

NEW DESALINATION SYSTEMS BASED ON THERMOSENSITIVE HYDROGELS

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Abstract

The novel technique of sea water desalination is advised. The technique is based on low molecular-weight salt concentration redistribution between two polymer networks with dissimilar ionization degree. Firmly ionised polyelectrolyte gel placed in salt solution accumulates desalinated water. Therefore, desalinated water is removed from polyelectrolyte gel for the duration of the contact with thermosensitive hydrogel. Thermosensitive hydrogel undertakes phase transition (collapse of the gel) while heating. Aforementioned approach gives prospect to collect desalinated water by heating of thermosensitive hydrogel by sun emission.

Key words: innovation environment, thermosensitive hydrogels, commercialization of desalination technology, polyelectrolyte gel

1. INTRODUCTION

It is now established that the systems containing polyelectrolyte hydrogels have inhomogeneous distribution of the low molecular weight components [1, 2]. Thus, polyelectrolyte network placed in a solution of low molecular weight salt 1:1. It accumulates lean solution, while the salt concentration in the solution above the gel, in contrast, increases [1]. Low molecular weight acid behaves in the similar way [2], with the difference that part of the hydrogen ions can bond with network, synthesized on the basis of weak polyacids.

This effect can be the basis of the water purifying and desalination technologies [3]. Namely, it is possible to implement a cycle in the first stage of which the hydrogel will accumulate lean solution which is separated from the network at the second stage of the cycle. In the cited paper for the implementation of the second stage were encouraged to utilise electric current, using the contraction phenomenon [4,5].

This approach requires a significant amount of energy, so the search for other ways is prevailing, to separate the lean solution from the swollen polymer network.

It can be assumed that for this purpose is acceptable to utilise thermosensitive hydrogels, brought into contact with the swollen polyelectrolyte network. In this case, part of the lean solution, on the low molecular weight component, is accumulated by thermosensitive hydrogel. Next, the solution is separated from it by heating. Significantly [6,7], that the gels synthesized on the base of polymers having a lower critical solubility temperature, have a relatively low temperature of thermally induced collapse. In particular, the temperature lying in the range 35 - 45°C is achievable. It allows to utilise solar energy to separate the lean solution from the swollen network. Thus, it is possible to actualize the technology of enrichment or leaning the solution of low molecular weight substance, which functions directly on solar energy.

However, as shown in this paper, in contact with a thermosensitive hydrogels polyelectrolyte networks swollen in a low molecular weight salt solution, there is a new, not previously described in the literature phenomenon. It consists in fact that the redistribution of concentrations effect described in

[1,2], also shown in contact of the above type networks. In contrast to the previously studied comparatively simple systems, the nature of redistribution of concentrations is influenced by osmotic effects.

The effectiveness and efficiency of the suggested demineralization method of aqueous solutions is provided by integration the approach discussed above with methods in which enrichment/depletion of the solution is provided by applying mechanical pressure to the cross-linked polymer network.

It should be emphasized; the elastic and mechanical properties of cross-linked polymer networks have been studied in detail. Studying various mechanical deformations of hydrogels [8], including when they are swollen [9] attract researchers' attention for a long time. This is dictated by both academic interest and practical considerations (e.g., the medical use of hydrogels [10, 11] requires ensuring their strength). In [12] it was noted that "scope of hydrogel applications, however, is often severely limited by their mechanical behaviour". It is also well known that mechanical pressure results in compression of the swollen polymer network, accompanied by separation of the accumulated water [13]. In the literature, attention is paid to gels that can significantly change volume due to various, including mechanical factors [14-16], which were used for complex composition gels, filled with nanoparticles gels and so on.

In this paper, new physico-chemical phenomenon was found, it occurs when a mechanical impact polymer gel swollen in the low molecular weight salt solution. This phenomenon is that during the influence on the network of the mechanical load the salt unevenly distributed between the fluid released from the gel under the load and the liquid remaining inside the gel. Separated liquid is enriched in the low molecular weight component, which can be regarded as Le Chatelier's general scientific principle.

2. EXPERIMENTAL

2.1. Materials

Acrylic acid (AA) containing the 99% of main product and 2-hydroxyethyl acrylate (HEA) containing 96% of main product manufactured by "Sigma-Aldrich Co." (USA) was further purified by passing through a column filled with Al_2O_3 , B.P. = $139^\circ\text{C}/760\text{ mm.Hg}$, $n_D^{20} = 1.4180\text{-}1.4220$.

N-Isopropylacrylamide containing 98.9% of main substance, and ammonium persulfate "chemically pure" grade containing 99.9% of main product manufactured by "PanReac AppliChem" (China) was utilised without further purification.

The thermosensitive hydrogels for experiment were prepared by copolymerization of *N*-isopropylacrilamid (NIPAM), and 2-hydroxyethyl acrylate (HEA), utilizing N, N'-methylenebis(acrylamide) (BIS) as cross-linking agent and ammonium persulfate as initiator. For synthesis of thermosensitive hydrogel used in the experiment and capable to thermo-induced collapse in the temperature range of $40\text{-}45^\circ\text{C}$ initial monomer mixture (IMM) was utilised, containing NIPAM and HEA in equimolar ratio (50/50 mol.%).

Strongly swellable gel synthesized on the base of polyacrylic acid containing 75 mol % of carboxyl groups neutralized (sodium acrylate) was utilised in the experiments. To obtain this gel a 50% aqueous solution a calculated amount of AA and 10 molal aqueous NaOH solution was added. The solution was adjusted to 10 wt.% based on the AA by the addition of distilled water; then initiator (0,005 mol/l) and a corresponding amount of the cross-linking agent (CA) were injected. Hydrogels were prepared by three-dimensional radical copolymerization using BIS as a cross-linking agent. The copolymerization was carried out in the aqueous solution in molybdenum glass ampoules. The initial monomer mixture and was poured into ampoules for 40 min, purged with argon to remove oxygen, and then sealed. The process was initiated by thermal decomposition of the initiator ammonium persulfate at 60°C .

The samples obtained after the synthesis of hydrogels were washed in 2-3 weeks separating the sol fraction.

2.2. Methods

Experiments were conducted by the following procedure, which illustrates Figure 1. Sample of polyelectrolyte gel (m_{AA}) is contacted with a solution of sodium chloride ($C_{NaCl,0}$). Upon reaching the swelling equilibrium, it was removed from the solution and brought into contact with the sample of dry thermosensitive gel (m_{dry}). Simultaneously conductance-measuring was recorded concentration of low molecular weight salt solution over the gel ($C_{NaCl,e}$).

The concentration was measured utilizing a conductivity meter - salimeter HM Digital PSC-54 manufactured by HM Digital, Inc. (South Korea), drawing calibration curves.

Upon reaching equilibrium, the swollen mass of thermosensitive gel is measured (m_{swell}), and then this gel is heated above the critical temperature. When heated, the accumulated solution in gel was separated due contraction of the polymer network, its concentration ($C_{NaCl,i}$) conductance-measuring was recorded (Table 2).

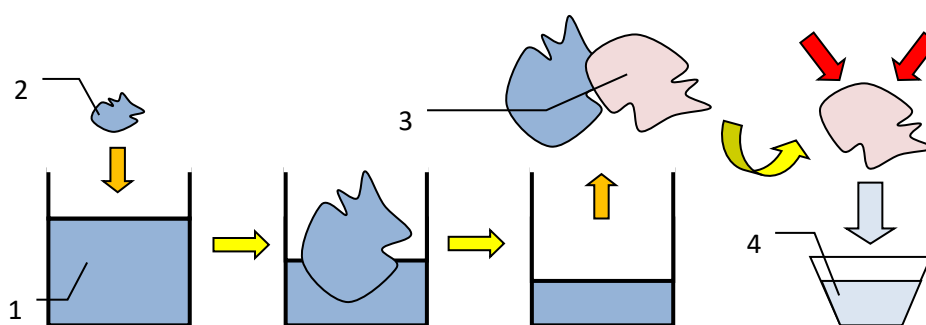


Figure 1. Diagram of the experiment, 1 - initial solution, 2 - polyelectrolyte hydrogel, 3 - thermosensitive hydrogel 4, - tested solution.

