



# Complex Formation of Divalent Cations with Carboxylic Acid Resins as a Factor Determining Different Stationary States of Their Swelling

Ekaterina A. Karpyuk, Oksana I. Titova, Alexander V. Pastukhov, Vadim A. Davankov, Sergei I. Kargov & Vladimir A. Ivanov

**To cite this article:** Ekaterina A. Karpyuk, Oksana I. Titova, Alexander V. Pastukhov, Vadim A. Davankov, Sergei I. Kargov & Vladimir A. Ivanov (2016) Complex Formation of Divalent Cations with Carboxylic Acid Resins as a Factor Determining Different Stationary States of Their Swelling, *Solvent Extraction and Ion Exchange*, 34:4, 362-374, DOI: [10.1080/07366299.2016.1155898](https://doi.org/10.1080/07366299.2016.1155898)

**To link to this article:** <http://dx.doi.org/10.1080/07366299.2016.1155898>



Accepted author version posted online: 18 Feb 2016.  
Published online: 18 Feb 2016.



Submit your article to this journal [↗](#)



Article views: 34



View related articles [↗](#)



View Crossmark data [↗](#)



## Complex Formation of Divalent Cations with Carboxylic Acid Resins as a Factor Determining Different Stationary States of Their Swelling

Ekaterina A. Karpyuk<sup>a</sup>, Oksana I. Titova<sup>a</sup>, Alexander V. Pastukhov<sup>b</sup>, Vadim A. Davankov<sup>b</sup>, Sergei I. Kargov<sup>a</sup>, and Vladimir A. Ivanov<sup>a</sup>

<sup>a</sup>Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia; <sup>b</sup>Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Sciences, Moscow, Russia

### ABSTRACT

Three samples of carboxylic acid gel-type cross-linked polyelectrolytes were examined by registering the extent and kinetics of their volume change depending on the temperature, concentration, and nature of external electrolyte solutions, as well as the initial state (ionic form, water content) of the bead. It is found that in some systems the swelling of the bead (as a result of lowering the temperature) proceeds much more slowly than the preceding shrinking (as a result of the increase of temperature). Moreover, the initial volume of the bead is not restored, and a new stationary state of swelling is established. By means of optical dilatometry, it is found that in the systems in which the differences in the stationary states of swelling are found, the beads display plasto-elastic properties, whereas in the absence of such differences the beads show elastic properties. It is found that different stationary states of swelling are also established when the beads of copolymer of methacrylic acid cross-linked with divinylbenzene in Na<sup>+</sup> form in the dry state and in the NaCl solution-swollen state are placed into a solution of a divalent cation salt. The difference in the stationary states of swelling reaches 12% in 4 N NiCl<sub>2</sub> solution. The substantial differences in the swelling behavior and viscoelastic properties of the resins in their Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Ni<sup>2+</sup> forms are interpreted in terms of formation of different kinds of complexes of functional groups of the polymer with Ca<sup>2+</sup> and Ni<sup>2+</sup> ions.

### KEYWORDS

Carboxylic cross-linked polyelectrolytes; ion exchangers; swelling kinetics; dilatometry; viscoelastic properties; bivalent cations complexing

### Introduction

The ability of cross-linked polyelectrolytes (CPEs) and hydrophilic polymers to absorb water and other polar liquids is used in various processes. There are also endeavors to use for separation purposes the influence of temperature on the swelling of weakly cross-linked hydrophilic gels that considerably change their degree of swelling in a rather narrow temperature range. Such gels are called temperature-sensitive or thermoresponsive gels.<sup>[1–5]</sup> The critical volume transition with temperature change is observed for nonionic acrylamide-type gels and also for their ionic counterparts with some amounts of ionizable carboxylic groups.<sup>[6–8]</sup> In the process of swelling at room temperature, these gels selectively extract the solvent from solutions containing high-molecular-weight substances (various proteins, lignin, etc.), thus increasing their concentration.<sup>[9–22]</sup>

Upon heating, the swollen thermoresponsive hydrogel shrinks and liberates the absorbed water. When being placed again into the cool solution, such polymer absorbs water and further concentrates the solution. Because, for thermoresponsive gels, only weakly bound water is redistributed upon temperature changes,<sup>[23]</sup> and because the transition takes place in a very narrow temperature

range, the dual-temperature concentration processes require considerably less energy than conventional concentration techniques, such as solvent evaporation.

When studying the concentration processes of high-molecular-weight substances using temperature-sensitive gels, it was noted<sup>[9–13]</sup> that the effectiveness of such separation processes increases with the increase of the degree of cross-linking and with the increase of the molecular size of the solute. In contrast, low-molecular-weight substances are absorbed and released by weakly cross-linked gels simultaneously with the solvent, thus showing no concentration effect.

Nevertheless, it was supposed<sup>[24,25]</sup> that temperature-sensitive gels can also be used for analogous dual-temperature concentrating of low-molecular-weight mineral electrolytes. However, no considerable progress was initially achieved in this direction. Only recently, a real possibility of practical application of this effect for concentration and purification of electrolyte solutions was found, and an applicable process developed. The latter was realized using a commercial polymethacrylic cation-exchanger cross-linked with divinylbenzene (about 1 mol of cross-links to 60 mol of methacrylic monomers).<sup>[26,27]</sup> In this dual-temperature process, the initial electrolyte solution (e.g.,  $\text{CaCl}_2$ ) is passed through the column with the cation-exchanger in the  $\text{Ca}^{2+}$  ionic form, while its temperature is periodically changed. As a result of the temperature increase, the resin in the column shrinks; the water from it migrates into the intergranular solution and dilutes it. This portion of the solution with the reduced concentration is displaced from the column by the continuous fluid flow and then the temperature of the column is decreased again. The resin in the column swells, absorbing water from the intergranular solution and concentrating it. This portion of the solution with the increased concentration is displaced from the column. As a result of such temperature change, the initial feed solution is divided in two parts—with the increased and with the decreased concentrations. On the polymethacrylic resin, the concentrations of the two portions may differ by a factor as high as 2.

It turned out, however, that a real separation effect can be achieved only on a very few types of CPEs.<sup>[27]</sup> It was also found that an important role in the process is played not only by the magnitude of the change in the degree of swelling of the CPE with temperature, but also by the kinetics of the uptake and the discharge of the solvent by the CPE phase. Moreover, even the optimal types of CPE demonstrate substantial differences in their behavior depending on the nature of counterions.

In the present work, both kinetic features and the extent of changes in the degree of swelling of carboxylic CPE in forms of different counterions are studied as a function of temperature. Special attention is paid to the discovered effect of attaining different stationary states of swelling of the resin.

