

## HIGH- AND LOW-VOLTAGE PAPER ELECTROPHORETIC INVESTIGATION OF THE SOLUTION CHEMISTRY OF MERCURIC IONS IN NITRIC ACID

S. K. SHUKLA AND J. P. ADLOFF

*Centre de Recherches Nucléaires, Département de Chimie Nucléaire, Strasbourg (France)\**

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A knowledge of the nature of the ionic species of an element present in aqueous solution which affects many of the physical and chemical properties of the solution<sup>1</sup> is of considerable interest in determining the method to be employed for the separation of the element in question and its quantitative isolation, as well as in the interpretation of the reactions or processes which take place in such a medium. Recently anion exchange chromatography<sup>2-4</sup> and solvent extraction<sup>5</sup> techniques have been employed as tools for investigating the state of combination of different elements in aqueous solution. For metal ions which have strong affinity for the ligands present in the aqueous system, thus forming stable complex species, the indications given by adsorption studies on anion exchangers may be reliable. But, as has already been pointed out by WAKI<sup>4</sup>, "it is often observed that a metallic element may be significantly adsorbed on an anion exchange resin even from a solution in which the presence of any complex anion seems hardly to be considered". It is believed that the resin is an extremely concentrated solution of electrolytes<sup>5</sup> with low effective dielectric constants<sup>6</sup> and where the water has less effect<sup>7</sup> may bind to itself the cations or complex ions of low stability by converting them into anionic species. Similar reasoning can be extended to the solvent extraction systems using long-chain aliphatic amines, where the electrolyte is concentrated into the organic phase of very low dielectric constant; the amines are there as binders for the anionic species and thus serve as stabilizers of the complex anions.

The advantage of paper electrophoresis as an easy and valuable tool for the study of the nature of the ionic species present in a solution, as well as in the isolation of pure species for the study of their other properties, has recently been recognized<sup>8-10</sup> and the technique has already been applied to the study of the solution chemistry of many elements.

Mercuric nitrate, like the sulphate and perchlorate, is known to be ionized and highly dissociated in solution<sup>11</sup>. Furthermore, the nitrate ion, next to the perchlorate ion, is a ligand which is very reluctant to form covalent bonds with an element. Recently, however, the existence of  $[\text{Hg}(\text{NO}_3)_3]^-$  and  $[\text{Hg}(\text{NO}_3)_4]^{2-}$  in solution has been concluded from adsorption studies<sup>4</sup>. If the existence of such anionic species of mercury in 0.2 N  $\text{HNO}_3$ , as reported by CHOI AND TUCK<sup>5</sup>, is accepted, then the exchange between  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  should be slow<sup>12</sup>, while the contrary has been reported<sup>13</sup>. We therefore thought it of interest to investigate the nature of the ionic

\* Full address: Centre de Recherches Nucléaires, Département de Chimie Nucléaire, rue du Loess, Strasbourg-Cronenbourg, France.

species furnished by  $\text{Hg}^{2+}$  in nitric acid solutions by paper electrophoresis, which permits a direct examination of the species without introduction of undesirable foreign substances in the system under study.

#### EXPERIMENTAL

The mercuric nitrate solution, tagged with  $^{203}\text{Hg}$  (half-life = 47 days and specific activity 128.5 mC/g), used in these studies was supplied by C.E.A., Saclay. This solution was evaporated several times with nitric acid and finally redissolved in nitric acid of the desired strength. The solution was diluted so as to have suitable activity for paper electrophoretic studies. The concentration of nitric acid in the solution to be tested and that in the electrolyte was always kept the same. Studies were made in the concentration range 0.2–8 *N*  $\text{HNO}_3$ . In order to see how the mercuric species in relatively concentrated nitric acid behaves when placed in nitric acid of lower concentration, the solution of  $^{203}\text{Hg}$  in 8 *N*  $\text{HNO}_3$  was examined by electrophoresis in electrolytes of varying concentrations.

