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The chromatography and electrophoresis of the perbromate ion

The existence of the perbromate ion and of perbromic acid was discovered only recently by APPELMAN¹. The first gram quantities of KBrO_4 were synthesised somewhat later by the same author² by oxidising KBrO_3 with F_2 .

We were interested in studying the chromatographic and electrophoretic behaviour of this new inorganic ion and the first results obtained are reported here.

The material used in this work was 100 mg of KBrO_4 kindly given to us by Dr. APPELMAN and the Argonne National Laboratory. It contained a small amount of KBrO_3 as impurity and all work carried out was done with a saturated solution prepared by placing about 5 mg of KBrO_4 in a glass-stoppered 1-ml weighing bottle and adding several drops of distilled water which, however, did not suffice to dissolve all the crystals present.

Spot tests on paper

Perbromate gives a bright red spot on a blue background when the paper chromatogram is dipped into an aqueous solution of methylene blue. Perchlorate gives the same reaction, while periodate does not react.

Perbromate yields a spot of free iodine (dark brown) when sprayed or dipped into a solution of KI in 1 *N* to 10 *N* HCl. It reacts rather slowly on ion-exchange papers developed with nitrates while the same reaction with BrO_3^- , IO_3^- and IO_4^- is instantaneous. On the same chromatograms, the perbromate spot first reacts at certain points giving a speckled appearance for some minutes.

Perchlorate does not react with the KI-HCl reagent. Chlorate does not react unless the HCl concentration is above 5 *N*.

Paper partition chromatography

With ethanol-water-conc. ammonia (60:20:10) run overnight for 30 cm, perbromate yields a round, well-defined spot, but connected with a comet to an equally strong bromate spot. As the bromate spot is much weaker in other systems, we think that some reduction takes place during development.

In butanol-1.5 *N* NH_4OH , the reduction is still more pronounced, yielding only a long, ill-defined tail starting from the region of the bromate spot.

Somewhat better results were obtained with the solvent butanol-pyridine-1 *N* ammonia (60:30:60). Here perbromate gives a definite spot and a less intense tail to the bromate spot. The solvent cannot be recommended for analytical work, but permits accurate R_F values to be measured for comparison with the other halates. These R_F values are reported in Table I and show that BrO_4^- usually has a high R_F value and, depending on the solvent, may move ahead or behind the ClO_4^- spot.

Partition thin-layer systems

As reduction was assumed to be responsible for the tail formation on paper partition chromatograms, we tried one of the paper chromatography solvents on a range of ready thin layers with development for about 1-2 h in a large tank saturated with the vapours of the solvent, as shown in Table II.

While a cellulose thin layer gave a slight comet, separations of BrO_4^- and BrO_3^- without any visible reduction comet could be effected on a whole range of silica gel thin-layer media. In some we only examined perbromate and bromate, since only samples of the thin layers were available and our interest lay more in the presence or absence of a reduction comet than in the comparison of the various halates (which was done more accurately on paper chromatograms).

Ion-exchange paper chromatography

The R_F values of halides, halates and perhalates on SB-2 strong anion-exchange

TABLE I

R_F VALUES OF PERBROMATE AND OTHER PERHALATES AND HALATES IN PAPER PARTITION CHROMATOGRAPHY

Paper: Whatman No. 1. Eluents: 1 = ethanol-water-conc. ammonia (60:20:10); 2 = butanol-pyridine-1 N ammonia (60:30:60).

Ion	Eluent	
	1	2
BrO_4^-	0.76 (comet to 0.61)	0.71 (comet down to 0.23)
BrO_3^-	0.61	0.23
ClO_4^-	0.80-0.85	0.60-0.64
ClO_3^-	0.70	0.44
IO_4^-	0.0 (forward tail to 0.26)	0.0 (forward tail to 0.08)
IO_3^-	0.26	0.08

TABLE II

THIN-LAYER PARTITION CHROMATOGRAMS OF PERBROMATE AND HALATES

Eluent: butanol-pyridine-1 N ammonia (60:30:60). Thin layer: I = Carlo Erba ready cellulose thin layer (on aluminium foil) (developed 88 mm in 2 h); II = Carlo Erba ready silica gel thin layer (on aluminium foil) (developed 112 mm in 2 h); III = Baker Flex silica gel IB-F; IV = Gelman glass fibre paper sheets impregnated with silica gel.