## Experimental

### Materials

AMAC was synthesized according to the usual technique by suspension copolymerization of their methyl esters followed by alkaline hydrolysis of ester groups.<sup>[28]</sup>

The characteristics of the CPE used in this work are summarized in Table 1. All CPE samples were carefully washed with hot water and ethanol to remove the residual adsorbed surfactants and to extract other possible leachables from the polymers. All carboxylic CPE used in this study had an exchange capacity of over 6 mequiv/g and had the form of transparent colorless beads. Only defectless spherical beads were selected under the microscope for all measurements.

### Conversion of CPE into $\text{Na}^+$ Form

Before the experiments, the polymeric materials were converted into the  $\text{Na}^+$  form. To this effect, a twofold excess (with respect to the ion exchange capacity) of 0.5 N HCl solution was passed through the CPE placed in a column. Then the CPE was washed with water and converted into  $\text{Na}^+$  form by means of passing of twofold excess (with respect to the capacity) of 0.5 N NaOH solution through the column. To remove excess of the alkali from the intergrain space, the column was washed with

**Table 1.** Characteristics of the cross-linked polyelectrolytes (CPEs) used in this work.

CPE	Type	Chemical composition	Cross-linking agent
KB-4P2, commercially available (Russia)	weakly acidic gel-type cation exchanger	poly(methacrylate)	divinylbenzene, 1 mol to 60 mol of methacrylic monomer
KB-2e3, commercially available (Russia)	weakly acidic gel-type cation exchanger	poly(acrylate)	dimethacrylate triethyleneglycol, 1 mol to 100 mol of acrylic monomer
AMAC, synthesized in the laboratory	weakly acidic gel-type cation exchanger	copolymer of acrylic and methacrylic acids, molar ratio 170:150	divinylbenzene, 1 mol to respectively 170 mol and 150 mol of acrylic and methacrylic monomers

approximately twofold excess (with respect to the volume of the CPE in the column) of distilled water or 2.5 N NaCl solution at pH ~8–9. In the course of washing, hydrolysis of sodium carboxylate groups is possible, but under these conditions only a negligible part (<0.01%) of the groups could have been converted into their hydrogen form.

### **Conversion of CPE into the Form of Bivalent Metal Ions ( $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ni}^{2+}$ )**

A 0.5 N solution of the respective metal chloride was passed through the column with the CPE in the  $\text{Na}^+$  form. The pH values of  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solutions were adjusted to pH ~8. At this pH value,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions occupy more than 90% of the carboxylate capacity of the resin, with no formation of hydroxide precipitates. To prevent the formation of nickel hydroxide precipitate (that begins to form already at pH 6.7–7.7 depending on the concentration), the pH of the 0.5 N  $\text{NiCl}_2$  solution was adjusted to 5.5–5.9 by addition of 0.5 N HCl. Because of the high selectivity of carboxylate groups to  $\text{Ni}^{2+}$  ions (higher than that to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions), more than 90% of the carboxylate capacity of the CPE at this pH is occupied by Ni ions.

### **Study of CPE Swelling by Optical Dilatometry**

For this study, an apparatus was assembled in which an optical microscope was combined with a digital camera and a computer. A thermostatted quartz cell with 1 cm optical path containing 3 mL gas-free solution of a definite composition was placed on the microscope stage. A spherical bead of CPE (with the diameter of 0.2–0.5 mm when in the dry state) was placed into the cell. At stated time intervals, a series of photographs of the bead was taken, and with the use of a computer program, the areas of the obtained images and the volumes of the bead were calculated (the bead was considered an ideal sphere, which is accurate within 0.2%). Because the extent of bead swelling depends both on temperature and on the composition of the solution, two kinds of kinetic measurements were conducted.

In the first set of experiments, the bead of resin in the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Ni}^{2+}$  forms was placed in the cell with 3 ml of respective  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , or  $\text{NiCl}_2$  solutions of some definite concentration at 293 K. After equilibration, the sustained bead volume was measured. Then the solution in the cell was heated rapidly to 363 K and the changes of the bead volume with time were registered until a constant volume was reached (the solution in the cell attained this temperature in no more than 3–5 minutes). The results of the measurements were represented as the values of temperature swelling factors  $f_T = V_{363}/V_{293}$ , where  $V_{363}$  and  $V_{293}$  are the volumes of the bead at 363 K and 293 K, respectively.

In the second set of experiments, the volume changes of a dry and the same swollen CPE bead in the  $\text{Na}^+$  form were compared at the constant temperature of 293 K. First the dry bead was placed into respective  $\text{CaCl}_2$  or  $\text{NiCl}_2$  solution, and the changes of the bead volume with time were registered until a constant value was reached. After that, the same bead was converted back into the  $\text{Na}^+$  form. For this purpose, the equilibrium solution was removed from the cell by a syringe, and

then the cell was filled with 0.5 N HCl solution. After about 1 hour, the solution was changed with a fresh acid solution. Very large excess of acid ensured complete removal of polyvalent ions from the bead. The constancy of bead volume after that additionally guaranteed the completed ionic transformation. After that, the solution of acid was substituted for 0.5 N NaOH solution. After two hours, the bead in the  $\text{Na}^+$  form was rinsed with 0.5 N NaCl solution thoroughly to prevent calcium or nickel hydroxides precipitation and again placed into the respective  $\text{CaCl}_2$  or  $\text{NiCl}_2$  solution. Then the changes of the bead volume with time were registered again, now from the swollen initial state. The results of the measurements were represented as the ratio of the current measured bead volume  $V_{\text{Me}}$  to the volume of the swollen bead in its  $\text{Na}^+$  form  $V_{\text{Na}}$ .

### **Study of Viscoelastic Properties of CPE**

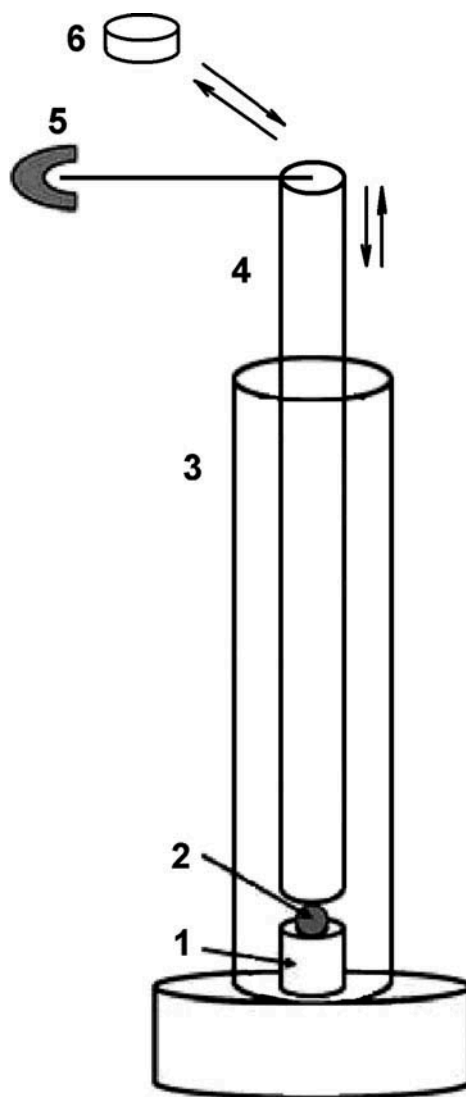
The standard equipment UIP-70 (Russia) adapted for precise dilatometric measurements on a single spherical polymeric sample (Figure 1) was used for the experiments. The adaptation of the equipment and its use for the study of swelling processes was described elsewhere.<sup>[29–31]</sup> A spherical defect-free swollen bead of 0.25–0.5 mm in diameter (measured under a microscope) and a droplet of ~0.02–0.03 mL of the corresponding equilibrium electrolyte solution were placed into a shallow spherical pit in a quartz plate. A quartz sliding rod 190 mm in length and 4 mm in diameter 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 displacement of the rod into electronic information by the instrument's capacitive sensor) that automatically registers the changes in the size of the swollen bead.

