



Low-voltage thin-layer electrophoresis of inorganic anions on silica gel-G and titanium (IV) tungstate layers: separation of coexisting F^- , Cl^- , Br^- and I^- , IO_3^- and IO_4^- , $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$

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Abstract

The electrophoretic behavior of twenty anions has been studied on silica gel-G, titanium (IV) tungstate and silica gel-G-titanium (IV) tungstate admixture layers using 0.1 M solutions of oxalic acid, citric acid, tartaric acid, succinic acid and acetic acid as background electrolyte. The mechanism of migration is explained in terms of adsorption and the solubility of various sodium or potassium salts of the anions in water. Titanium (IV) tungstate behaves only as an adsorbent and not as an ion exchanger. Being a cation exchanger, there is no exchange phenomenon occurring with anions. The migration of halides increase linearly with an increase in the bare ion radii of these ions. Differential migration of the anions on silica gel-G layers led to binary, ternary and quaternary separations of similar anions such as $F^- - Cl^- - Br^- - I^-$, $I^- - IO_3^- - IO_4^-$, $BrO_3^- - IO_3^-$ and $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$. The two cyanoferrate ions are separated from industrial waste water and from fixer and bleach solutions. The migration of anions has also been found to be in accordance with their lyotropic numbers.

Keywords Low-voltage thin-layer electrophoresis · Silica gel-G layers · Ti (IV) tungstate layers · Separation of inorganic anions · Lyotropic number

Introduction

Thin-layer electrophoresis (TLE) is a simple, convenient and inexpensive technique for the separation of metal ions and anions. Since 1962, TLE of these ions has been carried out on different adsorbent materials. However, most of the TLE studies were performed on metal ions [1–12] and much lesser attention has been paid to the TLE of anions. 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 background electrolytes at high voltage [13]. It is, therefore, advisable to apply low voltage for TLE of anions.

Dobici et al. [14] were the first to separate iodate and periodate on gypsum layers using TLE. Moghissi [15]

separated anions using thin layers of kieselguhr. Later, Mori et al. [16] studied TLE of twenty anions and achieved a number of useful separations using silica gel thin layers. Some other TLE separation of anions were also reported [17, 18]. In 1995, after a long gap, low-voltage TLE of anions and metal ions on silica gel-G-starch admixture layers has been carried out. [7]. This was probably the last publication on TLE of anions. Sharma [19] in 2002, extensively reviewed the paper electrophoresis (PE) and TLE of metal ions and anions and the separations achieved using both these techniques. A literature survey for the period 2002–2019 reveals that, though recently there has been a resurgence of interest in thin-layer chromatography (TLC) of metal ions [20–31] and reversed-phase TLC of metal ions and anions [32, 33], but TLE of metal ions and anions has not been attempted. As such, a strong need is felt to explore further possibilities of TLE separation of anions for which much lesser work is reported.

Synthetic inorganic ion exchanges have been widely used for chromatographic separation of metal ions. Among these, titanium (IV) tungstate is known to possess promising thermal and chemical stability [34]. It has successfully been used as a cation exchanger but it does not behave as anion exchanger

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and as such taken here as an adsorbent only. Interestingly, silica gel-G acts both as cation and anion exchanger [35–38]. We have, therefore, decided to use silica gel-G for the low-voltage TLE of anions. Further, titanium (IV) tungstate and its admixture with silica gel-G, has also been used for the same. Titanium (IV) tungstate decomposes at high pH. Hence, aqueous solutions of weak acids such as oxalic, citric, tartaric, succinic and acetic acid are chosen as background electrolytes in order to prevent the hydrolysis of the exchanger material.

Though the methodology is not new, but it is much easier and inexpensive and can be practiced in a laboratory without modern research facilities and where non-instrumental methods are adopted. The results are summarized in the following pages.

Experimental

Apparatus

Thin-layer electrophoresis was performed on glass plates (25 × 2.5 cm) using a horizontal electrophoresis apparatus (Bio-Chem India Ltd.) with an electronic regulated power supply unit (Metrex Ltd., India).

