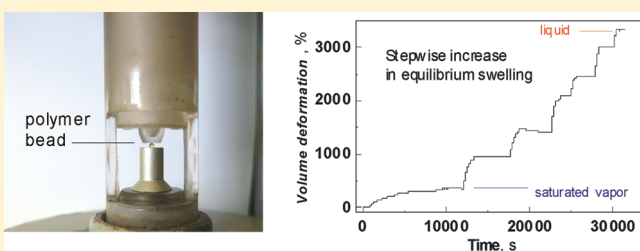


Paradoxes of Thermodynamics of Swelling Equilibria of Polymers in Liquids and Vapors

Vadim A. Davankov* and Alexander V. Pastukhov

Nesmeyanov-Institute of Organo-Element Compounds, Russian Academy of Sciences, Vavilov st. 28, 119991 Moscow, Russia

ABSTRACT: An automatic registration of the changing size of a single spherical microbead of a cross-linked polymer was applied for studying the swelling process of the bead by the sorption of vapors and/or liquids. Many representatives of all three basic types of polymeric networks, gel-type, hypercross-linked, and macroporous, were examined. Only the first two display large volume changes and prove suitable for following the kinetics and extent of swelling by the above dilatometric technique. The results unambiguously prove that swelling of all polymeric networks in liquids is always higher than in corresponding saturated vapors (Schroeder's paradox). The general nature of this phenomenon implies that the absolute activity of any sorbate in its liquid form is always larger than in the form of its saturated vapor. Surprisingly, gels with any solvent contents, which fall into the broad range between the vapor-equilibrated and liquid-equilibrated extreme contents, retain their volumes constant in the saturated vapor atmosphere. This paradox of a wide range of gels swollen to a different extent and, nevertheless, standing in equilibrium with saturated vapor is explained by the specificity of the network polymers, namely, that the energy of the solvent–polymer interactions is easily compensated by the energy of remaining between-chain interactions at any solvent content in the above range. Therefore, the strain-free swollen gels do not generate enhanced vapor pressure, but neither display the ability to take up more sorbate from its vapor.



INTRODUCTION

When developing basic notions of modern thermodynamics by the end of 19th century, Gibbs introduced the chemical potential of a compound as a new entity that characterizes the contribution of the compound to the total free energy of a system and its ability to participate in interphase equilibria. The chemical potential of any component that is common for two phases standing at equilibrium was postulated to be equal. Thus, chemical potentials of water molecules in liquid water and in saturated vapor at any temperature were said to be equal, in spite of the fact that *all physical properties* of the liquid and vapor strongly differ from each other. The notion of chemical potential proved to be applicable in the thermodynamic description of equilibria between two phases. The first problem arose in the interpretation of situation with a three-phase system, when in addition to the liquid and vapor, a gel emerged in contact with these phases. The term gel is generally used to describe an insoluble (polymeric) solid that is capable of incorporating a low-molecular weight component which exists in the system in the form of a liquid or vapor.

As early as 1903, Schroeder published¹ results of a simple but very convincing and vivid experiment where a plate of gelatin was partially immersed into water in a sealed vessel. After the system equilibrated, the swelling of the water-wetted part of the sample was observed to be substantially stronger (1139%) than that of the part contacting the saturated water vapor (41%). The author corroborated this observation with several thorough weighing experiments. From the viewpoint of common sense, this difference

in the swelling extents appears to be rather logical, considering the fact that the concentration of water molecules in liquid water is over 10 000 times higher than that in the saturated vapor. But, in view of the generally accepted framework of phase equilibrium thermodynamics,^{2,3} the solvent uptake by cross-linked polymers is solely linked to solvent chemical potential in the fluid phase, irrespective of the state of the fluid phase. The chemical potentials of water in the pure liquid and saturated vapor phases are assumed to be equal (sometimes even the activity of water both in pure liquid and saturated vapor is said to be equal, namely, unity). For this reason, the difference in solvent uptake by a solid polymer sample, when exposed to a saturated vapor versus a pure liquid, was termed Schroeder's paradox.

Schroeder's data have been re-examined and basically confirmed.^{4–6} It was found that the swelling difference in water and its vapors is really large, though the exact numbers are difficult to reproduce because properties of gelatin samples depend on the source of the material and, moreover, the gel is prone to slow hydrolysis and fouling. It was also noted that a water-swollen gelatin sample, when placed in the atmosphere of saturated vapor, slowly loses water, so that its water content in two weeks drops from 1076 to 343%,^{1,6} thus creating an impression that it tends to reach the above value of 41% characteristic of the gelatin/vapor system. (At that time it was not yet known that

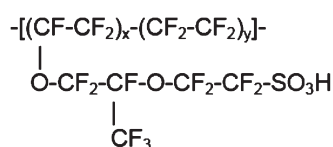
Received: August 25, 2011

Revised: October 31, 2011

Published: November 11, 2011

gelatin molecules form gels due to combinations of weak physical cross-links, namely, hydrogen bonds, which rearrange with time, thus enhancing the density of the swollen gel.) In general, Schroeder's paradox has been treated as an experimental artifact and attributed to inadequate thermostating or slow kinetics of the approach to a true thermodynamic equilibrium in the system vapor/gelatin, which should be identical to that of water/gelatin.^{7–9} The paradox has been then disregarded for several decades.

The swelling of polar polymers in water and water vapors became again the topic of high importance by the beginning of 21st century in connection with the development of conducting membranes for fuel cells. Water is frequently introduced in the feed stream to the fuel cell, and water is produced at the cathode. Both the conductivity and the water permeation of water- and ion-transporting polymeric membranes strongly depend on their water content. Most attention was devoted to Nafion membranes, cast from copolymers of tetrafluoroethylene with a monomer containing a sulfonyl group in the rather long and flexible side chain:



We can assume that, because of the flexibility of the side chains and large difference in the polarity of the perfluorocarbon-type matrix of the membrane and sulfonic groups, the latter tend to segregate into microclusters and channels with a high affinity to water.