After the bead with the equilibrium solution was fixed on the support plate, the quartz sliding rod was loaded at its top with the load of 5 g and the changing of the vertical size of the bead in time was registered. After the size of the bead ceased to change, the sliding rod was unloaded, and the relaxation of the bead with time was again registered. In the same manner, the deformation of the bead was sequentially registered under increasing loads of 5, 10, 20, 50, 100 g (and 200 g in some experiments). The results were plotted as the dependence of relative axial deformation on time ( $\Delta D/D_0$ ,  $\Delta D = D - D_0$ , where  $D$  and  $D_0$  are the current and the initial diameter of the bead sample, respectively). The accuracy of determining the axial 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 wide range from 1 to 60%.

## **Results and Discussion**

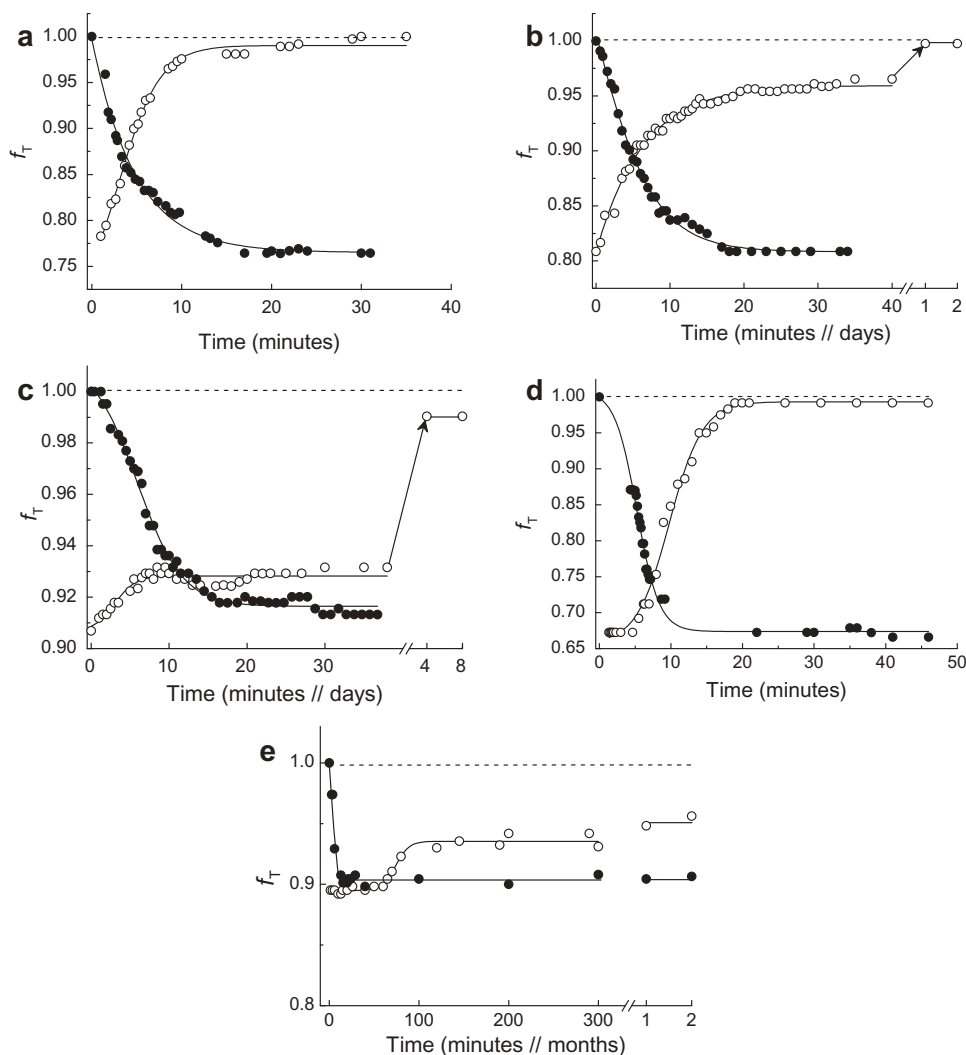
### **Temperature-induced Swelling**

Figure 2 shows the kinetics of swelling and shrinking of two carboxylic resin beads immersed into the corresponding equilibrium solutions on temperature changes. The results indicate that different resins belonging to the same narrow carboxylic gel-type of CPE can behave differently. The rates of shrinking of polymethacrylic KB-4P2 cation exchanger and of the acrylic-methacrylic copolymer AMAC cross-linked with DVB in the  $\text{Ca}^{2+}$  form (on increasing the temperature) and of its swelling back (on lowering the temperature) are sufficiently high, so that the initial volume of the bead is rapidly restored after heating and subsequent cooling (Figure 2a,d). Though there exists some difference in the rates of these two stages, this difference is not as great as in the case of other weakly cross-linked hydrophilic gels that were formerly used in dual-temperature processes of concentrating high-molecular-weight substances.<sup>[32–34]</sup> We found that the process of swelling can be well described by the well-known diffusion model proposed by Tanaka.<sup>[35]</sup> The evaluation of the diffusion coefficient of the polymer network upon swelling of the gel according to this model gives the value  $5 \times 10^{-8} \text{ cm}^2/\text{s}$ , which agrees well with



**Figure 1.** Equipment for registering the size changes of a swollen polymer bead on loading: 1, quartz support; 2, swollen polymeric bead; 3, glass tube; 4, quartz sliding rod; 5, mechanical motion transducer; 6, load.

the known data for hydrophilic gels.<sup>[32,35,36]</sup> The same KB-4P2 cation exchanger in the  $\text{Mg}^{2+}$  form behaves analogously in solutions with relatively low concentrations of  $\text{MgCl}_2$ . However, at concentrations of  $\text{MgCl}_2$  solution higher than 2 equivalents per liter, the rate of swelling upon cooling decreases substantially (Figure 2b). For the  $\text{Ni}^{2+}$  form of the resin, even at low concentrations of the external solution, the swelling proceeds considerably slower than shrinking, and the initial volume of the bead is not restored (Figure 2c). For the polyacrylic cation exchange resin KB-2e3 in the  $\text{Ca}^{2+}$  form, the shrinking of the bead on heating proceeds very rapidly. But the subsequent swelling on cooling proceeds extremely slowly and the equilibrium extent of sorption of additional amounts of water is not reached even after 2 months: after this time the volume of the bead increased only by ~6% (Figure 2e). This suggests that being once heated by 70 degrees, this resin upon cooling attains a new stationary state of swelling.



