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# Dissociation of Water Molecules in Systems with Ion-exchange Membranes

V.I.Zabolotskii, N.V.Shel'deshov, and N.P.Gnusin

The principles of the dissociation of water molecules in membrane systems containing cation-exchange, anion-exchange, and dipolar membranes are examined. The characteristics of the attainment of the limiting state at the membrane-solution boundary and the differences in the behaviour of cation-exchange and anion-exchange membranes are discussed from the standpoint of the possibility of the dissociation of water at the interfaces. The mechanisms and the kinetics of the dissociation of water in membrane systems involving catalytically active centres† are considered.
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## I. INTRODUCTION

The problem of the dissociation of water molecules in a membrane system when an electric current flows through the latter is one of the central problems in the electrochemistry of membranes. This is associated with the complications arising from the dissociation of water in membrane systems and with the new possibilities for electrochemical technology opened up by its use. In the demineralisation of solutions by electrodialysis, the dissociation of water in the region of the membrane–solution boundary leads to the participation of the $H^+$ and $OH^-$ ions in transport across cation-exchange and anion-exchange membranes. As a consequence of this, the limiting current decreases,[1] there is an additional consumption of electrical energy on demineralisation, the pH changes in the electrodialyser chambers, and chemical reactions sensitive to changes in the acidity of the medium occur, including the crystallisation of calcium carbonate and magnesium hydroxide in the concentration chambers, where the pH is in excess of 7, or reactions sensitive to the precipitation of silicic acid in the desalination chambers, in which the medium is acid.

Since the transport of the water dissociation products across the membrane begins after the attainment of the limiting state when the concentration of the $H^+$ and $OH^-$ ions in the region of solution near the membrane becomes comparable to the electrolyte concentration,[2–4] attention has been concentrated on the search for signs preceding the onset of limiting state in order to have reliable ways of maintaining the membrane system in the pre-limiting state, where water does not decompose.

Recently there has been a growth of interest in the decomposition of water in membrane systems for several reasons. Firstly, this is associated with the appearance of dipolar membranes and their use in electrodialysers for the preparation of acids and alkalis or for other chemical reactions with participation of hydrogen and hydroxide ions. The decomposition of water in such systems is the "working" process and the efficiency of the entire electromembrane technology depends on the overpotential and current yield with which the $H^+$ and $OH^-$ ions are generated.[5,6] The joint demineralisation and preparation of acid and alkali can be achieved in the so-called "semidipolar" membranes,[7–9] which are obtained by depositing a unipolar cation or anion exchanger on the membrane and also by the coprecipitation of the ion exchanger and polyelectrolyte.

Secondly, the problem of the intensification of the mass transfer in membrane systems has come to the fore and the applications of electrodialysis have been extended to the preparation of deionised or ultrapure water. The electrodiffusion process is then carried out under postlimiting conditions (the current is greater than the limiting diffusion current), where water decomposes very quickly and this process itself can intensity the mass transfer of electrolyte across membranes[10,11] by increasing the electrolyte concentration in the region of the diffusion layer near the membrane and by increasing thereby the migration current (the so called "current exaltation effect"). Finally, there has been a growth of interest in the role which the transport of $H^+$ ions across biological membranes plays, especially in photosynthetic processes,[12,13] where local electric fields in membranes initiate the heterolytic cleavage of water molecules and the injection of $H^+$ into the membrane.

## II. DISSOCIATION OF WATER MOLECULES AT THE MEMBRANE–SOLUTION BOUNDARY

The possibility of the dissociation of water when an electric current is passed through ion-exchange membranes was established a long time ago. As early as 1914, Bete and Toropoff[14] observed the transport of water dissociation products through certain membranes (gelatin, parchment, and collodion membranes). The involvement of $H^+$ and $OH^-$ ions in transport across ion-exchange membranes was observed in 1946 by Frilette[15] and independently by Kressman and Tye[16] and was later confirmed by many workers.[17–27]

It has now been established reliably that the rate of decomposition of water and the fluxes of $H^+$ and $OH^-$ ions in the membrane system depend greatly on the nature of the ionogenic groups.[11,19–24,28–30]

† This article was planned for publication in issue No.6 (1988) of this journal, which was devoted to the problem of polymer membranes.

