

ELECTROMIGRATION STUDIES OF SOME COMPLEXES OF SOME GROUP III METALS

R. A. BAILEY AND A. STEGER

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N.Y. (U.S.A.)

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INTRODUCTION

Zone electromigration of metal ions in complex-forming media has often been used in the study of complex formation in solution. It is useful particularly when the ligands are anionic, so that a change in the direction of motion of the metal ion from cationic to anionic shows that a complex has been formed. In such systems it is common to find that the mobility changes sharply with pH or ligand concentration only when the predominant species in solution changes; otherwise it is fairly uniform. From this, it has been possible to estimate values of the complex stability constant if the identities of the species concerned can be assumed^{1,2}. In a more qualitative way, however, electromigration is a simple technique to show relative stabilities and the effect of changes of conditions on complex formation.

We have investigated the behavior of several trivalent ions with "complexone" type ligands. Most of these are expected to form 1:1 complexes with the metals, although one or more water molecules (or hydroxyl ions) may be coordinated at the same time.

EXPERIMENTAL

The electromigration was carried out by the closed strip technique, as described previously³. Whatman 3MM filter paper strips were used with two or three ions being run side by side on each strip. Migration times and voltages were taken to give a reasonable movement of the zone. The migrant solutions (about 0.1 ml, 0.001 *M*) were made up from the metal nitrates, with just sufficient excess HNO₃ to prevent precipitation of hydrolysis products. The background solutions were 0.05 *M* NaNO₃-0.01 *M* complexing agent with the pH adjusted to the desired value by the addition of HNO₃ or NaOH. (At the lowest pH values, the complexing agents were not all soluble to the extent of 0.01 *M*. In such cases, saturated solutions were used.) The NaNO₃ served to give a sharper zone with less adsorption by the paper, as well as to provide a more uniform ionic strength for comparison of runs at different pH. Detection of the migrant zones was by alizarin.

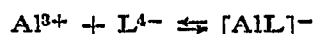
Chromatographic experiments showed that in all cases the metal ions moved with the solvent front, so that adsorption effects by the paper are not important.

RESULTS AND DISCUSSION

The results of the electromigration studies are shown in Figs. 1-6. With few exceptions, it may be seen that complexing takes place even near pH 1. The mobilities of the ions in 0.05 M NaNO₃ solution at low pH values were: Ga, 6; In, 8; Al, 11; Y, 14; La, 14 × 10⁻³ cm². V⁻¹. min⁻¹. These may be taken to be the mobilities of the aqua-complexes and would be the values expected if no complexing took place (*i.e.*, at low pH values). As can be seen, only in a few cases did an apparently non-complexed metal species exist in solution. (The actual mobility may be sensitive to substances which effect interaction with the paper, such as the non-ionized ligand, so that not too much significance can be attached to the fact that the limiting mobilities in the acidic complexing agents do not always agree with the values given above.)

The results in ethylenediaminetetraacetic acid (EDTA) (Fig. 1) indicate only a single anionic species for all of the metals studied. While this ligand may be sexadentate, it has been shown to be pentadentate for the lanthanide compounds^{4,5} and probably the Al, Ga, and In compounds also⁶. One carboxyl group is free, with the sixth coordination site on the metal occupied by a water molecule. Such a structure is even more likely in solution, but the electromigration experiments show that either the free carboxyl group or the coordinated water molecule is ionized even at pH 1-2. (The actual anionic species in solution is of course uncertain and may not be that isolated. The EDTA may be less than pentadentate, and coordination numbers greater than 6 are conceivable.)

For aluminum, the only metal showing a cationic plateau in this complexing agent, a value of the stability constant can be estimated by the method of JOKL¹, using the pH at which the mobility is midway between the anionic and cationic plateau values. One must assume the identities of the species concerned. If one assumes the equilibrium is (neglecting H₂O)



$\log K = 16.2$. This compares with an accepted value of 16.1⁷, although this agreement may be fortuitous. The mobility-pH plots of Y and La agree with those of KISO².

MOELLER AND HORWITZ⁵ report that (1,2-cyclohexylenedinitrilo)-tetraacetic acid (DCTA) forms compounds with the lanthanides which are similar to those obtained with EDTA. The results of electromigration (Fig. 2) show that Al, Y, and La are similar to the former in solution in that only a single anionic species, existing even at pH 1 is evident. Gallium and indium are much different, however; two cationic species are observed, while the single anionic species is only formed above pH 7. The high mobility compared to that of the anionic Al, Y, and La species implies a different structure or charge. There is no indication of a neutral species with any significant range of existence.