**Figure 2.** Changes of the swelling factor  $f_r$  for the KB-4P2 cation exchanger in its (a)  $\text{Ca}^{2+}$ , (b)  $\text{Mg}^{2+}$ , (c)  $\text{Ni}^{2+}$  forms in 4 N solutions of metal chlorides; (d) for the weakly cross-linked gel AMAC and (e) KB-2e3 cation exchanger in their  $\text{Ca}^{2+}$  forms in 2.5 N  $\text{CaCl}_2$ . The temperature of the samples rapidly changes from 293 K to 363 K (filled symbols) and from 363 K to 293 K (open symbols). Solid lines are approximating curves.

The discovered difference of stationary states of swelling of hydrophilic gels appears to be a very unusual phenomenon, and it may even seem improbable. However, it is appropriate to recall the work<sup>[34]</sup> in which the authors observed an incomplete collapse of temperature-sensitive poly(*N*-isopropylacrylamide) hydrogel after increasing the temperature.

The reasons for such a behavior of the CPE of carboxylic kind were elucidated by the second set of experiments.

### ***Ion-induced Swelling***

Figure 3 shows photographs obtained after a dry bead of the KB-4P2 resin in the  $\text{Na}^+$  form was placed into a 1 N  $\text{NiCl}_2$  solution. It can be seen that at the initial stages, there exists a boundary

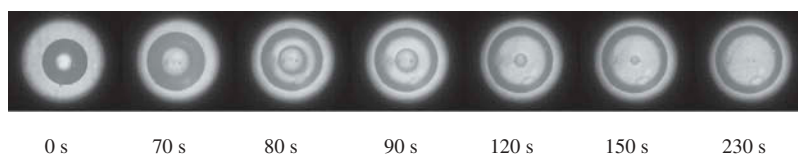


between the dry core and the swollen outer layer of the bead. As the bead swells, the dry core diminishes and finally disappears.

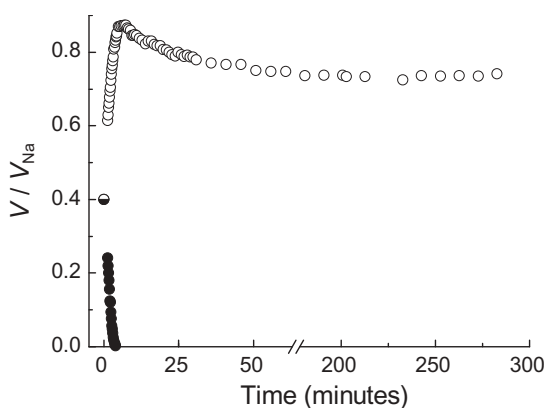
Earlier, analogous moving boundaries inside the beads were observed as well. [37–39] The authors used a weakly cross-linked copolymer—poly(0.75 sodium acrylate/0.25 acrylic acid) cross-linked with 0.06% mole fraction *N,N*-methylene-bis-acrylamide. The initially dry spherical beads with the radius from 0.05 to 0.1 mm were placed in aqueous solutions of  $\text{CuSO}_4$  or  $\text{AgNO}_3$ .

Time dependencies of the volumes of the KB-4P2 bead and its dry core in our experiments are shown in Figure 4. The total volume of the bead first increases quickly, then decreases much more slowly, reaching the stationary value. The initial dramatic increase is caused by rapid penetration of water into the  $\text{Na}^+$  form CPE bead, and the subsequent decrease by the more slow process of the exchange of  $\text{Na}^+$  ions for  $\text{Ni}^{2+}$  ions. As a result of this exchange, a more dense zone of the  $\text{Ni}^{2+}$  salt forms on the surface of the bead and gradually propagates to the center (the boundary between the  $\text{Ni}^{2+}$  and  $\text{Na}^+$  forms in the photos is indiscernible). Noteworthy is the fact that the swelling of the bead with the disappearance of the dry core completes in a few minutes, while the ion exchange with replacing of the initial system of ionic-type bonds carboxylate– $\text{Na}^+$  by the system of coordination-type bonds of  $\text{Ni}^{2+}$  ion with several carboxylate ligands takes more than an hour. The latter process is necessarily associated with the approach of several functional groups of the polymer network to the complexing metal ion and with the slow rearrangement of the conformation of respective segments of polymer chains, which results in the decrease of the volume of the swollen bead.

With the increase of the concentration of  $\text{NiCl}_2$  solution, the rate of hydration of the dry core decreases, and the approach to the equilibrium volume (or rather, to the stationary volume) of the bead also slows down. This fact reveals the role of the forming outer shell of the  $\text{Ni}^{2+}$  form. The shell



**Figure 3.** Photographs of the KB-4P2 bead showing the changes with time of the dry core and the swelling shell in 1 N  $\text{NiCl}_2$  solution at the constant temperature of 293 K. The time in seconds is indicated under the photos. The photos correspond to the initial part of the curves in Figure 4. The  $\text{NiCl}_2$  solution looks as the outer light spherical layer. The boundary between this layer and the next dark layer shows the outer boundary of the swelling bead growing in time. The dry core of the bead looks as the central sphere diminishing in time.



