# MODERN ASPECTS OF ELECTROCHEMISTRY

## No. 12

Edited by
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# Preface

The first chapter in the present volume takes up a well-known theme in modern context: the ideas concerning non-Stokesian mechanisms of ion transport. We are happy that one of the great pioneers of modern electrochemistry, T. Erdey-Grúz, in collaboration with S. Lengyel, has consented to write this article for us. Along with it is a solution-oriented article in spectroscopic vein, namely, that by A. Covington and K. E. Newman on the analysis of solution constituents by means of nuclear magnetic resonance studies.

Progress in the electrochemistry of the double layer has perked up, and the advances have been triggered from critical experiments, one showing that fluoride ions are specifically adsorbed, and the other showing that the position of maximum disorder of the water molecules occurs at a charge opposite to that needed for interpretations of capacitance humps in terms of water molecules. M. A. Habib, who has contributed to the theory in this area, reviews the consequences of these changes in information.

The rise in the price of energy toward a situation in which sources other than the fossil fuels become economical implies much for the fuel cell and electrocatalysis. It has long been known that electrocatalysis in real situations was more than a consideration of exchange current densities, and a gap remains in the formulation of the theory of supports for such catalysts, although Boudart has stressed so much the vital nature of them. P. Stonehart and K. A. Kinoshita describe progress in this area.

Lastly, the Bockris and Reddy prediction that the eventual largest area of application of electrochemistry would come in biology and medicine has advanced apace, and some of this intriguing material is described by F. Gutmann and J. P. Farges.

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# 1

# Proton Transfer in Solution

T. Erdey-Grúz and S. Lengyel

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## I. INTRODUCTION

The understanding of the role of proton transfer in the mechanism of transport processes in solution is based on three accepted concepts:

1. In a solution containing ions produced by dissociation of solvent molecules, rapid charge transfer may take place between these ions and solvent molecules when they collide. This charge transfer and the sudden charge displacement (jump) that is involved, e.g., between a hydrogen ion and a water molecule or a $CH_3O^-$ ion and a methanol molecule, may contribute to the transport of current in solution. This possibility was recognized as early as 1905 by Danneel.[1]

2. Successive charge transfers in a particular direction (e.g., under the influence of an external electric field) are necessary for this contribution. A series of successive transfers can take place only if each jump is followed by structural rearrangement in the liquid. As an example of such rearrangements, rotation of solvent molecules was also mentioned by Danneel.[1]

3. No free protons exist permanently in aqueous solutions. The hydrogen ion is the monohydrate of the proton, i.e., the hydronium (or oxonium) ion, $H_3O^+$. Recognition of this ion was first substantiated by Goldschmidt and Udby[2] in their theory of kinetics of acid-catalyzed esterification reactions. Recognizing the hydrogen ion as $H_3O^+$ also meant identifying Danneel's charge transfer as proton transfer from $H_3O^+$ to $H_2O$.

In liquids in which proton transfer contributes to transport processes, the structure is much influenced by the presence of hydrogen bonds. It was Latimer and Rodebush[3] who first recognized that "a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together," or in the more general form, "the hydrogen nucleus held between two octets constitutes a weak bond." This was the first formulation of the hydrogen bond. Latimer and Rodebush also understood the role the hydrogen bond might play in promoting proton-transfer "shifting of hydrogen nuclei from one water molecule to another." Recognition of the hydrogen bond may thus be considered, along with the three concepts enumerated above, as forming the groundwork for theories of proton transfer in transport processes in solution.

The hydrogen bond and proton transfer are decisive factors for a number of phenomena. In many crystalline hydrates, the hydrogen bond plays an important structure-influencing role. On the other hand, in some solids, such as $KH_2PO_4$, the hydrogen bond is responsible for ferroelectric properties. In biological materials, characteristic structural features are determined by hydrogen bonds; the $\alpha$-helix structure, myoglobin and lysozyme structures of polypeptide chains, and the double helix of DNA should be mentioned as examples, together with the suggestion[4] that proton tunneling in nucleic acid–base pairs may affect the transmission of genetic information. In liquids, association by hydrogen bonding has long been recognized as related to high dielectric constants. Proton transfer is a part of the mechanism of acid, base, and enzymatic catalysis. In this chapter, we shall focus our attention on the exchange reactions of proton transfer and their contribution to transport processes in solution.

