On the Schroeder Paradox for Ion-Exchange Polymers

V. I. Roldughin[a, b,]* and L. V. Karpenko-Jereb[c]

[a]*Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, bldg 4. Moscow, 119071 Russia*
[b]*Department of Chemistry, Moscow State University, Moscow, 119991 Russia*
[c]*Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, Graz, 8010 Austria*
*e-mail: vroldugin@yandex.ru

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Abstract—The known Schroeder paradox, i.e., a difference in the degree of swelling of ion-exchange polymers at equilibrium with liquid water and its vapor, has been discussed. It has been noted that there is no paradoxicality in this phenomenon. An example of different "swelling" based on trivial physical considerations has been presented. A simple mechanism has been proposed for increased swelling of an ion-exchange polymer immersed in liquid water, this mechanism being associated with the action of the Maxwell stresses at a polymer/electrolyte interface. The predicted values of the "excess" swelling have been shown to correspond to the data of real experiments.

INTRODUCTION

An effect that was discovered about 100 years ago and is referred to as the "Schroeder paradox" remains to be discussed in the scientific literature [1]. We shall consider this effect with respect to ion-exchange polymers (membranes). Its essence consists in the following. A polymer swells in different manners in vapor and liquid phases, which are at equilibrium with one another. It is the difference in the swelling that is the Schroeder paradox, because the polymer swells due to water sorption, while the chemical potentials of water molecules in liquid and vapor phases are obviously equal. That is, water molecules having the same chemical potential cause different degrees of swelling depending on the polymer environment, which, seemingly, should not be.

This effect plays a key role in membrane processes, because polymer membranes may simultaneously be in contact with vapor and liquid phases. Therefore, repeated attempts were made to explain the paradox theoretically. For this purpose, diverse (sometimes, exotic) models have been proposed (a long list of works devoted to the Schroeder paradox may be found in [2–7]). In this article, we shall not discuss the proposed models. It should only be noted that the Schroeder effect is of a general character; i.e., it is observed in diverse systems. Therefore, its explanation must, in our opinion, be based on fundamental laws. Below, we propose a simple explanation of the Schroeder paradox for ion-exchange polymers, with this explanation being based on fundamental principles. In fact, our explanation does not involve any model considerations. We shall just draw attention to the obvious difference between the states of an ion-exchange polymer occurring in contact with vapor and liquid phases and show that, in the case of the liquid phase, additional forces arise to stretch the polymer. The estimated value of these additional forces shows that they are sufficient to explain the "Schroeder paradox."

The Schroeder effect for nonionogenic polymers will be explained in a subsequent communication.

A TRIVIAL EXAMPLE

Let us present a simple example that may be considered to be an illustration of the Schroeder paradox. Take two similar salt (or sugar) crystals and place one of them into liquid water and the other into water vapor. The crystal placed into the liquid water will dissolve, and the salt will be distributed over the entire volume (infinite swelling). What will happen to the crystal in the vapor phase?

The crystal placed into the vapor phase will begin to sorb water, and a droplet will be formed and start growing, because, according to the Raoult law, the equilibrium vapor pressure over a solution is lower than equilibrium pressure p_0 over a pure solvent. However, as the droplet grows, the solution concentration (molar fraction of the salt) will decrease according to the following law (for the case of a low concentration):

$$c(r) = m_0 V_m / (4\pi r^3 / 3), \qquad (1)$$

where r is the droplet size, m_0 is the number of salt moles in the crystal, and V_m is the molar volume of

water. The equilibrium vapor pressure over the solution of the droplet will approach p_0 in accordance with the following law:

$$p = p_0[1 - m_0 V_{\mathrm{m}}/(4\pi r^3/3)]. \qquad (2)$$

However, the droplet will not grow infinitely, because the equilibrium vapor pressure over a droplet (which have a curved surface) is well known to be higher than p_0 due to the capillary pressure. The equilibrium pressure (for a rather large spherical droplet) is

$$p = p_0\left(1 + \frac{2\sigma V_{\mathrm{m}}}{rRT}\right), \qquad (3)$$

where R is the gas constant, T is the absolute temperature, and σ is water surface tension (the difference between the surface tensions of a solution and a pure solvent is ignored).

