Electromigration Method in Tracer Studies of Complex Chemistry. I. General

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The method of electromigration in the study of complex chemistry is presented. The physical factors influencing the migration are treated in detail with reference to measured data. In addition to offering a possibility of studying both trace and macro amounts of metal, electromigration has the advantages of being a direct method, measuring the average ionic charge and dimensions, and of being sensitive to both weak and strong interactions. Equations for calculating formation constants and hydration numbers, based on the estimation of the migration velocity for a given species, are given. A model for correlating the transport properties of $+1$, $+2$, $+3$ and $+4$ ions with ionic charge and radius is also presented.

The method of electromigration is based on the measurement of the average velocity obtained by a metal ion moving in a solution under the force of an applied electric field. The variation in velocity with the introduction of a complexing agent reflects possible changes in charge and size, allowing the species to be characterized.

Although the electromigration method has been employed for some 20 years for quantitative studies in complex chemistry, it has not gained very extensive use. The majority of the published work, including the first studies, has been made in the field of radiochemistry, especially for the actinides, by Soviet scientists as reviewed by Makarova and Stepanov.[1] Electromigration was used not only for the investigation of complex equilibria in solution but also as a tool for studying the kinetics of reactions. It is somewhat surprising that this method has been utilized so little considering its unique advantages of (1) directly measuring the mean physical properties z (charge) and r (radius), (2) its applicability to both very

strong and very weak complexation (interactions), and (3) its applicability of even sub-micro amounts of the metal (10−100 detected atoms). The various other methods used in complex chemistry[2−4] utilizes some other physical property that the particular species may have, allowing z or some related function like n (mean ligand number or formation function) to be deduced. In this respect only electromigration or similar methods can be classified as direct.

Electromigration methods are sometimes criticized because of difficulties encountered in interpreting the results. Studies reported in the literature do not give a satisfactory description of the experimental variables. There are many factors influencing the migration, e.g., the choice of support (paper, glass fibers, gel, etc.), viscosity of the electrolyte, and extent of hydration. It is felt that the electromigration method has received less attention that it deserves, and it is the purpose of this work to show the usefulness of the method. The experimental factors inluencing the migration velocity are thoroughly treated, and the basic laws are tested with various transport data. Finally, a method for calculating formation constants is presented based on an estimation of the migration velocity for a given species. The composition of the existing species can also be predicted.

EXPERIMENTAL

Description of apparatus. The apparatus used for the electromigration studies is shown in Fig. 1. It consists of a brass support for 1−4 paper strips and electrolyte compartments. The brass support is internally channeled for water cooling. The top surface is milled planar to ± 0.01 mm and is
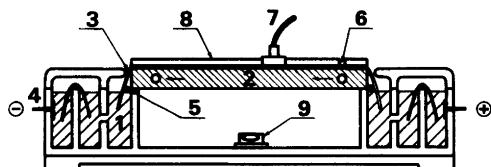
Fig. 1. Electromigration apparatus. (1) electrolyte, (2) watercooled brass support, (3) filter strip, (4) working electrode, (5) platinum wire, (6) sample introduction, (7) surface-barrier detector, (8) cover, (9) $x - y$ level indicator.

covered/insulated with a sprayed acrylic layer plus a self-adhesive vinyl film (0.02 mm). The electrolyte compartments are divided by plexiglass baffles into three sections. Liquid contact between the sections is provided by 5 mm Ø holes plugged with paper and by filter-strip bridges. Two sizes of compartments were used, 60 ml (2 × 3 × 10 cm) and 600 ml (2 × 3 × 100 cm). A potential of 100 − 500 V was applied across platinum electrodes inserted into the outer electrolyte compartments. The potential gradient across the paper strips was accurately measured over thin Pt-wires attached to the paper strip ends. The paper strips were enclosed under a cover of either 10 mm plexiglass or a thin acrylic plastic film (0.05 mm). At the beginning of an experiment 20 mm wide paper strips were firmly applied to the brass support with a little silicone high-vacuum grease at the ends of the paper. Vacuum grease was also spread in a thin layer parallel to the strips, preventing possible lateral flow of the electrolyte. The strips were marked (starting point) and were totally enclosed, except for a 5 mm Ø hole for sample loading. After the electrolyte was added, the paper strips were wetted for 10 − 30 min, depending on the viscocity. Another 20 − 40 min was used to allow the establishment of equilibrium before the samples (5 − 20 μl) and voltage were applied. A power supply delivering a constant potential 0 − 500 V (0 − 500 mA) was used. The potential across the paper strip was constant within ±0.3 % and the cooling water temperature was thermostated to ±0.1 °C.

