DOI 10.15415/jce.2015.12010

Electrophoretic Study of d-Block Metal Ions on Plain and Tri-n-Butylamine (TBA) Impregnated Titanium (IV) Tungstate Layers

SD SHARMA[1] AND MRIDUL GUPTA[2]

[1]School of Sciences, IFTM University, Moradabad, Uttar Pradesh, India

[2]J.S. Hindu college, Amroha, JP Nagar, Uttar Pradesh, India

Email: mridul_bhalwar@yahoo.com

Received: Oct 13, 2014| Revised: Nov 19, 2014| Accepted: Nov 21, 2014

Abstract: RPTLE of ninteen d block metal ion studied on TBA impregnated titanium(IV)tungstate layer in nine solvent system among them three are complex forming acids OA,TA, CA to study the effect of complexation on migration. Electrophoretic migration also correlated with Ionc potential,Kd of metal ions and Ka of acids,pH of electrolytes.The spots are well defined in RPTLE and Mi is positive.

Keywords: RPTLE-reversed phase thin layer electrophresis, TBA-tri n butylamine, OA-oxalic acid, TA-tartaric acid, CA-citric acid, Kd-distribution coefficient, Ka-ionization constant, Mi-migration on untreated layers-migration on impregnated layers

1. INTRODUCTION

Since 1946, thin layer electrophoresis (TLE) has been employed for the separation of organic substances (Consden, R. et. al. 1946). It is also a simple, inexpensive and convenient technique for the separation of metal ions. It has distinct advantages over thin layer chromatography (TLC) i.e. greater detection possibilities, more rapid ionic migration, better separation possibilities due to difference in direction of migration, of similar type of metal ions etc. Various adsorbetns such as silica gel-G, cellulose Makrova,T.P et. al. (1972), Gypsum (Dobici, F 1963), Kieselguhr (Mogissi, A 1964), Silica gel-H (Frachl, R et. al. 1973) etc. have frequently been used in TLE of metal ions and anions. The admixture of silica gel-G and Starch (Sharma, S.D et. al. 1995) have also been used which increases the degree of selectivity in ionic migration.

A survey of literature reveals that in the last fifteen years reversed phase thin layer chromatography (RPTLC) has been used extensively to study the retention behaviour of metal ions. As such RPTLC of metal ions has become

Journal of Chemistry,
Environmental Sciences
and its Applications
Vol. 1, No. 2
March 2015
pp. 97–109

very popular, Shimizu. T(1995) sharma, S.D (1995 to 2001) et. al. However, no effort has been made to study the electro chromatographic behaviour of metal ions on the layers of in organic ion exchangers using reversed phase thin layer electrophoresis (RPTLE). Among the synthetic inorganic ion exchangers of zirconium phosphate type, titanium (iv) tungstate is known to possess promising thermal and chemical stability (Qureshi, M 1973). It shows high selectivity at low pH and decomposes at high pH, hence solutions of weak acids were chosen as background electrolytes in order to prevent the hydrolysis of the exchanger. The complexing acids used as background electrolytes are oxalic, citric and tartaric.Tri-n-butylamine (TBA), being nonpolar in nature was successfully used as an impregnating material (Sharma, S.D 1995) in earlier study. It has, therefore, been decided to investigate RPTLE behaviour of some d-block metal ions on titanium (iv) tungstate layers impregnated with TBA. As a result of the combined effect of the electric field, ion exchange and complexation, a number of analytically important and useful metal ion separations were achieved.

2. EXPERIMENTAL

2.1 Apparatus and Reagents

Thin layer electrophoresis was performed on glass plates (2.5 × 25cm) using a horizontal electrophoresis apparatus operated with an electronic regulated power supply unit (Metrex Ltd. India). Chemicals and solvents used were either E. Merck, or B.D.H analytical reagent grade. Solutions of metal ions and detection reagents were prepared and used as Anal – R. grade

2.2 Preparation of ion exchange papers

Whatman No. 1 paper strips were impregnated with 0.25M solutions of both titanic chloride and sodium tungstate were prepared in distilled water. Paper strips were first passed through the titanic chloride solution for 3 to 5s and the excess titanic chloride was removed by placing the strips on a filter paper sheet. The strips were then dipped in the sodium tungstate solution for 5s and the excess reagents, allowed to dry at room temperature for 12hr., and used as such. These papers were found to possess considerable ion exchange capacity. For K^+ ion (K^+-H^+ exchange) the exchange capacity is 0.35 meq per g of the treated paper, as determined by column experiment (Saturation method)Frache,R (1973)et. al. A qualitative test for titanium in the solution was negative. This proves that the exchanger is chemically stable in the electrolytes used when kept for 12hr.

