

PAPER-ELECTROPHORETIC STUDIES OF THE
SOLUTION CHEMISTRY OF
RaD (^{210}Pb), RaE (^{210}Bi) AND RaF (^{210}Po)
II. IN NITRIC ACID AND PERCHLORIC ACID

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In a recent communication¹ we described the behaviour of RaD, RaE and RaF on paper electrophoresis in hydrochloric acid. The present paper concerns the study by the same technique of the separability and of the nature of the ionic species of these radio-elements in acids with which complexes are less likely to be formed, namely nitric and perchloric acids.

EXPERIMENTAL

The general experimental procedure and the apparatus used in this study remain the same as those described in Part I. For experiments with nitric acid, the solution of RaD, RaE, and RaF (in radioactive equilibrium) in N HNO_3 was applied on the paper while the solution of these elements in N HClO_4 formed the test solution when perchloric acid was used as electrolyte. Electrophoresis was carried out on Arches 302 paper strips (2.7×40 cm) sandwiched between two glass plates (8×30 cm) by applying a potential difference of 300 V D.C. for 45 min. The position of the elements on the electropherogram was located using the Frieseke-Hoepfner FH 452 automatic scanner by the method already described.

RESULTS AND DISCUSSION

(1) *In nitric acid*

In Table I, we present the electrophoretic displacement on paper of RaD, RaE and RaF in nitric acid in the concentration range 0.0005 N to 3.6 N . Fig. 2 shows some of the typical electropherograms obtained when the concentration of nitric acid was varied. As the NO_3^- ion has little tendency to complex formation, the hydrolysis of the ions in low concentrations of this acid is very marked. The three elements in question, being variously charged, undergo hydrolysis to different extent; RaD with two positive charges is less hydrolysed, the great tendency of RaE to give a number of complex hydrolysis products in dilute nitric acid is well known², while RaF with four positive charges has the greatest tendency to complex formation and consequently also to hydrolysis³. In very dilute nitric acid, e.g. 0.0005 N , all three elements are hydrolysed and lie as a single band at the point of application (Fig. 1, a).

TABLE I
ELECTROPHORETIC DISPLACEMENT (300 V, 45 min) OF RaD, RaE AND RaF IN NITRIC ACID MEDIUM

Normality of the acid	Displacement (mm)		
	RaD	RaE	RaF
0.0005	The three elements lie in a single band (from +4.8 to -12.0, maximum at 0).		
0.001	RaD and RaE lie in a single band (from +3.0 to -24.0, maximum at -4.8).		0
0.01	RaD and RaE lie in a single band (from +2.4 to -24.6, maximum at -14.4).		0
0.025	RaD and RaE lie in a single band (from +3.0 to -24.0, maximum at -10.2).		0
0.05	RaD and RaE lie in a single band (from +3.0 to -24.0, maximum at -12.6).		- 1.8
0.1	RaE still trails from +1.8 while some of RaD begins to move faster. The two elements thus give a large diffused band from +1.8 to -72.0 with a maximum at -24.0.		- 2.4
0.2	-43.2 (trailing from -13.2 to -72.0)	-15.3 (trailing from 0 to -24.0)	- 2.4
0.25	-58.8	-31.2 (trailing from - 7.8 to -39.0)	- 4.8
0.3	-60.0	-33.0 (trailing from - 6.0 to -39.0)	- 7.2
0.35	-65.1	-36.6 (trailing from -15.0 to -45.0)	- 7.8
0.4	-72.6	-51.6 (trailing from -30.0 to -54.0)	-14.0
0.45	-77.4	-52.8 (trailing from -30.0 to -60.0)	-16.2
0.5	-76.2	-56.4 (trailing from -39.0 to -63.6)	-22.8
0.6	-68.7	-52.2 (trailing from -36.0 to -58.8)	-21.9

(continued on p. 457)

TABLE I (continued)

Normality of the acid	Displacement (mm)		
	RaD	RaE	RaF
0.75	— 71.0	— 56.4	— 25.2
0.8	— 65.4	— 52.8	— 24.0
0.9	— 58.2	— 46.8	— 20.7
1.0	— 50.4	— 39.9	— 15.6
1.2	— 49.2	— 42.2	— 19.2
1.4	— 44.4	— 38.4	— 17.4
1.6	— 39.5	— 31.2	— 13.8
1.8	— 36.0	— 33.0	— 16.8
1.9	— 34.8	— 34.8	— 14.4
2.0	— 33.0	— 33.0	— 13.8
2.25	— 24.0	— 24.0	— 8.7
2.5	— 22.8	— 22.8	— 7.5
3.0	— 15.0	— 15.0	— 4.2
3.25	— 13.8	— 13.8	— 3.2
3.5	— 18.0	— 18.0	— 3.3
3.6	— 2.7	— 2.7	— 2.7

