

Partition of potassium nitrate between polyacrylamide gel and aqueous methanol solutions

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Summary

Samples of nonionic polyacrylamide (PAAm) gel were equilibrated in water-methanol-KNO₃ mixtures and distribution of salt and methanol between gel and surrounding liquid was examined. In water and mixtures of low methanol concentration the both components were almost equally partitioned. On the other hand, in methanol-rich media the accumulation of KNO₃ and water uptake in the gel were observed. Changes in the salt and solvent distribution occurred around the same mixture composition which correspond to the Θ -solvent composition for linear PAAm. The results point to the importance of preferential gel hydration in salt partitioning. However, possible role of other factors (e.g., the specific ion binding to the polymer) in the salt distribution is also shown.

Introduction

Gels have found widespread applications in a variety of areas like, for instance, medicine, pharmacy or biotechnology [1]. They are becoming increasingly important also in separation processes [2]. The practical importance of gels has motivated much research, concerning different aspects such as, e.g., the swelling and shrinking processes [3, 4], the elastic properties of gels [4, 5] and the structure of solvents inside a gel [6, 7]. An important issue is also an equilibrium partitioning of a solute between a gel and a surrounding coexisting fluid [8].

Recently, it has been reported that the volume phase transition of poly(N-isopropylacrylamide) gel has a significant effect on the equilibrium distribution of simple salts between the gel and the external aqueous salt solution [9]. Also, in the case of nonionic PAAm gels immersed in aqueous salt solutions it was observed that the difference between the concentration of the solute in the gel and the surrounding liquid increased when the gels collapsed [10].

The aim of this work was to examine the effect of swelling degree of a gel on the partition of a simple salt between the gel and external liquid. A nonionic PAAm gel immersed in water-methanol mixtures was chosen to be studied. Water is a good solvent for PAAm, whereas methanol is a nonsolvent [11]. PAAm gels without any ionizable groups exhibit a continuous change in the degree of swelling with changing composition of water-methanol mixtures [12]. The same swelling behavior of nonionic PAAm gels was observed in water-acetone mixtures [13, 14]. Potassium nitrate was the salt used.

Experimental

Materials

In order to obtain PAAm gel, to 100 cm³ of aqueous solution containing 12.1 g of acrylamide and 2.14 g of N,N'-methylene-diacrylamide, at first 5 cm³ of 3% aqueous solution of ammonium persulfate and then 195 cm³ of water were introduced upon stirring. Next, 0.25 cm³ of N',N',N',N'-tetramethylene-di-amine was added and the solution was poured into glass pipes of 10 mm diameter. After completion of polymerisation the gel was squeezed out of the pipes and cut into pieces of about 5 g each. Thus prepared gel samples were washed in flowing water for a few days (conductivity of water in a washing compartment was controlled), then some of them were dried at 80°C to constant weight and the others were left in water. The chemicals used for the preparation of PAAm gel were purchased from Aldrich.

In electrophoretic experiments linear PAAm (prod. BDH) with molecular weight of 75·10³ has been used. No further purification was employed. The degree of PAAm hydrolysis, determined on the basis of elemental analysis data, was 0.00 ± 0.01. Colloidal dispersions of PAAm in water-methanol-KNO₃ mixtures were obtained by mixing, in appropriate proportions, a solution of PAAm in water, an aqueous solution of KNO₃ and methanol.

Swelling ratio

The dried PAAm gel samples were weighted, immersed in 7.00 cm³ of water-methanol-KNO₃ mixtures and allowed to swell to equilibrium. The highest salt concentration in the mixture, used in the study, was more than three times as low as the saturation concentration of KNO₃ in a water-methanol mixture of the methanol volume fraction, x_m , equal to 0.8 and at temperature 25°C [15]. Once the equilibrium was reached, the gels were removed from vials, blotted with a tissue to remove surface solvents and then weighted again. The swelling ratio, Q , was defined as:

$$Q = \frac{W_s - W_d}{W_0 - W_d} \quad (1)$$

where W_d and W_s are the weights of the dry and swollen samples, respectively and W_0 is the weight of the sample swollen in water.

The fact of reaching the equilibrium was judged from parallel experiments in which non-dried PAAm gel samples were equilibrated in a relatively large volume of water-methanol-salt mixtures. We assumed that the equilibrium was reached if Q values obtained for dried and non-dried samples equilibrated in mixtures of identical composition were the same.

Swelling experiments were performed at 20°C. Each swelling ratio reported in the article is an average of at least 5 separate measurements.