For cation-exchange membranes at currents exceeding the limiting current by a factor of 1.5–2, the change in the pH of the solutions near the membrane is insignificant[31] and the transport numbers of the $H^+$ ions are in the range from $4 \times 10^{-5}$ to 0.11.[4,18,26,29,32,33] On the other hand, the transport of $OH^-$ ions across anion-exchange membranes takes place at a much higher rate and the transport numbers reach 0.03–0.6.[4,17-19,26,29,32-36]

Since the concentrations of $H^+$ and $OH^-$ ions in the spontaneous decomposition of water molecules in water are identical, while the mobility of $H^+$ ions in ion-exchange resins is greater than that of $OH^-$, this finding is in conflict with the usual ideas about the electrodiffusion character of the transport of ions across membranes. Many workers therefore assumed that the transport of $H^+$ ions across a cation-exchange membrane is suppressed by some factor and they introduced the additional hypothesis that the states of the interfaces at the cation-exchange and anion-exchange membranes are different. Thus it has been postulated[37,38] that, at high current densities, an intense flux of electrolyte ions induces the partial disruption of the diffusion layer. The effect of the disruption of this layer is greater on the side of the cations, since they are more hydrated. This results in the appearance of additional possibilities for increasing the electrolyte flux, while the transport of $H^+$ ions across the cation-exchange membrane is suppressed.

Similar ideas were developed in other studies.[15,33,34,39] The decomposition of the diffusion layer has been attributed[15] to the establishment of electro-osmotic fluxes on the surface of the membrane owing to its inhomogeneity, while other workers[33,34,39] attributed it to the appearance of local convective currents near the interface as a consequence of the evolution of joule heat in the desalinated layer of solution. By applying the schlieren method and photography with the aid of Toepler's apparatus, Varentsov and Pevnitskaya[34] confirmed experimentally that the local thermoconvection arises at a cation-exchange membrane for electric currents exceeding the limiting diffusion current, while at an anion-exchange membrane this effect is very weak. The results obtained were explained by the different degrees of hydration of anions and cations (Mandersloot's mechanism[37,38]) and also by the existence on the surface of anion-exchange membranes of films with a low concentration of fixed groups.[33,34,39] Kononov and Vrevskii[4] explain the preferential transport of $OH^-$ ions across anion-exchange membranes by their high selectivity with respect to hydroxide ions. After converting the membranes from the salt to the hydroxide-forms, they observed an increase in the rate of dissociation of water. Measurement of the electrolyte concentration at the interface using the commutator method (the current interruption method) made it possible to establish[18] that, at currents close to the limiting diffusion current, the limiting electrolyte concentration near the cation-exchange membrane does not attain low values comparable to the concentrations of the $H^+$ and $OH^-$ ions in water, while at an anion-exchange membrane they are attained readily. Subsequently these results were confirmed in a study[40] using analogous methods and in other investigations[41–44] in which modern direct methods for recording electrolyte concentrations with the aid of laser holography were employed.

The earlier conclusions[34,39] that local convection arises in the solution at the surface of a cation-exchange membrane were confirmed and specified in greater detail by the methods of laser holographic interferometry[41,43,45] and also by measuring the electrochemical noise in membrane systems.[46–50] At currents only slightly exceeding the limiting current, the convective streams are laminar in character and do not influence the electrical resistance of membrane systems.[48] When the limiting current is exceeded by a factor of three, laminar convection is converted into turbulent convection, causing random oscillations in the resistance of the desalinated layer of solution, which is manifested by the appearance of flicker noise.[48] After the attainment of the turbulent thermoconvection regime, the electrical resistance of the membrane system falls.[48] By an additional series of elegant experiments, the authors[48] demonstrated that the convective currents generated obey known laws: with increase in the viscosity of the system by the addition of a non-ionisable water-soluble polymer, with decrease in the temperature of the solution, or for the horizontal disposition of the cation-exchange membrane (the desalinated layer of the solutions lies below), the noise induced by convection weakens. The frequency-independent "white" noise, associated with the water dissociation reaction, is not observed in a system with a cation-exchange membrane.[47]

On the other hand, convective currents in the desalinated layer of solution have not been observed at an anion-exchange membrane for currents close to the limiting value either from the form of the interferograms[45] or by analysing the frequency spectrum of the noise[47,49] but the "white" noise has been distinctly observed, indicating the decomposition of water. With increase in the current, the intensity of the "white" noise increased linearly and, after the attainment of the limiting current, it began to grow faster than predicted by a linear law.[49] Only at very low current densities, exceeding the limiting current by a factor greater than three, does a weak flicker noise appear for an anion-exchange membrane, indicating the occurrence of thermoconvection.

