THE PAPER ELECTROPHORETIC STUDY OF ION PAIR FORMATION. II*

M. LEDERER AND M. MAZZEI

Laboratorio di Cromatografia del CNR, Istituto di Chimica Generale ed Inorganica, Rome (Italy)

(Received March 21st, 1968)

SUMMARY

Ion pair formation between cobalt(III) complexes and organic anions and between anionic complex cyanides and polyvalent metal ions was studied by paper electrophoresis. It was shown that complexes of the type $[CoA_6]^{3+}$ can move anionically (for example in trichloroacetate) and that complexes of the type $[M(CN)_6]^{2- \text{ or } 3-}$ can move cationically (for example in aluminium or zirconium chloride).

INTRODUCTION

In the first part of this paper[1] we showed that the interaction between Co(III) complexes and anions can be studied by high-voltage electrophoresis and that the mobilities of complexes are considerably influenced by the anions surrounding it even to the extent of producing anionically moving ions pairs (for example $Co(en)_3^{3+}$ in sodium sulphate).

We have now extended this investigation to the study of the movement of Co(III) complexes in several series of anions as well as to movement of complex anions in solutions of numerous metal ions. We feel that we have demonstrated ion pair formation (or outer-sphere complex formation) to an extent which was not thought likely before.

TECHNIQUE

Paper electrophoresis was carried out in a Camag high-voltage electrophoresis apparatus as described before[1] at 15° and using hydrogen peroxide as indicator of electroosmotic flow.

The complexes were dissolved in the electrolyte to be studied and were detected after electrophoresis with ammonium sulphide (Co complexes) or ferric chloride (anionic cyanocomplexes).

The behaviour of $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, $Co(dip)_3^{3+}$ and $Co(o\text{-}phen)_3^{3+}$ in several salts of organic acids

Table I shows the electrophoretic movement of four Co(III) complexes in mono-

---

* Dedicated to Prof. E. LEDERER on his 60th birthday.

TABLE I

ELECTROPHORETIC MOVEMENT OF COBALT COMPLEXES IN SOME ORGANIC ACIDS

Electrolyte		Voltage	Time (min)	Electrophoretic movement (mm)			
				$Co(NH_3)_6^{3+}$	$Co(en)_3^{3+}$	$Co(dip)_3^{3+}$	$Co(o\text{-}phen)_3^{3+}$
Monochloroacetate pH 4.5	0.1 M	1500	30	113	78	67	60
	0.5 M			114	74	65	55
	1.0 M			109	69	62	50
Dichloroacetate pH 4.5	0.1 M	1500	30	78	54	42	36
	0.5 M			89	54	43	30
	1.0 M			87	48	28	15
Trichloroacetate, pH 4.5	0.1 M	1500	30	115	76	54	41
	0.5 M			100	58	24	14
	1.0 M			76	38	0	— 8
Propionate	0.1 M	1500	30	122 T*	86 T	78 T	69 T
	0.5 M			115	77	69	63
	1.0 M			104	75	69	60
Oxalate	0.1 M	1500	30	insoluble	25	54	51
Malonate	0.1 M	1500	30	96	69	72	65
	0.5 M			75	48	58	49
	1.0 M			69	46	51	37
Succinate	0.1 M	1500	30	102	73	73	64

* T = tailing.

chloroacetate, dichloroacetate, trichloroacetate, propionate, oxalate, malonate and succinate.

The results are best visualised in a graph as shown in Fig. 1. From Fig. 1a it is evident that the tendency for ion pair formation increases from acetate to trichloroacetate and from hexammine-Co(III)$^{3+}$ to tris (o-phenanthroline)-Co(III)$^{3+}$ producing actual anionic movement only in the case of tris(o-phenanthroline)-Co(III)$^{3+}$ in 1 N trichloroacetate.

The sequence in divalent anions is radically different from that in monovalent anions. Fig. 1b shows that here especially the $Co(en)_3^{3+}$ ion is most retarded and in some cases also $Co(NH_3)_6^{3+}$. However, this effect is much smaller with malonate and succinate than with sulphate, oxalate and phthalate. It seems that the distance between the two anionic groups is rather important.