Salt partition

A portion of 3.00 cm³ of the medium in which equilibration of dry PAAm gel

took place was dried at 110°C to constant weight and a residue was dissolved in 3.00 cm³ of water. Next, the conductance of the solution obtained was measured using an automatic bridge B905 A (Wagne Kerr) at 25.0°C. The concentration of KNO₃, c_s , in the solution was found from a calibration plot of molar KNO₃ conductance versus $\sqrt{c_s}$ at 25.0°C. The partition coefficient, K_p , defined as a ratio of equilibrium KNO₃ concentrations in the media inside and outside the gel, was then calculated from the material balance. Triplicate experiments were performed for each examined composition of the system. The results were averaged.

Methanol distribution

Methanol content in the medium after equilibration of dry PAAm gel was determined by means of gas chromatography. A Chrom 5 (Laboratorni Pstroje, Praha) gas chromatograph equipped with a katharometer was used with a Carbowax 1560 column. Helium was used as a carrier gas. A sample of the medium of initial composition was used as a reference. Distribution of methanol and water between the gel and the dispersion medium was calculated from the material balance. Distribution experiments were performed in triplicate for each system composition.

Electrophoresis

Electrophoretic mobilities were measured with the aid of Laser Zee dzetameter, model 501 (Pen Kem, Inc., USA). The effective electrophoretic mobilities, u_{eff} , were calculated from Eq.(2):

$$u_{\text{eff}} = \frac{6\pi\eta e}{\epsilon kT} u \quad (2)$$

where η is the viscosity coefficient, e denotes the elementary charge, ϵ - dielectric constant of the dispersion medium, T - absolute temperature and u is the electrophoretic mobility measured. Each reported mobility value represents the average of at least 9 measurements.

Results and discussion

Figure 1 shows the equilibrium swelling degree of PAAm gel, Q , as a function of the volume fraction of methanol, x_m ; the dependencies were determined at different salt concentrations. As follows, with increasing methanol content the extent of swelling of PAAm gel decreases continuously. No effect of the electrolyte concentration on Q values is observed.

Figure 2 summarises the results of the studies on the distribution of KNO₃ between PAAm gel and water-methanol mixtures. As seen, in water the salt is almost equally partitioned between gel and aqueous phases, independently of c_s . Also, below a certain methanol content, which is around $x_m = 0.4$, the values of the partition coefficient, K_p , are almost equal to unity; the differences between KNO₃ concentrations in the gel and the surrounding liquid are mostly within the

experimental uncertainty. The differences depend on the total salt concentration in the system; the larger c_s the greater K_p . When $x_m \approx 0.4$ is reached, the differences between salt concentrations in both phases start to increase; the accumulation of KNO_3 in the gel takes place. The higher the methanol and salt concentrations the larger the value of K_p .

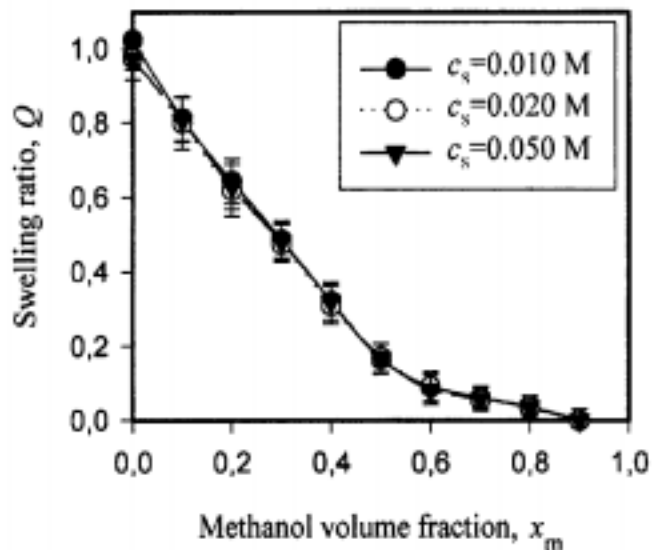


Figure 1. The dependence of the equilibrium swelling ratio of the PAAm gel on the methanol volume fraction at different KNO_3 concentrations. Error bars were estimated on the basis of standard deviations.