Regarding chemical reactions controlled by proton transfer, the dynamics of the formation and dissociation of hydrogen bonds, and the effect of hydrogen bonding on reaction rates, we refer to reviews and monographs on this topic.[5–8]

Since Conway[9] published an excellent detailed analysis of theories concerning proton-transfer processes in solution in this series in 1964, we restrict ourselves here to referring to well-known findings and theories and focus our attention on the advances described in the literature after 1964.

## II. EXPERIMENTAL FINDINGS

### 1. Anomalous Mobility of Ions of the Solvent Molecule in a One-Component Solvent

The limiting value of the equivalent conductance of atomic or other simple inorganic ions in aqueous solutions at 25°C is about 35–80 $\Omega^{-1}$ cm$^2$ equiv$^{-1}$. The hydrogen and the hydroxide ions are exceptions, with the much higher values of 350 and 192,[10] respectively. If we use a model of spherical charged particles subject to resisting forces proportional to their velocity and moving in a homogeneous fluid of definite viscosity, and apply Stokes's law, we obtain reasonable values for ionic radii in the range 1.2–4.4 Å. They are approximately in accordance with the hydrated radii.[11,12] However, the value expected for the hydrogen ion is unreasonably small, no free protons exist permanently in aqueous solutions, and the chemical species that actually exist, $H_3O^+$ and $OH^-$, have dimensions near that of a water molecule, which, if considered to be roughly a sphere, has a radius of about 1.4 Å.

As in the case of hydrogen and hydroxyl ions in aqueous solutions, anomalously high conductances were found for the $CH_3O^-$ ion in methanol by Dempwolff[13] and Tijmstra,[14] for the pyridinium ion ($C_5H_5NH^+$) in pyridine, the formate ion in formic acid, and the acetate ion in acetic acid by Hantzsch and Caldwell[15] in the years 1904, 1905, and 1907, respectively. The generalization that all ions produced by dissociation of the solvent molecule have anomalously high conductance was first suggested by Danneel.[1]

For these ions, in contrast to the hydrodynamic migration of the others, a different mechanism of current transport was proposed as early as 1905.[1] In the case of other ions, ion–solvent interactions (hydration, solvation) had to be considered in order to explain differences between Stokes and crystallographic radii and other facts.

The presence of the $H_3O^+$ ion in solids as well, namely, in crystal hydrates, could be detected,[16,17] and its molecular geometry was recently determined by Lundgren and Williams[18] by neutron scattering on *p*-toluenesulfonic acid monohydrate single crystal.* This crystal proved to be ionic, with the chemical species $H_3O^+$ at cation positions. According to this study, the $H_3O^+$ ion has a pyramidal

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*For earlier studies on the structure of $H_3O^+$, see Ref. 9, pp. 53–56.

structure with three O—H distances of 1.01 Å and H—O—H angles of 110.4°. The oxygen nucleus is at a distance of 0.32 Å above the plane formed by the three protons. The shape and size of the whole ion do not differ too much from those of the water molecule, and taken as a sphere, it can be assumed to be an intermediate between the ions of sodium and potassium, closer to the latter. Thus, we also have crystallographic radius for $H_3O^+$. A Stokes radius cannot be calculated directly from conductance because of a non-Stokesian mechanism of transport. However, hydrodynamic migration ("bodily transport") by the chemical species $H_3O^+$ cannot be excluded. Consequently, at least two mechanisms for the transport of current by protons must be supposed.