2.3 Test solution and detectors

Solutions of 0.1M, of chlorides, nitrates or sulphates of most of the metal ions were prepared in 0.1M solutions of the corresponding acids. Antimony, bismuth and tin chloride solution of the corresponding acids. Antimony, bismuth and tin chloride solutions, 0.1M, were prepared in 3.6 M or 4 M HCl. Cerric sulphate solution, 0.1M, was prepared in 3.6 N H_2SO_4 Solutions of sodium selnite, sodium molybdate, sodium tungstate, potassium chloride, caesium chloride and rubidium chloride, 0.1M, were prepared in demineralised water. Detection was made by the following reagents:-

Pb^{2+}, Ag^+, Hg_2^{2+}, Hg^{2+}, Tl^+, Bi^{3+}, pd^{2+},Sb^{3+}, Cd^{2+}, Sn^{2+}, Sn^{4+} spots were detected with yellow ammonium sulphide solutions. Fe^{3+}, VO^{2+}, UO_2^{2+} were detected with 1% aqueous $K_4[Fe(CN)_6]$ solution. Aqueous K_3 (Fe(CN$_6$] was used to detect Fe^{2+}, 1% alcoholic diphenyl carbazide was used to detect Cr^{3+}, Mn^{2+} and Zn^{2+} spots and 01% alcoholic alizarin Red-S solution for Zr^{4+}, Th^{4+}, Ce^{4+}, Ce^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Ru^{3+} spots. A fresh solution of sodium cobalfinitrate was used k^+, Rb^+ and $Cs^{+,}$ Al^{3+} was detected with aluminon solution. Fresh aqueous sodium rhodizonate solution in neutral medium was used to detect Ba^{2+} and sr^{2+}, 0.1M stannous chloride solution in 4M HCl was used to detect Au^{3+}, SeO_3^{2-}, MoO_4^{2-}, Pt^{4+} and WO_4^{2-}, Co^{2+} and Ni^{2+} were detected with 1% ammonical dimethyl glyoxime.

2.4 Ion exchange capacity

The ion exchange capacity of titanium (IV) tungstate impregnated papers was 0.35 meq/gm. For titanium (IV) tungstate exchanger prepared as above, it is 0.58 meq/gm as determined by column experiment by Saturation method (Quershi.M et. al.1970)

2.5 Procedure

The electrophoresis apparatus was filled to the mark with background electrolyte and paper strips were placed in position and allowed to become saturated with the electrolyte solution. Whereupon a small drop (0.02ml) of the test solution containing 2×10^{-6} moles of the ions was applied separately with the help of the lambda pipette on each strip in the middle. In all cases electrochromatography was continued for 3 hr. At constant potential difference of 100 V. There was no significant heating during the process.

3. RESULTS AND DISCUSSION

Electochromatography of some d-block metal ions on plain and TBA impregnated titanium (IV) tungstate layers has been performed in the following background electrolytes: E_1 to E_6 ; 1M to 0.00001M HNO_3, E_7 ; 0.1M oxalic acid (O.A.), E_8 ; 0.1M citric acid (C.A), E_9 ; 0.1M tartaric acid (T.A). The movement of the centre of the zones was measured in cm. A positive sign indicates the movement of the ions towards cathode and a negative sign the movement towards anode. The eolectrochromatograhic migration of metal ions on plain and impregnated titanium (IV) tungstate layers. As a result of significant difference in the migration of chemically similar elements, fantastic separation possibilities arise. Some of the important separations actually achieved are (a) Cu^{2+} - Ag^{+} in 0.1M HNO_3, (b) Cu^{2+} or Ag^{+} and Fe^{2+} - Fe^{3+} in 0.1M oxalic acid and (c) Fe^{2+} -Fe^{3+} in 0.1M citric acid. These separation

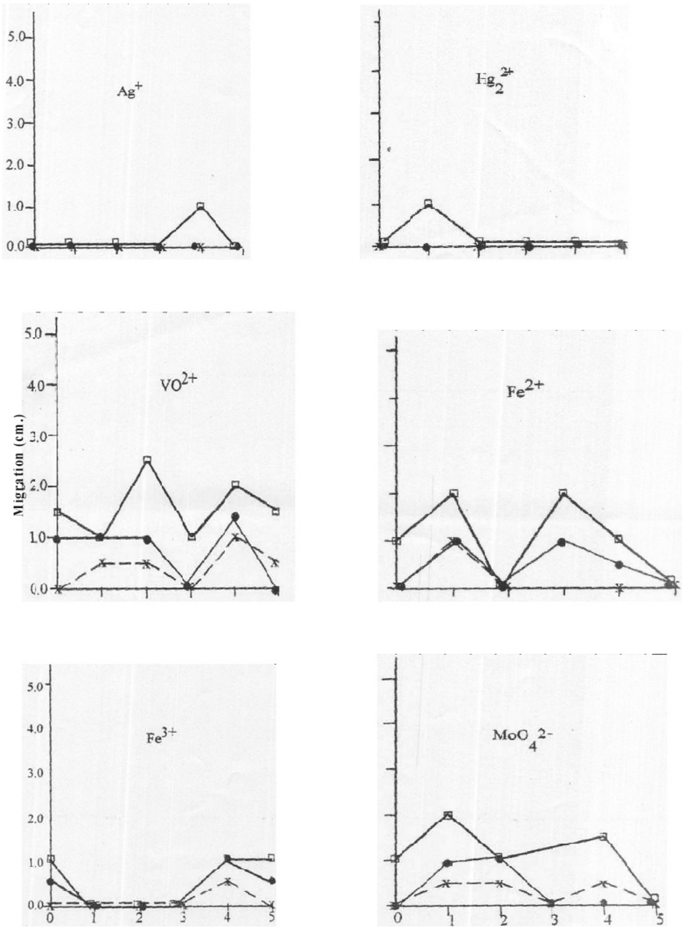


Figure 1-a: Plots of Electrophoretic Migration (cm.) of Metal Ions Versus pH of Electrolytes on (●) Plain, (X) Impregnated Titanium (IV) Tungustate Layers, and (□) Titanium (IV) Tungstate Impregnated Papers.

possibilities arise from the combination of three effects (a) the complexing acids chosen as background electrolytes form complexes with most of the metal ions, (b) titanium (IV) tungstate layers selectively adsorb certain metal ions and (c) electric field applied. A comparative study of electrophoretic behaviour of metal ions using titanium (IV) tungstate impregnated papers and titanium (IV) tungstate layers (both prepared by using same solutions of titanium (IV) tungstate layers (both prepared by using same solution of titanium (IV) chloride and sodium tungstate) and also keeping all other conditions such as voltage, time, background electrolytes etc. Same is quite revealing (Figure 1a-1d). The salient features of the study are:

(1) For almost all the metal ions, there ia a decrease in migration on thin layers probably due to higher adsorption. The higher ion exchange capacity of thin layer in comparison to that of impregnated papers may also be the reason for this decrease (the ion exchange capacity of titanium (IV) tungstate is 0.58 meq/gm and that for titanium (IV) tungstate impregnated papers is 0.35 meq/gm).

(2) All the metal ions except Pd^2, Pt^{4+} and Hg^{2+} move towards cathode.

(3) The plots of migration v/s pH (Figure- 1) show that for almost all metal ions the migration is maximum at pH1. Beyond this, there is a gradual decrease in migration.

(4) The most interesting features of the study is the zero migration of Ag+ at all pH. This is probably due to the interaction of Ag+ with the exchanger. It has been shown by Murray et.al. (1968) that the metal ions are preferably exchanged when the gel has a negative surface charge but Ag^+ is considerably exchanged even when the gel has a positive charge. They have explained this by the assumption that the adsorption of Ag+ is due to Ag^+ - matrix interaction.

To study the effect of complexation, plots of migration v/s metal ions in 0.1M oxalic acid and 0.1M HNO_3, used as back-ground electrolytes, were drawn (Figure- 2. It is observed that for almost all metal ions, the migration is much lower in oxalic acid media than in HNO_3 due to the formation of oxalato complexes. However, zero migration for some metal ions in oxalic acid media is probably due to precipitation (Table 1) oxalic acid is a good precipitating agent. Also Pd^{2+} and Pt^{4+} both move towards anode showing similar electrophoretic behaviour as they are chemically similar in nature.

For citric acid media, the plots of electrophoretic migration v/s pK_1 of metal citrate complexes are quite interesting (Figure-3). For metal ions such as Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} the migration increases with an increase in pK_1 of their citrate complexes. This can be explained on the basis of the fact

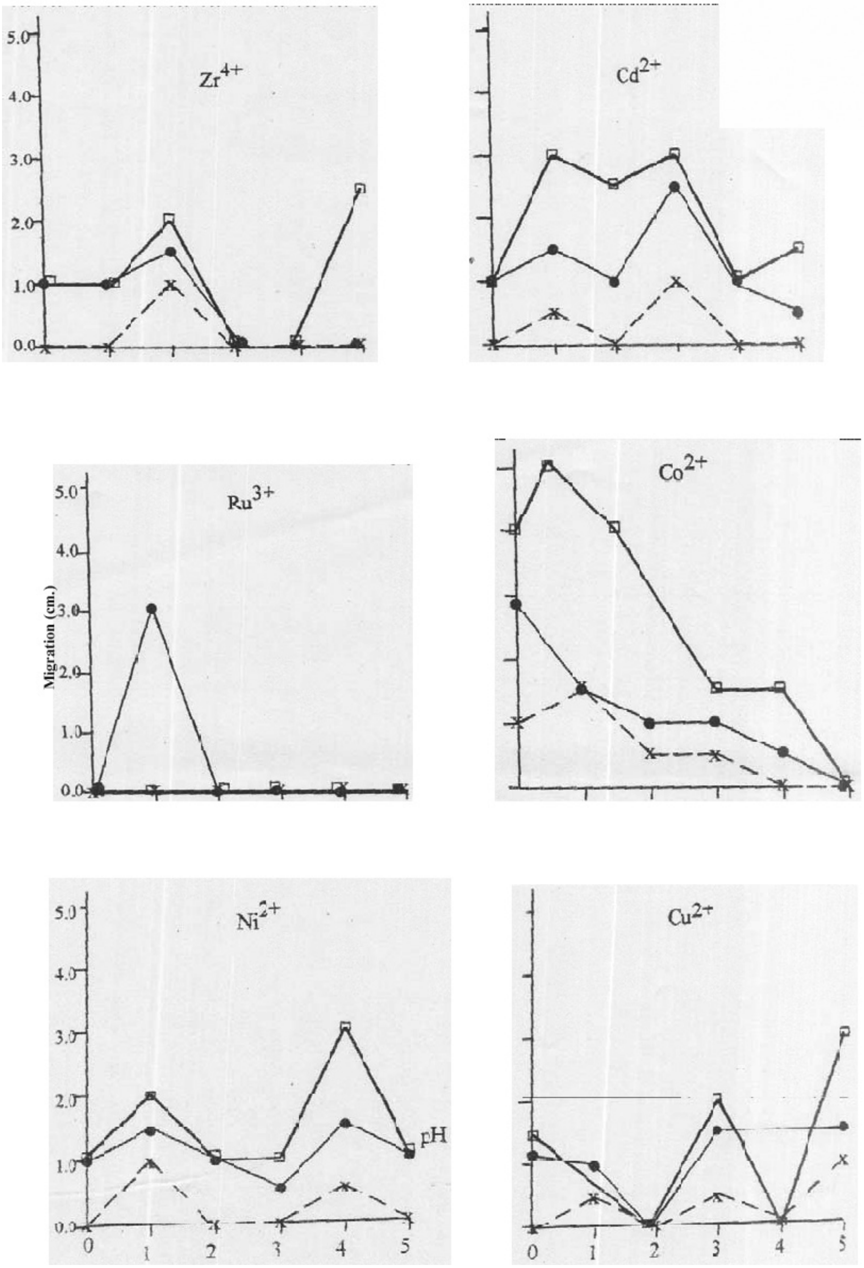


Figure 1b: Plots of Electrophoretic Migration (cm.) of Metal Ions Versus pH of Electrolytes on (●) Plain, (X) Impregnated Titanium (IV) Tungustate Layers, and (□) Titanium (IV) Tungstate Impregnated Papers.

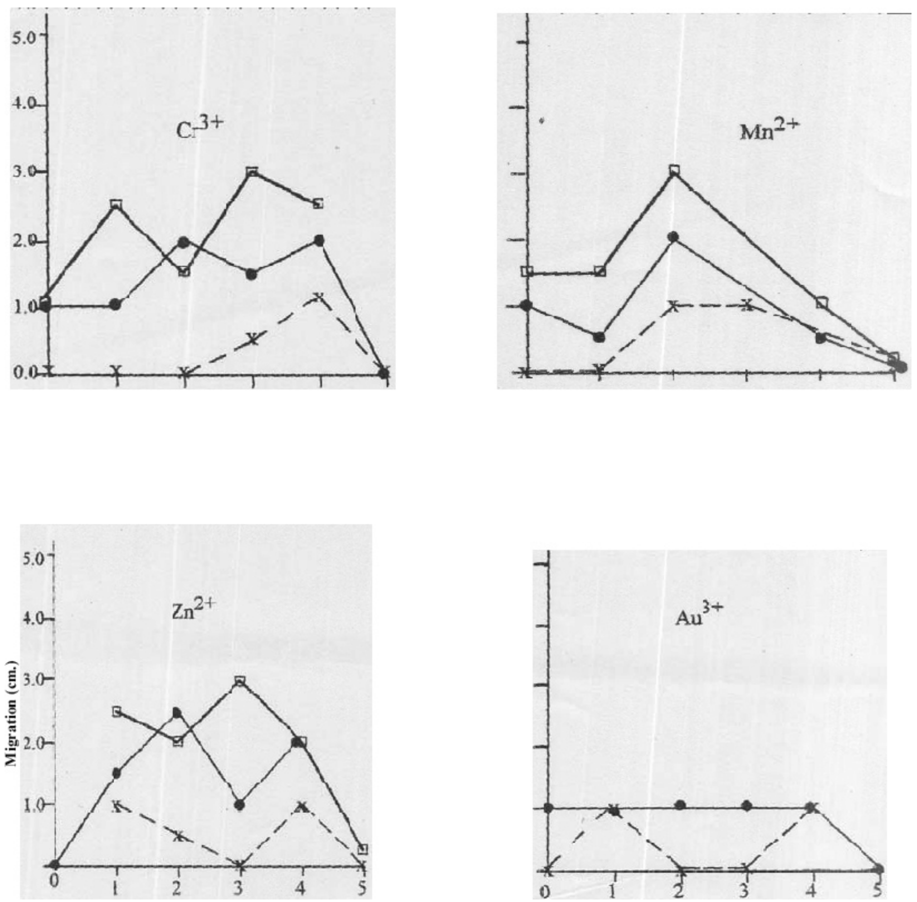


Figure 1c: Plots of Electrophoretic Migration (cm.) of Metal Ions Versus pH of Electrolytes on (●) Plain, (X) Impregnated Titanium (IV) Tungustate Layers, And (□) Titanium (IV) Tungstate Impregnated Papers.

that when pK_1 increases, the dissociation of metal citrate complexes decreases thereby causing higher migration. However, the migration for Fe^{3+} and Cu^{2+} is much lower inspite of having higher adsorption of Cu-citrate complexes whereas higher adsorption of Cu-citrate complex on thin layers may be the reason for this behaviour.