As the droplet grows, correction $m_0 V_{\mathrm{m}}/(4\pi r^3/3)$ in Eq. (2) decreases faster than correction $2\sigma V_{\mathrm{m}}/(rRT)$ in Eq. (3) does; therefore, the droplet ceases to grow after a certain size is reached. This size is determined from the condition for the cancellation of the corrections in Eqs. (2) and (3):

$$r_{\mathrm{e}} = (3m_0 RT/8\pi\sigma)^{1/2}. \qquad (4)$$

This size corresponds to a stable state of the droplet. It may be stated that the salt crystal has been substantially less "swollen" in the vapor phase than in the bulk liquid phase. That is, the Schroeder effect takes place. At the same time, there is no paradox in this case.

The following important circumstance must be noted: the water chemical potential is, in both cases, the same (a change in the chemical potential of the bulk water phase due to the dissolution of the small salt crystal is ignored). That is, neither the idea that there is a difference between chemical potentials nor other additional assumptions need to be introduced to explain the difference in the "swelling." This "Schroeder effect" has been explained within the framework of simple physical assumptions.

REAL ION-EXCHANGE POLYMERS

Preliminary Considerations

Let us consider real ion-exchange polymers. First of all, one *logical mistake* must be noted, which has been made by almost all researchers who study the Schroeder paradox. Commonly, it is implicitly believed that the equality of water chemical potentials must *inevitably* lead to the same swelling (in another case, no paradox would take place). However, water may have the same chemical potential in membranes occurring in absolutely different states. For example, we may take two identical membranes, stretch one of them with external forces, and place them both into a vapor atmosphere. The membranes will sorb water

molecules until thermodynamic equilibrium is reached in each of them. It is clear that the chemical potentials of water molecules in the stretched and nonstretched membranes will be equal; however, the states of the membranes will be completely different. Thus, *there is no reason to require the same swelling* for membranes occurring in liquid water and its vapor, which is to say, as a matter of fact, that there is no Schroeder paradox. It has appeared as a result of a logical mistake: the identity of polymer states has begun to be required based on the equality of water chemical potentials. There is no reason for this requirement!

Nevertheless, the difference in the swelling of an ion-exchange polymer in vapor and liquid phases must be explained in this or that manner. We shall consider two variants of the explanation, with one of them being formal, while another one implying a rather simple and physically clear mechanism for excess swelling of an ion-exchange polymer in a water phase.

Formal Explanation

Now, we shall show that the states of an ion-exchange polymer in vaporous and liquid water are different. Indeed, the vapor phase consists of just water molecules (if we ignore an inert gas medium). The liquid phase does not represent just water molecules; it contains H^+ and OH^- ions (if we consider a primitive model). If an ion-exchange polymer occurs in (to be more specific) a sodium form, Na^+ ions cannot pass to the vapor phase, while they freely pass to liquid water. This leads to the appearance of the Donnan potential, which cannot exist for a polymer in a vapor phase.

Quantum-chemical calculations have shown that ionogenic groups of a membrane dissociate after water molecules are sorbed [8]. That is, "free" ions are also present in a polymer swollen in water vapor. However, the ions are not evaporated into the vapor at normal temperature (image forces prevent the ions from leaving the polymer or electrolyte). Therefore, the Donnan potential cannot be introduced for a polymer in water vapor. Thus, even with a cursory glance at polymer/vapor and polymer/water systems, we can see that the states of the polymer in them must be different. In the former system, the equilibrium is determined by the equality of the chemical potentials of water in the vapor phase and in the polymer alone, while, in the latter case, it is necessary to provide equality of the chemical (electrochemical) potentials of not only water, but also H^+, OH^-, and Na^+ ions. It is quite obvious that the aforementioned equilibrium conditions are not identical. Thus, there is no reason to require the same degree of swelling for polymers occurring in different states, in particular, with respect to the concentrations of H^+, OH^-, and Na^+ ions and, hence, the concentration of water molecules. That is, the difference in polymer swelling is due to the non-

(a)

(b)

