A PAPER ELECTROPHORETIC STUDY OF ION PAIR FORMATION

V. PAPER ELECTROPHORESIS AND ANION-EXCHANGE PAPER CHROMATOGRAPHY OF INORGANIC ANIONS WITH VARIOUS ELECTROLYTES

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SUMMARY

Inorganic anions were studied by paper electrophoresis and ion-exchange paper chromatography employing electrolytes and eluents with various metal ions (Mg^{2+}, Al^{3+} and Cd^{2+}). It was found that the metal ion has a strong effect on the movement of anions in paper electrophoresis both by ion pair and complex formation In ion-exchange paper chromatography the effect is small. Data are given for twenty inorganic anions.

INTRODUCTION

Separations by paper electrophoresis are usually effected by choosing suitable conditions of pH or complexation (with borate for example) or by permitting the ions to move over large distances with high potentials. We have recently shown that there exists still another factor able to improve separations, namely ion pairing or outer-sphere complexing[1,2] and have shown that the separation of quarternary ammonium compounds can be improved by choosing suitable electrolytes and electrolyte concentrations[3].

In this paper we report a similar study for inorganic anions. Paper electrophoresis of inorganic anions has been effected in several alkaline electrolytes, and there is little difference in the separations obtained in *e.g.* NaOH or ammonium carbonate[4-7]. pH variations cannot be used very effectively for inorganic anions as many are unstable below neutrality. Thus improvement of separations can be obtained, as will be shown here, either by complex formation or by ion pair formation. We also thought it of interest to compare the effect of ion pairing in paper electrophoresis and ion-exchange chromatography. While the effect is considerable in the first and improves separations, it is not very marked in ion exchange.

EXPERIMENTAL

Paper electrophoresis

A Camag high-potential electrophoresis apparatus was used with Whatman

TABLE I

HIGH-VOLTAGE ELECTROPHORESIS OF INORGANIC ANIONS IN AMMONIUM NITRATE AS ELECTROLYTE
Whatman No. 1 paper; 1000 V for 30 min at 7–8°. The values are corrected for electroosmotic flow (movement of H_2O_2) and results of different sheets are compared by assuming the movement of ferricyanide (run on all sheets) constant. Chromatographic R_F values are given for each concentration to show where adsorption occurs, but no correction to the electrophoretic movement was made.

Anion	1.0 M		0.5 M		0.1 M	
	R_F	mm	R_F	mm	R_F	mm
F^-	1.0	73	1.0	63	1.0	57
Cl^-	1.0	114	1.0	96	1.0	89
Br^-	1.0	108	1.0	101	1.0	90
I^-	0.90	110	0.88	95	0.89	87
SCN^-	0.85	82	0.85	79	0.85	72
ClO_3^-	1.0	86	1.0	80	1.0	75
BrO_3^-	1.0	68	1.0	65	1.0	66
IO_3^-	1.0	41	1.0	38	1.0	39t
ClO_4^-	0.88	80	0.86	75	0.86	71
IO_4^-	0.90	44	0.87	39	0.90	38
ReO_4^-	0.84	57	0.80	52	0.83	53
$HCOO^-$	1.0	73	1.0	67	1.0	66
CH_3COO^-	1.0	50	1.0	46	1.0	42
Ox^{2-}	1.0	71	1.0	65	1.0	68
$Cr_2O_7^{2-}$	0.77	71	0.78	63	0.80	70
CrO_4^{2-}	0.77	75	0.78	68	0.80	65
$S_2O_3^{2-}$	1.0	82	1.0	78	1.0	77
$S_2O_8^{2-}$	1.0	87	1.0	76	1.0	74
SeO_3^{2-}	1.0	39	1.0	40	1.0	41
$Fe(CN)_6^{3-}$	1.0	91[a]	1.0	81[a]	1.0	78[a]
SO_4^{2-}	1.0	78	1.0	68	1.0	65

[a] Anion run on all sheets.
t = tailing.

No. 1 paper, water circulating at 7–8°, applying a potential of 1000 V for 30 min. During this time the current increased. However, we preferred such conditions to efficient cooling as they led to a fast separation. To compare the movement of ions from different electropherograms, we ran ferricyanide on all of them and recalculated the movement to the mean distance moved by ferricyanide (as indicated in the tables). For $Cd(NO_3)_2$ as electrolyte, perchlorate was used as standard instead of ferricyanide.

Adsorption on Whatman No. 1 paper was examined by chromatographing at about 5° by ascending development with the electrolyte. Electroosmotic movement was measured by observing the movement of H_2O_2, and the results shown in Tables I–V are corrected for electroosmotic flow. The movement of the anions in various concentrations of ammonium, magnesium and aluminium nitrates is shown in the tables. Some were insoluble under certain conditions and thus are not shown.

Generally there are two important changes in the movement of anions from NH_4^+ to Mg^{2+} and Al^{3+}. The divalent anions are slowed down as the charge of the metal ion increases while the halides move with about the same speed and there is a considerable difference in the separation of chlorate–bromate–iodate.

The greater tendency of oxyhalide anions to ion pairing is evident compared

TABLE II

HIGH-VOLTAGE ELECTROPHORESIS OF INORGANIC ANIONS IN MAGNESIUM NITRATE AS ELECTROLYTE

Conditions as in Table I.

Anion	1.0 M		0.5 M		0.1 M	
	R_F	mm	R_F	mm	R_F	mm
F^-	—	—	—	—	—	—
Cl^-	1.0	74	1.0	83	1.0	83
Br^-	0.90	77	1.0	86	0.92	85
I^-	0.82	75	0.86	84	0.83	83
SCN^-	0.83	56	0.82	73	0.82	66
ClO_3^-	1.0	64	1.0	72	1.0	68
BrO_3^-	1.0	44	1.0	51	1.0	56
IO_3^-	0.91	16	0.88	21t	0.92	25
ClO_4^-	0.90	67	1.0	76	0.86	72
IO_4^-	1.0–0.35	18–30	0.87t	22	0.89t	27
ReO_4^-	0.77	42	0.75	49	0.72	48
$HCOO^-$	1.0	21	1.0	37	1.0	47
CH_3COO^-	1.0	16	1.0	24	1.0	32
Ox^{2-}	—	—	—	—	—	—
$Cr_2O_7^{2-}$	0.70t	46–34	0.70	51	0.74	48t
CrO_4^{2-}	0.92t	33	0.90t	41	0.91t	46
$S_2O_3^{2-}$	1.0	38	1.0	45	1.0	49
$S_2O_8^{2-}$	1.0	62	1.0	69	1.0	67
SeO_3^{2-}	1.0	14	0.90	17	0.89	23
$Fe(CN)_6^{3-}$	1.0	41[a]	1.0	51[a]	1.0	55[a]
SO_4^{2-}	1.0	22	1.0	26	1.0	37

[a] Anion run on all sheets.
t = tailing.

TABLE III

HIGH-VOLTAGE ELECTROPHORESIS OF INORGANIC ANIONS IN ALUMINIUM NITRATE AS ELECTROLYTE

Conditions as in Table I.