Reagents

Titanium (IV) chloride (Riedel, Germany) was used. Silica gel-G was of chromatographic grade obtained from Qualigens Fine Chemicals, Glaxo, India. All other chemicals used were of analytical reagents grade from British Drug House (London, U.K.).

Test solutions and detectors

Test solutions (0.1 M) of anions are prepared by dissolving sodium or potassium salts of anions in demineralized water.

Detection was made by the following reagents: saturated solutions of AgNO₃ in methanol for Cl⁻, Br⁻, I⁻, AsO₃³⁻, AsO₄³⁻, CrO₄²⁻, Cr₂O₇²⁻, S₂O₃²⁻, and IO₄⁴⁻; 1% solution of FeCl₃ in 2 M HCl for Fe(CN)₆³⁻, Fe(CN)₆⁴⁻, SCN⁻, and N³⁻; 2% methanolic diphenylamine solution containing 4 M H₂SO₄ for BrO₃⁻, NO₂⁻, NO₃⁻, VO₃⁻, MnO₄⁻, and IO₃⁻; 2% alcoholic solution of pyrogallol for MoO₄²⁻ and WO₄²⁻; aqueous molybdate followed by SnCl₂ solution in 4 M HCl for PO₄³⁻; dilute ZrCl₄ solution in HCl and 0.1 M alcoholic alizarin red S for F⁻; and ferrous sulfate solution in 30% phosphoric acid for SeO₃²⁻.

Synthesis of titanium (IV) tungstate

Titanium (IV) tungstate was prepared as reported earlier [34].

Preparation of spiked solutions of fixer and bleach

Fixer and bleach solution (5 mL) from the photography lab (Anmol Digital Colour Lab, Moradabad, India) was spiked with Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ salts (100 mg each).

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 demineralized water with constant stirring for about 5 min. The slurry was immediately coated on the clean glass plates with the help of an applicator (Toshniwal, India) and uniform thin layers (≈0.15 mm thick) were obtained. The plates of silica gel-G were first dried at room temperature and then in an electric oven for 1 h at 100 °C. For use, titanium (IV) tungstate layers were dried at room temperature. The admixture layers were dried at 60 °C in an electric oven for 1 h.

Procedure

The electrophoresis apparatus was filled to the mark with the background electrolyte. The electrode compartments were filled to equal heights and the apparatus was placed horizontally to remove the siphoning effect. Activated plates, which form the stabilization medium, were placed in position. The contact between the electrode compartments and the layers was made with two pieces of Whatman No.1 paper and the layers were allowed to become saturated with the electrolyte. Whereupon, a small drop (0.02 mL) of the test solution containing 2×10^{-6} mol of ions was then applied separately, with the help of thin glass capillaries, on each thin layer in the middle. In all cases, electrophoresis was continued for 2 h at a constant potential difference of 100 V. The current was 4.40 mA and there was no significant heating during electrophoresis.

Results and discussion

Electrophoresis of twenty anions has been 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 0.1 M oxalic acid (E₁), 0.1 M citric acid, (E₂), 0.1 M tartaric acid (E₃), 0.1 M succinic acid (E₄) and 0.1 M acetic acid (E₅). The movement of the centre of the zones is measured in cm. As all the anions move towards anode, only migration of anions (with no sign) is given. The results are summarized in Tables 1, 2 and 3.

The most interesting feature of this study is the considerable difference in the migration of chemically similar anions on silica-gel-G layers leading to various separation

Table 1 Migration of anions (cm) on silica gel-G layers in different electrolytes