Then the process was repeated again utilizing the new sample of dry thermosensitive gel. This sample of dry thermosensitive gel was brought into contact with polyelectrolyte hydrogel, which has partially lost the accumulated solution in the previous stage of the cycle.

Sample weights portions utilised in experiments were summarized in Table 1. It was conducted three series of experiments differing initial concentration of sodium chloride and the equilibrium degree of swelling of hydrogels.

In the first two series of experiments utilised relatively weakly cross-linked gel; equilibrium degree of swelling in water (α_{AA}) and sodium chloride concentration used ($\alpha_{AA, NaCl}$) also is shown in Table 2. In the third series of experiments, a tighter cross-linked polymer network was utilised.

Experiments of mechanical pressure effect on a grid, swollen in a solution of a low molecular weight salt, were performed according to the following technique.

The experiment was performed by setting Figure 2. The installation includes a metal cylinder (1), at the end of which was reinforced 0.7 mm fine screen (2), on top of which was placed a cloth filter. Inside the cylinder was inserted the piston (3), to which was carried a holder (4) for the goods (5). Installation was mounted on a tripod, allowing the use of loads weighting up to 30 kg.

Table 1. Sample weights of polyelectrolyte (m_{AA}) and a thermosensitive (m_{dry} , m_{swell}) gels utilised in three series of experiments.

	m_{AA} , g	1 st cycle	2 nd cycle	3 rd cycle
m_{dry} , g (E1)	1,50	3,49	3,9	-
m_{swell} , g (E1)		24,32	16,96	-
m_{dry} , g (E2)	2,02	3,708	4,01	3,85
m_{swell} , g (E2)		11,6	26,22	6,08
m_{dry} , g (E3)	5,14	3,87	3,82	2,74
m_{swell} , g (E3)		26,52	21,72	10,61

Table 2. Results of the measurement of concentrations in three series of experiments.

α_{AA} , (α_{AA} , NaCl) g/g	$C_{NaCl,0}$, %	$C_{NaCl,e}$, %	$C_{NaCl,i(1)}$, %	$C_{NaCl,i(2)}$, %	$C_{NaCl,i(3)}$, %
332,6 (92,33)	0,1	0,14	0,125	1,11	-
332,6 (92,33)	0,2	0,253	0,265	0,261	0,266
103 (42,12)	0,2	0,275	0,318	0,275	0,224

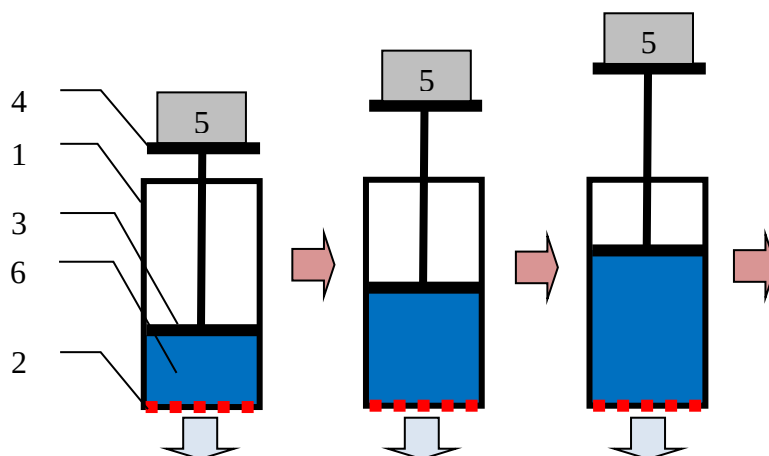


Figure 2. The scheme of the experiment with cyclically repeated mechanical action.

The dispersion of the hydrogel solution poured red blood salt at a concentration of 0,02058 wt.% and it was adjusted to equilibrate for 1 day. Next, the hydrogel was removed from the dispersion solution using a filter paper. After equilibrium is reached the concentration of salt in the solution above the gel was measured. The concentration was measured by a spectrophotometer utilizing a previously constructed calibration curves for three wavelengths ($\lambda = 261, 440, 420$ nm). We utilised the average value of concentration.