Both newly cast films and commercially available membrane samples of Nafion 112, 115, 117, 1110, 1123, and 211, and so forth (with a membrane thickness in the range between 50 and 600 μm and probably a different morphology) were tested by different research groups, who finally arrived at strongly contradicting results and conclusions.

Still, most authors agree that each sulfonic group acquires up to 15–16 water molecules from saturated water vapor and about 22–23 molecules from pure water, which corroborates the reality of Schroeder's paradox.^{10–13}

Besides the cation-exchanging Nafion membranes, differences in solvent uptake from the liquid versus corresponding saturated vapors have been reported for many solvent/cross-linked polymer systems, for example, water/cation exchange resin Dowex,¹³ water/sulfonated polyimide membranes,¹⁴ water/anion exchange membranes,¹⁵ methanol/Nafion membrane,¹⁶ 2-propanol/cross-linked polydimethylsiloxane,¹⁷ carbon tetrachloride/lightly vulcanized rubber,¹⁸ and several others. Importantly, the difference in water uptake from a liquid and saturated vapor environment is also markedly expressed for Na^+ - and Li^+ -forms of sulfonated membrane Nafion 117 and cationite Dowex 50Wx4. Herewith, Bass and Freger^{13,19} examined a wide range of water activities by adding sodium or lithium poly(vinylsulfonate) ($M_w \sim 2000$) to the aqueous phase. This linear polymer is strongly excluded from the resin or membrane network due to Donnan and size exclusion effects. For isopiestic measurements, membrane and resin samples in a sodium or lithium form were exposed directly to a vapor atmosphere, while in immersion tests the samples were fully immersed in the solution. The results indicate that Schroeder's paradox exists in the whole range of activities, not just at water activity of $a \rightarrow 1$.

Another approach to testing the action of a liquid and its vapor on a polymeric network is measuring permeability of polymeric membranes. Thus, Nafion membranes have been examined with liquid water or saturated vapor moving along one side of the membrane, the other being swept with nitrogen.^{11,20} These permeation measurements showed that the water fluxes from liquid water were roughly 2 times higher than from water vapor, consistent with the enhanced activity of the liquid and stronger swelling of the membrane in liquid water in accordance with Schroeder's paradox. The difference in the water flux was accentuated at higher temperatures. Similar differences were observed for water permeation through an alginate-based film,²¹ as well as for the transport of heptane or toluene through polyethylene-type membranes.²²

There is no generally accepted explanation of Schroeder's paradox. Against thermodynamic predictions, liquids obviously display the ability of expanding pores and even opening and filling new smallest pores in the polymeric network, thus enhancing both the swelling and permeability of the material, whereas in the gaseous phase saturated vapors fail to act as efficiently. As early as 1912 Bancroft⁴ suggested the presence of small water droplets in the water-swollen gelatin phase, which produce in gaseous environment an enhanced vapor pressure due to the curvature of the droplet surface. Some recent authors also tend to consider surface tension on hypothetical convex vapor–liquid borders at the openings of pores and involve this tension into complicated calculations of pore diameters.^{23–25} Weber and Newman^{26,27} assume capillary pressure to be a part of the chemical potential of the liquid in the swollen polymer. However, it is easy to imagine that a minimal loss of the sorbate from the surface of the sample would immediately convert the convex meniscus at the opening of a pore into a concave one, so that the surface tension and capillary pressure would start causing the opposite action on the swelling equilibrium. Some other authors,¹⁷ by using the Frenkel–Flory–Rehner model of gels, try to find two local potential minima for the free energy of the polymer/solvent system, one presumably corresponding to vapor equilibration and the other to liquid equilibration.

It must be mentioned, however, that some authors challenge the very presence of Schroeder's paradox. Ohnishi et al.²⁸ claimed the complete absence of the paradox since they found both the water uptake and proton conductivity of Nafion 117 to strongly depend on the pretreatment of the membrane but nearly coincide for samples equilibrated with liquid water or saturated vapor. In a more recent paper Jeck et al.²⁹ examined the Nafion 115 membrane (125 μm) that was previously swollen with water and partially dried at a vapor pressure of $p/p_0 = 0.75$. The membrane was then exposed to water vapor in the range of activities from $a_w = 0.75$ to $a_w = 1.00$ and with corresponding equilibrium aqueous solutions of poly(vinyl pyrrolidone), $M_w > 25\,000$ Da. In the latter case, however, the Nafion sample was separated from the solution by a commercial cellulose dialysis membrane (cut off 1000 Da) to prevent an accidental penetration of PVP into the Nafion sample. Though at the ultimate value of $a_w = 1$ the swelling extent of the membrane was found to be higher in pure water, the authors arrive at the conclusion that their “study does not show any evidence of Schroeder's paradox for water-swollen Nafion ionomer membranes and water uptake rather depends solely on solvent activity, regardless of whether the equilibrium fluid phase is vapor or liquid”. In an earlier similar study³⁰ the same authors made an analogous denial statement after examining a poly(vinyl alcohol) membrane that was obtained by cryostructuring of the polymer ($-20\text{ }^\circ\text{C}$, water/DMSO of 50:50);

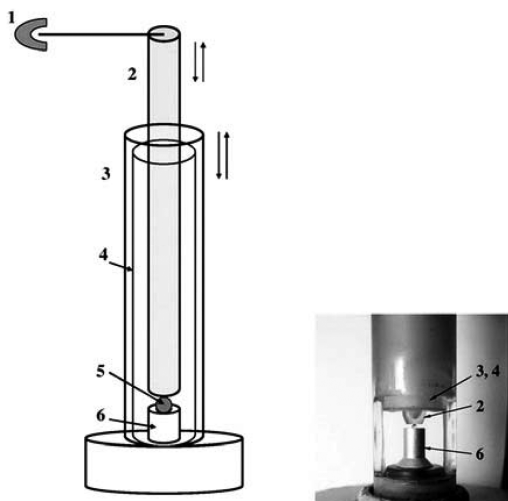


Figure 1. Equipment for registering the volume changes of a polymer sample on swelling with saturated vapor or droplets of the corresponding liquid: 1, mechanical motion transducer; 2, quartz sliding rod; 3, sliding glass tube; 4, inlay cylinder of filter paper; 5, spherical polymeric sample; 6, quartz or metal support with a small pit for the sample.

microcrystalline domains served there as physical cross-links between the flexible chains. No noticeable differences in the behavior of membranes immersed into liquids or corresponding saturated vapors have been noticed in a few other reports.^{31–34}

In summary, debates over the reality of the Schroeder's paradox have continued for over 100 years. Explanations for the paradox thus far offered in the literature are controversial, inconsistent, and not yet satisfactory and comprehensive.