Anion	0.5 M		0.3 M		0.2 M		0.05 M	
	R_F	mm	R_F	mm	R_F	mm	R_F	mm
F^-	—	—	—	—	—	—	—	—
Cl^-	1.0	70	1.0	78	1.0	77	1.0	82
Br^-	0.95	78	0.92	84	0.92	81	0.93	86
I^-	0.84	69	0.86	83	0.86	86	0.86	72
SCN^-	0.84	50	0.80	55	0.80	61	0.81	60
ClO_3^-	1.0	59	1.0	63	1.0	69	1.0	63
BrO_3^-	1.0	42	1.0	46	1.0	50	1.0	54
IO_3^-	1.0	9	0.90	11	0.88	14	0.85t	22t
ClO_4^-	0.88	64	0.85	67	0.83	73	0.88	70
IO_4^-	—	—	—	—	—	—	—	—
ReO_4^-	0.73	44	0.75	46	0.76	48	0.75	47
$HCOO^-$	—	—	—	—	—	—	—	—
CH_3COO^-	—	—	—	—	—	—	—	—
Ox^{2-}	—	—	—	—	—	—	—	—
$Cr_2O_7^{2-}$	0.75	44	0.80	46	0.82	49; 0.79	0.70	45; 38
CrO_4^{2-}	0.76	47	0.76	46	0.75	42; 0.76	0.68	46; 36
$S_2O_3^{2-}$	1.0	29	1.0	32	1.0	33	1.0	31
$S_2O_8^{2-}$	1.0	58	1.0	60	1.0	63	1.0	60
SeO_3^{2-}	1.0	+12	1.0	+4	0.91	0	0.84	0
$Fe(CN)_6^{3-}$	1.0	38[a]	1.0	41[a]	1.0	43[a]	1.0	37[a]
SO_4^{2-}	—	—	—	—	—	—	—	—

[a] Anion run on all sheets.
t = tailing.

TABLE IV

HIGH-VOLTAGE ELECTROPHORESIS OF INORGANIC ANIONS IN CADMIUM NITRATE
Perchlorate is used as reference anion for comparison of different sheets. Conditions as in Table I.

Anion	1.0 M		0.5 M		0.1 M	
	R_F	mm	R_F	mm	R_F	mm
F^-	1.0	15–52	1.0	23–60	1.0	63–38–0
Cl^-	0.92	+11	0.88	+ 7	0.92	8; +1
Br^-	0.89	+15	0.88	+ 9	0.85	+ 2
I^-	0.80	+15	0.84	+11	0.82	+12
SCN^-	0.85	+15	0.87	+13	0.82	+ 2
ClO_3^-	1.0	58	1.0	60	1.0	71
BrO_3^-	0.91	37	1.0	40	1.0	53
IO_3^-	0.88	0	0.80	5	0.85	16t
ClO_4^-	0.88	61[a]	0.78	65[a]	0.86	71[a]
IO_4^-	—	—	—	—	—	—
ReO_4^-	0.76	37	0.73	42	0.68	49
$HCOO^-$	1.0	+2	1.0	+2	1.0	0
CH_3COO^-	1.0	+2	1.0	+2	1.0	0
Ox^{2-}	—	—	—	—	—	—
$Cr_2O_7^{2-}$	0.68	40t	0.70	46	0.65	49
CrO_4^{2-}	—	—	—	—	—	—
$S_2O_3^{2-}$	1.0	0	1.0	+4	0.90	0
$S_2O_8^{2-}$	1.0	58	1.0	64	1.0	68
SeO_3^{2-}	0.87	+6	0.87	+4	0.81	0
$Fe(CN)_6^{3-}$	—	—	—	—	—	—
SO_4^{2-}	1.0	14	1.0	19	1.0	0(?)

[a] Anion used as reference.
t = tailing.

TABLE V

R_F VALUES OF INORGANIC ANIONS ON STRONGLY BASIC ANION-EXCHANGE RESIN PAPER AMBERLITE SB-2 IN THE NITRATE FORM
The last column gives the R_F values in 1 N KNO_3 on cellulose Whatman No. 1 paper to show where adsorption on cellulose occurs. The values for KNO_3 are taken from ref. 5.