Quantitative allowance for thermoconvection in a rigorous description of electrodiffusion is a complex task and involves many difficulties already in the stage of its formulation. Theoretically, thermoconvection can be taken into account indirectly by assuming that the electrolyte concentration at the interface does not diminish below a certain value as a result of thermoconvection. Here it has been shown[51] that, instead of a horizontal plateau on the voltage–current plot, a section corresponding to a retarded growth of current with increasing potential appears.

The reason for the different behaviour of cation-exchange and anion-exchange membranes has not been elucidated.[44–50] It also remains obscure why thermoconvection is observed near a cation-exchange membrane but not near an anion-exchange membrane, although, it follows from results of these workers and those of other investigators[18,40,43] that the boundary electrolyte concentration near an anion-exchange membrane in the limiting state is lower than near a cation-exchange membrane and that the liberation of joule heat because of this should be more intense near an anion-exchange membrane.

In our view, the appearance of thermoconvection and the consequent growth of the concentration of the counterions at the cation exchanger–solution interface are a consequence and not the cause of the low rate of decomposition of water. In fact, the dissociation of water, which occurs with a large negative heat change (the enthalpy of dissociation of water is 56.6 kJ $mol^{-1}$ [52]), compensates for the liberation of joule heat on passage of the current through the highly desalinated layer of solution at the interface, so that thermoconvection is very significant near an anion-exchange membrane, while the concentration of counterions diminishes to values comparable to the concentrations of $H^+$ and $OH^-$ ions.[18,40,43,44,53] Around a cation-exchange membrane, the endothermic water dissociation process takes place at a very low rate and the passage of current therefore causes local heating of the solution at the interface and intense thermoconvection with all the consequences arising from it.

This approach explains the differences in the hydrodynamic state of the interfaces of cation-exchange and anion-exchange membranes observed in practice but leaves open the question of the causes of the different rates of decomposition of water at these membranes. The solution of this problem requires primarily the elucidation of the characteristic features of the mechanism of the dissociation of water in membrane systems.

If it is assumed that in a membrane system water decomposes at the same rate as in the usual aqueous solutions (the dissociation rate constant is $k_d = 2.5 \times 10^{-5}$ $s^{-1}$ [54]) and the concept of the reaction layer is used,[55] the current transported by the $H^+$ and $OH^-$ ions across the membrane ($i_w$) can be expressed in terms of the rate constants for the forward ($k_d$) and reverse ($k_r$) reactions, the concentrations of water ($c_{H_2O}$) and $H^+$ and $OH^-$ ions ($c_H$ and $c_{OH}$ respectively), and the thickness of the reaction layer ($\lambda$):

$$i_w = F\int_0^{\lambda}(k_d c_{H_2O} - k_r c_H c_{OH})\,dx \leqslant F k_d c_{H_2O}\lambda. \qquad (1)$$

As can be seen from Eqn.(1), the partial electric current involving hydrogen or hydroxide ions ($i_w$) has an upper limit: under stationary conditions, the fluxes of $H^+$ and $OH^-$ ions across membranes cannot be greater than the rate of formation of these ions in the reaction layer and the latter quantity is limited by the values of $k_d$ and $\lambda$. The upper limit to $i_w$ has been estimated[35,36] as $2 \times 10^{-4}$ A $m^{-2}$ at 25 °C, i.e. it is $10^7$ times smaller than the current due to $H^+$ and $OH^-$ ions actually observed in membrane systems.

Despite the approximate character of these estimates (the approach adopted by Simons and co-workers[35,56] is strictly applicable only in the presence of a supporting electrolyte when the electromigration transport of the ions formed in the reaction can be neglected[55]), a marked inconsistency is observed between the results of the calculation and the real rates. Even allowance for the electromigration ion transport[57] does not greatly improve the estimate.[36] The high rates of dissociation of water in the membrane–solution system cannot be explained from the standpoint of the Wien effect for weak electrolytes. The strength of the electric field arising in the region of the membrane–solution boundary is too low and the rate constant for the dissociation of water hardly differs from its value in the absence of the field.[58] The very fact of the decomposition of water and of the transport of $H^+$ and $OH^-$ ions at the experimentally observed rates is therefore surprising and requires explanation, and not the ability of cation-exchange membranes to "suppress" the dissociation of water.[15,34,37–39]

The low limiting kinetic current for the water dissociation reaction in solution and marked dependence of the transport numbers of the $H^+$ and $OH^-$ ions on the nature of the ion-exchange membranes lead to the conclusion that the cause of the high rate of this process should be sought not in the properties of the solution but in the characteristic features of the ion-exchange membranes.