Anions	(E ₁)	(E ₂)	(E ₃)	(E ₄)	(E ₅)
1. Cl ⁻	0.0	2.5	4.5	1.0	0.0
2. Br ⁻	1.5	4.0	5.5	1.0	1.0
3. I ⁻	2.5	3.0	6.5	5.5	2.0
4. F ⁻	0.0	0.0	0.0	0.0	0.0
5. IO ₃ ⁻	0.0	3.0	4.2	5.0	1.5
6. IO ₄ ⁻	1.0	3.0	4.5	4.5	3.0
7. BrO ₃ ⁻	ND	5.0	0.0	5.0	6.0
8. AsO ₃ ³⁻	1.0	1.5	1.0	2.0	2.5
9. AsO ₄ ³⁻	1.5	1.0	1.5	2.5	2.5
10. SCN ⁻	1.5	2.0	3.5	4.0	4.5
11. S ²⁻	0.0	0.0	0.0	2.0	2.5
12. N ₃ ⁻	2.0	0.0	2.0	4.0	4.5
13. CrO ₄ ²⁻	1.6	2.0	3.0	2.0	2.0
14. Cr ₂ O ₇ ²⁻	0.0	0.0	1.5	1.5	2.5
15. S ₂ O ₃ ²⁻	3.0	2.0	3.5	0.0	4.0
16. Fe(CN) ₆ ³⁻	3.5	2.5	3.5	0.0	3.0
17. Fe(CN) ₆ ⁴⁻	1.0	0.0	4.0	0.0	N.D.
18. CH ₃ COO ⁻	N.D.	1.0	3.0	1.0	N.D.
19. VO ₃ ⁻	0.0	2.0	0.0	0.0	0.0
20. MnO ₄ ⁻	N.D.	0.0	1.0	1.0	1.5

N.D. Not detected

possibilities. Some separations actually achieved are given in Table 4. The important ones are:

- (a) I⁻ from Br⁻, Cl⁻ and F⁻ (b) I⁻ from IO₃⁻ and IO₄⁻
- (c) Fe(CN)₆³⁻ from Fe(CN)₆⁴⁻ (d) IO₃⁻ from BrO₃⁻

However, the separation of I⁻, IO₃⁻ and IO₄⁻ is somewhat difficult as these ions are interconvertible. In dilute aqueous

Table 2 Migration of anions (cm) on Ti (IV) tungstate layers in different electrolytes

Anions	(E ₁)	(E ₂)	(E ₃)	(E ₄)	(E ₅)
1. Cl ⁻	0.0	1.0	2.0	0.0	0.5
2. Br ⁻	1.0	1.5	2.2	1.0	0.0
3. I ⁻	1.5	2.0	3.0	2.0	1.0
4. F ⁻	0.0	N.D.	N.D.	0.0	0.0
5. IO ₃ ⁻	0.5	1.5	1.0	2.0	1.0
6. IO ₄ ⁻	0.0	1.0	0.5	1.5	1.5
7. BrO ₃ ⁻	1.0	2.0	0.0	2.5	2.5
8. AsO ₃ ³⁻	0.5	1.0	0.0	1.0	1.0
9. AsO ₄ ³⁻	0.0	0.0	1.0	0.0	1.5
10. SCN ⁻	1.0	0.5	1.5	1.0	1.6
11. S ²⁻	0.0	0.5	N.D.	0.0	1.0
12. N ₃ ⁻	0.5	1.0	0.0	1.0	1.0
13. CrO ₄ ²⁻	0.0	0.5	1.0	0.0	0.5
14. Cr ₂ O ₇ ²⁻	0.0	0.0	0.5	0.0	0.0
15. S ₂ O ₃ ²⁻	1.0	1.0	0.0	0.0	1.0
16. Fe(CN) ₆ ³⁻	2.0	1.0	1.0	0.0	1.5
17. Fe(CN) ₆ ⁴⁻	0.0	0.0	1.0	0.5	0.0
18. CH ₃ COO ⁻	0.0	0.5	1.0	N.D.	N.D.
19. VO ₃ ⁻	0.0	1.0	0.0	0.0	0.5
20. 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 of silica gel-G and Ti (IV) tungstate (1:1) in different electrolytes