Anion	Eluent									KNO_3
	KNO_3			$Mg(NO_3)_2$			$Al(NO_3)_3$			
	0.1 N	0.5 N	1 N	0.1 N	0.5 N	1 N	0.1 N	0.5 N	1 N	1 N
Cl^-	0.22	0.51	0.66				0.30	0.60	0.72	1.0
Br^-	0.10	0.33	0.43	0.12	0.36	0.52	0.12	0.36	0.50	1.0
I^-	0.03	0.07	0.12	0.02	0.08	0.15	0.03	0.06	0.15	0.84
SCN^-	0.02	0.06	0.10	0.01	0.08	0.14	0.02	0.06	0.12	0.81
ClO_3^-	0.12	0.34	0.49	0.14	0.30	0.49	0.11	0.35	0.44	1.0
BrO_3^-	0.28	0.60	0.75	0.36	0.67	0.81	0.34	0.70	0.82	1.0
IO_3^-	0.60	0.87	0.88	0.65; 0.95	0.85; 1.0	0.93	0.64; 0.92	0.80; 0.92	1.0	1.0
IO_4^-	0	0.05	0.07	0.01	0.04	0.08	0.02	0.04	0.09	1.0
$Cr_2O_7^{2-}$	—	—	—	0	0.01	0.03	0.01	0.02	0.03	—
CrO_4^{2-}	0.03	0.06	0–0.17	0	0.01	0.03	0.01	0.02	0.03	1.0
$S_2O_3^{2-}$	0.08	0.43	0.83	0.16	0.17 (0.70)	0.95	0.17	0.73; 0.93	1.0	1.0
$Fe(CN)_6^{3-}$	0	0	0	0	0	0	0	0	0.01	1.0

to that of the halides. This was also noted in previous studies on the ion pairing of cobalt(III) complexes[1]. With cadmium nitrate as electrolyte which acts mainly as a complexant unlike the previous electrolytes which should essentially form outer-sphere complexes, we obtained again interesting separations (Table IV). Halides move cationically, presumably as CdX^+. There is an excellent separation of oxyhalides with a tendency of the heavier being being most retarded. Some divalent anions such as persulphate and dichromate are moving anionically while others, thiosulphate and selenite, are almost isoelectric.

These results clearly show that excellent separations can be obtained with complexing agents and that a study of other complexing cations may be rewarding.

Chromatography on ion-exchange resins

One of us (L.O.) had published the R_F values of a series of inorganic anions on Amberlite SB-2 paper developing with 0.1, 0.5 and 1 N KNO_3 (ref. 8). Table V

TABLE VI

R_F VALUES OF INORGANIC ANIONS ON MACHEREY, NAGEL & CO. STRONGLY BASIC QUARTERNARY AMMONIUM CELLULOSE PAPER IN THE NITRATE FORM

Eluents: ammonium, magnesium and aluminium nitrates.

Ion	Eluent								
	NH_4NO_3			$Mg(NO_3)_2$			$Al(NO_3)_3$		
	0.1N	0.5N	1N	0.2N	1N	2N	0.15N	0.4N	0.9N
F^-	0.83 (0.50)	0.90	0.88	—	—	—	—	—	—
Cl^-	0.43	0.74	0.80	0.56–0.84	0.86	0.85	0.59–0.74	0.87	0.87
Br^-	0.57	0.73	0.80	0.56	0.78	0.84	0.56	0.80	0.81
I^-	0.45	0.73	0.77	0.45	0.68	0.73	0.49	0.69	0.75
SCN^-	0.47	0.70	0.76	0.45	0.64	0.74	0.46	0.63	0.66
ClO_3^-	0.44	0.71	0.77	0.64	0.84	0.85	0.72	0.83	0.83
BrO_3^-	0.47	0.76	0.83	0.67	0.81	0.87	0.68	0.83	0.86
IO_3^-	0.40–0.54	0.78	0.82	0.86	0.81	0.90	0.90	0.87	0.91
ClO_4^-	0.27	0.56	0.62	0.47	0.73	0.73	0.47	0.65	0.67
IO_4^-	0.42	0.73	0.85	0.61	0.76	0.90	—	—	—
ReO_4^-	0.32	0.46	0.55	0.33	0.57	0.66	0.32	0.49	0.55
$HCOO^-$	0.75	0.80	0.84	0.90	0.90	0.91	—	—	—
CH_3COO^-	0.80	0.90	0.91	0.82–0.88	0.88–0.96	0.88–0.93	—	—	—
Ox^{2-}	0.86	0.93	0.89	—	—	—	—	—	—
$Cr_2O_7^{2-}$	0.18	0.40	0.53	0.12	0.37	0.50	0.18	0.43	0.41
CrO_4^{2-}	0.15	0.37	0.52	0.12; 0.41	0.37; 0.82	0.44; 0.83	0.20	0.45	0.42
$S_2O_3^{2-}$	0.90	0.89	0.90	0.87	0.89	0.89	0.95	—	—
$S_2O_8^{2-}$	0.10	0.51	0.67	0.25	0.63	0.75	0.27	0.60	0.68
SeO_3^{2-}	0.80	0.84	0.86	0.72	0.88	0.91	0.76	0.82	0.82
$Fe(CN)_6^{3-}$	0.12	0.30	0.47	0.08	0.47	0.67	0.15	0.62	0.48
Pyrophosphate	0.96	1.0	1.0	—	—	—	—	—	—
PO_4^{3-}	0.85	0.95	1.0	—	—	—	—	—	—
$H_2PO_4^-$	0.82	0.88	0.88	—	—	—	—	—	—
$HAsO_4^{2-}$	0.85 (0.38)	0.85	0.88	—	—	—	—	—	—
TeO_4^{2-}	0.82	0.87	0.93	—	—	—	—	—	—