Effects of the electrolysis on the electrolyte. Application of a potential over the outer electrolyte compartments produced hydrogen ions at the anode and hydroxyl ions at the cathode by electrolysis. In order to prevent changes in the composition of the electrolyte around the ends of the filter strip, the inner electrolysis compartments were separated by two baffles. The effectiveness of this arrangement was demonstrated by determining changes in H^+ in the electrode compartments after high current electrolysis. Even though considerable changes in pH might occur at the electrodes, there were only negligible effects in the inner compartments so that

the pH could be held constant to within ±0.01 unit also for neutral solutions. Furthermore, it was observed that the paper strip itself acts as a baffle arrangement. The pH on the strip, measured directly with a flat-bottom-type glass electrode, was nearly constant even if the pH in the inner compartments would be altered. The reason for this is that the mass transport of the anions (ClO_4^- and OH^-) and cations (H^+ and Na^+) is constant during the electrolysis and hence the electrolyte composition at any point on the strip remains the same.

Choice of paper. Primarily, the filter paper serves as a support material for the electrolyte during the electromigration, but certain other properties are also required. The time needed to move ions an appreciable distance should be minimized so that the effect of the electrolysis on the electrolyte can be neglected and so that short-lived nuclides will not disappear by decay. Also, the electrical resistance of the paper soaked with electrolyte should be as high as possible because the total heat that can be removed by water cooling, without an increase in temperature is limited to approx. 25 W per 20 mm wide paper strip. Furthermore, the surface density must be kept as low as possible so that α-particles can be detected. For the above reasons, a thin and fast (porous) filter paper, Whatman 41 (0.19 mm, 91 g/m² dry, 150 g H_2O ads/m²) was chosen. Glass-fiber papers were generally too thick and absorbed too much electrolyte. However, Whatman GF/A glass microfiber paper (0.25 mm, 52 g/m² dry, 275 g H_2O ads/m²) was also used. Thin-layer cellulose, backed by plastic films, might offer possibilities for rapid electromigration but it was considered to be less advantageous under the present conditions.

Nuclides and chemicals. All nuclides were radiochemically pure and were normally prepared as 10^5 dpm/ml in 0.1 M $HClO_4$. When required, the sample, 10 − 20 μl, was evaporated to dryness and the activity dissolved in 10 μl of electrolyte before application. The electrolyte was made by weighing 8 M $NaClO_4$, purified as previously,[5] and 12 M $HClO_4$ stock solutions, and diluted to appropriate volume. All other reagents were of p.a. grade and used without further purification. pH measurements were made with a modified glass-calomel combination electrode.[5]

Counting techniques. The distribution of radioactive nuclides along the electrophoresis paper was measured by both a continuous (A) and a discontinuous (B) method:

(A) A surface-barrier detector placed over the paper strip covered with the plastic film made it possible to detect α-particles from the migrating ions (Fig. 1). The counting efficiency was low, 1 − 10 %, requiring around 10^2 dpm to 10^4 dpm for the determination of the center and leading positions, respectively, with an accuracy of 1 %. The detector

was placed 5 – 10 mm in front of the approaching leading boundary and the pulse-time events while the sample passed were recorded. Then the procedure was repeated up to 20 times for a run. The centre position corresponded to the maximum pulse rate, and the time at which the leading boundary passed the detector was arbitrarily taken as the event of the 10th recorded pulse.

(B) In the case of using a mixture of nuclides of very low activities, $<10^2$ dpm of α, or using β- or γ-emitting nuclides, method (A) was not applicable. The filter paper was instead dried and cut into 5 or 10 mm sections. These strips were then analyzed for their radioactive content with various suitable detectors (Intertechnique automatic scintillation counter or Ge(Li) gamma-spectrometer, a set of surface barrier detectors for alfa-spectroscopy and gas-proportional detectors for beta-analysis). In case of alfa-spectroscopy the nuclides were transferred from the strip cuts into mass-free samples.

Viscosity measurements. The viscosity η of the perchlorate media used was measured by Ostwald's capillary method, using an Ubbelohde viscosimeter. The time t required for a known volume of solution (density ρ) to discharge through a capillary under the force of its own weight was calculated as $\eta = \rho t \eta_{H_2O}/(\rho_{H_2O})$.

MIGRATION IN NON-COMPLEXING MEDIA

The velocity (v) acquired by a spherical ion with an appreciably large radius (r) moving in an ideal hydrodynamic continuum with the viscocity (η) under the influence of the force (F) was calculated by Stokes:[6]

$$v = F/(6\pi\eta r) \tag{1}$$

The force exerted on the ion of charge (ze) by the electric field (E) is $F = E|z|e$, and hence the radius is:

$$r = E|z|e/(6\pi\eta v) \tag{2}$$

For aqueous solutions it has been shown that Stokes' law gives somewhat too large calculated radii for ions with hydrated radii smaller than 5 Å. Nightingale, however, has developed a method for correcting the calculated Stokes' law radii r_s into proper hydrated radii r_h.[7] For many metal ions the correction is rather small, e.g., 12 % for the lanthanides, but is increasingly important for less charged ions (see Table 1). The dimension of an hydrate ion, which is one of its most important physical properties, can thus be measured quite conveniently. Its corresponding hydration number h is then simply obtained by division of the hydrated volume by the volume of one water molecule.

