

ION PAIR FORMATION IN THE SEPARATION OF METAL COMPLEXES BY PAPER ELECTROPHORESIS

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A rather large effect due to ion pair formation has been observed repeatedly in paper electrophoresis and, for example, CHAKRABORTTY¹ showed that in $M/2$ Na_2SO_4 the $\text{Co}(\text{NH}_3)_6^{3+}$ ion moves more slowly than $\text{Co}(\text{II})$, also that several hexaquo- $\text{M}(\text{III})$ ions are almost neutral.

The effect of the chloride concentration on the separation of several pairs of *cis-trans* isomers was shown recently by BLASIUS AND BILAL². These authors found that adding AlCl_3 to an acetate buffer increased the separation effect and interpreted this as being due to ion pair formation.

The present study of the effect of ion pair formation in paper electrophoresis began with the examination of the purity of several $\text{Co}(\text{III})$ complexes which decomposed in paper chromatography but travelled without change in several buffers.

Acetate buffers were employed and it was found that the sequence of the speeds of the $\text{Co}(\text{III})$ complexes was not that of their ionic volumes as would be expected from the work of EDWARD AND WALDRON-EDWARD³. In perchlorate the sequence did agree qualitatively with the ionic volumes and this decided us to investigate a range of electrolytes for various series of complexes as relatively little data of this kind seem to exist in the literature (see BASOLO AND PEARSON⁴) and had obvious applications in the separation of complexes.

TECHNIQUE

The Camag high voltage electrophoresis apparatus was used with circulating tap water at about 15° and (unless specified otherwise) at 1500 V for 30 min. The samples were applied to the centre of the paper strip and a spot of H_2O_2 was run on the same paper to correct for electroosmotic effects (in all the electrolytes H_2O_2 did not move).

The complexes were detected by spraying the paper lightly with ammonium sulphide.

(A) THE BEHAVIOUR OF $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{dip})_3^{3+}$ AND $\text{Co}(\text{o-phen})_3^{3+}$

Hexamminecobalt(III) chloride, tris(ethylenediammine)cobalt(III) chloride and tris(dipyridyl)cobalt(III) chloride were prepared by the usual methods. The tris(*o*-phenanthroline)cobalt(III) complex was obtained by oxidising the $\text{Co}(\text{II})$

TABLE I
ELECTROPHORETIC MOBILITIES OF COBALT(III) COMPLEXES IN MONOVALENT ELECTROLYTES

<i>Electrolyte</i>		<i>Electrophoretic movement in mm in 30 min with 1500 V</i>				<i>Movement relative to Co(NH₃)₆³⁺</i>		
		<i>Co(NH₃)₆³⁺</i>	<i>Co(en)₃³⁺</i>	<i>Co(dip)₃³⁺</i>	<i>Co(o₃phen)₃³⁺</i>	<i>Co(en)₃³⁺</i>	<i>Co(dip)₃³⁺</i>	<i>Co(o₃phen)₃³⁺</i>
Na acetate-HAc	0.05 N	124	83	74	69	0.67	0.60	0.56
	0.1 N	105	71	65	59	0.67	0.62	0.56
	0.5 N	92	60	57	51	0.66	0.62	0.56
	1.0 N	80	49	50	42	0.63	0.62	0.52
NaClO ₄ at pH ₄	0.05 N	129	86	48	39	0.66	0.37	0.30
	0.1 N	156	99	46	37	0.64	0.30	0.24
	0.5 N	110	72	14	8	0.65	0.13	0.07
LiCl at pH ₄ (only 1000 V)	0.05 N	126	83	69	63	0.66	0.55	0.50
	0.1 N	137	87	70	65	0.64	0.51	0.47
	0.5 N	128	74	68	63	0.58	0.53	0.49
	1.0 N	61	33	31	27	0.54	0.51	0.44
BaCl ₂ at pH ₄	0.1 N	138	88	69	63	0.64	0.50	0.46
AlCl ₃ at pH ₄	0.1 N	123	79	66	61	0.64	0.53	0.49
LiBr at pH ₄	0.05 N	134	89	64	56	0.66	0.48	0.42
	0.1 N	130	80	58	51	0.62	0.45	0.39
NaBr at pH ₄ (only for 20 min) (with 750 V for 30 min)	0.05 N	140	91	71	63	0.65	0.51	0.41
	0.1 N	129	82	61	53	0.64	0.47	0.41
	0.5 N	73	41	32	26	0.56	0.44	0.36
	1.0 N	49	23	17	13	0.47	0.35	0.27

