Journal of Chromatography, 77 (1973) 464–466

CHROM. 6509

Note

Cross-electrophoresis on paper of some inorganic systems

The principle of cross-electrophoresis was first demonstrated by GRASSMANN AND HÜBNER[1] and extensive work on protein–protein interactions has been carried out during the last 20 years[2]. We have tried repeatedly to apply it to reversible reactions between two inorganic ions and have not always had great success. It was sometimes observed that when an anion traversed a band of a cation, a coloured zone was formed, but without any transformation of the cation band at the point where the anion traversed it, in spite of the fact that a well known complex had been formed.

This note contains a series of observations on systems in which we have a rather good knowledge of the complexing reactions that take place.

Technique

A simple paper electrophoretic apparatus was used, in which Whatman No. 1 paper strips, 57 × 6 cm, were sandwiched between glass plates 3 mm thick (50 × 7 cm), which were clamped together.

A thin band of the metal ion was applied to the paper strip and a round spot of the anion placed in front of it, as shown schematically in Fig. 1a. Fig. 1b shows a typical positive result after applying a potential of 200 V for 1 h. When the metal ion traverses the anion as a straight unbroken line, we call this a negative result.

Results

Interaction of Fe(III) with various inorganic anions in 0.1 N HCl. A 0.05 *M* solution of Fe^{3+} dissolved in 0.1 *N* HCl was placed as a fine line on a paper strip moistened with 0.1 *N* HCl. Then 0.1 *N* solutions of CNS^-, I^-, Br^-, SO_4^{2-}, NO_3^-, F^- or

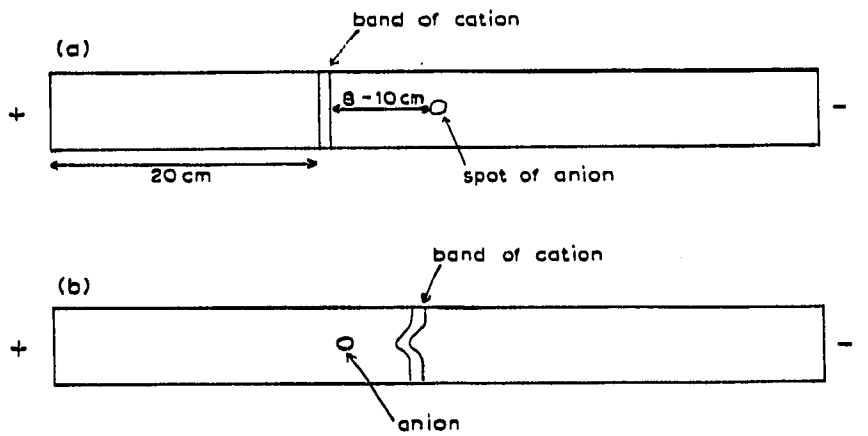

Fig. 1. (a) Schematic picture of the position of the cation band and the anion spot before electrophoresis. (b) Schematic picture of a positive result in cross-electrophoresis.

ClO_4^- were allowed to migrate through it and the band of Fe^{3+} was made visible with ammonium sulphide.

Only with CNS^- and F^- could a disturbance of the Fe^{3+} be observed. Here the strongly bound complexes clearly give a positive result while anions that either do not or poorly complex Fe(III) yield a negative result.

Interaction of $Co(en)_3^{3+}$ with various anions in 0.1 N HCl. A 0.05 *M* solution of $Co(en)_3^{3+}$ was allowed to migrate on paper moistened with 0.1 *N* HCl against spots of 0.1 *N* solutions of CNS^-, I^-, Br^-, SO_4^{2-}, NO_3^-, F^- and ClO_4^-. The complex was made visible by spraying with ammonium sulphide. Positive results were obtained with SO_4^{2-} and ClO_4^-, which both form well known outer-sphere complexes with $Co(en)_3^{3+}$.

Interaction of Cd(II) with inorganic anions on paper moistened with various electrolytes. A 0.05 *M* solution of Cd(II) in the respective electrolyte (0.1 *N*) was allowed to migrate against a range of inorganic anions and the cadmium band detected with ammoniacal oxine in ethanol. The results are shown in Table I.

TABLE I

CROSS-ELECTROPHORESIS OF Cd^{2+} AGAINST VARIOUS ANIONS IN DIFFERENT BACKGROUND ELECTROLYTES

Anion	*Background electrolyte*		
	0.1 N $HClO_4$	*0.1 N H_2SO_4*	*0.1 N HNO_3*
Cl^-	−	−	+
Br^-	−	−	+
I^-	+ (slight)	−	+
F^-	−	−	−
NO_3^-		−	
SO_4^{2-}	−		−
ClO_4^-		−	

Discussion

The few experiments described above clearly illustrate that the only result that cross-electrophoresis can give in inorganic systems is to indicate when the metal ion changes its charge. In the experiments with Fe(III) in 0.1 *N* HCl, it is known that the Fe(III) exists mainly as $FeCl^{2+}$. Thus, when the complexed chloride is substituted by Br^- or I^-, still yielding complexes of the type FeX^{2+}, a negative result will be obtained, whereas when stronger complexing agents such as CNS^- and F^- produce a lower charged complex, a V-shaped notch appears in the Fe(III) band.

The experiments with $Co(en)_3^{3+}$ show clearly that positive results can also be obtained when ion-pair formation (or outer-sphere complexing) reduces the charge of the metal ions, *i.e.*, the method is certainly of no use for detecting complexes.

In the experiments with Cd(II), when $HClO_4$ or H_2SO_4 is used as electrolyte, Cd(II) forms rather strong ion pairs with ClO_4^- or SO_4^{2-}, and hence there is no change in charge with Cl^-, Br^- and only a slight change with I^-. On the other hand, the halides give a strongly positive result in HNO_3, which does not form strong ion pairs with Cd(II).

In conclusion, we would like to point out that cross-electrophoresis has no value in inorganic reactions for indicating complex formation. All that it indicates is a change of charge on the metal ion under the conditions of the experiment.

Laboratorio di Cromatografia del C.N.R.,
Via Romagnosi 18/A, Rome (Italy)

VALERIA MOSINI
M. LEDERER

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Received December 2nd, 1972