Measurement of the free migration velocity $v°$ must be made in infinitely diluted aqueous solutions and without support matrix (paper etc.). For this purpose conductivity measurement are valuable. Although conductivity measurements only give the sum of cations and anions, single ion conductivities $\lambda°$ can be calculated from several experiments. Stokes' law for the limiting molar conductivity $\lambda°$ has the form:

$$\lambda° = |z|F^2/(6\pi N\eta° r) \tag{3}$$

Table 1. Correction factors for transforming Stokes' law radii r_s into true hydrated radii r_h, for some metal ions.

Metal ion	$\lambda°$ [a] cm² Ω⁻¹ ekv⁻¹	r_h Å	r_h [b] Å	Correction factor r_s/r_h
Li⁺	38.68	2.37	3.77	1.59
Na⁺	50.10	1.83	3.52	1.92
K⁺	73.5	1.25	3.25	2.08
Rb⁺	77.8	1.18	3.24	2.75
Cs⁺	77.3	1.19	3.24	2.72
Be²⁺	45	4.08	4.58	1.12
Mg²⁺	53.1	3.46	4.28	1.24
Ca²⁺	59.5	3.09	4.10	1.33
Sr²⁺	59.5	3.09	4.10	1.33
Ba²⁺	63.6	2.88	4.02	1.39
La³⁺	69.75	3.95	4.52	1.14
Eu³⁺	67.8	4.08	4.61	1.13
Yb³⁺	65.6	4.21	4.63	1.10

[a] Limiting molar conductivity, Ref. 14. [b] Corrected according to Ref. 7.

where F is Faraday's constant and N is Avogadro's number.

Stokes' law enables us to calculate the hydrated radius, but it cannot be used to predict $v°$ or $\lambda°$. In order to accomplish this, we must obtain a relation between the hydrated radius and a common and independently derived radius. It would therefore be useful if r_h could be related to the crystal radius r_c by a simple electrostatic model. Stokes has convincingly shown that accurate ($\pm 2\%$) values for various properties of $+1$, $+2$ and $+3$ ions, having noble gas electronic structure, can be calculated using a refined electrostatic model.[8,9] Values of van der Waal's radius, electrostatic self energy for gaseous and aqueous ions, free energy of hydration, and crystal lattice energies were derived. Here, however, no exact calculations will be made since it would be very complicated and the general trend would be hidden. We will instead proceed as follows. The r_h of hard ions can be related to the entropy change of hydration ΔS_h since the loss in freedom for the h water molecules, when bonded by the metal, is proportional to the entropy change. The hydrated volume of the metal is assumed to be equal to the bonded water molecules, neglecting the volume of the naked metal ion:

$$r_h^3 \sim \Delta S_h \qquad (4)$$

Now, ΔS_h can be shown to be proportional to z^2/r_c, either by plotting experimental data or by the following derivation. The ΔS_h is obtained by differentiating the free energy of hydration ΔG_h with respect to temperature. ΔG_h can in its turn be estimated from the electrostatic self energy of the gaseous ion since this is the dominating term (80 -90%).[8] The Born equation gives:[8]

$$-\Delta G_h = \frac{Nz^2 e^2}{2r_v \varepsilon} = \frac{694.8 z^2}{r_v} \text{ (kJ mol}^{-1}\text{ Å)} \qquad (5)$$

where r_v is the van der Waal's radius and ε is the dielectric constant, resulting in

$$\Delta S_h \sim \frac{z^2}{r_v} \qquad (6)$$

Combining eqn. (6) and eqn. (7), we obtain the relation

$$r_h \sim z^{2/3} r_v^{-1/3} \qquad (7)$$
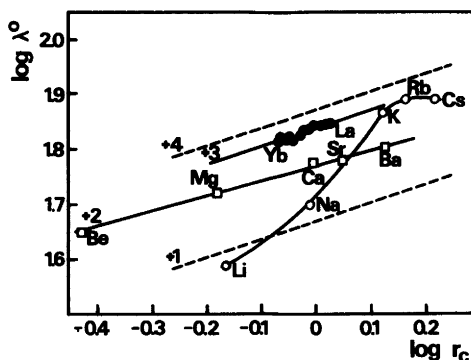
which inserted in Stokes' law gives

Fig. 2. Limiting molar conductivity $\lambda°$ of momo-, bi-, and trivalent ions as a function of the crystal ionic radius r_c. The relations between $\lambda°$ and r_c shown for the lanthanide ions ($+3$) and the Group IIA ($+2$) ions follow closely the expression $\lambda° = \text{const. } |z|^{1/3} r_c^{1/3}$. The broken lines show the expected function for the Group IA ($+1$) ions and the predicted function for $+4$ ions, respectively.

$$v° \text{ or } \lambda° \sim z^{1/3} r_v^{1/3} \qquad (8)$$

Although the use of van der Waal's radius in eqn. (8) is more correct, the use of the crystal radius would be more convenient. The relation with the crystal radius is expected to be similar even if the ratio r_c/r_v varies somewhat.