In view of this situation, we performed an extensive study of swelling of typical representatives of all basic types of polymeric networks both in saturated vapors and corresponding liquids. The behavior of polar polymers toward water and polar solvents was examined, as well as the swelling of nonpolar polymeric materials in suitable media. The new technique applied permitted a direct registration of volume deformations of single small spherical polymer samples and rapidly provided unambiguous information on both the kinetics and extent of volume changes of the bead. Our first results proving that the swelling of polymeric networks in liquid media is always higher than that in corresponding saturated vapors recently appeared.³⁵

EXPERIMENTAL METHODS

Measurement Technique. In ref 36 we described the adaptation of a standard equipment UIP-70 (Russia) for thermomechanical studies of polymers for precise dilatometric measurements on a single spherical polymeric sample (Figure 1). A defect-free bead of regular spherical shape and 0.6–0.8 mm in diameter (precisely measured under a microscope with the accuracy of ± 0.001 mm) was placed into a shallow spherical pit in a quartz (or metal) plate. A quartz sliding rod ($L = 190$ mm, $D = 4$ mm) with a polished flat end pressed against the bead with a load of 0.2–0.5 g, which would not yet distort the regular spherical shape of the swollen bead. While being fixed in the pit with the rod, the bead is prevented from rotational movements during the measurement. The sliding rod is connected to the mechanical motion transducer (for transforming mechanical motion into

electronic information by the instrument's capacitive sensor) that automatically registers changes in the diameter of the swelling bead with an accuracy of ± 0.5 μm . The area around the bead and the rod in contact with it is limited by a glass tube ($L = 140$ mm, $D_{\text{internal}} = 8$ mm) that incorporates an inlay cylinder of filter paper. The latter can be wetted with water or other liquids, to quickly provide the space within the glass tube with a source of the liquid vapor. The small volume of the formed chamber and the small size of the polymeric sample guaranteed rapid saturation of the chamber atmosphere with the vapor of the corresponding liquid and rapid swelling of the initially dry polymeric bead. At any desired moment, the glass tube can be slightly lifted, thus giving access to the bead and allowing wetting directly with a microdrop of the corresponding liquid with the help of a syringe. Though such manipulation results in a short-term distortion of the saturated vapor atmosphere in the chamber, this short-term effect cannot confuse the obvious general trends in the swelling process.

The thus-registered swelling of the bead upon the absorption of a solvent was expressed as bulk deformation ϵ_{sw} calculated according to the equation

$$\epsilon_{\text{sw}} = (v_{\text{sw}} - v)/v = [(D_{\text{sw}}/D)^3 - 1] \times 100$$

where D and v are the diameter and volume of a dry bead and D_{sw} and v_{sw} are the diameter and volume of the bead during the swelling process. The accuracy of determining the volume deformation by the above dilatometric technique is estimated to be better than 0.8%. Note that deformations considered in the present study vary in the range from 10 to 3000%.

To specialists experienced in ion exchange technology, it is a familiar fact that individual beads of an ion-exchange resin batch may slightly differ in their size, color, and mechanical strength. They also differ in a range of about 10% in the absolute values of their swelling, even in the case that no defects can be detected on the beads under the microscope. In this work, however, the important factor was the general rate and extent of swelling in vapor and liquid of any single bead, rather than the absolute values of volume swelling of different beads.

Materials. Samples of ion exchange resins and polymer sorbents, both commercially available and synthesized in our laboratory, were tested in this work. All samples were carefully washed with hot water and ethanol, to remove the rests of adsorbed surfactants and extract possible leachables from the polymers. Only defect-less spherical beads of appropriate size have been selected under microscope for the dilatometric measurements. The list of polymers examined includes the following.

Gel-Type Polymers. KU-2x8 is a gel styrene–divinylbenzene sulfonated cation exchanger (Russia).

PCA-433 is a gel styrene–divinylbenzene anion exchanger (Purolite).

Amberlite IRA-402 is a gel styrene–divinylbenzene anion exchanger (Rohm and Haas).

Dowex-1x10 is a gel styrene–divinylbenzene anion exchanger (DOW).

C-104 is a gel weakly acidic poly(acrylate) cation exchanger (Purolite).

A-850 is a gel poly(acrylate) anion exchanger (Purolite).

Polyacrylic acid prepared by suspension copolymerization of methylacrylate with 0.5% divinylbenzene, followed by alkaline hydrolysis of ester functions.

Polymers of Hypercrosslinked Structure. LPX-200X is a hypercrosslinked polystyrene, obtained by cross-linking to 200% of linear polystyrene with *p*-xylene dichloride.

CPS(0.2)-100E, CPS(0.6)-100E, CPS(0.2)-200E, CPS(0.2)-43E, CPS(0.6)-43E, and CPS(1.4)-100E are hypercrosslinked polystyrenes (degree of cross-linking with monochlorodimethyl ether, from 43 to 200%) on a base of gel styrene copolymers with 0.2, 0.6, and 1.4 wt % of DVB.

DT is a microporous polydivinylbenzene, obtained in the presence of 60% toluene.

MN-270 is a microporous, hypercrosslinked polystyrene sorbent (Purolite).

