

Dependence of the mobility of tracer ions in aqueous perchlorate solutions on the hydrogen ion concentration

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The dependence of the absolute individual ion mobility (AIIM) of the carrier-free radioactive ions [$^{137}\text{Cs}]\text{Cs}^+$, [$^{201}\text{Tl}]\text{Tl}^+$ and [$^{57}\text{Co}]\text{Co}^{2+}$ on the hydrogen ion concentration in aqueous perchlorate electrolyte mixtures was studied by means of the electromigration technique. The AIIM of the radioactive ions was found to decrease as the hydrogen ion concentration of the electrolyte mixture increases. Above $\text{pH} > 4$ there is a fairly good agreement between experimental and calculated values. Below $\text{pH} 4$ the experimentally observed decrease of the AIIM is not explained by the extended Debye–Hückel–Onsager limiting law. The effect can possibly be explained by a change of the dynamical properties of electrolyte bulk water due to the increasing presence of an excess of hydrated protons in the bulk solution. From the variation of the rotational reorientation time of bulk water molecules in HClO_4 electrolytes with the proton concentration, a value of 0.69 ps^{-1} is derived for the rate constant for proton transfer between the hydronium ions and the acceptor water molecules. For the proton hopping length a value of 2.46 \AA was found. These two values are in good agreement with the literature values. Finally, we propose a relation for mobility of tracer ions in HClO_4 electrolytes involving the proton hopping time and length.

I Introduction

All ions are hydrated in aqueous solutions and the extent of hydration together with the ionic charge play an important role in many chemical reactions. Thus the investigation of the structural and dynamical properties of hydrated ions in aqueous solutions is of fundamental importance in physical chemistry.

The static properties of hydration, *i.e.* the hydration numbers and distances between the ions and oxygen atoms of hydrated water molecules, as well as the dynamical properties, *i.e.* the residence time and rotational behavior of water molecules in the first hydration shell, have been extensively investigated using X-ray and neutron diffraction, X-ray extended absorption fine structure, nuclear magnetic resonance, quasi-elastic neutron scattering and molecular dynamic simulation. A recent compilation of the results gained by the techniques mentioned above may be found elsewhere.¹

Information on the dynamical properties of water molecules in the hydration shells of ions may also be deduced from the measurements of the transport properties of ions in solutions. The behavior of the limiting ionic mobility, u° , at zero concentration of added electrolyte reflects the complex relation existing between the water structure around the ion and the dynamics of ion-hydration. For a long time u° has been used as a probe to get insight into the dynamical aspects of ion–water interactions. Various theoretical models, from the initial solventberg model to molecular approach, have been employed to try to describe the dynamics of ions in solutions.^{2,3} More recently a self-consistent microscopic theory based on the microscopic version of the dielectric friction including rotational and translational friction of the solvent has been successfully employed to calculate the mobility of univalent ions in various polar solvents.^{4,5}

At non-zero electrolyte concentrations, the ion atmosphere relaxation and electrophoretic effects contribute to a decrease

of the ion mobility. In the range of very low electrolyte concentrations, the ion mobility is described without ambiguity by the well known Debye–Hückel–Onsager (DHO) limiting law.^{6,7} At higher electrolyte concentrations ($c \leq 0.2 \text{ mol dm}^{-3}$), an extension of the DHO limiting law based on the introduction of ion atmosphere parameters [see eqn. (11) in Section II B] leads to reasonable values for the ion mobility and diffusion coefficient for uni- and divalent ions in various neutral ($\text{pH} \sim 7$) aqueous electrolytes.^{8,9} Recent molecular dynamics simulations of NaCl and KCl solutions show that the decrease of the ionic diffusion coefficient at increasing concentrations is correlated with the increase of the residence time τ_r of water molecules in the hydration shell of the ions as well as with the decrease of the bulk water diffusion coefficient, $D_{\text{H}_2\text{O}}$.¹⁰ At low electrolyte concentrations the product $\tau_r D_{\text{H}_2\text{O}}$ is constant and the hydration number remains unchanged.

Most of the experimental and theoretical studies deal with the determination of the transport properties of ions in neutral aqueous electrolytes. Studies of the dynamical properties of ions in acidic aqueous electrolytes are scarce. In previous work,¹¹ the absolute individual ion mobilities (AIIM) of carrier-free trivalent lanthanide ions, determined by means of the electromigration method, were found to be influenced by the hydrogen ion concentration in aqueous $\text{HClO}_4 + \text{NaClO}_4$ solutions at constant overall ionic strength, $\mu = 0.1 \text{ mol dm}^{-3}$ and $T = 298.1 \text{ K}$. Although the macroscopic properties of the two electrolytes, such as viscosity and density, are very close, the values of the AIIM of the lanthanide ions in $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ were about 15% lower than those in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$. Thus transport of metal cations is affected by an excess of protons in the solution. The structure of acidic electrolytes is largely different from that of neutral electrolytes because the individual proton of the acid is directly transferred to a water molecule of the bulk and never returns as the nearest neighbour of its counter-ion.¹² The interaction of protons with water molecules leads to the formation of complexes of the

type H_5O_2^+ or H_9O_4^+ .^{13,14} It is also well established that the migration of the excess proton in water occurs *via* a process of structural diffusion (Grötthaus mechanism) in which charge transfer takes place through an interchange of covalent and hydrogen bonds.¹⁵ This mechanism is responsible for the proton's well known abnormally high mobility ($u_p = 36.24 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 298.1 \text{ K}$). Fundamental results on the dynamics of the proton transfer in water may be found elsewhere.^{16–24} Since protons migrate very rapidly, they continuously interact with a great number of water molecules, in turn affecting the dynamics of bulk water. As the dynamical properties of the bulk water are coupled with those of the water molecules in the hydration shell of the ions, a difference in the transport properties of the ions in neutral and acidic media may be expected.

In this paper, we investigate by means of the electromigration method the influence of the hydrogen ion concentration of chemically inert aqueous perchlorate electrolyte solutions on the absolute individual ion mobilities of the carrier-free radioactive ions [¹³⁷Cs]Cs⁺, [²⁰¹Tl]Tl⁺ and [⁵⁷Co]Co²⁺ at tracer scale concentrations ($\approx 10^{-11} \text{ mol}$). One major advantage of the radio-tracer technique is that the overall composition of the supporting electrolyte is not affected by the minute presence of the radioactive tracer ions. A change of the structural and dynamical properties of the supporting electrolyte on the other hand is then reflected by a modification of the mobility of the migrating radioactive ions.

The experimental values of the AIIM for the radioactive tracer ions investigated here are compared with the values predicted by the extended DHO limiting law. Using the migration data obtained in this work and those obtained for other radioactive ions in previous work,^{11,25} a systematic analysis of the variation of the AIIM with the hydrogen ion concentration of perchlorate electrolyte mixtures is performed assuming an equilibrium between two alternative dynamical states of the hydrated radioactive ion. This results in a semi-empirical relation for the dependence of the AIIM of the migrating ions on the overall electrolyte ionic strength and the hydrogen ion concentration.

The variation of the AIIM of the metal cations with increasing hydrogen ion concentration is also discussed in terms of a change of the dynamical properties of the electrolyte bulk water. The rate constant for proton transfer between the hydronium ions and water molecules is deduced from the hydrogen ion concentration dependence of the rotational reorientation time of bulk water molecules in HClO_4 electrolytes.

The proton hopping length is calculated from the proton mobility using the Einstein relation.

II Theory

A Ion mobility, ion micro-viscosity and rotational reorientation time of water molecules

The mobility of an ion can be related to the solution viscosity by the Stokes–Einstein equation for perfect sticking^{26,27}

$$u_i = \frac{e|z_i|}{6\pi\eta r_s} \quad (1)$$

where e is the elementary charge ($1.6022 \times 10^{-19} \text{ C}$), z_i the charge number of the ion, η the solution viscosity ($\text{kg m}^{-1} \text{ s}^{-1}$) and r_s the Stokes radius (m). As the experimental results are generally difficult to interpret on the basis of the Stokes radius, Stokes' law may be used in its microscopic form

$$u_i = \frac{e|z_i|}{6\pi\tilde{\eta}_i r_i} \quad (2)$$

which connects the ion mobility to the ion micro-viscosity, where $\tilde{\eta}_i$ is the ion micro-viscosity ($\text{kg m}^{-1} \text{ s}^{-1}$), defined as the viscosity of the water molecules in the first hydration shell of the ion, and r_i is the ionic radius (m).