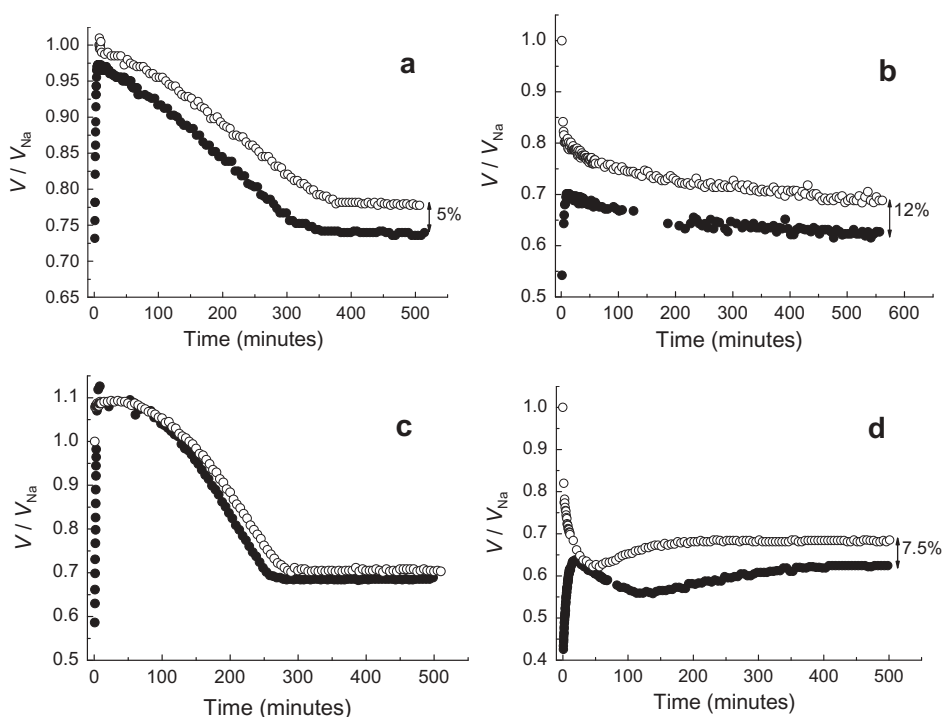
**Figure 4.** Time dependencies of the volume of the KB-4P2 bead (open symbols) and its dry core (filled symbols) in 1 N  $\text{NiCl}_2$  solution.  $V_{\text{Na}}$  is the volume of the swollen bead in the  $\text{Na}^+$  form. The initial part of the curves corresponds to the photos in Figure 3.



becomes more dense with the concentration of the solution, which hinders the interphase transfer of water and the exchange of ions, but to an even greater degree retards the conformational restructuring of the polymer network.

The role of “rigidity” or “low elasticity” of the outer shell of the bead in the  $\text{Ni}^+$  form was confirmed in the following experiments. Figure 5a,b compares the results of experiments in which the same KB-4P2 bead in the  $\text{Na}^+$  form (in the dry state in the first experiment and in the water-swollen state in the second experiment) was placed into solutions of  $\text{NiCl}_2$  or  $\text{CaCl}_2$ . Note that the final stationary volumes of the same bead in  $\text{NiCl}_2$  solution are different: the initially dry bead does not reach the final volume of the initially swollen bead. The difference in the final volumes increases with the concentration of the external solution. The data of XAFS-spectroscopy show that the beads do not contain nickel hydroxide, formation of which could be expected because of possible hydrolysis of the salt in the alkaline media inside the initial bead in its  $\text{Na}^+$  form.<sup>[40]</sup> The data of XAFS-spectroscopy also show that, regardless of the way of obtaining the final sample, from the dry or from water-swollen states, the structure of the first coordination sphere of  $\text{Ni}^{2+}$  ions, comprising at least two carboxylic groups, is virtually the same. These data indicate that the differences in the properties of KB-4P2 bead in the  $\text{Ni}^{2+}$  form obtained from different initial states are caused not by the differences in the immediate structure of complexes of  $\text{Ni}^{2+}$  in the polymer, but rather by the differences in the sets of carboxylate groups fixed in the coordination sphere of the complexing ion and, accordingly, by the differences in the conformational states of polymer chains of the gel network.

Indeed, the difference in the volumes of the same CPE bead in these two stationary states must be caused by the fact that the process of the exchange of  $\text{Na}^+$  for  $\text{Ni}^{2+}$  (Figure 5a,b) in the outer layer of the initially dry bead proceeds at a substantially lower hydration degree of polymeric chains. As a



**Figure 5.** Time dependencies of bead volumes in the experiments when the same KB-4P2 bead in  $\text{Na}^+$  form in the dry state (filled symbols) and in the 0.5 N NaCl solution-swollen state (open symbols) was placed into (a, b)  $\text{NiCl}_2$  solution and (c, d)  $\text{CaCl}_2$  solution with concentration (a, c) 0.005 N and (b, d) 4 N at constant temperature of 293 K.  $V_{\text{Na}}$  is the volume of the bead in the  $\text{Na}^+$  form swollen in the 0.5 N NaCl solution.

result of different initial distances between carboxylate ligands involved in formation of sufficiently stable dicarboxylate complexes, different sets of carboxylic groups react with migrating  $\text{Ni}^{2+}$  ions in the case of the initially dry bead compared with the situation in the preliminarily swollen bead. Here, a direct analogy is observed with the well-documented fact that upon cross-linking of linear polymeric chains in solutions by bifunctional reagents, the swelling ability of the formed gel rapidly decreases with the concentration of the initial polymer solution. [41]

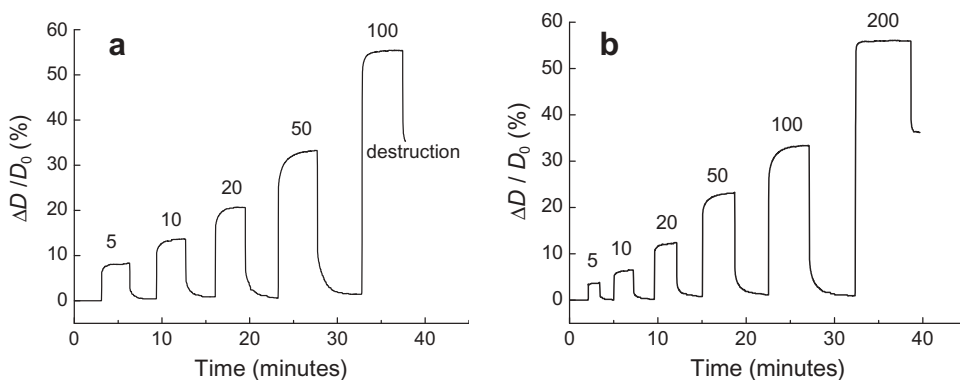
The two plots in Figure 5c show that the stationary values of the swelling factor of the KB-4P2 bead obtained from its dry and swollen initial states in dilute  $\text{CaCl}_2$  solution virtually coincide. It means that the final states of sorption of both water and calcium ions are close to the equilibrium and are slowly reached from any initial states of the bead. However, for a concentrated solution (Figure 5d), a somewhat different picture is observed. The volume of the dry bead placed into  $\text{CaCl}_2$  solution first increases because of the rapid sorption of water, then decreases as a result of the reaction of ion exchange, and then the bead continues to swell to reach the final stationary state. During this period a restructuring of the system of electrostatic bonds of calcium ions with carboxylic anions probably takes place. The salts of calcium with carboxylic groups have rather ionic than coordination character. They are much more labile than complexes of nickel, and rapidly exchange carboxylate ligands, which allow polymeric chains to change their conformational states and gradually reduce the local strains of the whole network.

