Low-Voltage Paper Electrophoretic Study of Ion-Pair Formation and Electrochromatography of Inorganic Anions on Papers Impregnated with Titanium (IV) Tungstate

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Abstract

The ion-pair formation and electrochromatographic behavior of 22 anions are studied on plain and titanium (IV) tungstate impregnated papers using 0.1N and 1N solutions of NaNO₃, Mg(NO₃)₂, Al(NO₃)₃, Cr(NO₃)₃, and Co(NO₃)₂ as background electrolytes. The effect of ion-pair formation on the migration of anions is studied. In general, the mechanism of migration is explained in terms of adsorption, precipitation, and complex formation. A number of binary and ternary separations are achieved. In Mg(NO₃)₂ media, the migration is correlated with the solubility of their magnesium salts for SO₃²⁻, C₂O₄²⁻, SeO₃²⁻, AsO₄³⁻, and Fe(CN)₆⁴⁻.

Introduction

As proved by a previous study, the separation of anions by paper electrophoresis is usually affected by the selection of suitable electrolytes and their concentrations (l). In later studies, it was observed that the metal ions of the salt solutions used as background electrolytes has a strong effect on the movement of anions because of both ion-pair and complex formation. A literature survey reveals that very little work has been reported in the field (2,3). The paper electrophoretic study of ion-pair formation started with Co(III) complexes. This method shows that the metal ion of the electrolyte can influence the sequence and migration distance of various metal complexes to a large degree (4,5). The separation of anions can be obtained successfully by using salts of ammonium, cadmium, magnesium, and aluminum as background electrolytes (2). Such a study has serious practical limitations because many anions (e.g., sulfates and phosphates) get precipitated with the electrolytes at a high voltage (3). Also, pH variations cannot be used very effectively for inorganic anions because many anions are unstable below neutrality (2). Therefore, anions are studied less

frequently than cations. In order to overcome these problems, it is advisable to use electrolyte solutions of suitable pH at a low voltage. Recently, we have studied the low-voltage thin-layer ionophoresis of anions (6). In order to extend this work, we decided to perform a low-voltage paper electrophoresis of several anions at 100 V for 3 h and study the ion-pair formation by using suitable electrolytes of different cations.

When electrochromatographic migration is combined with ion exchange, more interesting results are achieved and the potential of this technique increases considerably. Titanium (IV) tungstate possesses high chemical stability and exhibits good ion-exchange properties (7,8). Recently, papers impregnated with titanium (IV) tungstate have been used more extensively for the planar chromatographic (9,10) and electrophoretic study (11,12) of metal ions. In view of this fact, the low-voltage electrophoresis of many anions on titanium (IV) tungstate impregnated papers using electrolyte solutions at a suitable pH has been carried out, and some analytically important separations were achieved.

Experimental

Apparatus

The electrochromatographic studies were performed on Whatman (Maidstone, Kent, U.K.) No. 1 strips $(46.4 \times 2.75 \text{ cm})$ using a horizontal electrophoresis apparatus operated with an electronic regulated power supply unit (Matrex Ltd., New Delhi, India).

Reagents

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

Preparation of ion-exchange papers

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Papers impregnated with titanium (IV) tungstate were pre-

pared in the same manner as reported in a previous study (13). These papers were found to possess a considerable ion-exchange capacity. For K^+ (K^+ – H^+ exchange) the ion-exchange capacity was 0.35 mequiv/g of the treated paper, as determined by column experiments (saturation method) (13).

Test solutions

Test solutions of anions were prepared by dissolving the sodium or potassium salts of anions in demineralized water.

Detectors

The following reagents were used for detection purposes: a silver nitrate solution in methanol for Cl⁻, Br⁻, I⁻, IO₄⁻, S₂O₃²⁻, CrO₄²⁻, Cr₂O₇²⁻, S²⁻, AsO₄³⁻, and AsO₃³⁻; ferric chloride for Fe(CN)₆⁴⁻, Fe(CN)₆³⁻, SCN⁻, and N₃⁻; diphenyl amine for BrO₃³⁻, VO₃⁻, MnO₄⁻, IO₃⁻, and SO₃²⁻; zirconium tetrachloride and alizarin for F-; phenolphthalein for CO₃²⁻; acidic KMnO₄ for C₂O₄²⁻; and sodium nitro pruside for SO₃²⁻.