The values of the ion micro-viscosity in pure water, $\tilde{\eta}_i^\circ$ calculated from the ion mobility in pure water, u_i° at 298.15 K ²⁸ for the ions investigated in this work are listed in Table 1. The ratio of $\tilde{\eta}_i^\circ$ against η° , the viscosity of water ($\eta^\circ = 8.903 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ at 298.15 K ²⁹), reflects the effect of the ion on the structure of water. Here, $\tilde{\eta}_i^\circ < \eta^\circ$ corresponds to the case of low charge density ions (Cs⁺, Tl⁺, *etc.*), referred to as structure-breakers, while $\tilde{\eta}_i^\circ > \eta^\circ$ corresponds to the case of high charge density ions (Sr²⁺, Co²⁺, La³⁺, *etc.*), classified as structure-makers. The ion micro-viscosity can be related to the vibrational frequency ν_i (s^{-1}) of the ion–water bond in the first hydration sphere as³⁰

$$\tilde{\eta}_i = \frac{2\nu_i M_{\text{H}_2\text{O}}}{d_i N_A} \chi_i \quad (3)$$

$M_{\text{H}_2\text{O}}$ the molar mass of H_2O (kg mol^{-1}), d_i the distance between the central ion and the oxygen atom of the hydrated water molecules (m), and N_A the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$). The factor χ_i takes into account the electrostriction, *i.e.* the reduction of the effective radius of the

Table 1 Parameters of hydrated ions in pure water ($T = 298.15 \text{ K}$). u_i° is the absolute individual ion mobility at $\mu = 0$ [refs. 28,49,50], $\tilde{\eta}_i^\circ$ the ion micro-viscosity, τ_i° the rotational reorientation time of water molecules in the first hydration shell of the ion, N the coordination number [ref. 1] and Δn the number of water molecules leaving the hydration shell during the exchange process with the bulk. r_i is the ionic radius [refs. 51 and 52]. $\text{p}K^\circ$ is the first hydrolysis constant at 298.15 K for $\mu \rightarrow 0$ [ref. 53]

Ion	$r_i/10^{-10} \text{ m}$	$u_i^\circ/10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\tilde{\eta}_i^\circ$ [eqn. (2)]/ $10^{-4} \text{ kg}^{-1} \text{ s}^{-1}$	$\tilde{\eta}_i^\circ$ [eqn. (3)]/ $10^{-4} \text{ kg}^{-1} \text{ s}^{-1}$	$\tau_i^{\circ a} / 10^{-12} \text{ s}$	N	Δn	$\text{p}K^\circ$
Cs ⁺	1.67	8.00	6.4	6.7	5.9	8	6.0	—
Tl ⁺	1.50	7.74	7.3	8.0	6.8	6	4.2	13.2
Na ⁺	1.02	5.19	16.0	16.5	14.9	6	2.6	14.2
Sr ²⁺	1.26	6.16	21.9	20.5	20.4	8	2.7	13.3
Co ²⁺	0.65	5.70	45.9	42.2	42.8	6	1.0	9.7
La ³⁺	1.16	6.85	32.1	31.7	29.9	9	2.2	8.5
Gd ³⁺	1.05	6.62	36.7	35.6	34.2	8	1.7	8.0
Tb ³⁺	1.04	6.48	37.8	36.0	35.3	8	1.7	7.9
Tm ³⁺	0.99	6.48	39.8	38.0	37.0	8	1.6	7.7
Yb ³⁺	0.99	6.45	39.9	38.4	37.2	8	1.6	7.7
Am ³⁺	1.095	7.30	31.9	33.6	29.7	9	2.2	8.2
ClO_4^-	2.40	6.97	5.1	4.1	4.7	8	6.9	—

^a Calculated from the data of column 4 with eqn. (6).

water molecule caused by the electrostatic field of the ion. It can be calculated using Conway's equation:³¹

$$\chi_i = \left(1.1 \times 10^{-19} \left(\frac{z_i e}{\epsilon_0 \epsilon_r d_i^2} \right)^2 + 1 \right)^{-0.05} \quad (4)$$

where ϵ_0 is the permittivity of the vacuum ($8.8541 \times 10^{-12} \text{ F m}^{-1}$), and ϵ_r the dielectric constant of water (78.36 at 298.15 K ²⁸). Using the harmonic oscillator as a model for the ion-water system, the vibrational frequency of the ion-water bond may be connected to the hydration enthalpy ΔH_{hyd} (J mol^{-1}) as³⁰

$$\nu_i = \frac{1}{2\pi} \left(\frac{2\Delta H_{\text{hyd}}}{d_i^2 M_{\text{red}}} \right)^{1/2} \quad (5)$$

where M_{red} is the reduced mass of the quasi-molecule ion-OH₂. For calculation of $\tilde{\eta}_i^\circ$ by means of eqns. (3)–(5), the values of ΔH_{hyd} obtained by means of the TATB extra-thermodynamic assumption ($\Delta H_{\text{hyd}}[\text{C}_6\text{H}_5)_4\text{As}^+] = \Delta H_{\text{hyd}}[\text{B}(\text{C}_6\text{H}_5)_4^-]$) were employed.³² The value of d_i was set equal to $r_i + (\delta/2)$, with δ being the thickness of the hydration shell. For univalent, divalent and trivalent ions, the values of δ were taken as 2.404 , 2.334 and $2.276 \cdot 10^{-10} \text{ m}$, respectively.³³ As shown in Table 1, the values of $\tilde{\eta}_i^\circ$ obtained by eqn. (3) agree closely with those given by eqn. (2), based on sticking conditions.

It is also possible to determine the rotational reorientation time τ_i for water molecules in the hydration shell of the ion from the ion micro-viscosity using the Debye–Stokes–Einstein (DSE) relation:

$$\tau_i = \frac{\alpha \pi \tilde{\eta}_i \theta^3}{kT} \quad (6)$$

where α is a numerical constant, θ the effective radius of the water molecule ($1.38 \times 10^{-10} \text{ m}$), k the Boltzmann constant ($1.3807 \times 10^{-23} \text{ J K}^{-1}$) and T the absolute temperature (K). Assuming that the DSE relation holds for pure water and using a rotational reorientation time of $\tau_{\text{H}_2\text{O}}^\circ = 8.3 \text{ ps}$ (the Debye relaxation time of water at 298.15 K)^{34,35} and a viscosity of $8.903 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$, we obtain $\alpha = 4.65$. The value of α increases weakly as the temperature increases with a change of about 0.1% per degree in the range 273 – 328 K . The diffusion coefficient of pure water calculated with the parameters above, ($D_{\text{H}_2\text{O}}^\circ = \theta^2/\tau_{\text{H}_2\text{O}}^\circ = 2.29 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) is in good agreement with the best known experimental value,³⁶ $2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. For the structure-breaker ions we find $\tau_i^\circ < \tau_{\text{H}_2\text{O}}^\circ$ and for the structure-maker ions $\tau_i^\circ > \tau_{\text{H}_2\text{O}}^\circ$.

As the break-up of the first hydration shell is initiated principally by molecular reorientation, the number of water molecules leaving the hydration sphere over the period of time in which the outer bulk water shell is renewed, may be given by³

$$\Delta n = N[1 - e^{-\tau_{\text{H}_2\text{O}}^\circ/\tau_i}] \quad (7)$$

where N is the number of water molecules in the first hydration sphere at time zero, *i.e.* the coordination number. The number of water molecules remaining in the hydration shell during the exchange process is thus $N - \Delta n$. The values of τ_i° (in pure water) as well as the values of N and Δn for the ions investigated in this work are listed in Table 1. The relative exchange rate of water molecules between the hydration sphere and the bulk, $\Delta n/N$, appears as an important quantity for the exchange process. As shown in Fig. 1 for the cations in pure water, $\Delta n/N$ may be expressed as a complicated exponential function of the surface charge density of the ion, $\sigma = |z_i|e/4\pi r_i^2$ (C m^{-2}):

$$\frac{\Delta n}{N} = e^{-4\pi\sigma} [e^{-\sigma_s} (e^{p\sigma} - e^{q\sigma}) + e^{q\sigma} - 1] \quad (8)$$

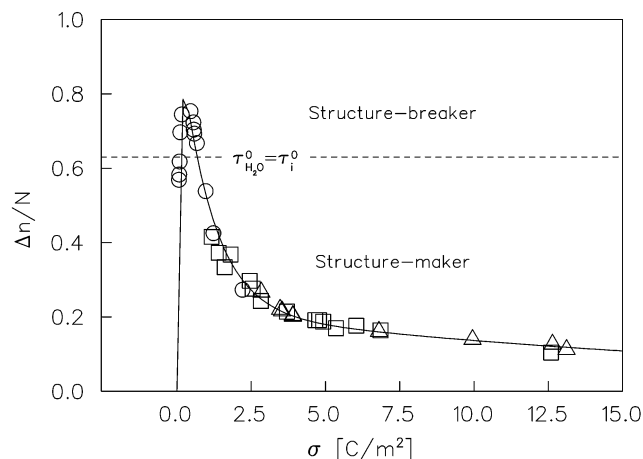


Fig. 1 Relative exchange rate of water molecules between the first hydration sphere and the bulk, $\Delta n/N$, versus surface charge density σ of the ion in pure water at 298.15 K . The circles represent the univalent ions (Pe_4N^+ , Bu_4N^+ , Pr_4N^+ , Et_4N^+ , Me_4N^+ , NH_4^+ , Cs^+ , Rb^+ , K^+ , Tl^+ , Ag^+ , Na^+ , Li^+); the squares the divalent ions (Ra^{2+} , Ba^{2+} , Pb^{2+} , Sr^{2+} , Hg^{2+} , Ca^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Be^{2+}) and the triangles the trivalent ions (La^{3+} , Gd^{3+} , Gd^{3+} , Tb^{3+} , Tm^{3+} , Yb^{3+} , Am^{3+} , Sc^{3+} , Fe^{3+} , Al^{3+}). The solid line is the fit of the data with eqn. (8). The ratio $\Delta n/N$ was calculated by means of eqns. (7,6,2) using ionic radii from Shannon⁵¹ for monatomic ions and thermochemical radii from Jenkins and Thakur⁵² for polyatomic ions. The values of the ion mobility in pure water were taken from [ref. 28] except for lanthanide ions [ref. 49,50].