Anions	(E ₁)	(E ₂)	(E ₃)	(E ₄)	(E ₅)
1. Cl ⁻	0.0	2.0	4.0	1.0	1.0
2. Br ⁻	1.5	3.5	5.0	2.0	0.5
3. I ⁻	2.0	2.5	5.0	4.0	1.5
4. F ⁻	1.0	0.0	0.0	0.0	0.0
5. IO ₃ ⁻	1.0	2.5	4.0	4.0	3.5
6. IO ₄ ⁻	1.0	2.5	2.5	3.5	3.0
7. BrO ₃ ⁻	1.5	4.0	0.0	4.0	5.5
8. AsO ₃ ³⁻	1.5	1.5	1.0	1.5	2.0
9. AsO ₄ ³⁻	1.0	1.0	1.0	2.0	2.0
10. SCN ⁻	1.4	2.0	2.5	3.0	3.5
11. S ²⁻	0.0	1.0	0.0	1.0	2.0
12. N ₃ ⁻	1.5	1.5	N.D.	3.0	3.5
13. CrO ₄ ²⁻	1.5	0.0	2.0	1.0	1.0
14. Cr ₂ O ₇ ²⁻	1.0	1.0	1.5	1.0	0.5
15. S ₂ O ₃ ²⁻	2.5	1.5	2.0	0.0	3.0
16. Fe(CN) ₆ ³⁻	3.0	2.0	3.0	0.5	2.5
17. Fe(CN) ₆ ⁴⁻	1.0	0.0	3.0	1.0	0.0
18. CH ₃ COO ⁻	N.D.	1.0	2.0	1.0	N.D.
19. VO ₃ ⁻	0.0	1.5	0.0	0.0	1.0
20. MnO ₄ ⁻	N.D.	0.0	N.D.	0.5	1.0

N.D. Not detected

acid solutions (e.g., 0.1 M to 2.0 M HCl) IO₃⁻ can be reduced to I₂ whereas in an aqueous alkaline media, I₂ may react with OH⁻ ions to give I⁻ and IO₄⁻ ions. In order to study the effect of the nature of adsorbents on migration of anions, plots of migration versus anions for each of the three type of layers in different background electrolytes are drawn. The figures are not given for the sake of brevity. It is interesting to note that among halides F⁻ is strongly adsorbed on all the layers because sodium fluoride is much less soluble as compared to other sodium halides. The solubility of NaF, NaCl, NaBr and NaI is 4.17, 36, 90.5 and 178.7 g/100 g. of water at 20 °C, respectively. This happens because the governing factor is the lattice energy which increases as the ionic radii decreases. Also, for good number of anions the migration is higher (ranging from 2.5–6.5 cm.) on silica gel-G layers. On the other hand, migration of anions on titanium (IV) tungstate layers is much lower (ranging from 0.0–3.0 cm) which may be

Table 4 Separations of anions achieved on silica gel-G layers

Background electrolyte	Separations achieved Anion (Migration in cm)
E ₁	Cl ⁻ (0.0) – I ⁻ (2.6), S ²⁻ (0.0) – S ₂ O ₃ ²⁻ (3.0) Fe(CN) ₆ ⁴⁻ (1.0) – Fe (CN) ₆ ³⁻ (3.5)
E ₂	IO ₃ ⁻ (3.0) – BrO ₃ ⁻ (5.0)
E ₃	F ⁻ (0.0) – Cl ⁻ (4.5) – Br ⁻ (5.5) – I ⁻ (6.5) S ²⁻ (0.0) – SCN ⁻ (3.5)
E ₄	F ⁻ (0.0) – Br ⁻ (3.0) – I ⁻ (5.5) S ²⁻ (0.0) – S ₂ O ₃ ²⁻ (2.0) – SCN ⁻ (4.0)
E ₅	I ⁻ (2.0) – IO ₃ ⁻ (4.5) – IO ₄ ⁻ (3.0) S ²⁻ (2.5) – SCN ⁻ (4.5)