Polymers of Macroporous Structure. KU-23 is a macroporous styrene–divinylbenzene sulfonated cation exchanger (Russia).

Amberlyst-15 is a macroporous styrene–divinylbenzene sulfonated cation exchanger (Rohm and Haas).

CT-175 is a macroporous styrene–divinylbenzene sulfonated cation exchanger (Purolite).

DH is a macroporous polydivinylbenzene, obtained in the presence of 60% hexane.

MN-500 is a biporous, hypercrosslinked polystyrene sulfonated cation exchanger (Purolite).

MN-200 is a biporous, hypercrosslinked polystyrene sorbent (Purolite).

Amberlite XAD-4 is a mesoporous polydivinylbenzene sorbent (Rohm and Haas).

A-830 is a macroporous poly(acrylate) anion exchanger (Purolite).

Amberlite XAD-7 is a mesoporous poly(acrylate) sorbent (Rohm and Haas).

Though all of the above-mentioned polymers were tested in this work, only typical results are presented below.

■ RESULTS AND DISCUSSION

Basic Types of Polymeric Networks. While linear polymers dissolve in suitable solvents, networks (or polymers having cross-links between linear chains) display a limited uptake of the solvent, herewith forming a gel phase, in addition to the excess liquid (or vapor) phase. Depending on the preparation procedure, networks may have a different structure, topology, and morphology, which all may strongly influence the behavior of the network with respect to the solvents. Surprisingly, the most researchers, while examining the reality of Schroeder's paradox, did not pay sufficient attention to the structure of the networks, which partially can explain serious disagreements between results reported thus far. Therefore, we find it necessary to summarize here the main distinguishing features of three basic types of polymeric networks, namely, gel-type, hypercrosslinked, and macroporous polymeric materials.

Gel-type networks are three-dimensional spatial structures composed of relatively long and flexible polymeric chain segments and certain crossbridges between them. The network is relatively mobile which manifests itself in the high increase in the volume of the material on its swelling in an appropriate solvent and reversible decrease in the volume on drying or contacting a nonsolvent. From thermodynamic viewpoint, swollen gel-type materials present *homogeneous single-phase two-component (polymer + solvent) systems*, transparent both in the swollen and dry state. In the latter case, organic gel polymers have a density that is close to 1 g/cm³ and display no obvious porosity, being impenetrable to gas molecules due to the close contacts between

the constituent polymeric chains. Importantly, gel-type networks swell only in a limited number of solvents that are able of strongly solvating polymeric chains or their functional groups, thus breaking the interchain contacts and replacing them with polymer–solvent interactions. Naturally, nonpolar materials swell only in organic solvents while polar materials—in water and polar solvents.

Porous polymers are materials of reduced density. They are permeable to gas molecules and any solvents, independently of their thermodynamic affinity toward the polymer. Porosity results from the presence of an inert diluent (porogen) in the process of network formation. To prevent reduction of the total volume of the gel by close packing of chains of the network upon the removal of the porogen, the three-dimensional spatial network must display a high rigidity. The network rigidity is provided by rather short distances between network junctions and restricted conformational mobility of short polymer segments between them.

If the porogen is not compatible with the three-dimensional polymer under formation, the phase separation of the system occurs during the synthesis process, resulting in macroporous nontransparent heterogeneous (*two-phase = polymer + porogen or air*) material. Macroporous polymers always contain an elevated amount of the cross-linking agent and, therefore, exhibit a very weak swelling ability. Though any liquid can penetrate the macropores, a volume increase of the matrix is only possible in thermodynamically good solvents.

If the porogen used in the synthesis solvates the formed three-dimensional network well and there is no microphase separation upon synthesis, a transparent homogeneous single-phase polymer with an expanded network is formed. Such open-network polymers are referred to as *hypercrosslinked*^{37–39} *microporous*, though the term “pore” loses here its sense since there are no pore walls in the form of a separate solid polymer phase. Rather, the rigid skeleton network of hypercrosslinked polymers is formed from individual polymer chains. Due to the open-network skeleton, hypercrosslinked polymers possess relatively high mobility. In contrast to macroporous materials, the microporous hypercrosslinked networks grow considerably in volume when the free space between polymer chains is filled with liquid. Remarkably, hypercrosslinked materials strongly swell with any liquid, regardless of its affinity to the polymer.

It is clear from the above that, by registering the volume changes of a single bead, the Schroeder's effect can be detected most distinctly in the case of gel-type and hypercrosslinked networks, which exhibit large deformations on swelling while remaining single-phase materials both in dry and swollen state. The barely swelling macroporous materials seem to be least suitable for observing the difference in their interaction with vapors and liquids by using the dilatometric technique.

Schroeder's Paradox as a General Logical Phenomenon.

While trying to find an answer to a long-standing problem, namely, the contradiction between the theoretically expected equality of water chemical potentials in pure liquid and saturated vapor, on the one hand, and the difference in the swelling of certain polar polymers in these two fluids (Schroeder's paradox), on the other hand, we suggested an ultimate miniaturization of the experiment.³⁶ A single spherical polymeric microbead of less than 1 μ L in volume was first immersed into a saturated vapor atmosphere and then directly wetted by the corresponding liquid. The automatic registration of the size of the bead allowed following both the kinetics and the extent of the two stages of swelling. The fast equilibration of the micro sample with the environment

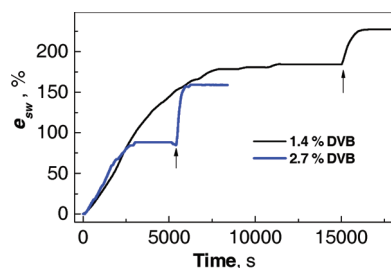


Figure 2. Volume deformation of styrene-DVB copolymers 1.4% DVB and 2.7% DVB on swelling with toluene vapors to the maximum and then in liquid toluene (shown with an arrow).