with $p = 11.65 \text{ (m}^2 \text{ C}^{-1})$, $q = 12.52 \text{ (m}^2 \text{ C}^{-1})$ and $\sigma_s = 0.24 \text{ C m}^{-2}$. The surface charge density σ_s corresponds to the maximum value of $\Delta n/N$. Interestingly, the radii derived from σ_s , which are 2.30 , 3.26 , and $4.00 \times 10^{-10} \text{ m}$ for $z_i = 1, 2$ and 3 , respectively, are correlated through a proportionality factor of $\sqrt{4/6}$ with the Hubbard–Onsager lengths, $R_{\text{H-O}}$, commonly used as solvent parameters. $R_{\text{H-O}}$ may be calculated using the following expression³⁷

$$R_{\text{H-O}} = \left[\frac{z_i^2 e^2}{16\pi\eta^\circ \epsilon_0 \epsilon_r^2} (\epsilon_r - \epsilon_\infty) \tau_{\text{H}_2\text{O}}^\circ \right]^{1/4} \quad (9)$$

with ϵ_∞ the high-frequency dielectric constant of water (5.2 at 298.15 K).²⁸ From eqns. (9) and (6), the surface charge density term σ_s appears to be only dependent on the solvent properties at a given temperature

$$\sigma_s = \frac{6\epsilon_r}{\theta} \left[\frac{\epsilon_0 kT}{(\epsilon_r - \epsilon_\infty)\alpha\theta} \right]^{1/2} \quad (10)$$

The value of σ_s decreases weakly as the temperature increases with a change of about 0.1% per degree in the range 273 – 328 K . Finally, inserting the above expression σ_s for in eqn. (8) we obtain a general expression which describes well the transport properties of ions in pure water as a function of the characteristics of the ions (ionic radius and charge) and of the solvent properties. Furthermore, it is possible from eqn. (8) to derive an analytical expression of the Stokes radius r_s using eqn. (2).

B Ion mobility in electrolyte mixtures, ionic strength dependence

According to Onsager's theory based on the Debye–Hückel treatment of the ion atmosphere in dilute solutions³⁸ and according to corrections proposed by Stokes *et al.* for finite ion-size effects³⁹ in connection with dielectric saturation and local hydration of the ions,⁴⁰ the ion mobility of an individual ion present at very low concentration ($c_i \approx 0$) in a chemically inert background electrolyte may be given by the following

relation:

$$u_i = u_i^\circ - \frac{2.802 \times 10^6 z_i^2 u_i^\circ (1 - \sqrt{d(\omega_i)})}{(\epsilon_r T)^{3/2}} \times \frac{\sqrt{\mu}}{(1 + \kappa a)(1 + \kappa a/\sqrt{2})} \quad (11)$$

where u_i° is the limiting mobility of ion i ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$), $d(\omega_i)$ a mobility function, μ the overall ionic strength of the electrolyte (mol dm^{-3}), $\kappa = \sqrt{\mu}/3.041 \times 10^{-10}$ (m^{-1}) the reciprocal radius of the ion atmosphere,⁴¹ and a (m) the distance of closest approach between oppositely charged ions of the background electrolyte.⁴² The mobility function may be expressed by:

$$d(\omega_i) = \frac{1}{2\mu} \sum_j \frac{c_j |z_j| u_j^\circ}{u_j^\circ / |z_j| + u_i^\circ / |z_i|} \quad (12)$$

where c_j and z_j are the concentration and the charge of the j th component of the background electrolyte. Eqn. (11), called the extended DHO limiting law, is valid only for electrolyte concentrations lower than about 0.2 mol dm^{-3} . For higher electrolyte concentrations, the ion mobility (or the diffusion coefficient) increases and reaches a maximum value (generally higher than the limiting value in pure water) at about 1.2 mol dm^{-3} before it decreases again.⁹ Unfortunately, no pertinent law exists to describe the behavior of transport properties of an individual ion in electrolyte solutions of concentrations higher than 0.2 mol dm^{-3} .

In the case of a mixed background electrolyte of type MX/HX composed of univalent ions (in our experiments $\text{NaClO}_4/\text{HClO}_4$), for which the overall ionic strength is kept constant, the change of the pH of the solution is obtained by replacing M^+ ions by H^+ ions ($\mu = [\text{M}^+] + [\text{H}^+] = [\text{X}^-]$). The mobility function can then be expressed as a function of the hydrogen ion concentration $[\text{H}^+]$

$$d(\omega_i) = \frac{1}{\mu} [d(\omega_i^{\text{HX}})[\text{H}^+] + d(\omega_i^{\text{MX}})(\mu - [\text{H}^+])] \quad (13)$$

where $d(\omega_i^{\text{HX}})$ and $d(\omega_i^{\text{MX}})$ are the mobility functions of the individual ions for the electrolytes HX and MX. The change in the parameter a , the mean value of the distance between oppositely charged ions, with the pH of the electrolyte mixture may be expressed similarly by

$$a = \frac{1}{\mu} [a^{\text{HX}}[\text{H}^+] + a^{\text{MX}}(\mu - [\text{H}^+])] \quad (14)$$

where a^{HX} and a^{MX} are the distances of closest approach for the ions of the electrolytes HX and MX.

For a mixed electrolyte of type $\text{NX}_2/\text{MX}/\text{HX}$, composed of uni- and divalent ions (in our experiment $\text{Co}(\text{ClO}_4)_2/\text{NaClO}_4/\text{HClO}_4$), for which the overall ionic strength $\mu = \mu^{\text{NX}_2} + \mu^{\text{MX}}$ is kept constant, and the change of the pH of the solution is achieved by replacing M^+ ions by H^+ ions, the mobility function is given as a function of the proton concentration $[\text{H}^+]$ by

$$d(\omega_i) = \frac{1}{\mu} [d(\omega_i^{\text{NX}_2})\mu^{\text{NX}_2} + d(\omega_i^{\text{HX}})[\text{H}^+] + d(\omega_i^{\text{MX}})(\mu - [\text{H}^+])] \quad (15)$$

where $d(\omega_i^{\text{NX}_2})$, $d(\omega_i^{\text{HX}})$ and $d(\omega_i^{\text{MX}})$ are the mobility functions of the individual ions for the electrolytes NX_2 , HX and MX. The change of the parameter a with the pH of the electrolyte mixture may be expressed by

$$a = \frac{1}{\mu} [a^{\text{NX}_2}\mu^{\text{NX}_2} + a^{\text{HX}}[\text{H}^+] + a^{\text{MX}}(\mu - [\text{H}^+])] \quad (16)$$

where a^{NX_2} , a^{HX} and a^{MX} are the distances of closest approach for the individual electrolytes NX_2 , HX and MX.

If the migrating tracer cations are not involved in hydrolysis equilibria ($\text{M}^{n+} + m\text{H}_2\text{O} \rightleftharpoons \text{M}(\text{OH})_m^{(n-m)+} + m\text{H}^+$), which is

Table 2 Electrolyte parameters used to calculate the absolute individual ion mobilities by means of eqns. (9)–(14) at $T = 298.15 \text{ K}$

$u^\circ/10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$				$a/10^{-10} \text{ m}$		
Na^+	ClO_4^-	Co^{2+}	H^+	NaClO_4	HClO_4	$\text{Co}(\text{ClO}_4)_2$
5.19 ^a	6.97 ^a	5.70 ^a	36.24 ^a	4.04 ^b	5.09 ^b	6.73 ^c

^a Ref. 28. ^b Ref. 42. ^c Interpolated from the relation $a = 75.56 (r_+ + r_-)^{-1} - 18.06$ obtained for the perchlorate data: $a(\text{NaClO}_4) = 4.04 \text{ \AA}$, $a(\text{LiClO}_4) = 5.63 \text{ \AA}$, $a(\text{Zn}(\text{ClO}_4)_2) = 6.18 \text{ \AA}$ [ref. 41] with r_+ the ionic radius of the cation and r_- that of the anion/ Å .

in fact the case for our experimental study (for the onset of the hydrolysis reactions see the pK° -values in Table 1), the AIIM of the cations can be calculated for various pH values of the mixed electrolyte (for overall ionic strength lower than 0.2 mol dm^{-3}) using eqns. (11), (13) and (14) and (11), (15) and (16) respectively. The electrolyte parameters employed for the calculations are listed in Table 2. The pH-dependence of AIIM of Cs^+ , Tl^+ and Co^{2+} ions is shown in Fig. 2.