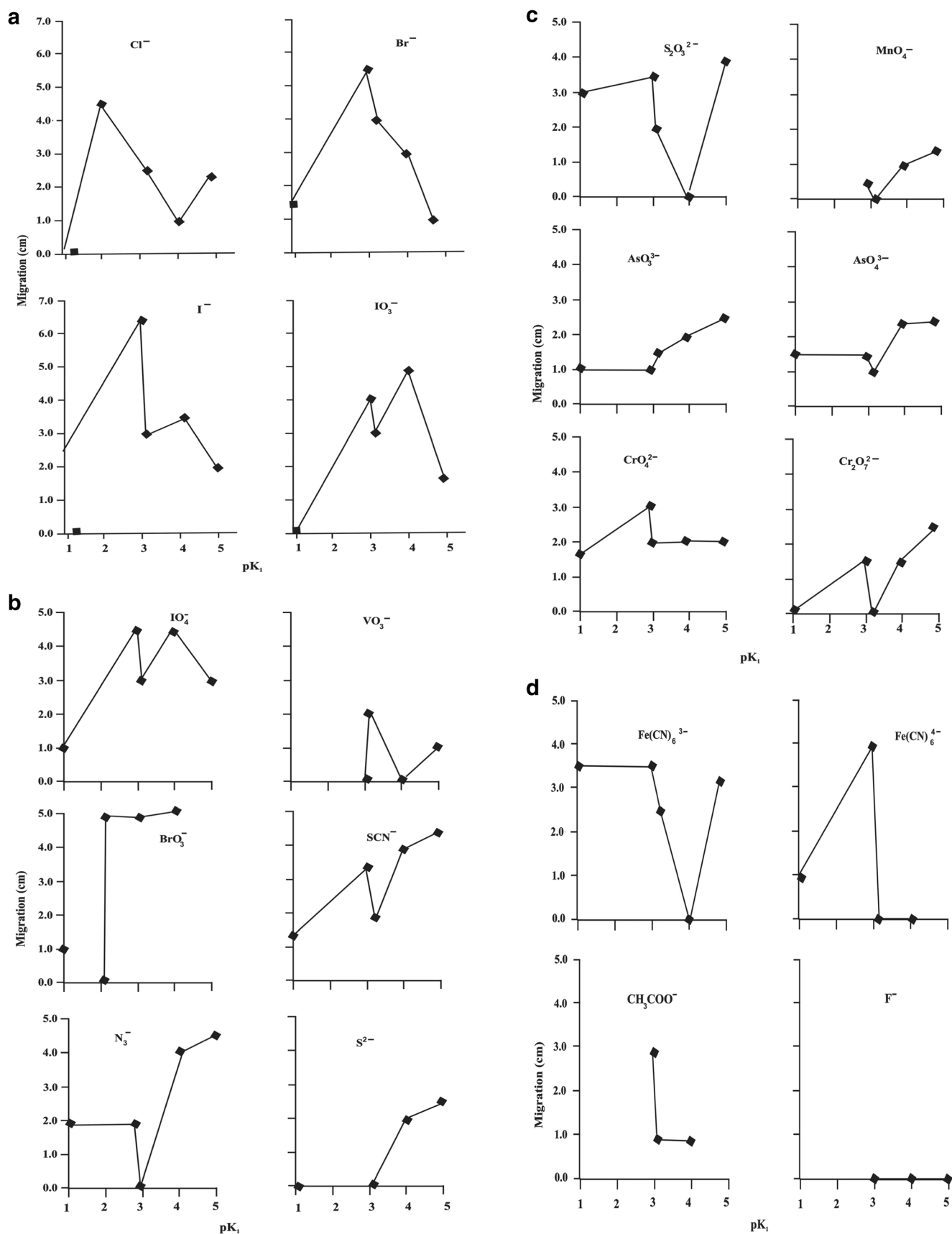


Fig. 1 a–d Plots of migration of anions versus pK₁ of acids used as electrolytes on silica gel-G layers

