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Swelling and mechanical behavior of ionized poly(acrylamide-*co*-*N*,*N*'-diethylacrylamide) gels in water/acetone mixtures and in water at various temperatures

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Summary

Ionized networks of random copolymers of acrylamide (AAm) and N,N'-diethylacrylamide (DEAAm) (mole ratios of $x_{\mathrm{AAm}}/x_{\mathrm{DEAAm}}$ = 1/0, 0.75/0.25, 0.5/0.5, 0.30/70, 0.15/0.85, 0/1) with various amounts of ionic comonomer-sodium methacrylate (MNa) (mole ratios to all monomers x_{MNa} = 0.0, 0.025, 0.05) and crosslinker - N,N'-methylenbisacrylamide (MBAAm) were prepared at high dilution in water. Their swelling and mechanical behavior was investigated in water at various temperatures (from 10 to 90°C) and in water/acetone (*w/a*) mixtures at room temperature. For some copolymers the transition region from expanded to collapsed state was observed at critical concentration of acetone, a_c, in *w/a* mixtures or at critical temperature, T_c, in water. It was found that with increasing content of DEAAm component in copolymers the a_c values increase; the similar increase was observed with increasing x_{MNa}. Neat PDEAAm and copolymers with the highest DEAAm content exhibit temperature transition; both increasing amount of AAm and charges bound on the chains (x_{MNa}) in copolymers shifts the T_c temperatures to higher values very efficiently (for more than 20°C).

Introduction

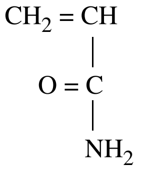
Polyelectrolyte hydrogels exhibit high swelling and the first order phase transition (collapse) caused by a small changes in external parameters such as temperature, solvent composition, electric field and etc. [1-4]. While in charged poly(acrylamide) (PAAm) networks the collapse can be brought about by changes in the solvent compositions (e.g. water/acetone), in poly(*N,N'*-isopropylacrylamide) (PIPAAm) and poly(*N,N'*-diethylacrylamide) (PDEAAm) gels (both polymers exhibit low critical solution temperature (LCST) at ~ 30°C), the transition can be induced in neat water by temperature changes [3,5,6]. Both the extent of the collapse and the critical acetone concentration, a_c, or transition temperature, T_c, are dependent on network formation procedure and on amount of charges bound on the chain [5,6].

Copolymerization of two monomers is an effective method of modification of physical properties of polymers and gels. Several authors [7–11], who have studied temperature collapse in PIPAAm hydrogels, reported that while incorporation of a hydrophilic comonomer leads to a higher LCST, incorporation of a hydrophobic monomer lowers the critical temperature T_c. From the investigations of swelling behavior of ionized networks of statistical copolymers of *N*-vinylcaprolactam and 1-vinyl-2-pyrrolidone in water/ethanol mixtures, it was found that critical acetone concentration at the transition, a_c, slightly increased with increasing amount of more hydrophobic *N*-vinylcaprolactam component [12].

This work investigates the effect of amount of bound charges and composition of poly(acrylamide-*co*-*N*,*N*'-diethylacrylamide) ionized networks on their swelling and mechanical behavior in water/acetone mixtures at room temperature and in water at various temperatures. One can expect that some of these networks will simultaneously exhibit the transition on solvent composition as well as on temperature, and critical values of a_c and/or T_c will be affected by charge concentration and composition of copolymer. As in last decades thermo-sensitive hydrogels have been used in various biotechnological fields [4,13], one can expect that changes in composition and ionization allow to direct physical properties of hydrogels to practical applications.

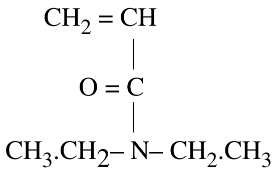
Experimental

Materials: Commercial acrylamide (AAm) and *N*,*N*'-diethylacrylamide (DEAAm) were used:



$$CH_2=CH-C(=O)-NH_2$$

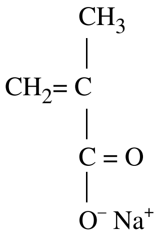
acrylamide



$$CH_2=CH-C(=O)-N(CH_2.CH_3)_2$$

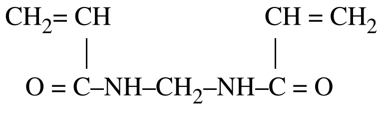
N,N'-diethylacrylamide

Sodium methacrylate (MNa) was used as negatively charged comonomer and *N,N'*-methylenbisacrylamide (MBAAm) was used as crosslinker:



