MEASUREMENT OF THE DIFFUSION COEFFICIENTS OF OH AND OD RADICALS AND OF H AND D ATOMS IN AQUEOUS ELECTROLYTE SOLUTIONS

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During illumination of an electrode immersed into the solution of an electrolyte which does not absorb light, a photocurrent is generated which is caused by the consecutive processes of electron photoemission from the metal into the solution, thermalization and solvation of the emitted electrons, their capture by scavengers introduced into the solution, and electrode reactions of the solvated electrons and scavenging products [1-3]. The current measured is

$$j=j_0-j_e\pm j_a, \tag{1}$$

where j_0, j_e, and j_a are the photoemission current, the current of solvated electrons returning to the electrode, and the current of the scavenging products, respectively. The sign of j_a depends on whether the scavenging product is reduced (+) or oxidized (−) at the electrode. By measuring the photocurrent kinetics one can determine the rates of the bulk and electrode reactions of the solvated electrons (e_{aq}^-) and scavenging products; these products can be almost any intermediate species of chemical reactions. In particular, OH radicals and H atoms will be formed when N_2O and H_3O^+ are used as scavengers:

$$e_{aq}^-+N_2O\rightarrow N_2+OH^-+OH^\cdot; \tag{2}$$

$$e_{aq}^-+H_3O^+\rightarrow H_2O+H^\cdot. \tag{3}$$

The fundamentals of the technique are given in [1-4]. Photoemission into electrolyte solutions is used in the present work to determine the diffusion coefficients of OH radicals and H atoms in electrolyte solutions.

For the concentrations of solvated electrons (n_e) and of scavenging products (n_a) the following equations hold:

$$\frac{\partial n_e}{\partial t}=D_e\frac{\partial^2 n_e}{\partial x^2}-k_aN_an_e+F(x)\varphi(t); \tag{4}$$

$$\frac{\partial n_a}{\partial t}=D_a\frac{\partial^2 n_a}{\partial x^2}-\frac{1}{\tau_a}n_a+k_aN_an_e \tag{5}$$

with the boundary and initial conditions

$$n_e(x,0)=n_a(x,0)=n_e(\infty,t)=n_a(\infty,t)=0; \tag{6}$$

$$D_e\left(\frac{\partial n_e}{\partial x}\right)_{x=0}=\varkappa_e n_e(0,t),\quad D_a\left(\frac{\partial n_a}{\partial x}\right)_{x=0}=\varkappa_a n_a(0,t), \tag{7}$$

where D_e and D_a are the diffusion coefficients of e_{aq}^- and of the scavenging product, respectively, k_a is the rate constant of e_{aq}^- capture by the scavenger present in the solution at the concentration N_a, τ_a is the lifetime of the scavenging product in the solution (in the case of $H^\cdot$ and $OH^\cdot$, $\tau_a^{-1}=0$), $\varkappa_e$ and $\varkappa_a$ are the electrode reaction rates, F(x) is the distribution function of the solvated electrons along the solvation path which is characterized by the effective length $l_0=25\pm4$ Å [5], and φ(t) is the shape of the light pulse. It follows from (4) to (7) that at measuring times t such that

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$$l_0/\sqrt{D_e t},\quad l_0/\sqrt{D_a t} \ll 1,\quad D_e/\varkappa_e^2 t,\quad D_a/\varkappa_a^2 t \ll 1 \tag{8}$$

the shape of the kinetic curves is independent of F(x), $\varkappa_e$, and $\varkappa_a$, and governed only by the rates of e_{aq}^- capture by the scavenger and of diffusion of e_{aq}^- and the scavenging product to the electrode. With D_e, $D_a \leq 10^{-4}$ $cm^2 \cdot sec^{-1}$, $\varkappa_e$, $\varkappa_a \geq 10^2$ $cm \cdot sec^{-1}$, and the above value of l_0, relations (8) will hold for $t \geq 10^{-8}$ sec. Then, provided the scavenging product is reduced at the electrode, the kinetics of the charge emitted into the solution will be governed by the relation

$$Q(t) = \int_0^t j(t')\,dt' = Q_\infty \left(1 - \frac{1}{2\sqrt{\pi k_a N_a \delta t}}\right), \tag{9}$$

where $\delta = D_a/D_e$. Barker had first pointed out [4] that the quantity $k_a N_a$ can be found by comparing Q_∞ and Q(t) in solutions not containing a scavenger ($k_a N_a \simeq 0$) when the drop in Q(t) is attributed to the e_{aq}^- returning to the electrode:

$$Q_\infty / Q_{N_a = 0}(t) = 2\sqrt{\pi k_a N_a t}. \tag{10}$$

Thus, using (9) and (10) one can find the absolute values of the reaction rate constants of e_{aq}^- with scavengers and the relative values of the diffusion coefficients of intermediate species, i.e., δ, from measurements of Q(t) at $N_a = 0$ and at scavenger concentrations where $k_a N_a t \simeq 1$.

An LGI-21 nitrogen laser ($\lambda = 3371$ Å) with a pulse length of 14 nsec and a repetition rate of 12 Hz was used as the light source in the present measurements. The signal which was proportional to the emitted charge was amplified with a wide-band amplifier (10 kHz to 40 MHz), fed to an S-7-5 stroboscopic oscillograph, and recorded. The stroboscopic recording mode yielded an instrumental input sensitivity of 20-30 μV, so that the δ values could be measured with an accuracy not inferior to 30%. The intensity of the light reaching the electrode was not above 100-200 $kW \cdot cm^{-2}$.* The results reported below were obtained at a mercury electrode in 1 N KCl solution.

