Impact of ion exchange membrane surface charge and hydrophobicity on electroconvection at underlimiting and overlimiting currents

K.A. Nebavskaya[a], V.V. Sarapulova[a], K.G. Sabbatovskiy[b], V.D. Sobolev[b], N.D. Pismenskaya[a], P. Sistat[c], M. Cretin[c], V.V. Nikonenko[a,*,1]

[a] Kuban State University, Stavropolskaya st., 149, Krasnodar, Russia
[b] Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninsky prospect 31, Moscow, Russia
[c] European Membrane Institute, University of Montpellier, Place Eugèfigne Bataillon, Montpellier Cédex 5, France

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ABSTRACT

The mechanism of electroconvection at a permselective surface presents a high interest for electrodialysis separation processes as well as for microfluidics and other applications. We have studied a commercial Neosepta AMX-Sb anion-exchange membrane and its three modifications differing in the surface charge and, as a consequence, in the degree of hydrophobicity. The zeta-potential and the contact angle were measured; the membranes were characterized by chronopotentiometry and voltammetry. It is shown that at the current densities slightly lower or equal to the limiting current density, the mass transfer rate is mainly affected by the membrane surface charge. However, at the higher current densities, the main factor is the degree of hydrophobicity: the samples with a weakly charged highly hydrophobic surface show lower voltage under the same current density. This peculiarity is explained by the fact that the mechanism of electroconvection (EC) depends on the current density. At underlimiting currents and low voltages, EC occurs as electroosmosis of the first kind; the surface charge determines the parameters of the (quasi)equilibrium electric double layer (EDL), playing the main role in the phenomenon. At overlimiting currents and high voltages, it is the extended space charge region (much thicker than the EDL), which controls EC occurring apparently as electroosmosis of the second kind (nonequilibium EC). Then the contribution of the EDL is less important, while the impact of hydrophobicity increases. It is shown that the equilibrium EC may be quite strong at the AMX-Sb membrane having a highly developed surface roughness of different scales. In the range of 0.03–0.06 V there is an "anomaly": with increasing current density the potential drop over the AMX-Sb is decreasing instead of increasing.

1. Introduction

Electrodialysis is widely used for production of potable water from brackish water sources, as well as for production of high quality industrial process water or treatment of certain industrial effluents [1]. Its broader employment is hindered by the low mass transport rate when treating the dilute solutions [2], mainly due to the decrease of electrolyte concentration at ion exchange membrane/solution boundary caused by the passage of electric current [3]. Under condition that electrodiffusion is the only mechanism of mass transfer, the formation of such a concentration gradient (known as concentration polarization) leads to the phenomenon of limiting current (i_{lim}), which is attained when the concentration gradient reaches its maximum value. This state relates to the nearly vanishing electrolyte concentration at the surface.

However, the limiting current may be exceeded if additional mass transfer mechanisms, such as gravitational convection or electroconvection [4,5], arise, or new charge carriers are produced by water splitting [6,7] or ampholyte dissociation. In dilute solutions, EC, which is caused by the action of electric force on space charge in the depleted solution near the ion selective surface, is of major importance.

EC aids to mix the solution near the ion exchange surface, which enhances the mass transfer rate in electrodialysis. Along with electrodialysis, this phenomenon is important, and even makes the basis of functioning, for micro- and nanofluidic devices, such as electrokinetic micropumps, nanomixers [8] and other [9]. It is significant in analytical chemistry for solution pre-concentration [10], in the processes of electro-sedimentation [11], electrophoresis and others.

Generally, space charge region (SCR) at ion-exchange membrane

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* Corresponding author.
  E-mail addresses: littlegreenchemist@yandex.ru (K.A. Nebavskaya), sabbat07@mail.ru (K.G. Sabbatovskiy), marc.cretin@iemm.univ-montp2.fr (M. Cretin).
  [1] v_nikonenko@mail.ru

(IEM) surface involves equilibrium electric double layer (EDL), which occurs at the surface even in the absence of electric current, and extended SCR, which forms when the current density exceeds i_{lim} [4]. When a current flows across an ion-exchange membrane, electrolyte interfacial concentration, C_s, decreases (in the depleting solution). The (quasi)equilibrium EDL thickness, λ, increases being proportional to $(C_s)^{-1/2}$, but its structure remains unchanged. The extended SCR is essentially non-equilibrium, it appears when $C_s \ll C_O$ (C_O is the electrolyte concentration in the bulk solution). While λ is of the order of nanometer, the thickness of the extended SCR can be a few µm [12]. Depending on what part of the SCR the electric force is applied, electroconvection may be equilibrium or nonequilibrium [13]. Usually, equilibrium EC is considered as the classical electroosmosis (EO), i.e. a fluid slip along the surface induced by the tangential component of applied electric force. When an electric force is applied to a SCR involving its extended part, two situations are possible. If the electric force contains its tangential component, EC can occur in EO mode (as a slip). Dukhin and Mishchuk [14–16] call this mechanism "EO of the second kind" (keeping term "EO of the first kind" to the classical EO, where no extended SCR appears). EO of the second time may be stable or instable, when a certain voltage threshold is overcome. According to Mishchuk et al., [17], to produce this kind of EC, two sufficiently high components of electric field are needed. The normal one is to form an extended SCR, and a tangential one, to yield the fluid slip.

However, even in the condition where no tangential field is applied, intensive EC is possible due to electro-osmotic instability discovered by Rubinstein and Zaltzman [18]. This kind of electroconvection arises, when a small perturbation of concentration or electric or fluid velocity fields does not decay with time, but induces higher deviations from the steady state. In this case, oscillations of potential (when the current is fixed) or current (when the potential is fixed) are observed in simulations [18–22], as well as in experiments [23–25]. In particular, tangential component of electric field arises changing its magnitude and direction with time.

