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New Analysis of the $OH^{\ominus}$ Conductance Mechanism in Aqueous Solution

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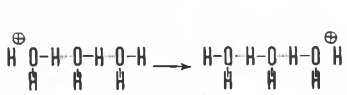
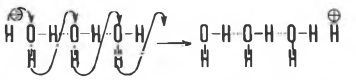
Abstract: It is shown that the commonly used schematic representation of the $OH^{\ominus}$ conductance mechanism in aqueous solution is not the analogue of the corresponding diagrams for the $H^{\oplus}$ ion. The experimental finding of only comparatively slow motion in these solutions prompted us to derive a relation between the equivalent conductance, the $OH^{\ominus}$ drift velocity, and the parameters of $OH^{\ominus}$ exchange of the water molecules. With some remarks the connection to the analogous treatment referring to the $H^{\oplus}$ conductance is outlined.

It is generally accepted that the electrical conductance mechanism of $H^{\oplus}$ in water may be represented schematically in the form



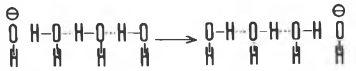
(Ia)

This scheme is not without problems. Firstly, there is no net displacement of the protons which should at least symbolically indicate that in the presence of an electric current, e.g. causing the electrolysis, the constituent H moves towards the cathode where hydrogen gas is formed. We have emphasized this point in a paper treating the $H^{\oplus}$ conductance mechanism in aqueous solution in a way analogous to that given below[1]. Secondly, in the right-hand side of scheme (Ia) the water hydrogen atoms are partly displaced with respect to the positions in the left-hand side of the diagram. However, during the electrolysis the mean displacement of the water hydrogen atoms, apart from minor partial molar volume effects, must be zero. This condition is fulfilled by a rotation of the water molecules following the preceding two steps. Usually this H_2O rotation is considered as having the function of the achievement of a correct acceptor position for the next transfer process. In contrast to this, actually the water rotation is part of the electric current J because it is strictly connected with J, as has been shown elsewhere[1]. But if one chooses proper entrance positions of $H^{\oplus}$ in the water molecule, then according to scheme (Ib) this water proton contribution to J can be eliminated in principle.



(Ib)

There exists one text-book representation by *Atkins* following this scheme[2a], however in the second edition the author has revised the diagram to give essentially scheme (Ia), although slightly modified by adding the rotational rate determining step mentioned before[2b]. Furthermore, in the text books as a schematic representation of the electric conductance mechanism of the hydroxide ion diagram (II) is given.



(II)

It is interesting to remark that this mechanism is treated with less detail, or sometimes is entirely omitted. In fact, it seems that so far it has been overlooked that scheme (II) *is not* the analogue of scheme (Ia). In the latter case the jumping species is the ion $H^{\oplus}$ and it represents that element which is evolved at the cathode. In contrast to this, in scheme (II) the oxygen which is evolved at the anode (or the ion $OH^{\ominus}$ whose concentration decreases in the electrode compartments) is not the jumping particle. In scheme (II) the rotation of the water molecules which reinstalls the previous water hydrogen positions is not the material oxygen flux which partly constitutes the electric current J leading to the evolution of O_2 at the anode. Also, a scheme analogous to (Ib) cannot be constructed from (II). It follows definitely that the correct analogue to scheme (Ia) is scheme (IIIa).

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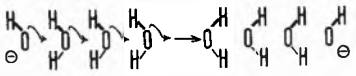
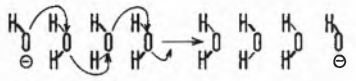


(IIIa)

After process (IIIa) the oxygen atoms belonging to the water molecules have to be moved back to the starting positions, and this occurs by a rotation about the (vertical) H · · · H axes. Again this motion contributes directly to the total oxygen flux, *that is to J*, during the electrolysis. The analogue to scheme (Ib) is:



(IIIb)

in which case *no water* oxygen is part of the electric current. But there exists extraconductivity for the ion $OH^{\ominus}$, thus its drift velocity $\vec{v}_{OH}$ per unit electric field strength ∇U should be high if scheme (IIIb) is correct.

$$u_{OH\ominus} = \frac{|\vec{v}_{OH}|}{|\nabla U|} = \frac{\lambda_{OH\ominus}}{F} \qquad (1)$$

($\lambda_{OH\ominus}$ is the equivalent conductance of $OH^{\ominus}$, F the Faraday constant).

