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NOTE

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Abstract

The electrophoretic behavior of 19 metal ions on thorium phosphate papers is described. Seven background electrolytes were used for these studies to allow different time intervals. On the basis of the differential mobilities of the metal ions, which depend on the ion exchange properties of thorium phosphate and the nature of the complexes formed with the electrolyte, some important binary, ternary, and quaternary separations have been achieved.

The importance of synthetic inorganic ion exchangers in the field of separation science has been reviewed (*1–4*). Papers impregnated with inorganic ion exchangers have been extensively used for chromatographic separations of metal ions. The electrophoresis of cations has also been investigated in order to achieve some important and difficult separations. In this case the ion-exchange property of these exchangers combines with the electrophoretic migration of the metal ions under an applied electrical potential to yield interesting results. Some studies on electrophoresis on paper impregnated with inorganic ion exchangers have been reported (*3–8*). These papers are highly selective, and excellent separations of metal ions have been achieved (*1–16*). However, electrophoretic work on paper impregnated with thorium-based exchangers is lacking. In our laboratory we have prepared thorium phosphate ion exchangers which are fibrous and suitable for chromatographic work (*17–19*). In the present work the electrophoretic behavior of metal ions on thorium phosphate-impregnated papers has been described. The same operation was repeated on ordinary Whatman No. 1 paper for comparison. On the basis of the ion-exchange properties and the migration of metal ions under the electrical potential applied, some difficult and important separations are reported.

EXPERIMENTAL

Apparatus

Electrophoretic work was done with an electrophoresis apparatus (Toshniwal, India, Type CM01/0 Sr. No. 124).

Reagent

Thorium nitrate tetrahydrate used was of Reagent grade (M & B) quality. All other reagents were of either of E. Merck pro analysi or BDH AnalaR grade. Whatman No. 1 chromatographic paper (45 × 2.5 cm) was used for electrophoretic work.

Preparation of Ion Exchange Papers

Thorium phosphate paper was prepared as follows. Thorium nitrate tetrahydrate (0.1 *M*) in 1 *M* nitric acid and 0.25 *M* phosphoric acid solution were prepared. The paper strips were first soaked with thorium nitrate solution for 3 to 5 sec, then the excess thorium nitrate solution was removed by a blotting paper sheet, and then the strips were dried at room temperature. The strips were then passed through a 0.25 *M* phosphoric acid solution for 15 to 20 sec. The excess phosphoric acid was removed by a blotting paper sheet and again the strips were dried overnight at room temperature. After they were dried, the strips were washed with water to pH 3–3.5 and finally dried at room temperature before being used as ion exchange papers.

Cation Solutions

Solutions of nitrates, sulfates, or chlorides of most of the cations were prepared (metal ion, 4 mg/ml). Bismuth nitrate solution was prepared in dilute nitric acid, and antimony solution was prepared in dilute hydrochloric acid.

Background Electrolytes

Seven aqueous background electrolyte solutions were used for electrophoretic work:

(1) 0.1 *M* Nitric acid.
(2) 0.5 *M* Perchrloric acid.
(3) 0.1 *M* Potassium hydrogen phthalate solution.
(4) 0.1 *M* Citric acid solution.
(5) 0.1 *M* EDTA solution.
(6) 0.05 *M* Hydrochloric acid + 0.09 *M* potassium chloride.
(7) 0.1 *M* Acetic acid + 0.1 *M* sodium acetate solution.

Detection Reagents

Yellow ammonium sulfide solution was used for the detection of Ag^+, $Hg_2{}^{2+}$, Hg^{2+}, Pb^{2+}, Tl^+, and Bi^{3+} zones. Fe^{3+}, $UO_2{}^{2+}$, VO^{2+}, and Cu^{2+} were detected with potassium ferrocyanide solution. Fe^{2+} was detected with potassium ferricyanide solution. Cd^{2+} and As^{3+} were detected with dithizone in carbon tetrachloride. Mn^{2+} and Zn^{2+} were detected with a mixture of trisodium pentacyanoamminoferrate and rubeanic acid. Ni^{2+} and Co^{2+} were detected with dimethyl glyoxime solution.