Since EDL is always present at charged surfaces of ion exchange membranes, equilibrium EC occurs in no threshold mode. At the same time, unstable non-equilibrium electroconvection (both the Rubinstein-Zaltzman or Dukhin-Mishchuk modes) requires some threshold value of potential drop to be reached. At small excesses of overlimiting current density (at potential drops about 0.3 V across one membrane) the extended SCR is formed, but EC can be stable [20]. At further increase of potential drop (to about 1 V), the transition to regime of electrokinetic instability occurs [18,26].

Until recently it was thought [26] that only the non-equilibrium EC can cause oscillations of potential drop under a constant current. Zholkovskij et al. [27] have shown theoretically that equilibrium EO near a perfectly perm-selective surface cannot yield instability. However, in their recent work [13], Rubinstein and Zaltzman have predicted theoretically that the oscillations of current caused by equilibrium EC can arise, if the membrane is not ideally selective. In Refs. [28,29], it was found experimentally that, really, in some cases (undulated membrane surface, alternation of well and poorly conductive regions on the membrane surface, its high hydrophobicity) these oscillations are observed in transition regime at small potential drops and at times significantly lower than the transition time.

The velocity of electroosmotic slip, u, caused by equilibrium EO, is a strong function of the surface charge. According to Rubinstein and Zaltzman [13,26], u increases with zeta potential ζ as:

$$u = \left(\zeta \frac{F}{RT} \left(\frac{F}{RT} \frac{\partial \varphi}{\partial x} + \frac{1}{C} \frac{\partial C}{\partial x} \right) - \frac{4}{C} \frac{\partial C}{\partial x} \ln \frac{1 + e^{\left(\frac{\zeta F}{2RT} \right)}}{2} \right) \frac{\varepsilon \varepsilon_0 (RT)^2}{4\pi \eta F^2}$$

(1)

where C is the electrolyte concentration, T is the absolute temperature, η is the dynamic viscosity of solution, $F = 96485$ C mol^{-1} is the Faraday constant, R $= 8.314$ J mol^{-1} K^{-1} is the gas constant, ε is the relative

permittivity of solution, $\varepsilon_O = 8.85 \cdot 10^{-12}$ F·m^{-1} is the vacuum permittivity. ζ is defined as the potential drop between the slip plate and the outer border of EDL, its value increases with surface charge, σ, according to the Grahame equation [30]:

$$\sigma = \sqrt{8\varepsilon\varepsilon_0 CRT} \times \sinh\left(\frac{\zeta F}{2RT} \right)$$

(2)

Eq. (1) is a generalization of the Smoluchowski equation deduced when accounting for polarization of the EDL by the applied tangential electric field [13]. The relation between the surface charge and intensity of EC was also theoretically discussed by Andersen et al. [31], who connected the propensity to develop electroosmotic instability with the membrane surface charge density, which can be a function of applied current. When H$^+$ and OH$^-$ ions are generated at the depleted surface (water splitting), the surface charge can be reduced, e.g. due to deprotonation of fixed amino groups (current-induced discharge [31]).

Generally, it is possible to change the value of surface charge (by changing the concentration of the fixed ions on the surface of IEM or by charging the surface of channels in microfluidic devices [32]). Hence, it is important to study how ion transport and electroconvection respond to the variation of membrane surface charge. However, as far as we know, no such studies were carried out.

As it is follows from Eqs. (1) and (2), with increasing σ (ζ), electroconvection should increase. However, there is another factor, which affects EC. Really, when increasing surface charge, its hydrophobicity will decrease. Nevertheless, as it was shown experimentally [33,34] and via simulation [20,35], increasing hydrophobicity leads to increasing overlimiting transfer caused by a more intensive EC. This effect is explained by easier fluid slip over the highly hydrophobic regions [36]. Properties of water near a hydrophobic surface differ from those of bulk water. There is local reduction of water density [37–39], which is accompanied by a decrease in the viscosity [40] and in dielectric permittivity [37], which in turn compresses the EDL. The change in water properties affects the velocity of electroosmotic slip at a hydrophobic surface [37,41–43].

There is a number of studies where the tangential streaming potential/zeta potential was measured for ultrafiltration and reverse osmosis membranes [44–48]. In particular, Szymczyk et al. [47] found that a chemical modification of an UF membrane leads to a charge reversal (from negative to positive) of the porous substructure of the membrane, while the overall charge of the external surface remains negative, although with diminished magnitude. However, only few of papers reported the results of similar measurements for ion-exchange membranes [49,50]. Lee et al. characterized the AEM fouling in terms of zeta potential [51]. A new promising method for determening the lateral electrical conductivity of ion-exchange membranes based on the measurements of tangential streaming current and streaming potential was developed by Sedkaoui et al. [50].

In this work we prepare a series of ion-exchange membranes with similar properties, but differing in surface charge and, as a consequence, in the degree of hydrophobicity. To evaluate the surface charge, we measure the tangential streaming potential and then determine the zeta potential and use Eq. (2) to find σ. By applying chronopotentiometry and voltammetry, we try to find out how the membrane surface properties affect the development and mechanism of electroconvection at low and high voltages.

2. Experimental

2.1. Membranes

We studied a Neosepta AMX-Sb homogeneous anion exchange membrane (manufactured by Astom, Japan) and three its modifications. The AMX-Sb sample was prepared from a commercial membrane subjected to standard salt pretreatment. Additionally, we stu-