nitrate as developing solvents. There seems to be little difference between K^+, shows the R_F values on the same resin paper using magnesium nitrate and aluminium Mg^{2+} and Al^{3+} as eluent, the R_F values of the halides and oxyhalides being almost identical in all three.

Chromatography on anion-exchange cellulose paper

In this section we report for the first time data for a range of inorganic anions on an anion-exchange cellulose (Macherey, Nagel & Co. quarternary ammonium cellulose paper). From an analytical point of view the results are rather disappointing as most substances have rather high R_F values. Also there are no large differences between halides or between oxyhalides.

TABLE VII

R_F VALUES OF INORGANIC ANIONS ON MACHEREY, NAGEL & CO. STRONGLY BASIC QUARTERNARY AMMONIUM CELLULOSE PAPER IN THE NITRATE FORM

Eluent: cadmium nitrate.

Anion	Normality		
	0.1	0.5	1
F^-	0.85	0.88	0.88
Cl^-	0.70	0.74	0.75
Br^-	0.77	0.79	0.81
I^-	0.77	0.80	0.80
SCN^-	0.56	0.76	0.80
ClO_3^-	0.67	0.76	0.83
BrO_3^-	0.86	0.86	0.90
IO_3^-	0.88	0.92	0.90
ClO_4^-	0.45	0.64	0.70
ReO_4^-	0.31	0.48	0.53
$Cr_2O_7^{2-}$	0.10	0.36	0.42
$S_2O_3^{2-}$	0.72	0.87	0.89
$S_2O_8^{2-}$	0.18–0.35	0.60	0.67
SeO_3^{2-}	0.80	0.85	0.85

Table VI further shows that generally there are no marked differences between R_F values in ammonium, magnesium and aluminium nitrates. Chromatography with a complexing cation, i.e. with cadmium, does not change the picture very much either (see Table VII).

DISCUSSION

The work reported here shows that improvement of electrophoretic separations of anions may be obtained if electrolytes of suitable metal ions capable of ion pairing are employed. Highly hydrated monovalent anions do not separate better, but oxyhaides which are less hydrated are subject to ion pairing as are polyvalent anions.

A rather unexpected result of this work was that the cation of the developer had little effect in ion-exchange chromatography. This seems to be due to the fact

that in the law of mass action equation the activity of the polyvalent metal ion is diminished by ion pairing with the nitrate (used as eluent), and thus although there is also ion pairing with the anion under study the two effects cancel each other. What is surprising however is that there are not even small differences. From studies in solution it can also be assumed that the quarternary ammonium groups of the resin form ion pairs with anions. It is equally remarkable that there is no effect due to the differences in ion pairing ability of different anions with the groups of the resin and the metal ions in solution.

Complexing with cadmium produces rather spectacular results in paper electrophoresis with sequences that could have been predicted in most cases from the complex chemistry of cadmium. Ion-exchange chromatography on cellulose anion-exchange paper yields rather poor results as the complexed anions are all moving with high R_F values.

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