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. Then, a small drop (0.02 mL) of the test solution containing 2×10^{-6} mol of the ion was applied separately with the help of a lambda pipette on the middle of each strip. In all cases, electrochromatography was continued for 3 h at a constant potential difference of 100 V. There was no significant heating during electrophoresis.

Results and Discussion

The electrochromatography of anions on titanium (IV) tungstate impregnated papers was performed in the following background electrolytes: 1N sodium nitrate for E_1 ; 0.1N sodium nitrate for E_2 ; 1N magnesium nitrate for E_3 ; 0.1N magnesium nitrate for E_4 ; 1N aluminum nitrate for E_5 ; 0.1N aluminum nitrate for E_6 ; 1N chromium nitrate for E_7 ; 0.1N chromium nitrate for E_8 ; 1N cobalt nitrate for E_9 ; and 0.1N cobalt nitrate for E_{10} . The movement of the center of the zones was measured in millimeters. A negative sign indicated the movement of the ions towards the anode (i.e., negatively charged species).

The migration of anions on Whatman No. 1 and titanium (IV) tungstate papers is given in Table I.

In general, the migration of anions was much higher on unimpregnated papers than on impregnated ones, possibly because of the higher adsorption on impregnated papers (Table I). Furthermore, the migration of anions in the $Co(NO_3)_2$ solution

Table I. Migration in Millimeters of Anions on Titanium (IV) Tungstate and Whatman No. 1 Papers in Different Background Electrolytes

									Back	ground	electrol	ytes								
	E	1	E ₂		E ₃		E4	ļ	E ₅	-	E	6	E ₇	,	E ₈		Eg		E ₁₀)
	a*	b†	a	b	a	b	а	b	a	b	a	b	a	b	a	b	а	b	a	b
CI-	-40	-45	-50	-75	-10	-30	-30	-40	-30	-65	-10	-75	-40	-30	-20	-30	0	0	0	-10
Br-	-20	-25	-50	-50	-10	-25	-20	-50	-55	-60	-25	-75	-50	-40	n.d.‡	-40	0	-20	0	-30
ŀ	-35	-45	-50	-65	-15	-30	-45	-75	-65	-75	-75	-125	-30	-60	-40	-40	0	-20	0	-20
F-	-20	-20	-10	-20	0	0	0	0	0	-30	-25	-45	0	0	0	n.d.	0	0	0	0
IO ₃ -	-10	-10	-20	-35	0	0	-40	-70	-10	-70	-15	-55	n.d.	-35	0	-40	0	-15	0	-10
IO_4^-	0	-5	-15	-30	-10	-25	-20	-30	n.d.	-65	-10	-50	-20	-30	-50	0	0	-30	0	-10
BrO_3^-	0	-30	-40	-45	-30	-30	-30	-45	-45	-70	-20	-80	-50	-60	-30	-30	0	-15	0	-5
N ₃ -	-35	-40	n.d.	-75	-15	-35	-10	-80	-10	-30	-10	-20	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.
SCN-	-40	-60	-45	-95	-35	-10	n.d.	-80	-50	-70	-10	-80	-30	-30	-15	0	0	-15	0	-10
S ²⁻	-35	-55	-40	-70	-30	n.d.	-55	-60	-30	-45	-20	-50	-20	-20	0	-40	0	-15	0	-5
S ₂ O ₃ ²⁻	-20	-15	-20	-60	-25	-30	-45	-50	-45	-35	-5	-10	0	-10	0	-5	0	-10	0	-10
VO ₃ -	-30	-45	-10	-80	0	-30	-25	-45	-25	-25	-20	-10	-15	0	-20	0	0	0	0	0
MoO42-	-25	-35	-40	-30	0	-35	-30	-25	-15	-35	-10	-25	0	-40	0	0	0	n.d.	0	0
WO42-	-	-20	-	-25	-	-20	-	-20	-	0	-	0	-	-50	-	0	-	0	-	0
SeO32-	-15	-15	-10	-40	0	0	-30	-60	0	0	-75	0	0	0	0	0	0	0	0	0
MnO_4^-	0	0	0	0	-10	-15	-15	-30	0	0	-5	-25	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	0
Fe(CN) ₆ ³⁻	-25	-60	-40	-35	-15	-40	-30	-60	0	-50	-25	-70	0	-10	0	-25	0	0	0	0
Fe(CN) ₆ ⁴⁻	-35	-20	-25	-30	-10	-20	-15	-50	-30	-35	-80	0	-10	-10	0	0	0	0	0	-5
CrO ₄ ²⁻	-40	-50	-25	-80	0	-35	-30	-85	-40	0	-35	-85	-20	-15	-40	-20	0	0	0	0
Cr ₂ O ₇ ²⁻	-20	-45	-20	-70	0	-20	-30	-70	-30	0	-25	-10.5	-25	-30	-20	-40	0	-10	0	0
AsO43-	-10	-40	-10	-40	-35	0	-10	-40	0	-15	-10	-15	0	0	-10	-10	0	0	0	0
AsO ₃ ³⁻	-45	-20	0	-25	-30	-15	-30	-15	-10	-10	0	-10	0	n.d.	0	-10	0	0	0	0

