

ZONE ELECTROMIGRATION OF SOME GALLIUM AND INDIUM COMPLEXES

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INTRODUCTION

Zone electromigration is a simple technique for obtaining information about complex ions in solution. The sign of the charge on the moving species is immediately evident from the direction of motion so that this technique is particularly useful for studying complexes of metal ions with anionic ligands. In addition, data may be obtained on the conditions under which a given species can exist in solution.

The observed zone mobility of a metal ion in a complexing medium is actually the weighted mean of the zone mobilities of all of the metal-containing species which are present in equilibrium with one another¹. Thus it is influenced by the formation constants of the system. The variation of zone mobility with pH or ligand concentration is expected to be abrupt only in those regions where the predominating complex species is being replaced by another of different charge. Experimental results often show the character of a roughly constant zone mobility changing more or less sharply to another constant value over a narrow range of pH. This has been used in the estimation of complex formation constants^{2,3}. The relation between mobility and charge or structure of a given species is complicated by such factors as partial ionization and absorption by the paper. However, complex ions with the same charge and similar structure would be expected to have similar mobilities, although the molecular weight may enter into this as well².

If a metal ion forms two species in solution which exchange with one another very slowly, two distinct zones may be observed on electromigration. An intermediate exchange rate may lead to an elongated, or comet-shaped spot. This may be the cause of part of the trailing sometimes observed in complexing media, although other factors also lead to this¹.

We have applied zone electromigration to the study of gallium(III) and indium(III) ions in a number of organic acid solutions. It is known that these ions are complexed by ligands of this type, although only slight attention has been given to their study.

EXPERIMENTAL

A closed strip technique was used in which the paper was sandwiched between two metal plates insulated with polyethylene and cooled with tapwater. Four strips could be run in parallel. Electrolyte reservoirs were not used; the ends of the paper

were in direct contact with platinum foil electrodes. By using suitable buffer solutions of the acid and its salts at the ends, pH changes arising from electrolysis were localized. Measurements showed that the pH of the strip where migration took place remained constant. This technique minimized electroosmosis, and separate experiments showed that it was negligible.

The solutions of complexing agents were made up to 0.1 *M* in free acid and the pH adjusted shortly before use with 1 *M* NaOH or HNO₃. Fumaric, phthalic, and salicylic acids were not soluble to the extent of 0.1 mole/l, so that saturated solutions were used.

Whatman No. 3 MM chromatography paper (4 cm × 25 cm) was used as supporting medium; in each experiment, spots of Ga and In were run side by side on the same strip. Migration times of about 1 h at a voltage gradient of about 15 V/cm were generally suitable. The absorbance was maintained near 0.025 ml/cm². Roughly 0.01 ml of migrant solution at concentrations less than 0.05 *M* were used.

The gallium(III) and indium(III) were in solution as the nitrates, with an excess HNO₃ content just sufficient to prevent precipitation of the hydroxides. Too high an acidity interfered with migration and led to non-reproducible results. The migrant zones were detected with alcoholic alizarin solution, followed by exposure to NH₃ vapor when necessary.

Paper chromatograms were obtained using the ascending technique.

Mobilities and R_F values were determined by measuring from the center of the zone to the starting point. When comet-shaped or trailing zones occurred, measurement was made from the center of the most intensely colored region.

RESULTS AND DISCUSSION

Zone mobilities are collected in Table I, and chromatographic R_F values in Table II. Comet-shaped zones are indicated by c, and precipitation at the starting point with no motion, by p. The R_F values labelled c refer to spots that streaked back to the starting point. The systems in which strong complexing was indicated by electromigration gave R_F values close to unity, but for some of the others lower values were found. With gallic and salicylic acids at low pH values, two solvent fronts were indicated by zones of different pH on the chromatogram. The R_F values were measured with respect to the first front, but the spots actually moved with the second, more acidic, front.

These R_F values are included to give an indication of possible absorption by the paper. The mobility values could be corrected using these results, but this would not change the basic arguments which follow.

The behavior of gallium and indium is similar in each complexing medium investigated. The only notable difference lies in the appearance of anionic gallium complexes at a lower pH than those of indium, implying a stronger complexing tendency for the former. Anionic species are formed with all ligands which are likely to form chelate structures utilizing carboxyl or hydroxyl groups. Thus, oxalato and malonato complexes with relatively high, anionic mobilities are formed, while succinic acid, which could chelate only with the formation of an unstable seven-membered ring, gives almost no anionic motion. With the latter, precipitation takes place at pH 5-6, while in more strongly complexing media there is none until pH 9 or greater.

TABLE I
ZONE MOBILITIES OF GALLIUM AND INDIUM COMPLEXES

U = Mobility $\times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{min}^{-1}$; — = motion toward cathode; + = motion toward anode.