The relation found in eqn. (8) can be tested by plotting experimental values of $\log \lambda°$ versus $\log r_c$ for Group IA, IIA, and the trivalent lanthanides (Fig. 2). The $2+$ and $3+$ ions behave very regularly and the powers of z and r_c obtained from the slopes and distances in Fig. 2 are close to the predicted ones:

$$\lambda° \sim z^{0.36} r_c^{0.30} \qquad (9)$$

The $+1$ ions deviate, however, especially the largest ions (K^+, Cs^+ and Rb^+), from the calculated values represented by the broken line in Fig. 2. This should be expected because these ions have too small hydrated radii to obey Stokes' law. The difference in expected and actual hydrated volume quantitatively explains the deviation in Fig. 2. Although only some ions, isoelectronic with the noble gas ions, have been treated, the relation of eqn. (8) should be valid, at least for hard cations, but probably also for all other ions because every aqueous ion is hydrated to a large extent. In fact, soft metal ions for which data were avaulable did fit Fig. 2 (Ag^+, Tl^+, Cu^{2+}, Zn^{2+}, Co^{2+} and Pb^{2+}). Furthermore, the anions F^-, Cl^-, Br^-
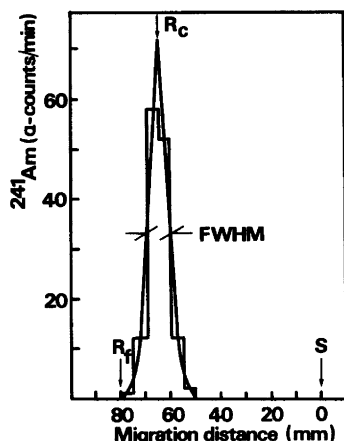
Fig. 3. Distribution of Am^{3+} along the filter strip following electromigration in 1 M (0.1 H, 0.9 Na)ClO_4 at 25 °C. R_f = front boundary, R_c = peak maximum, FWHM = full width at half maximum, S = start.

and I^- behave in analogy with the $+1$ Group IA elements, but the deviations are somewhat smaller and shifted towards larger r_c.

MIGRATION IN MATRIX

Various kinds of support material can be used, e.g., filter paper, glass fibers, and quartz powder, but here we will mainly deal with filter paper. It was observed that the distribution of the migrating ions always closely resembled that shown for Am^{3+} in Fig. 3. The

shape of the peak appeared nearly the same for different perchlorate compositions and ionic strengths. Thus the ratios of the full width at half maximum (FWHM) and the leading boundary position (R_c) to the peak maximum (R_c) were constant. R_c values are used in this report. The spreading across the 20 mm wide strips was found to attain an even distribution as the distance travelled became appreciable. The presence of the support material will reduce the electromigration velocity. The obstruction coefficient p is defined as the ratio between the observed migration velocity v_{obs} and the free migration velocity $v°$;

$$p = v_{obs}/v° \qquad (10)$$

If p is a constant for a given matrix, then v_{obs} should obey Stokes' law in the usual way. In order to investigate the validity of eqn. (10) we performed the following tests.

Ion properties. For an inert matrix there should be no variation in p with the ion properties (z and r). We have compared our observed electromigration velocities with free migration velocities for a number of elements of charge $+1$, $+2$ and $+3$ for which conductivity data exist (Table 2). The calculated values of p are constant (within experimental and extrapolation uncertainties), 0.66 ± 0.07, for the tested ions. Hence, all ions seem to be equally affected by the filter paper matrix. This conclusion is in good agreement with conductance measurements of various electrolytes in a comparable type of filter paper, from which it was derived that $p=0.57 \pm 0.01.$[10] Furthermore, it was assumed that the

Table 2. The relation between the observed electromigration velocities v_{obs} and the limiting molar conductivity $\lambda°$. Whatman 41 filter paper, 7.94 V/cm and 25 °C.

Element	r_c Å	v_{obs} 0.1 M NaClO$_4$ mm/min	1 M NaClO$_4$ mm/min	H$_2$O [a] mm/min	$\lambda°$ H$_2$O [b] cm$^2\Omega^{-1}$ekv^{-1}	H$_2$O [c] mm/min	p H$_2$O
Na$^+$	0.97	1.80(5)	1.58(5)	2.02(10)	50.10	2.47	0.77(5)
Ag$^+$	1.26	1.71(6)	1.26(5)	1.91(10)	61.9	3.06	0.62(5)
K$^+$	1.33	2.38(9)	1.88(6)	2.52(10)	73.50	3.63	0.69(5)
Cs$^+$	1.67	2.43(9)	1.93(7)	2.65(10)	77.2	3.81	0.70(4)
Ca^{2+}	0.99	1.76(6)	1.19(6)	2.00(10)	59.5	2.94	0.68(4)
Sr^{2+}	1.12	1.76(6)	2.10(8)	1.62(10)	59.4	2.93	0.58(7)
Eu^{3+}	0.95	1.80(5)	1.46(5)	1.95(10)	67.8	3.34	0.59(5)
						Mean:	0.66(7)

[a] Extrapolated, using Jones-Doles equation. [b] Ref. 15. [c] $v° = 0.0494 \times \lambda°$ (at 7.94 V/cm).
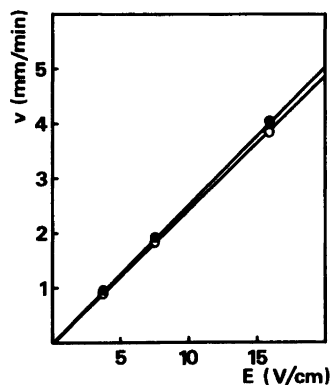
Fig. 4. Effect of electric field strength E (V/cm) on electromigration velocity v (mm/min) in 0.1 M $HClO_4$ at 25 °C. (●) denotes $^{241}Am^{3+}$ and (○) $^{22}Na^+$.

obstructive factors are the same for all ions.[11] A few experiments were made with glass fiber filter paper Whatman GF/A, and they all showed very similar migration velocities as for the cellulose paper Whatman 41.

External variables. The migration velocity was found to be proportional to the *electric field* by varying the applied potential in the range of 0 – 15 V/cm. The experiments were carried out with Am^{3+} in 0.1 M $HClO_4$, giving a linear correlation with E (Fig. 4).
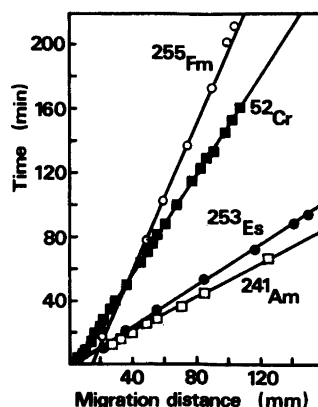

Fig. 5. The front boundary migration of Cr^{3+}, Am^{3+}, Es^{3+} and Fm^{3+} as a function of time during electromigration in perchlorate media at 25 °C. Due to diffusion/mixing during the sampling, the straight lines do not necessarily go through origo. (□) ^{241}Am and (●) ^{253}Es in 1 M (0.1 H, 0.9 Na)ClO_4, (■) ^{52}Cr (2 μl 1 M Cr^{3+}) in 4.7 M (0.1 H, 4.6 Na)ClO_4 and (○) ^{255}Fm in 8 M (0.1 H, 7.9 Na)ClO_4.

Strict linearity ($\pm 1 \%$) of the migrated distance *vs. time* was found for Cr^{3+}, Am^{3+}, Cm^{3+}, Es^{3+} and Fm^{3+} for all tested electrolytes. The migration was followed by a determination of the front, visually (Cr^{3+}) or with an α-surface barrier detector, and a typical result is shown in Fig. 5. The *temperature*

Table 3. Viscosity of perchlorate solutions relative to H_2O at 25 °C.

Solution	Viscosity rel. H_2O [a] ($\sigma = \pm 0.010$)			ρ g/ml ($\sigma = \pm 0.005$)
0.5 M (0.1 H, 0.4 Na)ClO_4	1.022			1.041
1 M (0.1 H, 0.9 Na)ClO_4	1.032			1.075
2 M (0.1 H, 1.9 Na)ClO_4	1.151			1.163
3 M (0.1 H, 2.9 Na)ClO_4	1.305			1.228
4 M (0.1 H, 3.9 Na)ClO_4	1.570			1.298
4.5 M (0.1 H, 4.4 Na)ClO_4	1.846			1.330
5 M (0.1 H, 4.9 Na)ClO_4	2.003			1.375
6 M (0.1 H, 5.9 Na)ClO_4	2.554			1.456
7 M (0.1 H, 6.9 Na)ClO_4	3.248			1.509
8 M (0.1 H, 7.9 Na)ClO_4	5.034			1.587
0.1 M $HClO_4$	1.024			1.012
1 M $HClO_4$	0.988	1.0065 [b]		1.060
0.1 M $NaClO_4$	1.011			1.005
1 M $NaClO_4$	1.036	1.0369 [b]	1.049 [c]	1.077
2 M $NaClO_4$	1.140	1.150 [c]		1.143
3 M $NaClO_4$	1.302			1.218

[a] $\eta_{H_2O} = 0.8903$ centipoise at 25 °C, Ref. 15. [b] Ref. 16. [c] Ref. 13.

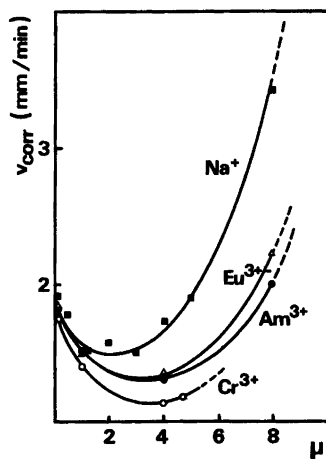*Fig. 6.* Migration velocities corrected for the influence of viscosity ($v_{corr} = v \times \eta/\eta°$) as a function of ironic strength μ. 0 – 8 M (Na,H)ClO$_4$ at pH 1 and 25 °C. (■) ^{22}Na$^+$, (△) $^{152/154}$Eu^{3+}, (●) ^{241}Am^{3+} and (○) ^{nat}Cr^{3+}.

dependency was not investigated. The main effect will probably be due to the simultaneous change in viscosity.