(c)
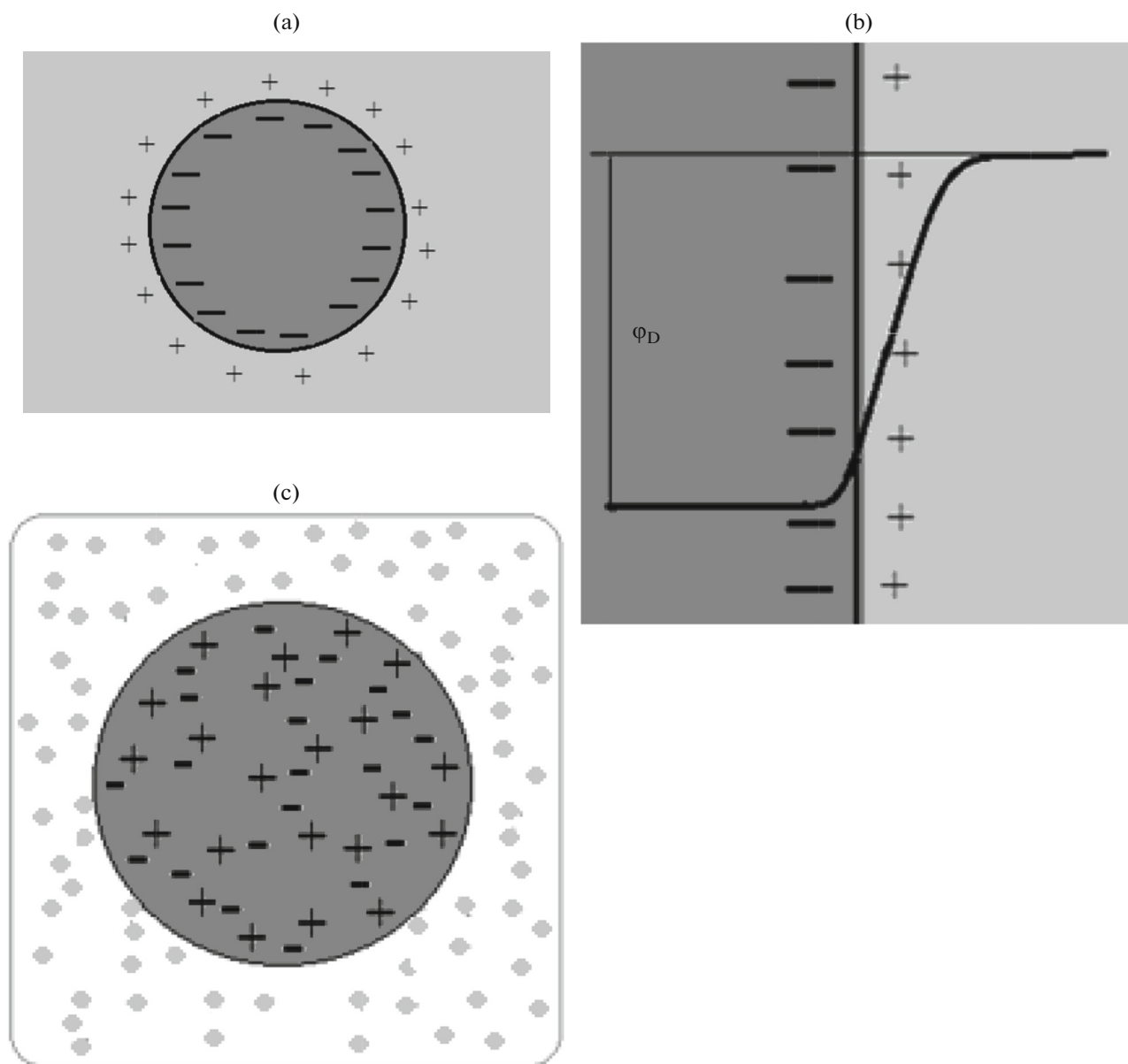
Fig. 1. (a) The charge distribution at the surface of an ion-exchange polymer, (b) the pattern of the electrostatic potential in liquid water, and (c) the charge distribution at the polymer in water vapor.

identity in the conditions of the thermodynamic equilibrium in the two cases under consideration.

Moreover, in the case of ion-exchange polymers occurring in liquid water, there is one more mechanism for their increased swelling, this mechanism being incapable of manifesting itself in water vapor.

