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Low Voltage Thin Layer Electrophoresis of Anions on Silica Gel-G And Titanium (IV) Tungstate Layers

S.D. SHARMA[1] AND MRIDUL GUPTA [2#]

[1.] School of Sciences, IFTM University, Moradabad (U.P.)

[2] J.S. Hindu Degree College, Amroha, J.P. Nagar (U.P.)

***Email : mridul_bhalwar@yahoo.com**

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Abstract The low voltage thin layer electrophoresis of anions has been studied on Silica Gel-G and titanium (iv) tungstate layers in in various complexing acid media such as Oxalic acid (O.A), Citric acid(C.A), Tartaric acid (T.A) and Succinic acid (S.A).The electrophoretic migration of anions also correlated with lyotropic number, N. The Spots are well defined in electrophoresis.

Keywords : Elecrophoresis, O. A-Oxalic acid, T.A–Tartaric acid, C.A–Citric acid lyotropic number(N)

1. INTRODUCTION

Earlier, thin layer electrophoresis (TLE) of metal ions has been studied on different adsorbent materials. However, a scare attention has been paid to the separation of anions by using this technique. This is probably due to the problems in their detection along with some practical limitations as many anions e.g. sulphates, phosphates etc get precipitated with the background electrolytes at high voltage [1]. To overcome this difficulty it is advisable to apply low voltage for TLE of anions.

Dobici et al[2] were the first to separate iodate and periodate on gypsum layer. Moghissi [3] separated anions using thin layer on kiselguhr. However, TLE was not employed for the study of anions for almost more than three decades. Only recently, low voltage thin layer inophoresis of anions and cation on Silica Gel-G –starch admixture layer has been carried out [4]. The various adsorbents employed for TLE of cation and anions, silica gel-G is considered to be the most suitable due to the ease of employment and cleanness of separations.

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Synthetic ion exchangers have been widely used for the chromatographic separations of metal ions. Among these, titanium (iv) tungstate is known to possess promising thermal and chemical stability [5].It has successfully been used as acation exchanger but it does not behave as an anion exchanger. Interestingly, silica gel-G act both as cation and anion exchanger [6-9]. We, have, therefore, decided to use silica gel-Gas an adsorbent for the TLE of anions. The effect of the addition of titanium (iv) tungstate to silica gel-G has also been studied. Titanium (iv) tungstate shows high selectivity at low pH and decomposes at high pH. Hence, aqueous solutions of weak comlexing acids such as oxalic, citric, tartaric, succinic and acetic acid were chosen as background electrolytes in order to prevent, the hydrolysis of the exchanger materials.

2. EXPERIMENTAL

2.1 Apparatus and Reagents :

Thin layer electrophoresis was performed on glass plates (2.5 · 2.5cm) using a horizontal electrophoresis apparatus operated with on electronic regulated power supply unit (Metrex Ltd. India)

Titanium(iv) chloride (Riedel, Germany) was used. All other chemicals and solvents used were of analytical regent grade from British Drug House (London, U.K.)

2.2 Test Solution and detectors :

Test solutions of anions were prepared by dissolving the sodium and potassium salts of anions in demineralised water. Following reagents were used for detection purpose:

Silver nitrate solution in methanol for Cl^-, Br^-,I^-, $IO4,^-$ $S_2O_3^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, S^{2-}, AsO_4^{+3}, $AsO3_3^{-3}$, ferric chloride for $\{Fe(CN_6)\}^{3-}$,$\{Fe(CN_6)\}^{4-}$, SCN^-, N^{3-}, diphenyl amine for BrO^{3-},VO^{3-},MnO^{4-},IO^{3-}, zirconium tetrachloride alizarin for F^-, phenolphthale in for CO^{3-},acidic $KMnO_4$ for C_2O_4 and sodium nitroprusside for SO_3^-

2.3 Synthesis of Titanium (IV) tungstate :

Titanium IV tungstate was prepared by mixing 0. 30M solution of titanium (IV) chloride and sodium tungstate in the volume ratio of 1:1, at p H and digesting the resulting precipitate at room temperature for 24 hr. After filtering and drying the precipitate was cracked in dematerialized water and then placed in 2M HNO_3 to convert it in the H^+ form. The material was finally washed with dematerialized water and the slurry was made by grinding the mixture vigorously in glass mortar for a long time. This step proved to be very important for complete adhesion. The grinding of the granules must be complete and the slurry should be in the form of a fine paste without any solid particles being left. The slurry was then spread over the clean glass plate with the help of an applicator to give 0.1 mm. thick layers. The plates were ready for use after drying at room temperature. For RPTLE, thin layer were then impregnated with 20% mixture of try-n-butyl amine in diethyl ether. Di ethyl ether was evaporated by heating the plate in an electric oven at 40 ± 5 C for 1 hr. The plates were stored in desiccators at room temperature and used for electro chromatography. Its ion exchange capacity was found to be 0.58 mg/gm. of exchanger as determined by column experiment.