$$CH_2=C(CH_3)-C(=O)-O^-\,Na^+$$

sodium methacrylate



$$CH_2=CH-C(=O)-NH-CH_2-NH-C(=O)-CH=CH_2$$

N,N'-methylene-*bis*-acrylamide

Preparation of networks: acrylamide, *N,N'*-diethylacrylamide, and sodium methacrylate were used for preparation of ionized networks of copolymers of P(AAm-*co*-DEAAm) with various mole ratios of AAm/DEAAm ($x_{\text{AAm}}/x_{\text{DEAAm}}$ = 1/0, 0.75/0.25, 0.5/0.5, 0.3/7, 0.15/0.85, 0/1) and with mole fractions of MNa related to sum of AAm and DEAAm monomers (x_{MNa} = 0, 0.025, 0.05; Table 1). Networks were formed in presence of the crosslinker - *N,N'*-methylenbisacrylamide (x_{MBAAm} = 0.003); as an initiator redox system - N,N,N',N'-tetramethylethylenediamine and ammonium persulfate - was used. Crosslinking copolymerization of water/monomers mixtures (10 g of all monomers was dissolved in total 100 ml of aqueous solutions flushed with nitrogen) was performed in glass ampoules (~ 10 mm in diameter) at room temperature for 24 h; the volume fractions of all monomers in mixtures were $v_{\text{m}} = 0.1/\rho_{\text{m}}$ (ρ_{m} is the density of monomer mixtures; ρ_{m} = 1.122 for AAm and 0.923 g.cm^{-3} for DEAAm; for mixtures ρ_{m} was calculated from weight fractions of AAm and DEAAm). After copolymerization the networks were removed from ampoules, cut into cylinders ~10 mm in height and extracted with redistilled water.

Swelling and mechanical measurements: After extraction, the samples (~ 1 cm^3 in volume) were immersed in 100 ml water/acetone (*w/a*) mixtures or in neat water flushed with nitrogen; swelling proceeded for one month in *w/a* mixtures at room temperature or 4 days at various constant temperatures. Then the inverse swelling ratio X, relative to the network formation state, was calculated from [5]

$$X = (D^*/D)^3 = V^*/V \qquad \textbf{(1)}$$

where D^* and D, respectively, are the sample diameters after preparation and swelling in mixtures or in water at chosen temperature and V^* and V are corresponding sample volumes. The sample diameters were measured with a traveling microscope (Abe comparator). From X values, the volume fractions of dry polymer in the swollen state $v_2 = v_1 X$ were determined; $v_1 = v_{\text{m}}(\rho_{\text{m}}/\rho_{\text{d}}) = 0.1/\rho_{\text{d}}$ is the volume fraction of dry polymer at network formation, ρ_{d} is the dry density of networks (ρ_{d} = 1.35, 1.28, 1.20, 1.14, 1.10 and 1.07 g.cm^{-3} for networks with x_{AAm} = 1, 0.75, 0.5, 0.3, 0.15 and 0, respectively). The equilibrium swelling degrees relative to the dry state, $Q = 1/v_2$, were also determined; the swelling degrees of all networks in water at room temperature, Q_{w}, are shown in Table 1.

The mechanical experiments were carried out in uniaxial compression [5] on the same samples which were used in swelling measurements. In the apparatus temperature chamber (which could be filled by diluents through which nitrogen is passing) was used. The sample (immersed in water heated to chosen temperature or in *w/a* mixture at room temperature) was compressed to a ratio λ ($\lambda = l/l_0$ where l and l_0, respectively, are compressed and initial heights) and force f was measured after 30 s relaxation (time sufficiently long for attaining equilibrium). Usually ten values of λ and f were determined ($0.8 < \lambda < 1$); the shear modulus G was calculated from [5]

$$G = f/[S_0(\lambda^{-2} - \lambda)] \qquad \textbf{(2)}$$

where S_0 is the initial cross-section of the specimen. As one measurement lasted 300 s no systematic weight changes of samples were observed before and after measurements.