Procedure

The electrode and electrode vessels were washed with deionized water and dried. The base plate which contains electrode was kept in the horizontal position. Equal volumes of electrolyte were poured into these vessels. The paper strips were soaked with the corresponding electrolyte, and excess electrolyte was removed by a blotting paper sheet. These sheets, which act as a carrier, were placed in position in the cassette. Then the metal ion solution (4 mg/ml) was applied separately on each strip in the middle with the help of a thin glass capillary. The cassette was then covered and a potential difference was applied for a fixed time. The time of migration and the potential difference applied is specified in each case (Table 1). The migration of the zones of metal ions toward anode or cathode was measured after detection of the spot from the point of application up to the middle of the zone. On the basis of the results of experiments and distance traveled by the metal ions by electrical migration, synthetic mixtures of particular ions were applied as in the case of individual ions for separations.

TABLE 1

Movements of Metal Ions in Different Electrolytes on Thorium Phospate Papers and on Ordinary Whatman No. 1 Papers (in cm)

Electrolyte

Metal ion	0.1 *M* HNO_3[a]	0.5 *M* $HClO_4$[b]	0.1 *M* Citric acid[c]	0.1 *M* $KHC_8H_5O_4$[d]	0.1 *M* EDTA[e]	0.5 *M* HCL + 0.9 *M* KCl[f]	0.1 *M* CH_3COOH + 0.1 *M* CH_3COONa[g]
Ag^+	−1.0(−0.1)	−1.0(−0.2)	−1.0(−1.0)	−0.7(−1.3)	−0.5(−0.5)	—	−1.0(h)
Hg_2^{2+}	0.0(−0.5)	h(h)	0.0(0.0)	h(h)	+1.2(+4.0)	—	h(h)
Hg^{2+}	0.0(−0.3)	0.0(−0.3)	−0.5(+1.0)	0.0(+1.7)	+2.0(+4.5)	—	0.0(0.0)
Tl^+	−9.0(−10.4)	−3.3(−4.0)	0.0(h)	h(h)	−3.0(−6.5)	—	−3.0(h)
Pb^{2+}	−0.8(−7.5)	−2.8(−3.6)	−0.4(−9.5)	0.0(0.0)	+1.5(+3.5)	—	0.0(−6.0)
Cu^{2+}	−5.0(−6.2)	−2.4(−2.5)	−8.0(−8.0)	−1.5(0.0)	+2.2(−4.3)	−4.5(−6.0)	−4.5(+1.2)
Cd^{2+}	−6.0(−6.0)	h(h)	−10.3(h)	−3.8(−1.4)	+1.5(+4.5)	−3.2(−3.0)	−1.0(−5.5)
Zn^{2+}	−5.8(−7.6)	h(h)	−11.0(h)	−4.7(−3.0)	+2.3(h)	−4.3(−4.5)	−2.5(−7.0)
Mn^{2+}	−4.5(−8.7)	h(h)	h(h)	−6.0(−4.5)	h(h)	−3.8(−4.8)	−2.5(h)
Fe^{3+}	−0.3(−5.3)	−1.2(−2.8)	−0.6(−3.0)	0.0(0.0)	+0.2(+1.9)	0.0(−4.4)	0.0(h)
Fe^{2+}	−6.0(−6.6)	−2.6(−3.0)	0.0(h)	Trail(+2.0)	h(h)	h(h)	−5.0(h)
Ni^{2+}	−6.0(−5.9)	−2.1(−2.6)	−13.4(−13.6)	−6.0(−3.8)	h(h)	−4.0(−6.0)	−5.0(−9.4)
Co^{2+}	−6.2(−5.7)	−3.2(−3.2)	−7.5(h)	−7.1(−4.5)	h(h)	−3.5(−6.2)	−5.1(−9.2)
As^{3+}	0.0(−1.2)	−0.3(−1.0)	−2.2(0.0)	−2.0(−2.7)	−1.8(−0.5)	h(h)	−2.5(0.0)
Sb^{3+}	0.0(−1.4)	−0.6(−1.4)	+0.2(+3.0)	h(h)	h(h)	h(h)	0.0(0.0)
Bi^{3+}	0.0(0.0)	−0.3(trail)	0.0(0.0)	0.0(0.0)	−1.0(+1.5)	+0.5(−0.0)	0.0(h)
UO_2^{2+}	−2.0(−4.8)	−1.2(−2.1)	−0.2(−1.6)	h(h)	+0.8(+3.7)	0.0(−4.5)	0.0(h)
VO^{2+}	−4.6(−5.6)	−1.1(−2.5)	−1.3(−1.0)	−0.1(+1.6)	h(h)	−1.6(−4.0)	−0.8(−0.8)
Cr^{3+}	—	—	—	0.0(−1.5)	0.0(+2.5)	—	—

[a] 100 V applied potential, 4 hr.

[b] 80 V applied potential, 4 hr.

[c] 150 V applied potential, 5 hr.

[d] 250 V applied potential, 8 hr.

[e] 200 V applied potential, 4 hr.

[f] 80 V applied potential, 3 hr.

[g] 120 V applied potential, 5 hr.

[h] Diffused bands; cannot be measured.

RESULTS AND DISCUSSION

Electrophoresis is based on the differential migration of charged particles in an electric field. The distance of the center of the zone from the middle of the paper where the metal ion was originally spotted is given in centimeters, with a negative sign indicating movement of the ion toward the cathode and a positive sign used for the distance traveled toward the anode, while ions which do not show any movement are marked as 0.00. The electrophoretic behavior of 19 metal ions on thorium phosphate papers and on ordinary Whatman No. 1 papers has been studied using seven background electrolytes. These results are given in Table 1.

In Table 1 the figures within parentheses indicate the movement of metal ions on ordinary Whatman No. 1 papers. When a potential difference is applied, the rate of migration increases with the charge of the components and with decreasing molecular weight and adsorption on the carrier. For the metal ions which are strongly adsorbed on thorium phosphate paper, the rates of migration are generally low. But ordinary Whatman No. 1 papers do not show such behavior. Moreover, the spots on thorium phosphate paper (after development) are much better defined and sharper than those obtained on ordinary Whatman No. 1 paper.

Table 1 shows that the rates of movements of metal ions which are strongly adsorbed by thorium phosphate ion exchanger, e.g., Fe^{3+}, Bi^{3+}, Pb^{2+}, $UO_2{}^{2+}$, and VO^{2+} (*17*), are comparatively low. Thus these ions can be separated from numerous metal ions. Some important separations are shown in Table 2. The figures within parenthesis denote the distance migrated by the metal ions (in cm).

The above results show that electrophoretic study on thorium phosphate papers has many interesting possibilities for analytical separations of metal ions which are not feasible on ordinary chromatographic paper. Some important binary, ternary, and quaternary separations are easily achieved, e.g., Fe^{3+}/Cu^{2+}, Fe^{3+}/Co^{2+}, Pb^{2+}/Tl^{+}, Bi^{3+}/As^{3+}, VO^{2+}/Ni^{2+}, $Fe^{3+}/UO_2{}^{2+}/VO^{2+}$, $Fe^{3+}/Cu^{2+}/Ni^{2+}$, and $UO_2{}^{2+}/VO^{2+}/Mn^{2+}$.

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TABLE 2

Separations of Metal Ions Actually Achieved on Thorium Phosphate Papers by Electrophoretic Technique