It is interesting to correlate the electrophoretic migration of some d-block metal ions with their ionic potential Lurie .J. et. al (1975) et. al i.e. the ratio of the charge of the ion to its radius, in 0.1M HNO_3 media. Two series of d-block metal ions were considered on the basis of their electronic set up in

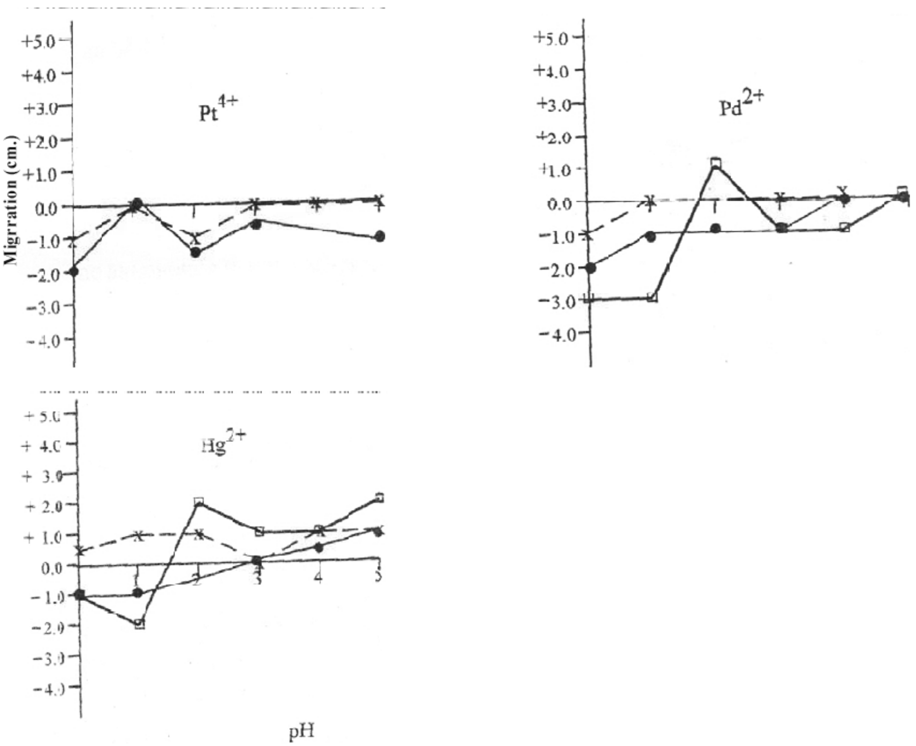


Figure 1d: Plots of Electrophoretic Migration (cm.) of Metal Ions Versus pH of Electrolytes on (•) Plain, (X) Impregnated Titanium (IV) Tungustate Layers, And (□) Titanium (IV) Tungstate Impregnated Papers.

outermost orbit. Metal ions, their respective ionic potentials and electrophoretic migrations are given below:

(a) Metal ions having incomplete 18 electrons in external layer.

Metal ion :	Mn^{2+},	Fe^{2-},	Co^{2+},	Ni^{2+},	Fe^{3+},	Cr^{3+}
Ionic Potential:	2.2	2.4	2.4	2.6	4.5	4.6
Electrophoretic Migration (cm.):	0.5	1.0	1.5	2.0	0.0	1.0

(b) Metal ions having complete 18 electrons in external layer.

Metal ion :	Ag^{+},	Cu^{2-},	Hg^{2+},	Cd^{2+},	$Zn2^{+}$
Ionic Potential: 0.9	1.0	1.8	1.9	2.4	
Electrophoretic Migration (cm.):	0.0	1.0	1.0	1.5	1.5

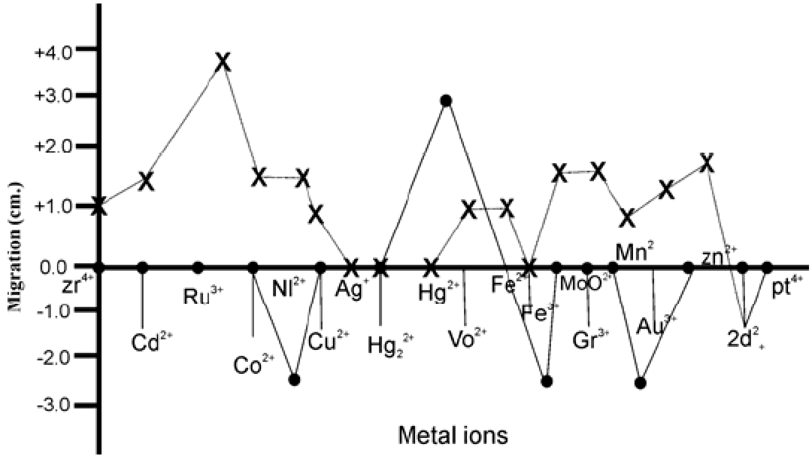


Figure 2: Plots of Electrophoretic Migration Versus d-Block Metal Ions on Titanium (IV) Tungustate Layers in (●) 0.1M Oxalic Acid and (x) 0.1M HNO_3.