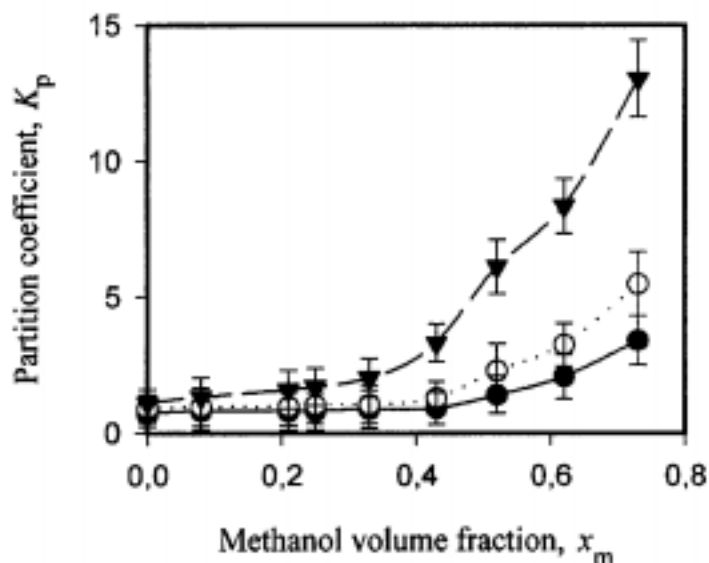


Figure 2. The dependence of the coefficient of KNO_3 partition between PAAm gel and surrounding liquid on the methanol volume fraction at different salt concentrations. Error bars were estimated on the basis of standard deviations.

The composition of water-methanol mixture, at which the increase in K_p begins, corresponds roughly to the composition of a mixture determined as Θ -solvent of linear PAAm at room temperature. The reported compositions of water-methanol mixtures, corresponding to Θ -solvent, range between 0.37 and 0.46 volume fraction of methanol [16-19]. Moreover, Zhu and Napper [20] found that the coil-to-globule transition of interfacial PAAm chains in water-methanol mixtures starts to occur around $x_m = 0.45$. All the determinations of Θ -solvent composition were performed in the presence of salts; no effect of salt concentration on the cloud-point parameters was observed [12, 19]. Taking the above into consideration we can conclude that the accumulation of KNO_3 in the PAAm gel begins when the water-methanol mixture approaches the bad solvent composition. With a further deterioration of solvent quality an increase in K_p takes place.

Kawasaki *et al.* [9] suggested that in the case of poly(N-isopropylacrylamide) gels in aqueous salt solutions the distribution of salts between gel and surrounding liquid depended on the water content in the gel. However, in that case the salts were excluded from the gel because the collapse, caused by the temperature change, involved a decrease in the water content in the gel. On the other hand, when gels are immersed in mixed solvents the phenomenon of preferential solvation can occur [21]. Preferential hydration of PAAm in water-methanol mixture was already reported [22]; in the case of linear high-molecular weight PAAm the water adsorption of about 0.1 cm^3 per 1 g of dry polymer was found at $x_m = 0.38$ and NaCl concentration equal to 0.1 mole/dm^3 . Thus, one can suppose that an increase of KNO_3 concentration in the gel phase, observed in methanol-rich mixtures, might be due to a higher water concentration in the gel as compared to that in the external liquid, which - in turn - results from the preferential hydration of the polymer. In order to verify this hypothesis the extent of preferential hydration of PAAm gel as a function of mixture composition was examined. The results obtained are shown in Figure 3, where the water content in PAAm gel is plotted versus x_m in the external solution; two different salt concentrations in the system were examined. As follows, the preferential hydration of PAAm gel was found only in methanol-rich mixtures; the lowest alcohol contents at which it was observed being around $x_m = 0.4$. The increase in c_s reduced the extent of hydration. We must emphasise here, however, that although the method applied for the methanol determination is very accurate, the scattering of the results was significant, especially in the x_m range in which the volume of gel absorbed medium was very small. Therefore, the results concerning the preferential hydration of PAAm gel can be treated only qualitatively. Nonetheless, a correlation between the hydration extent of the gel and the partition coefficient of the salt can be concluded, especially that the uptake of salt and water in the gel began around the same value of x_m . Moreover, Pałecz *et al.* [23] on the basis of enthalpies of KNO_3 solution in aqueous methanol solutions calculated the enthalpic pair interaction coefficient between methanol molecules and KNO_3 in water and obtained its positive value, which means that the ions of this electrolyte interact weakly with methanol and strongly with water molecules. Thus, the tendency of KNO_3 to accumulate in a water-rich phase can be expected.