2.4 Preparation of chromatoplates :

The chromatoplates of silica gel-G, titanium (IV) tungstate and their admixture (1:1) were prepared by mixing each of them separately with dematerialized water with constant stirring for about 5 min. The slurry was immediately coated on the clean glass plate with the help of an applicator and uniform thin layer (≈0.15 mm. thick) were obtained. The plates of silica gel –G were first dried at room temperature and then in electric oven for 1hr. at 100°C. For titanium (IV) tungstate layers were dried at room temperature. The admixtures were dried at 60 °C in electric oven for 1 hr.

2.5 Procedure :

The electrophoresis apparatus was filled to the mark with background electrolyte. Activated plates, which form the stabilization medium, were placed in position and allowed to become saturated with electrolyte. A small drop of the test solution was then applied in the middle. In all cases, electrophoresis was continued for 3 hr. at a constant potential difference of 100V. There was no significant heating during electrophoresis.

3. RESULTS AND DISCUSSION

Electro chromatography of twenty anions was performed on thin layers of (a) Silica gel-G; (b) Titanium (IV) tungstate; (c) Admixture of silica gel-G and titanium (IV) tungstate (1:1). The background electrolytes used were 0.1M Oxalic acid, 0.1 Citric acid, 0.1 Tartaric acid, 0.1 Succinic acid, and 0.1 Acetic acid. The movement of the centre of the zones was measured in cm. The negative sign indicates the movement of ions towards anode i.e. negatively charged species. The result are summarized in table 1,2 and 3.

Table 1 : Migration of Anions (cm) on Silica Gel-G Layers in different Electrolytes

ANIONS	0.1M OXALIC ACID	0.1M CITRIC ACID	0.1M TARTARIC ACID	0.1M SUCCINIC ACID	0.1 M ACETIC ACID
Cl^-	0.0	–2.5	–4.5	–1,0	0.0
Br^-	–1.5	–4.0	–5.5	–3.0	–1,0
I^-	–2.5	–3.0	–6.5	–5.5	–2.0
F^-	0.0	0.0	0.0	0.0	0.0
IO_3^-	0.0	–3.0	–4.2	–5.0	–4.5
IO_4^-	–1.0	–3.0	–4.5	–4.5	–3.0
BrO_3^-	N.D	–5.0	0.0	–5.0	–6.0
AsO_3^{3-}	–1.0	–1.5	–1.0	–2.0	–2.5
AsO_4^{3-}	–1.5	–1.0	–1.5	–2.5	–2.5
SCN^-	–1.5	–2.0	–3.5	–4.0	–4.5
S^{2-}	0.0	0.0	0.0	–2.0	–2.5
N_3^-	–2.0	0.0	–2.0	–4.0	–4.5
CrO_4^{2-}	–1.6	–1.0	–3.0	–2.0	–2.0
$Cr_2O_7^{2-}$	0.0	0.0	–1.5	–1.5	–2.5
$S_2O_3^{2-}$	–3.0	–2.0	–3.5	0.0	–4.0
$K_3\{Fe(CN)_6\}^{3-}$	–3.5	–2.5	–3.5	0.0	–3.0
$K_4\{Fe(CN)_6\}^{4-}$	–1.0	0.0	–4.0	0.0	N.D
CH_3COO^-	N.D	–1.0	–3.0	–1.0	N.D
VO_3^-	0.0	–2.0	0.0	0.0	–1.0
MnO_4^-	N.D	0.0	–1.0	–1.0	–1.5

N.D. Not detected

The interesting feature of this study is the considerable difference in the migration of chemically similar anions leading to fantastic separation possibilities. Some of the important ones actually achieved are:

(a) I^- from Cl^- and Br^-
(b) I^- from IO_3^- and IO_4^-
(c) $\{Fe(CN)_6\}^{3-}$ from $\{Fe(CN)_6\}^{4-}$
(d) IO_3^- from BrO_3^-

In order to study the effect of the nature of adsorbents on migration of anions, plot of migration versus anions on all the three type of layers in different background electrolytes are drawn {Fig.1 (a), (b), (c), (d), (e)}. It is interesting