III Experiment

A Sample preparation

The carrier-free radioisotopes ^{137}Cs , ^{57}Co , (CSI Diagnostik GmbH) and ^{201}Tl (Mallinckrodt Medical BV) were used. Aliquots of solutions of ^{137}Cs (400 MBq mL^{-1} , $1 \text{ mol dm}^{-3} \text{ HCl}$) and ^{57}Co (80 MBq mL^{-1} , $1 \text{ mol dm}^{-3} \text{ HCl}$) were diluted with deionized water to obtain specific volume activities of about 40 MBq mL^{-1} for both cations. In the case of ^{201}Tl , isotonic solutions of thallium chloride (37 MBq mL^{-1} , $0.16 \text{ mol dm}^{-3} \text{ NaCl}$) were used directly.

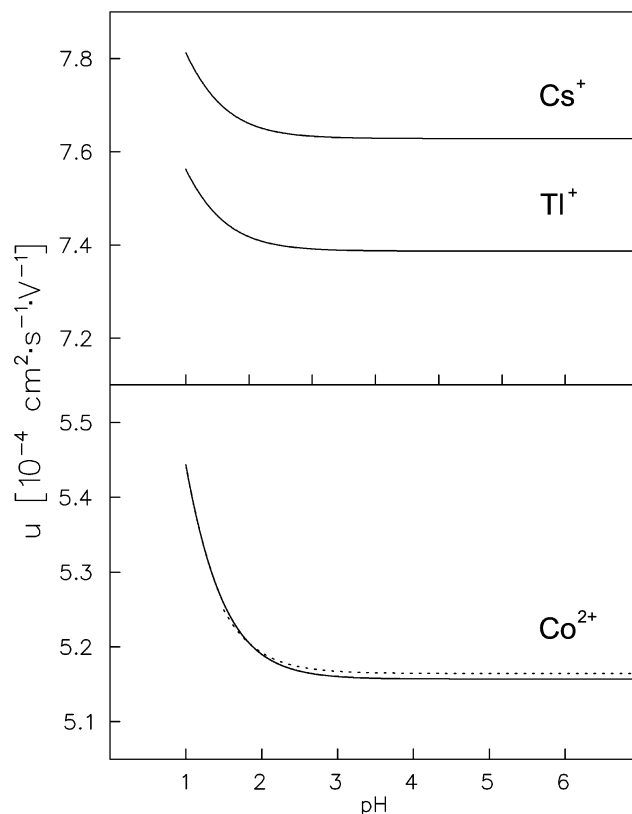


Fig. 2 Variation of the ion mobility of Cs^+ , Tl^+ and Co^{2+} ions according to the pH of inert electrolyte mixtures of overall ionic strength $\mu = 0.1 \text{ mol dm}^{-3}$ (solid line: $\text{Na}(\text{H})\text{ClO}_4$, dashed line: $\text{Co}(\text{ClO}_4)_2/\text{Na}(\text{H})\text{ClO}_4$) calculated with the extended limiting law, eqn. (11).

Background electrolyte mixtures of the type $\text{NaClO}_4/\text{HClO}_4$ and $\text{Co}(\text{ClO}_4)_2/\text{NaClO}_4/\text{HClO}_4$ were prepared from deionized water and analytical grade chemicals. The overall ionic strength was $\mu = 0.10 \text{ mol dm}^{-3}$ for all electrolytes. The concentration of $\text{Co}(\text{ClO}_4)_2$ was fixed to $0.023 \text{ mol dm}^{-3}$.

The pH of the electrolytes was measured by means of pre-calibrated glass electrode using standard buffer solutions. The estimated uncertainty was ± 0.02 in pH units.

B Measurement of the ion mobility

The measurement of the AIIM of the radioactive ions was performed by means of the free-electrolyte continuous electromigration technique. The apparatus used in this work as well as the analytical procedure for the on-line determination of the migration velocities of radioactive ions are described in detail elsewhere.^{8,43} In order to eliminate electroosmosis, the inner surface of the migration tube was coated with a monomolecular layer of non-cross-linked polyacrylamide according to the method proposed by Hjertén.⁴⁴

The migration tube (id 3 mm, length 500 mm) was filled with the electrolyte mixture of a given composition. To exclude convection flows, the migration tube was connected to the electrode cells *via* hydrodynamic resistors (polycarbonate membranes). A bolus of 1–5 μL of the solution containing the radio-isotope ($\sim 10^{-11}$ mol) under investigation was injected into the migration tube. An electric field intensity of 2.5 or 10 V cm^{-1} was applied over the migration zone by the use of platinum electrodes immersed in the electrode cells. To ensure a constancy of electrolyte composition and pH in the migration tube, the electrolyte solution in the electrode cells was continuously refreshed by means of a peristaltic pump. The electromigration experiments were carried out at a temperature of 298.1(5) K using an appropriate thermostating system.

The migration of the radio-ions was studied over a period of 30 min by continuously scanning the migration tube with a well collimated bismuth germanate (BGO) scintillation detector. For each scan, the absolute position of the ions was determined by analysis of the recorded activity distribution with a Gaussian or Lorentzian, setting a preferential fit on the front of the migration. The migration velocity of the radioactive ions was calculated on-line from the slope of the linear relation obtained between the position of the radioactive ions and the time. The absolute individual ion mobility was determined by dividing the migration velocity by the intensity of the electric field.

Each value of the AIIM reported in this study is an average of two to four independent measurements with a precision ranging between 0.5 and 2%. The standard deviations on the average value of the AIIM range from 2 to 4%.

III Results

A pH dependence of the AIIM

The AIIM of the Cs^+ , Tl^+ and Co^{2+} radioactive ions *versus* the pH of the inert electrolyte mixtures is plotted in Fig. 3. The AIIM increases as the pH is raised from pH 1 to pH 4. Up to pH 4 the AIIM is constant. The increase of the AIIM at decreasing hydrogen ion concentrations was not expected since changes of electrolyte parameters like density, viscosity, dielectric constant or others between pH 1 and 7 can be neglected. For example, the viscosity of 0.10 mol dm^{-3} NaClO_4 is $9.001 \times 10^{-4} \text{ kg}^{-1} \text{ s}^{-1}$ and that of 0.10 mol dm^{-3} HClO_4 is $9.117 \times 10^{-4} \text{ kg}^{-1} \text{ s}^{-1}$.⁴⁵ The difference in the viscosity is only 1.3%, while the AIIM of the ions studied for the two electrolytes differ by 10 to 20%. Furthermore, no metal-ligand complexation equilibria, redox reactions or protonization equilibria may have an influence on the mobility of the investigated ions. The coating of the inner surface of the migration tube for suppression of the electroosmosis performed well since no change in the height and shape of the measured radioactive distributions was detected during the electromigration runs. No adsorption of the radioactive ions on the wall of the migration tube was observed. Similar dependences of the ion mobility on the pH of inert aqueous solutions have been found for the lanthanide ions in previous study (Fig. 4).¹¹ The two levels of the migration data obtained for the neutral and acidic electrolytes are given in Table 3 and Table 4 respectively.

Phenomenologically, the variation of the AIIM with the pH of the electrolyte mixtures may be divided into three zones whose characteristics depend significantly on the pH of the inert electrolyte mixture.

In the zone of $7 > \text{pH} > 3$ to 5, the AIIM is constant. The value of the AIIM is in close agreement with the theoretical value given by the extended DHO limiting law for each of the Cs^+ , Tl^+ , and Co^{2+} ions. In the case of the trivalent lanthanide and actinide ions the experimentally determined AIIM¹¹ are 10 to 20% higher than the value predicted by the extended limiting law.

