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## A PAPER ELECTROPHORETIC STUDY OF ION-PAIR FORMATION

## VII. THE EFFECT OF IONIC SIZE ON ION-PAIR FORMATION

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SUMMARY

The electrophoretic movement of chlorate, bromate and iodate was studied using a wide range of metal salts as electrolytes. The separation effects were interpreted as differences in the degree of ion-pair formation. In Fe(III), Zr(IV) and Th(IV) nitrates iodate moves cationically.

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## INTRODUCTION

Our paper-electrophoretic study of ion-pair formation started with a paper-electrophoretic examination of some Co(III) complexes where we found that the anion of the electrolyte can influence the sequence and migration distances of various complexes to a large degree<sup>1</sup>. This work was then extended to organic cations<sup>2</sup> and later we showed that improved separations of anions could be obtained with Mg(II) or Al(III) as cation of the electrolyte instead of the ammonium or sodium ion used in previous studies<sup>3</sup>. So far, no data are available on the effect of the size of the cation (*e.g.* Mg, Ca, Sr and Ba) of the electrolyte on the separation of anions, and the present paper deals with this question.

Such a study has serious practical limitations as many anions such as sulphate, phosphate, *etc.* precipitate with many cations, and in order to have comparative results we decided to limit our study to three anions, namely chlorate, bromate and iodate. All three usually exhibit little tendency to form complexes with metal ions, have few insoluble salts, are relatively strong acids and, as we found during this work, are not reduced to an appreciable extent during an electrophoretic run even in acid media. They are all detected readily with the same reagent (KI in 5 N HCl) yielding brown spots which are readily visible even in the presence of coloured cations.

As we desired to compare electrolytes with different cations, it was of course impossible to perform electrophoresis with identical V/cm values. Furthermore, conditions for fast runs did not permit the maintenance of a constant current during the run. As we realised that ionic mobilities increase by about 20 % for an increase of 7°, it seemed useless to try to establish conditions where mobilities could be expressed in mm/V/h or similar units.

We preferred to express all results as the movement of bromate or iodate rela-

tive to the movement of chlorate. In other words, we established essentially the separation effect obtained, which is often the practice in chromatographic techniques where only relative retention volumes or retention times are reported. This method had the advantage, however, that reproducible results were obtained which gave exactly the information which we wanted.

#### EXPERIMENTAL AND RESULTS

A CAMAG high voltage electrophoresis apparatus was used with water at 7° circulating through it. Electrophoresis was performed on Whatman No. 1 paper with 1000 V for 30 min (unless otherwise specified).

##### *Ionic mobilities and electrophoretic mobilities*

Table I summarises results from published data. It is remarkable that the ratio of the ionic mobilities measured by conductivity and those in paper electrophoresis with dilute ammonium carbonate or sodium hydroxide are almost identical. This should not be interpreted as the "ionic cloud" being non-existent, but rather that all three ions are affected in almost the same way. In the electrolytes given in Table I, the ionic cloud is sufficiently strong to reduce the speed of di- and trivalent anions to that of a monovalent one. However, these data give us a useful starting point for comparing the behaviour of these anions in other electrolytes.

##### *The effect of the concentration of the electrolyte*

The effect of the concentration of the electrolyte is shown in Table II which contains the data obtained in a previous study<sup>3</sup>. While the bromate ion is slowed down by only about 10% from 0.1 to 1.0 M in ammonium and magnesium nitrates, a rather strong effect is already noticeable for the iodate ion.