As already mentioned, the rate of dissociation of water at cation-exchange (sulphonic acid) membranes in solutions of alkali metal salts is very low even when the actual current exceeds the limiting diffusion current by a large factor. However, as shown for the first time by Oda and Yawataya,[20] the dissociation of water increases sharply in this system when alkali metal cations are replaced by the $Ca^{2+}$, $Mg^{2+}$, and $NH_4^+$ cations. This effect was observed in the electrodialysis of sea water.[50] Subsequently it was established[60] that also certain other cations of weakly dissociating bases ($Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$) are able to accelerate the decomposition of water, the reaction being accelerated not by the above ions themselves but by their hydroxides which are deposited on the surfaces of the membranes in electrodialysis and under postlimiting conditions are deposited especially on the surface of the cation-exchange membrane. The compounds $Cu(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, and $MnCO_3$ also exhibit a catalytic activity. On the other hand, deposits of the compounds $Zn(OH)_2$, $CaSO_4$, $BaSO_4$, and $CaCO_3$ on the surface of the cation-exchange membrane do not influence the rate of decomposition of water.[60] This shows that the diffusion-dependent obstacles to the transport of electrolyte across the solid phase of the deposit on the membrane surface and the associated additional concentration polarisation are not the causes of the intensification of the dissociation of water.

The observed acceleration can be explained (at least qualitatively) by assuming that certain weakly dissociating substances are involved directly in the dissociation of water, for example, in accordance with the scheme

$$Mg(OH)_2 \rightleftarrows MgOH^+ + OH^-,$$
$$MgOH^+ + 2H_2O \rightleftarrows (MgOH)_2 + H_3O^+.$$

The rate constant for the heterolytic decomposition of water on groups of the type of $MgOH^+$ can be higher by several orders of magnitude than the rate constant for the non-catalytic reaction; the reaction can also be accelerated by the electric field at the deposit–membrane interface, where the space charge is localised. According to the data of Tanaka and Seno,[60] the formation of the deposits on the boundary between the membrane and the diffusion layer, which serves as the recipient of the counter ions, fails to influence the rate of decomposition of water in all cases.

In principle, the simple cations of weakly dissociating bases can also possess catalytic activity, for example, as a result of their participation in the reactions[36]

$$Mg^{2+} + 4H_2O \rightleftarrows Mg(OH)_2 + 2H_3O^+. \qquad (2)$$

$$Mg(OH)_2 \rightleftarrows Mg^{2+} + 2OH^-. \qquad (3)$$

The detailed mechanism of the dissociation of water in solutions with catalytically active inorganic ions is obscure as yet; the studies carried out hitherto on this question[20,59,60] have been qualitative. In particular, the claim by Tanaka and Seno[60] that the acceleration of the water dissociation reaction takes place in all cases only after the formation of the solid phase of the deposit, is incomprehensible and requires additional experimental confirmation. From the standpoint of Simon's scheme[36] [Eqns.(2) and (3)], the acceleration can be promoted by catalytically active cations of the type of $Mg^{2+}$ present in the double layer at the membrane–solution interface, while the presence of the solid phase of the insoluble compound is not obligatory.

It has been shown[25,35,36] that the dissociation of water can be accelerated by certain organic bases B and acids AH, in particular compounds with tertiary amino-groups:

$$B + H_2O \rightleftarrows BH^+ + OH^-, \qquad (4)$$

$$BH^+ + H_2O \rightleftarrows B + H_3O^+, \qquad (5)$$

$$A^- + H_2O \rightleftarrows AH + OH^-, \qquad (6)$$

$$AH + H_2O \rightleftarrows A^- + H_3O^+, \qquad (7)$$

and that the dissociation can be accelerated both by the groups contained in the membrane[25] and introduced into the solution.[36] Having compared, in terms of the reaction layer approximation, the rates of decomposition of water in the catalytic reaction [Eqns.(4) to (7)] and the usual reaction

$$H_2O \rightleftarrows H^+ + OH^- \qquad (8)$$

Simons[36] showed that the acceleration of the reaction as a result of catalysis by organic substances can be very great.