(Hydroxyethyl)ethylenediaminetriacetic acid is most likely to act as a pentadentate ligand, with the weakly coordinating hydroxyethyl group free. This has been observed with lanthanide complexes⁵. Electromigration results (Fig. 3) show that gallium and indium form only a single cationic and a single anionic species. However, lanthanum, and probably also yttrium and aluminum, form at least two cationic species as well as the anionic one. (The mobility of the cationic Ga and In species is quite low, and this plateau may not represent the aqua-complex.) The anionic motion

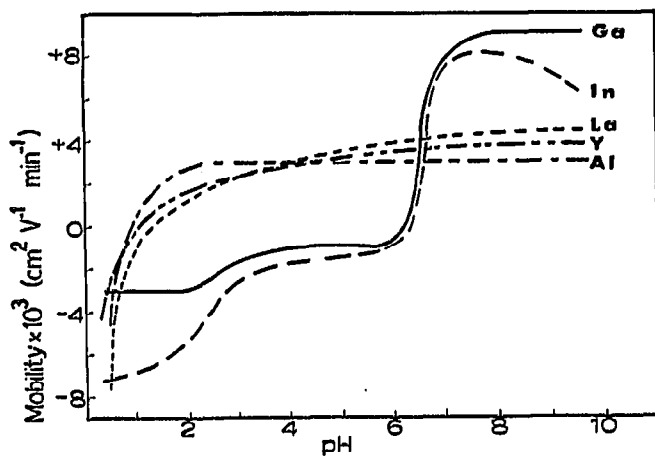
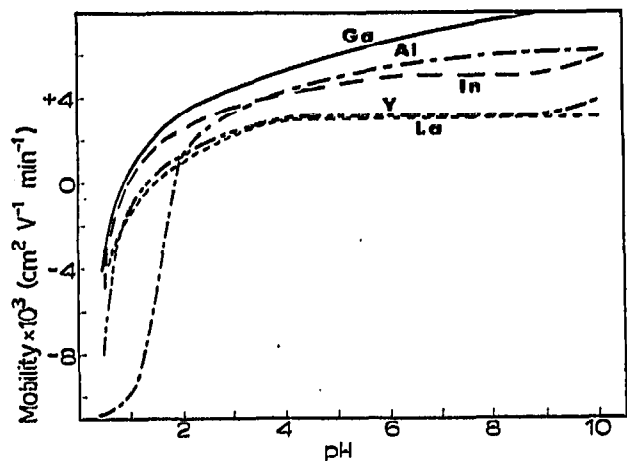


Fig. 1. Zone mobilities as a function of pH in EDTA.

Fig. 2. Zone mobilities as a function of pH in DCTA.

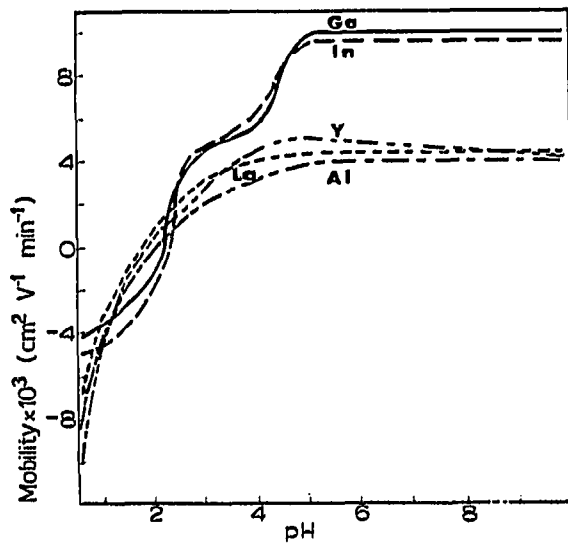
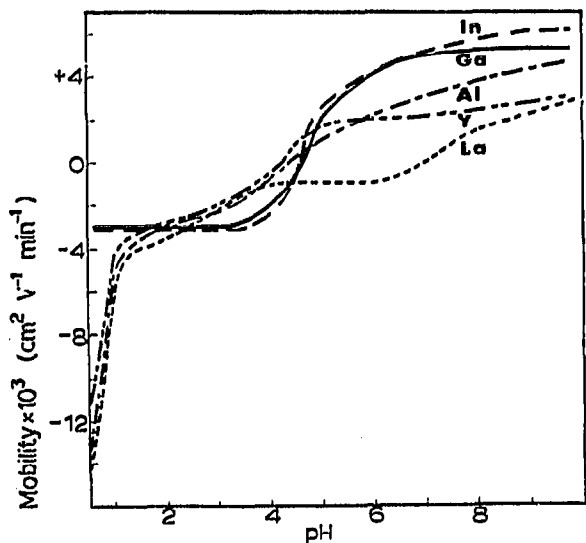


Fig. 3. Zone mobilities as a function of pH in (hydroxyethyl)ethylenediaminetriacetic acid.