TABLE II

ELECTROPHORETIC MOBILITIES OF Co(III) COMPLEXES IN POLYVALENT ELECTROLYTES AND SOME ORGANIC ACIDS

Electrolyte	Electrophoretic movement in mm in 30 min with 1500 V				Movement relative to $\text{Co}(\text{NH}_3)_6^{3+}$			
	$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Co}(\text{en})_3^{3+}$	$\text{Co}(\text{dip})_3^{3+}$	$\text{Co}(\text{o phen})_3^{3+}$	$\text{Co}(\text{en})_3^{3+}$	$\text{Co}(\text{dip})_3^{3+}$	$\text{Co}(\text{o phen})_3^{3+}$	
Na_2SO_4 pH ~ 5 (750 V only)	0.05 N	25	12	64	62	0.48	2.6	2.5
	0.1 N	16	3	55	54	0.19	3.4	3.4
	0.5 N	12	— 2	58	57	0.07	4.8	4.7
	1.0 N	6	— 2	22	21	0.11	3.7	3.5
NaH_2PO_4	0.05 N	99	69	75	67	0.70	0.76	0.68
	0.1 N	97	70	75	67	0.72	0.77	0.69
	0.5 N	63	44	60	57	0.70	0.95	0.90
	1.0 N	39	23	45	42	0.59	1.1	1.1
$\text{Na}_2\text{S}_2\text{O}_3$	0.1 N	11	— 5	decomposes	43	—	—	3.9
KH phthalate pH 4	0.1 N	55	32	50	38	0.58	0.91	0.69
Na benzoate pH 6	0.1 N	124	74	61	49	0.60	0.49	0.43

complex with hydrogen peroxide in the solution of the electrolyte and the solution yielded usually a second spot due to the unoxidised Co(II) complex.

Table I shows the distances moved in electrophoresis when all four complexes were run on the same sheet of paper in a given electrolyte. The mobilities relative to $\text{Co}(\text{NH}_3)_6^{3+}$ are also given in Table I. It is evident that $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{dip})_3^{3+}$ move with almost the same speeds in acetate buffer although the organic skeleton of the latter should retard it considerably with respect to the first. In sodium perchlorate the sequence is that of the presumed ionic volumes, however here the *o*-phenanthroline complex hardly moves at all, indicating that also here there is considerable interaction between the complex cation and the perchlorate anion. In lithium chloride, lithium bromide and sodium bromide the sequence is essentially like that in perchlorate except that the larger ions (dipyridyl and *o*-phenanthroline complexes) move faster than in perchlorate. The cation of the electrolyte seems to have no important function, barium and aluminium chlorides giving the same relative sequences as lithium chloride.

Rather spectacular results are obtained with divalent anions as electrolyte as shown in Table II. The sequence is completely reversed, the smaller complex ions moving slower than the larger ones and the $\text{Co}(\text{en})_3^{3+}$ becomes almost neutral at 1 *N* sulphate or thiosulphate.

Sodium dihydrogen phosphate as electrolyte shows a much lower interaction than would be expected and is less reactive than sulphate. Phthalate (taken as an example of a divalent organic acid) has essentially the same effect as sulphate while benzoate is even less effective than acetate.

The results shown here strongly suggest that there is more than one type of interaction responsible for the ion pair formation. There is the electrostatic attraction factor, as is obvious from the much stronger effect of divalent ions compared to monovalent ones, but in addition there seem to be configurational effects which cause such things as: the equal speeds of $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{dip})_3^{3+}$ in acetate, and the slowing down of $\text{Co}(\text{o-phen})_3^{3+}$ in perchlorate when compared to chloride or bromide.

It is also interesting to note that it was possible to change the electrophoretic sequence at will by choosing the right electrolyte.

(B) THE BEHAVIOUR OF SEVERAL PAIRS OF *cis-trans* $\text{Co}(\text{en})_2\text{X}_2^+$ COMPLEXES

The compounds *cis* and *trans* $\text{Co}(\text{en})_2\text{Cl}_2^+$, $\text{Co}(\text{en})_2(\text{acetato})_2^+$, $\text{Co}(\text{en})_2(\text{phenylacetato})_2^+$ and $\text{Co}(\text{en})_2(m\text{-nitrobenzoato})_2^+$ were gifts from Dr. MONACELLI and Dr. MASPERO of this institute.