In a number of studies, the description of the voltage–current plots for membrane systems by the authors assumes a local equilibrium in the water dissociation reaction at all points within the system,[61,62] which is equivalent to considering the reaction as "rapid". Despite the controversial nature of this assumption, Zholkovskii and co-workers[61,62] were able to describe qualitatively the shape of the voltage–current plots.

## III. DISSOCIATION OF WATER MOLECULES IN DIPOLAR MEMBRANES

The term dipolar ion-exchange membranes is applied to layered membranes consisting of at least one cation-exchange and one anion-exchange layer which are in contact. In an electric field, dipolar membranes are arranged in such a way that the layers represent series-connected resistances in relation to the electric current passing through the system. If the cation-exchange layer is directed towards the cathode and the anion-exchange layer towards the anode, then, on passing of the electric current, the electrolyte concentration in the region of contact between the layers diminishes and, from a certain instant, the $H^+$ and $OH^-$ ions formed in this region on dissociation of water are included in the transport process.

The dipolar membranes operating under conditions involving the generation of $H^+$ and $OH^-$ ions have undoubted advantages over the membrane–solution system from the standpoint of the possibility of investigating the dissociation of water. Instead of the diffusion layer, which arises, for example, near a cation-exchange membrane, in a dipolar membrane there exists an anion-exchange layer which suppresses the influence of convection in solution, is selective with respect to anions, and thereby diminishes the transport of cations. This results in a high current yield of the $H^+$ and $OH^-$ ions, reaching 0.9–0.96.[63] Furthermore, more reproducible data have been obtained at dipolar membranes than in a membrane–solution system.

The high current densities with respect to $H^+$ and $OH^-$ ions, reaching $10^3$ A $m^{-2}$, are a unique feature of dipolar membranes.[64] This exceeds by many orders of magnitude the limiting kinetic current for the water dissociation reaction [Eqn.(1)]. For a long time no attention was paid to this paradox and the water dissociation reaction was regarded as rapid[65] without any explanation.

Greben' et al.[66] were the first to point out the important role of the ionogenic groups in the dissociation of water, having assumed that the ionogenic group can participate directly in the reaction, accelerating it. They investigated by the voltammetric method dipolar membranes containing sulphonic, carboxylic, and phosphonic acid groups and concluded that the decrease in the potential differences in the membranes in the sequence

$$-SO_3H > -COOH > -PO(OH)_2$$

can be explained by the decrease of the energy barrier to the interaction of the ionogenic groups with water molecules as the p$K$ of the cation-exchange groups increase in the same sequence.

The available quantitative information about the dissociation of water in dipolar membranes[67–74] includes voltage–current plots for the dipolar region, which are inaccessible to direct d.c. measurements, the effective dissociation and recombination rate constants, and equilibrium constants. The authors of the above studies used for the investigation of dipolar membranes the method of the frequency spectrum of the electrochemical impedance[67] with simultaneous polarisation of the membranes with a direct current. Analysis of the frequency spectrum made it possible to isolate from the overall impedance its component which refers to the dipolar region[69] and to calculate the effective reaction constants.[68] The mechanism of the dissociation, postulated in the calculations, does not take into account the role of the ionogenic groups in the reaction; as a result of this, the calculated constants are merely effective quantities. Nevertheless, this approach made it possible to compare the properties of dipolar membranes differing from one another by the nature of the ionogenic groups.[74]

The brands of the dipolar membranes and of the cation- and anion-exchange resins used for this preparation.[75]

| No. | Brand | | | No. | Brand | | |
|---|---|---|---|---|---|---|---|
| | of dipolar membrane | of cation-exchange resin | of anion-exchange resin | | of dipolar membrane | of cation-exchange resin | of anion-exchange resin |
| 1 | MB-4 | KF-1 | AV-23M | 6 | MB-51 | SG-1 | AV-17 |
| 2 | MB-31 | KF-1 | EDE-10P | 7 | MB-6 | KU-2 | AN-22 |
| 3 | MB-3 | KF-1 | AV-17 | 8 | MB-1 | KU-2 | EDE-10P |
| 4 | MB-42 | SG-1 | AV-23M | 9 | MB-2 | KU-2 | AV-17 |
| 5 | MB-13 | SG-1 | EDE-10P | | | | |

Note. The brand names of the industrial MB-1, MB-2, MB-3, and MB-4 membranes are as given in a catalogue (Ref.75, p.15). The MB-2 membrane has been alkylated with methyl iodide.[70] The remaining membranes are experimental (conventional brand names) and have been prepared at the "Plastmassy" [Plastics] NPO.

