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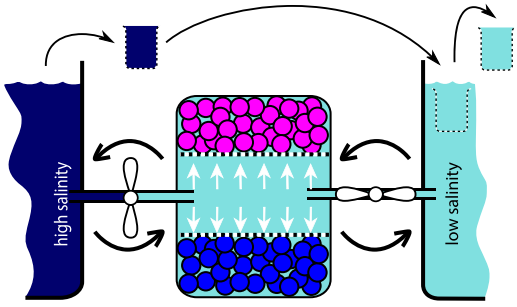
Thermodynamic model for a reversible desalination cycle using weak polyelectrolyte hydrogels

Oleg Rud[a,b,*], Oleg Borisov[a,c,d], Peter Košovan[b]

[a] Institute of Macromolecular Compounds of Russian Academy of Sciences, 199004, Bolshoy pr. 31, Saint-Petersburg, Russia
[b] Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, Praha 2 128 00, Czech Republic
[c] Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR 5254 CNRS UPPA, Pau, France
[d] Saint-Petersburg National University of Informational Technologies, Mechanics and Optics, Lomonosova st. 9, 197101 Saint-Petersburg, Russia

GRAPHICAL ABSTRACT



ABSTRACT

The recently proposed use of hydrogels for water desalination is based on the decrease of salt concentration in the gel upon compression. In the first experiments, desalination cycles using hydrogels involved an irreversible mixing step, which inevitably reduced the thermodynamic efficiency. This approach could become competitive with membrane-based desalination methods if it could work close to maximum thermodynamic efficiency. In this work, we develop a thermodynamic model for compression of weak polyelectrolyte hydrogels in open and closed systems. We use this model to design a fully reversible desalination cycle which can, in principle, achieve maximum thermodynamic efficiency.

We also show that compressing weak polyelectrolyte hydrogels at low salinity decreases their ionization, thereby leading to a non-monotonic dependence of salt concentration on the gel compression. Therefore, our model shows how to redesign the desalination cycle when using weak polyelectrolytes at low salinities.

1. Introduction

Desalination offers an option to satisfy the increasing demand for potable water, lack of which is becoming a problem for about a quarter of the world's population, according to the world health organization [1].

Most common desalination methods comprise distillation, reverse osmosis (RO) and forward osmosis (FO) [2]. To date, reverse osmosis is the most widespread, followed by the distillation [3]. Compared to the distillation process, the reverse osmosis can operate much closer to the theoretical maximum thermodynamic efficiency. On the other hand, the membrane-based processes (FO and RO) are more sensitive to the

* Corresponding author at: Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, Praha 2 128 00, Czech Republic.
E-mail address: oleg.rud@natur.cuni.cz (O. Rud).

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quality of the feed water. Water pre-treatment is required to prevent biofouling and clogging of the membranes used in FO and RO [4]. This adds extra costs in terms of energy consumption as well as running costs for the maintenance of the membranes [5]. The energy consumption and sensitivity to water quality pose major challenges in modern desalination research.

An alternative desalination method using polyelectrolyte hydrogels has been proposed recently [6-8]. It can be viewed as a modification of forward osmosis (FO) method, where the gel acts both as the draw solute and as the separation membrane [7,9]. The key idea is that the salt concentration inside a polyelectrolyte hydrogel is lower than outside due to the Donnan partitioning of ions [6,10]. In the experiments, poly(acrylic acid) hydrogels were swollen in the solution of NaCl, and then compressed to yield water with a lower salt concentration than the initial solution [6]. The originally proposed desalination cycle included a recovery step by re-swelling the compressed gel in the high-salinity solution. This step is thermodynamically irreversible, which limits the maximum efficiency that can be theoretically achieved in this cycle [11]. The recent experimental examination of desalination efficiency of this cycle came to similar conclusions [7].

The poly(acrylic acid) hydrogel, used in the desalination experiment, is a weak polyelectrolyte, and its ionization depends on the outer salinity and pH, as well as on the state of compression [12]. The use of poly(acrylic acid) was motivated by its low cost and broad availability which makes it a good candidate for large scale production [6,13,7]. However, its variable ionization was neglected in the recent theoretical analysis, where constant degree of ionization was assumed [11], as well as in the interpretation of the experiments [7]. In this work, we address the questions, how the variable ionization of the weak polyelectrolyte affects the performance of the desalination cycle, and how to design a thermodynamically reversible desalination cycle based on the compression and re-swelling of polyelectrolyte hydrogels.

Properties of weak polyelectrolyte gels have been extensively studied by experiments in the context of stimuli-responsive materials, where the change of external conditions in the environment triggers structural changes in the gel [14,15].