Acid

Oxalic	pH	0.3	1.0	1.3	2.0	3.0	4.0	5.0	6.0	7.0	9.5
	U_{Ga}	-1.5	+4.5	+8	+11	+11.5	+11	+11c	+10.5c	+11; +5.5	+12; +7
	U_{In}	-4	+1	+2	+10	+10	+10	+10.5	+9.5	+9.5; +3.5	+9.5; +5
Citric	pH	0.3	1.0	2.0	3.0	4.0	4.3	5.0	6.0	7.0	9.0
	U_{Ga}	-4	+3	+4.5c	+7	+6.5	+7	+7.5c	+7.5c	+7.5c	+6.5c
	U_{In}	-4	+1	+2	+6.5	+7c	+7.5	+7.5	+8	+8.5	+8
Malonic	pH	0.3	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	10.3
	U_{Ga}	-7	-6	+6.5	+7	+8	+9.5c	+7.5c	+9	+8.5	+9
	U_{In}	-6.5	-7	+2.5	+5	+7.5	+9	+7.5	+9.5	+9c	+9
Tartaric	pH	0.3	1.0	2.0	3.0	4.0	5.0	5.4	6.0	7.0	9.0
	U_{Ga}	-7	-1	-0.5	+5	+6c	+5.5c	+5.5c	+8c	+8c	+7.5c
	U_{In}	-8	-2.5	-2.5	+4	+6	+5.5	+5.5	+8	+7.5	+7
Malic	pH	2.0	3.0	4.0	5.0	5.5	6.0	7.0			
	U_{Ga}	+1.5c	+4c	+5.5c	+5.5c	+5.5c	+5.5c	+5.5c			
	U_{In}	-2.5c	+2	+5.5	+6.5	+6	+9	+7			

Gallic	pH	2.0	3.0	4.0	5.1	6.0	7.0
	U Ga	-1c	+1c	+2c	+2.5c	+2.5c	+2.5c
	U In	-3	-1	+1.5	+2c	+1.5c	+2.5c
Lactic	pH	2.0	3.0	4.0	5.0	6.0	7.0
	U Ga	-5	-2.5	+3c	+3c	+2c	+3c
	U In	-5c	-5	+2.5	+2c	+1.5c	+1.5c
Salicylic	pH	2.0	3.0	4.0	5.0	6.0	7.0
	U Ga	-2.5c	-3c	+1c	+1.5	+2c	+1c
	U In	-5	-3.5c	-0.5c	-2c	-1c	-2c
Succinic	pH	2.0	3.0	4.0	5.0	6.0	
	U Ga	-8c	-3.5c	-1.5c	p	p	
	U In	-6.5	-4	-1	+2.5c	p	
Phthalic	pH	2.0	3.0	3.9	5.0	6.0	7.0
	U Ga	-6c	-1c	-0.5c	+1c	p	p
	U In	-5.5	-2	-1c	+1c	+1c	p
Fumaric	pH	2.0	3.0	4.0	5.0		
	U Ga	-6.5	-2.5c	p	p		
	U In	-6	-2.5	p	p		

c = comet-shaped zone.

p = precipitation at the starting point.

TABLE II

 R_F VALUES OF GALLIUM AND INDIUM COMPLEXES

Acid								
Oxalic	R_F	pH	0.3	1.0	3.0	5.0	7.0	9.5
		Ga	I	I	I	I	I	I
		In	I	I	I	I	I	0.9
Citric	R_F	pH	0.3	1.0	3.0	5.0	7.0	
		Ga	I	I	I	I	I	
		In	I	I	I	I	I	
Malonic	R_F	pH	0.3	1.0	3.0	5.0	7.0	10.3
		Ga	I	I	I	I	I	0.8
		In	I	I	I	I	0.9	0.9
Tartaric	R_F	pH	0.3	1.0	3.0	5.0	7.0	9.0
		Ga	I	I	0.9	0.9	0.9	0.9
		In	I	I	I	I	I	I
Malic	R_F	pH	2.0	4.0	5.5	7.0		
		Ga	I	I	I	I		
		In	I	I	I	I		
Gallic	R_F	pH	2.0	3.0	4.0	7.0		
		Ga	0.6*	0.8*	I	0.9		
		In	0.6*	0.8*	0.9	0.9		
Lactic	R_F	pH	2.0	4.0	6.0	7.0		
		Ga	0.9	0.8	1.0	1.0		
		In	0.9	0.7	0.5c	0.3c		
Salicylic	R_F	pH	2.0	3.0	4.0	7.0		
		Ga	0.6*	0.5*	0.5c	0.5c		
		In	0.6*	0.5*	0.3c	0.3c		
Succinic	R_F	pH	2.0	3.0	4.0	6.0		
		Ga	0.9	0.6	0.3c	p		
		In	0.9	0.7	0.8	p		
Phthalic	R_F	pH	2.0	3.0	3.9	5.0		
		Ga	0.8	0.6	0.4c	0.2c		
		In	0.8	0.7	0.6	0.3		
Fumaric	R_F	pH	2.0	3.0	5.0			
		Ga	0.9	0.4	p			
		In	I	0.5	p			

* Two solvent fronts.

c = spot streaks back to the starting point.

p = precipitation at the starting point.