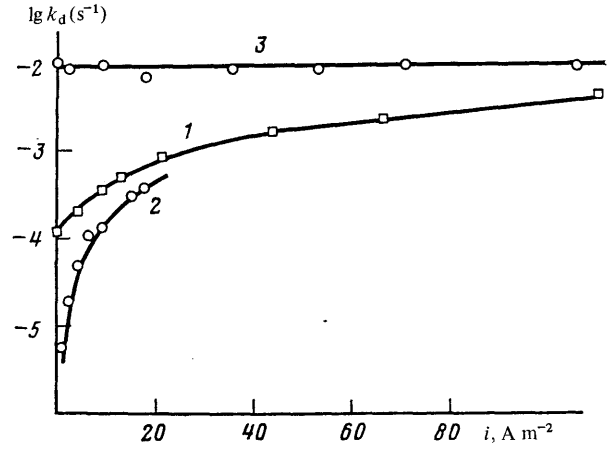



**Figure 1.** Dependence of the rate constants for the dissociation of water in the dipolar region of MB-1 (curve *1*) and MB-2 (curve *2*) membranes at 25 °C and the MB-3 membrane (curve *3*) at 4 °C on the current density. The logarithm of the rate constant for the dissociation of water is -4.6 at 25 °C and -5.5 at 4 °C.[72]

The rate constants for the dissociation of water in dipolar membranes (the bands of the membranes are indicated in the Table) differ sharply from the corresponding constants for the same reaction in pure water (Fig.1); they depend on the nature of the ionogenic group and the current density. Phosphonic acid groups have

such a marked catalytic effect that the increase in the reaction rate constant due to the electric field applied to the membrane from outside cannot be seen against this background (Fig.1, curve *3*). At low current densities, sulphonic acid groups hardly accelerate the dissociation (Fig.1, curve *2*) and the rate constant is in this case almost the same as in pure water. At high current densities, the constant increases, the field effect predominating under these conditions. The involvement of the tertiary amino-groups in the dissociation of water in dipolar membranes has been confirmed:[70] the alkylation of tertiary amino-groups of the dipole membrane sharply increases the overpotential and decreases the rate constant for the dissociation of water. This effect also shows that sulphonic acid groups have a significantly weaker catalytic activity than the tertiary amino-groups.

The extremely low overpotential in the dipolar region of the membranes containing phosphonic acid groups can be explained from the standpoint of the catalytic mechanism.[71] Calculation showed[72] that, among all the possible water dissociation reactions in these membranes

$$H_2O + H_2O \underset{1,4\cdot10^{11}}{\overset{2,5\cdot10^{-5}}{\rightleftharpoons}} H_3O^+ + OH^-; \quad K = 1,8\cdot10^{-16} \qquad (9)$$

$$R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH + H_2O \underset{10^{10}-10^{11}}{\overset{2\cdot10^{8}-2\cdot10^{7}}{\rightleftharpoons}} R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O^- + H_3O^+; \quad K_A = 2\cdot10^{-4} \qquad (10)$$

$$R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O^- + H_2O \underset{10^{6}-10^{10}}{\overset{5\cdot10^{-6}-5\cdot10^{-7}}{\rightleftharpoons}} R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}OH + OH^-; \quad K_B = 5\cdot10^{-11} \qquad (11)$$

$$R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O^- + H_2O \underset{10^{10}-10^{11}}{\overset{10^{3}-10^{4}}{\rightleftharpoons}} \left[R{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{P}}{-}O\right]^{2-} + H_3O^+; \quad K_A = 10^{-7} \qquad (12)$$

$$\left[R{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{P}}{-}O\right]^{2-} + H_2O \underset{10^{6}-10^{10}}{\overset{10^{1}-10^{3}}{\rightleftharpoons}} R{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O^- + OH^-; \quad K_B = 10^{-7} \qquad (13)$$

(the rate constants, in $s^{-1}$ expressed for the forward reaction and in litre $mole^{-1}$ $s^{-1}$ for the reverse reaction, are indicated above and below the arrows; the equilibrium constants, in mole $litre^{-1}$, are indicated after the reactions), the last two make the main contribution. In order to ensure the dissociation of water, reactions (10) and (11) or (12) and (13) (or both pairs simultaneously) must take place consecutively in the forward direction. In each pair of reactions, the rate of dissociation is limited by the stage with the lowest rate constant [stages (11) and (13)]. Since both pairs of reactions can take place simultaneously, and the rate constant for stage (13) in the forward direction is greater by a factor of $2 \times 10^3$ than the rate constant for stage (11), reactions (12) and (13) make the greatest contribution to the dissociation.

The catalytic mechanism of the dissociation of water in dipolar membranes is confirmed by the dependence of the rate constant for the rate-limiting stage of the dissociation of water, found for reactions (9)–(13), on the effective equilibrium constant for the dissociation calculated from the impedance frequency spectra (Fig.2). In terms of the catalytic effectiveness, the ionogenic groups of dipolar membranes can be arranged in a sequence in order of increasing rate constants for the dissociation of water involving their participation:[74]

| $-N(CH_3)_3$ | $<$ | $-SO_3H$ | $<$ | $-PO_3H^-$ | $<$ | $=NH$, $-NH_2$ | $<$ | $\equiv N$ | $<$ | $-COO^-$ | $<$ | $-PO_3^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $k\ (s^{-1}) = 0$ | | $3\cdot10^{-3}$ | | $3\cdot10^{-2}$ | | $10^{-1}$ | | 1 | | 10 | | $10^3$ |

The dependence of the activation energy for the dissociation of water on the nature of the ionogenic groups (Fig.3) is important evidence in support of the catalytic mechanism for the dissociation of water in dipolar membranes. The activation energy for membranes with a weak catalytic effect (MB-1 membrane, 45 kJ $mol^{-1}$) is close to the activation energy in pure water (56 kJ $mol^{-1}$), while phosphonic acid groups reduce sharply this quantity (MB-3 membrane, 26 kJ $mol^{-1}$). The low activation energies for the MB-2 membrane (32.5 kJ $mol^{-1}$) are associated with the pronounced heating of its dipolar region.[77]

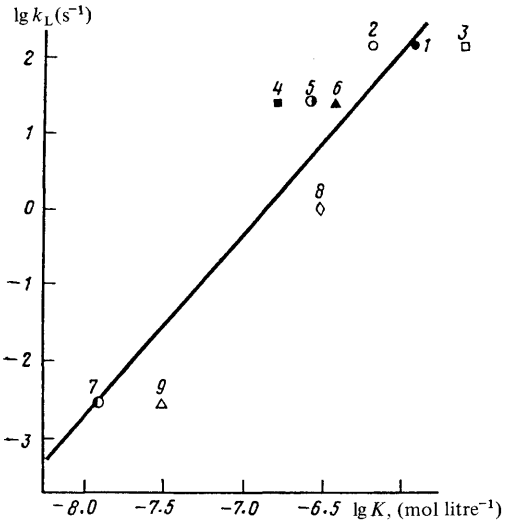



**Figure 2.** Dependence of the rate constant for the rate-limiting stage ($k_L$) of the dissociation of water on the effective equilibrium constant of the water dissociation reaction calculated from the impedance frequence spectra.[74] The numerals opposite the symbols correspond to the numbers of the membranes in the Table.

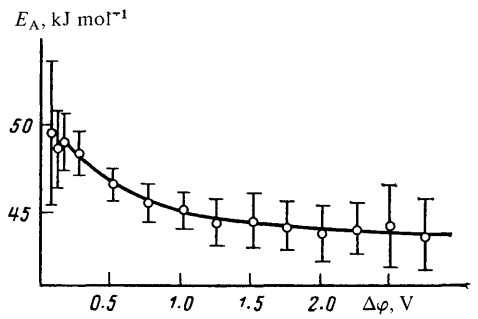



**Figure 3.** Dependence of the activation energy for the dissociation of water in the MB-1 membrane[69] on the overpotential of the dipolar region. The activation energy for the dissociation reaction is 56 kJ $mol^{-1}$ in pure water,[76] 32.5 kJ $mol^{-1}$ in the MB-2 dipolar membrane,[66] and 26 kJ $mol^{-1}$ in the MB-3 membrane.[66]