Fig. 1c shows in comparison with Fig. 1a the behaviour of some inorganic monovalent anions (data from ref. 1) to illustrate that in both cases the ion-pair formation is strongest with large anions and least with small ones. We have thus more ion-pair formation with perchlorate than with chloride and more with trichloroacetate than with acetate, which is contrary to the tendency for complex formation. A recent spectrophotometric study of ion-pair formation[2] employs perchlorate as background electrolyte in 0.06 N concentration and this does not seem to be a very happy choice at all.

Fig. 1d gives an example of the effect of the concentration of the anion. Only the results with trichloroacetate are given but most other anions show identical
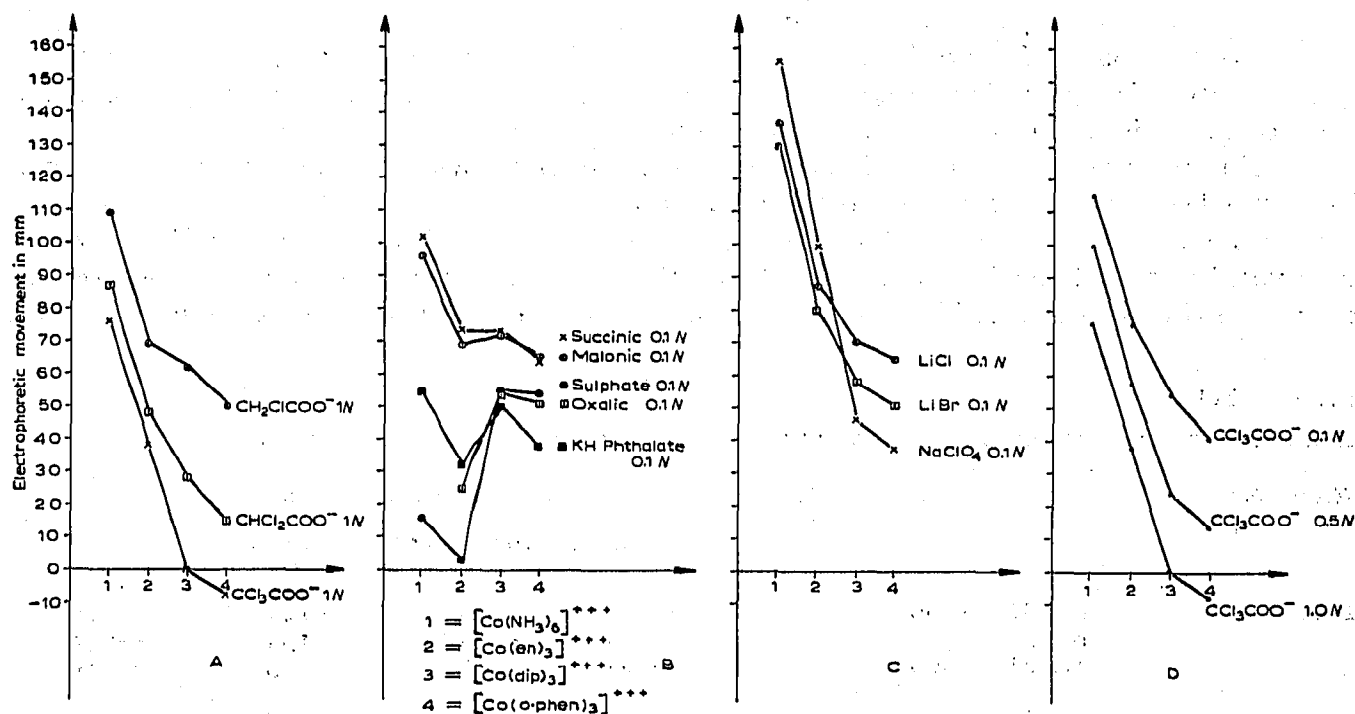
Fig. 1. Graphical representation of the electrophoretic movement of Co(III) complexes in various electrolytes. (A) Comparison of mono-, di- and trichloroacetate (1 N). (B) Comparison of several divalent anions (all 0.1 N). (C) Comparison of lithium chloride, lithium bromide and sodium perchlorate (0.1 N). (D) Comparison of 0.1, 0.5 and 1 N trichloroacetate. The order of the complexes is: (1) Hexamminecobalt(III); (2) tris(ethylenediammine)cobalt(III); (3) tris(dipyridyl)cobalt(III); (4) tris(o-phenanthroline)cobalt(III).