A Model of Excess Ion-Exchange Polymer Swelling in Liquid Water

Let us describe a possible mechanism of the enhanced swelling of an ion-exchange polymer immersed in liquid water. This mechanism is not realized for a polymer occurring in water vapor, because, as has

been mentioned above, ions cannot evaporate and the polymer remains to be electrically neutral (Fig. 1).

We consider the standard mechanism for the appearance of Donnan potential φ_D (Fig. 1). The Donnan potential results from the passage (or exchange) of ions from a polymer to a liquid water phase (aqueous electrolyte solution). It is generated by immobile charges that are located in a thin surface layer (with a thickness nearly equal to Debye radius r_D) and screened by mobile ions present in an electrolyte. It is known [9] that the charges distributed over the surface of a conductor (an ion-exchange polymer may be considered to be a conductor) do not create a field

in its internal part. In this case, the distribution of a field at the polymer surface may be represented as follows. In a polymer, the field exists only in the region of a thin charged layer, while it does not exist in the internal region. In an electrolyte solution, the field is generated by all charges of the surface layer and reaches the thickness of the Debye layer, beyond which it is screened by counterions. An important difference between vapor and liquid phases surrounding the polymer consists in the following: in the case of liquid water, the charge on a polymer surface is screened by ions of an external electrolyte, while, in a vapor phase, all charges are screened by ions located in the polymer. In other words, in the case of a liquid phase, the polymer is charged (in a thin surface layer), while, in the case of water vapor, it is not. It should be emphasized that, in liquid water, a polymer must be charged to provide the equality of the electrochemical potentials of ions located in water and the polymer. This equality is provided by the charges rigidly bonded to the polymer (the mobile ions are involved in the formation of an electrical double layer). This difference is schematically represented in Fig. 1.

Now, let us discuss what transpires with charged surface groups of a polymer. These groups are repulsed from each other by electrostatic (Coulomb) forces. This repulsion stretches the polymer. These tensile stresses have been calculated in [9] to be equal to

$$\Pi_{Mnn} = \frac{1}{2} q_s E, \tag{5}$$

where Π_{Mnn} is the stress tensor component normal to the polymer surface, q_s is the surface charge density, and E is the electric field strength at the polymer surface. Then, the physical meaning of these stresses becomes quite obvious. Parameter $q_s E$ is the force applied from the side of an electric to the surface charges. Since the field is generated by the same charges, a factor of 1/2 arises, which excludes the action of each charge on itself. Note that these stresses lead to other well-known effects: a reduction in the surface tension of charged droplets and breakage of strongly charged solids.

Combination (5) is, in fact, part of the Maxwell stress tensor

$$\Pi_{Mnn} = \frac{1}{2} q_s E = \frac{\varepsilon_0 \varepsilon E^2}{2}, \tag{6}$$

where ε_0 is the electric constant and ε is the dielectric permittivity of water. Remember that, in the general case, a corresponding Maxwell stress tensor component has the following form [9]:

$$\Pi_{Mnn} = \frac{\varepsilon_0 E^2}{2} \left(\varepsilon + \rho \frac{\partial \varepsilon}{\partial \rho} \right), \tag{7}$$

where ρ is the density of the dielectric medium. The addend in the right-hand side of Eq. (7) is responsible

for the electrostriction effects, which have been ignored here for simplicity.

Thus, the Maxwell stresses, which manifest themselves only for a polymer immersed in a liquid water phase, cause the excess swelling of the polymer observed in experiments.

Let us estimate the strains caused by the Maxwell stresses relevant to polymer surface charging. We consider a spherical fragment of an ion-exchange polymer (the sample shape is insignificant; an effect of the same magnitude may be obtained for a sample of an arbitrary shape, Fig. 2). The strain caused in a spherical sample by the stresses normal to the surface is easy to determine by the standard formulas as [10]

$$\Delta r_m = \Pi_{Mnn} r_m \frac{1 - 2\sigma_P}{E_Y}, \tag{8}$$

where r_m is the radius of the polymer sample, E_Y is the Young modulus of the polymer, and σ_P is its Poisson modulus.