Experimental Q(t) curves in solutions with different N_2O concentrations are given in Fig. 1a, and in Fig. 1b these dependences are plotted as Q against $1/\sqrt{t}$. For the different N_a one obtains, in harmony with (9) and (10), a set of parallel straight lines with a slope which is independent of electrode potential; this is an indication that the electrodic reduction rate of the OH radicals satisfies condition (8) for $t > 3 \times 10^{-8}$ sec, and has no effect on the results of the measurements.

In solutions of acids, the Q(t) relations are complicated by the fact that the electrochemical desorption rate of the atomic hydrogen is rather low.† Nevertheless at electrode potentials between −0.9 and −1.3 V (sce) and $N_a \leq 2 \times 10^{-2}$ M one can distinguish a section on the kinetic curves for $t \gtrsim 10^{-6}$ sec which is described by relations (8) and (9) and where the slope of $Q(1/\sqrt{t})$ does not depend on electrode potential (Fig. 2). Similar measurements were made in D_2O solutions. The values found for the rate constants of reactions (2) and (3) and for δ are reported in Table 1.

In accordance with the results of pulse radiolysis [6, 7], the isotope effect for the rate constants of reactions (2) and (3) is small. It must be noted that reactions (2) and (3) yield short-lived intermediates (N_2O^- or O^- and $H_3O^{\cdot}$, respectively). But their lifetime is not above 10^{-9} sec, which has no effect on the results of the present work.

The diffusion coefficient of e_{aq}^- in H_2O solutions is 4.7×10^{-5} $cm^2 \cdot sec^{-1}$ [6], so that the diffusion coefficients of the OH radicals and of H atoms are $(1 \pm 0.3) \times 10^{-5}$ $cm^2 \cdot sec^{-1}$ and $(7 \pm 2) \times 10^{-5}$ $cm^2 \cdot sec^{-1}$, respectively. The value of $D_{e_{aq}^-}$ in D_2O solutions is not known, but the fact that there is no isotope effect for the reaction rate constants of e_{aq}^- [6] indicates that it is close to that reported above for H_2O solutions. It can be seen from the data of Table 1 that the OH radical, in contrast to the hydroxyl ion, has no anomalous mobility, while the mobility of the H atoms is close to that of the H_3O^+ ions, and is characterized by approximately the same magnitude of the isotope effect (according to [8], $D_{H_3O^+} = 6.7 \times 10^{-5}$ $cm^2 \cdot sec^{-1}$ and $D_{D_3O^+} = 3.2 \times 10^{-5}$ $cm^2 \cdot sec^{-1}$ in 1 N KCl solution). The data obtained allow us to suggest that H atoms move in water via the same mechanism as the protons [9], by the transfer of H atoms from one cluster to another.

* The decrease in light intensity is desirable in order to reduce disturbing effects associated with heating of the electrode and with bimolecular reactions in the solution.

† Results of the investigations of H-atom electrode reactions will be given in a separate publication.

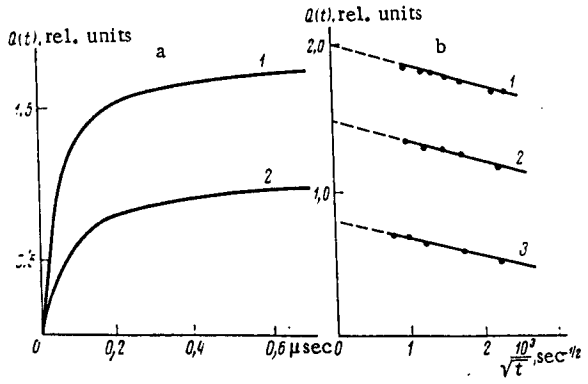

Fig. 1

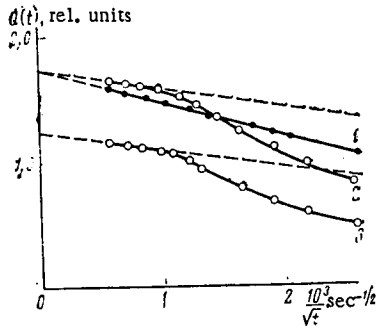

Fig. 2

Fig. 1. a) The kinetics of emitted charge, Q(t), in 1 N KCl solution with N_2O concentrations of 2.3×10^{-2} M (1) and 4.6×10^{-3} M (2); b) the $Q(1/\sqrt{t})$ relations for different N_2O concentrations: 1) 2.3×10^{-2} M, 2) 1.3×10^{-2} M, 3) 3.8×10^{-3} M.

Fig. 2. The $Q(1/\sqrt{t})$ relations in 1 N KCl solution containing 2.3×10^{-2} M N_2O (1), 2×10^{-2} M H_3O^+ (2), or 1×10^{-2} M H_3O^+ (3).

TABLE 1

Reaction No.	Medium	$k_R \cdot 10^{-9}$, $M^{-1} \cdot sec^{-1}$	Capture product	δ
2	H_2O	6±1	$OH^\bullet$	0,2
2	D_2O	6±1	$OD^\bullet$	0,2
3	H_2O	8±1,5	$H^\bullet$	1,5
3	D_2O	8±1,5	$D^\bullet$	0,8

Thus, it is the main conclusion of the present work that H and D atoms in aqueous electrolyte solutions have mobilities which are approximately 4 and 8 times higher than those of OH and OD radicals, which do not exhibit anomalous mobilities.

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