Diffusion Coefficients for HCl under Conditions approaching Neutrality

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Direct measurement of HCl diffusion under near-neutral conditions demonstrates much lower neutral diffusion coefficients than previously demonstrated.

Water can be considered to be a condensed phase with a randomly arranged hydrogen bonded structure.[1] The formation and dissolution of hydrogen bonds, which involves protons as well as water molecules, occurs on a time scale of 10^{-12} s.[2] Within this network, the proton exists principally in bound form as H_3O^+ with a surrounding hydration shell. The transfer of protons through water occurs *via* a jump mechanism largely consistent with that enunciated by Grotthas. There, a proton passes from one water molecule to the next, through formation of a new hydrogen bond, with local charge

Table 1. Diffusion coefficients for HCl through a dialysis membrane and underlying spacer.

pH[a]	D_{HCl} /cm^2 s^{-1} × 10^6
7.46	0.34
6.44	0.79
5.46	1.18
4.52	1.71
3.50	5.56

[a] Midpoint of an individual pH jump.

due to the proton leading to reorientation of the water molecule.[3] Coupled with this, the diffusion of sites with attached protons may also be important.[4] This microscopic picture is seen as the basis for the high anomalous mobility of protons in water. The limiting molar conductivity for H^+ ($349.8 \times 10^{-4}\ \Omega^{-1}\ m^2\ mol^{-1}$ at 25 °C[5]) is five- to nine-fold greater than that of alkali metal cations, and the mutual diffusion coefficient of HCl (D_{HCl}) as measured by diffusion chamber apparatus is approximately two-fold greater than that for the corresponding alkali metal salts.[2]

Hitherto, D_{HCl} has shown only minor reduction as HCl concentration is lowered; thus, the value at 0.05 M (3.07×10^{-5} cm^2 s^{-1} at 25 °C) is 10.6% of that at 1.0 M.[6] Direct measurement of D_{HCl} under conditions approaching neutrality, have not been possible, however, in view of the practical difficulty of achieving reliable pH gradients without buffering. We have, therefore, used a simplified single compartment electrode system to estimate D_{HCl} over the pH range 3—7. Dynamic responses at a glass pH electrode were monitored, where the electrode tip was mounted with a single dialysis membrane and a nylon spacer; a 60 μm unstirred film layer. Step changes in pH were induced in a vigorously stirred external solution containing 20 g l^{-1} albumin[7] at 23 °C, and D_{HCl} computed using a diffusion boundary layer model[8] for ion selective electrode dynamic response.

The time to complete 99% of the response (t_{99}) varied from 1—2 min at low pH to 20 min at high pH, and was an order of magnitude greater than t_{99} for the bare electrode throughout the pH range used (<1 s). When a double thickness nylon spacer was used, t_{99} was correspondingly increased; on taking the altered diffusion layer into account, the computed D_{HCl} values remained unaltered within experimental error.

Representative D_{HCl} values for individual pH jumps (Table 1) demonstrate an order of magnitude reduction compared with 0.05 M HCl, and also a marked further reduction towards neutrality where the minimum D_{HCl} is reached. NMR relaxation data[9] indicate that the proton jump mechanism is unaffected by pH. The reasons for observed D_{HCl} changes are, therefore, obscure, though they may relate to modification in coupling to the alternative diffusional route to proton movement.[4] Irrespective of the mechanism, the results are of wide general significance for reactions involving protons under near-neutral conditions. In addition, they have implications for pH equilibration within biological systems.

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