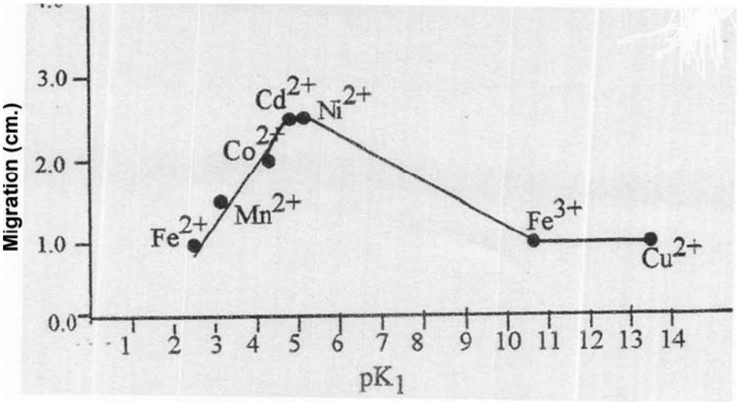
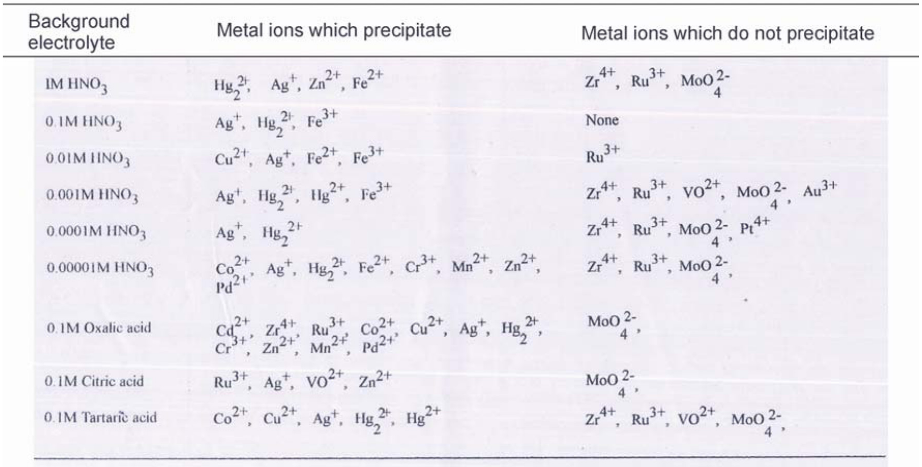


Figure 3: Plots of Electrophoretic Migration Versus pk_1 of Metal Citrate Complexes in 0.1M Citric Acid.

It is clear from the above data that for metal ions, electrophoretic migration increases with an increase in their ionic.
Potentials except in case of Fe^{3+} and Cr^{3+}. The zero migration of Fe^{3+} due to the formation of ferric tungstate which is insoluble in 0.1M HNO_3 as evident from table 1, and hence there is no movement of the ion. In case of Cr^{3+}, the relatively lower migration that expected on the basis of its ionic potential is

Table 1: Precipitation of Metal Ions from Solution after Addition of Sodium Tungstate Followed by Electrolyte.



Background electrolyte	Metal ions which precipitate	Metal ions which do not precipitate
1M HNO_3	Hg_2^{2+}, Ag^+, Zn^{2+}, Fe^{2+}	Zr^{4+}, Ru^{3+}, MoO_4^{2-}
0.1M HNO_3	Ag^+, Hg_2^{2+}, Fe^{3+}	None
0.01M HNO_3	Cu^{2+}, Ag^+, Fe^{2+}, Fe^{3+}	Ru^{3+}
0.001M HNO_3	Ag^+, Hg_2^{2+}, Hg^{2+}, Fe^{3+}	Zr^{4+}, Ru^{3+}, VO^{2+}, MoO_4^{2-}, Au^{3+}
0.0001M HNO_3	Ag^+, Hg_2^{2+}	Zr^{4+}, Ru^{3+}, MoO_4^{2-}, Pt^{4+}
0.00001M HNO_3	Co^{2+}, Ag^+, Hg_2^{2+}, Fe^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Pd^{2+}	Zr^{4+}, Ru^{3+}, MoO_4^{2-},
0.1M Oxalic acid	Cd^{2+}, Zr^{4+}, Ru^{3+}, Co^{2+}, Cu^{2+}, Ag^+, Hg_2^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Pd^{2+}	MoO_4^{2-},
0.1M Citric acid	Ru^{3+}, Ag^+, VO^{2+}, Zn^{2+}	MoO_4^{2-},
0.1M Tartaric acid	Co^{2+}, Cu^{2+}, Ag^+, Hg_2^{2+}, Hg^{2+}	Zr^{4+}, Ru^{3+}, VO^{2+}, MoO_4^{2-},