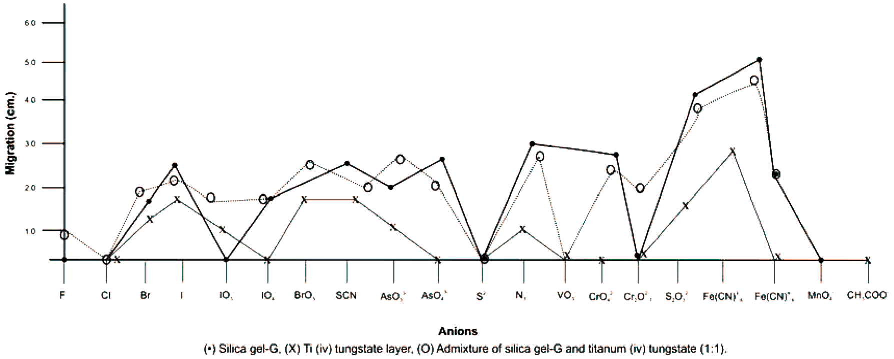

Figure 1 (a) : Plots of Electrophoretic Migration Versus Anions in 0.1M Oxalic acid on Different Layers

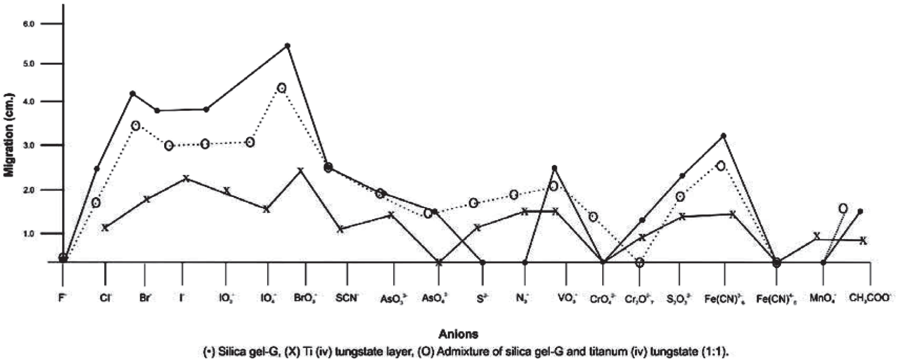

Figure 1 (b): Plots of Electrophoretic migration versus anions in 0.1M Citric acid on different layers

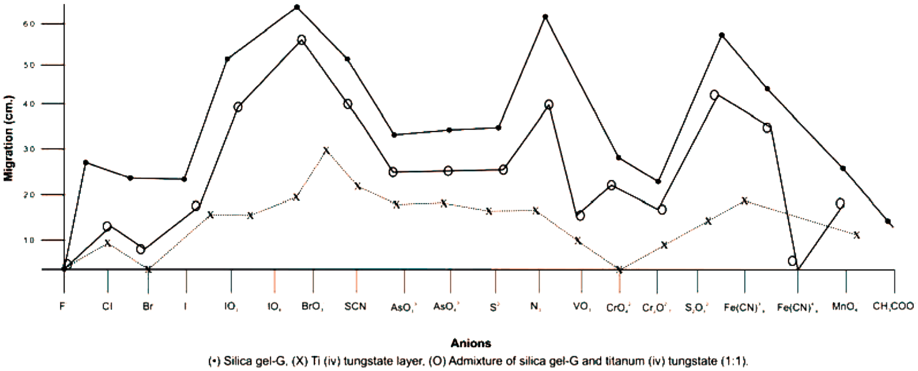

Figure 1 (c): Plots of Electrophoretic migration versus anions in 0.1M Tartaric acid on different layers

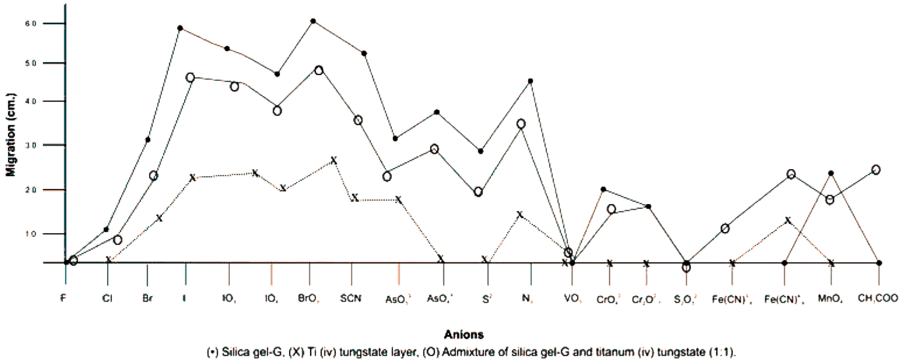

Figure 1 (d) : Plots of Electrophoretic migration versus anions in 0.1M Succinic acid on different layers