The Π_{Mnn} value of a typical ion-exchange polymer is determined as follows. For a polymer charged to potential ϕ_D, the electric field strength at its surface on the side of a 1 : 1 electrolyte is equal to [11]

$$E = \left| \frac{d\varphi}{dx} \right| = \frac{1}{r_D} \frac{2kT}{e} \sinh\left(\frac{e\varphi_D}{2kT} \right), \tag{9}$$

where k is the Boltzmann constant, T is the temperature, and e is the proton charge. For the Donnan potential, we take a moderate value $\varphi_D = 100$ mV [12]; then, $E \approx 330$ mV/r_D. Assuming that $r_D = 3$ nm (a centimolar electrolyte solution) and $\varepsilon = 80$ for water, we obtain $\Pi_{Mnn} \approx 4 \times 10^6$ Pa. Note that the normal component of the pressure tensor (this component governing the action from the side of the electrolyte on the charged surface) coincides with the hydrostatic pressure in the electrolyte far from the surface [11]. Therefore, the total "excess" effect is determined by the aforementioned value of Π_{Mnn}.

It should be noted once more that this is the additional tensile stress applied to the polymer in the liquid water phase. In order to determine the total stress, it is necessary to additionally take into account, e.g., water osmotic pressure and other effects. However, we have, here, confined ourselves to the consideration of the contribution that is, for sure, absent in the polymer occurring in water vapor.

Using the elasticity modulus of Nafion membranes equal to nearly 50 MPa [13] at 95% humidity (i.e., a strongly overestimated value), we obtain that the linear degree of swelling (a change in the radius) related to the action of the electrostatic forces is 4–8% and, accordingly, the change in the polymer sample volume is 12–30%. As the humidity increases, the elasticity modulus of the polymer decreases, and its swelling, accordingly, increases. As has been mentioned above,
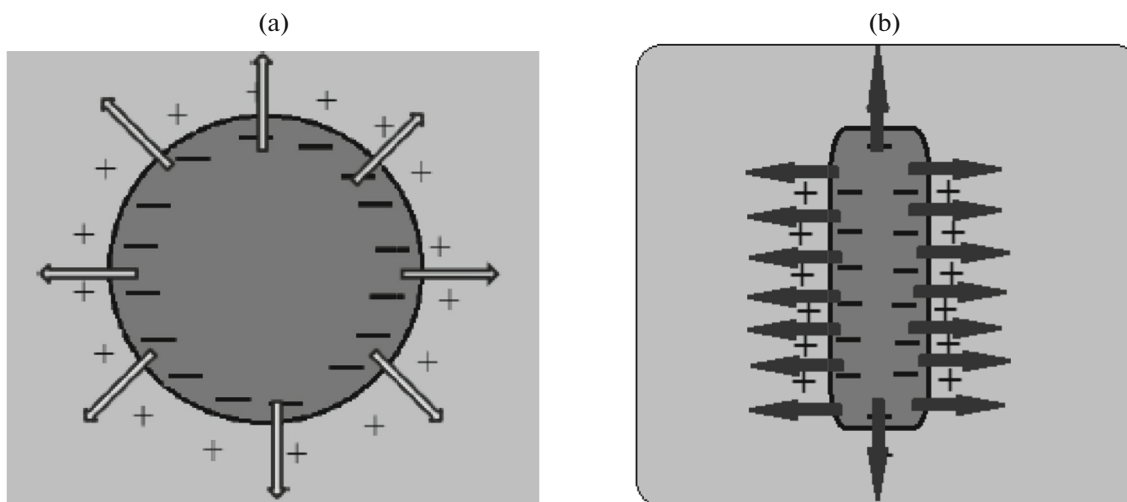
(a)   (b)

Fig. 2. Schematic representation of the action of Maxwell stresses for (a) spherical and (b) rectangular polymer samples.

in a real system, we should take into account the influence of other factors, which will be analyzed in subsequent publications.

CONCLUSIONS

It has been shown that ion-exchange polymers must have different swellabilities in liquid water and its vapor. The specific physicochemical analysis has shown the *unavoidability* of such behavior of a polymer in these two phases; i.e., the Schroeder paradox comprises no paradoxicality. The increased swelling of ion-exchange polymers in liquid water is due to the Maxwell stresses acting on their charged surfaces, with these stresses being absent in the case of water vapor. The estimation of the stresses for the polymer Nafion in water yields values of "excess" swelling comparable with those observed in real experiments.

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