probably due to the kinetic inertness of Cr^{3+}. It has been explained that ion exchange behaviour of Cr(III) is characterised by the tendency of the element to held tenaciously on cation exchanger and as such it not easily desorbed. This isa consequence of the kinetic inertness of Cr(III)Toube. H(1952) et. al.. The specific behavius of Cr^{3+} on the basis of its kinetic inertness was explained in the study of TLC of metal ions on stannic arsenate thin layers. Quereshi.M (1978) et. al.

Further, the average mobility (M) of the metal ions studied increases with an increase in ionisation constant (K_a) of the acid used as background electrolyte which is in order T.A < C.A < O.A. This behaviour is probably due to the increase in number of H^+ ions which compete with the metal ions for the exchange sites.

It has been observed that the electrophoretic migrations of metal ins on papers impregnated with titanium (IV) based exchangers are inversely proportional their distribution coefficients Qureshi.M (1973) et. al.. This behaviour is expected because when K_d is higher, the metal ion is more strongly held by the ion exchanger and move less easily. On titanium (IV) tungstate also, this trend was confirmed by determining the migratin of some common metal ions on titanium (IV) tungstate layers in 0.01M HNO_3 as the background electrolyte. The K_d values for these metal ions in 0.01M HNO_3 are already reported Qureshi.M (1973) et. al. shows that for these metal ions the sequence of K_d values is the same as the one predicted from the electrophoretic migration. The K_d values and the electrohoretic migrations of some metal ions

Table 2: K_d Values and Electrophoretic Migration of Metal Ions in 0.01M HNO_3.

Metal ions	Kd	Migration (cm)
Hg^{2+}	0.10	3.5
Zn^{2+}	0.25	2.5
Mn^{2+}	0.25	2.0
Zr^{2+}	1.30	1.5
Cd^{2+}	3.20	1.0
Co^{2+}	7.90	1.0

are given in table 2. It is observed that the sequence of K_d values is the same as predicted from electrophoretic migrations.

K_d value : $Hg^{2+} < Zn^{2+} = Mn^{2+} < Zr^{4+} < Cd^{2+} < Co^{2+}$;
Electrophoretic migration $Hg^{2+} > Zn^{2+} > Mn^{2+} > Zr^{4+} > Cd^{2+} = Co^{2+}$

The same is not, however, true for all the metal ions studied. It is considered that elution sequence can be predicted from K_d values. It follows that the electrophoretic migrations are not reliable for such prediction because (a) in electrochromatography, the movement of background electrolyte is too fast for equilibrium to be established and (b) some of the metal ions interact in different manner on the layers than on columns.

In the RPTLE of d-block metal ions on TBA impregnated layers, the spots are well defined and no tailing is observed. The migration was found to be reproducible and variation does not exceed 5% of the average value. The impregnated layers are quite stable and firm and are capable of withstanding the background electrolyte and chemical operations. For impregnated layers, 20% TBA was used as an impregnant of the basis of earlier experience. Sharma. S.D (1999) et. al.

In order to study the effect of pH of the background electrolytes on the migration of some some d-Block metal ions on tungstate layers, plots of electrophoretic migration v/s pH were drawn (Fig-1)

It is observed that for a number of metal ions except Zr^{4+}, Co^{2+}, VO^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+} and Zn2+, the electrophoretic migration first with an increase in pH till it becomes 1. For Ni^{2+}, Cu^{2+}, and Cr^{3+} the migration is maximum at pH 4. The migration is almost zero for all metal ions except Ni^{2+}, Cu^{2+} and Hg^{2+} at PH 5. This may be due to precipitation of these ions at this pH (Table III). For Cu^{2+}, Ni^{2+} and Hg^{2+}, Some specific interaction with the stationary phase may be the reason for their exceptional behaviour.

Figure-1 shows that the adsorption on TBA impregnated titanium (IV) tungstate layers was lower than on untreated ones, as indicated by the positive value of Mi (Mi = migration on untreated layers-Migration on impregnated layers). Thus, impregnation leads to increased adsorption for most of the metal ions studied. This might be due to the nonpolar nature of TBA (which is insolable in water). Due to being polar in nature, untreated layer s adsorb the ions with decreasing polarity of the adsorbent surface was also reported in earlier studies out by Sharma. S.D and Sharma. S.C. (1999 et. al.) on the RPTLC of metal ions on silica gel-G layers impregnated with TBP and TBA.