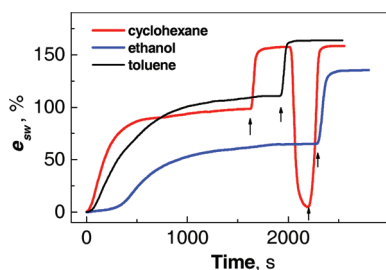


Figure 3. Volume deformation of hypercrosslinked microporous polystyrene CPS(0.2)-100E upon swelling in vapor (up to maximum deformation) and subsequent contact with liquid solvent (shown by the arrow).

reduced the time of the experiment to about 1 h and permitted fast examination of many dozens of various polymers representing all three basic types of networks. It can be mentioned here that the same automatic technique revealed such unusual and unpredicted effects as a nonlinear contraction of porous materials on drying⁴⁰ and the contraction of nanoporous hypercrosslinked polymers in solutions of electrolytes with large, excluded ions.⁴¹

If, according to the huge difference in the volume concentration of a substance in its liquid and gaseous state, the absolute activities and chemical potentials of the substance in these phases differ, what we strongly believe, then the action of the liquid and saturated vapor on a third (polymeric) partner of a system must also differ. This effect must be of a general character and not only peculiar to the action of water on gelatin or Nafion membranes. Figure 2 presents results of testing beads of styrene–divinylbenzene copolymers, the most typical nonpolar gel-type polymeric network. The recorded stepwise increase in the bead volume leaves no doubt in the fact that liquid toluene causes quicker and stronger swelling of the copolymers compared to swelling in saturated toluene vapor.

The same trend is valid for swelling in toluene (Figure 3) of a typical hypercrosslinked polystyrene sample with a cross-linking degree of 100%. In contrast to the above gel-type polystyrene, the hypercrosslinked network swells not only in the thermodynamically good solvent, toluene, but also in a Θ -solvent, cyclohexane, and even in the precipitator for polystyrene, ethanol, though to a slightly smaller extent. By comparing Figures 2 and 3 one also notes that swelling of hypercrosslinked materials takes place much faster than that of conventional gels cross-linked to a degree as low as 1.4%.³⁶ Material deformations on swelling and drying are fully reversible, as shown by the reproducibility of data in the swelling–drying–swelling cycle in cyclohexane. Still, the most

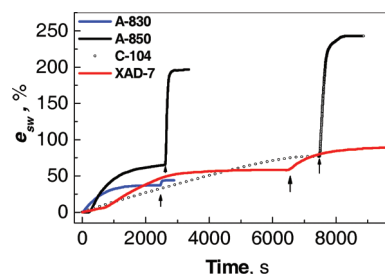


Figure 4. Volume deformation of gel-type polyacrylic anion exchanger A-830 in Cl^- -form and cation exchanger C-104 in H^+ -form, macroporous anion exchanger A-830 in Cl^- -form, and neutral porous sorbent Amberlite XAD-7 in water vapor up to maximum deformation and subsequent contact with liquid water (shown by the arrows).

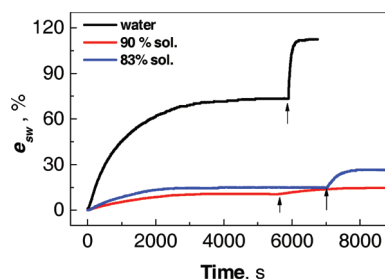


Figure 5. Volume deformation of polystyrene-type Amberlite IRA-402 anion exchanger in vapors over pure water and over PEG-600 solutions of 83% and 90% and in corresponding liquids (shown by the arrows).

important fact here is the marked Schroeder's effect in any type of solvating media.

Naturally, polar polymers will readily swell in water (and polar solvents). Figure 4 demonstrates a big difference in swelling of polyacrylic gel-type anion and cation exchangers (plots for A-850 and C-104, respectively) in saturated water vapor and liquid water. On the contrary, in a plot related to a macroporous acrylic network A-830, the difference between two levels of swelling is hardly visible, and the total extent of swelling is also small. Mesoporous polar sorbent Amberlite XAD-7 shows a moderate Schroeder's effect.

Schroeder's effect must reveal itself not only with pure liquids and corresponding vapors at $p_s/p_o = 1$, but also at lower activities of the volatile component of the system. In the experiment presented in Figure 5, the activity of water was heavily reduced by dissolving polyethylene glycol PEG-600 to final concentrations of the solution as high as 83 and 90 wt %. The gel-type anion exchanger IRA-402 does not swell in the neutral PEG oligomer of that size. Therefore it was assumed that only water molecules can enter the polymeric phase from both the aqueous PEG solution and saturated vapor over it. Though the swelling extent of the resin drops substantially in these concentrated solutions, compared with swelling in pure water, the Schroeder's effect remains intact.

Historically, the most popular technique for examining the swelling process is gravimetry. We felt it necessary to apply it to appropriate samples. Two pieces (0.23 and 0.28 g) of vulcanized natural caoutchouc (vacuum rubber 7889) were held in toluene vapors and in liquid toluene, respectively. Because of the larger size of the samples needed for accurate weighing, the establishment of equilibrium swelling from the vapor required

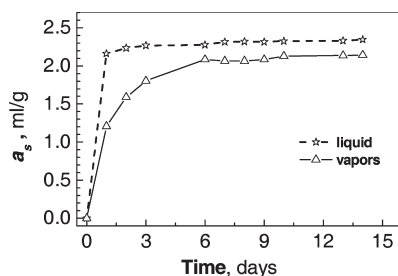


Figure 6. Sorption of toluene by nonporous rubber samples from liquid and saturated vapors.

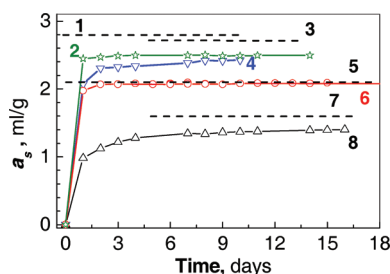


Figure 7. Swelling of hypercrosslinked polystyrene obtained by additional cross-linking of styrene–0.3% DVB copolymer to cross-linking degrees of 100% (1–4) and 43% (5–8) in liquid toluene (1, 5) and its vapor (2, 6) and in liquid ethanol (3, 7) and its vapor (4, 8).