The hydrodynamic fraction of this conductance can be estimated, starting from assumed values for the radii of ionic spheres. Lorenz[19] used radii of the H atom and the $OH^-$ ion, calculated from atomic volumes by Reinganum's formula. A more adequate way of estimation is to take $H_3O^+$ as a sphere of a size intermediate between that of $Na^+$ and $K^+$ and assume a corresponding hydrodynamic mobility (a value between 50.1 and 73.5 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1}$).[10]

A higher value of 85 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1}$ results if we assume the hydrodynamic mobilities $\lambda$ of the species $H_3O^+$ and $H_2O$ to be approximately equal and calculate the latter from the experimental value of the self-diffusion coefficient of the water molecule ($D^* = 2.25 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$)[20] by using Nernst's expression in the form

$$D^* = (\lambda/e_0F)kT$$

Here $e_0$ denotes electronic charge, $F$ the Faraday constant, and $k$ Boltzmann's constant.

A higher value for the radius of the hydrated $H_3O^+$ ion is obtained from thermodynamic ionic properties (heat capacities[21,22] and activity coefficients[23]) of solutions of lithium halides and $LiClO_4$ and salts of other alkali metals with those of acid solutions. This comparison shows that the behavior of the $Li^+$ ion comes closest to that of the $H_3O^+$ ion.

If we take the hydroxide ion as a sphere of the same radius as that of the isoelectronic fluoride ion, we obtain by Stokes's formula $\lambda = 55\,\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{equiv}^{-1}$. A fraction of the conductance of $OH^-$ corresponding approximately to this value is due, then, to hydrodynamic migration.

The differences between the total and the hydrodynamic conductances must be explained by a special conductance mechanism for both the $H_3O^+$ and the $OH^-$ ion.

The temperature dependence of the total equivalent conductance (relative mobility) of $H_3O^+$ differs from that of other ions.[9,10,24–27] Since the structure of water changes with temperature, the temperature dependence of the equivalent ionic conductance cannot be fitted by a single apparent activation energy over a longer range of temperature. However, if values of apparent activation energies calculated for the same temperature interval are compared, the values of $H_3O^+$ and $OH^-$ are smaller than those of any other simple ion. In the interval 0–156°C, the activation energy decreases with increasing temperature for all simple ions. However, this decrease is more rapid for $H_3O^+$ and $OH^-$.

As was shown by Hückel,[24] the differences $\lambda_{H^+} - \lambda_{Na^+}$ (or $\lambda_{H^+} - \lambda_{K^+}$) can be taken approximately as the nonhydrodynamic fraction of the conductance of the hydrogen ion. The apparent activation energies calculated from these values are lower than the apparent activation energies of other ions. Their decrease with increasing temperature is very rapid.

In contrast to other ions, the equivalent conductance of the hydrogen ion increases with increasing pressure.[28–33] Correspondingly, the activation volume calculated from the pressure dependence of the abnormal contribution to proton mobility is negative.

Bernal and Fowler assumed[25] that "the effective mobility of the isotope D must be less than that of the ordinary H." Since hydrodynamic and transfer mechanisms are influenced to a different degree by the isotope effect, it is important to know the ratio of the mobilities of $H^+$ in $H_2O$ to $D^+$ in $D_2O$. At 25°C, it is 1.42.[27] This ratio can be derived from measurements of the conductances of hydrochloric acid and potassium chloride in ordinary water and in nearly pure $D_2O$.[34] (See also the footnote on p. 836 of Ref. 27.) Alternatively, it can be derived from the diffusion coefficients calculated by the corrected form of the Ilkovic equation from the polarographically measured diffusion currents.[35] However, the ratio (1.52) derived from the latter approach[36] differs slightly from the above-mentioned value. This ratio has been studied as a function of the concentration of the supporting electrolyte in solutions of some alkali halides and tetraalkylammonium bromides.[35,36]

Assuming a hydrodynamic mobility mechanism only, we should expect a smaller value for $\lambda_{H^+}/\lambda_{D^+}$, corresponding to the differences between viscosities and dielectric constants of $H_2O$ and $D_2O$, respectively. Supposing, on the other hand, that in the mechanism involving proton (or deuteron) transfer (usually referred to as the *prototropic mechanism*), it is this transfer, not a structural rearrangement, that is the rate-determining step; we should then expect a higher value for $\lambda_{H^+}/\lambda_{D^+}$ than that observed, due to the mass effect on transfer probability.