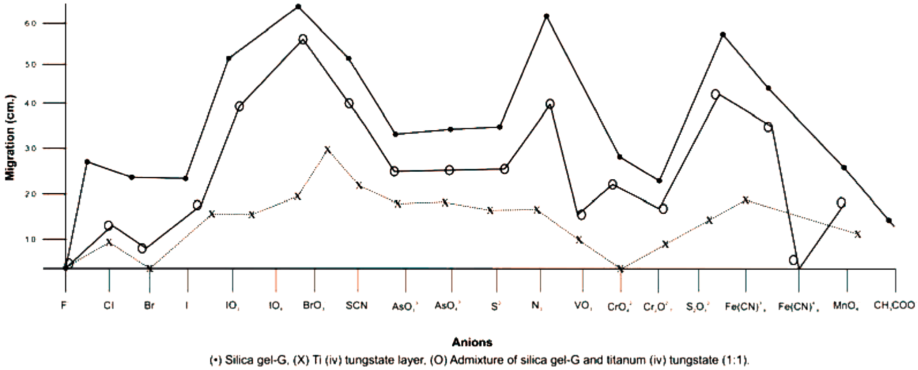

Figure 1 (e) : Plots of Electrophoretic migration versus anions in 0.1M Acetric acid on different layers

to note that among halide F^- is strongly adsorbed on all the layers because sodium fluoride is less soluble as compared to other salts. The solubility of NaF, NaCl, NaBr, NaI is 4.17, 36, 90.5,and 178.7gm./100gm. of water at 20C respectively. In order to study the effect of the nature of adsorbents on migration of anions, plot of migration versus anions on all the three type of layers in different background electrolytes are drawn {Fig. 1(a),(b),(c),(d),(e)}. It is interesting to note that among halide F^- is strongly adsorbed on all the layers because sodium fluoride is less soluble as compared to other salts. The solubility of NaF, NaCl, NaBr, NaI is 4.17, 36, 90.5,and 178.7gm./100gm. of water at 20C respectively. This happen because the governing factor is the lattice energy which increases as the ionic radii decreases.

Table 2.: Migration of Anions (cm) on Titanium (IV) Tungstate Layers in Different Electrolytes

ANIONS	0.1M OXALIC ACID	0.1M CITRIC ACID	0.1M TARTARIC ACID	0.1M SUCCINIC ACID	0.1 M ACETIC ACID
Cl^-	0.0	–1.0	–2.0	0.0	–0.5
Br^-	–1.0	–1.5	–2.2	–1.0	0.0
I^-	–1.5	–2.0	–3.0	–2.02	–1.0
F^-	0.0	N.D	N.D	0.0	0.0
IO_3^-	–0.5	–1.5	–1.0	–2.0	–1.0
IO_4^-	0.0	–1.0	–0.5	–1.5	–1.5
BrO_3^-	–1.0	–2.0	0.0	–2.5	–2.5
AsO_3^{3-}	–0.5	–1.0	0.0	–1.0	–1.0
AsO_4^{3-}	0.0	0.0	–1.0	0.0	–1.5
SCN^-	–1.0	–0.5	–1.5	–1.0	–1.6
S^{2-}	0.0	–0.5	N.D	0.0	–1.0
N_3^-	–0.5	–1.0	0.0	–1.0	–1.0
CrO_4^{2-}	0.0	–0.5	–1.0	0.0	–0.5
$Cr_2O_7^{2-}$	0.0	0.0	–0.5	0.0	0.0
$S_2O_3^{2-}$	–1.0	–1.0	0.0	0.0	–1.0
$K_3\{Fe(CN)_6\}^{3-}$	–2.0	–1.0	–1.0	0.0	–1.5
$K_4\{Fe(CN)_6\}^{4-}$	0.0	0.0	–1.0	–0.5	0.0
CH_3COO^-	0.0	–0.5	–1.0	N.D.	N.D.
VO_3^-	0.0	–1.0	0.0	0.0	–0.5
MnO_4^-	N.D.	–0.5(T)	0.0	0.0	–0.5

N.D. Not detected

Table 3: Migration of Anions (cm) on Admixture Layers on Silica Gel–G And Titanium (IV) Tungstate Layers In Different Electrolytes

ANIONS	0.1M OXALIC ACID	0.1M CITRIC ACID	0.1M TARTARIC ACID	0.1M SUCCINIC ACID	0.1 M ACETIC ACID
Cl^-	0.0	–2.0	–4.0	–1.0	–1.0
Br^-	–1.5	–3.5	–5.0	–2.0	–0.5
I^-	–2.0	–2.05	–5.0	–4.0	–1.5