The solution was examined both by high- and low-voltage electrophoresis. The glass-plate (30 × 8 cm) technique described by LEDERER AND WARD<sup>14</sup> was employed for low-voltage electrophoresis. High-voltage electrophoresis was carried out with a locally made high-voltage electrophoresis apparatus described by GROSS<sup>15</sup>. Arches No. 302 paper strips (2.7 cm wide of suitable length, 30 cm long for low-voltage and 44 cm long for high-voltage electrophoresis) were used. Electrophoretic migrations were also observed in each case on glass paper (Whatman No. GF/C) strips.

The position of the  $^{203}\text{Hg}$ (II) species on the electropherogram was located by scanning with the Frieske Hoepfner FH 452 automatic chromatogram scanner, using a 3 mm wide slit.

#### RESULTS AND DISCUSSION

The sequence of displacement of the mercuric species in different concentrations of nitric acid was the same under high- and low-voltage electrophoresis as well as on the electropherograms on glass paper and Arches 302. Because of the better displacements, only those results that are obtained with high-voltage electrophoresis using Arches 302 paper strips are shown in Figs. 1 and 2 as typical. It is seen that the mercuric ion has a greater cationic speed in the concentration range 0.2–4 *N*  $\text{HNO}_3$ , while the displacement in the electrolyte at higher concentrations becomes relatively smaller. We conclude, therefore, that in the concentration range 0.2–4 *N*  $\text{HNO}_3$ ,  $\text{Hg}^{2+}$  exists as an aquocomplex  $[\text{Hg}(\text{H}_2\text{O})_4]^{2+}$ , which combines with  $\text{NO}_3^-$  in higher concentrations of nitric acid to give  $[\text{Hg}(\text{H}_2\text{O})_3(\text{NO}_3)]^+$ , a complex with a lower net positive charge. The presence of the neutral complex  $[\text{Hg}(\text{H}_2\text{O})_2(\text{NO}_3)_2]^0$  was not revealed by electrophoresis in the concentration range of nitric acid studied and may be due to its low stability constant<sup>16</sup>. It may exist in nitric acid of higher concentration. However, in disagreement with the results of anion exchange and solvent extraction studies, electrophoretic results did not show the presence of an anionic species formed by  $\text{Hg}^{2+}$  with  $\text{NO}_3^-$ , which has been reported to be very marked in dilute nitric acid<sup>4,5</sup>. It is considered, therefore, that the adsorption of  $\text{Hg}^{2+}$  on the anion exchanger and its extraction in methyldioctylamine solution in chloroform