The difference between the equivalent conductances of $H^+$ and $OH^-$ is also important. The conductance of $OH^-$ is less than that of the ion $H^+$.

Roberts and Northey[36] calculated from their polarographic measurements of the limiting diffusion current a limiting value of $D^0_{H^+} = 9.4 \times 10^{-5}\,\mathrm{cm^2\,sec^{-1}}$ for the diffusion coefficient of $H^+$ at 25°C. According to Nernst's formula, this corresponds to an equivalent conductance of $\lambda_{H^+} = 352\,\Omega^{-1}\,\mathrm{cm^2\,equiv^{-1}}$. This experimental evidence for equal mobilities in diffusion and current transport was preceded by the observations of Woolf[37] that the presence of "supporting" electrolytes decreases tracer diffusion of $H^+$ to a higher degree than that of any other ion. Correspondingly, Glietenberg *et al.*[38] found a particularly large effect from $Li^+$ ions. These effects were interpreted by structural changes caused by ion–solvent interactions, i.e., hydration of the ions of the supporting electrolyte. These changes lead to structures less favorable for proton transfer.

A comparison of the equivalent conductances of other ions with those of the hydrogen ion in solvents such as methanol and ethanol[9] also shows abnormal proton mobility. This abnormality is explained by consecutive processes of proton transfer and structural rearrangements. Temporary clusters of solvent molecules, bound by hydrogen bonds, certainly play an important role in this mechanism.

Experimental evidence shows that a contribution to transport processes from a transfer reaction is not limited to proton transfer. Electronic conductivity in solutions was predicted by Frumkin, as noted by Levich in his review.[39] The increase of diffusion by electron transfer was measured by Ruff *et al.* in the systems ferrocene and ferricinium ion [i.e., biscyclopentadienyl complexes of Fe(II) and Fe(III)] in alcohols,[40] ferroin and ferriin [tris1,10-phenantroline complexes of Fe(II) and Fe(III)] ions in water,[41] and ferrous and ferric forms of cytochrome *c* in water.[42] A contribution of the transfer of atoms or molecules to diffusion was also measured in systems containing sulfide and disulfide ions,[43] triiodide and iodide ions,[44] and tribromide and bromide ions[45] in aqueous solution. For systems containing antimony trichloride and aliphatic alcohols, acids, amides of carboxylic acids, and alkyl halides, there is, in addition to proton transfer, a contribution to the electrical conductivity from the transfer of atomic chlorine.[46,47]

## 2. Effect of Structural Changes on Proton-Transfer Mobility

Hydrogen bonds seem to be a precondition for proton transfer from $H_3O^+$ to $H_2O$; at least, quantum mechanical calculations of proton tunneling probability are usually based on hydrogen-bonded models.

The addition of nonelectrolytes to aqueous electrolyte solutions affects the structure of the solvent mainly by dissolving a fraction of the hydrogen bonds and changing the size of clusters held together by these bonds. The addition of electrolytes may have either a structure-breaking or a structure-forming effect on water. However, the added ions affect electrical conductivity by their own current transport. Separating these two influences has been the aim of many authors in studying the effect of the addition of nonelectrolytes on the conductance of the oxonium and the hydroxide ions. In this respect, Wulff and Hartmann[48] were the first to carry out studies on the influence of the dioxane content in hydrochloric acid solutions in water–dioxane mixtures on viscosity, dielectric constant, and equivalent conductance.

Nonelectrolytes that are highly soluble in water usually contain hydroxyl groups, have a characteristic structure, and show current transport by a prototropic mechanism in their pure state.

