Diffusion of ^{22}Na$^+$ in inert aqueous electrolytes – pH dependence.

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In order to study the effect of an excess of protons in solutions on the transport properties of ions, the diffusion coefficients of Na$^+$ ions labelled with ^{22}Na ($T_{1/2}$ = 2.603 y) were measured by the open-ended capillary method according to the pH of the following electrolytes: NaClO$_4$/HClO$_4$, μ = 0.5, LiClO$_4$/HClO$_4$, μ = 0.1 and NaClO$_4$, μ = 0.1, at 289.1 K.

Capillaries in Teflon were first filled with the electrolyte of a given composition and pH labelled with the investigated radioisotope. The capillaries were then immersed in a thermostated non radioactive solution of identical chemical composition. During the diffusion run time, which was of the order of 1 hour, a constant stirring speed of 2 cm/min was applied to the support of the capillaries in order to avoid a radio-tracer accumulation at the open end of the capillary, without convection. The activities of the solution in the capillaries before (A_i) and after (A_f) diffusion were measured using a GeLi detector. The experimental diffusion coefficient, D, was calculated as follows:

$$D = \frac{4l^2}{\pi^2 t} \ln\left(\frac{8}{\pi^2 \gamma}\right) + \frac{4l^2 \pi^{14} \gamma^8}{9t8^8} \quad (1)$$

where t is the time of diffusion, l the length of the capillary (3.8 mm) and γ the ratio A_f/A_i.

The experimental diffusion coefficients of Na$^+$ in the neutral electrolytes (pH=6) as well as the theoretical values calculated using the limiting law (LL, Onsager law) and the extended limiting law (ELL) are given in Table 1. The later law takes into account the closest distance of approach between the ions composing the electrolyte. For the diffusion of Na$^+$ in neutral NaClO$_4$ electrolytes (self-diffusion), the experimental value agrees well with the ELL value. But, in the case of the diffusion of Na$^+$ in the neutral LiClO$_4$ electrolyte (tracer-diffusion) a large difference between the experimental and the theoretical values is observed.

The variation of the experimental diffusion coefficient with the pH of the electrolytes is shown in Fig.1. The diffusion coefficient remains constant over a wide range of pH before to increase for self-diffusion or to decrease for tracer-diffusion as the proton concentration increases (pH < 1.5). Using the equation obtained for the change of the experimental ion mobility with the pH [1] and the Nernst-Einstein relationship, the diffusion coefficient of Na$^+$ in Li(H)ClO$_4$ electrolytes may be given as a function of the proton concentration by (solid line in Fig. 1):

$$D = D_{LiClO_4}\left(1 - \frac{0.18\beta[H^+]}{1+\beta[H^+]}\right) \quad (2)$$

with D_{LiClO_4} = 0.96 10^{-9} m$^2\cdot$s^{-1} and β = 2215 L$\cdot$mol^{-1}.
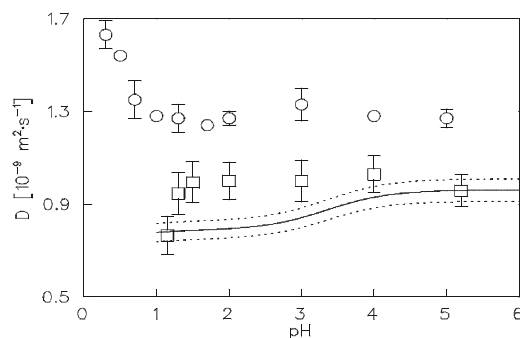

Fig. 1. Experimental diffusion coefficient of Na$^+$ versus pH of NaClO$_4$/HClO$_4$, μ = 0.5, (circles) and LiClO$_4$/HClO$_4$ μ = 0.1 (squares) electrolytes. The solid line is the diffusion coefficient from Eq.(2). The dashed lines are the uncertainties on the values of Eq.(2).

Table 1. Diffusion coefficients of Na$^+$ in neutral electrolytes of various ionic strength (μ). T = 298.1K. LL: limiting law; ELL: extended limiting law.

Electrolyte	μ	$D \times 10^9$ [m$^2\cdot$s^{-1}]		
		LL	ELL	Exp
NaClO$_4$	0.1	1.24	1.28	1.32(6)
NaClO$_4$	0.5	1.13	1.27	1.26(3)
LiClO$_4$	0.1	1.24	1.29	0.96(7)

The difference between the experimental diffusion coefficients and the diffusion coefficients calculated from the absolute individual ion mobilities leads to the assumption that the charge of the moving ion is not constant and equal to the formal charge when the pH of the solution is less than 4. The concept of "apparent charge", z_{ap}, was first introduced by Magdelenat et al. [2] and reflects the complexity of the structure of charged particles in electrolyte solutions. z_{ap} may be given from the experimental transport properties by:

$$z_{ap} = \frac{kT u_{exp}}{e D_{exp}} \quad (3).$$

A comparison between experimental sel-diffusion coefficients and electrophoretic mobilities (u) should thus be useful to point out the variation of the apparent charge of the migrating ion in acidic media.

[1] E. Mauerhofer, F. Rösch, Effect of the pH on the ion mobility of non-carrier-added radioelements in chemically inert aqueous electrolytes, to be published. [2] Magdelenat H. et al. Apparent ionic charge in electrolyte and polyelectrolyte solutions, J. Chem. Education, 55, (1978)12.