For example, weak polyacid gels respond to an increase in pH by increasing their ionization degree, which increases their swelling ratio [16,17]. Thermo-responsive polymers, such as poly(n-isopropyl acrylamide) (PNiPAAm), undergo a transition from good to poor solvent conditions upon an increase in temperature which results in shrinkage of the gel [18,19]. Copolymers of PNiPAAm and PAA combine the high swelling capacity of polyelectrolyte gels with thermo-responsive and pH-responsive properties. Thermo-responsive shrinking can be exploited for desalination using hydrogels, as an alternative to mechanical compression [20,21].

In the context of desalination, we address the reverse problem compared to the stimuli-responsive systems: we apply mechanical force on the gel, and by deforming the gel we trigger changes in its environment — increasing or decreasing salinity. Studies addressing the use of polyelectrolyte hydrogels for desalination are scarce as compared to those addressing their stimuli-responsive properties. Wilhelm and coworkers published several articles describing the use of hydrogels for desalination by applying mechanical pressure [7,6]. More recently, a similar procedure was described by Yu et al. [8].

Other authors proposed to use stimuli-responsive microgels or hydrogel layers as draw solutes in forward osmosis [21,9,13,22]. Various mechanisms and stimuli have been proposed in this context, such as electric field [23], magnetic field [24-26], and temperature-induced collapse of thermo-responsive microgels [20,21].

The main advantage of using responsive microgels as draw solutes in FO is their re-usability, and ease of separation by simple filtration methods. In general, the use of hydrogels in water desalination appears to be an emerging field, the potential of which is waiting to be fully exploited.

In the next section, we introduce a thermodynamic model of a weak polyelectrolyte hydrogel swelling in a salt solution. Then in Section 3, we use this model to analyze the swelling and compression of polyelectrolyte hydrogels in open systems (constant salt concentration) and in closed systems (constant total number of ions). We specifically focus on the amount of ions present in the gel and in the surrounding medium which is the key feature for desalination. We also contrast the behavior of strong and weak polyelectrolyte gels in order to understand under which conditions the variable ionization of weak polyelectrolyte gels is important. Finally, in Section 4 we use the knowledge from the previous analysis to design two thermodynamically reversible desalination cycles based on compression and re-swelling of strong and weak polyelectrolyte gels, respectively.

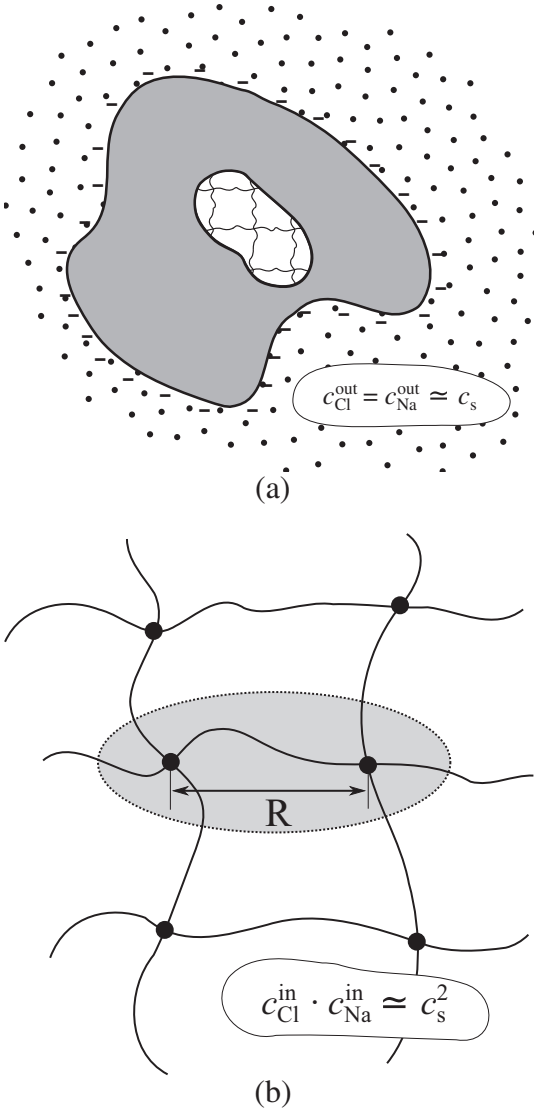

Fig. 1. Schematic representations of polyelectrolyte gels in solution: (a) Gel microparticle in solution of monovalent salt. Electric charge concentrated at surface raises The Donnan potential is schematically depicted as negative charges accumulated at the gel-solution interface. (b) Gel as the network of polyelectrolyte chains connected through crosslinks. Average polymer density in the gel is proportional to R^{-3}.

2. The thermodynamic model

We represent the polyelectrolyte gel as a network composed of polyelectrolyte (polyacid or polybase) chains of N monomers connected by crosslinks. The experimental studies of desalination using hydrogels