Several authors studied the effect of varying the concentration of added nonelectrolytes on the electrical conductance of aqueous acid and base solutions. Some investigated the variation of conductance with the nature of the added nonelectrolytes and their concentrations. Thus, the conductance of aqueous hydrochloric acid solutions containing methanol and ethanol has already been investigated, mainly by Goldschmidt and Dahl,[49] Walden,[50] Thomas and Marum,[51] Berman and Verhock,[52] Kortüm and Wilski,[53]

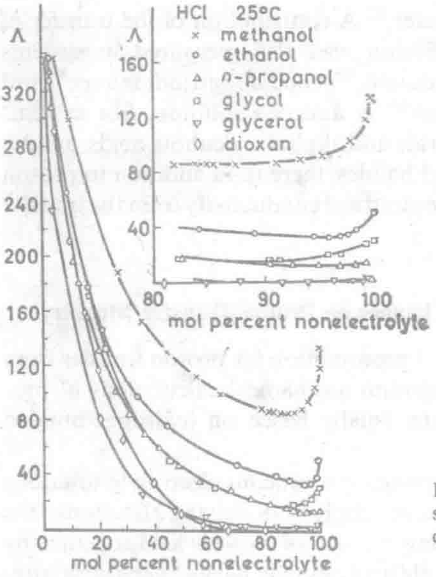

Figure 1. Conductance of 0.01 *m* solutions of HCl as a function of the concentration of various nonelectrolytes at 25°C.

Dnieprov,[54] el Aggan *et al.*,[55] and Tourky and Mikhail.[56] The change in conductance of aqueous hydrochloric acid solutions on the addition of ethylene glycol has been studied by Dnieprov[54] and Kirby and Maass,[57] while the effect of glycerol has been measured by Dnieprov,[54] Conway *et al.*,[27] Woolf,[58] and Accascina *et al.*[59]; further, the effect of butanol has been investigated by Accascina *et al.*[60] It has been found that the equivalent conductance of aqueous hydrochloric acid solutions decreases rapidly on the additions of alcohols; with increasing alcohol concentration, it passes through a minimum and increases again in solutions containing very small amounts of water. According to Tourky *et al.*,[61] and Abdel Hamid *et al.*,[62] the conductance of hydrochloric acid varies similarly in mixtures of propanol, *t*-butanol, and water. The influence of water on proton migration in 1-pentanol has been studied by de Lisi and Goffredi.[63] Figures 1 and 2 show how the equivalent conductances of dilute (0.01 *M*) hydrochloric acid and potassium hydroxide solutions vary with the concentration of the nonelectrolyte (methanol, ethanol, *n*-propanol, ethylene glycol, glycerol, and dioxane) added to aqueous solutions. These studies were made by Erdey-Grúz *et al.*[64,65] The results for HCl coincide qualitatively with those of former authors. However, more detailed information can be derived from recent studies. The conductance minimum occurs at about 90 mol percent alcohol content of the solvent (see detailed figure for the range 80–100 mol percent). On the curve for methanol, a sharp minimum can be seen, while it is smoothed out in the cases of *n*-propanol and glycerol.

The equivalent conductance of KOH solutions falls rapidly with the increasing concentration of the nonelectrolyte (Fig. 2), but a smooth minimum appears only on the curve for methanol, at about 75 mol percent of the nonelectrolyte.

Hydrodynamic mobilities depend on the viscosity of the solution. For the model of spherical charged particles subject to resisting forces proportional to their velocity and moving in a homogeneous fluid of definite viscosity, Walden's rule

$$\Lambda^0\eta^0 = (0.82 \times 10^{-8})/r = \text{const}$$

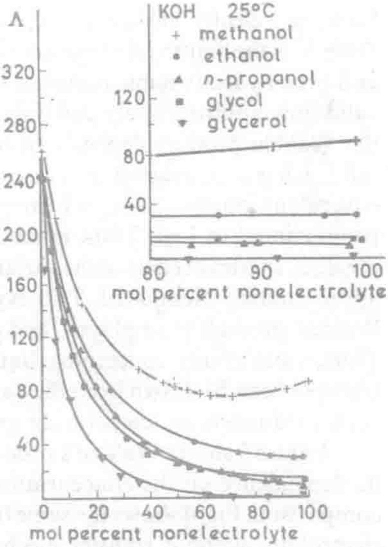

Figure 2. Conductance of 0.01 *m* solutions of KOH as a function of the concentration of various nonelectrolytes at 25°C.