F^-	–1.0	0.0	–0.0	0.0	0.0
IO_3^-	–1.0	–2.05	–4.0	–4.0	–3.5
IO_4^-	–1.0	–2.05	–2.05	–3.5	–3.0
BrO_3^-	–1.5	–4.0	0.0	–4.0	–5.5
AsO_3^{3-}	–1.5	–1.5	–1.0	–1.5	–2.0
AsO_4^{3-}	–1.0	–1.0	–1.0	–2.0	–2.0
SCN^-	–1.4	–2.0	–2.5	–3.0	–3.5
S^{2-}	0.0	–1.0	0.0	–1.0	–2.0
N_3^-	–1.5	–1.5	N.D.	–3.0	–3.5
CrO_4^{2-}	–1.5	0.0	–2.0	–1.0	–1.0
$Cr_2O_7^{2-}$	–1.0	–1.0	–1.5	–1.0	–0.5
$S_2O_3^{2-}$	–2.5	–1.5	–2.0	0.0	–3.0
$K_3\{Fe(CN)_6\}^{3-}$	–3.0	–2.0	–3.0	–0.5	–2.5
$K_4\{Fe(CN)_6\}^{4-}$	1.0	0.0	–3.0	–1.0	0.0
CH_3COO^-	N.D.	–1.0	–2.0	–1.0	N.D.
VO_3^-	0.0	–1.5	0.0	0.0	–1.0
MnO_4^-	N.D.	0.0	N.D.	–0.5	–1.0

N.D. Not detected.

Also, for almost all anions the migration is higher on silica gel-G layers. On the other hand, the migration of anions on titaniumIV tungstate layers is much lower which may be due to the formation of less soluble titanium salt of various anions studied. Ti (IV) tungstate is a cation exchanger and as such there is no exchange phenomenon occuring with anions Thus for anions, it behaves only as an adsorbent and not as an ion exchanger. However, on mixing silica gel-G with ti(IV) tungstate in1:1 ratio, the migration of anion is found to increase considerably in all the background electrolytes thereby enhancing the better separation possibilities for anions.

To study the effect of various organic acids used as background electrolytes on the electrophoretic behaviour of anions, plots of migration v/s pK1of acids were drawn (Fig. 2). A cursory inspection of these plots lead to following conclusions.

1. I^-,IO_4^-,SCN^- show higher migration in all the background electrolytes. It may be due to higher solubility of the sodium salts of these ions.
2. In citric acid media, the anions such as Cl^-, Br^-, IO_3^- BrO_3^-, S_2O_3, CrO_4 and $\{Fe(CN)_6\}^{4-}$ give much higher migration as compared to the values reported for other background electrolytes. It is probably due to higher

solubility of sodium or potassium salts of these anions in citric acid media.

3. In oxalic acid media, the migration for almost all the anions is very low or zero, probably due to low ionization constant of this acids.

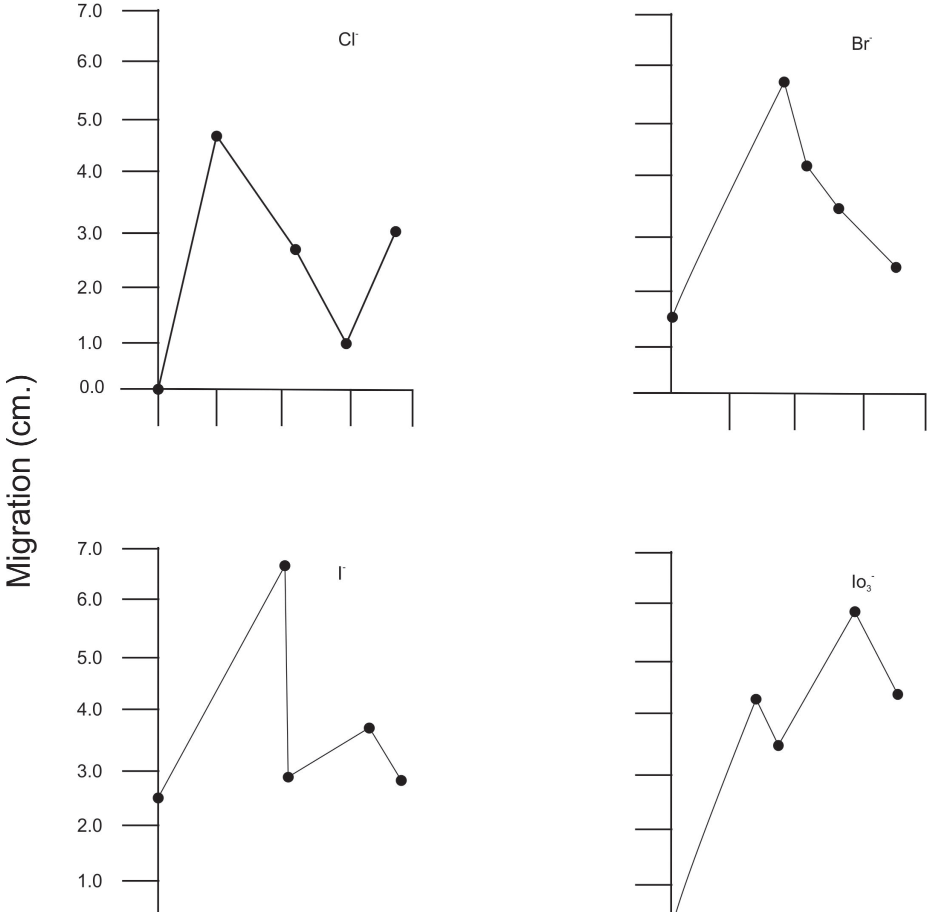

Figure 2 (a): Plots of migration of anions versus pKa of acids used as electrolytes on Silica Gel-G layers.