* a, migration of anions on titanium (IV) tungstate impregnated papers.

⁺ b, migration of anions on Whatman No. 1 papers.

* n.d., not detected

was found to be quite low. This behavior can be explained on the basis that aqueous cobalt (II) salts are more easily oxidized than cobalt (III) salts, which has a tendency to form numerous complexes that are kinetically inert and thus move less on Whatman No. 1 papers. However, the migration of all the anions is zero on titanium (IV) tungstate impregnated papers in this media. This is probably caused by the precipitation mechanism, because all of the anions gave a precipitate upon mixing their solutions with a $Co(NO_3)_2$ solution followed by the addition of sodium tungstate (Table II).

It is interesting to note that on Whatman No. 1 papers the migration of halides (except F-) was almost similar in NaNO₃ and $Mg(NO_3)_2$ solutions, but in the Al(NO₃)₃ solution the migration was much higher because of the fact that halides form ion-pair complexes (15) with Al^{3+} of the type AlF_6^{3-} , $AlCl_4^{-}$, and $AlBr_4^{-}$. However, the behavior of halides is somewhat exceptional when chromium nitrate and cobalt nitrate solutions are used as electrolytes. In these electrolytes, the migration of halides is remarkably lower than in the case of the Al(NO₃)₃ solution, possibly because of the formation of heavier complexes (15) such as (Co X_4)^{2–} and (CrX₆)^{3–}. In the case of F– the migration was low because metal fluorides are quite insoluble (the solubility order being $I^- >$ Br > Cl > F). This happens because the governing factor is the lattice energy, which increases as the ionic radii decreases. It is noticed that the solubility order is found only among the alkali and alkaline earth metal halides.

The greater tendency of oxyhalide anions to ion pairing was evident as compared with that of halides, which has been reported earlier (2). There was an excellent separation possibility for the ion pair of oxyhalides with the metal ion of the electrolyte solution because of the tendency of heavier being the most retarded forming. This has been demonstrated earlier by using cadmium nitrate as an electrolyte, which acts mainly as a complexant while other electrolytes form outer-sphere complexes (2).

The divalent anions were generally slowed down as the charge of

the cationic part of the background electrolyte increased. In spite of being monovalent, N_3^- , VO_3^- , and SCN- had the same migration as divalent anions. This interesting aspect was probably because of their larger size or polyatomic structure. In a 1N Al(NO₃)₃ solution, most of the divalent anions (such as WO_4^{2-} , SeO_3^{2-} , CrO_4^{2-} , and $Cr_2O_7^{2-}$) and a monovalent anion (MnO_4^-) gave zero migration, which was attributed to precipitation because these anions gave a precipitate when the solution of their salts were mixed with the solution of background electrolytes used.

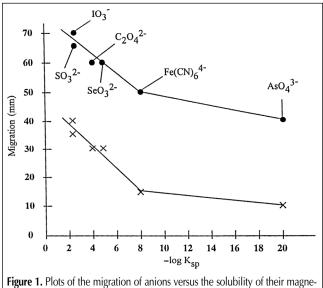
Regarding the effect of electrolyte concentration on the migration of anions with the change in concentration from 1N to 0.1N, the migration of anions gradually increased because ions moved more frequently with a decrease in the concentration of the electrolyte solution both on Whatman No. 1 and titanium (IV) tungstate impregnated papers (Table I).