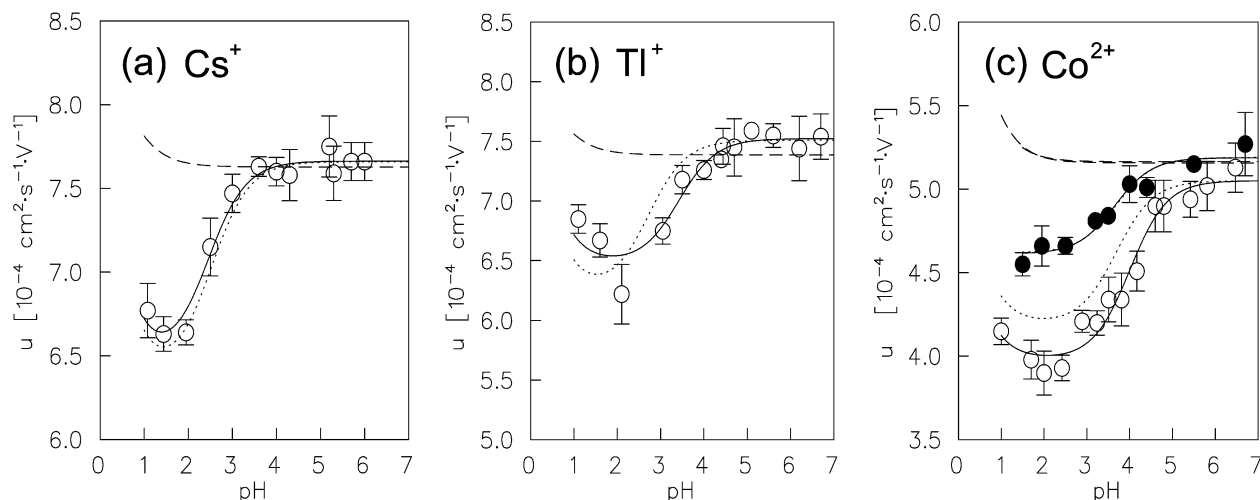


Fig. 3 (a) Ion mobility of Cs^+ in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$). (b) Ion mobility of Tl^+ in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$). (c) Ion mobility of Co^{2+} in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$), open symbols; ion mobility of Co^{2+} in $\text{Co}(\text{ClO}_4)_2/\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$, $\mu_{\text{Co}(\text{ClO}_4)_2} = 0.068 \text{ mol dm}^{-3}$, $\mu_{\text{Na}(\text{H})\text{ClO}_4} = 0.032 \text{ mol dm}^{-3}$), close symbols. The solid line is the fit of experimental data using eqn. (19), the dashed line is the ion mobility calculated using eqn. (11), the dotted line is the ion mobility calculated using eqn. (24).

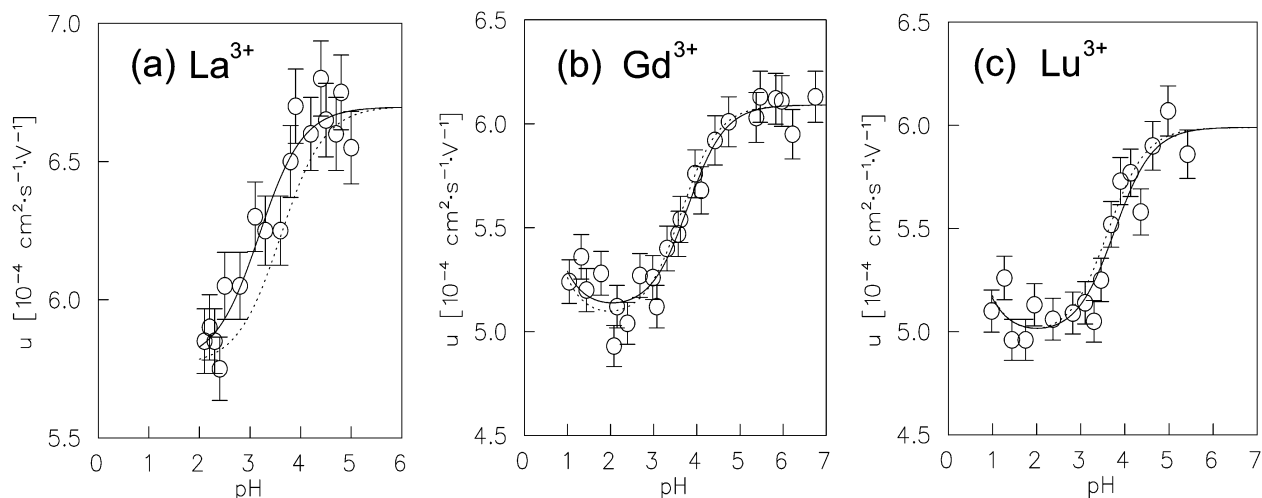


Fig. 4 (a) Ion mobility of La^{3+} in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.01 \text{ mol dm}^{-3}$). (b) Ion mobility of Gd^{3+} in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$). (c) Ion mobility of Lu^{3+} in $\text{Na}(\text{H})\text{ClO}_4$ ($\mu = 0.10 \text{ mol dm}^{-3}$). The solid line is the fit of experimental data using eqn. (21), the dotted line is the ion mobility calculated using eqn. (24).

In the intermediate zone of $3 > \text{pH} > 2$, the AIIM decreases at increasing hydrogen ion concentration and reaches a minimum at about pH 2.

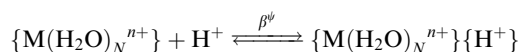
In the acidic zone, $2 > \text{pH} > 1$, a small increase of the AIIM is observed, which is qualitatively in agreement with the prediction given by the extended limiting law.

Furthermore, there is one important observation: As shown in Fig. 3(c), the variation of the AIIM of Co^{2+} ions with pH is less pronounced when the ions move in $\text{Co}(\text{ClO}_4)/\text{Na}(\text{H})\text{ClO}_4$ electrolytes rather than in “Co-free” $\text{Na}(\text{H})\text{ClO}_4$ electrolytes. This indicates that the pH-mobility effect of the ions depends also on the structure affecting properties of the cation composing the electrolyte. As Na^+ ions are replaced by hydrogen ions in the $\text{Co}(\text{ClO}_4)/\text{Na}(\text{H})\text{ClO}_4$ electrolyte, not only the pH increases but also the “structureness” of the electrolyte bulk water increases, (*i.e.* the rotational freedom of the bulk water decreases, since Co^{2+} is a stronger structure-maker ion than Na^+).

B Analysis of the migration data

For a first, qualitative interpretation of the change of the AIIM with the pH of the solution, two alternative dynamical states of the hydrated radioactive cation acting in equilibrium

were assumed:¹¹



$$\beta^\psi = \frac{[\{\text{M}(\text{H}_2\text{O})_N^{n+}\}\{\text{H}^+\}]}{[\{\text{M}(\text{H}_2\text{O})_N^{n+}\}][\text{H}^+]}. \quad (17)$$

Using the symbolic representations $\{\text{M}(\text{H}_2\text{O})_N^{n+}\}$ and $\{\text{M}(\text{H}_2\text{O})_N^{n+}\}\{\text{H}^+\}$ we try to describe two different types of interaction of the migrating radioactive ion with the components of the chemically inert electrolyte, in particular the hydrogen ion concentration $[\text{H}^+]$. We aim to reflect the change of the dynamical properties of the water molecules in the hydration shell of the ion. The phenomenological stoichiometric equilibrium constant of the system is represented by β^ψ ($\text{dm}^3 \text{ mol}^{-1}$).

For a quantitative discussion the overall ion mobility may be written as⁴⁵

$$u = \sum_{i=1}^n u_i \alpha_i \varphi \quad (18)$$

where u_i is the absolute individual ion mobility of the ionic species i (for $\alpha_i = 1$), α_i the partial mole fraction of the ionic

Table 3 Parameters of hydrated ions in the neutral aqueous perchlorate electrolyte. u_i is the experimental absolute individual ion mobility, $\bar{\eta}_i$ the ion micro-viscosity, and τ_i the rotational reorientation time of water molecules in the first hydration shell. r_i is the ionic radius. $T = 298.1(5) \text{ K}$

Ion	$r_i/10^{-10} \text{ m}$	$u_i/10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\bar{\eta}_i$ [eqn. (2)]/ $10^{-4} \text{ kg}^{-1} \text{ s}^{-1}$	τ_i [eqn. (6)]/ 10^{-12} s	τ_i [eqn. (26)]/ 10^{-12} s
$\text{NaClO}_4, \mu = 0.1$					
Cs^+	1.67	7.66(2) ^a	6.6	6.2	6.1
Tl^+	1.50	7.51(4) ^a	7.5	7.0	7.1
Co^{2+}	0.65	5.05(5) ^a	51.8	48.3	44.6
Sr^{2+}	1.26	5.87(5) ^b	23.0	21.4	21.3
Gd^{3+}	1.05	6.09(4) ^c	39.9	37.2	35.6
Tb^{3+}	1.04	5.77(4) ^c	42.5	39.6	36.8
Tm^{3+}	0.99	5.91(5) ^c	43.6	40.6	38.6
Yb^{3+}	0.99	6.28(7) ^c	41.0	38.2	38.8
Lu^{3+}	0.97	5.99(9) ^c	43.9	40.9	—
Am^{3+}	1.095	7.00(12) ^c	32.0	29.8	31.0
$\text{NaClO}_4, \mu = 0.01$					
La^{3+}	1.16	6.70(5) ^c	32.8	30.6	30.5
$\text{Co}(\text{ClO}_4)/\text{NaClO}_4, \mu = 0.1$					
Co^{2+}	0.65	5.19(4) ^a	50.4	46.9	45.9

^a This work. ^b Ref. 25. ^c Ref. 11.

