+0.6) > Th^{4+} (+0.5)$.

The same is true for plain papers, the order now being $K^+ \approx Rb^+ \approx Cs^+ (+19.0) > Tl^+ (+18.3) > Sr^{2+} \approx Ba^{2+} (+12.0) > Mn^{2+} (+10.8) > Zn^{2+} (+10.3) > Co^{2+} \approx Cd^{2+} \approx Mg^{2+} (+9.5) > Sb^{5+} (+9.0) > Ni^{2+} \approx Be^{2+} (+8.5) > Pb^{2+} (+5.8) > Ca^{2+} (+4.5) > Cu^{2+} (+4.1) > Pr^{3+} (+3.8) > La^{3+} \approx Ce^{3+} \approx Ce^{4+} \approx Y^{3+} \approx Sm^{3+} \approx Nd^{3+} \approx In^{3+} (+3.0) > Al^{3+} (+2.4) > Ag^+ (+1.5) > UO_2^{2+} (+1.2) > Ir^{3+} (+0.8) > VO^{2+} (+0.6) > Hg_2^{2+} (+0.5)$. Consistent with their charges, a glance at the order of migration on stannic arsenate papers clearly shows that the monovalent ions move the farthest followed by the divalent, the trivalent, and the tetravalent ions. This is because the ions with a higher charge are adsorbed more strongly and hence move less. There is only one exception

TABLE 5
Precipitation of Cations in the Mixture of Background Electrolyte and Impregnating Material

| Background electrolyte | Cations + background electrolyte | | Cations + sodium arsenate + background electrolyte | |
|------------------------|--|---|--|--|
| | Cations which precipitate | Cations do not precipitate | Cations which precipitate | Cations do not precipitate |
| 0.5 M Citric acid | Nil | Hg^{2+} , Bi^{3+} , Ti^{4+} , Th^{4+} , Pd^{2+} | Ag^+ , Hg^{2+} , Pb^{2+} , UO_2^{2+} | Cr^{3+} , Hg_2^{2+} , Ti^{4+} |
| 0.5 M Tartaric acid | Nil | Sb^{3+} , Hg_2^{2+} , Hg^{2+} , Ir^{3+} | Th^{4+} , UO_2^{2+} , Bi^{3+} | Fe^{3+} , Sb^{3+} |
| 0.5 M Oxalic acid | Co^{2+} , Cu^{2+} , Zn^{2+} , Ce^{4+} , Pb^{2+} , Hg^{2+} , Th^{4+} , Pr^{3+} , Hg_2^{2+} , Sm^{3+} , Nd^{3+} , Ce^{3+} | Zr^{4+} , Ni^{2+} , Ag^+ , Fe^{2+} | Ag^+ , Ba^{2+} , Sr^{2+} , Cd^{2+} , Cu^{2+} , Pr^{3+} , Pb^{2+} , Hg_2^{2+} , Ce^{4+} , Th^{4+} , Y^{3+} , La^{3+} , Ce^{3+} , Sm^{3+} , Nd^{3+} | Co^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , Ti^{4+} , Fe^{2+} , Sn^{2+} , Zr^{4+} |

and that is Cu^{2+} which comes after the trivalent ions. This is because Cu^{2+} forms a highly insoluble arsenate (II) with a K_{sp} of 7.6×10^{-36} . That this explanation is correct is confirmed by the fact that on plain papers the position of Cu^{2+} is before the trivalent ions as it should be if the charge on the ion is the deciding factor.

(4). Ions which have zero migration may do so owing to (a) precipitation, (b) ion exchange, (c) complexation to form uncharged complexes, and (d) strong adsorption owing to high charge.

On mixing solutions of the cations with the background electrolyte oxalic acid, it was found that in the cases of Co^{2+} , Cu^{2+} , Zn^{2+} , Ce^{4+} , Pb^{2+} , Hg^{2+} , Th^{4+} , Pr^{3+} , Hg_2^{2+} , Ce^{3+} , Sm^{3+} , and Nd^{3+} a precipitate was obtained. In such cases, zero migration on plain papers is therefore due to precipitation mechanism. In order to simulate conditions on impregnated papers, sodium arsenate was added to the cation solution followed by the background electrolyte. A number of ions precipitate under these conditions (see Table 5). In these cases also the precipitation mechanism holds good.

(5). To study the effect of complexation, migration was studied in

HNO_3 of $\text{pH} = 1$. In most cases there is a decrease in mobility due to complex formation, e.g., Th^{4+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} , Be^{2+} , Hg^{2+} , Mg^{2+} , Ba^{2+} , and Al^{3+} , when HNO_3 is replaced by 0.5 M citric, tartaric, or oxalic acid solutions as background electrolytes.

(6). In order to study the electrophoretic effect, some ions were electrochromatographed for 6 hr at 50 and 100 V. It was observed that in some cases, i.e., K^+ , Rb^+ , Al^{3+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Cs^+ , Sr^{2+} , and Ba^{2+} , the migration at 100 V is more than double that at 50 V.

Acknowledgments

The authors thank Dr. R. N. Gupta and Dr. B. C. Banerjee for providing research facilities.

REFERENCES

1. M. Qureshi and A. H. Israili, *Anal. Chim. Acta*, **41**, 523 (1968).
2. M. Qureshi, K. G. Varshney, and F. Khan, *Sep. Sci.*, **6**(4), 559 (1971).
3. M. Qureshi, K. G. Varshney, and R. P. S. Rajpoot, *Ann. Chim.*, In Press.
4. J. P. Rawat and P. Singh, *Ibid.*, **64**, 873 (1974).
5. G. Alberti, A. Conte, G. Grassini, and M. Lederer, *Electroanal. Chem.*, **4**, 301 (1962).
6. Ying-Bo-Hai, *Acta Chim. Sinica*, **31**, 263 (1965).
7. M. Qureshi, J. Kishore, and R. G. Varshneya, *Electroanal. Chem.*, In Press.
8. T. R. Sato, W. P. Norris, and H. H. Strain, *Anal. Chem.*, **27**, 521 (1955).
9. M. Qureshi, H. S. Rathore, and R. Kumar, *J. Chem. Soc., A*, **2**, 1986 (1970).
10. M. Qureshi, R. Kumar, and H. S. Rathore, *Ibid.*, **2**, 272 (1970).
11. M. Qureshi and S. D. Sharma, *Anal. Chem.*, **45**(7), 1283 (1973).
12. R. Belcher and C. L. Wilson, *New Methods in Analytical Chemistry*, 2nd impression, Asia Publishing House, New Delhi, 1956, p. 12.
13. Ref. 12, p. 13.
14. A. A. Grinberg, *An Introduction to the Chemistry of Complex Compounds*, Addison-Wesley, Reading, Massachusetts, 1962, p. 338.
15. M. T. Beck, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold, London, 1970, p. 250.
16. Ref. 15, p. 104.

Received by editor January 24, 1978