INTRODUCTION

It is well known to specialists in the field of sorption technologies that ion-exchange resins increase their volume in a wet atmosphere and even more strongly in aqueous media. At each of these two phases of polymer swelling, enormous forces (swelling pressure) arise that can break a column initially filled with a dry ion-exchange resin. As early as 1903, Schroeder published the results of a simple experiment: in a closed vial filled with water, a gelatin plate was immersed in a liquid to half its length [1]. After equilibrium was achieved in the system, it was found that the moisture content in the upper part of the sample (which was in contact only with saturated water vapor) was much less than that of the part of the plate immersed in water. According to this experiment, a gelatin plate brought into a contact with saturated vapor greatly increases its volume upon immersion in liquid water.

The considerable distinction between the equilibrium degree of swelling for a hydrophilic polymer in saturated aqueous vapor and in liquid water; it is experimentally verified by the registration of increasing volume of spherical polymer samples upon the processes of vapor and liquid water sorption. Specimens of three main classes of hydrophilic cross-linked polymers were tested. These had gel, hypercrosslinked, and macroporous structures that differed by the scale of the Schroeder effect. A similar effect is typical also for hydrophobic polymers upon swelling in liquid organic solvents and their saturated vapor. The paradox is explained by the lower activity of a sorbate in a saturated vapor compared to its activity in a liquid phase. The ability of many samples of cross-linked polymers with different degrees of saturation with a sorbate to be at equilibrium with the saturated vapor of a sorbate is explained by the differences in the inner structure of these samples, i.e., by differing in the swelling combinations and the intensity of the interchain interactions in a polymer network.

Thermodynamic of Liquid–Vapor Equilibrium

The basic thermodynamics postulated for an equilibrium single-component heterogeneous liquid–saturated vapor system is the equality of the chemical potentials of a substance (e.g., water) in these phases:

\[ \tilde{\mu}_w = \mu_w, \]

which is usually represented by the empirical ratio

\[ \tilde{\mu}_w^\circ + RT \ln a_w = \mu_w^\circ + RT \ln a_w, \]

where \( \tilde{\mu}_w, \mu_w, \tilde{\mu}_w^\circ, \mu_w^\circ \) are the chemical potentials and standard chemical potentials of vapor and liquid water, respectively.

In 1975, IUPAC defined a pure substance \( (\kappa = 1) \) in the state of an ideal gas with a pressure of \( p^\circ = 1 \) atm \( (1.01 \times 10^5 \text{ Pa}) \) at any fixed temperature as the standard state for all gaseous substances. At the same time, these conditions are apparently not strictly fixed, since less precise definitions for a gas are found in the literature, such as "The standard value \( \mu^\circ(T) \) is the chemical potential at unitary pressure (e.g., 1 atm)" [2, p. 229].
For solid and liquid substances, the main standard state is a pure substance ($x^o = 1$) at an external pressure of $p^o = 1$ atm. Since thermodynamics in any case assigns the different standard states mentioned above to water in the vapor and liquid states, the standard chemical potentials for these phases should differ: $\mu^w_a \neq \mu^o_a$. It then clearly follows from postulated Eq. (2) that the activities of water in vapor and liquid also could not be equal: $\tilde{a}_w \neq a_w$. But these values are under the logarithm sign and therefore should be non-dimensional numbers. We can use several methods for a nondimensional expression of a substance’s activity. In spite of the obvious inequality of these two activity values, however, in thermodynamics it is most convenient to conventionally consider as a unit both the activity of water in a pure liquid and the activity of water in saturated vapor, however not at a pressure of $p^o = 1$ atm (which could somehow connect the vapor activity with its standard state) but at partial vapor pressure under pure water, i.e., $p_0 = 0.0312$ atm = 23.75 mmHg at 25°C. This simplification allows us to present vapor activity with a partial pressure of $p$ in multicomponent systems as a simple dimensionless ratio, $\tilde{a}_w = p/p_0$. For liquid solutions, it is convenient to define water activity as its molar fraction $a_w = x$, also in relative units.

The fundamental impossibility of determining experimentally both standard chemical potentials and absolute activity values (which are not measurable physical properties of matter) in aggregate with the inaccuracy of the postulates mentioned above leads to main equation (1) being ignored, and the activities of both pure water and saturated vapor being simply equated with the same unit. Working with these units in calculating thermodynamic functions sometimes leads to illogical conclusions, e.g., in solutions “for a pure component $A$, the value $\mu^o_{A,\text{gas}} = \mu^o_A$, i.e., the standard value $\mu^o_{A,\text{gas}}$ (at $p = p^o_A$) coincides with the chemical potential of pure liquid component $A^o$ [2, p. 277]. If the standard chemical potentials and activities of pure water in a liquid and vapor state coincide, what are the differences (from a thermodynamic point of view) between these two equilibrium phases?

**Thermodynamics of Polymer–Water (Vapor and Liquid) Equilibrium**

The erroneous nature of these simplified ideas cannot help but be revealed in the Schroeder experiment [1], where the activities of vapor and liquid water were compared in their ability to produce swelling of a hydrophilic polymer. Schroeder found that gelatin swells in water 25 times more (1139 wt %) than in saturated water vapor (41.4 wt %). An increase in network swelling upon the transition from saturated vapor to liquid is a fairly regular phenomenon, since the concentration of water molecules in the environment outside a polymer grows step-wise by ten of thousands of times. However, this effect does not follow from the statement about the equality of water activities in liquid and vapor, and is therefore called “Schroeder’s paradox.”

The Schroeder effect was thoroughly reexamined and confirmed in [3]. The following explanations of the effect were recognized as satisfactory: gelatin swells too slowly in vapor and the true value in a system is not attained, or that the heterogeneity of a gelatin structure appears upon contact with liquid water and “free” water microdrops penetrate into its pores [4, 5]. It was only in recent decades that Schroeder’s paradox drew the attention of researchers once again, in connection with great importance of moisture absorption by ion-exchange conducting polymer membranes of the Nafion type (a copolymer of sulfocontaining monomer with tetrafluorethylene). A great many contradictory publications have appeared, but most investigators have come to the conclusion that each sulfogroup in a membrane is firmly bound to 5–6 water molecules, and the maximum water uptake of a polymer is 15–16 water molecules per $\text{SO}_3\text{H}$-group from saturated vapor or 22–23 $\text{H}_2\text{O}$ molecules from liquid water. The difference in swelling in water and its saturated vapor was then revealed for a series of ion-exchange materials of ionic chemical nature [6, 7]. It was shown that organic solvents and their vapor also exhibit the Schroeder effect with respect to network polymers [8, 9].

In clarifying the nature of the Schroeder paradox, the authors of [10] concluded that “The reason for this difference is that the surface energy of the sorption phase affects the chemical potential of the sorption phase in a different extent in the liquid and saturated vapor sorption.” In other words, the main requirement for interface equilibrium is violated under sorption conditions, i.e., Eq. (1) for the chemical potentials of liquid water and saturated vapor.

We believe there are no grounds for such a radical rejection of the model of chemical potentials proposed by Gibbs and Lewis at the beginning of 20th century, since the reason for the Schroeder paradox is not buried in the violation of criterion (1) by a solid polymer, but in ignoring the inequality of the activities of liquid water and saturated vapor $\tilde{a}_w \neq a_w$, validated above. Let us consider in pairs the equilibrium between the following phases: polymer, saturated vapor, liquid water, and polymer. Let us write the expressions for the chemical potentials of water in these four phases: