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ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES

KYIV 2016

National Academy of Science of Ukraine
V.I. Vernadskii Institute of General and Inorganic Chemistry
Ege University, Turkish Republic

ENVIRONMENTAL PROTECTION: FROM SORBENTS TO MEMBRANES

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ART OK Publisher

KYIV 2016

УДК 544.018.2: 544.472.3 + 555.11+666.22

Колективна монографія «Environmental Protection: from Sorbents to Membranes» - під ред. проф. Н. Кабай, докт. хім. наук Ю. С. Дзязько, проф. М. Арда, докт. хім. наук К.О. Каздобіна - 108 с.

Колективна монографія включає статті за матеріалами українсько-турецького семінару, який було проведено 11 листопада 2016 р. на базі Інституту загальної та неорганічної хімії ім. В. І. Вернадського НАН України за участю фахівців Егейського університету (Турецька республіка) та за підтримки Відділення хімії НАН України, Відділу міжнародних зв'язків НАН України, а також Наукової та Технічної дослідної Ради Турецької республіки TÜBİTAK. У монографії наведено результати досліджень, які направлені на вилучення токсичних і цінних компонентів із розчинів техногенного та природного походження, зокрема з біологічних рідин, із застосуванням сорбційних та мембранних методів. Результати робіт можуть бути застосовані у водопідготовці, хімічній, фармацевтичній, харчовій промисловості. Особливу увагу приділено синтезу нових матеріалів для процесів розділення та впливу структури цих матеріалів на їх функціональні властивості: проникну здатність, електропровідність, каталітичну спроможність тощо.

Монографія є корисною для фахівців в області мембранних та сорбційних технологій, а також для студентів вищих навчальних закладів.

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Рекомендовано до друку Вченою радою ІЗНХ ім. В. І. Вернадського НАН України (протокол № 15 від 19 жовтня 2016 р.).

ISBN 978-966-97621-2-2

UDC 544.6.018.22

THE NATURE OF INTERPHASE POTENTIAL UNDER FORCED MOVEMENT OF THE PROTON IN WATER/OXYGEN SYSTEM

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Abstract. *The effect of oxygen bubbles on the formation of the membrane interfacial potential under microgravity in water media was considered. The braking of the proton motion and changes of pH under microgravity in water/oxygen systems depend on the O_2 gas bubble size distribution, that have a much larger variance in acid solutions than in basic solution.*

Keywords: *membrane, proton, oxygen, interphase potential*

Introduction. The main point that has to be considered in the water management is the behavior of the proton in presence of oxygen and porous membrane. This is ideal since the electrode needs to remain hydrated to promote high levels of proton transfer in presence of O_2 and is especially important for design of effective portable fuel cells [1]. In such case the water transfers protons through the membrane due own structure and exchanging of pressure in porous media [2, 3]. The presence of dodecahedral substitutional sites in the structure of liquid water promotes the hydration of individual water molecules, introduced into these cavities [4, 5]. The substitution of water molecules by oxygen molecules change the structure of existing hydrated complexes of water with change in degree of proton-donor activity and the transport of oxygen to the cathode. These effects increase in the presence of porous membrane.

The aim of this work is to study the effect of oxygen bubbles on the formation of the membrane interfacial potential under microgravity in water media.

Experimental. In the experiment distilled water, degassed for 1.5 - 2 hrs by refluxing was used. Water (80 - 85 ^{0}C) was placed in a sealed measuring cell, which was cooled to 20±2 ^{0}C then pH and redox - potential Eh were measured. Temperature settings were selected according to the oxygen solubility in water (at 80 ^{0}C virtually no dissolved oxygen) ($[O_2] \approx 10^{-7}$ M), whereas at 20 ^{0}C $[O_2]\approx 3\times10^{-4}$ M. The mechanical action exerted on the water by filtration through filters of different structure. The measurements were performed on ion-meter EV-74 with glass and platinum electrode and Ag/AgCl reference electrode with measurement error ± 5%. The standard and isolated from the air thin-layer cell with the water layer thickness of 0.5 mm were used for measurements. The experiment was conducted in two stages. First, the initial pH and Eh were measured in the degassed distilled water. In the second step into the cell with degassed water fed oxygen for one minute. Oxygen was bubbled through a saturated NaOH solution to remove CO_2. Then measurements of pH and Eh were repeated.

The microtexture of samples was studied using the SEM Mira 3 FESEM Tescan USA Inc. with high resolution on the cathode with field emission SEM HV - 10 KeV and automatic measurement in the image.

Magnetization of the water was performed with an inhomogeneous magnetic field intensity H = 0.074 Tl during 30 s.

Results and discussion. The shift of Eh potential values of degassed water in the cathode region after filtration through membranes with various nature and pore size was experimentally found (fig. 1). In the absence of concentration changes, it formally indicates the decrease in oxygen content [6]. And in this case, a change in the redox potential is possible due to the impact of double electric layer, DL, at the interphase of the water cluster/amorphous water/membrane surface, i. e interphase potential, caused by the forced movement of the proton across porous membrane. It's known that the electrical surface potential of pure water arise due to the net alignment of the dipole and quadrupole moments of water molecules at the interface and only changes in the surface potential can be measured experimentally, the small surface potential of pure water is not easily determined. The general sign convention for the surface potential is taken as measured from the air into the solution and the electrical surface potential is estimated to be between 0.1 and 0.2 V, corresponding to having the water hydrogens pointing slightly toward the bulk [7].

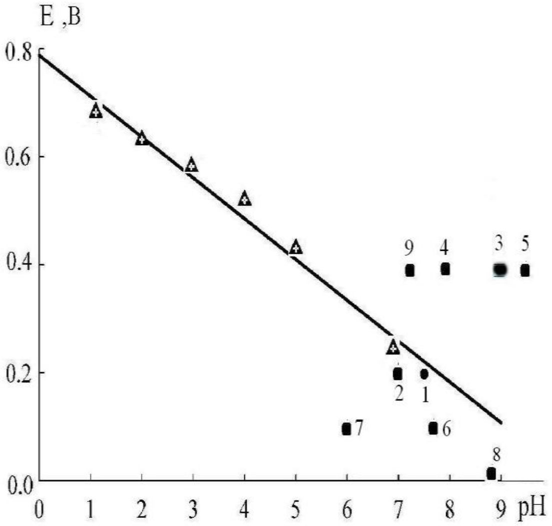

Fig. 1. *Isoelectric Point of Various Kinds of Water, Passed through Membranes of different Pore Size and Nature. Etalon - 0.01M Solution of NaCl with O_2 (▲).*

(1- Distilled Water; 2- Distilled Water without Oxygen; 3- Distilled Water without Oxygen, Passed through Polymer Membranes with pore size of 11-12nm ; 4- Distilled Water without Oxygen, Passed through Paper Membranes with Pore size of 200 nm; 5- Distilled Water Containing Oxygen, Passed through Polymer Membranes with Pore Size of 11-12 nm ; 6- Tap Water; 7 - Distilled Water Containing Carbon Dioxide ; 8 - Magnetized Distilled Water ; 9 - Distilled Water without Oxygen, Passed through Paper Membranes with Pore Size of 300nm).

In this case, the proton electrochemical potential can be expressed by the equation given by Nernst - Peters [7]:

$$\Delta\overline{\mu_{H^+}} = F\Delta\varphi - 2{,}3RT\Delta pH \qquad (1)$$

where ΔpH - interphase gradient of pH (or the concentration of protons) and Δφ - an electric potential difference at the phase interfaces (capacity of the DLs). The equation shows that the electrochemical potential difference of H^+ consists of two components - the concentration (pH gradient) and electrical (Δφ). The value of $\Delta\overline{\mu_{H^+}}$ can be regarded as the force acting on the protons, which determines the flow of H^+ across interphase border. If we taken the resulting potential to one coulomb of electricity, we get specific electromotive force (EMF) for the proton transfer:

$$\Delta E_{H^+} = \frac{\Delta\overline{\mu}}{F} = \Delta\varphi\frac{2{,}3RT}{F}\Delta pH \qquad (2)$$

Fixed experimental changes in pH and Eh potential values and the values of the isoelectric points removal corresponds to the mathematical regularity eq.2. If the pH removes in the basic site, the values of $\Delta E_H{}^+$ increases with increasing of the ΔpH. It has created energy barriers for oxygen motion in this case. Thus, the membrane, under conditions of lack of dissolved oxygen, "encapsulates" it within a clusters, i.e. it translates into a molecular - dissolved state and eliminates the effect of proton EMF. In equilibrium state, the active (electrical) proton flux at the interphases is balanced by a passive flow of H^+ (concentration gradient). The stationary state is reached usually for 100 – 200 s.

The occurrence of the interphase potential explains the absence of differences in the values of the redox potential in the conditions of pH change by passing degassed water and water containing oxygen through the track (nano-scale) membrane (Fig. 2). The small pore sizes (11-12 nm) cause higher Laplace pressure values in this case.

$$P_L = \frac{2\sigma}{R} \qquad (3)$$

where σ - the surface tension, R - the pore radius of curvature.

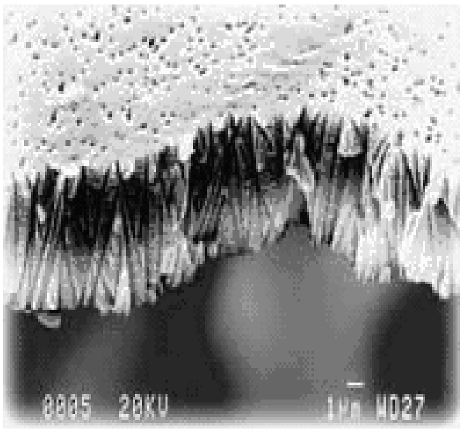

Fig. 2. *Electron Micrograph of the Track Membrane*

Taking into account that the bubble O_2 gas forms closed the membranes surface due to natural convection and that under microgravity environment the bubble curtain thickness increases with decreasing electrode potential, the O_2 gas bubble size distribution shows a much larger variance in acids solution than in basic solution under microgravity. The variance increases from ±0.05mm at −0.4V to ±0.2 mm at −0.8 V. [8]. And when the pore sizes are smaller than the size of the bubble the curvature radius increases exponentially, as result - the elimination of concentration component. Then according to the equation 2 $\Delta pH = 0$ and interfacial potential value becomes zero.

The presence of dissolved oxygen increase the concentration of protons at the interface of the oxygen / water, that causes the proton concentration gradient (fig 3). So to mitigate this effect the external pressure P_0 on the surface of the membrane should be increased or the pore size is to be increased, too.

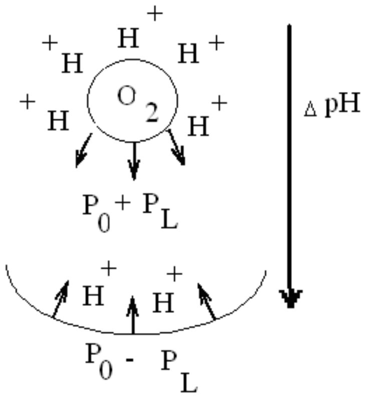

Fig. 3. *The Mechanism Scheme of the Proton Gradient Formation within the Nanoporous Membrane in the Presence of* O_2 *Bubble (External Pressure –* P_0*, Laplace Pressure-* P_L*).*

Conclusions. The membrane, under conditions of lack of dissolved oxygen, translates oxygen bubbles into a molecular - dissolved state and eliminates the effect of proton EMF. Changes of pH under microgravity in water/oxygen systems depend on the O_2 gas bubble size distribution, that have a much larger variance in acids solution than in basic solution. Modeling of cross-border potential have shown that when the pore sizes are smaller than the size of the bubble the curvature radius increases exponentially, as result - the elimination of concentration component and cross-border potential value becomes zero. This model is in agreement with experiment. If the porous size larger than size of oxygen bubbles –the cross-border potential is decreased. In case of the smaller porous (the smaller than bubble size) is observed an increase in concentration of the protons at the oxygen / water interphase. So to mitigate this effect should be increased external pressure P_0 on the surface of the membrane or increase the pore size.

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УДК 544.6.018.22

ПРИРОДА ТРАНСГРАНИЧНОГО ПОТЕНЦІАЛУ ПІД ЧАС ПРИМУСОВОГО РУХУ ПРОТОНУ В СИСТЕМІ ВОДА-КИСЕНЬ

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Резюме. *Розглянуто вплив бульбашок кисню на формування мембранного потенціалу на межі розділу фаз в умовах мікрогравітації у водних середовищах. Показано, що усунення руху протонів і зміни pH при мікрогравітації в системі вода / кисень залежить від розподілу розмірів бульбашок газу* O_2*, які мають набагато більшу дисперсію в розчині кислоти, ніж в лужному розчині.*

Ключові слова: *мембрана, протон, кисень, трансграничний потенціал.*