behaviour. The differences in degree of ion-pair formation increase considerably with the increase in anion concentration. The effects due to ion-pair formation are also observable in ion exchange chromatography when the adsorption of the cation is due to electrostatic attraction. As shown in Table II all four Co(III) complexes are strongly adsorbed on Macherey Nagel sulphonic cellulose exchange paper from 0.1 N trichloroacetate (and unadsorbed on Whatman No. 1 paper). In 0.5 N and 1 N trichloroacetate the dipyridyl and o-phenanthroline complexes are on the liquid front (i.e. unadsorbed) while the hexammine and the ethylenediammine complexes are still very strongly held. The behaviour is thus analogous to that in electrophoresis (see Table I).

TABLE II

R_F VALUES OF METAL COMPLEXES ON ION EXCHANGE PAPERS

Eluent: aqueous trichloroacetate at pH 4.5.
Papers: Whatman No. 1 (W1).
Amberlite SA-2 (sulphonic) Na+ form (SA-2).
Macherey Nagel sulphonic cellulose paper Na+ form (MN).

	0.1 M			0.5 M			1.0 M		
	W1	SA-2	MN	W1	SA-2	MN	W1	SA-2	MN
Co(NH₃)₆³⁺	0.91	0.0	0.0	0.89	0.0	0.05	0.87	0.0	0.17
Co(en)₃³⁺	0.93	0.0	0.0	0.90	0.0	0.07	0.98	0.0	0.29
Co(dip)₃³⁺	0.97	0.0	0.02	0.97	0.0	0.95	0.99	0.25T	0.91
Co(o-phen)₃³⁺	0.91	0.0	0.03	0.93	0.0	0.92	0.93	0.18T	0.91

Some results with complex anions of the type $M(CN)_6^{n-}$

We compared four anions, *viz.* CNS⁻, a rather large monovalent anion, ferricyanide, $Os(CN)_6^{2-}$ and $Ru(CN)_6^{2-}$. The three complex cyanides are all very stable and all four ions yield coloured spots with an acid solution of ferric chloride.

The movement of the anions in various metal chlorides as electrolytes is shown in Table III, expressed in millimeters moved.

The first observation that can be made is that in LiCl, KCl and NH₄Cl, where we would expect least ion pair formation, all the complex cyanides move approximately with the speed of CNS⁻, *i.e.* they appear to have about one negative charge only.