The dependence of K_p on the salt concentration suggests that there are also other factors influencing the partition of KNO_3 between the gel and surrounding liquid. One of such factors can be the ion binding to the polymer. It was reported that intrinsic viscosities of nonionic PAAm in aqueous salt solutions increased with increasing salt concentration [24, 25]. This behavior was attributed to the site binding of cations (Na^+ , K^+ and NH_4^+) with electron-rich polar amide groups on PAAm, resulting in a pseudopolyelectrolyte [24]. In water-methanol media the extent of this binding may increase due to the reduction of the dielectric constant compared to

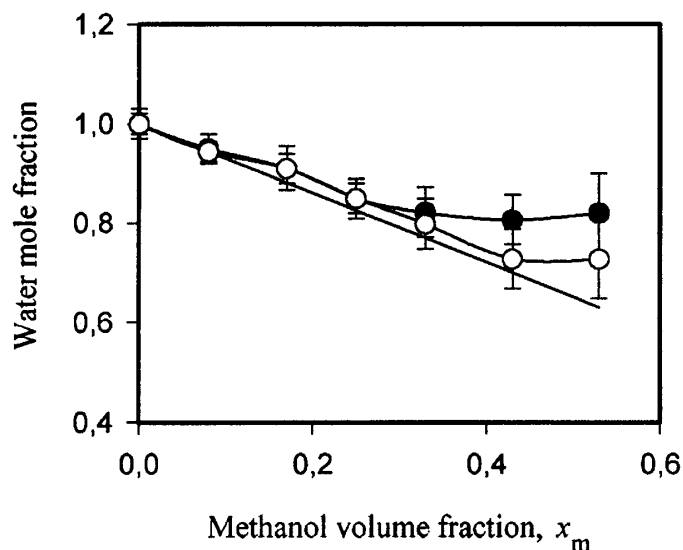


Figure 3. The water uptake in the gel as a function of methanol volume fraction determined at two different KNO_3 concentrations. Error bars were estimated on the basis of standard deviations

that of water ($\epsilon = 80$). The effective dielectric constant of the gel should also decrease with decreasing Q , and hence, increasing concentration of PAAm in the gel phase; the dielectric constant of PAAm is about unity [26] while that of methanol is 33.

The introduction of a sufficient amount of methanol into the aqueous solution of linear PAAm induces the phase separation which yields colloidal dispersions of the polymer [12, 19]. We have performed the electrophoretic studies of these dispersions containing different concentrations of methanol and KNO_3 . The electrophoretic mobilities of PAAm particles were measured just after the polymer precipitation. The obtained results are presented in Figure 4. As follows, in the absence of the salt PAAm particles carried negative charges which probably originated from the hydrolysis of some amide groups into carboxylic moieties [27]. The introduction of KNO_3 influenced the electrophoretic mobilities of the particles. At low values of c_s a reduction of their mobilities was observed, whereas at higher salt concentrations the charge reversal took place. The reduction of mobilities can be explained by the screening effect of the electrolyte, resulting in the compression of the electrical double layer or the reduction of the surface charge of particles. On the other hand, the reversal of the sign of electrophoretic mobilities indicates the specific binding of

cations to the polymer. However, other reasons for the dependence of u_{eff} on c_s like, for example, a difference between solubilities of cations and anions in the polymer-rich phase, which can produce a potential difference [28] and, hence, influence the electrophoretic mobilities of particles, cannot be excluded.

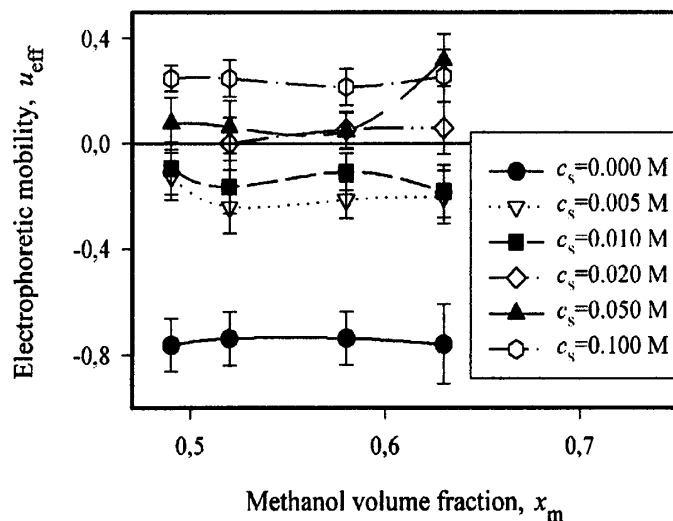


Figure 4. Dimensionless electrophoretic mobility of PAAm particles in water-methanol- KNO_3 mixtures as a function of methanol volume fraction at different KNO_3 concentrations. Error bars were calculated on the basis of standard deviations

Conclusions

Although the studied, nonionic PAAm gel exhibits a continuous change in the swelling ratio with the change in the composition of water-methanol mixtures, a distinct change in the coefficient of salt partition between gel and surrounding liquid takes place when the mixture approaches the Θ -solvent composition for linear PAAm. The preferential hydration of gel is an important parameter influencing the salt partition coefficient. However, there are also other factors like, for instance, the specific ion binding to the polymer, which affect the salt distribution.

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