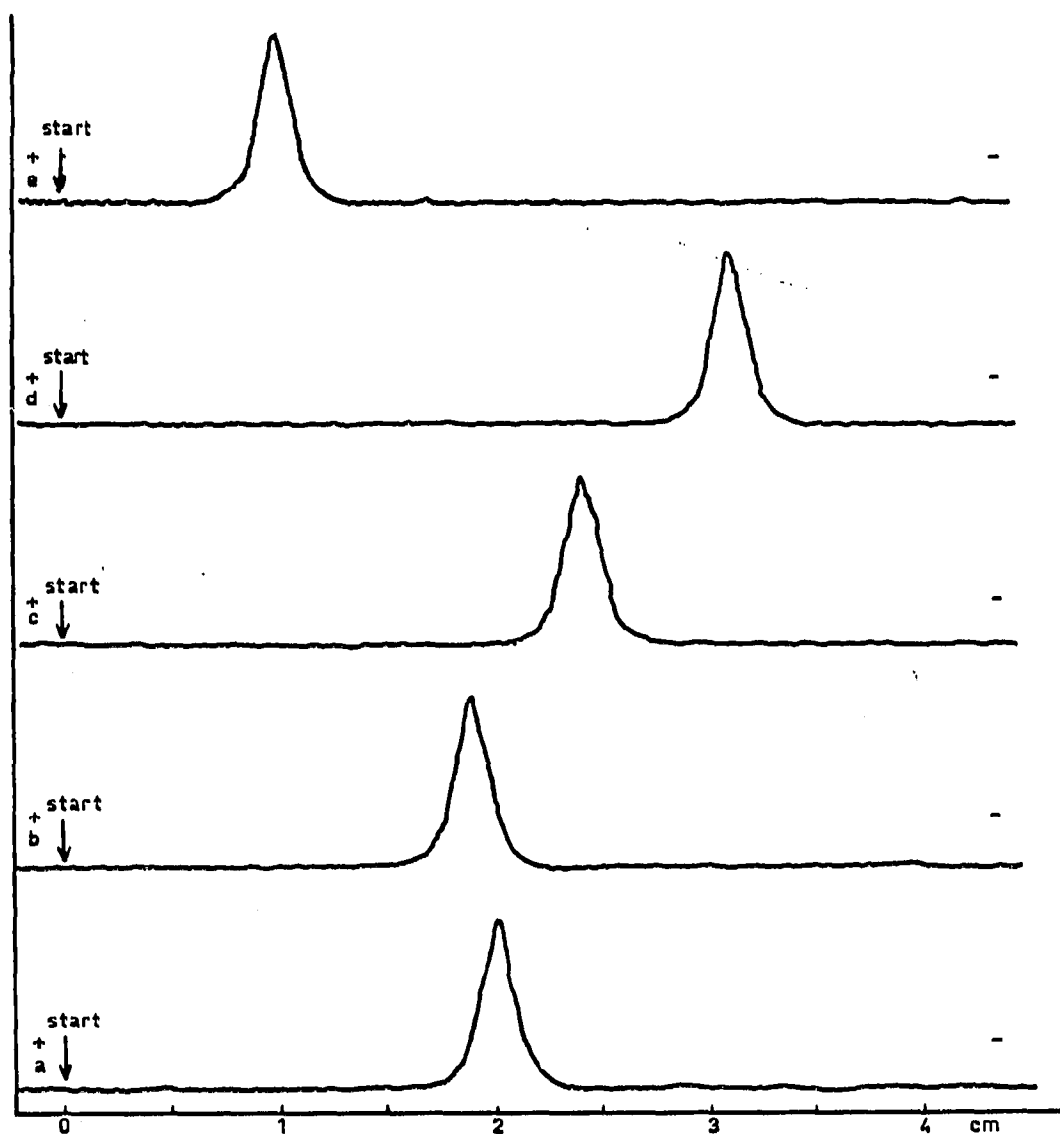


Fig. 1. High-voltage electropherograms of  $^{203}\text{Hg}(\text{NO}_3)_2$  solutions on Arches 302 paper ( $44 \times 2.7$  cm). Conditions: (a) Electrolyte =  $0.2 \text{ N HNO}_3$ ; 2500 V, 100 mA, 0.5 h; (b) Electrolyte =  $0.5 \text{ N HNO}_3$ ; 1400 V, 125 mA, 1.0 h; (c) Electrolyte =  $1.0 \text{ N HNO}_3$ ; 650 V, 150 mA, 1.0 h; and (d) Electrolyte =  $2.0 \text{ N HNO}_3$ ; 620 V, 150 mA, 2.0 h.

might have been due to the high concentration of nitric acid in these systems of low dielectric constant and of low water content, favouring the stabilization of an otherwise unstable anionic species of mercuric ion in an aqueous system. The decreased adsorption as well as extraction with increase in the concentration of nitric acid may be accounted for by the saturation of the adsorbing or extracting system by several layers of undissociated nitric acid. This prevents the  $\text{Hg}^{2+}$  from coming in contact with the resin or the amine which contributed to stabilization of the anionic species in a lower concentration of the acid.

The electrophoretic mobility of  $\text{Hg}(\text{II})$  in dilute nitric acid was almost the same as that of  $\text{Hg}(\text{II})$  dissolved in  $8 \text{ N HNO}_3$  electrophorised in the same electrolyte. This indicates the labile nature of the nitratocomplexes formed by  $\text{Hg}(\text{II})$ .