##### *The effect of the metal ion of the electrolyte*

Table III gives the movement of chlorate, bromate and iodate in 0.1 M solutions of a number of divalent, trivalent and tetravalent metal ions. With the divalent metal ions it is rather remarkable that there are no differences between Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> and only slight slowing down of iodate in Cd<sup>2+</sup>. On the one hand, there is definite evidence of ion pairing because the BrO<sub>3</sub><sup>-</sup>/ClO<sub>3</sub><sup>-</sup> ratio is about 0.78 and not 0.88 as in dilute solutions of monovalent metal ions, and the IO<sub>3</sub><sup>-</sup>/ClO<sub>3</sub><sup>-</sup> ratio is still less, being about 0.35 instead of 0.52. On the other hand, the solubilities of Ca(II), Sr(II) and Ba(II) chlorates, bromates and iodates differ enormously as shown in Table IV and the forces acting in saturated solutions thus seem to be absent in 0.1 M solutions of metal ions when interacting with very dilute solutions of the anions.

The trivalent and tetravalent metal ions have only a small influence on the BrO<sub>3</sub><sup>-</sup>/ClO<sub>3</sub><sup>-</sup> ratio, but a spectacular one on the movement of IO<sub>3</sub><sup>-</sup>, which becomes cationic in Fe(III), Th(IV) and Zr(IV). Also, from Al(III) to the rare earths La(III) and Ce(III), iodate changes its speed by a factor of four.

The cationic movement of IO<sub>3</sub><sup>-</sup> comes somewhat as a surprise as from our previous work we would not have suspected the possibility that an interaction between a monovalent anion and a polyvalent cation would lead to such a strong interaction. It is interesting to note that this occurs with metal ions which in "neutral" solutions are strongly hydrolysed, *i.e.* exist as Fe(OH)<sup>2+</sup>, ZrO<sup>2+</sup> and Th(OH)<sup>3+</sup>.

TABLE I

ELECTROPHORETIC AND IONIC MOBILITIES OF CHLORATE, BROMATE AND IODATE IONS

Anion	Electrophoretic mobilities				Ionic mobilities $\Lambda_{\infty}$ (conductivity) <sup>8</sup>			
	0.1 M $(\text{NH}_4)_2\text{CO}_3$ (ref. 5)		2% $(\text{NH}_4)_2\text{CO}_3$ (ref. 6)		0.1 N NaOH (ref. 7)		18°C	25°C
	Distance moved (mm)	Movement relative to $\text{ClO}_3^-$	Distance moved (mm)	Movement relative to $\text{ClO}_3^-$	Distance moved (mm)	Movement relative to $\text{ClO}_3^-$	Mobility relative to $\text{ClO}_3^-$	Mobility relative to $\text{ClO}_3^-$
$\text{ClO}_3^-$	-84		-76		-74		55.8	64.6
$\text{BrO}_3^-$	-73	0.87	-67	0.88	-62	0.84	49.0	55.7
$\text{IO}_3^-$	-49	0.58	-50	0.66	-41	0.55	34.8	40.7

TABLE II

ELECTROPHORETIC MOVEMENT IN  $\text{NH}_4\text{NO}_3$  AND  $\text{Mg}(\text{NO}_3)_2$  ELECTROLYTES<sup>3</sup>

Electrolyte	Concentration (M)	Electrophoretic movement in 30 min with 1000 V (mm)			Movement relative to $\text{ClO}_3^-$		
		$\text{ClO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$	
$\text{NH}_4\text{NO}_3$	0.1	-75	-66	-39	0.88	0.52	
	0.5	-80	-65	-38	0.81	0.48	
	1.0	-86	-68	-41	0.79	0.48	
$\text{Mg}(\text{NO}_3)_2$	0.1	-68	-56	-25	0.82	0.37	
	0.5	-72	-51	-21	0.71	0.29	
	1.0	-64	-44	-16	0.69	0.25	

It occurred to us that there may be an analogy between this interaction and that occurring on the hydrous oxides. We thus impregnated paper with freshly precipitated thorium hydroxide (for preparation see ref. 4) and chromatographed  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$  and  $\text{IO}_3^-$  on it using 0.1 M  $\text{LiNO}_3$  as eluent.  $\text{IO}_3^-$  ions were strongly absorbed while the other two travelled with the liquid front.