The mechanical experiments were done also just after networks preparation at room temperature (modulus G_1, Table 1). From G_1, the concentration of elastically active network chains (EANCs) relative to the dry state υ_{d} was determined from [5]

$$\upsilon_d = G_1/(R\ v_1\ T_1) \qquad (\mathbf{3})$$

where R is the gas constant and T_1 = 298 K is temperature of measurements (Table 1). From modulus G and G_1 the reduced modulus

$$G_r = G/G_1 \qquad (\mathbf{4})$$

was also determined.

Table 1. Composition, mechanical and swelling parameters of poly(AAm-*co*-DEAAm) hydrogels

x_{AAm}/ x_{DEAAm}	x_{MNa}	G_1 kPa	$\upsilon_d.10^5$ mol cm^{-3}	Q_w. 25 °C	χ	Φ
1.00/0.00	0	9.8	4.96	20.7	0.492	–
0.75/0.25	0	11.1	5.38	19.3	0.498	–
0.50/0.50	0	10.8	5.02	17.5	0.500	–
0.30/0.70	0	9.6	4.32	16.2	0.510	–
0.15/0.85	0	9.3	4.04	14.4	0.507	–
0.00/1.00	0	9.7	4.11	12.6	0.512	–
1.00/0.00	0.025	9.8	4.96	70.1		0.36
0.75/0.25	0.025	10.8	5.24	51.1		0.31
0.50/0.50	0.025	11.2	5.16	41.3		0.20
0.30/0.70	0.025	11.1	4.99	34.1		0.21
0.15/0.85	0.025	10.4	4.53	33.3		0.15
0.00/1.00	0.025	10.3	4.38	31.2		0.13
1.00/0.00	0.05	10.1	5.11	111.9		0.28
0.75/0.25	0.05	11.4	5.53	100.5		0.25
0.50/0.50	0.05	11.8	5.48	80.3		0.21
0.30/0.70	0.05	11.1	4.99	79.7		0.18
0.15/0.85	0.05	10.5	4.59	66.2		0.15
0.00/1.00	0.05	11.8	5.02	61.6		0.14

Results and discussion

Coil-to-globule transition in poly(*N*,*N*'-dialkylacrylamides) single chains and gels has been usually explained as a result of balance between hydrophilic and hydrophobic forces [14,15]. In most cases, hydrophilic forces are facilitated by hydrogen bonding interactions of –CONH$_2$ group with water while hydrophobic interactions are driven by intermolecular association of hydrophobic groups, such as ethyl groups of PDEAAm. As was pointed out [16], none of suggestions can explain why a simple change in chemical structure between AAm and IPAAm results in completely different temperature phase diagrams for their polymers in water. Ilmain *et al.* [17] suggested that behavior of PAAm in water is due to hydrogen bonding while that of PIPAAm is due to hydrophobic association, although no attempt was made to explain what exactly that association meant. The extended chain conformation is energetically favored by lower enthalpy due to hydrogen bonding between the amide group of polymer and hydrogen of water. So, the free-energy of polymer chains at temperatures below the LCST is dominated by enthalpy. But the highly directional hydrogen bonding also constrains the thermal fluctuations of polymer chains. Thus, the energy expended by polymer chain to accommodate hydrogen bonding increases with temperature and can reach a critical point where it seeks entropic compensation. So, coil-to-globule transition occurs if entropic gain at the critical temperature offsets the increased enthalpy due to hydrogen-bond-breaking; unbound amide and carbonyl groups are energetically expensive. The polymer chains remain in a stable globular conformation only if the increase in conformational entropy is also facilitated by intramolecular hydrogen bonding between amide and carbonyl groups thus decreasing the bond enthalpy. PAAm and PDEAAm are quite similar in their chemical structure; the former is a hydrogenous version of the latter. In PAAm, collapsed globule conformation is not energetically favorable since the unpaired proton on amide group results in higher enthalpy. This requires that water is absorbed in large amounts at all temperatures and the polymer remains in extended chain conformation – enthalpy dominates entropy at all temperatures.