Thin layer	Ion	R_F value
I	BrO_4^-	0.67 (only slight comet)
	BrO_3^-	0.27
	IO_4^-	0.10
	IO_3^-	0.07
II	BrO_4^-	0.63 (slight spot of BrO_3^- but no comet)
	BrO_3^-	0.21
	IO_4^-	0.105 (with slight spot at 0.0)
	IO_3^-	0.07
III	BrO_4^-	0.73 (with slight forward tail and slight bromate spot but no reduction comet)
	BrO_3^-	0.26
IV	BrO_4^-	0.90 (slight bromate spot but no comet)
	BrO_3^-	0.52 (rather flat spot which seems to move on a demixion front)

resin paper (nitrate form) and developed with aqueous sodium nitrate are shown in Fig. 1 and Table III.

On SB-2 paper, development of 10–15 cm takes about 20 min and under these conditions no reduction tail was observed for perbromate. Both perbromate and bromate travel just behind the liquid front when developed with 1 N NaNO₃ on Whatman No. 1 paper, *i.e.* there is negligible adsorption on cellulose.

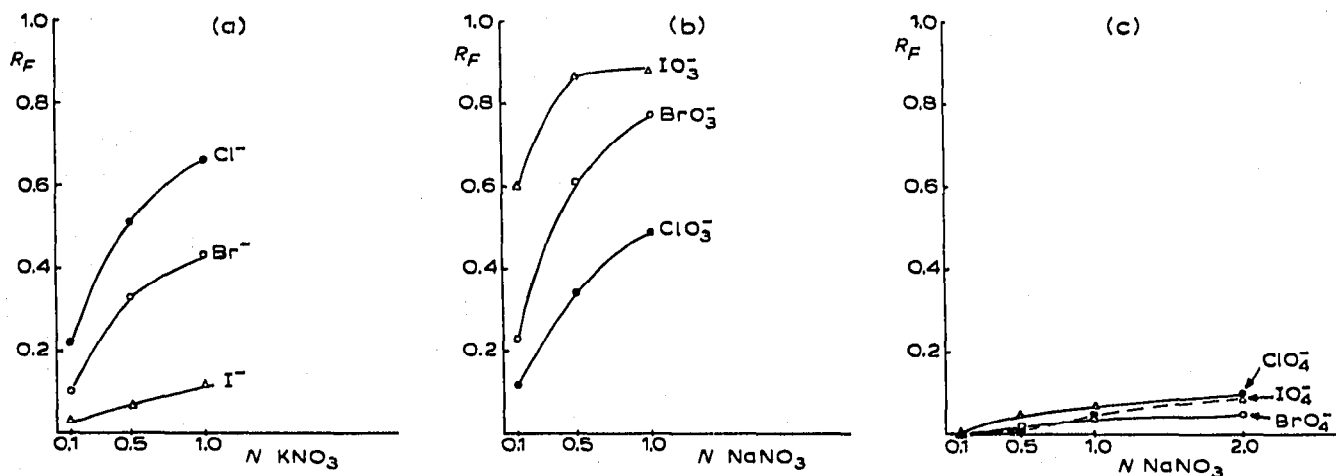


Fig. 1. R_F values of (a) halides, (b) halates and (c) perhalates plotted against the NaNO_3 concentration (KNO_3 in (a)) on the strongly basic anion-exchange resin paper SB-2 (in the nitrate form).

TABLE III

R_F VALUES OF HALIDES, HALATES AND PERHALATES ON SB-2 PAPER (NITRATE FORM)

Eluent: sodium nitrate.

Ion	Normality			
	0.1	0.5	1.0	2.0
BrO_4^-	0.0	0.02	0.04	0.05
BrO_3^-	0.23	0.61	0.77	
ClO_4^-	0.0	0.01	0.05	0.10
ClO_3^-	0.12	0.34	0.49	
IO_4^-	0.0	0.05	0.07	0.09
IO_3^-	0.60	0.87	0.88	

TABLE IV

R_F VALUES OF THE PERHALATES ON MN STRONGLY BASIC ION-EXCHANGE CELLULOSE PAPER

Eluent: sodium nitrate.