4. The migration of $Cr_2O_7^{2-}$ is lower than that of $CrO4^{2-}$ in all the background electrolytes. It may be due to larger size of $Cr_2O_7^{2-}$ Another reasons for this, may be low solubility of potassium dichromate as compared to potassium chromate (solubility of $K_2Cr_2O_7$ is 61.7 and K_2CrO_4 is 13.1 /100gm. of water at 20C respectively).

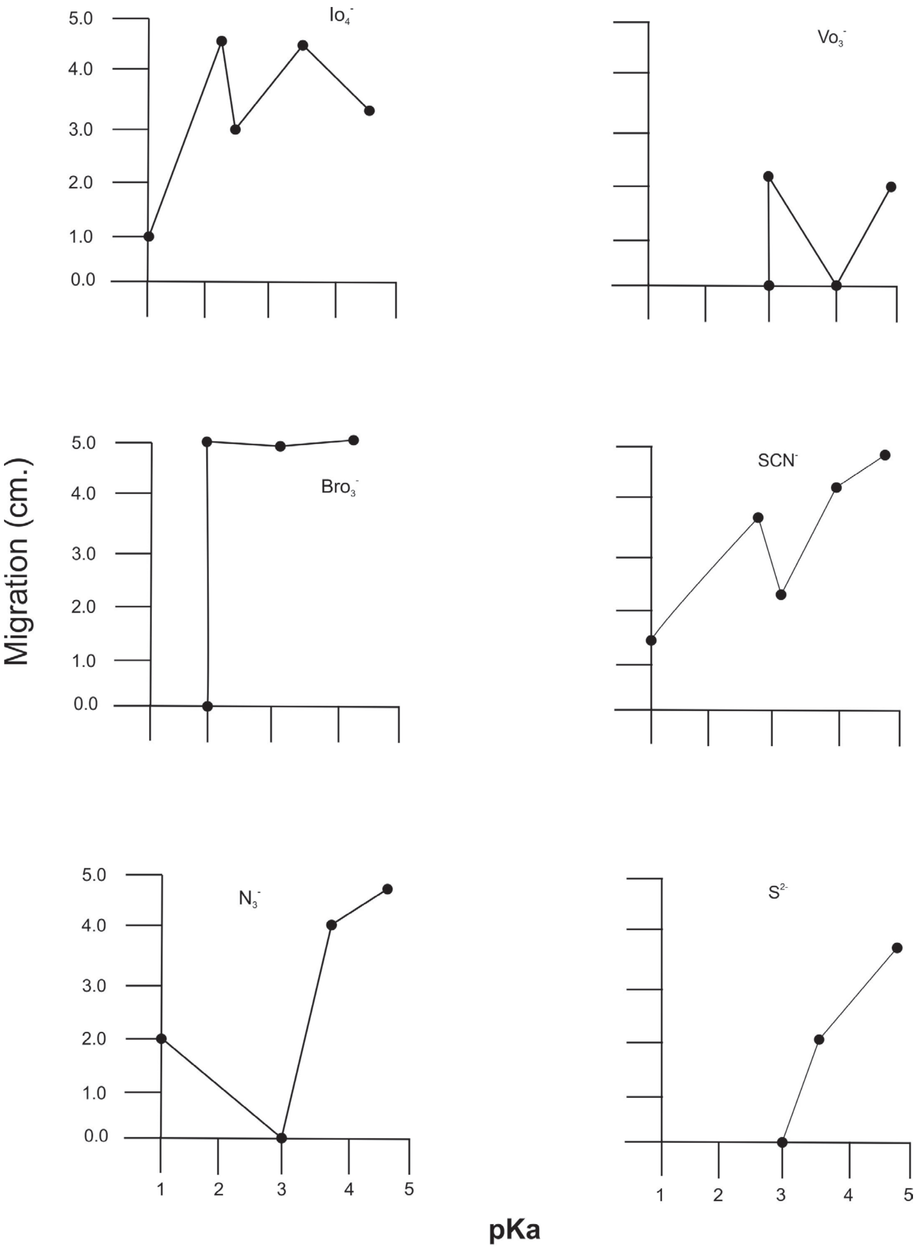

Figure 2 (b) : Plots of migration of anions versus pKa of acids used as Electrolytes on Silica Gel-G layers.