10 days, distinct from 1 to 2 h which are sufficient in the case of microbeads. The result of the test (Figure 6) was positive in that the rubber samples accumulated more toluene from the liquid than from vapor.

Less impressive turned out to be results obtained by the same weighing technique on multibeaded samples of hypercrosslinked polystyrene and toluene and ethanol as sorbates (compare Figures 3 and 7). Here, much smaller differences between solvent uptake from vapor phase versus liquid were found than could be expected from the above data obtained for a single bead of a similar polymer. In fact, the isopiestic technique encounters problems of precise thermostating of the system over a very long period of time. The problem manifests itself in occasional condensation of saturated vapors on the walls of the hermetic vessel. No doubt, condensation must also occur in contact points of different beads, which act as micropores with enhanced sorption activity of narrow slits between two spheres. The condensation process results in the formation of a liquid phase in immediate contact with the vapor-swollen gel phase. The gel will absorb this condensed liquid, thus mimicking a slow approach of the swelling extent to the value characteristic of the equilibrium in the gel–liquid system.

Actually, the same condensation process must take place in the case of swelling of permanently porous materials in saturated vapors. Capillary condensation of vapors in the pores will create a liquid phase, and the polymer gel will find itself in contact with the liquid. Under this situation, there will be no difference in the swelling values in vapor and liquid media. Indeed, isopiestic measurements on samples of industrial porous hypercrosslinked sorbents of the MN-series showed no sign of Schroeder's paradox, though the total weight–solvent uptake by these materials is really high (Table 1).

Paradox of the Broad Equilibrium Range of the System: Swollen Polymer Gel–Saturated Vapor. The characteristic shape of the plots presented above as well in the previous publication³⁵ and in all our other experiments that were made with the use of the microdilatometric technique, convincingly disprove the version that much more time is needed for the sorption process from vapor phase, to arrive at the ultimate “equilibrium” uptake of the solvent, which is quickly achieved from the liquid environment. We definitely observe two different solvation states of the polymer, one for vapor equilibration, the other for liquid equilibration. However, we noticed that a polymer, swollen to a maximum extent by immersing into a liquid and then placed into the atmosphere of saturated vapor, does not show any tendency of loosing excess sorbate and returning to the lower degree of swelling that was considered to be the equilibrium state of the polymer–vapor system. In fact, to reject and loose the sorbate, the polymer gel has to generate vapor pressure that is higher than that of saturated vapor over the surface of a pure liquid. What reasons could be suggested for such an enhanced vapor pressure?

One possibility is the very old suggestion by Bancroft⁴ that small water droplets remain on the surface of the gelatin sample that was removed from the liquid, which produces an enhanced vapor pressure due to the curvature of the droplet surface. However, such microdroplets would be highly unstable for the two reasons: enhanced vapor pressure over the convex surface of the droplet and enhanced liquid pressure under that surface. The latter factor would inject excess liquid from the droplet into the gel phase causing extension of its network. In any way, excess water droplets on the gel surface and in the openings of its pores will quickly disappear, thus removing the stimulus for an enhanced evaporation. On the contrary, evaporation would create convex meniscus in the openings of pores, which would immediately invert the action of the two above factors and stimulate additional condensation from the saturated environment.

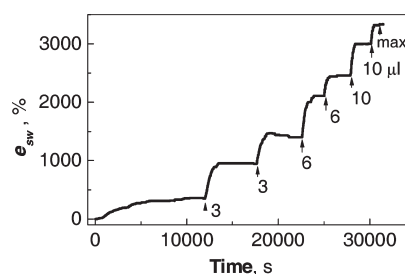
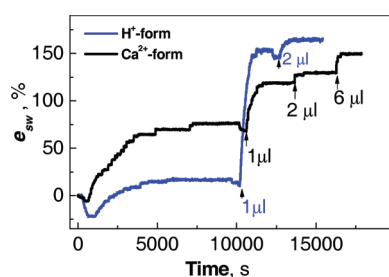
Another possibility of loosing excess water could be the enhanced chemical potential of water within the ultimately swollen gel phase. This case would correspond to the assumption of Weber and Newman^{26,27} that capillary pressure is a part of chemical potential of the liquid in the swollen polymer. Again, loose speculations concerning the chemical potential of liquid in the gel would involve manipulations with surface tensions on the vapor–liquid, vapor–swollen gel, and liquid–swollen gel borders. Only the first one is well-defined and experimentally measurable. In any case, the presumed enhanced chemical potential of the liquid in the gel phase (over the chemical potential of pure liquid) would emerge only in the very moment when the swollen sample was taken out of the liquid. But, we do not see any physical reason for such a sudden jump of the chemical potential or activity of water on such a manipulation.

Obviously, when taken out of water, the swollen gel would not start generating vapor pressure higher than that over pure water.

We do not consider a cross-linked polymer, especially a swollen one, as a principally nonequilibrium phase. In the presence of a plasticizing solvent, the gel-type network has the possibility to rearrange the conformation of its segments to arrive at a minimum free energy of the system. In this minimum energy state, the solvation forces of solvent–polymer interactions are compensated by the forces of remaining polymer–polymer interactions and the growing stretching of the network. At any activity (or partial pressure) of the solvent in the vapor phase, a corresponding swelling equilibrium step will be established. A marked increase in the solvent activity on replacing saturated vapor by