### Deformation under Load

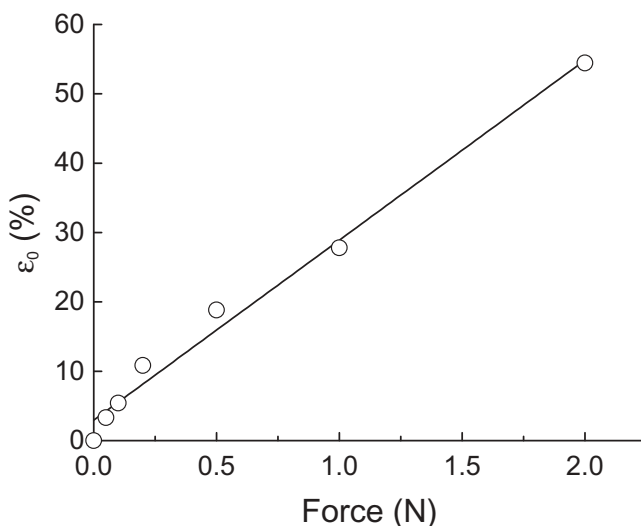
The influence of the ionic form of CPE and the concentration of the external solution manifests itself also on examining viscoelastic properties of the beads. For polymethacrylic and polyacrylic CPE in the  $\text{Na}^+$  form swollen in water, elastic deformation behavior is typical on uniaxial compression of a spherical sample. This is clearly seen in the plots of axial deformation (here  $D_0$  is the initial diameter of the bead and  $D$  is the current vertical size of the same bead under load) on periodic loading and unloading of the sample (Figure 6). The deformations proportionally increase with the magnitude of the compressive force, but rapidly vanish upon unloading, that is, remain completely reversible.

A linear dependence of the instantaneous elastic deformation on the magnitude of the compressive force is observed (Figure 7). The residual deformations do not exceed 1%, that is, remain within the measurement accuracy of the applied experimental method.

The deformation behavior of swollen-in-water KB-4P2 and KB-2e3 beads in their  $\text{Na}^+$  form allows to characterize these polymers as typical elastomers with a small modulus of elasticity. A similar elastic deformation behavior is also characteristic for the  $\text{Ca}^{2+}$  and  $\text{Ni}^{2+}$  forms of KB-4P2 and KB-2e3 beads in dilute solutions of  $\text{Me}^{2+}$  chlorides. However, the compression amplitude for the  $\text{Ca}^{2+}$  form is



**Figure 6.** Axial deformations of swollen beads of (a) KB-2e3 and (b) KB-4P2 in  $\text{Na}^+$  form on periodic loading and unloading of the samples. The load in grams is indicated over each "peak".



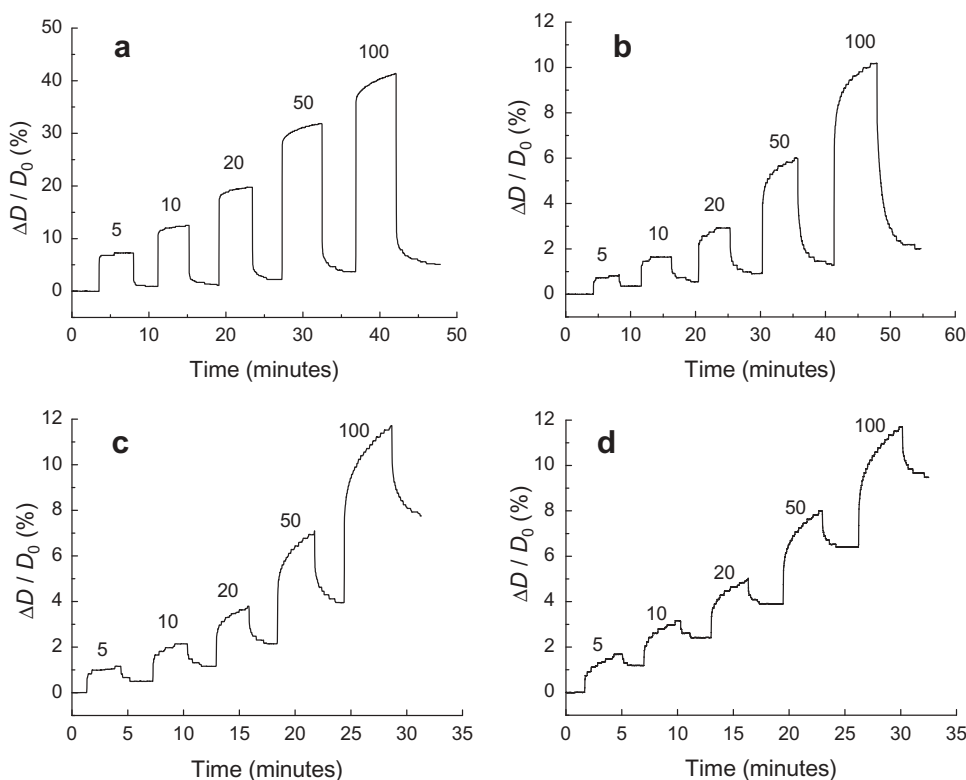
**Figure 7.** Dependence of the instantaneous elastic deformation of the swollen KB-4P2 bead in the Na-form on the magnitude of compressive force.  $R^2 = 0.988$ .

considerably smaller (about 40% for an axial force of 1 N) and for the  $\text{Ni}^{2+}$  form even smaller (not exceeding 10%) (Figure 8a,b), as compared to the flexibility (deformations amounting to 60% under the same stress) for the  $\text{Na}^+$  form of the beads (Figure 6). The more rigid structure of the polymer in the  $\text{Ca}^{2+}$  and, in particular,  $\text{Ni}^{2+}$  form can be attributed to the fact that the bivalent cations act as cross-links of the network by interacting simultaneously with two carboxylate ions. By that, in comparison with  $\text{Ca}^{2+}$  ion,  $\text{Ni}^{2+}$  ion displays a pronounced tendency to form stable complexes or chelates, which is characteristic of all transition metal ions. Apart from the electron deficiency of its  $d$ -shell, of importance is also the fact that the ionic radius of  $\text{Ni}^{2+}$  (0.7 Å) is smaller than the ionic radius of  $\text{Ca}^{2+}$  (0.94 Å), which enhances its polarizing action and increases the bond strength with electron-donating carboxylate ligands.