Fig. 4. Zone mobilities as a function of pH in diethylenetriaminepentaacetic acid.

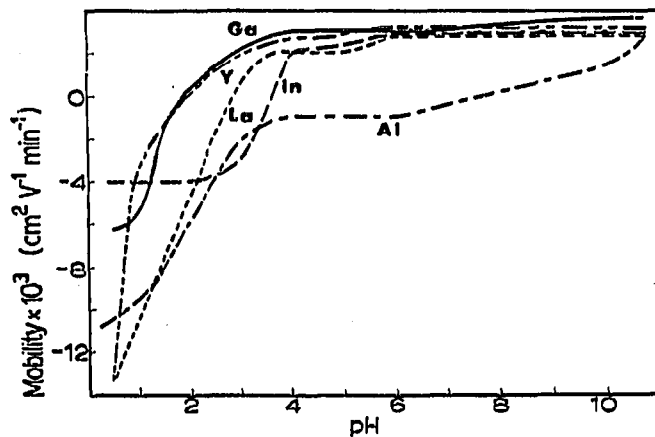
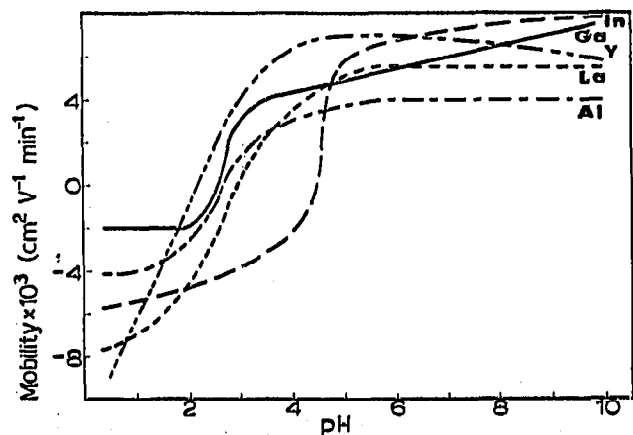
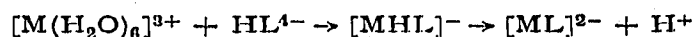


Fig. 5. Zone mobilities as a function of pH in nitrilotriacetic acid.

Fig. 6. Zone mobilities as a function of pH in EGTA.

does not occur until pH 4 or above, in contrast to the behavior of EDTA. However, it is clear that either the hydroxyethyl group, or coordinated water, is ionized here. The lack of a definite plateau for Al and Y in particular indicates several species in solution in the range of pH 1 to 3.

Diethylenetriaminepentaacetic acid has five ionizable carboxyl groups and eight donor sites. The electromigration results (Fig. 4) indicate the existence of only one anionic complex for Al, Y, and La, but two for Ga and In as well as the cationic species. It would appear that the species present at pH > 5 for Ga and In is quite different from that for the other three metals, perhaps having a greater charge, as the mobilities are much greater. There is thus a similarity to the DCTA system. One would be tempted to propose the equilibrium



but if the complexes are 6-coordinate, this would imply that the two nitrogens were not coordinated in the latter case. However, it is possible for non-coordinated carboxyl groups to be ionized. Since this occurs with only two of the metals, it is most likely associated with a change in coordination; either a carboxyl replacing a nitrogen atom, or a water molecule.

Nitrilotriacetic acid can act as a quadridentate ligand with a charge of 3-. The anionic complexes formed (Fig. 5) indicate either that two ligands are attached to each metal ion, or that a hydroxo-species is formed. In all cases only a single anionic and a single cationic species are indicated. Notable is the low stability of the In complex as compared to the other metals.

Little is known about the structure of ethyleneglycoltetraacetic acid (EGTA) complexes. All species studied exhibit a single anionic complex as well as a cationic species (Fig. 6). Only aluminum exhibits a third form, which moves very slowly as a cation, but may be neutral. The apparent motion could be due to the aqua species migrating from the neutral complex if the exchange process were slow. For this case, the zones always streaked from the starting point.

The overall complex-forming behavior of these systems shows that gallium and indium frequently form different species than the other three metals. Aluminum stands somewhat apart, but is more similar to Y and La (except in EGTA). Depending on the ligand, the relative stabilities may vary considerably, but as the identities of the species concerned are unknown, there is no significance in estimating stability constants, although with further information this would be possible in several cases. The formation of anionic species even at quite low pH values is notable.

SUMMARY

Zone electromigration of Al, Ga, In, Y, and La ions in the presence of several ligands of the "complexone" type was investigated as a function of pH. The formation of anionic species was noted even at low pH values, indicating strong ionization of the carboxyl groups of the ligand or of coordinated water molecules. Information was also obtained on the comparative behavior of these ions.

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