

SEPARATIONS OF INORGANIC IONS BY PAPER ELECTROPHORESIS IN SOLUTIONS OF N-(2-HYDROXYETHYL)IMINODIACETIC ACID

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INTRODUCTION

The majority of the electrophoretic separations of metal ions succeed when the ions are in the form of complexes with anionic ligands. In such cases, the charge on the ions undergoes a change and the value of this charge which affects their electrophoretic mobility can be influenced. The choice of a suitable complexing agent and determination of the fundamental conditions of the migration are of chief importance in the development of a separation. A convenient complexing agent is one which possesses a wide efficiency in forming complexes which migrate as zones of very different electrophoretic mobilities.

Complexes with analogous structure, derived from central ions with the same charge, have very similar mobilities¹. These can, however, differ one from another under conditions of the partial complex formation, if the stability of the complexes differs². The degree of association of a given complex is generally determined by the free ligand concentration in the supporting electrolyte. In the case of the complexes of weak acids, both the analytical concentration and the pH value of the solution are important³. For this reason, it is very useful, when determining the optimal conditions of electrophoretic separations, to examine extensively the dependence of the mobilities on pH ("electrophoretic mobility curves") and subsequently compare these curves.

Various aminopolycarboxylic acids are widely used as complexing agents. Their low solubility in aqueous solution, however, is a disadvantage for electrophoretic purposes: it is not possible to achieve the required concentrations in the supporting electrolyte. Certain functional groups can increase the solubility of the reagent without decreasing its complexing properties. An example of a complexone of this type is N-(2-hydroxyethyl)iminodiacetic acid (HIDA). Its complexing power is similar to that of the nitrilotriacetic acid, but its solubility in water is far greater. The electrophoretic behaviour of the chelates of HIDA with certain common metal ions was investigated within the framework of a study dealing with the chelating properties of HIDA⁶. A very good electrophoretic separation of rare earths with this reagent was reported recently⁴. The successful application of this reagent for the separation of other elements was also assumed. In this communication, an investigation of the electrophoretic behaviour of numerous elements in solutions of HIDA is described, for the purpose of establishing the separation possibilities. On the basis of

the results obtained, some examples are given for the separation of model mixtures from which some concrete analytical problems can be resolved.

EXPERIMENTAL

Apparatus

The technique of horizontal water-cooled electrophoresis was used, as described previously⁴. Instead of the foam rubber, a porous polyurethane layer was used to press the electropherogram towards the cooling plate. Whatman No. 1 chromatography paper was used; the liquid content of the electrolyte-treated paper was 120%. The rectifier produced a potential gradient of 15 V/cm; the temperature was 20°.

Chemicals

N-(2-Hydroxyethyl)iminodiacetic acid was prepared according to VIELES *et al.*⁵. The supporting electrolytes used for impregnation of the electropherograms, which contained 0.05 M HIDA, were prepared by dilution of an 0.2 M solution of the monosodium salt and adjustment of the pH value to the required value by addition of suitable buffer systems where necessary; this has been described previously⁴. In the study of sodium mobilities, potassium-containing electrolytes were used.

The above-mentioned concentration of HIDA ensures complex formation directly after the sample has been spotted to the pretreated paper or in the first phase of migration. Therefore, it is not necessary to prepare the complexes or their solutions directly. In all cases, *ca.* 1–2 μ l of 0.05 M solutions of simple salts were used; cations as their nitrates or chlorides, while anions were in the form of their sodium or potassium salts. Ti(IV) was in the form of the oxysulfate, Zr(IV) in the form of the oxychloride and U(VI) in the form of the uranyl nitrate.

Procedure

When measuring the mobilities for plotting as mobility curves (60 min runs) a simple apparatus without electrode vessels was used. The electrical connection of the platinum wire electrodes with the electropherogram was achieved by means of filter paper bridges. The electrolyte pretreated paper strip and the bridges were placed on the cooling plate insulated with polythene sheet. After 15–20 min equilibration, the samples were spotted and the electrophoresis carried out. The strips were dried and cut, if necessary, and the spots visualised.

For the separation runs (1.5–3 h), the arrangement with the electrode vessels was used⁴.

Evaluation

The following reagents were used for detection: zinc uranyl acetate for Na; nitrito-cobaltate for K, Rb and Cs; sodium rhodizonate for Sr and Ba; 8-hydroxyquinoline for Li and Mg; "phthalein complexone" for Ca; stannous chloride-potassium thiocyanate for Mo, W, Re(VII), Au, Se(IV), Te(IV) and As(III); molybdate for As(V); Zn²⁺-hydrogen peroxide⁶ and benzidine for Mn and Cr(III); ammonium sulphide for Cu, Cd, Co, Ni, Pb, Hg and Tl; and alizarin (acidified alcoholic solution⁴) for the others. The strips were generally sprayed well with 0.2 M HCl and dried to destroy the strong HIDA complexes before finally locating the spots.