It is interesting to correlate the migration of some of the anions in Mg(NO₃)₂ media with the solubility of their magnesium salts. For this purpose, IO_3^- , SO_3^{2-} , $C_2O_4^{2-}$, SeO_3^{2-} , $Fe(CN)_6^{4-}$, and AsO_4^{3-} were studied in $Mg(NO_3)_2$ media. The plot of migration versus the solubility of the magnesium salts of these anions (Figure 1) revealed that the migration on anions increased with an increase in the solubility. This relationship held good both for Whatman No. 1 and titanium (IV) tungstate papers because the nature of the curve for both papers was almost identical. Furthermore, the increase in migration was more pronounced in the higher solubility range (i.e., beyond 10-9). Interestingly, the difference in migration on both of the papers was almost constant, which was probably a result of the difference in their adsorption behavior. Solubility data is relevant only in the regions of saturated solutions, but cannot indicate how an ion will behave when it is present at a dilution far below saturation. This is shown in Table I by the lack of difference in the migration of the majority of the anions in NaNO₃, Mg(NO₃)₂, and Al(NO₃)₃ media. However, there was a significant difference in migration when $Cr(NO_3)_3$ and $Co(NO_3)_2$ were used as background electrolytes. This behavior

Background electrolyte	Anion + sodium tungstate + background electrolyte		Anion + background electrolyte					
		Р*	NP ⁺	P NP				
E ₁	IO ₃ ⁻ , BrO ₃ ⁻ , MnO ₄ ⁻	_	MnO ₄ -	_				
E ₂	MnO ₄ ⁻ , AsO ₃ ³⁻	_	-	-				
E ₃	IO ₃ ⁻ , VO ₃ ⁻ , MoO ₄ ²⁻ , SeO ₃ ²⁻	F-	SeO ₃ ^{2–} , AsO ₄ ^{3–}	_				
E ₄	CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻	F-	-	-				
E ₅	SeO ₃ ²⁻ , MnO ₄ ⁻ , AsO ₄ ³⁻	Fe(CN) ₆ ³⁻	WO4 ²⁻ , SeO3 ²⁻ , MnO4 ²⁻ , CrO4 ²⁻ , Cr ₂ O7 ²⁻	-				
E ₆	AsO ₃ ³⁻	IO ₃ -	Fe(CN) ₆ ⁴⁻	-				
E ₇	MoO ₄ ²⁻ , SeO ₃ ²⁻ , Fe(CN) ₆ ³⁻ , AsO ₄ ³⁻ , AsO ₃ ³⁻	F-	SeO ₃ ^{2–} , AsO ₄ ^{3–}	F-, VO3-				
E ₈	IO ₃ ⁻ , S ₂ O ₃ ²⁻ , MoO ₄ ²⁻ , SeO ₃ ²⁻ , Fe(CN) ₆ ³⁻ , Fe(CN) ₆ ⁴⁻ , AsO ₃ ³⁻	_	WO ₄ ^{2–} SeO ₃ ^{2–} , MoO ₄ ^{2–}	VO3 ⁻ , Fe(CN)6 ⁴⁻				
E ₉	all anions were precipitated	_	VO ₃ ⁻ , WO ₄ ⁻ , SeO ₃ ²⁻ , MoO ₄ ²⁻ , AsO ₃ ³⁻ , AsO ₄ ³⁻ , Fe(CN) ₆ ⁴⁻ , CrO ₄ ²⁻	Cl ⁻ , F ⁻ , MnO ₄ ⁻ , Fe(CN) ₆				
E ₁₀	all anions were precipitated	-	VO ₃ ⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻ , SeO ₃ ²⁻ , CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻ , AsO ₃ ³⁻ , AsO ₄ ³⁻	F ⁻ , MnO ₄ ⁻ , Fe(CN) ₆ ³⁻				

can be attributed to the higher complex-forming ability of chromium and cobalt.

Contrary to our expectations, the electrochromatography of anions was not very effective on papers impregnated with inorganic ion exchangers such as titanium (IV) tungstate because the activity of anions was diminished in the presence of the polyvalent metal ion of the exchanger. It can also be assumed that tetravalent



sium salts: (•) Whatman No. 1 papers and (x) titanium (IV) tungstate papers.