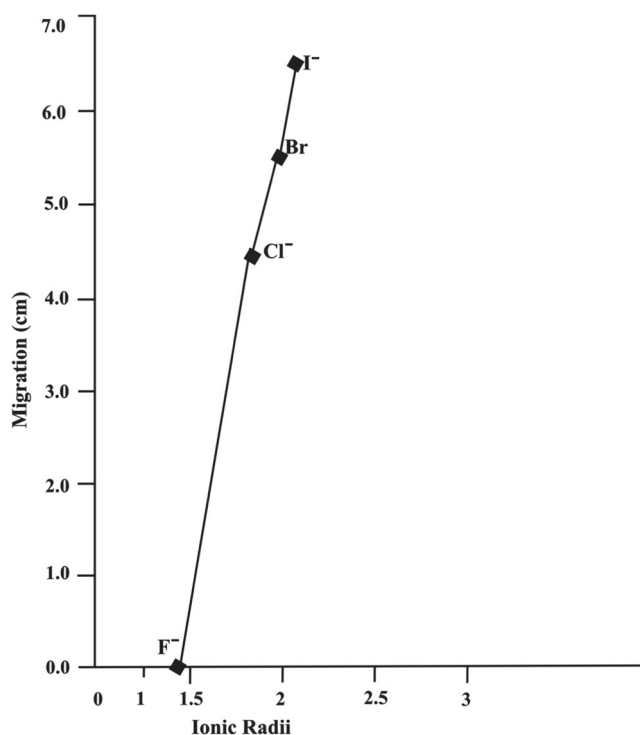
Table 5 Migration of some anions and their lyotropic numbers (N)

Anions	N ^[45]	Migration (cm) ^a
F ⁻	4.8	0.0
IO ₃ ⁻	6.3	4.5
BrO ₃ ⁻	9.7	3.0
Cl ⁻	10.0	2.5
Br ⁻	11.5	2.0
I ⁻	12.5	2.0
SCN ⁻	13.0/13.3	1.5

^a Value obtained with 0.1 M NaCl as mobile phase

due to the formation of less soluble titanium salts of various anions studied. Titanium (IV) tungstate is a cation exchanger and as such there is no exchange phenomenon occurring with anions. Thus for anions, it behaves only as an adsorbent and not as an ion exchanger. However, on mixing silica gel-G with titanium (IV) tungstate in 1:1 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 behavior of anions, plots of migration of anions on silica gel-G layers v/s pK₁ of acids were drawn (Fig. 1a–d). A cursory inspection of these plots led to following conclusions.

**Fig. 2** Plots of migration versus ionic radii of halides on silica gel-G layers in 0.1 M tartaric acid**Table 6** Separation of Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ present in a binary mixture on silica gel-G layers in 0.1 M oxalic acid (E₁)

Sample ^a	Migration (cm)	
	Fe (CN) ₆ ⁴⁻	Fe (CN) ₆ ³⁻
Distilled water	1.0	3.5
Hard water	1.1	3.5
Industrial waste water	0.8	3.3
Fixer	1.0	3.7
Bleach	0.8	3.5

^a 0.1 M solutions of potassium ferrocyanide and potassium ferricyanide were prepared directly in hard water and industrial waste water. The two cyanoferrate ions could not be detected in unspiked fixer and bleach samples

1. I⁻, IO₄⁻, SCN⁻, show higher migration in all the background electrolytes when compared to the migration of majority of anions under study. It may be due to the higher solubility of the sodium salts of these ions.
2. In citric acid and tartaric acid media, the anions such as Cl⁻, Br⁻, IO₃⁻, BrO₃⁻, S₂O₃²⁻ and CrO₄²⁻ give higher migration as compared to the values reported for other background electrolytes. It is probably due to higher solubility of the sodium or potassium salts of these anions in both the media.
3. In oxalic acid media, the migration for almost all the anions is low or zero, probably due to the higher ionization of the acid which suppresses the ionization of weak anionic acids in the solution resulting in lower concentration of anions.
4. The migration of Cr₂O₇²⁻ is lower than that of CrO₄²⁻ in all the background electrolytes. It may be due to larger size of Cr₂O₇²⁻ causing higher adsorption on silica gel-G layers. Another reason for this may be the lower solubility of potassium dichromate as compared to potassium chromate (solubility of K₂CrO₄ is 61.7 g and that of K₂Cr₂O₇ is 13.1 g/100 g of water at 20 °C).
5. The behavior of S²⁻, BrO₃⁻, AsO₃³⁻ and AsO₄³⁻ is quite interesting as their migration does not change in the pK₁ range 1 to 3. However, on further increase in pK₁, the migration gradually increases. This is probably due to the decrease in the number of H⁺ ions in the solution causing an increase in conc. of anions owing to common ion effect and consequently the ionophoretic migration of anions increases.
6. In oxalic acid media, MnO₄⁻ escapes detection probably due to its reduction.