Ion	Normality	
	0.05	0.1
ClO_4^-	0.34	0.45
BrO_4^-	0.28 (with a faint spot at 0.42)	0.39 (with a faint spot at 0.56)
IO_4^-	0.36	0.52

TABLE V

PAPER ELECTROPHORESIS OF PERHALATES AND HALATES

Potential, 1000 V; time, 30 min; temperature, 7-8°; paper, Whatman No. 1.

Salt	Concentration	Electrophoretic movement						Movement relative to ClO_4^-					
		ClO_4^-	ClO_3^-	BrO_4^-	BrO_3^-	IO_4^-	IO_3^-	ClO_3^-	BrO_4^-	BrO_3^-	IO_4^-	IO_3^-	
NaOH	0.1 M	-73	-75	-68 T	-64	0	-38	1.03	0.93	0.88	0	0.52	
$(\text{NH}_4)_2\text{CO}_3$	2%	-66	-75	-67	-61	$\begin{cases} -36 \\ -2 \end{cases}$	-36	1.14	1.01	0.92	1.39	0.54	
NH_4NO_3	0.1 M	-77	-77	-66 T	-65	-38	-36	1.0	0.86	0.84	0.49	0.47	
NH_4NO_3	0.5 M	-83	-86	-77	-72	-46	-45	1.04	0.93	0.87	0.55	0.54	
$\text{Mg}(\text{NO}_3)_2$	0.1 M	-82	-79	-71 T	-62	-34	-34	0.96	0.87	0.76	0.41	0.41	
$\text{Al}(\text{NO}_3)_3$	0.1 M	-72	-70	-66 T	-51	-17 T	-17	0.97	0.92	0.71	0.24	0.24	
ZrOCl_2	0.1 M	-66	-58	-62	-31	$\begin{cases} +35 \\ 0 \\ +13 \end{cases}$	+30	0.88	0.94	0.47	—	—	
$\text{Th}(\text{NO}_3)_4$	0.1 M	-73	-68	-66	-47	+29-0	+31	0.93	0.90	0.65	—	—	

From Fig. 1, it is obvious that perbromate behaves in a manner very similar to perchlorate and periodate. However, it is difficult to establish the sequence of the three perhalates in a region where R_F values cannot be measured with good accuracy. The results obtained indicate that perbromate is somewhat more adsorbed than both perchlorate and periodate.

To obtain comparative data on another anion-exchange paper, we examined the movement of the perhalates on MN strongly basic cellulose ion-exchange paper (cellulose with quaternary ammonium groups) which yielded again the sequence periodate > perchlorate > perbromate as shown in Table IV.

Paper electrophoresis

The movement of halates and perhalates in a number of electrolytes is shown in Table V.

It is rather striking that the halate-perhalate pairs have almost the same mobility in all electrolytes except those where ion-pairing is very strong. These results suggest that the ionic mobility of perbromate should be of the order of 50 (at 18°). They also show that paper electrophoresis offers excellent separations of perbromate from all halates and other perhalates, except from ClO_3^- , in thorium nitrate as well as in zirconyl chloride.

Discussion

The chromatographic properties of the perbromate ion may thus be summarised as follows.

(1) In partition systems, perbromate moves with high R_F values in solvents such as ethanol- NH_4OH or butanol-pyridine-ammonia. On paper, it is reduced during the run, but on silica gel thin layers it seems to move without decomposition. A sequence for the perhalate ions is difficult to establish because periodate moves little (this may be partly due to complex formation with the cellulose) and for two solvents examined the sequence ClO_4^- - BrO_4^- is not the same.

(2) In ion-exchange resin paper chromatography, perbromate is strongly adsorbed and moves with R_F values very similar to those for ClO_4^- and IO_4^- . The sequence of movement indicated by small R_F differences is $\text{IO}_4^- > \text{ClO}_4^- > \text{BrO}_4^-$.

(3) In paper electrophoresis, the pairs IO_3^- - IO_4^- , BrO_3^- - BrO_4^- and ClO_3^- - ClO_4^- are not separated unless the cation of the electrolyte favours ion-pair formation (e.g. Th(IV) or Zr(IV)).

Separations of BrO_3^- and BrO_4^- are readily obtained with both partition and ion-exchange systems. Separations of ClO_4^- - BrO_4^- - IO_4^- are better in paper electrophoresis. The separation and identification of BrO_4^- in the presence of all other halides halates and perhalates is possible by employing several systems.

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