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On Schroeder's paradox

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Abstract

In 1903, von Schroeder reported a difference in solvent uptake (i.e. swelling) by a solid polymer sample (i.e., gel or membrane) when the sample was exposed to a saturated vapor versus a pure liquid. While "Schroeder's paradox" has been disregarded for a long time, it has been recently reported for several systems, which involve either glassy or ion exchange polymers and small polar molecules. In this work, we report the apparent occurrence of the paradox for a simple system based on an elastomer (crosslinked polydimethylsiloxane) swollen in 2-propanol. The phenomenon is not general (i.e. it depends on the type of system) and is shown to be reversible when it does occur. Contrary to previous explanations based on non-equilibrium or permanent pores in the polymeric matrix, an interpretation based on the classical phase equilibrium equation for gels is proposed. The implications in terms of mass transfer in dense membranes and the numerous lingering questions related to this paradox are discussed.
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Keywords: Membranes; Gels; Stability; Equilibrium; Paradox

1. Introduction

In 1903, Schroeder reported a puzzling experimental observation: when a polymer sample made of pure gelatin is put into contact with saturated water vapor versus pure liquid water under isothermal conditions, a significant difference in terms of the mass gain of the gel phase (i.e. its water content) is obtained [1]. The possibility for this type of binary system to achieve two distinct equilibrium states under strictly identical conditions in terms of water chemical potential cannot be accounted for by simple phase equilibrium considerations, according to the thermodynamics framework, which has been postulated for polymers and gels for decades. In fact, a solution approach is almost unanimously taken in the field of equilibria involving polymers, dense membranes and (xero)gels, since the pioneering work of Flory [2]; thus, the nature of the fluid phase, which is put into contact with the polymer is not supposed to play a role in the mass uptake (i.e. swelling). The sole value of the chemical potential has, in principle, to be taken into account. Such

a statement is a cornerstone in the field of phase equilibrium thermodynamics with polymers, be it for material preparation, polymer devolatilization, or membrane and chromatographic processes for instance [3–7].

The experimental results reported by Schroeder were immediately questioned. The phenomenon has been attributed to artifacts such as the failure to attain proper vapor saturation or to the slowness of equilibration. Other propositions include the ability of free polymer molecules to leach in the liquid phase but not in the vapor, or morphological changes in the polymer [8]. For a long period, the paradox went largely ignored. An isolated work concluded later on that it was indeed an experimental artifact, given the inability to obtain gravimetric measurements in a saturated vapor and a pure liquid under identical conditions [9]. Nevertheless, a series of recent studies performed on several hydrophilic polymers under precise conditions add new support to the existence of a systematic and effective discrepancy between saturated vapor and pure liquid sorption [10–12]. A near-exhaustive literature review of studies mentioning Schroeder's paradox is summarized in Table 1.

Controversial (if any) explanations are, nowadays, proposed when this subject is mentioned. A first category of comments

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Table 1
Systems already reported to develop Schroeder's paradox in scientific literature

Polymer	Solvent	Reference
Gelatin	Water	Schroeder [1]
Polyvinyl alcohol	Water Ethanol	Heintz and Stephan [17]
Nafion 117	Water Methanol	Gates and Newman [12]
Sulfonated polyethylene	Water	Freger et al. [11]
Sulfonated polyimide	Water	Cornet et al. [10]

leads to the conclusion that it is impossible to describe this type of behavior based on equilibrium thermodynamics considerations, given its history dependency, such as the one, which has been reported for the Nafion/water system [10]. Differences between the characteristics of a vapor and that of a liquid, such as the existence of an interface for the latter, have been proposed recently for the water/Nafion system [13]. It is important to stress, however, that this theory requires the existence of a permanent porous structure in the polymeric matrix: the mechanistic interpretation of the phenomenon is based on the differential wetting of micropores between the pure liquid and the vapor.

In fact, Table 1 suggests that Schroeder's paradox is restricted to strongly interacting systems, systems in which the polymer undergoes a very high degree of swelling. The systems concerned exclusively seem to involve small polar molecules in glassy or ion-exchange polymers. This type of system, which involves complex matrices, could possibly be consistent with the presence of hypothetical pores in the polymeric phase. At present, this interpretation is considered to give the best qualitative explanation of the paradox [10–11].

It is the intention of this work to reassess the previous work in this area discussed above, as well as to tentatively offer a different interpretation:

(i) First, the possible occurrence of Schroeder's paradox is reported for the first time in a simple system, which consists of a non-polar elastomeric matrix swollen in an organic solvent.

(ii) Secondly, the reversible character of the phenomenon and its system specificity are reported.

(iii) In contrast to previous statements, the experimental data are interpreted, in a last step, based on thermodynamics (i.e. phase equilibrium). It is shown that a simple equilibrium relationship based on crosslinked polymers swollen in a single solvent is not incompatible with the occurrence of Schroeder's paradox. In fact, a so-called van der Waals loop (i.e. a double root solution for the Gibbs stability criteria) can be obtained under a certain set of conditions. This peculiarity leads to a bifurcation of part of the sorption isotherm, typical of the experimental data associated with Schroeder's paradox.

2. Materials and methods

2.1. Polymers

Two types of silicone rubber (polydimethylsiloxane, PDMS) samples were used.

(i) Silastic^{TM} thick (5 mm), flat sheet samples, provided by Dow Corning (LPI, France), which contains around 30% of silica filler (weight basis) [14].

(ii) Rhodorsil RTV 141, provided by Rhodia Silicones (France), which is a two-part room temperature (RTV) vulcanization kit, consisting of pure silicone rubber [15]. Thick samples (around 1 cm) have been crosslinked in the lab according to the recommended protocol (10 parts of A and 1 part of B, 48 h crosslinking after careful mixing at room temperature). Each sample was visually screened in order to ensure that no air bubbles were trapped in the matrix before use. The samples were subjected to repeated immersion in pure chloroform followed by drying in an oven until they attained a constant dry weight after each cycle. This step is of utmost importance to ensure that uncrosslinked chains have been completely leached from the rubber matrix, and thus, cannot induce a weight change following liquid immersion.

2.2. Solvent swelling determination

Pure liquid and saturated vapor swelling measurements have been performed in closed glass vessels. The polymer samples were placed in two PTFE gaskets (one in the liquid phase, one in the vapor phase). A series of the vessels depicted in Fig. 1a were closed under atmospheric pressure conditions and placed in a thermostated oven in order to attain thermodynamic equilibrium. This type of system is similar to the system originally used by Schroeder, which is shown in Fig. 1b [1].

The solvent mass uptake was determined periodically by quickly removing the sample, blotting it with paper (for liquid phase immersed samples only) and inserting it into a dry glass vessel. The mass of the closed sampling vessel (including the swollen polymer sample) was determined using a precision balance. The weight gain was then calculated in order to express the relative solvent uptake as a percentage of the dry mass of the sample (S). This is an established procedure for the determination of polymer swelling determination in liquid phases [16,17]. Nevertheless, several precautions and checking tests were performed in order estimate the reproducibility of the protocol, as well as the uncertainty associated with the sample-blotting step or evaporation interferences. Since thick polymer samples were used, these two effects (which depend heavily on the interfacial area of the sample) are minimized. As a consequence, a maximal absolute error around 20 mg has been estimated according to this protocol. This uncertainty is far below the changes, which are experimentally observed when a Schroeder's paradox situation is obtained. Table 2