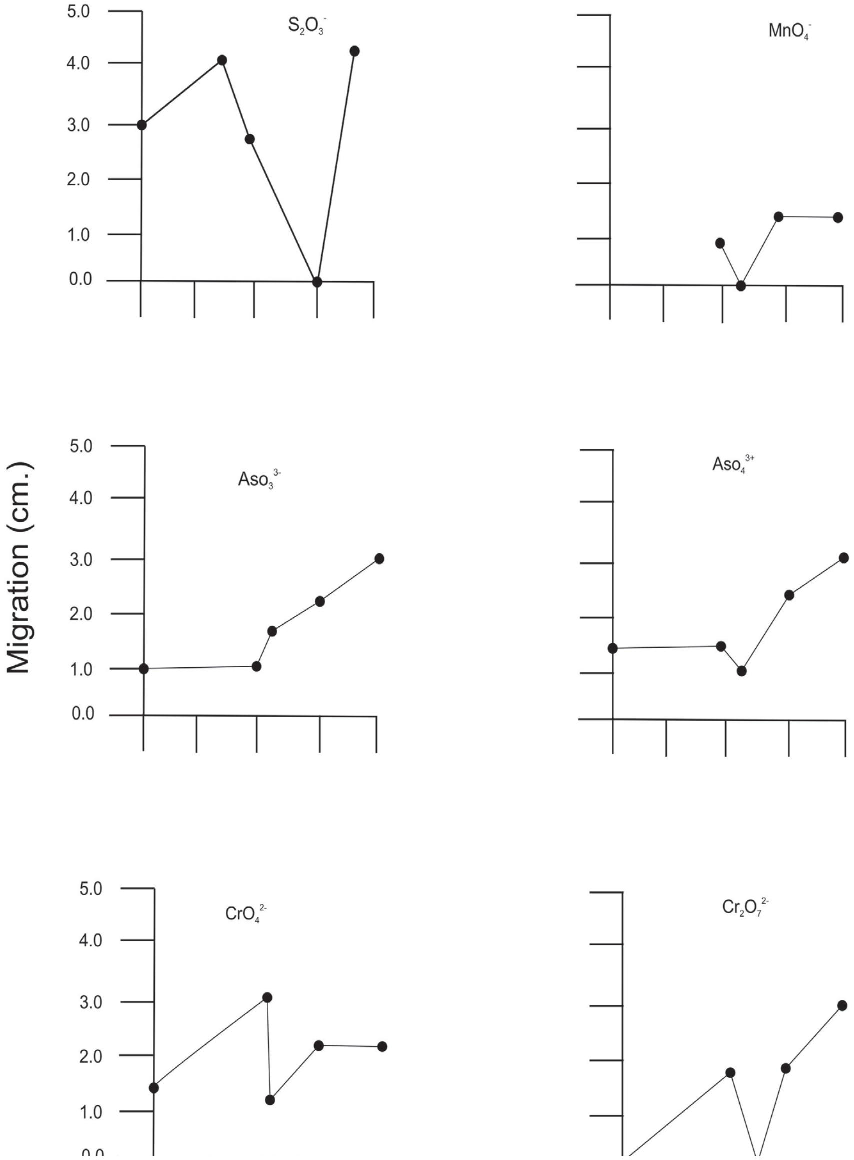

Figure 2 (c): Plots of migration of anions versus pKa of acids used as Electroytes on Silica Gel-G layers.

5. The behaviour of S^{2-}, BrO^{3-}, As O_3^{3-} and As O_4^{3-} is quite interesting as their migration increase with on increase in the ionization constant of the background electrolyte. This is probably due to increase in the