In 0.001 *N* HNO₃, there is already a visible tendency for RaD to move cationically. As the concentration of the acid in the electrolyte is increased, the hydrolytic effect on the ions becomes less and less and they begin to move faster. The sequence of

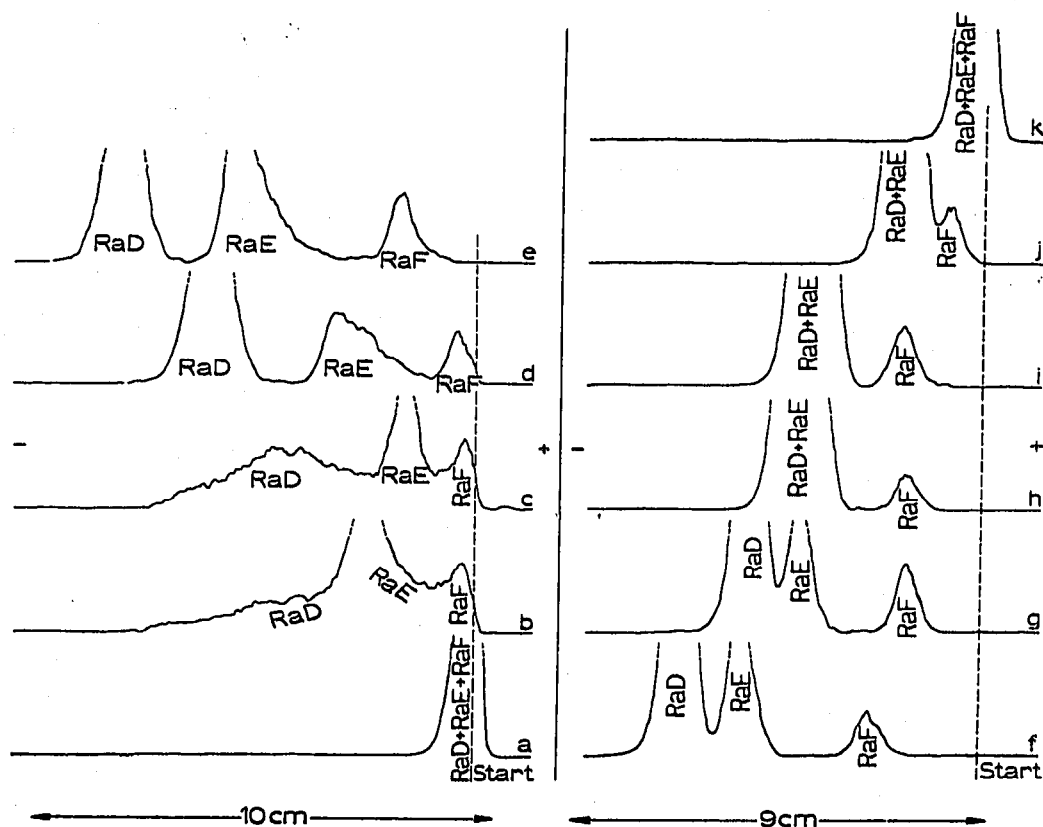


Fig. 1. Electropherograms (300 V, 45 min) of RaD, RaE and RaF in nitric acid as electrolyte. (a) 0.0005 *N*; (b) 0.1 *N*; (c) 0.2 *N*; (d) 0.25 *N*; (e) 0.45 *N*; (f) 0.8 *N*; (g) 1.0 *N*; (h) 1.5 *N*; (i) 1.8 *N*; (j) 2.5 *N*; (k) 3.6 *N*.