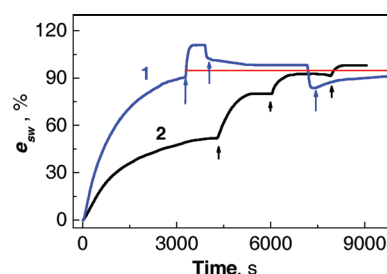
Table 1. Sorption of Water, Ethanol, and Toluene by Hypercrosslinked Polymeric Sorbents with a Mesoporous and Biporous Structure, when Measured by Isopiestic and Immersion Techniques

polymer	water, mL/g	water vapor, mL/g	ethanol, mL/g	ethanol vapor, mL/g	toluene, mL/g	toluene vapor, mL/g	surface area, S_{sp} , m ² /g
MN-270	1.22	1.12	1.27	1.29	1.38	1.33	1300
MN-200	1.54	1.54	1.91	1.83	1.92	1.94	1100
MN-202	1.30	1.26	1.61	1.56	1.58	1.50	670
MN-600	1.34	1.33	1.48	1.42	1.44	1.44	700

**Figure 8.** Volume deformation of a polyacrylic cation exchanger (0.5% DVB) in Na⁺-form equilibrated with saturated water vapor and then wetted six times with water microdroplets to a maximal swelling extent.**Figure 9.** Volume deformation of a polyacrylic cation exchanger (0.5% DVB) in H⁺-form and Ca²⁺-form equilibrated with saturated water vapor and then wetted several times with water microdroplets to a maximal swelling extent.

pure liquid stimulates a rapid increase in the swelling extent with establishing a new equilibrium. But, what will happen, if a microdroplet of the solvent will be placed on the surface of the vapor-equilibrated sample? Obviously, the droplet will be taken up by the polymer with a certain increase in its volume. Will the sample try to reject that excessive amount of the solvent by generating a vapor pressure higher than that of the surrounding saturated vapor? Will the new situation stimulate an accelerated uptake of the vapor to arrive at the ultimately swollen state? The both questions must be answered with “no”.

Figures 8 and 9 present results of such stepwise wettings of beads initially equilibrated with saturated water vapor and then kept in this saturated atmosphere. The sorbent tested was a Na⁺-salt of poly(acrylic acid) cross-linked with 0.5% divinylbenzene. Because of high hydrophilicity and low cross-linking degree, the polymer exhibits a high ultimate swelling extent (up to 3000%) and extremely large Schroeder's effect. Each wetting event of the vapor-equilibrated bead with small droplets results in a new stable state of the system. This situation is also characteristic for both the H⁺ and Ca²⁺-forms of the resin, though the swelling of the resin is now much lower.

**Figure 10.** Volume deformation of a polystyrene-type anion exchanger Amberlite IRA-402 (Cl[−] form) in the following subsequent processes: (1) swelling in saturated water vapor, swelling in liquid water, partial drying, another partial drying; (2) swelling in saturated water vapor and then wetting with three microdroplets of water. After each manipulation the sample remains in saturated water atmosphere.

The same behavior was found for a polystyrene-type anion exchanger Amberlite IRA-402 on its stepwise wetting with small portions of water (Figure 10, plot 2). One can make similar steps in the opposite direction (Figure 10, plot 1). After partial drying, the ultimately swollen bead retains in saturated water atmosphere its slightly reduced volume for a long period of time, without showing any tendency of approaching any of the two characteristic swelling extents. Only after the second partial drying event, the sample finds itself below the state of equilibration with saturated vapor. Naturally, it takes up some additional water to acquire the expected vapor-equilibrated state.

The real paradox in the above experiments is that there is not just one single state of the polymeric gel that would correspond to equilibrium with saturated vapor. Depending on the prehistory of the sample, any content of the solvating substance in the polymer, which falls into the range between the vapor-saturated and liquid-saturated extremes, can guarantee a stable situation in equilibrium with saturated vapor. In fact, there is a wide range of polymeric gel compositions which are free of uncompensated strains, since polymer–solvent interactions with the accumulated (in one way or another) solvent are fully balanced with remaining interchain interactions. This situation with polymeric networks is possible, because the energy of solvation gradually decreases on adsorption of the solvating media, while the energy of remaining polymer–polymer interactions gradually increases. This means that each new portion of the sorbate binds at less active sorption sites of the material, while each new extension of the network must break stronger between-chain interactions and cause a stronger strain of the network. Because of that, the two equilibrium states which correspond to the activity (and/or chemical potential) of the sorbate in its vapor and liquid form, correspondingly, are well-defined and strongly reproducible. However, all intermediate swelling compositions of the gel (which are artificially attainable by adding of small portions of the liquid or partial drying of the swollen gel) provide systems equally stable in

the atmosphere of saturated vapor. The network gels in these thermodynamically stable states have no reason to reject and loose the acquired sorbate and no power to gain more of it from the surrounding vapor.

Of course, a self-consistent interpretation of this paradox in terms of accepted notions on activity and chemical potentials of the solvating media in the three phases under discussion, liquid, vapor, and gel, if possible at all, remains to be found. It is obvious that, on moving from the vapor-equilibrated to solvent-equilibrated states, the solvent concentration and solvent activity within the gel phase gradually increase. It is difficult to imagine that the solvent chemical potential in the tree equilibrated phases was identical from the very beginning and did not experience any changes on gradual moving from one equilibrium state to another within the above-discussed wide range that corresponds to Schroeder's effect.

CONCLUSION

Results obtained in this study, combined with numerous literature data, unambiguously prove that all polymeric networks tend to swell stronger in any liquid than in its saturated vapor. This logical phenomenon appears as a paradox only in frames of the postulate that chemical potentials of a volatile component that is common to liquid and gaseous phases standing at equilibrium are equal. One can affirm, at least, that the absolute activity of that common component in its liquid form is higher than that in saturated vapor form.

Surprisingly, a gel with any content of solvation media, between the vapor-saturated and the liquid-saturated extremes, exists in equilibrium with saturated vapor. Instead of a local potential energy minimum for the system polymer network–sorbate (if plotted against swelling extent of the gel), there is a whole flat wide valley extending from the polymer-saturated vapor state to the maximum content of the sorbate generated by wetting the gel with excess pure liquid.

AUTHOR INFORMATION

Corresponding Author

*E-mail: davank@ineos.ac.ru.