A similar soluble form of an insoluble polymeric salt was also encountered previously<sup>1</sup> namely a cationic ferrocyanide in zirconyl chloride as electrolyte.

#### *The effect of the anion of the electrolyte*

In this account of the variables influencing the paper-electrophoretic separation of  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$  and  $\text{IO}_3^-$ , we feel that we should investigate the influence of the anion of the electrolyte. Table V shows the results obtained with magnesium sulphate, perchlorate, nitrate and chloride. As the anion of the electrolyte tends to form stronger ion pairs with the cation, it competes with the anions to be separated and the movement becomes more like that at "infinite dilution". Thus the degree of separation decreases in the order chloride, nitrate, perchlorate, sulphate.

TABLE III

ELECTROPHORETIC MOVEMENT IN 0.1 M ELECTROLYTE SOLUTIONS

Electrolyte	Electrophoretic movement in 30 min with 1000 V (mm)			Movement relative to $\text{ClO}_3^-$	
	$\text{ClO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$
$\text{Ca}(\text{NO}_3)_2$	-81	-62	-31	0.77	0.38
$\text{Sr}(\text{NO}_3)_2$	-85	-67	-33	0.79	0.39
$\text{Ba}(\text{NO}_3)_2$	-74	-56	-25	0.76	0.34
$\text{Co}(\text{NO}_3)_2$	-76	-58	-27	0.76	0.36
$\text{Ni}(\text{NO}_3)_2$	-82	-64	-29	0.78	0.35
$\text{Zn}(\text{NO}_3)_2$	-79	-62	-27	0.78	0.34
$\text{Cd}(\text{NO}_3)_2$	-79	-62	-22	0.78	0.28
$\text{Al}(\text{NO}_3)_3$	-69	-53	-18	0.77	0.26
$\text{Fe}(\text{NO}_3)_3$	-72	-55	+17	0.76	—
$\text{La}(\text{NO}_3)_3$	-61	-46	-4	0.75	0.07
$\text{Ce}(\text{NO}_3)_3$	-67	-49	-6	0.73	0.09
$\text{Th}(\text{NO}_3)_4$	-67	-47	+30	0.70	—
$\text{ZrOCl}_2$	-61	-33	+39	0.54	—

TABLE IV

SOLUBILITY IN COLD WATER<sup>0</sup>

Salt	Solubility (g/100 ml)	Salt	Solubility (g/100 ml)	Salt	Solubility (g/100 ml)
$\text{Ca}(\text{ClO}_3)_2$	s	$\text{Sr}(\text{ClO}_3)_2$	174.9	$\text{Ba}(\text{ClO}_3)_2$	27.4
$\text{Ca}(\text{BrO}_3)_2$	vs	$\text{Sr}(\text{BrO}_3)_2$	33	$\text{Ba}(\text{BrO}_3)_2$	0.3
$\text{Ca}(\text{IO}_3)_2$	0.20	$\text{Sr}(\text{IO}_3)_2$	0.03	$\text{Ba}(\text{IO}_3)_2$	0.008

s = soluble; vs = very soluble.

TABLE V

ELECTROPHORETIC MOVEMENT IN 0.1 M ELECTROLYTE SOLUTIONS

Electrolyte	Electrophoretic movement in 30 min with 1000 V (mm)			Movement relative to $\text{ClO}_3^-$	
	$\text{ClO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$
$\text{MgSO}_4$	-75	-66	-35	0.88	0.47
$\text{Mg}(\text{ClO}_4)_2$	-69	-55	-29	0.80	0.42
$\text{Mg}(\text{NO}_3)_2$	-78	-63	-31	0.81	0.40
$\text{MgCl}_2$	-79	-61	-32	0.77	0.40

TABLE VI

ELECTROPHORETIC MOVEMENT IN HCl ELECTROLYTE

HCl concentration (N)	Conditions	Electrophoretic movement (mm)			Movement relative to $\text{ClO}_3^-$	
		$\text{ClO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$	$\text{BrO}_3^-$	$\text{IO}_3^-$
0.1	30 min with 1000 V	-91	-76	-37	0.84	0.41
0.5	45 min with 500 V	-63	-50	-18	0.79	0.29

*The effect of the hydrogen ion concentration*

In the electrolytes with trivalent and tetravalent metal ions, hydrolysis produces a high  $\text{H}^+$  concentration. This seems to have little influence on the three anions studied. As shown in Table VI, there is essentially the same separation in 0.1 N HCl as in 0.1 N NaOH and 0.1 N  $\text{NH}_4\text{NO}_3$ .