Bulk properties. The *viscosity* of the electrolyte was varied by varying the sodium perchlorate concentration in the range 0.1 to 8 M (see Table 3). The migration velocity can be normalized by multiplying by the viscosity, and the product $v\eta/\eta°$ is shown as a function of the ionic strength for Na$^+$, Cr^{3+}, Eu^{3+} and Am^{3+} in Fig. 6. According to Stokes' law, the value of the product $v\eta/\eta°$ should be constant. However, this is not the case as is apparent from the figure. The deviations are due to weak interactions with the electrolyte ions, such as ion-pair formation with ClO$_1^-$ and loss of water molecules from the metal ions.[12] The influence of the salt concentration follows the Jones-Doles law for conductivities, as can be seen from Fig. 7. The migration velocities are linear functions of $\sqrt{c}$, c being the molar electrolyte concentration. The mobilities of ions in relation to the viscosity of electrolytes has been reviewed by Stokes and Mills.[13]

MIGRATION OF COMPLEX IONS

The introduction of a complexing agent X^{a-} will produce complexes with the metal cation M^{m+} according to the reaction equilibria

$$M^{m+}(aq) + iX^{a-}(aq) \rightleftharpoons MX_i^{z_i+}(aq) + lH_2O \qquad (11)$$

with the corresponding formation constant β_i and where l is the number of released water molecules. Polymeric species are not taken into account here but may be included. The migration velocity v_i of the complex MX$_i^{z_i+}$(aq) will depend upon its charge z_i ($= m - ia$) and its total hydrated volume V_i as obtained from Stokes' law. Comparing the migration velocity to that of the uncomplexed metal ion, we find that the charge is the dominating factor (see Table 4). Experimental values of the relative migration velocity for a number of metal complexes are compared with their relative charge z_i/m. In most cases the correlation between the migration velocity v_i and the charge z_i is within 20 %, but rather large deviations (up to 60 %) may be found.

Estimating the migration velocity. It seems appropriate to introduce the following relation

$$v_i = f_i v \qquad (12)$$

where the coefficient f_i can be divided into two factors, the charge ratio z_i/m and the volume factor g_i

$$f_i = \frac{z_i}{m} g_i \qquad (13)$$

Experimentally obtained values of the coefficients g_i vary from 0.6 to 1.2 with an average of 1.0 ± 0.2 as can be seen from Table 4. The values of g_i can be calculated from Stokes' law as follows:
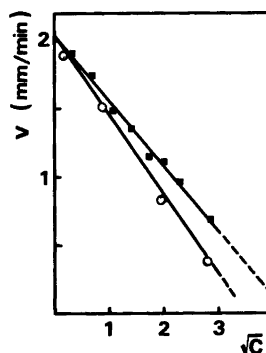
$$g_i = r_h/r_{h,i} = (V/V_i)^{1/3} \qquad (14)$$

Fig. 7. Jones-Doles plot of the migration velocity v *versus* the square root of the electrolyte concentration $\sqrt{c}$. 0.1 – 8 M (Na,H)ClO$_4$ at pH 1 and 25 °C. (■) denotes ^{22}Na$^+$ and (○) ^{241}Am^{3+} (or $^{152/154}$Eu^{3+}).

Table 4. Relation between the migration velocities v and v_i, of a given metal ion (M^{m+}) and its complex ($MX_i^{z_i+}$), and their respective charges. The ratio v/v_i is calculated from data for a number of metal-ligand systems under various conditions (ionic strength, temperature, *etc.*). $v_i = vf_i$, where $f_i = z_ig_i/m$.