Also we fixed volume of gel reaching state of equilibrium. Volumes of dispersions were measured by utilizing the measuring cylinders, the mass of the gel before and after swelling - gravimetrically.

Based on these data, the concentration of low-molecular salt inside C_i gel calculated by the obvious formula

$$C_i w + C_e(1 - w) = C_0$$

Where C_e – the salt concentration in the solution above the gel; C_0 – the salt concentration in the original solution; w - the proportion of the total amount oncoming to the hydrogel.

In the experiments, the cylinder (1) filled with a dispersion of the hydrogel (6) swollen to equilibrium state in a solution of utilised salt.

Then, on the dispersion of the swollen gel provided a mechanical action using a load (5), holding the gel under the load until equilibrium is reached. (In all experiments the pressure was fixed and was created with 1.5 kg load because further pressure increase led to a mechanical destruction of the hydrogel particles.)

Concentration was measured and the volume of water separated from the gel under the influence of mechanical pressure. Measurements were also carried out by spectrophotometry as described above. After reaching the equilibration, the gel was removed from the cylinder, and it was filled with initial concentration of low molecular weight salt solution. Further swelling - loading cycle was repeated again.

3. RESULTS AND DISCUSSION

Concentration measurement results are shown in Table 2, in the same specified number of cycles for each series of measurements.

It is seen that in contact with thermosensitive gel with polyelectrolyte network, it is the redistribution of concentrations. Namely, the thermosensitive gel accumulates solution enriched in a low molecular weight component. In a first approximation, the nature of this phenomenon can be set based on the analogy with the effect of redistribution of the concentration in the hydrogel system - a solution of [1,2]. As shown further in [1], the presence of its own counterion in polyelectrolyte hydrogel, formed upon the dissociation of functional groups of cross-linked networks, resulting in its partial volume displacement of ions, formed during dissociation of low molecular weight salts. Neutral environment condition leads to the fact that the salt concentration in the solution above the gel is higher than its concentration in its volume.

The thermosensitive gel is a non-ionic network, so it can be expected that the effect is similar to [1, 2] will also take place in contact of considered gels` types. This conclusion is confirmed by the results of the first series of experiments (E1, Table 2).

It is seen that initially thermosensitive gel, brought into contact with polyelectrolyte gel, accumulates the solution which concentration is slightly lower than the concentration of the solution over the gel (the first step of the experiment, the polyelectrolyte gel - solution system), but higher than the initial concentration of the solution. Wherein the volume of the gel is depleted by a low molecular weight component, so in the next cycle – concentration of the accumulated solution by thermosensitive gel lowered more, but still remains above the initial.

The second series of experiments (E2) also gives the results interpreted by analogy with [1,2]. Namely, [1] it was shown that the smaller the ratio of the concentration of the initial solution to the network density then the difference between the concentrations of solution inside and outside the gel is greater. Consequently, an increase in the initial concentration of the solution makes this effect less noticeable (E2); relatively small amounts of thermosensitive gel brought into contact with polyelectrolyte almost cease to affect the salt concentration within the latter.

The situation changes when moving to a network with higher density (E3). In this case, attention is drawn to the concentration $C_{NaCl,i}$ (1) exceeds the initial concentration $C_{NaCl,0}$ of solution, and the concentration of $C_{NaCl,e}$. This suggests that the measured redistribution of concentrations affects not only factors considered in [1]. We can assume the additional contribution made by osmotic

phenomena, common interpretation which may be given on the basis of Le Chatelier's principle. Polyelectrolyte gel displaces from its volume the ions that prevent its swelling due to the shielding effect.

Thus, the interaction of the polyelectrolyte and the thermosensitive polymer networks has an effect on redistribution of concentrations expressed in that the non-ionic network pulls the solution to itself, enriched in low molecular weight component. Repeated contact polyelectrolyte hydrogel with the thermosensitive gel allows to reduce the concentration of the solution removed from the cross-linked polymer network due to this type of contact. This effect can be the basis for an improved method of enrichment/depletion of aqueous solutions based on the utilisation of a polyelectrolyte hydrogel in contraction - swelling mode.

Qualitatively, Figure 2 illustrates the behaviour of the gel in the experiments with superposition of mechanical pressure. The Figure highlights that as the cycle number increased the residual volume of the gel increased as well (under a fixed mechanical load). In the first cycle the gel volume is reduced by 30%, then this parameter increases. In the fifth cycle, the gel doesn't change the volume.

Quantitatively, the observed effect is illustrated in Figure 3, which shows the concentration in the solution above the gel and in the gel depending on the number of cycle. For comparison, the same Figure shows the dependence of the concentration in the solution separated from the gel under the influence of mechanical load.

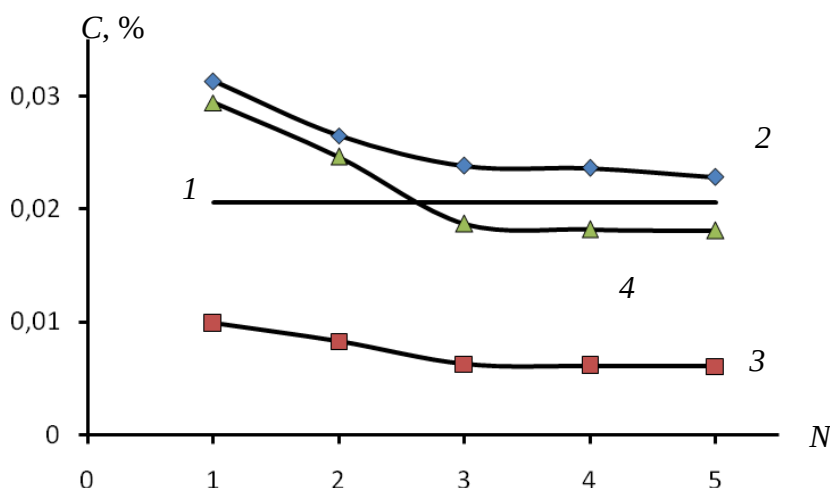


Figure 3. Dependencies of red blood salt concentrations from number of cycle;
1 is the concentration of initial solution, 2 - the salt concentration in the enriched solution above the gel 3 - salt concentration inside the gel, 4 - the salt concentration in the solution, separated from the gel under the influence of mechanical load.

It can be seen that the concentration of solution separated from the gel in the first swelling - loading cycle, considerably higher than the concentration of the initial solution. At the same time the concentration inside the gel solution (from which the liquid was pressed out) is significantly lower than the initial concentration, which can be explained by the existence of the concentration redistribution effect [1].

This result shows that from swollen gel in the low molecular weight salt solution, enriched with low molecular weight component liquid is separated. It fully meets the Le Chatelier's scientific principle, according to which the impact on the system in stable equilibrium, leads to intensifying processes in the system for compensation of external effects.

In this case, the compensation of the external factor (mechanical) impact is to reduce the salt concentration inside the gel. It is known that low molecular weight salt ions shield the charges of the functional groups of the network, resulting in its ability to swell (and, consequently, to counteract external mechanical impact) is reduced.

In accordance with this, the separation of the gel from excess low molecular salts (in experiments, it is observed as an increase in the concentration of the solution which is separated from the gel under the influence of mechanical load) provides increased resistance of the system to external mechanical impact.

The desalination system design basis on the concentrations redistribution effect upon contact of two polymer hydrogels. The example scheme of device providing water demineralization utilising described above phenomena is shown in Fig 4.