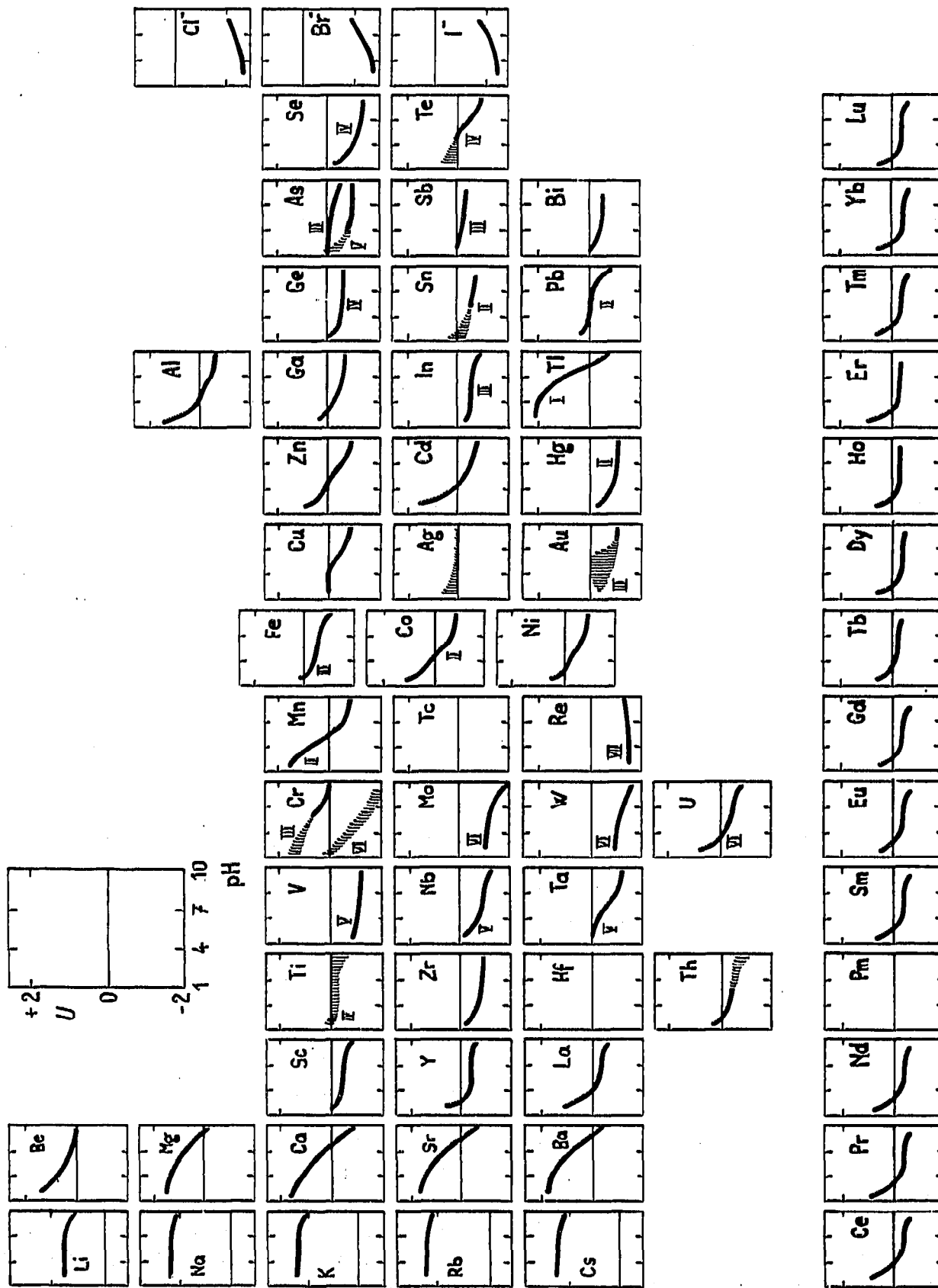


Fig. 1. Electrophoretic mobility curves in 0.05 M HIDA. U = electrophoretic mobility relative to $(C_2H_5)_4N^+$. Temperature: 20°.

The electrophoretic mobility data are relative values with respect to tetraethylammonium (spotted as an internal standard on each electropherogram) and corrected for electroosmosis (indicated by antipyrine or, below pH 3, by glucose).

MOBILITY CURVES

The comparison of the mobility curves gives a first indication about the feasibility of an electrophoretic separation. The dependence of the mobility, in 0.05 *M* HIDA, on the pH was studied for chemically stable ions of the majority of the elements, excepting the light non-metals of periods 2 and 3 of the periodic table, the platinum metals, and some heavy radioactive elements, Tc, Pm and Hf. The mobility data for some transition elements⁶ and rare earth elements⁴ were taken from literature. The arrangement of the results in the form of the periodic table permits the evaluation of similarities and differences in the electrophoretic behaviour of related elements, separated with difficulty. This behaviour is closely related to the existence of particular ionic species in solution under the given experimental conditions¹. However, the problem was not investigated here as to whether the mobility changes occur owing to complex formation or as a consequence of other processes.

The alkali metal ions have very similar mobilities and do not show any manifestation of complex formation with HIDA, except in the case of Li, where complex formation is slightly indicated. Other elements in this study (except Be and Cr(III)) tend to form anionic species as the pH values are increased.

This tendency shows, in many cases, a distinctly periodic character, increasing from group IIa to Vb, and is greater for lighter elements. In the alkaline earth group, calcium forms the strongest complex, and magnesium behaves similarly to barium. The same situation occurs in the rare earth group (which was discussed in detail elsewhere⁴); their HIDA-chelates were studied also potentiometrically⁸. In group IVb tailing occurs with Ti(IV) and to some extent with Th, probably as a result of the adsorption or reduced solubility of hydrolysis products. Both Cr(III) and chromate form elongated zones, limiting the separations in many cases. Molybdate and tungstate have very close mobilities; an incomplete separation is possible but only in an alkaline solution. The mobility curve of the uranyl ion corresponds obviously to complex formation with HIDA, in accordance with the literature⁷. This finding is also true of the mobility curves of Mn(II), Fe(III), Co(II), Ni, Cu, Zn, Cd and Pb⁶, whose complexes in solution have been studied by other physico-chemical methods⁹⁻¹¹.

In the case of Ag and Au(III), a strong tailing or precipitation occurs, probably due to reduction. Hg(II) shows an anionic species only, which is a very stable HIDA complex. The trivalent ions of group IIIa possess an increasing complexing affinity from aluminium up to indium; but Tl(I) migrates in the main pH range to the cathode, in accordance with its weak tendency to complex formation. Undefined anionic species are formed by Ge(IV), Sn(II) and elements of group Va. Selenite, tellurite and halides migrate as original anions.

CONDITIONS FOR SEPARATIONS

The mobility curves show that the suitable pH for separation of most of the metal ions, in a solution of HIDA, is in the range pH 2-3. Under these conditions, the

strong, heavy metal-HIDA complexes are in equilibrium with comparable concentrations of the free central ion or its lower complexes. This fact influences the zone mobilities, according to the different stabilities of the complexes³: the most stable ones show an anodic or only weakly cathodic mobility. The weaker the complex, the higher is the cathodic mobility of the zone. A higher acidity generally increases the cathodic mobilities, with respect to the changed complex formation equilibrium.

A similar equilibrium state exists in the case of weak complexes (*e.g.* those of the alkaline earths). Under our experimental conditions these occur in an alkaline solution only, which is therefore suitable for their separation. Some non-metallic ions and ions derived from acid oxides can also be separated in such a medium. The HIDA complexes of such ions are probably not formed; the waves on the mobility curves, if present, correspond to acid-base equilibria in the widest sense.