Metal and ligand	Complex, $MX_i^{z_i+}$	$v/v_i = \dfrac{1}{f_i}$	m/z_i	$\dfrac{(v/v_i)}{(m/z_i)} = \dfrac{1}{g_i}$	Ref.
Mn^{2+}, CH_2NOH (formaldoxime)	$Mn(CH_2NO)_3^-$	-2.3	-2	1.15	17
Fe^{3+}, CH_2NOH	$Fe(CH_2NO)^{2+}$	2.12	1.5	1.41	17
	$Fe(CH_2NO)_4^-$	-2.65	-3	0.88	17
	$Fe(CH_2NO)_5^{2-}$	-1.41	-1.5	0.94	17
	$Fe(CH_2NO)_6^{3-}$	-0.85	-1	0.85	17
Ln^{3+}, H_4Y (ethylenediamine-tetraacetic acid)	LaY^-	-3.19	-3	1.06	18
	PmY^-	-3.02	-3	1.01	18
	EuY^-	-2.99	-3	1.00	18
	CeY^-	-3.19	-3	1.06	18
Y^{3+}, H_4Y	YY^-	-2.99	-3	1.00	18
Co^{2+}, H_4Y	CoY^{2-}	-1.63	-1	1.63	17
UO_2^{2+}, $H_2C_2O_4$ (oxalic acid)	$UO_2(C_2O_4)_2^{2-}$	-1.00	-1	1.00	20
Tl^+, $H_2C_2O_4$	$Tl(C_2O_4)^-$	-0.93	-1	0.93	21
Cu^{2+}, $H_2C_2O_4$	$Cu(C_2O_4)_2^{2-}$	-1.17	-1	1.17	17
Ln^{3+}, H_2tar (tartaric acid)	$Ce(tar)^+$	2.57	3	0.86	22
	$Ce(tar)_2^-$	-2.49	-3	0.83	22
	$Eu(tar)^+$	2.48	3	0.83	22
	$Eu(tar)_2^-$	-2.45	-3	0.82	22
Am^{3+}, H_2CO_3 (carbonate)	$Am(CO_3)_2^-$	-3.7	-3	1.2	12
Am^{3+} and Cm^{3+}, H_8A (ethylenediaminetetra-methylphosphonic acid)	$An(H_2A)^{3-}$	-1.03	-1	1.03	23
	AnA^{5-}	-1.65	-1.67	0.99	23
Ce^{3+}, H_8A	$Ce(HA)^{4-}$	-1.41	-1.33	1.05	23

where V and V_i are the total hydrated volume of M^{m+} and $MX_i^{z_i+}$, respectively.

The crucial point is now to estimate V_i, which may be done in several ways, depending on the specific metal-ligand system. Different approaches should be used to ascertain optimal predictability for each individual case depending on the information available, *e.g.* physical properties and general basic chemical considerations such as class of reaction (inner or outer sphere), *etc*. If the volume V_i is not directly available from a corresponding plateau in the electromigration diagram, then it can be estimated in one of the following ways:

(a) Assumption of additivity of the volumes in the reaction. According to eqn. (11), we have

$$V_i = V + iV_x - l_iV_{H_2O} \qquad (15)$$

Very accurate additivity is often found for electrostatic models,[9] and hence V_i can be calculated from estimated l_i values (V and V_x are assumed to be directly measured). For outer sphere reactions l_i might be around 1 to 3, whereas a complete dehydration may occur for inner-sphere complexation. l_i can also be calculated from the entropy change ΔS of the reaction, eqn. (11).
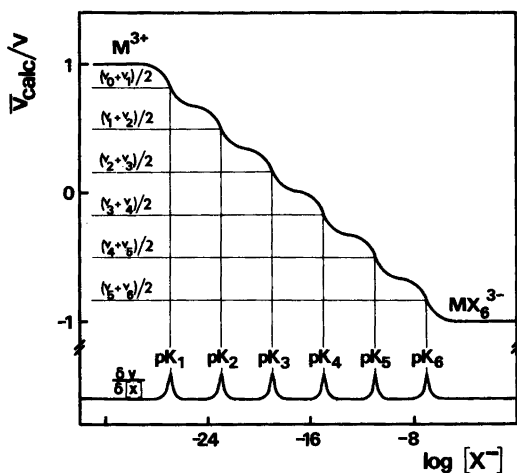
(b) Use of some semiempirical relation. Jokl has

Fig. 8. General electromigration diagram. The calculated average relative migration velocity $\bar{v}_{calc}/v$ for the metal M(III) is shown as a function of the ligand concentration log $[X^-]$. Numerical values of pK_n for the complex formation, MX_{i-1}^{2-i} $+[X^-]\rightleftharpoons MX_i^{3-i}$, can be found by using the derivative $\delta v/\delta[X^-]$ or the average velocity of two consecutive complexes $(v_{i-1}+v_i)/2$.

found the relation $v_i/z_i = A\sqrt{M}+B$, where A and B are constants and M is the molecular weight. This relation has a variation coefficient of only $\pm 8.6\%$ for organic ions and metal complexes.

(c) Comparison with similar complexes of known hydrated volumes.

CALCULATION OF COMPLEXES

The average migration velocity of the metal in the presence of a complex forming agent X^{a-} can be calculated as the sum of the velocities of the individual species $MX_i^{z_i+}$ weighted with their relative concentration

$$\bar{v}_{calc} = \frac{\Sigma v_i[MX_i^{z_i+}]}{[M]_{total}} \qquad (16)$$

Inserting the relative migration coefficients f_i, eqn. (12), and the formation constants β_i, eqn. (11), we obtain

$$\bar{v}_{calc} = v\left[\frac{1+\Sigma f_i\beta_i[X^{a-}]^i}{1+\Sigma\beta_i[X^{a-}]^i}\right] \qquad (17)$$

By solving a set of equations of calculated and observed average migration velocities, the formation constants will be numerically determined. An especially suitable form of eqn. (17) is the dimensionless relative average migration velocity $(\bar{v}_{calc}/v)$.