The dissociation of water in the dipolar region takes place under conditions different from those in pure water or in aqueous solutions. This is associated not only with the presence of the polymer

matrix, the fixed ionogenic groups, and counterions but also with the presence of electrical double layer at the site of contact between the cation exchanger and the anion exchanger.[78] Within the limits of this layer, the concentration of both the counterions and co-ions is low compared with the concentration of the fixed ions and this region has come to be called the "exhausted" layer.

There are at least three causes of the increase in the rate of dissociation of water in the exhausted layer. Firstly, the decrease in the concentration of the $H^+$ and $OH^-$ ions in the exhausted layer increases the degree of dissociation of the ionogenic groups, and hence also the concentrations of the charged forms, and increases the rates of the proton transport reactions in which they participate.[79] The second cause is associated with the polarisation of the H—OH bond by the electric field of the ionogenic group and also by the external electric field applied to the exhausted layer:[80–84]

$$k_d = k_d(0)\exp\left(\beta E + \frac{\alpha FE}{RT}\right) ,$$

where $k_d$ is the rate constant for the heterolytic dissociation of water molecules in an electric field with a strength $E$, $k_d(0)$ is the corresponding constant in the absence of the field, and $\alpha$ and $\beta$ are parameters taking into account respectively the decrease in the activation energy for the dissociation of water in the electric field and the entropy effect accompanying the orientation of water molecules in the vicinity of the ionogenic group and its dissociation. Thirdly, the dependence of the rate of dissociation of water molecules on the potential applied to the membrane is due to the expansion of the region of the space charge where dissociation actually occurs.

The dependence of the rate constant for the dissociation of water on the electric field strength, predicted by the Onsager theory for the second Wien effect, has been used in a number of studies for the description of processes in dipolar membranes.[85–87] Despite the qualitative agreement with experiment, from the standpoint of these ideas, it is difficult to explain the marked dependence of the properties of the membranes on the nature of the ionogenic groups. The same difficulty arises when one uses the model of the "neutral" layer, which is assumed to exist btween the cation exchanger and the anion exchanger in the dipolar region.[56] For certain membranes with an increased electrical resistance, it is essential to take into account the increase in the rate constants for the dissociation of water owing to the heating of those membranes at high current densities.[77]

It is noteworthy that all the approaches used to describe the dissociation of water in dipolar membranes and the models of such membranes[56,81,85] are mutually exclusive, although each investigator has found good agreement when comparing his model with experiment.

Comparison of the known models for the dissociation of water in dipolar membranes with experiment has demonstrated that the model of Timashev and Kirganova[81] agrees with the experimental data in terms of the largest number of criteria. Unfortunately, the accuracy of the experimental data (the voltage—current plots, the impedance frequency spectra) does not at present make it possible to determine all the constants for the space charge region and the water dissociation reaction.

Thus the best model of the dipolar membrane under the conditions corresponding to the generation of $H^+$ and $OH^-$ ions, which takes into account the non-equilibrium nature of the processes occurring in the space charge region, is that proposed by Timashev and co-workers.[81–83] The ideas developed in these studies agree fully with the catalytic mechanism of the water dissociation reaction at the ionic groups of the membranes.

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One can now regard it as a reliably established fact that the dissociation of water molecules in membrane systems takes place preferentially in the regions of the localisation of the space charge in the membrane phase with active participation of the ionogenic groups. In membrane systems lacking catalytically active groups, the dissociation of water takes place via the usual mechanism as a non-catalytic homogeneous reaction. In order to intensify the dissociation of water in membrane systems, catalytically active groups can be introduced both into the polymer matrix of the membrane and into the solution around the membrane.

Further progress in the study of the water dissociation reaction in membrane systems is related to the need to examine the elementary processes occurring with participation of catalytic centres in the space charge regions and the interfaces. The knowledge of the characteristic features of the water dissociation reaction in such systems will make it possible to alter specifically the surface properties of the membranes in order to facilitate or suppress this reaction. The dissociation of water must be taken into account in a theoretical description of membrane systems and in the planning and operation of electromembrane apparatus.

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Kuban State University,
Krasnodar