their migration rate is $RaD > RaE > RaF$. Although the difference in the migration rate of the three ions is already noticeable on the electropherogram in the electrolyte $0.1 N HNO_3$ (Fig. 1, b), RaE moves as a wide diffused band which overlaps with RaF at its anionic end, and with RaD at the cationic one. It is only from $0.25 N HNO_3$ (Fig. 1, d) that the separation of the three elements is rendered possible where the RaE band still trails to touch the cationic extremity of the RaF band but is completely separated from the RaD band. The separation of the three elements is complete in the concentration range 0.35 to $0.6 N$ of nitric acid, $0.45 N HNO_3$ giving the best results (Fig. 1, e). In electrolyte more concentrated than $0.6 N HNO_3$, RaE is not hydrolysed and moves as a rapid compact band whose velocity approaches that of RaD . Overlapping between the extremities of the bands of RaD and RaE is therefore obtained (Fig. 1, f, g). Separation of the still slower RaF from the two other elements becomes more and more easy and distinct under these conditions. In $1.5 N HNO_3$ the electrophoretic bands of RaD and RaE are almost superimposed (Fig. 1, h). No distinction between the RaD and RaE bands is possible in concentrations higher than $1.8 N HNO_3$, but the separation of polonium is still feasible (Fig. 1, i). On the electropherograms in electrolytes of concentrations higher than $2.5 N HNO_3$ the migration rate of RaD and RaE approaches that of RaF (Fig. 1, j), due presumably to complexation with NO_3^- ions at high concentrations of nitric acid so that overlapping between the bands is obtained, but one can still separate most of the RaF from the RaD and RaE by electrophoresis on paper in nitric acid of concentration as high as $3.5 N$. In $3.6 N HNO_3$ (Fig. 1, k), the highest concentration that could be tried, RaD , RaE and RaF lie in a single band at -2.7 mm. Unfortunately, experiments using acid of higher concentrations could not be carried out because the acid attacked the paper. We can only conclude that the concentrations at which the change over from cationic to anionic nature takes place for RaD , RaE and RaF in nitric acid lie beyond $3.6 N HNO_3$. Paper electrophoresis of polonium in nitric acid showed similar behaviour to that shown in mixtures with RaD and RaE .

TABLE II

ELECTROPHORETIC DISPLACEMENT (300 V, 45 min) OF RaD , RaE AND RaF USING DIFFERENT MIXTURES OF NITRIC ACID AND POTASSIUM NITRATE SOLUTION AS ELECTROLYTE

Composition of the electrolyte	Displacement (mm)		
	RaD	RaE	RaF
$1 N HNO_3$	-50.4	-39.6	-16.2
$1 N HNO_3$ 95% + $1 N KNO_3$ 5%	-48.0	-30.6 (trailing from -15.0 to -37.8)	- 5.75
$1 N HNO_3$ 50% + $1 N KNO_3$ 50%	-50.4	-26.4 (trailing from - 3.0 to -33.0)	- 4.5
$1 N HNO_3$ 5% + $1 N KNO_3$ 95%	-41.4	-15.6 (trailing from 0 to -22.0)	- 2.4
$1 N KNO_3$	-29.1	- 0.9	- 0.9

(2) *In mixtures of nitric acid and potassium nitrate solution*

Table II summarises the electrophoretic migration on paper of RaD, RaE and RaF in different electrolytes where the concentration of NO_3^- is kept constant at 1 *N* but the pH of the solution is varied by replacing progressively the nitric acid by potassium nitrate. Even 5% KNO_3 in the electrolyte in place of nitric acid produces a considerable change in the electrophoretic mobility of the highly charged ions RaE and RaF, while the mobility of the relatively less charged RaD undergoes little change (Fig. 2, a, b). The sharp electrophoretic band of RaE in *N* HNO_3 is replaced by a band which trails, while the migration of RaF is reduced from -16.2 mm to -5.75 mm; thus RaF seems to be more sensitive to changes of pH than RaE. This effect is more and more pronounced as the proportion of potassium nitrate in the electrolyte is increased (Fig. 2 c, d). In *N* KNO_3 , RaE and RaF are completely hydrolysed and remain in a single band at the point of application while RaD still preserves its cationic nature (Fig. 2 e). Similar migration is observed for polonium when it is subjected to electrophoresis alone in the above media.

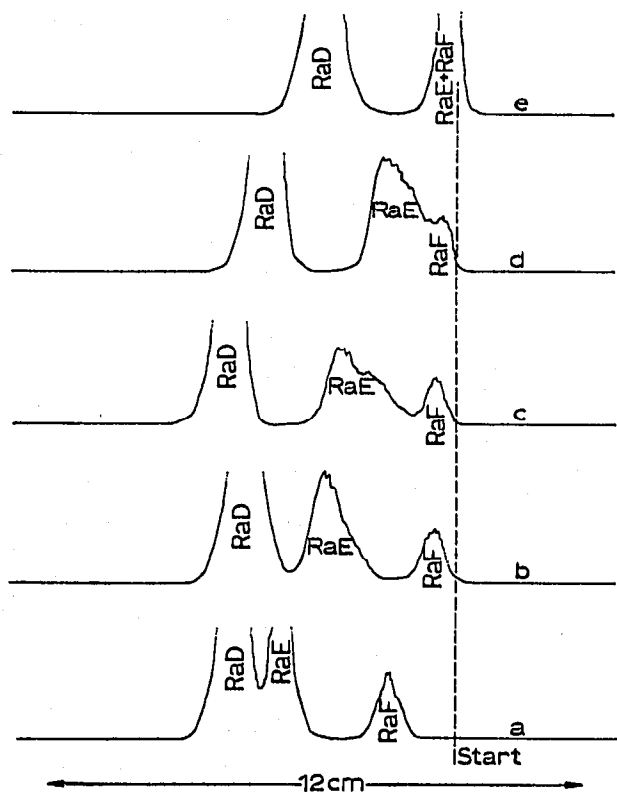


Fig. 2. Electropherograms (300 V, 45 min) of RaD, RaE and RaF in the electrolytes (a) *N* HNO_3 ; (b) *N* KNO_3 (5%) + *N* HNO_3 (95%); (c) *N* KNO_3 (50%) + *N* HNO_3 (50%); (d) *N* KNO_3 (95%) + *N* HNO_3 (5%); (e) *N* KNO_3 .