Table 4 Parameter of hydrated ions in acidic aqueous perchlorate electrolytes. u_i is the experimental absolute individual ion mobility, $\tilde{\eta}_i$ the ion micro-viscosity, and τ_i the rotational reorientation time of water molecules in the first hydration shell. r_i is the ionic radius. $T = 298.1(5)$ K

Ion	$r_i/10^{-10}$ m	$u_i/10^{-8}$ m ² V ⁻¹ s ⁻¹	$\tilde{\eta}_i$ [eqn. (2)]/ 10 ⁻⁴ kg ⁻¹ s ⁻¹	τ_i [eqn. (6)]/ 10 ⁻¹² s	τ_i [eqn. (26)]/ 10 ⁻¹² s
HClO ₄ , $\mu = 0.1$					
Cs ⁺	1.67	6.78(16) ^a	7.5	7.0	7.2
Tl ⁺	1.50	6.99(34) ^a	8.1	7.6	8.3
Co ²⁺	0.65	4.14(8) ^a	63.2	58.9	52.1
Sr ²⁺	1.26	5.38(3) ^b	25.1	23.4	24.8
Gd ³⁺	1.05	5.24(10) ^c	46.3	43.2	41.7
Tb ³⁺	1.04	5.12(10) ^c	47.9	44.6	43.0
Tm ³⁺	0.99	5.16(10) ^c	49.9	46.5	45.0
Yb ³⁺	0.99	5.08(10) ^c	50.7	47.3	45.3
Lu ³⁺	0.97	5.10(10) ^c	51.6	48.0	—
Am ³⁺	1.095	5.63(8) ^c	41.4	38.5	36.2
HClO ₄ , $\mu = 0.01$					
La ³⁺	1.16	5.77(8) ^c	38.1	35.5	32.6
Co(ClO ₄) ₂ /HClO ₄ , $\mu = 0.1$					
Co ²⁺	0.65	4.62(4) ^a	56.6	52.7	51.3

^a this work ^b [Ref. 25] ^c [Ref. 11]

species in the equilibrium and φ a function taking into account the change of the activity coefficients γ when switching from Na⁺ to H⁺ in the perchlorate solution of a constant overall ionic strength. Concerning the small increase of the AIIM of the radioactive cations observed between pH 2 and pH 1, the function φ can be expressed as

$$\varphi = \frac{1}{\mu} \left[\frac{\gamma_{\text{HClO}_4}}{\gamma_{\text{NaClO}_4}} \Big|_{\mu} [\text{H}^+] + (\mu - [\text{H}^+]) \right] \quad (19)$$

The values of the activity coefficients²⁸ of the aqueous electrolyte of HClO₄ and NaClO₄ at 298.15 K are given in Table 5. Since the activity coefficients are ionic strength dependent, the function φ for a Na(H)ClO₄ electrolyte mixture can be expressed by

$$\varphi = 1 + 0.321[\text{H}^+] \quad (20)$$

Using the equilibrium expression (17) and relation (18), the variation of the overall ion mobility of the radioactive cation with the pH of the electrolyte may now be expressed by

$$u = \frac{u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}} + \beta^\psi [\text{H}^+] u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}}{1 + \beta^\psi [\text{H}^+]} \varphi \quad (21)$$

The ion mobility $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}$ corresponds to the minimum value of the AIIM at about pH 2. The experimental data were fitted with the equation above. The obtained results are included in Table 5.

While the experimentally determined AIIM are different for all the cations investigated, the ratio between $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}$ and $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}}$ is constant for a given aqueous electrolyte and a given overall ionic strength. For the electrolyte mixture Na(H)ClO₄, the mean value of this ratio is 0.83(3) at $\mu = 0.1$ mol dm⁻³ and 0.86(1) at $\mu = 0.01$ mol dm⁻³ (the ratio is quoted by A in Table 5). As the ionic strength of the electrolyte mixture approaches zero (infinite dilution of the electrolyte) and thus the pH to 7, the value of A is expected to approach unity.

Using the migration data obtained in this work and from the experimental AIIM of Am³⁺ in neutral (NaClO₄) and acidic (HClO₄) aqueous perchlorate electrolytes of various ionic strength,²⁵ the variation of A with the overall ionic strength of the Na(H)ClO₄ electrolyte mixture ($\mu < 0.2$ mol dm⁻³) may be given by:

$$A = 1 - \frac{1.78\sqrt{\mu}}{1 + 6.69\sqrt{\mu}} \quad (22)$$

To complete the analysis of the migration data we should find an analytical expression for the stoichiometric equilibrium

Table 5 Results of the fit of the experimental electromigration data according to eqn. (21). $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}}$ is the ion mobility at the neutral level and $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}$ the ion mobility at the acidic level. β^ψ is the phenomenological stoichiometric equilibrium constant for eqn. (17). A is the ratio $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}/u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}}$. $T = 298.1(5)$ K

Ion	$r_i/10^{-10}$ m	$u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}}/10^{-8}$ m ² V ⁻¹ s ⁻¹	$u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}}/10^{-8}$ m ² V ⁻¹ s ⁻¹	A	$\log \beta^\psi$	$\log \beta^\psi$ [eqn. (23)]
NaClO ₄ /HClO ₄ , $\mu = 0.1$, $\gamma_{\text{NaClO}_4} = 0.777$, $\gamma_{\text{HClO}_4} = 0.803$						
Cs ⁺	1.67	7.66(3)	6.44(6)	0.84(1)	2.43(23)	2.54
Tl ⁺	1.50	7.52(6)	6.48(8)	0.86(1)	3.42(46)	2.71
Co ²⁺	0.65	5.05(5)	3.98(5)	0.79(1)	4.00(26)	3.69
Sr ²⁺	1.26	5.88(6)	5.10(5)	0.87(1)	3.30(58)	3.48
Gd ³⁺	1.05	6.09(4)	5.10(3)	0.84(1)	3.79(23)	3.64
Tb ³⁺	1.04	5.77(4)	4.92(5)	0.85(1)	3.39(26)	3.65
Tm ³⁺	0.99	5.92(5)	4.94(4)	0.83(1)	3.56(27)	3.66
Yb ³⁺	0.99	6.27(7)	5.06(7)	0.81(2)	3.47(30)	3.66
Lu ³⁺	0.97	5.99(8)	4.98(5)	0.83(2)	3.76(36)	—
Am ³⁺	1.095	6.99(11)	5.57(9)	0.80(2)	4.07(37)	3.60
NaClO ₄ /HClO ₄ , $\mu = 0.01$, $\gamma_{\text{NaClO}_4} = 0.903$, $\gamma_{\text{HClO}_4} = 0.906$						
La ³⁺	1.16	6.70(5)	5.77(8)	0.86(1)	3.18(41)	3.61
Co(ClO ₄) ₂ /NaClO ₄ /HClO ₄ , $\mu = 0.1$, $\gamma_{\text{NaClO}_4} = 0.856$, $\gamma_{\text{HClO}_4} = 0.860$						
Co ²⁺	0.65	5.19(4)	4.62(4)	0.89(1)	3.67(41)	3.69

constant β^ψ . The value of β^ψ (Table 5) increases with increasing structure-making properties of the ion. This may reflect the interaction of the ion with the electrolyte bulk water. Thus an analytical expression for β^ψ was obtained by plotting the product $\log \beta^\psi \cdot (\tau_i^\circ/\tau_{\text{H}_2\text{O}}^\circ)$ versus $(\tau_i^\circ/\tau_{\text{H}_2\text{O}}^\circ)$ (Fig. 5). In fact $\log \beta^\psi$ corresponds to the pH-value for which we have: $[\{\text{M}(\text{H}_2\text{O})_N^{n+}\}] = [\{\text{M}(\text{H}_2\text{O})_N^{n+}\} \{\text{H}^+\}]$. From the linear fit of the data plotted in Fig. 5 and using eqns. (6) and (2), the stoichiometric equilibrium constant may be expressed as a function of the diffusion coefficient of the ion in pure water, ($D_i^\circ = kT u_i^\circ / ez$), and of the diffusion coefficient of water, $D_{\text{H}_2\text{O}}^\circ$:

$$\beta^\psi = 7413 \exp\left(\frac{-2.82r_i D_i^\circ}{\theta D_{\text{H}_2\text{O}}^\circ}\right) \quad (23)$$

The $\log \beta^\psi$ values calculated with the equation above are listed in Table 5.