Background electrolyte	Electrical potential applied (V)	Time (hr)	Separations achieved
0.1 *M* Nitric acid	100	4	$Fe^{3+}(-0.3)/Ni^{2+}(6.1)$
			$Fe^{3+}(-0.25)/Fe^{2+}(-5.2)$
			$Fe^{3+}(-0.3)/Cu^{2+}(-5.4)$
			$Fe^{3+}(-0.3)/Zn^{2+}(-6.1)$
			$Fe^{3+}(-0.3)/Co^{2+}(-6.5)$
			$Fe^{3+}(-0.3)/Cd^{2+}(-5.5)$
			$Pb^{2+}(-0.9)/Tl^{+}(-8.5)$
			$Pb^{2+}(-0.8)/Cd^{2+}(-5.5)$
			$UO_2^{2+}(-1.8)/VO^{2+}(-4.5)$
			$Fe^{3+}(-0.25)/UO_2^{2+}(-1.8)/VO^{2+}(-4.5)$
0.1 *M* Potassium hydrogen phthalate	250	8	$Fe^{3+}(0.0)/Zn^{2+}(-5.0)$
			$VO^{2+}(0.0)/Mn^{2+}(-6.2)$
			$Bi^{3+}(0.0)/As^{3+}(-2.0)$
			$Bi^{3+}(0.0)/Cu^{2+}(-1.6)$
			$Fe^{3+}(0.0)/Cu^{2+}(-1.6)/Ni^{2+}(-6.1)/Co^{2+}(-7.3)$
			$Fe^{3+}(0.0)/Cu^{2+}(-1.7)/Mn^{2+}(-6.0)$
0.1 *M* Citric acid	150	5	$Fe^{3+}(-0.50)/Cu^{2+}(-7.8)$
			$UO_2^{2+}(-0.20)/Cu^{2+}(-7.9)$
			$Fe^{3+}(-0.52)/Ni^{2+}(-13.4)$
			$Pb^{2+}(-0.5)/Cd^{2+}(-10.6)$
			$Fe^{3+}(-0.5)/As^{3+}(-2.2)/Ni^{2+}(-13.5)$
			$UO_2^{2+}(-0.2)/As^{3+}(-2.3)/Cu^{2+}(-8.0)$
			$Fe^{3+}(-0.5)/Co^{2+}(-7.4)/Ni^{2+}(-13.4)$
			$UO_2^{2+}(-0.2)/VO^{2+}(-1.4)/Co^{2+}(-7.3)/Ni^{2+}(-13.4)$
0.1 *M* EDTA	200	4	$Fe^{3+}(+0.2)/Cu^{2+}(+2.2)$
			$Fe^{3+}(+0.2)/Zn^{2+}(2.3)$
			$Cr^{3+}(0.0)/Cu^{2+}(+2.2)$
0.05 *M* HCl + 0.09 *M* KCl (1:1)	80	3	$Fe^{3+}(0.0)/Mn^{2+}(-3.8)$
			$Fe^{3+}(0.0)/Zn^{2+}(-4.3)$
			$Fe^{3+}(0.0)/Cd^{2+}(-3.3)$
			$Fe^{3+}(0.0)/Cu^{2+}(-4.7)$
			$Fe^{3+}(0.0)/Ni^{2+}(-4.1)$
			$Fe^{3+}(0.0)/Co^{2+}(-3.6)$
			$UO_2^{2+}(0.2/Mn^{2+}(-3.9)$
			$UO_2^{2+}(0.0)/Cu^{2+}(-4.6)$
			$UO_2^{2+}(0.0)/Zn^{2+}(-4.4)$
			$UO_2^{2+}(0.0)/Cd^{2+}(-3.4)$
			$UO_2^{2+}(0.0)/Ni^{2+}(-4.0)$

(*continued*)

TABLE 2 (*continued*)

Background electrolyte	Electrical potential applied (V)	Time (hr)	Separations achieved
			UO_2^{2+}(0.0)/Co^{2+}(−3.7)
			VO^{2+}(−1.6)/Cu^{2+}(−4.6)
			VO^{2+}(−1.7)/Ni^{2+}(−4.1)
			VO^{2+}(−1.7)/Co^{2+}(−3.4)
0.05 *M* HCl + 0.09 *M* KCl	80	3	UO_2^{2+}(0.0)/VO^{2+}(−1.7)/Mn^{2+}(−3.8)
			UO_2^{2+}(0.0)/VO^{2+}(−1.8)/Zn^{2+}(−4.5)
			UO_2^{2+}(0.0)/VO^{2+}(−1.7)/Ni^{2+}(−4.0)
0.1 *M* Acetic acid + 0.1 *M* sodium acetate	120	5	Pb^{2+}(0.0)/Tl^{+}(−3.0)
			Cd^{2+}(−1.0)/Cu^{2+}(−4.5)
			Zn^{2+}(−2.5)/Cu^{2+}(−4.5)
			Zn^{2+}(−2.5)/Ni^{2+}(−5.0)
			Zn^{2+}(−2.4)/Co^{2+}(−5.1)
			Fe^{3+}(0.0)/Cu^{2+}(−4.6)
			Fe^{3+}(0.0)/Fe^{2+}(−5.0)
			Cd^{2+}(−1.0)/Ni^{2+}(−5.0)
			Cd^{2+}(−1.1)/Co^{2+}(−5.2)
			Cd^{2+}(−1.0)/Fe^{2+}(−5.0)
			UO_2^{2+}(0.0)/Cu^{2+}(−4.5)
			UO_2^{2+}(0.0)/Fe^{2+}(−5.1)
			UO_2^{2+}(0.0)/Ni^{2+}(−5.1)
			UO_2^{2+}(0.0)/Co^{2+}(−5.0)
			VO^{2+}(−0.9)/Cu^{2+}(−4.5)
			VO^{2+}(−0.8)/Ni^{2+}(−5.0)
			VO^{2+}(−0.8)/Co^{2+}(−5.0)

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