(3) *In perchloric acid*

Perchloric acid, being a very strong acid, attacks the paper even at a concentration of 1.0 *N*. Studies in this medium could therefore be made only in the concentration range 0.01 *N* to 1.0 *N*. Fig. 3 shows the typical electropherograms obtained. The elements are easily hydrolysed in perchloric acid; thus in 0.1 *N* HClO_4 even bivalent RaD is hydrolysed and gives a diffused cationic band while RaE and RaF undergo complete hydrolysis and lie in a single band at the point of application. It is only in concentrations higher than 0.25 *N* that RaD moves as a compact cationic band while

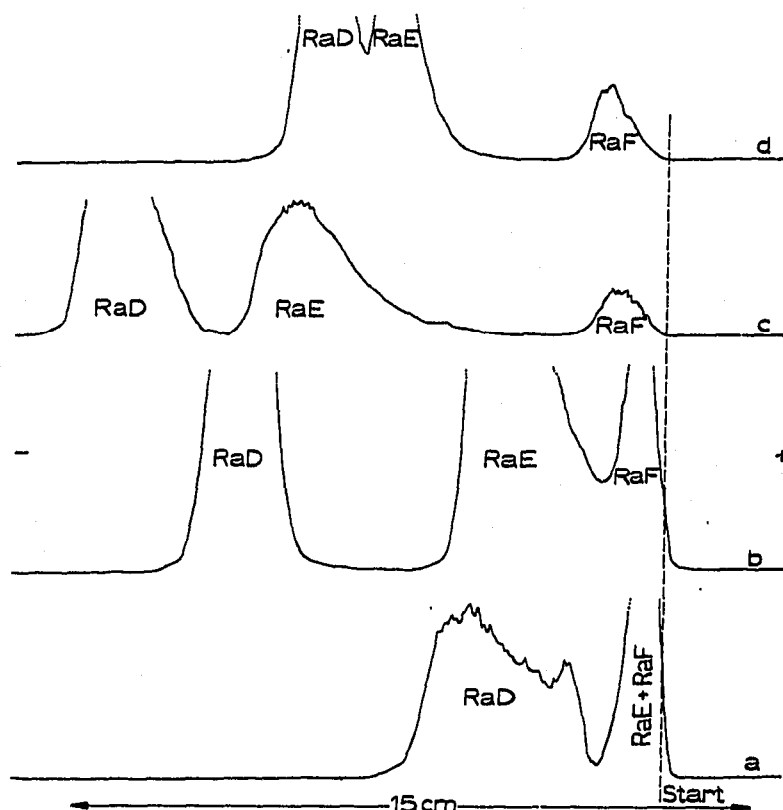


Fig. 3. Electropherograms (300 V, 45 min) of RaD, RaE and RaF in perchloric acid as electrolyte. (a) 0.1 *N*; (b) 0.25 *N*; (c) 0.6 *N*; (d) 1.0 *N*.

RaE, which is completely separated from RaD at this concentration, still trails in perchloric acid of concentrations as high as 0.85 *N*. One can, however, obtain the separation of RaD, RaE and RaF in concentrations of 0.25 *N* to 0.75 *N* HClO₄. With increase in the concentration of the acid, the distance between the RaE and RaF bands increases while RaD and RaE are less and less widely separated. Thus, in 1 *N* HClO₄ the bands of RaD and RaE overlap while the separation of RaF from the other two elements is very distinct. Trailing in the band of RaF is observed even in 1.0 *N* HClO₄ showing that even at this concentration this element is hydrolysed. Similar behaviour in paper electrophoresis for polonium alone applied to the paper was observed in this acid. This is presumably due to the high charge of the ion.

SUMMARY

An attempt has been made to define the concentration range of nitric and perchloric acids which give separations of RaD, RaE and RaF in electrophoresis on paper. The effect on the ionic nature of these elements of varying the concentration of these acids and also of the progressive replacement of nitric acid by potassium nitrate, keeping the NO₃⁻ ion concentration constant, has been examined.

REFERENCES

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