Finally, the variation of the ion mobility with the pH of the Na(H)ClO₄ electrolyte mixture of a constant overall ionic strength μ can be expressed as follows

$$u = u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}} \left[1 - \frac{f(\mu)\beta^\psi [\text{H}^+]}{1 + \beta^\psi [\text{H}^+]} \right] [1 + 0.321[\text{H}^+]] \quad (24)$$

where $f(\mu)$ corresponds to the second term on the right side of relation (22). As $u_{\{\text{M}(\text{H}_2\text{O})_N^{n+}\}}$ for the uni- and divalent ions studied here may be calculated from relation (9) (or by a similar relation for the lanthanide and actinide ions), the relation (24) reaches the general form: $u = u^\circ - g(\mu, [\text{H}^+])$. The variation of the AIIM with the pH of the inert electrolyte calculated by means of eqn. (24) is represented by the dotted lines in Fig. 4 and Fig. 5.

IV Discussion

The extended DHO limiting law does not predict a change of the AIIM with the pH of the inert electrolyte mixture. However a systematic effect of the hydrogen ion concentration on the electrophoretic mobilities of radioactive cations on tracer scale (10^{-11} mol) has been observed by means of the electromigration technique. From the systematic analysis of the experimental migration data a semi-empirical relation (24) was deduced. It reproduces well the change of the AIIM with the hydrogen ion concentration. However the cause of this effect which in our mind has so far never been observed with other methods based on the measurement of the individual transport properties of ions, still remains unknown. A change of the dynamical properties of the electrolyte bulk water with regard to the hydrogen ion concentration could be a possible explanation for this effect.

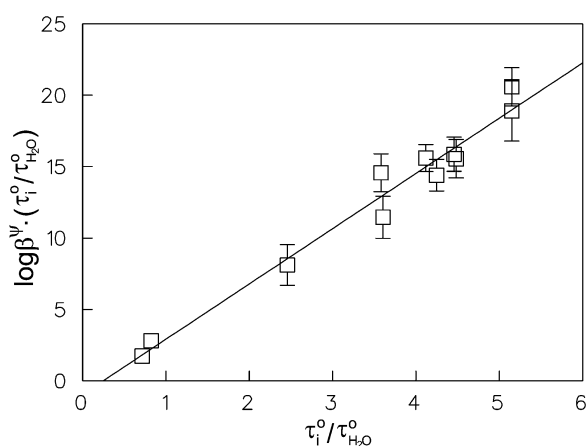


Fig. 5 Plot $\log \beta^\psi (\tau_i^\circ/\tau_{\text{H}_2\text{O}}^\circ)$ versus $\tau_i^\circ/\tau_{\text{H}_2\text{O}}^\circ$ at $T = 298.15$ K for the ions investigated. (Coefficient of correlation $r = 0.988$).

In the zone of $7 > \text{pH} > 3-5$, the hydrogen ion concentration appears to be too low to affect the dynamic properties of the bulk water. The values of the ion microviscosity η_i and of the reorientation time of water molecules in the hydration shell of the ion τ_i calculated from the experimental AIIM (Table 3) are somewhat higher than those obtained for pure water (Table 1). This is due mainly to the modification of the dynamical properties of bulk water induced by the hydrated ions of the electrolyte. We also observed that the pH value at which the decrease of the ion mobility begins appears to depend on the structure-affecting properties of the moving ion.

According to the microscopic version of Stokes law, eqn. (2), the decrease of the AIIM could be explained by an increase of the frictional forces exerted on the migrating ion due to an excess of hydrated protons in the electrolyte bulk water. It is well established that the migration of an excess of protons in water does not occur through hydrodynamics Stokes diffusion but *via* a process of structural diffusion (Grötthuss mechanism), in which charge transfer takes place through an interchange of covalent and hydrogen bonds.¹⁵ The mechanism of structural diffusion gives the proton a very high mobility, leading to the formation of hydrated protons, which are generally described with the limiting structures H_5O_2^+ (Zundel cation¹³) or H_9O_4^+ (Eigen cation¹⁴). Due to its high mobility, the proton can thus interact with a large number of water molecules. Hence, the non-negligible presence of hydrated protons could modify the dynamic (reorientation time) and structural properties (translational and orientational order) of the electrolyte bulk water. This results in an increase of the reorientation time of the water molecules in the hydration sphere of the ion and thus to a lowering of the ion mobility.

For the change of the rotational reorientation time of the electrolyte bulk water with the hydrogen ion concentration we propose the following relation

$$\tau_{\text{H}_2\text{O}} = \tau_{\text{H}_2\text{O}}^\circ \left[\frac{\sum_j c_j \tau_j}{\sum_j c_j \tau_j^\circ} \right] \quad (25)$$

where c_j is the concentration and τ_j the rotational reorientation time of the water molecule in the first hydration shell of the ion for the j th ion composing the electrolyte, except for the proton itself, ($j \neq \text{H}^+$). The variation of τ_j with the hydrogen ion concentration at a given overall ionic strength of the electrolyte mixture is obtained using relation (24). The values of the phenomenological stoichiometric equilibrium constants β^ψ derived from relation (22) are: 162(9), 2188(131), 4898(292) $\text{dm}^3 \text{mol}^{-1}$ for ClO_4^- , Na^+ and Co^{2+} respectively. The variation of the reorientation time of the bulk water molecules $\tau_{\text{H}_2\text{O}}$ with the hydrogen ion concentration of the various electrolytes mixtures is shown in Fig. 6. The values of $\tau_{\text{H}_2\text{O}}$ and of the corresponding diffusion coefficient of bulk water $D_{\text{H}_2\text{O}}$ for the neutral and acidic electrolyte solutions are listed in Table 6. A consequence of relation (25) is that the relative exchange rate of water molecules between the first hydration sphere of the ion and the bulk, $\Delta n/N$, remains constant for any electrolyte composition. We see no indication that more or less water molecules leave the hydration shell of the ion as the hydrogen ion concentration of the electrolyte increases, only the dynamical properties are affected. Hence the rotational reorientation time of the water molecules in the hydration shell of the migrating radioactive ion may be expressed as

$$\tau_i = \tau_i^\circ (\tau_{\text{H}_2\text{O}}/\tau_{\text{H}_2\text{O}}^\circ) \quad (26)$$

The values of τ_i calculated by means of eqn. (26) for the radioactive ions in neutral and acidic aqueous electrolytes are in fairly good agreement with the values derived from the experimental ion mobilities (Tables 3 and 4).

By means of eqn. (25), we can also calculate the value of the rotational reorientation time of bulk water, $\tau_{\text{H}_2\text{O}}$, in NaClO₄ and HClO₄ electrolytes of various ionic strength. The ionic

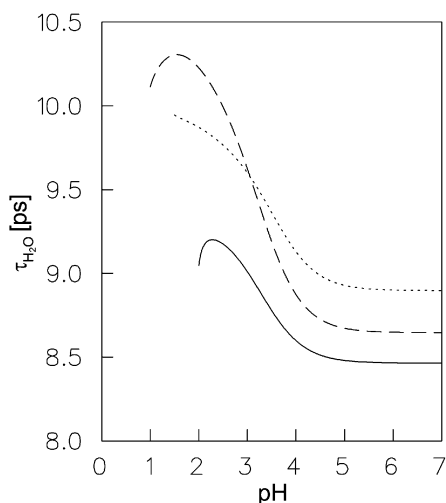


Fig. 6 Reorientation time of bulk water molecules of the electrolyte as function of the pH at 298.15 K. The solid line represents the electrolyte mixture Na(H)ClO₄ $\mu = 0.10 \text{ mol dm}^{-3}$; the dashed line the electrolyte mixture Na(H)ClO₄ $\mu = 0.01 \text{ mol dm}^{-3}$ and the dotted line the electrolyte mixture Co(ClO₄)₂/Na(H)ClO₄ $\mu = 0.10 \text{ mol dm}^{-3}$.

strength dependence of $\tau_{\text{H}_2\text{O}}$ for both electrolytes is displayed in Fig. 7. For the NaClO₄ electrolyte the value of $\tau_{\text{H}_2\text{O}}$ may be derived by a similar law as the extended DHO limiting law, since, as mentioned above, the hydrogen ion concentration is too low to affect the dynamical properties of the bulk water molecules. In the case of the HClO₄-electrolyte, the value of $\tau_{\text{H}_2\text{O}}$ increases significantly for increasing hydrogen ion concentrations and thus with the fraction of water molecules which exchange protons per unit time. The variation of the rotational reorientation time of bulk water with the proton concentration may be given by the following semi-empirical expression

$$\tau_{\text{H}_2\text{O}} = \tau_{\text{H}_2\text{O}}^\circ \left[1 - \frac{\tau_p}{\tau_{\text{H}_2\text{O}}^\circ} \left(1 - \exp\left(-b \frac{[\text{H}^+]}{[\text{H}_2\text{O}]}\right) \right) \right]^{-1} \quad (27)$$

where τ_p is the proton hopping time, $[\text{H}_2\text{O}] = 55.5 \text{ mol dm}^{-3}$ and b a numerical constant. The fit of the $\tau_{\text{H}_2\text{O}}$ data for HClO₄ electrolytes according to the relation (27) (solid line in Fig. 7) leads to a value for τ_p of 1.44(18) ps at 298.1(5) K. The inverse of this number corresponds to the rate constant for proton transfer between the hydronium ions and the acceptor water molecule. The value found here is 0.69(9) ps⁻¹ and compares well with the experimental value obtained from NMR studies of proton transfer in water,⁴⁶ 0.67 ps⁻¹ and with the values calculated by quantum molecular dynamic simulation¹⁸ which are 0.69 ps⁻¹ for proton transfer in the Eigen cation and 0.60 ps⁻¹ for proton transfer in the Zundel cation. The ratio $b/[\text{H}_2\text{O}]$ in expression (27) is 60.8(4) dm³ mol⁻¹.