Malic and tartaric acids which can form 5- or 6-membered chelate rings also lead to high anionic mobilities.

Possible species would be $[MA_3]^{3-}$ with the bidentate oxalate and malonate ligands, and $[MA_2]^{1-}$ with the tartrate and malate ions which can be tridentate. The relative mobility values would be in accord with such formulas, but there is no real proof that the completely chelated species are formed here. In all likelihood the citrate

ion is also tridentate; this would lead to an anionic bis-complex. The three carboxyl groups here lead to a possible charge of 3⁻ on the citrate ion, although they need not all be ionized in the complex.

The slight anionic motion observed with the monocarboxylic acids, lactic, gallic and salicylic, would imply at least partial ionization of the hydroxyl groups involved in chelation if tris-complexes are formed. Species with coordinated OH⁻ groups, or with more than three acid ions coordinated through only one position, may be contributing.

Phthalic and fumaric acids, which are unlikely to chelate well, lead to no significant anionic motion. The low mobilities observed do imply the formation of complexes, although the observed precipitation at comparatively low pH values indicates that these are weak.

The zone mobilities of gallium and indium in KNO₃ solution where complex formation is unlikely are -2.9 and $-4.0 \cdot 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{min}^{-1}$, respectively at low pH. These comparatively low values imply strong interactions with the supporting medium as would be expected for tervalent species. The mobility increases when a neutral hydroxyl ligand such as glycol is added, but the zones show considerable trailing. The much higher cationic mobilities at low pH values in some of the complexing media (malonic, tartaric, and succinic acids, in particular) may then be caused by the existence of cationic complex species, which, while having a reduced charge, interact much less strongly with the paper.

The results of this work cannot be related directly to other studies, most of which have been made at a constant (high) ionic strength. A comparison is of interest in several cases, however.

COZZI AND VIVARELLI⁴ studied indium complexes in tartrate, malate and succinate solutions by electrode potential measurements. For all of these complexing agents they proposed the species $[\text{In}(\text{HA})(\text{A})]$ at $\text{pH} < 3$, and $[\text{In}(\text{OH})(\text{A})_2]^{2-}$ at $\text{pH} > 3$. (The neutral acid would be represented by H₂A.) Moreover, the formation constants were the same for all three ligands. Our results indicate that the behavior of indium in succinic acid solutions is markedly different from that in the other two acids; the formation of anionic species is much reduced. In addition, there is no indication in any case of a predominating neutral species at low pH.

The gallium tartrate complexes proposed by SAVCHENKO AND GONCHAROV⁵ from potentiometry and conductance were $[\text{Ga}(\text{A})]^+$ at $\text{pH} 1.5$, $[\text{Ga}(\text{A})_2]^-$ at $\text{pH} > 3$, and a mixture of species, chiefly $[\text{Ga}(\text{HA})_2(\text{A})]^{1-}$ and $[\text{Ga}(\text{HA})(\text{A})_2]^{2-}$, at intermediate values. Our results do not disagree with these proposals.

DUTT AND BOSE⁶ have found that the mono-, bis-, and tris-malonato complexes of gallium exist in solution; the first predominates at $\text{pH} < 2.25$, the second, between $\text{pH} 2.25$ and 3.5 , and the last, at higher pH's. Again, while our results indicate that the cationic species ceases to be important at a lower pH, there is otherwise no disagreement.

ZELYANSKAYA AND BAUSOVA⁷ have polarographic evidence for $[\text{Ga}(\text{C}_6\text{H}_4\text{-OCOO})_3]^{3-}$ in salicylate solutions at $\text{pH} 2.5$ - 4.5 . Under our conditions, we have a cationic species changing to an anionic one at $\text{pH} 3$ - 4 . The low anionic mobility makes an ion with charge -3 unlikely as the predominating species.

At $\text{pH} 7$ and above there is definite evidence for the formation of two oxalato complexes with both gallium and indium. Evidently these do not exchange with one

another rapidly here, as the two zones observed for each metal were distinctly separated. The new species has a lower mobility, indicating either a lower negative charge or a very considerably different structure. DUTT AND SUR⁸ find that the bis-oxalato complex of gallium is very stable at low pH values, while the tris-complex exists at higher values. Polarographic studies of KUZNETSOVA⁹ show that the tris-complex $[\text{Ga}(\text{A})_3]^{3-}$ is most stable at pH 8.6-10. It is probable that one of the species responsible for the "double spots" observed is $[\text{M}(\text{A})_3]^{3-}$, the other may be $[\text{M}(\text{A})_2(\text{H}_2\text{O})_2]^{1-}$, or perhaps an hydroxo compound.

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SUMMARY

The zone electromigration of gallium and indium ions was carried out as a function of pH in 11 organic acid solutions. Results show the variation of complex formation with pH, and permit a comparison to be made of the complexing properties of the various acids.

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