The general picture of the migration diagram is shown in Fig. 8, where the migration velocity has been calculated using eqn. (17) as a function of $-\log[X^{a-}]$. In the example given it is assumed that a trivalent metal ion M^{3+} is complexed with a monovalent anion X^- through six consecutive steps, from MX^{2+} to MX_6^{3-}. The coefficients g_i are taken as unity for the sake of simplicity. The curve gives a considerable amount of information. Every species that dominates in some region is unambiguously identified by its plateau. Also, the stepwise formation constants K_n

$$MX_{i-1}^{(z_i-1)+} + X^{a-} \rightleftharpoons MX_i^{z_i+} \qquad (18)$$
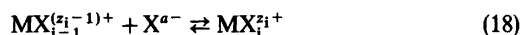
can easily be estimated from the positions of the inflection points between the plateaus. The corresponding value on the $-\log[X^{a-}]$ axis numerically gives pK_n. The derivative of the migration curve makes it easier to find the inflection points and the peaks correspond to pK_n. The values of pK_n can also be obtained from the intersection of the curve with the average relative migration velocities of two consecutive species $(v_{i-1}+v_i)/2$.

DISCUSSION

The use of electromigration offers several advantages compared with the classical conductivity method. Most important is that it permits direct measurement of the transport properties of an ion or complex and that it can be done in the presence of any other ions. Conductivity, however, is a measure of the combined transport properties of all ions present in the solution, both negative and positive. The usefulness of conductivity in complex chemistry studies is therefore very limited. The ligand can not be varied independently of the metal and almost zero ionic strength is required as no electrolyte ions, other than the metal salt, must be present.

The applicability of the electromigration method to any electrolyte system opens possibilities for advanced complex chemistry studies. The state of the ion, its thermodynamics, and the kinetics of complex formation can be determined. Both very strong

interactions, like complex formation with chelating agents, and very weak interactions, like ion-pair formation and van der Waal's forces, can be studied. Ion-pair formation is easily detected by the electromigration method since uncharged ion pairs have almost zero migration velocity. All transport methods are potential sources of information about the extent of solvation of cations because the transport properties depend on the effective size of the solvated ion. Knowledge of the effective solvation is essential for the determination of the entropy of the ion and for its reactions. Electromigration is therefore probably one of the best methods for studying thermodynamic hydration numbers h. Other methods, which are sensitive to a part of the hydration sphere only, $e.g.$, the inner solvation sphere, do not provide information on h. Another important advantage is that extremely small metal quantities can be used. In fact, the migration velocity can be determined to within $\pm 10\%$ with as little as 10 to 100 detected atoms. The maximum of the migrating zone (Fig. 2) is easily determined at any detectable concentration of the metal. The accuracy can be improved to $\pm 1\%$ by the use of a sufficiently large number of detected atoms in combination with an internal standard, $e.g.$, ^{22}Na, $versus$ which relative migration velocities are calculated.

For equilibrium studies there are some obvious requirements. Firstly, equilibrium must be attained rapidly in comparison with the migration velocity. If this is not the case, more than one migrating zone will be observed (useful for kinetic studies). Secondly, it is necessary that free ions, not ion pairs, are dominating. There are no problems with aqueous solutions but for non-aqueous systems this may be more troublesome, especially if the ionic strength is appreciable. For example, almost no migration of Am^{3+} was observed in 1 M perchlorate ethanolic solutions.[12] Thirdly, it is required that the sorption of the ions on the matrix material is negligible. However, in the neutral pH range there may be strong sorption, which has to be suppressed either by complexation or possibly by carrying out the experiments without a matrix.

The general electromigration curve $versus$ ligand concentration, as shown in Fig. 8, corresponds to ideal conditions with each stepwise complex dominating in a certain concentration range. Actually, the stepwise complex formation often proceeds gradually with several complexes coexisting so that no distinct plateaus for the intermediate complexes are obtained. Nevertheless,

examples with up to five plateaus can be found; Fe(III) formaldoxime (Table 4). The absence of distinct plateaus does not prevent derivation of formation constants, according to eqn. (17) or by using the average migration velocities $(v_{i-1}+v_i)/2$ of two consecutive complexes (Fig. 8), but the accuracy will be lowered since the migration velocities v_i then cannot be measured directly from the plateaus. The obtainable accuracy of the determined pK_n can be estimated to be around ± 0.07 units based on the inherent uncertainty in the migration velocities. The accuracy achievable by the electromigration method is thus quite comparable to other techniques available for tracer work (liquid − liquid partition, ion exchange, radiopolarography, cocrystallization, chromatographic methods, $etc.$).

It would be rather time consuming to obtain a complete curve in cases with so many plateaus as in Fig. 8 because every point requires one experiment. An automatization would here be of great value. An apparatus could be designed according to the following guidelines: The migrating zone is arranged as a column, which is automatically eluted and analyzed, or the voltage required to maintain a fixed position of the migrating zone in a moving electrolyte is determined.

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