From the value of τ_p it is also possible to determine the proton hopping length, r_{OO} , defined as the oxygen–oxygen distance between the hydronium ion and the acceptor water

Table 6 Rotational reorientation time $\tau_{\text{H}_2\text{O}}$ and diffusion coefficients $D_{\text{H}_2\text{O}}$ of bulk water molecules in neutral and acidic perchlorate electrolytes $T = 298.1(5) \text{ K}$

Electrolyte	$\mu/\text{mol dm}^{-3}$	$\tau_{\text{H}_2\text{O}}$ [eqn. (26)]/ 10^{-12} s	$D_{\text{H}_2\text{O}}/10^{-9} \text{ cm}^2 \text{ s}^{-1}$
NaClO ₄	0.10	8.65(7)	2.20(2)
NaClO ₄	0.01	8.47(7)	2.25(2)
Co(ClO ₄) ₂ /NaClO ₄	0.10	8.90(7)	2.14(2)
HClO ₄	0.10	10.11(10)	1.88(2)
HClO ₄	0.01	9.05(10)	2.10(2)
Co(ClO ₄) ₂ /HClO ₄	0.10	9.94(8)	1.92(2)

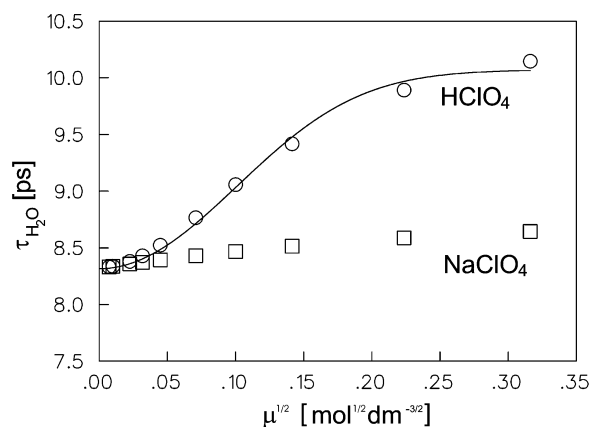


Fig. 7 Rotational reorientation time of bulk water versus ionic strength of the NaClO₄ and HClO₄ electrolytes. The solid line is eqn. (27).

molecule, by means of the Einstein relation:

$$r_{\text{OO}} = \sqrt{6\tau_p D_p} \quad (28)$$

where $D_p = 7.01 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ is the abnormal proton mobility, (difference between the proton diffusion coefficient, $9.31 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and water self-diffusion coefficient, $2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).^{15,28} With $\tau_p = 1.44(18) \text{ ps}$ we find a value for the proton hopping length of $r_{\text{OO}} = 2.46(15) \text{ \AA}$. This value agrees well with the experimental data obtained from thermal neutron and X-ray scattering studies, $r_{\text{OO}} = 2.5 \text{ \AA}$.⁴⁷ Molecular dynamic simulations lead to values of $r_{\text{OO}} = 2.40\text{--}2.49 \text{ \AA}$ for H_5O_2^+ and $r_{\text{OO}} = 2.50\text{--}2.60 \text{ \AA}$ for H_9O_4^+ .^{16,17,20} For comparison it should be remembered that the oxygen–oxygen distance between two water molecules in pure water is larger, about 2.8 \AA .

According to relations (26) and (27), the concentration dependence of the absolute individual ion mobility of an ion present at tracer scale in HClO₄ may be written as:

$$u_i = u_i^\circ \left[1 - \frac{\tau_p}{\tau_{\text{H}_2\text{O}}^\circ} \left(1 - \exp\left(-b \frac{[\text{H}^+]}{[\text{H}_2\text{O}]}\right) \right) \right] \quad (29)$$

The experimental values of the AIIM of La³⁺ ions in HClO₄,⁴⁸ the only migration data in acidic solutions found in the literature at the time of this work, are plotted as a function of the ionic strength of the electrolyte in Fig. 8. The values of the AIIM given by eqn. (29) using the parameters $\tau_p = 1.44 \text{ ps}$ and $b/[\text{H}_2\text{O}] = 60.8 \text{ dm}^3 \text{ mol}^{-1}$ are represented by the solid line in Fig. 8. The calculated values agree well with the experimental data. Thus, despite the great lack of absolute and accurate tracer migration data in perchloric acid for comparison, we can say that eqn. (29) leads to a good estimation of the transport properties of ions on tracer scale in HClO₄. For other acids such as HCl or HNO₃ for example, eqn. (29) cannot be applied directly for all metal ions because of the formation of complex species of various charges which greatly influence the overall ion mobility.

IV Conclusion

In acidic inert aqueous electrolytes, metal cations, particularly at very low concentrations, migrate completely differently from predictions by standard theories. As this is not due to the intrinsic properties of the migrating ion themselves, the structure and dynamics of the aqueous electrolytes with an excess of protons must be responsible.

In this paper we have investigated the dependence of the absolute individual ion mobility (AIIM) of the radioactive ions [¹³⁷Cs]Cs⁺, [²⁰¹Tl]Tl⁺ and [⁵⁷Co]Co²⁺ on the hydrogen ion

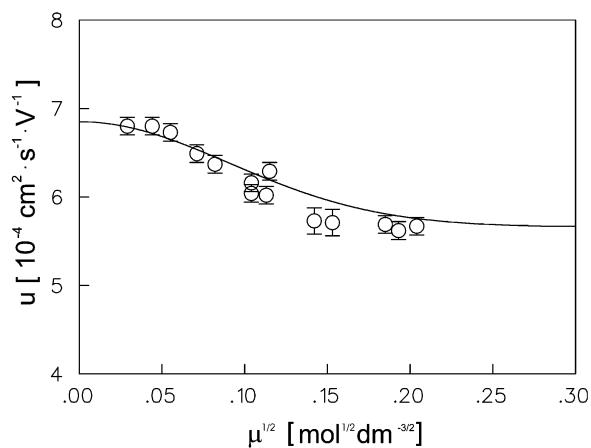


Fig. 8 Ion mobility of La^{3+} in HClO_4 . Experimental data (circles), calculated data from eqn. (29) (solid line).

concentration of inert aqueous perchlorate electrolyte mixtures by means of the electromigration technique. The AIIM of the radioactive ions is found to decrease as the hydrogen ion concentration of the electrolyte mixture increases. A similar behavior of the AIIM with regards to the hydrogen ion concentration of inert electrolytes was also observed in previous work for some di- and trivalent radioactive ions at tracer scale. The experimental values of the AIIM were compared to the theoretical values predicted by the extended DHO limiting law. For the neutral electrolyte mixtures of low hydrogen ion concentration ($\text{pH} > 4$) there is a fairly good agreement between experimental and calculated values. The experimentally observed decrease of the AIIM of the radioactive ions for higher hydrogen ion concentrations ($\text{pH} < 4$) is not explained by the extended DHO limiting law. A systematic analysis of the migration data was performed assuming a change of the dynamical properties of the water molecules in the hydration shell of the migrating radioactive ions. The resulting general relation for the variation of the AIIM with the hydrogen ion concentration as well as with the overall ionic strength μ of the electrolyte mixture is of the form: $u = u^\circ - f(\mu, [\text{H}^+])$ [see eqn. (24)].

The effect of the hydrogen ion concentration on the AIIM can be explained by a possible change of the dynamical properties of electrolyte bulk water due to the increasing presence of an excess of hydrated protons in the bulk. From the variation of the rotational reorientation time of bulk water molecules in HClO_4 electrolytes of various concentrations, a value of 0.69 ps^{-1} is derived for the rate constant of proton transfer between the hydronium ions and the acceptor water molecules. For the proton hopping length we find a value of 2.46 \AA . These two values are in good agreement with the literature values. Finally we propose a relation for the ion mobility of radioactive ions at tracer scale in HClO_4 electrolytes involving the values of the proton hopping time and length.

This study demonstrates the potential of the electromigration method to investigate the individual parameters of the migrating ion, but also to derive data on the dynamics of electrolyte systems. The approach might thus be applied to provide experimental data to check the validity of various theoretical models developed for understanding the dynamics of ions in solutions.

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