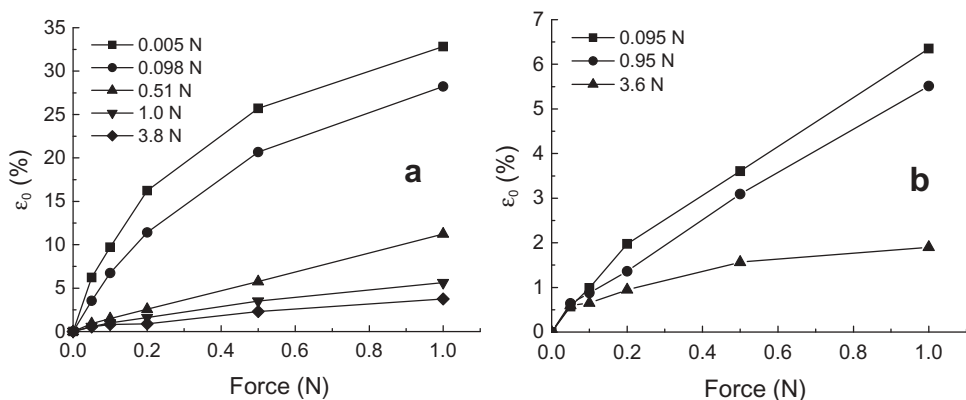
Noteworthy, with the increase of the concentration of the external  $\text{Me}^{2+}$  salt solution, both the degree of deformation of the bead under mechanical load (Figure 8) and the elastic part of deformation decrease. Accordingly, the contribution of viscoelastic deformations decreases, which manifests itself in the reduction of immediate elastic deformations (Figure 9) and in the growth of residual deformations. Here the influence of the concentration of the electrolyte on the water content of the CPE is clearly demonstrated: the lower the water content the higher the rigidity of the polymer (the extent of deformation decreases) and the slower the conformational restructuring of the polymer network under changing load (the contribution of residual deformations grows). Also clearly demonstrated is the higher rigidity of the beads substantially reinforced by the more stable nickel complex bridges. The deformability of beads in  $\text{Ni}^{2+}$  form is lower and residual deformation is higher than those for the  $\text{Ca}^{2+}$  form of CPE.

## Conclusions

Thus, it is discovered that the ion exchange resins of polymethacrylic and polyacrylic types in  $\text{Ca}^{2+}$  and  $\text{Ni}^{2+}$  forms can attain different stationary states of their swelling depending on the way of swelling. The rates of shrinking of polymethacrylic cation exchanger and of the acrylic-methacrylic copolymer cross-linked with DVB in the  $\text{Ca}^{2+}$  form (on increasing the temperature) and of its swelling back (on lowering the temperature) are sufficiently high, so that the initial volume of the bead is rapidly restored after heating and subsequent cooling. The same polymethacrylic resin in the  $\text{Mg}^{2+}$  form behaves analogously in solutions with relatively low concentrations of  $\text{MgCl}_2$ . However,



**Figure 8.** Axial deformations for KB-4P2 in (a, c)  $\text{Ca}^{2+}$  form and (b, d)  $\text{Ni}^{2+}$  form on periodic loading and unloading of the samples swollen in (a, b) 0.005 N and in (c, d) 3.8 N solutions of  $\text{CaCl}_2$  and  $\text{NiCl}_2$ , respectively. The load in grams is indicated over each "peak".



**Figure 9.** Isochronous dependencies of immediate elastic deformations of the KB-4P2 bead in the  $\text{Ca}^{2+}$  (a) and  $\text{Ni}^{2+}$  form (b) on the magnitude of compressive force for different concentrations of the external solution.

at concentrations of  $\text{MgCl}_2$  solution higher than 2 N, the rate of swelling upon cooling decreases substantially. For the  $\text{Ni}^{2+}$  form of the resin, even at low concentrations of the external solution, the swelling proceeds considerably slower than shrinking, and the initial volume of the bead is not restored. For the polyacrylic resin cross-linked with dimethacrylate triethyleneglycole in the  $\text{Ca}^{2+}$  form, the shrinking of the bead on heating proceeds very rapidly. But the subsequent swelling on cooling proceeds extremely slowly and the equilibrium extent of sorption of additional amount of

water is not reached even after 2 months. It is also discovered that the dry and the swollen in the 0.5 N NaCl solution beads of the polymethacrylic resin in the  $\text{Na}^+$  form after being placed in solution of  $\text{CaCl}_2$  or  $\text{NiCl}_2$  attain different stationary states of swelling. The difference in the degree of swelling increases with the concentration of the external solution. The ionic form of crosslinked polyelectrolytes of acrylic and methacrylic types and the concentration of the solution affects the elastic-plastic properties of the gel: in sodium chloride solutions either dilute or concentrated and in dilute solution of calcium chloride gels exhibit elastic properties, whereas in concentrated solutions of calcium chloride and in solutions of nickel chloride plasticity manifests itself in the deformation.

## References

1. Hirokawa, Y.; Tanaka, T. Volume phase transition in a non ionic gel. *J. Chem. Phys.* **1984**, *81*(12), 6379–6380.
2. Katayama, S.; Ohata, A. Communications to the editor (Phase transition of a cationic gel). *Macromolecules*. **1985**, *18*(12), 2781–2782.
3. Inomata, H.; Goto, S.; Saito, S. Phase transition of N-substituted acrylamide gels. *Macromolecules*. **1990**, *23*(22), 4887–4887.
4. Beltran, S.; Baker, J.; Hooper, H.; Blanch, H.; Prausnitz, J. Swelling equilibria for weakly ionizable, temperature-sensitive hydrogels. *Macromolecules*. **1991**, *24*(2), 549–551.
5. Katayama S. Chemical condition responsible for thermoswelling or thermoshinking of volume phase transition in gels. Effect of relative amounts of hydrophobic to hydrophilic groups in the side chain. *J. Phys. Chem.* **1992**, *96*(13), 5209–5210.
6. Hirotsu, Sh.; Hirokawa, Y.; Tanaka, T. Volume phase transitions of ionized N-isopropylacrylamide gels. *J. Chem. Phys.* **1987**, *87*(2), 1392–1395.
7. Cai, W.; Anderson, E. C.; Gupta, R. B. Separation of lignin from aqueous mixtures by ionic and nonionic temperature-sensitive hydrogels. *Ind. Eng. Chem.* **2001**, *40*(10), 2283–2288.
8. Yang, M.; Liu, C.; Li, Z.; Gao, G.; Liu, F. Temperature-responsive properties of poly(acrylic acid-co-acrylamide) hydrophobic association hydrogels with high mechanical strength. *Macromolecules*, **2010**, *43* (24) 10645–10651.
9. Gehrke, S. H.; Andrews, G. P.; Cussler, E. L. Chemical aspects of gel extraction. *Chem. Eng. Sci.* **1986**, *41*(8), 2153–2160.
10. Cussler, E. L. Temperature-sensitive method of size-selective extraction from solution. U.S. Pat. 4,828,701, **1989**.
11. Roepke, D. C.; Goyal, S. M.; Kelleher, C. J.; Halvorson, D. A.; Abraham, A. J.; Freitas, R. F. S.; Cussler, E. L. Use of temperature-sensitive gel for concentration of influenza virus from infected allantoic fluids. *J. Virological Methods*. **1987**, *15*, 25–31.
12. Freitas, R. F. S.; Cussler, E. L. Temperature sensitive gels as extraction solvents. *Chem. Eng. Sci.* **1987**, *42*(1), 97–103.
13. Cai, W.; Gupta, R. B. Poly(N-ethylacrylamide) hydrogels for lignin separation. *Ind. Eng. Chem.* **2001**, *40*(15), 3406–3412.
14. Kim, J. J.; Park, K. Smart hydrogels for bioseparation. *Bioseparation*. **1998**, *7*(4–5), 177–184.
15. Kim, J. J.; Park, K. *Applications of smart hydrogels in separation*, in *Smart Polymers for Bioseparation and Bioprocessing*; Mattiasson, B.; Galaev, I., Eds.; Taylor & Francis: London, UK and New York, NY, **2002**, p. 140–162.
16. He, Q. W.; Sun, Y. S.; Tong, S. X.; Zhou, X. Synthesis of temperature sensitive hydrogel beads and their separation properties. *Ion Exch. Adsorpt.* **1990**, *6*(6), 418–424.
17. Sun, Y. S.; Qiu, Z. Y.; Hong, Y. L. Application of nonionic temperature sensitive hydrogel for concentration of protein aqueous solution. *Chin. J. Polym. Sci.* **1992**, *10*(4), 311–318.
18. Park, C. H.; Igacio, O. A. Concentrating cellulases from fermented broth using a temperature-sensitive hydrogel. *Biotechnol. Prog.* **1992**, *8*, 521–526.
19. Park, C. H.; Igacio, O. A. Concentrating cellulases using a temperature-sensitive hydrogels: effect of gel particle size and geometry. *Biotechnol. Prog.* **1993**, *9*, 640–646.
20. Ichijo, H.; Kishi, R.; Hirasa, O.; Takiguchi, Y. Separation of organic substances with thermoresponsive polymer hydrogel. *Polymer Gels and Networks*. **1994**, *2*(3), 315–322.
21. Han, J.; Park, C. H.; Ruan, R. Concentrating alkaline serine protease, subtilisin, using a temperature-sensitive hydrogel. *Biotechnol. Lett.* **1995**, *17*(8), 851–852.
22. Park, J. H.; Park, C. H.; Chung, I. S. Concentrating autographa californica nuclear polyhedrosis virus and recombinant alkaline phosphatase from insect cells using a temperature-sensitive hydrogel. *Cytotechnology*. **1997**, *25*, 227–230.