The electrophoretic migration of Fe(CN)₆³⁻ and Fe(CN)₆⁴⁻ decreases in the order Fe(CN)₆³⁻ > Fe(CN)₆⁴⁻. This is analogous with the retention behavior of these ions on microcrystalline thin layers with acetone–ethyl acetate–water [39] as reported much

earlier and later on silica gel layers with acetone–water [40] as the mobile phase. The lesser migration of $\text{Fe}(\text{CN})_6^{4-}$ may be attributed to the following two reasons.

- The ion pair formation between $\text{Fe}(\text{CN})_6^{4-}$ and Ca^{2+} of the gypsum binder in silica gel-G, is stronger than with $\text{Fe}(\text{CN})_6^{3-}$ as is apparent from their formation constants [41, 42]. Thus, weakly bound ferrate (III) migrates faster through silica gel-G than ferrate (II).
- The greater hydrogen bond forming tendency of ferrate (II) with the surface hydroxyl groups of silica gel compared to ferrate (III) results in greater affinity of the former for silica [43, 44].

The migration behavior of anions could be reasonably interpreted by their lyotropic numbers. For this, the migrations of some anions (whose lyotropic numbers are known) in 0.1 M NaCl as electrolyte are determined (Table 5). The magnitude of migration is in accord with the order of lyotropic number [45] in colloid chemistry rather than with the radii of the hydrated ions [46]. These numbers (derived from the concentrations of the sodium salts of the different anions required to flocculate agar) are listed in Table 5. The lyotropic numbers for other anions are not known. The migration of some anions can be explained as follows.

The value of the lyotropic number 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 anion should increase with decrease in the lyotropic number of the anion. 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 anions are more strongly adsorbed on silica gel-G layers, causing lower migration. This behavior is very much in agreement with the data given in Table 1. The only exception being F^- which shows zero migration i.e. the migration much less than expected on the basis of its lyotropic number. It may be due to very low solubility of NaF as compared to other sodium halides.

As shown in Fig. 2 the migration of halides increase linearly with an increase in the bare ionic radii of these ions. The extent of hydration is much higher for F^- 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 aqueous media. Another reason for zero migration of F^- ion is the very low solubility of NaF in water.

In order to test the utility of this method for the separation of two hexacyanoferrate ions in different water samples and spiked fixer and bleach solutions, TLE was carried out. It was observed that the binary separation is quite clear (Table 6). The migration data shows that the presence of sulphates,

chlorides and bicarbonates of calcium and magnesium (hard water) has no effect on the separation. The electroplating industry waste water (containing Ni) when added to the sample also does not affect the separation. Thus, the method is applicable for the mutual separation of these two ions in different mixtures.

Conclusion

From the above discussion, it is concluded that in the electrophoresis of various anions, using aqueous organic acids as mobile phases, the solubility of sodium and potassium salts of these anions plays a significant role. In general, there is a substantial decrease in the migration of anions on titanium (IV) tungstate layers when compared to that of silica gel-G as it behaves only as an adsorbent and not as an ion exchanger. Interestingly, the migration of halides varies linearly with their bare ion radii. Silica gel-G layers were found quite effective in achieving some binary, ternary and quaternary separations at 100 V. A correlation is observed between the electrophoretic migration and lyotropic number of anions. The migrations of various anions are found to be in accordance with their lyotropic numbers.

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