 Table III. Conductance of Background Electrolyte Used in mho per Centimeter

Background electrolyte	Conductance
1N NaNO3	119.2
0.1N NaNO ₃	18.2
$1 \text{N} \text{Mg}(\text{NO}_3)_2$	98.7
$0.1 \text{NMg}(\text{NO}_3)_2$	16.0
1N Al(NO ₃) ₃	60.7
0.1N AI(NO ₃) ₃	10.0
$1N Co(NO_3)_2$	106.2
$0.1 \text{N Co}(\text{NO}_3)_2$	16.7
$1 \text{N} \text{Cr}(\text{NO}_3)_3$	127.3
0.1N Cr(NO ₃) ₃	22.6

Table IV. Separation of Anions on Titanium (IV) Tungstate and Whatman No. 1 Papers in Different Electrolytes

Background electrolyte	Separation on Whatman No. 1 papers	Separation on titanium (IV) tungstate papers
E ₁	$Fe(CN)_6^{4-}$ - $Fe(CN)_6^{3-}$, SCN^- - Br^- , MnO_4^- - SCN^- or S^{2-} or $Fe(CN)_6^{3-}$	AsO4 ³⁻ -AsO3 ³⁻
E ₂	SCNBrO ₃ - or F-, CrO ₄ ² BrO ₃ - or F-	VO ₃ Cl- or SCN-
E ₃	IO ₃ ⁻ -IO ₄ ⁻	IO_3^- –Br O_3^-
E ₄	MnO_4 Fe(CN) ₆ ⁴⁻ or Cr ₂ O ₇ ²⁻ , SCNS ²	² - VO ₃ S ² -, FCl-
E ₅	I-–CI-, F––IO $_3$ - or IO $_4$ - or BrO $_3$ -	-
E ₆	IO ₃ ⁻ -BrO ₃ ⁻ -CrO ₄ ²⁻ , IO ₄ ⁻ -I ⁻	I−–Br−

titanium forms an ion pair with anions. Therefore, from an analytical point of view, the results were rather disappointing because the majority of anions had low migration. There was no large difference between the migration of halides and oxyhalides.

In general, the migration of iodide, iodate, and periodate had been found to be in the following order: $I^- > IO_3^- > IO_4^-$. This order was possibly because of the fact that periodate is larger in size than iodate and iodide ions and thus is less hydrated and can form very stable complexes or an ion pair, causing lower migration. The order of migration of these ions is very much in agreement with this explanation.

In the majority of background electrolytes, the migration of $Cr_2O_7^{2-}$ was lower than that of CrO_4^{2-} . This may be caused by either the larger size of the $Cr_2O_7^{2-}$ ion or the lower solubility of potassium dichromate (the solubility of potassium dichromate and potassium chromate in grams per 100 grams of water is 13.1 and 61.7, respectively).

The conductance of various electrolytes used was measured and is given in Table III. Although, the behavior of a single electrolyte can be studied with great precision by means of conductivity measurements. However, the influence of an electrolyte in the concentration range of 0.1 to 1.0N on the solution chemistry of another ion in low concentration obviously cannot be studied by conductivity measurements. Thus, the conductance measurements could not be much help in the study of the electrolytic migration of anions.

On the basis of the differential migration of various anions, some binary separations were actually realized and are given in Table IV.

In the literature, suitable combinations of a stabilization medium and background electrolyte are available for the analysis of almost all metal ions. However, anions have been paid much less attention. This simple and inexpensive method for the separation of anions is applicable to the analysis of a variety of multicomponent mixtures of these anions and therefore have wider applications in geological, pharmaceutical, and environmental analysis.

Conclusions

The low-voltage paper electrophoresis and the study of ion-pair formation for 22 anions on Whatman No. 1 and titanium (IV) tungstate impregnated papers led to some useful separations. In general, the migration of anions is much higher on unimpregnated papers than impregnated ones. In the $Co(NO_3)_2$ media, the migration is very low on Whatman No. 1 papers and is almost zero on titanium (IV) tungstate impregnated papers because of complexation and precipitation in the network of support. Interestingly, the migration of divalent anions decreases as the charge of the cationic part of the electrolyte increases. The movement of anions increase with the increase in dilution of the electrolyte solution. Contrary to our expectation, the eletrophoresis of anions is not very effective in the study of ion-pair formation on titanium (IV) tungstate papers. The order of migration of I^- , IO_3^- , and IO_4^- depends on their size and the formation of ion pairs and complexes. The conductance measurements could not be of much help in the study of the electrochromatographic migration of anions.

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