*The movement in mixtures of monovalent and polyvalent electrolytes*

We studied two systems, one of weak ion-pair formation, namely  $\text{NH}_4\text{NO}_3$ - $\text{Al}(\text{NO}_3)_3$ , and one of very strong ion-pair formation,  $\text{NH}_4\text{NO}_3$ - $\text{Th}(\text{NO}_3)_4$ . The results are given in Figs. 1 and 2. In the first case there is a linear change as  $\text{Al}(\text{III})$  replaces  $\text{NH}_4^+$ , while in the case of  $\text{Th}(\text{IV})$  the movement of iodate changes from anionic to cationic in the range  $0-3 \cdot 10^{-3}$  M  $\text{Th}(\text{IV})$  (ionic concentration being constant at 0.1 N with  $\text{NH}_4^+$ ) and the rate of the cationic movement remains constant at  $\text{Th}(\text{IV})$  concentrations above 0.01 M. An interpretation of this phenomenon is made difficult by the fact that  $\text{Th}(\text{IV})$  in neutral nitrate is an equilibrium of various hydrolysed and polymerised species. The curve obtained is similar to that of  $\text{CrO}_4^{2-}$  which also forms a cationic species with  $\text{Th}(\text{IV})$  and  $\text{Zr}(\text{IV})$ .

## DISCUSSION

This work was carried out primarily to investigate some of the parameters of paper electrophoresis using ion pairing as the main differentiating factor, and the

effects of the variables have been described above. The cationic behaviour of iodate in  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Th}(\text{NO}_3)_4$  and  $\text{ZrOCl}_2$  was unexpected and requires some comment.

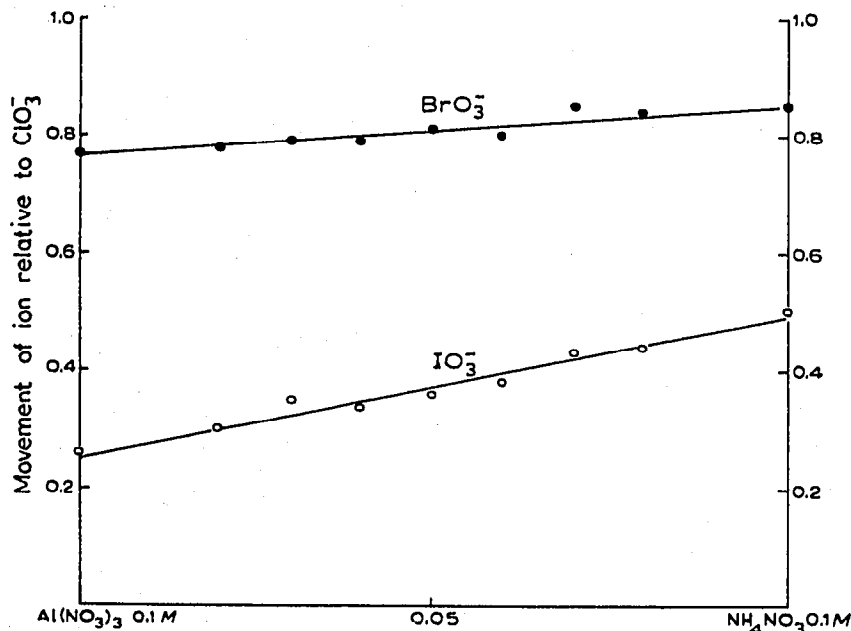


Fig. 1. Movement of  $\text{BrO}_3^-$  (●—●) and of  $\text{IO}_3^-$  (○—○) relative to the movement of  $\text{ClO}_3^-$  (plotted against the concentration of  $\text{Al}(\text{NO}_3)_3$  in  $\text{NH}_4\text{NO}_3$  as electrolyte (total concentration = 0.1 M).