REFERENCES

[1] Consden, R., Gorden, A.H and martin, A.J.P. (1946) J.Biochem, **40**, 33. ; Kunkel, H.G and Wallenius, G, (1955) Sciences, **122**, 288; Smithies, O, (1955) J. Biochem, **61**, 629; Groulade.J, Fine, J.M and Ollivier.C, (1961) Nature, **191**, 72; Marti, H.R. (1961) Experentia, **17**, 235; Honegger. C. G, Helv. (1961) Chim. Acta, **44**, 173; Pastuska, G and Trinks. H. (1961) Chemiker Zig **85**, 535; Vahvasel Ko. (1962) E, Nature, **193**, 474; Hollender, A., Scand. (1962) J.Clin. Lab. Invest **14**, 104; Raymond. S and Marumi.N. (1962) Anal. Biochem. **3**, 23; Pastuska, G and Trinks, H. (1962) Chemiker Zig, **86**, 135.

[2] Dobici. F and Grassini. G. (1963) J. Chromatogr. **10**, 98
http://dx.doi.org/10.1016/S0021-9673(01)92278-2

[3] Frache. R and Dadone. A. (1973) Chromatographia. **6**, 430
http://dx.doi.org/10.1007/BF02281022

[4] Frache. R and Dadone. A. (1973) Chromatographia. **6**, 266
http://dx.doi.org/10.1007/BF02281022

[5] Groulade. J, Fine. J.M and Ollivier. C. (1961) Nature, **191**, 72
http://dx.doi.org/10.1038/191072a0

[6] Hollender. A, Scand. (1962) J. Clin. Lab. Invest, **14**, 104

[7] Honegger. C.G, Helv. (1961) Chim. Acta, **44**, 173

[8] Lurie. J. (1975) Handbook of Analytical Chemistry, Mir Publishers, Mascow p 30.

[9] Makrova, T.P and Stapnov, A.V. (1972) Zh. Ana. Khim, **26(9)**, 1823; Sharma, S.D and Misra. S. (1991) J. Liq. Chromatogr. **14 (181)**, 1453

[10] Makrova. T.P and Stapnov. A. V. (1971) Zh. Anal. Khim. **26(9)**, 1823

[11] Martin. H.R. (1961) Experentia, **17**, 235 http://dx.doi.org/10.1007/BF02160641

[12] Moghissi. A. (1964) Anal. Chim. Acta. **80**, 91
http://dx.doi.org/10.1016/S0003-2670(00)88690-0

[13] Murray. D.J and Fuerstnu. M.C. (1968) J. Inorg. Nucl. Chem., **30**, 3325
http://dx.doi.org/10.1016/0022-1902(68)80129-0

[14] Pastuska. G and Trinks. H. (1961) Chemiker Ztg. **85**, 535

[15] Pastuska. G and Trinks. H. (1962) Chemiker Ztg. **86**, 135

[16] Qureshi. M, Kumar. R and Rathore. H.S. (1970) J. Chem. Soc. 272
http://dx.doi.org/10.1039/j19700000272

[17] Qureshi. M, Varshney. K.G and Fatima. N. (1978) Sepr. Sci and Technol., **13(4)**, 321.

[18] Qureshi. M, Zehra. N, Nabi. S.A and Kumar.V. (1973) Talanta, **20**, 609

http://dx.doi.org/10.1016/0039-9140(73)80111-0
[19] Raymond. S and Masumi. N. (1962) Anal. Biochem. **3**, 23 http://dx.doi.org/10.1016/0003-2697(62)90040-4
[20] Sharma. S.D and Gupta. Rachna. (2001) J. Ind. Chem. Soc. **78**, 301
[21] Sharma. S.D and Misra. S. (1991) J. Liq. Chromatogr. **14(8)**, 1453 http://dx.doi.org/10.1080/01483919108049627
[22] Sharma. S.D and Sharma. C. (2000) J. Planar Chromatogr. **13** 93
[23] Sharma. S.D and Sharma. S.C. (1999) J. Chromatogr. **841**, 263 http://dx.doi.org/10.1016/S0021-9673(99)00293-9
[24] Sharma. S.D, Misra. S and Agarwal. R. (1995) Chem. Environ. Res. **4 (1 & 2)**, 111.
[25] Sharma. S.D, Misra. S and Sharma.S.C. (1998) J. Ind. Chem. Soc. **75**, 81
[26] Sharma. S.D, Sharma. S.C and Sharma. C. (2001) J. Planar Chromatogr. **14**, 16
[27] Sharma. S.D, Sharma. S.C and Sharma.C. (1999) J. Planar Chromatogr, **12**, 440
[28] Shimizu. T, Tanake. T and Kobayashi. M, J. Planar Chromatogr., **8**, 469
[29] Shimizu. T, Tanake .T and Toyoshima .Y. (1994) J. Planar Chromatogr. **8**, 152
[30] Smithies. O. (1955) J .Biochem. **61**, 629
[31] Toube. H. (1952) Chem. Rev., **50**, 69 http://dx.doi.org/10.1021/cr60155a003
[32] Vahvaselko. E. (1962) Nature, **193**, 474 http://dx.doi.org/10.1038/193474a0