We made an experimental investigation searching to detect comparatively fast $OH^{\ominus}$ motion leading to a high $OH^{\ominus}$ drift velocity. We measured the mean hydrogen self-diffusion coefficient and the complete set of nuclear magnetic relaxation rates (^1H,^2H,^{17}O,^{23}Na) of an aqueous NaOH solution[3]. All these dynamical quantities show a strong slowing down with increasing NaOH concentration, the relative retardation approximately equals to that caused by $CaCl_2$ (see Fig. 1). Still from these data H_2O-$OH^{\ominus}$ and $Na^{\oplus}$-$OH^{\ominus}$ intermolecular relaxation rates were derived which yield the «local» self-diffusion coefficient of $OH^{\ominus}$, $D_{OH^{\ominus}}$ [4]. It has been shown that $D_{OH\ominus}$ is the equilibrium analogue to $u_{OH\ominus}$ in equation (1)[4]. We found that a low value $D_{OH\ominus} \approx D_{F\ominus}$ cannot be excluded. It follows that scheme (IIIb) is not the only correct possibility to explain $\lambda_{OH\ominus}$, we must also consider scheme (IIIa) and we give now the exact formal description of the quantity $\lambda_{OH\ominus}$.

Our object is an electrolysis cell with a Hg/Na cathode (x=0) and an oxygen anode (x=l) containing an aqueous NaOH solution. In the presence of an electric current J the chemical reaction in this cell is $NaOH \rightarrow Na + \frac{1}{2}H_2O + \frac{1}{4}O_2$. Now we consider the microscopic picture of this cell. The total position vector of all the oxygen nuclei per oxygen nucleus in the cell is

$$\vec{R}'_O = \sum_{i=1}^{N_O} \vec{r}_{Oi}/N_O \qquad (2)$$

with $N_O = N_{H_2O} + N_{NaOH}$. In the presence of the electric current J we find

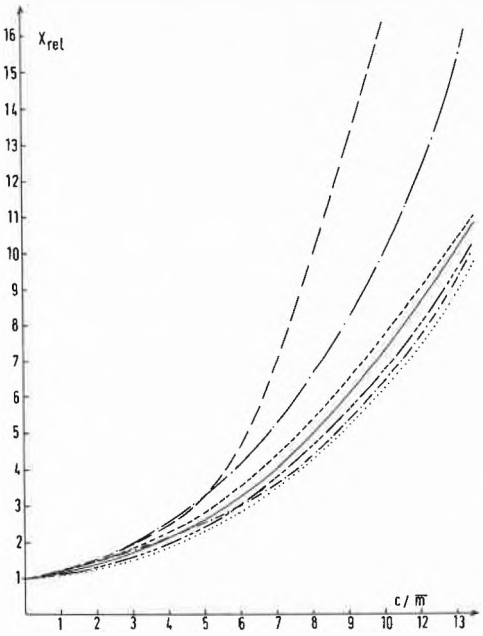


Fig. 1. Relative variations of a number of experimental quantities showing the slowing down of microdynamic processes: – – – $(\lambda_{OH\ominus})^{-1}$, – · – · – *viscosity*, ---- R_{1H}, —— D^{-1} *(inverse mean hydrogen self-diffusion coefficient)*, ---------- R_{2H}, –·–·–·–·– R_{23Na}, ... R_{17O}; $R_Y = (1/T_1)_Y$, $T = 25°\,C$[3].

$$N_O \frac{d\vec{R}'_O}{dt} = \sum_{i=1}^{N_O} \frac{d\vec{r}_{Oi}}{dt} = \sum_{i=1}^{N_O} \vec{v}_{Oi} = \vec{v}_O \neq 0 \qquad (3)$$

because at the anode (x=l) oxygen gas is evolved. $\vec{v}_O$ is the mean total velocity vector of the element oxygen. In the cathode compartment the relation holds $\partial c_{OH\ominus}/\partial t = \partial c_{NaOH}/\partial t \neq 0$ (c_{OH} = NaOH concentration).

This is a consequence of $-\mathrm{div} j_{OH} \neq 0$ at the cathode surface. j_{OH} is the particle flux of $OH^{\ominus}$. It follows also that in the homogeneous part of the cell between anode and cathode $\vec{v}'_O = \vec{v}_{OH} \neq 0$ with $\vec{v}_O = \vec{v}'_O + \vec{v}_{O(inhom)}$. $\vec{v}_{O(inhom)}$ is the contribution of the region around the anode to the total velocity vector $\vec{v}_O$. The $OH^{\ominus}$ ions are in aqueous solution. Thus we have to give a strict definition of the water molecule, in order to decide whether a given oxygen nucleus belongs to $OH^{\ominus}$ or to H_2O. For this purpose we construct a spherical shell of radius $r \approx 0.96$ Å and thickness δr around each proton (hydrogen nucleus). All oxygen nuclei which are located inside the overlap region of two shells we consider as belonging to the water molecule. The remaining oxygen nuclei which only reside in the shell of the OH-hydrogen constitute the $OH^{\ominus}$ ions. We choose the thickness δr such that the number of water molecules geometrically defined equals the number given by the analytical composition. Then the total OH velocity vector is

$$\vec{v}_{OH} = (\vec{v}_{OH})_{os} + (\vec{v}_{OH})_{is} = \vec{v}_{OH\ominus} + \vec{v}_{OH\ in\ H_2O}$$