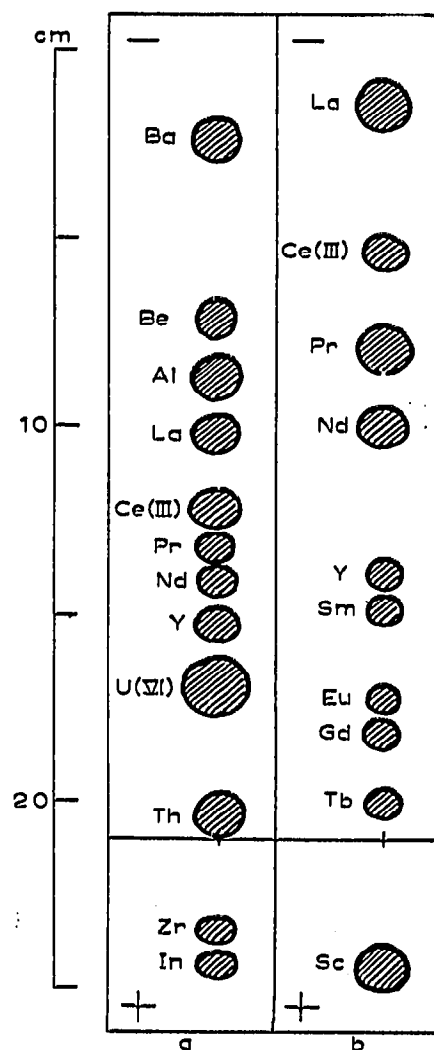
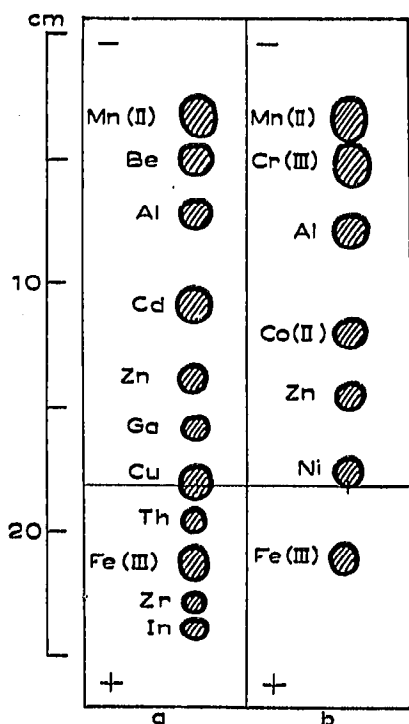
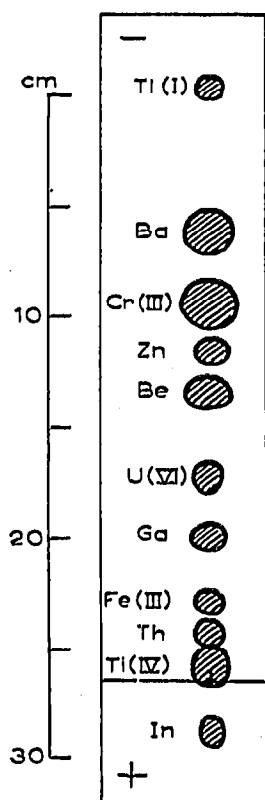


Fig. 2. Separation at pH 2.1. Time: 2 h. Potential gradient: 15 V/cm.

Fig. 3. Separations at pH 2.7. Time: 1.5 h. Potential gradient: 15 V/cm.

Fig. 4. (a) Separation at pH 2.6. Time: 3 h. Potential gradient 10 V/cm. (b) Separation at pH 2.4. Time: 3 h. Potential gradient: 15 V/cm.

Separations in acidic solution

In a relatively acid medium not even stable complexes are formed quantitatively and thus they can be successfully separated (Fig. 2). The best separation conditions, however, exist at an acidity about pH 2.5. Fig. 3a shows a separation of 11 ions in a single run. The separations Be-Al-Ga-In, Zn-Ga, Cd-In, Cd-Zn-Cu and Cu-Th-Zr are remarkable here. Under the same conditions, the common metal ions of group 3 in analysis can be separated, but the separation of Mn-Cr(III) is often defective (Fig. 3b).

A very good separation of Sc, Y and the lanthanides from La up to Tb was described in detail in a previous communication⁴. Their separation after electrophoresis at pH 2.4 is shown in Fig. 4b. Some rare earths can be separated one from another, and from zirconium, thorium, uranium and some other elements at a slightly elevated pH, as can be seen in Fig. 4a.