REFERENCES

- (1) Schroeder, P. Z. *Phys. Chem.* **1903**, 45, 75–117.
- (2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1973.
- (3) Maurer, G.; Prausnitz, J. M. *Fluid Phase Equilib.* **1996**, 115, 113–333.
- (4) Bancroft, W. D. *J. Phys. Chem.* **1912**, 16, 395–406.
- (5) Czapek, F. *Biochemie der Pflanzen*, 2nd ed.; G. Fischer: Jena, Germany, 1913; Vol. 1.
- (6) Shull, C. A.; Shull, S. P. *Am. J. Bot.* **1920**, 7, 318–326.
- (7) Wolff, L. K.; Büchner, E. H. Z. *Phys. Chem.* **1915**, 89, 271.
- (8) Katz, J. R. *Die Gesetze der Quellung. eine biochemische und kolloidchemische Studie* (Zugl. Diss. Amsterdam); Theodor Steinkopff: Dresden, Germany, 1917.
- (9) Ashpole, D. K. *Proc. R. Soc. A* **1952**, 212, 112–123.
- (10) Freger, V. *J. Phys. Chem. B* **2009**, 113, 24–36.
- (11) Majsztrik, P. W.; Satterfield, M. B.; Bocarsly, A. B.; Benziger, J. B. *J. Membr. Sci.* **2007**, 301, 93–106.
- (12) Elfring, G. J.; Struchtrup, H. *J. Membr. Sci.* **2007**, 297, 190–198.
- (13) Bass, M.; Freger, V. *Polymer* **2008**, 49, 497–506.
- (14) Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. *J. New Mater. Electrochem. Syst.* **2000**, 3, 33–42.
- (15) Li, Y. S.; Zhao, T. S.; Yang, W. W. *Int. J. Hydrogen Energy* **2010**, 35, 5656–5665.
- (16) Gates, C. M.; Newman, J. *AIChE J.* **2000**, 46, 2076–2085.
- (17) Vallieres, C.; Winkermann, D.; Roizard, D.; Favre, E.; Scharfer, P.; Kind, M. *J. Membr. Sci.* **2006**, 278, 357–364.
- (18) Musty, J. W. G.; Pattle, R. E.; Smith, P. J. A. *J. Appl. Chem.* **1996**, 16, 221–222.
- (19) Bass, M.; Freger, V. *Desalination* **2006**, 199, 277–279.
- (20) Romero, T.; Mérida, W. *J. Membr. Sci.* **2009**, 338, 135–144.
- (21) Hambleton, A.; Perpican-Saiz, N.; Fabra, M. J.; Voilley, A.; Debeaufort, F. *Food Chem.* **2011**, in press, doi:10.1016/j.foodchem.2011.03.009.
- (22) Friess, K.; Jansen, J. C.; Vopička, O.; Randova, A.; Hynek, V.; Šípek, M.; Bartovska, L.; Izák, P.; Dingemans, M.; Dewulf, J.; Van Langenhove, H.; Drioli, E. *J. Membr. Sci.* **2009**, 338, 161–174.
- (23) Choi, P.; Datta, R. *J. Electrochem. Soc.* **2003**, 150, E601–E607.
- (24) Choi, P.; Jalani, N. H.; Thampan, T. M.; Datta, R. *J. Polym. Sci., Part B* **2006**, 44, 2183–2200.
- (25) Elfring, G. J.; Struchtrup, H. *J. Membr. Sci.* **2007**, 297, 190–198.
- (26) Weber, A. Z.; Newman, J. *J. Electrochem. Soc.* **2003**, 150, A1008–A1015.
- (27) Weber, A. Z.; Newman, J. *J. Electrochem. Soc.* **2004**, 151, A311–A325.
- (28) Onishi, L.; Prausnitz, J.; Newman, J. *J. Phys. Chem. B* **2007**, 111, 10166–10173.
- (29) Jeck, S.; Scharfer, P.; Kind, M. *J. Membr. Sci.* **2011**, 373, 74–79.
- (30) Jeck, S.; Scharfer, P.; Kind, M. *J. Membr. Sci.* **2009**, 337, 291–296.
- (31) Cornet, N.; Gebel, G.; de Geyer, A. *J. Phys. IV Fr.* **1998**, 8, 63–68.
- (32) Peron, J.; Mani, A.; Zhao, X.; Edwards, D.; Adachi, M.; Soboleva, T.; Shi, Z.; Xie, Z.; Navessin, T.; Holdcroft, S. *J. Membr. Sci.* **2010**, 356, 44–51.
- (33) Schneider, N. S.; Rivin, D. *Polymer* **2010**, 51, 671–678.
- (34) Monroe, C. W.; Romero, T.; Mérida, W.; Eikerling, M. *J. Membr. Sci.* **2008**, 324, 1–6.
- (35) Davankov, V. A.; Pastukhov, A. V. *Russ. J. Phys. Chem. A* **2011**, 85, 719–727.
- (36) Pastukhov, A. V.; Davankov, V. A.; Sidorova, E. V.; Shkol'nikov, E. I.; Volkov, V. V. *Russ. Chem. Bull.* **2007**, 56, 484–493.
- (37) Davankov, V. A.; Tsyurupa, M. P. *Hypercrosslinked Polymeric Networks and Adsorbing Materials. Synthesis, Structure, Properties and Application. Comprehensive Analytical Chemistry*; Elsevier: Amsterdam, 2011; Vol. 56.
- (38) Tsyurupa, M. P.; Davankov, V. A. *React. Funct. Polym.* **2006**, 66, 768–779.
- (39) Tsyurupa, M. P.; Davankov, V. A. *React. Funct. Polym.* **2002**, 53, 193–203.
- (40) Pastukhov, A. V.; Davankov, V. A. *Dokl. Chem.* **2006**, 410, 182–184.
- (41) Pastukhov, A. V.; Davankov, V. A.; Tsyurupa, M. P.; Blinnikova, Z. K.; Kavalerskaya, N. E. *Russ. J. Phys. Chem. A* **2009**, 83, 457–464.