The subscripts os and is characterize outside and inside overlap of shells, respectively. Next we consider 1 cm^3 in the region of uniform composition in the cell, the corresponding partial velocity vectors are $\vec{v}^1_{OH\ominus}$ and $\vec{v}^1_{OH\ in\ H_2O}$. Then the relation holds

$$\frac{\lambda_{OH\ominus}}{F} = \frac{|\vec{v}^1_{OH}|}{N_{OH\ominus}|\nabla U|} = \frac{1}{N_{OH\ominus}|\nabla U|}(|\vec{v}^1_{OH\ominus}| + |\vec{v}^1_{OH\ in\ H_2O}|) \qquad (4)$$

$$N_{OH\ominus} = N_{OH\ominus}/V$$

Now let us choose such geometry of the cell that the hydrostatic pressures in the anode and cathode compartment are equal. As a consequence, the solvent water in the part of uniform composition is at rest. Thus, here we have for the total position vector of all the oxygen nuclei which form water molecules

$$\frac{d\vec{R}_{OH\ in\ H_2O}}{dt} = 0 \qquad (5)$$

Referring to a given water proton the $OH^{\ominus}$ leaves and enters its spherical shell at different positions. Let the mean vector connecting the point of entrance with that of previous exit be $\overline{\Delta\vec{X}'}$ ($J \neq 0$!). During the time τ_e between exit and entrance the spherical shell around the «water» proton is empty and during this time the one particle oxygen position vector formally moves from the exit to the entrance to «accept» a new oxygen. This corresponds to an effective backward velocity $-\overline{\Delta\vec{X}'}/\tau_e$. Then the total rate of change of displacement of the water OH is

$$\frac{d\vec{R}_{OH\ in\ H_2O}}{dt} = \vec{v}_{OH\ in\ H_2O} - \frac{\overline{\Delta\vec{X}'}N_e}{\tau_e} \qquad (6)$$

where N_e is the number of empty shells ($N_e \ll N_O$). Now it may be shown that the relation holds[1]

$$\frac{N_e}{\tau_e} = \frac{N_f}{\tau} \qquad (7)$$

where $N_f = N_{H_2O}$ is the number of filled overlapping shells, and τ is the mean lifetime of an OH group in the entity called water molecule. Then, if we refer equation (6) to unit volume it follows from (4)–(7)

$$\frac{\lambda_{OH\ominus}}{F} = \frac{1}{N_{OH\ominus}|\nabla U|}\left[|\vec{v}^1_{OH\ominus}| + \frac{|\overline{\Delta\vec{X}'}|}{\tau}\right] \qquad (8)$$

with $\overrightarrow{\Delta X}^1 = \overrightarrow{\Delta X}' N_{H_2O}/V$ which is our final result.

We give a numerical example: At 25 °C, $\tau \approx 2 \cdot 10^{-10}$ s for $c_{NaOH} = 1$ M [5]. Then with $\lambda_{OH^\ominus}/F \approx 2.0 \cdot 10^{-3}$ cm^2 s^{-1}V^{-1} and $\vec{v}^1_{OH^\ominus}/N_{OH^\ominus} \nabla U \approx 0.5 \cdot 10^{-3}$ cm^2 s^{-1}V^{-1} (which is the value for the ion $F^\ominus$) it follows $|\overrightarrow{\Delta X}'| \approx 5 \cdot 10^{-15}$ cm. One sees that the mean vector connecting entrance and exit of the OH group in the «water sphere» in the presence of $\nabla U = 1$V cm^{-1} is extremely small, so that, although scheme (IIIb) is not exactly correct, effectively it corresponds to reality: We have a slightly debalanced superposition of processes similar to (IIIa) in opposite directions.

We close this communication by quoting the formula for the equivalent conductance of the ion $H^\oplus$ which is the analogue of equation (8)[1]

$$\frac{\lambda_{H^\oplus}}{F} = \frac{1}{N_{H^\oplus}|\nabla U|}\left[|\vec{v}^1_{H^\oplus}| + \frac{|\overrightarrow{\Delta X}'|}{\tau}\right]$$

Here a torus construction defines the ionic species «$H^\oplus$», thus replacing the set of two overlapping spherical shells.

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[3] H. Hermann, H.G. Hertz, R. Maurer, unpublished.
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[5] See e.g. H.G. Hertz, H. Versmold, C. Yoon, *Ber. Bunsenges. Phys. Chem. 87* (1983) 577.