TABLE III

ELECTROPHORETIC MOVEMENT OF COMPLEX CYANIDES IN VARIOUS ELECTROLYTES

Electrolyte		Voltage	Time (min)	Electrophoretic movement (mm)			
				SCN^-	$Fe(CN)_6^{3-}$	$Ru(CN)_6^{2-}$	$Os(CN)_6^{2-}$
LiCl	0.1 M	1500	30	−141	−156	−141T	−134T
	0.5 M	1500	30	−164T	−173T	−159T	−157T
	1.0 M	1000	30	− 83	− 86	− 73	− 71
KCl	0.1 M	1500	30	−155	−172	−152T	−152
	0.5 M	1500	30	−167T	−181	−158T	−155T
	1.0 M	750	30	− 53	− 52	− 42	− 43
NH₄Cl	0.1 M	1500	30	−155	−174	−157T	−154T
	0.5 M	1500	30	−165	−181	−157	−154
	1.0 M	750	30	− 57	− 59	− 47	− 46
N(CH₃)₄Cl	0.1 M	1500	30	−134	− 98	−103T	−103T
	0.5 M	1500	30	−125	− 73	− 95	− 90
	1.0 M	1000	30	− 58	− 23	− 36	− 36
N(Et)₄Cl	0.1 M	1500	30	−114	− 80	− 90	− 86
	0.5 M	1500	30	−123	− 64	− 91	− 88
	1.0 M	750	30	− 42	− 14	− 22	− 21
Mg(NO₃)₂	0.1 M	1500	30	−146	−119	− 63	− 62
	0.5 M	1500	15	− 67	− 59	− 26	− 24
	1.0 M	750	30	− 51	− 37	− 13	− 13
CaCl₂	0.1 M	1500	30	−141	−119	− 65	− 65
	0.5 M	1500	30	−142	−120	− 63	− 63
	1.0 M	500	30	− 37	− 32	− 18	− 18
SrCl₂	0.1 M	1500	30	−128	−103	− 55	− 54
	0.5 M	1500	23	− 96	− 82	− 48	− 49
	1.0 M	500	30	− 34	− 29	− 19	− 18
BaCl₂	0.1 M	1500	30	−161	−121	− 66T	− 66T
	0.5 M	1500	20	− 88	− 75	− 40	− 36
	1.0 M	500	30	− 34	− 25	− 15	− 14
AlCl₃	0.1 M	1500	30	−113	− 78	+ 28	+ 29T
	0.5 M	1000	30	− 55	− 44T	+ 17	+ 18
	1.0 M	750	30	− 23	− 21T	+ 13	+ 14
ZrOCl₂	0.1 M	1500	30	− 93	+ 31	+ 57	+ 55
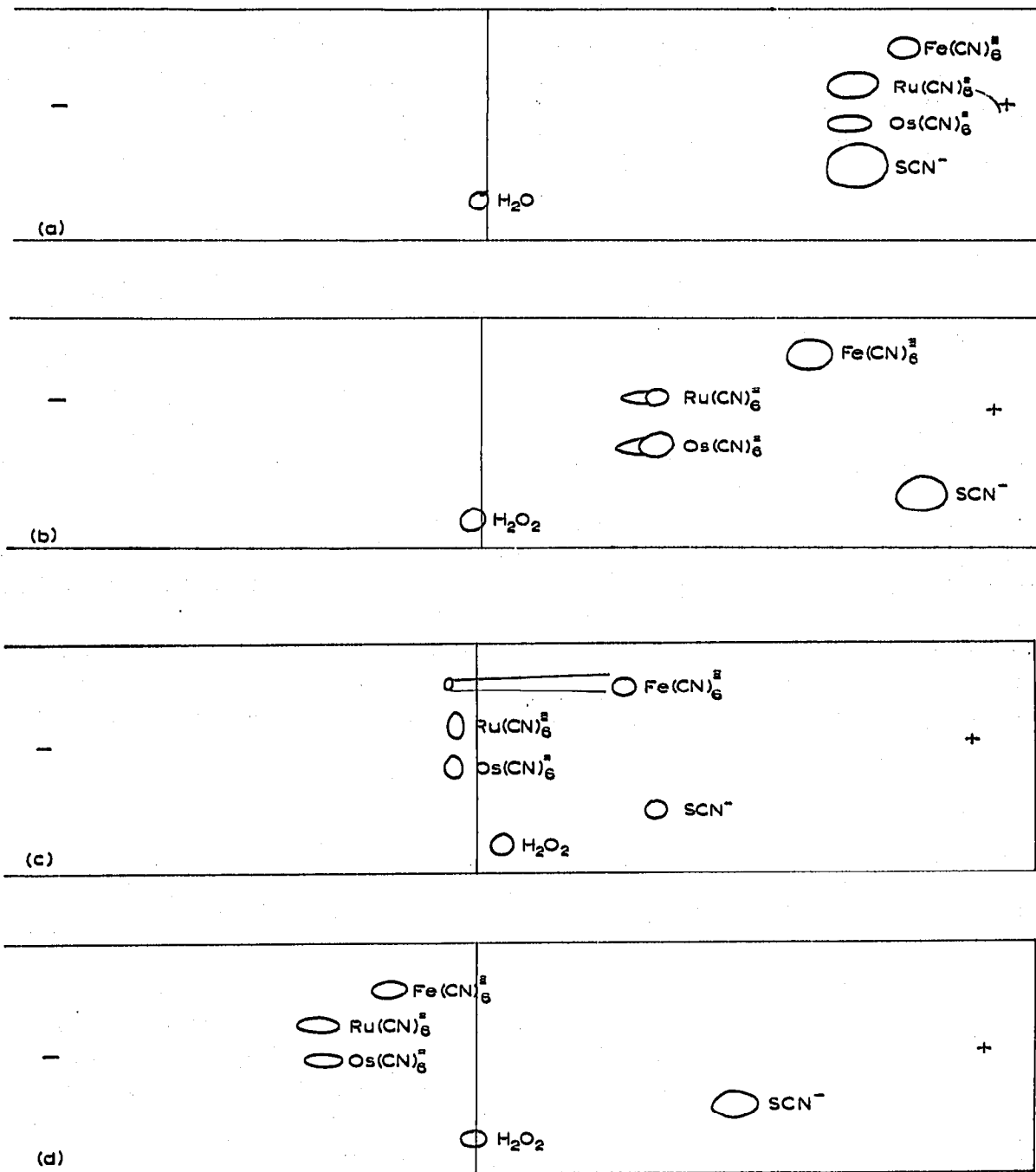
Fig. 2. Some electropherograms of CNS⁻, $Os(CN)_6^{2-}$, $Ru(CN)_6^{2-}$ and $Fe(CN)_6^{3-}$ in various electrolytes ($^3/_{10} \times$ actual size): (a) in 0.1 N LiCl for 30 min with 1500 V; (b) in 0.1 N $BaCl_2$ for 30 min with 1500 V; (c) in 0.5 N $AlCl_3$ for 30 min with 1000 V; (d) in 0.1 N $ZrOCl_2$ for 30 min with 1500 V. Hydrogen peroxide is used as indicator for electroosmotic flow.

This is of course not new and is evident also from conductivity as well as from numerous previous paper electrophoretic studies with ferrocyanide and other polyvalent anions.

In tetramethyl- and tetraethylammonium chloride the complex cyanides move already considerably less than CNS⁻ and in alkaline earths the effect is particularly

marked for the divalent complex cyanides $Os(CN)_6^{2-}$ and $Ru(CN)_6^{2-}$. *Actual cationic movement* was obtained in $AlCl_3$ for the divalent complex cyanides and for all three cyanides in zirconyl chloride, while the mobility of thiocyanate diminishes only to a marked extent at higher concentrations of divalent and trivalent metal chlorides.

Typical electropherograms are shown in Fig. 2.

DISCUSSION

Ion-pair or outer-sphere complex formation is a well-known phenomenon and may be studied by various methods (see BASOLO AND PEARSON[3], also ref. 2). We only extended the work on a semi-quantitative basis for several series of compounds. However, the data obtained raise a number of problems.

When a metal ion moves anionically in paper electrophoresis it is usually assumed that it has formed a complex with the anion of the electrolyte. There seems to be no method however to distinguish between outer and inner sphere complexes solely on the basis of electrophoretic movement.

The tendency of large and small hydrated anions (*e.g.* ClO_4^- and CCl_3COO^-) to form strong ion pairs poses another problem. Perchlorate has usually been used in complex chemistry as the least complexing anion and it now seems that the possibility of ion-pair formation has not been sufficiently considered.

We believe that we have opened up a new field for obtaining separations. The possibility to change the charge of polyvalent ions by ion-pair formation with suitable counter ions seems to offer numerous possibilities in paper electrophoresis as well as in ion exchange and other types of chromatography.

REFERENCES

1 M. MAZZEI AND M. LEDERER, *J. Chromatog.*, 31 (1967) 196.
2 N. TANAKA, Y. KOBAYASHI AND M. KAMADA, *Bull. Chem. Soc. Japan*, 40 (1967) 2970.
3 F. BASOLO AND R. G. PEARSON, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958, p. 376.