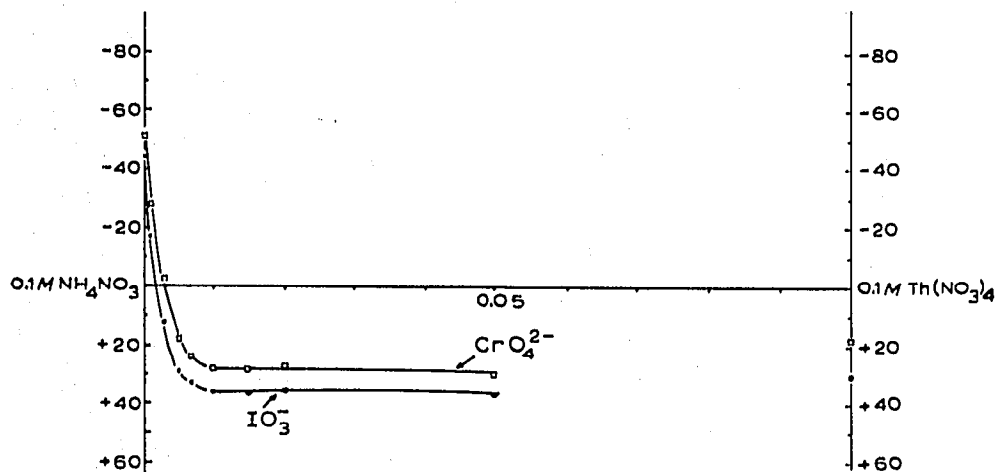


Fig. 2. Movement of iodate and chromate plotted against the  $\text{Th}(\text{NO}_3)_4$  concentration in  $\text{NH}_4\text{NO}_3$  (total concentration = 0.1 M). Potential, 1000 V; time, 30 min; paper, Whatman No. 1; temperature, 7–8°.

The whole group of  $\text{XO}_3^-$  halates is much less hydrated than the halides; however, the ionic weight of  $\text{ClO}_3^-$  is less than half that of  $\text{IO}_3^-$  and it is presumably much more hydrated for that reason.  $\text{IO}_3^-$  seems sufficiently large to be so little hydrated as to form very stable complexes or ion pairs. This picture, however, does not explain why the bromate ion behaves much like chlorate and is not intermediate between iodate and chlorate. We cannot offer an explanation for this at present. In this work,

we have also obtained data which may be of theoretical interest. The behaviour of a single electrolyte can be studied with great precision by means of conductivity measurements. The influence of an electrolyte (0.1–1.0 *M* range) on the solution chemistry of another ion in low concentrations obviously cannot be studied by conductivity measurements. Phase equilibrium methods such as ion-exchange equilibria give results which reflect equally the state of the ion in both phases. Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, for example, are adsorbed on anion-exchange resins to different degrees, but exhibit almost identical mobilities in paper electrophoresis as well as in conductivity measurements. Thus little information can be derived from ion-exchange or solvent-extraction studies.

Solubility measurements are relevant only in the region of saturated solutions but cannot indicate how an ion will behave when it is present at a dilution far below saturation. This is illustrated in this paper by the lack of difference between the mobilities of halate ions in 0.1 *N* calcium, strontium and barium nitrates.

A knowledge of the behaviour of dilute solutions of ions in another electrolyte may be interesting in a number of practical problems (such as sea water chemistry or the biochemistry of biological fluids) and we hope that the results presented here may give some useful indications in these fields.

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