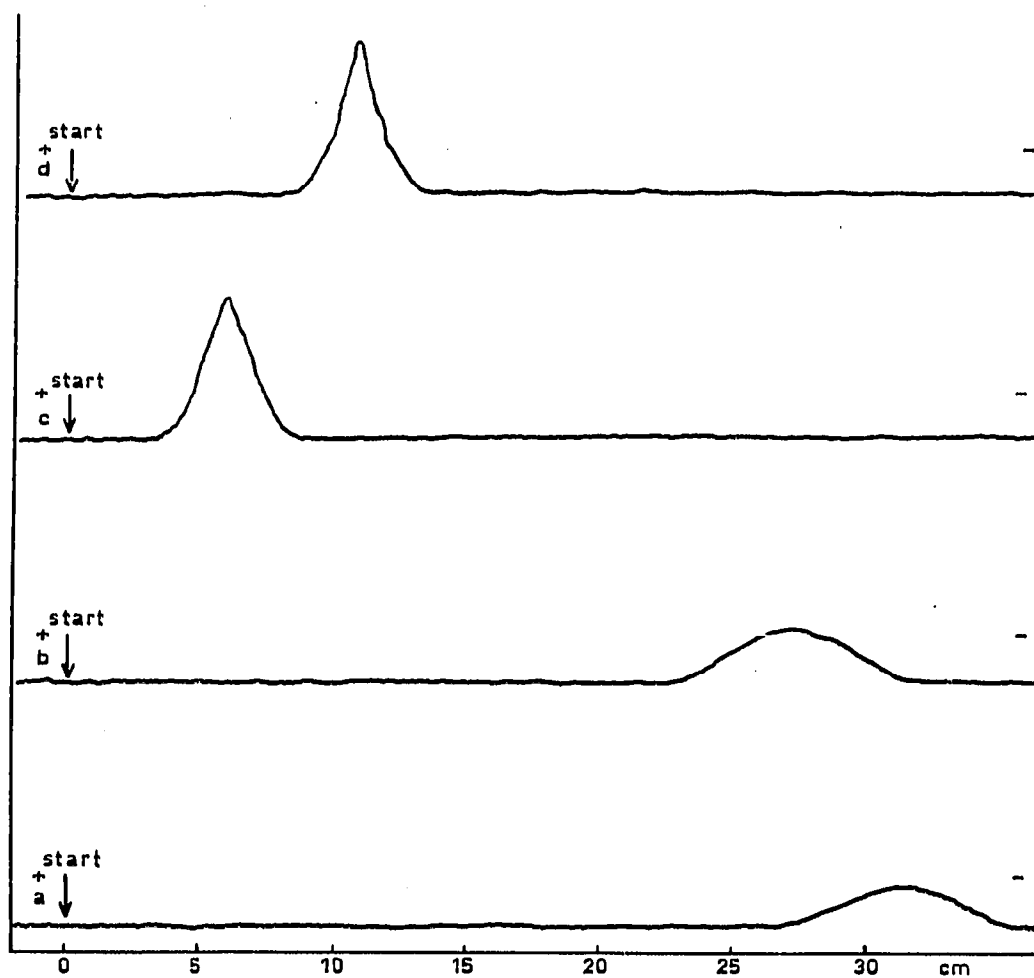


Fig. 2. High-voltage electropherograms of  $^{203}\text{Hg}(\text{NO}_3)_2$  solutions on Arches 302 paper ( $44 \times 2.7$  cm). Conditions: (a) Electrolyte =  $2.5 \text{ N HNO}_3$ ; 580 V, 150 mA, 0.5 h; (b) Electrolyte =  $4 \text{ N HNO}_3$ ; 460 V, 110 mA, 0.5 h; (c) Electrolyte =  $5 \text{ N HNO}_3$ ; 330 V, 140 mA, 2.5 h; (d) Electrolyte =  $6 \text{ N HNO}_3$ ; 340 V, 150 mA, 2.5 h; and (e) Electrolyte =  $8 \text{ N HNO}_3$ ; 130 V, 130 mA, 1.0 h.

#### SUMMARY

The nature of ionic species furnished by  $\text{Hg}^{2+}$  in nitric acid has been examined by paper electrophoresis in the concentration range  $0.2\text{--}8 \text{ N HNO}_3$ . Only cationic species  $[\text{Hg}(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{Hg}(\text{H}_2\text{O})_3(\text{NO}_3)]^+$  were found in the concentration range  $0.2\text{--}4 \text{ N}$  and  $4\text{--}8 \text{ N}$ , respectively. The solvent extraction and anion exchange adsorption results reported in literature have been explained by taking into consideration the properties of the extracting and the adsorbing system.

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