23. Karpuk, E. A.; Korotkikh, O. I.; Ivanov, V. A. Changes in thermodynamic functions in the two-temperature process of concentration and purification of electrolyte solutions on KB-4P2 polymethacrylic ionite. *Russian J. Phys. Chem.* **2012**, 86(2), 184–189.
24. Budtova, T.; Suleimenov, I. Physical principles of using polyelectrolyte hydrogels for purifying and enrichment technologies. *J. Appl. Polym. Sci.* **1995**, 57, 1653–1658.
25. Budtova, T. V.; Suleimenov, I. E.; Frenkel, S. Ya. Highly swelling polymer networks: some modern problems and perspectives, a review. *Zh. Prikladnoi Khim.* (Journal of Applied Chemistry, in Russian). **1997**, 70(4), 529–539.
26. Ivanov, V. A.; Gavlina, O. T.; Gorshkov, V. I.; Yaroslavl'tsev, A. A. Two-temperature concentrating of electrolyte solutions on ionites. *Russ. J. Phys. Chem.* **2005**, 79(7), 1174–1175.
27. Karpuk, E. A.; Korotkikh, O. I.; Gavlina, O. T.; Ivanov, V. A. Dual-temperature reagentless concentration of solutions of electrolytes based on the influence of temperature on the sorption of water by ionites. *Russ. J. Phys. Chem.* **2011**, 85(4), 684–689.
28. Toroptseva, A. M.; Belogorodskaya, K. V.; Bondarenko, V. M. Laboratory workshop on chemistry and technology of high-molecular compounds. Leningrad: Chemistry Publ. **1972**. 416 p. (In Russian).
29. Pastukhov, A. V.; Davankov, V. A.; Sidorova, E. V.; Shkol'nikov, E. I.; Volkov, V. V. Deformation of styrene-divinylbenzene copolymers and hypercrosslinked polystyrenes during solvent adsorption and desorption. *Russ. Chem. Bull.* **2007**, 56(3), 484–493.
30. Davankov, V. A.; Pastukhov, A. V. Paradoxes of Thermodynamics of Aqua-Vapor-Polymer Interface Equilibrium. *Russian J. Phys. Chem. A.* **2011**, 85(5), 721–729.
31. Davankov, V. A.; Pastukhov, A. V. Paradoxes of Thermodynamics of Swelling Equilibria of Polymers in Liquids and Vapors. *J. Phys. Chem. B.* **2011**, 115(51), 15188–15195.
32. Kabra, B. G.; Akhtar, M. K.; Gehrke, S. H. Volume change kinetics of temperature-sensitive poly(vinyl methyl ether) gel. *Polymer.* **1992**, 33(5), 990–995.
33. Park, C. H.; Orozco-Avila, I. Concentrating cellulases from fermented broth using a temperature-sensitive hydrogel. *Biotechnol. Prog.* **1992**, 8(6), 521–526.
34. Park, C. H.; Orozco-Avila, I. Concentrating cellulases using a temperature-sensitive hydrogel: effect of gel particle size and geometry. *Biotechnol. Prog.* **1993**, 9(6), 640–646.
35. Tanaka T.; Fillmore D. J. Kinetics of swelling of gels. *J. Chem. Phys.* **1979**, 70(3), 1214–1218.
36. Tanaka, T.; Sato, E.; Hirokawa, Y.; Hirotsu, S.; Peetermans, J. Critical kinetics of volume phase transition of gels. *Phys. Rev. Lett.* **1985**, 55(22), 2455–2458.
37. Budtova, T.; Suleimenov, I.; Frenkel, S. Peculiarities of the kinetics of polyelectrolyte hydrogel collapse in solutions of copper sulfate. *Polymer.* **1995**, 36(10), 2055–2058.
38. Budtova, T.; Navard, P. Swelling-Induced Birefringence of a Polyelectrolyte Gel Strongly Interacting with Metal Ions. *Macromolecules.* **1997**, 30(21), 6556–6558.
39. Budtova, T.; Navard, P. Swelling kinetics of a polyelectrolyte gel in water and salt solutions. Coexistence of swollen and collapsed phases. *Macromolecules.* **1998**, 31(25), 8845–8850.
40. Trofimova, N. N.; Titova, O. I.; Karpuk, E. A.; Ivanov, V. A.; Slovokhotov, Yu. L.; Zubavichus, Ya. V.; Pomogailo, A. D. Local coordination of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  cations in polyacrilate matrices. *Bull. Russ. Acad. Sci.: Physics.* **2013**, 77(9), 1127–1130.
41. Davankov, V. A.; Rogozhin, S. V.; Tsyurupa, M. P. Factors determining the swelling power of crosslinked polymers. *Angew. Makromol. Chem.* **1973**, 32, 145–151.