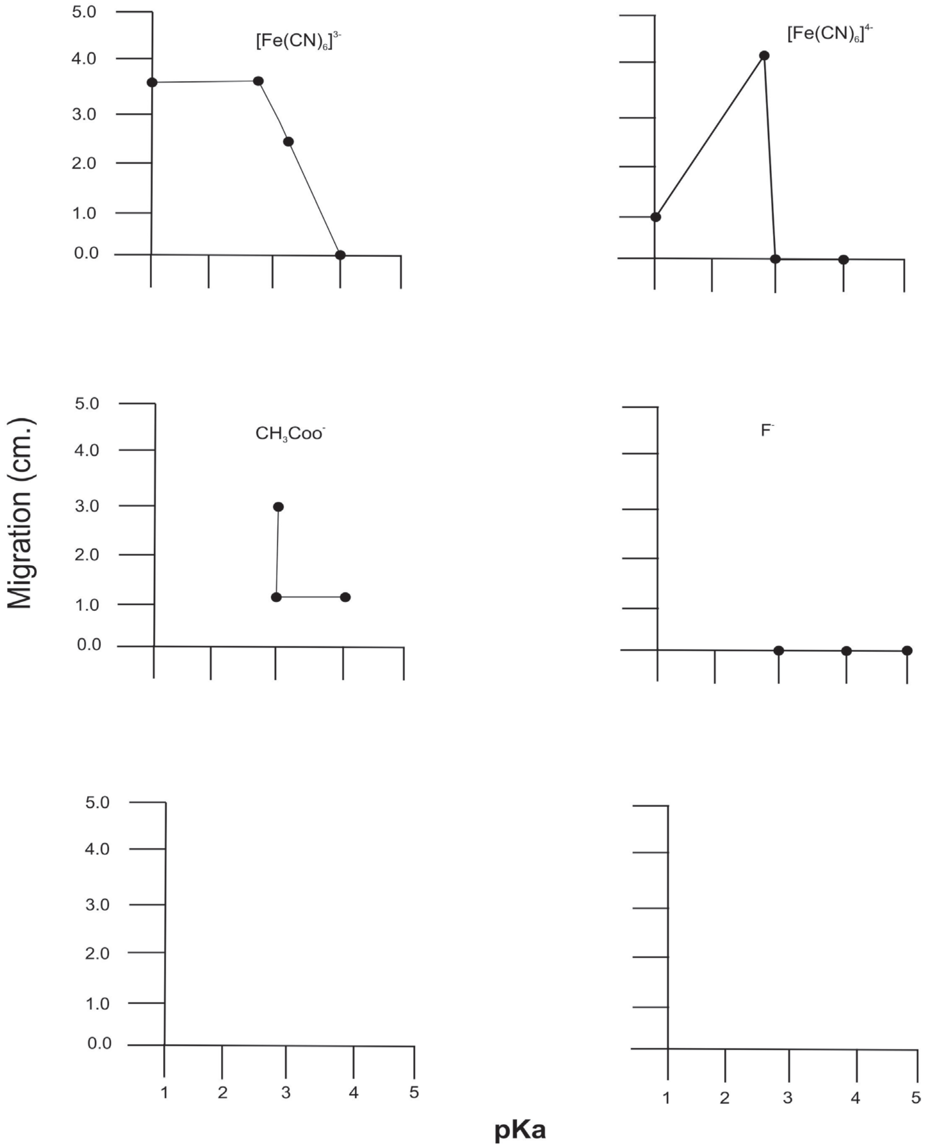

Figure 2 (d): Plots migration of anions versus pKa of acids used as Electrolytes on Silica Gel-G layers.

no. of H^+ ions in the solution causing higher exchange of H^+ ion and consequently the ionophoretic migration of anions increase.

6. In oxalic acid media MnO_4^- escape detection probably due to its reduction.

The migration behaviour of some anions could be reasonably interpreted by their lyotropic numbers. The magnitude of migration is in accord with the order of lyotropic no.[11] in colloid chemistry rather than with the radii of the hydrated ions. [12] These numbers (derived from the concentration of the sodium salts of the different required to flocculate agar) are listed in table 4. The migration of some anions can be explained as follows.

Table 4. Migration Of Some Anions And Their Lyotropic Numbers (N) [11]

ANIONS	N	Migration(cm.)
F^-	4.8	0.0
IO_3^-	6.3	4.5
BrO_3^-	9.7	3.0
CI^-	10.0	2.5
Br^-	11.5	2.0
I^-	12.5	2.0

The value of the lyotropic no. would depend on the extent of dehydration of the colloid due to hydration of these anions, in other words, the extent of hydration of the anions should increase with decrease in the lyotropic no. Therefore, the order of migration of anions should be comparable to that of the strength of hydration. It is considered that hydrophobic anions(anions with weak hydration) have a large capacity for interaction with the gel matrix causing pronounced adsorption. Thus the more hydrophobic more strongly adsorbed on silica gel-G layers, causing lower migration. This behaviour is very much in agreement with the data given in table 1. The only exception being F^- which show zero migration i.e. the migration much less than expected on the basis of its lyotropic no.

As shown in fig 3, the migration of halides increases linearly with an increase in the extent of hydration of these ions.

The extent of hydration As shown in fig 3, the migration of halides increase with an increase in the extent of hydration of these ions. The extent of hydration is much higher for F^- ion than for I^- as the smaller ion is hydrated to a larger extent. The larger size of hydrated F^- ion decreases its mobility. Thus, the migration of halides is in the same order as predicted for their degree of hydration in an aqueus media. Another reason for zero migration of F^- ion is due to the very low solubitily of NaF in water.

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