Their movement in various electrolytes is shown in Table III. There are small and relatively constant differences between the *cis* and the *trans* forms in monovalent electrolytes irrespective of the cation present. In sodium sulphate the separation is considerably greater for all four pairs and permits a ready separation in relatively short time. This is of practical interest because many pairs of complexes are unstable in aqueous solutions and cannot be separated when a run takes more than a few minutes.

The *cis* form is always slower than the *trans* form as noted previously by BLASIUŠ AND BILAL².

TABLE III

ELECTROPHORETIC MOBILITIES OF SOME PAIRS OF *cis-trans* $\text{Co(en)}_2\text{X}_2^+$ ISOMERS IN VARIOUS ELECTROLYTES

Compound	Movement in mm in 30 min with 1500 V		Movement of <i>cis</i> form relative to the <i>trans</i>	Electrolyte	
	<i>trans</i>	<i>cis</i>			
$\text{Co(en)}_2(\text{Cl}_2)_2^+$	64	59	0.92	Sodium acetate-acetic acid	0.05 N
	58	52	0.90		0.1 N
	49	43	0.88		0.5 N
$\text{Co(en)}_2(\text{acetato})_2^+$	51	46	0.90	Sodium acetate-acetic acid	0.05 N
	46	41	0.89		0.1 N
	39	33	0.85		0.5 N
$\text{Co(en)}_2(m\text{-nitrobenzoato})_2^+$	25	23	0.92	Sodium acetate-acetic acid	0.05 N
	24	21	0.87		0.1 N
	15	10	0.67		0.5 N
$\text{Co(en)}_2(\text{phenylacetato})_2^+$	30	27	0.9	Sodium acetate-acetic acid	0.05 N
	27	23	0.85		0.1 N
	24	20	0.83		0.5 N
	18	13	0.72		1.0 N
$\text{Co(en)}_2\text{Cl}_2^+$	50	44	0.88	Barium chloride	0.05 N
	50	40	0.80		0.1 N
	17	11	0.65		0.5 N
$\text{Co(en)}_2\text{Cl}_2^+$	55	32	0.58	Sodium sulphate	0.05 N
	41	20	0.49		0.1 N
$\text{Co(en)}_2(\text{acetato})_2^+$	44	29	0.66	Sodium sulphate	0.05 N
	37	23	0.62		0.1 N
$\text{Co(en)}_2(m\text{-nitrobenzoato})_2^+$	27 tail	13	0.48	Sodium sulphate	0.05 N
	21 tail	10	0.48		0.1 N
$\text{Co(en)}_2(\text{phenylacetato})_2^+$	31	20	0.65	Sodium sulphate	0.05 N
	25	13	0.52		0.1 N

TABLE IV

MOVEMENT OF SOME COBALT COMPLEXES IN AN OPTICALLY ACTIVE ELECTROLYTE

Electrolyte: 0.1 N (+)-camphor-10-sulphonic acid (β)-monohydrate.

Voltage: 1500 V.

	Distance moved in mm	
	in 30 min	in 1 h
$\text{Co}(\text{NH}_3)_6^{3+}$	137	runs off paper
$\text{CoII}(\text{dipyridyl})_3^{2+}$	91	244
$\text{CoIII}(\text{dipyridyl})_3^{3+}$	91	239
$\text{CoIII}(o\text{-phenanthroline})_3^{3+}$	77	207

(C) ELECTROPHORESIS IN AN OPTICALLY ACTIVE ELECTROLYTE

Since such excellent separations of *cis-trans* pairs were obtained, we also wanted to study the effect of an optically active electrolyte on those complexes which can be resolved into optical isomers by precipitation methods. Table IV shows the movement of several complexes in 0.1 *N* (+)-camphor-10-sulphonic acid (β)-monohydrate (Fluka, $\alpha = + 20^\circ$). None of the compounds separated into two spots but moved with a spot about as compact as that of $\text{Co}(\text{NH}_3)_6^{3+}$. If we assume that for a separation to be visible the centers of two spots have to move 10 mm apart, then if a separation of optical isomers occurred this must be less than 10 mm in a total movement of about 250 mm, *i.e.* that the difference in movement is less than 4%.

SUMMARY

Ion pair formation of cobalt complexes was studied by paper electrophoresis in a wide range of electrolytes. Quite strong interactions between divalent anions and complexes of the type $\text{Co}(\text{NH}_3)_6^{3+}$ were observed. The interactions seems to depend on the shape and size of the interacting ions as well as the charge. *Cis-trans* pairs of complexes separate very readily in sulphate (mobility differences about 40%) and much less in monovalent electrolytes (mobility differences about 10%). Optical isomers could not be resolved by paper electrophoresis.

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