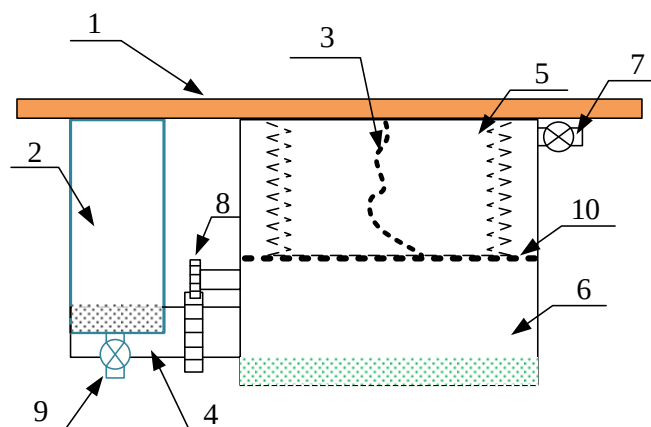


Figure 4. The seawater desalination facility's principal scheme that utilises two types of gels

The device consists of:

- Photovoltaic panel (1), which is also a heat source for all other system components operating.
- Reservoir filled with a thermosensitive polymer (2).
- Hygroscopic fuse (3), which ensures the piston functioning, utilising alcohol vapour.
- Rotating shutter (4), providing contact interruption between polyelectrolyte and thermosensitive hydrogels.
- Piston (5), conducting a mechanical separation from the gel of the low molecular weight salt enriched solution.
- Reservoir (6) filled with a working substance – a polyelectrolyte hydrogel, the reservoir bilge is permeable to the solution and is not permeable to the hydrogel dispersion particles.
- Channel (7) for desalinated water supply.
- Turning mechanism (8).
- Channel for collecting desalinated water (9).
- Grid (10) allowing hydraulic resistance of a desalinated liquid with the purpose of filling of space between the piston and walls of the reservoir.

The device operates as follows. In the initial state, the piston (5) is in the upper position; the hydrogel filling the reservoir (6) is in equilibrium with the swelling degree determined by the low molecular

weight component concentration in the initial solution. The initial state is effectuated by cooling the piston with desalinated water, flowing around the piston when supplied through the channel (7).

Then the channel (7) overlaps, and the working fluid (specifically, ethanol was utilised) warms, creating a mechanical pressure transferred to the polyelectrolyte hydrogel. The squeezed liquid is discharged through the grid bilge of the reservoir (6).

When the pressing is completed (the state in which the piston comes to lower position), the channel (7) opens again. In this case, there is interval to fill the space between the walls of the reservoir (6) and the piston (5) with a desalinated liquid, before contacting with swellable polyelectrolyte gel as a result of the hydraulic resistance of the grid (10). Due to this, the working fluid in the piston is cooled, the gel swelling undergoes at the same time, i.e. the desalinated liquid acts as a refrigerating medium. After the swelling is completed, the cycle is repeated again.

To maintain working fluid's continuous evaporation due to the subsidiary heat from the solar photovoltaic panel (1), a hygroscopic fuse (3) which absorbs ethanol is utilised. The fuse supplies working fluid directly to the backside of the solar photovoltaic panel (1).

Repeating cycles are carried out until the established mechanical pressure does not cease to facilitate the separation of the accumulated solution from the polyelectrolyte hydrogel.

At this stage, a turning mechanism (8) is activated, connected to a rotating shutter (4), one of whose parts is made of hygroscopic material reinforced with a grid. Then the thermosensitive gel comes into contact with the polyelectrolyte, the last accumulated liquid, partially passes into the dispersion filling the reservoir (2). The filled in dispersion, swelling, gradually increases in volume until the moment when it comes into contact with the backside of the solar photovoltaic panel (1). As a result, the thermosensitive gel contracts, separating the desalinated water.

4. CONCLUSION

Thus, the transition to the low molecular weight salt solutions, a well-known phenomenon of contraction of the gel under the influence of mechanical load, acquires nontrivial peculiarities. There is an effect of concentration redistribution, when the salt contained in the gel is redistributed unevenly between the solution separated from network, and the solution remaining inside the gel. The balance between these concentrations is defined as the mechanical and as osmotic factors, which suggests a specific osmo-mechanical nature of the observed phenomenon.

The observed phenomenon allows us to question the development of the varieties of enrichment technologies. To be precise, it is possible to utilise thermosensitive hydrogels to remove desalinated water from the hydrogel, which as a result of several swelling - loading cycles in saline solution is saturated with demineralized water.

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