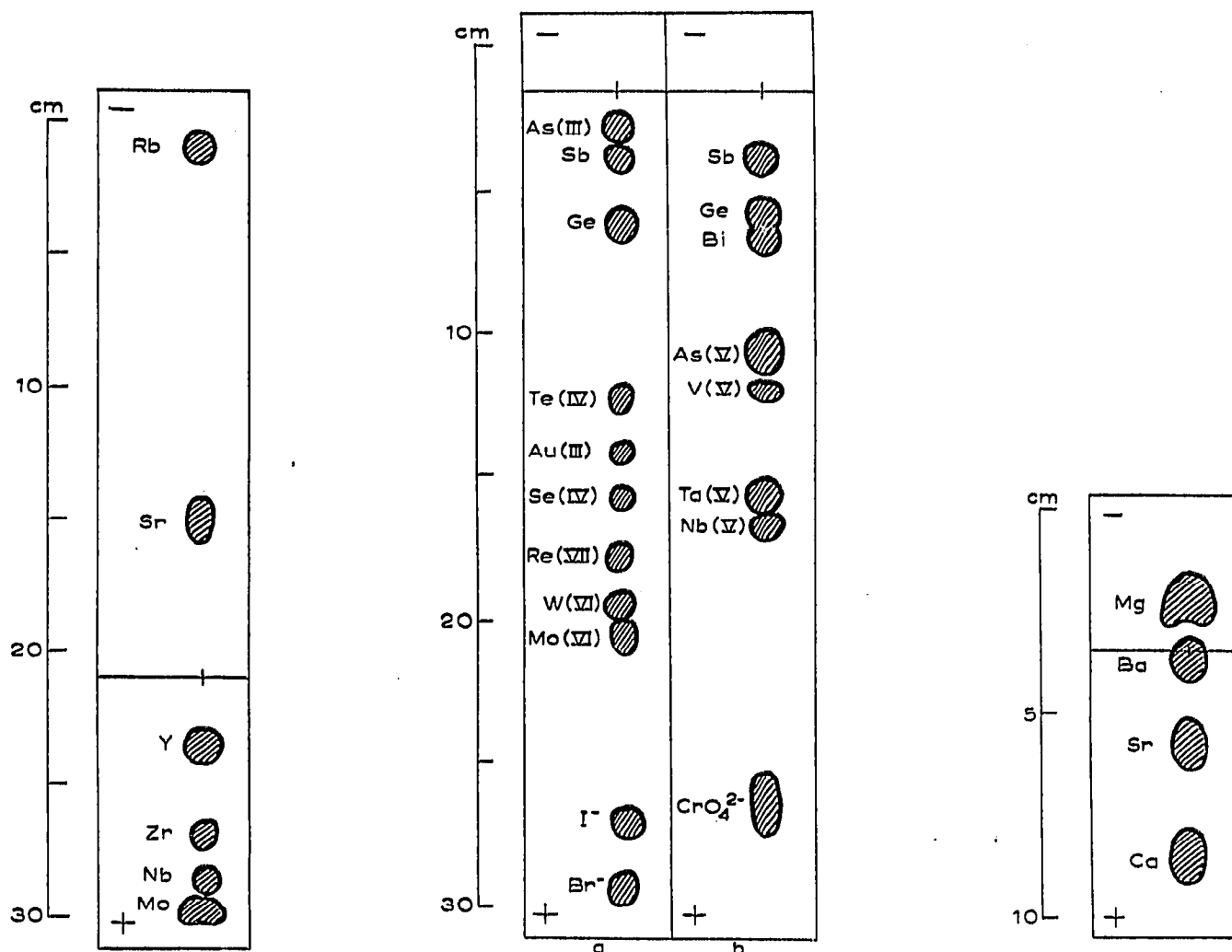


Fig. 5. Separation at pH 5.5. Time: 1 h. Potential gradient 15 V/cm.

Fig. 6. Separations at pH 9. Time: 1.5 h. Potential gradient 15 V/cm.

Fig. 7. Separation at pH 10. Time: 1 h. Potential gradient: 15 V/cm.

Separation in a neutral solution

The separation of adjacent elements of the periodic system, which possess quite different complexing abilities with HIDA, sometimes succeeds in an approximately neutral solution. A separation of a mixture of the period 5 elements, from Rb up to Mo, in an HIDA solution at pH 5.5 is shown in Fig. 5.

Separation in an alkaline solution

The second buffering range of HIDA (about pH 9) appears to be suitable for separations of some anions. Fig. 6 shows such combinations. It is possible to separate the adjacent group elements As–Se–Br and Sb–Te–I, as well as being able to carry out separations of elements one from another within a periodic group, although the separation molybdate–tungstate is rather incomplete and when the behaviour of a mixture of the group V homologues was investigated, the separation of tantalate–niobate did not succeed very well (Fig. 6b).

The alkaline earth elements can be separated one from another (Fig. 7) under these conditions, as calcium forms the most stable complex and magnesium the weakest.

It can be concluded that HIDA possesses an exceptional place in inorganic electrophoretic separations because of its efficiency and universality. Good results could be expected from other hydroxy-aminoacids with a favourable arrangement of donor functional groups. Our investigations in this direction are continuing.

SUMMARY

N-(2-Hydroxyethyl)iminodiacetic acid (HIDA) is a very suitable complexing agent for paper electrophoretic separations of inorganic ions. It is fairly soluble even in an acidified aqueous solution. Its complexes migrate as well defined zones with different mobilities, depending on their stability. The electrophoretic behaviour of 64 inorganic ions in solutions of HIDA as a function of pH value was studied (electrophoretic mobility curves). Separation at pH 2–3 yields the best results for many metal ions; some further separations succeed in an alkaline solution (pH 9–10). Examples of separations of a number of model mixtures are given.

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