Effect of Network Formation Conditions on the Network Structure: As follows from Table 1, at roughly constant network formation conditions (amount of water and crosslinker), the equilibrium modulus G_1 after network formation is in the first approximation independent of the copolymer composition and of the charge concentration. From that it follows that also crosslinking density υ_d related to the dry volume is constant. As expected, with increasing fraction of charges on the chain, x_{MNa}, the swelling degree in water at room temperature, Q_w, increases for all three network series. On the other hand, increasing amount of DEAAm in copolymers decreases the swelling degree in water; this fact means that amphiphilic DEAAm, due to two ethyl groups attached to nitrogen, is more hydrophobic than AAm.

Swelling and Mechanical Behavior in Water/Acetone Mixtures at Room Temperature: A continuous or jumpwise change in the volume of the gel (in the degree of swelling Q) with increasing volume concentration of acetone, a, in the w/a mixtures can be seen in Fig. 1. Incorporation of more hydrophobic DEAAm component into networks results in shifting of the transition region from expanded (low a values) to collapsed (high a values) state to higher acetone concentrations in all three series. While for uncharged networks the transition region interval lies in the range from ~40 to 95 vol. % of acetone for charged copolymers this interval is in the range from ~50 to 95 vol. %. This indicates that both increasing DEAAm and charge content in networks stabilizes hydration of chains. Acetone can interact with polymer segments through the polar and unpolar groups, while water lacks the non-polar group. With increasing hydrophobic DEAAm content in networks, acetone becomes a better solvent for gels. Shrinkage of gels is caused by dehydration of chains due to stronger hydrophobic interactions between acetone and polymer; once acetone molecules destroy a part of hydration shell, the damage propagates through entire hydration structure and dehydrated chains associate to form a collapsed structure. In this state, acetone molecules are adsorbed on collapsed structure.

As follows from Fig. 1 the jumpwise change in log Q in dependence on a takes place in most networks with $x_{MNa} \geq 0.025$; for two highest DEAAm contents only small decrease in log Q at a ~ 95–100 vol.% is observed. Fig. 2 shows that the critical acetone concentrations at which transition appeared, a_c, only slightly depend on the charge concentration (especially at high DEAAm content) and increase with DEAAm content; for uncharged networks the a_c values were determined as acetone concentrations where slope d(log Q)/da has a maximum. The dependences of the reduced modulus, G_r (Eq. (4)) on a in w/a mixtures are also shown in Fig. 1. As expected, a jump in the volume of the gel is reflected also in a jumpwise change in the reduced modulus. For copolymers with $x_{MNa} = 0$, continuous dependences of log *Q* on *a* are accompanied by continuous dependences of modulus G_r on *a*.

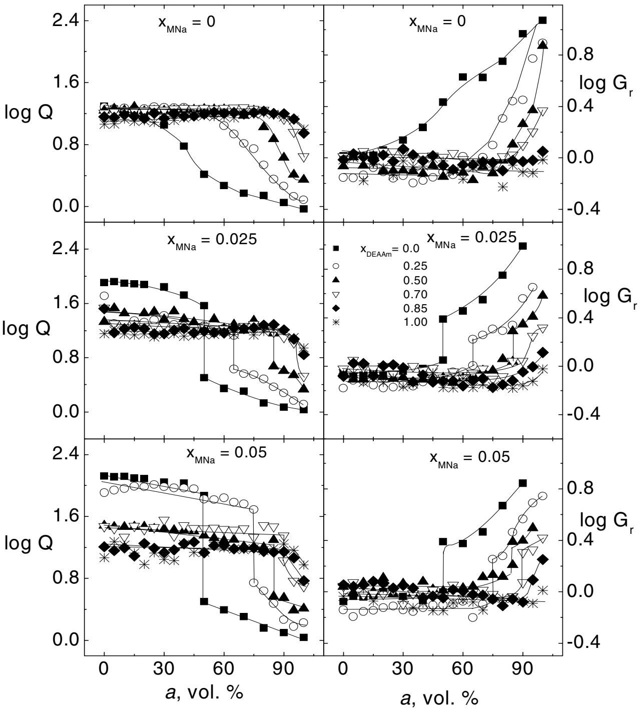


Figure 1. Dependence of the swelling degree, log *Q*, and reduce modulus log G_r on acetone concentrations *a*, for gels with indicated mole fractions of DEAAm, x_{DEAAm} and for indicated mole ratios of sodium methacrylate, x_{MNa}

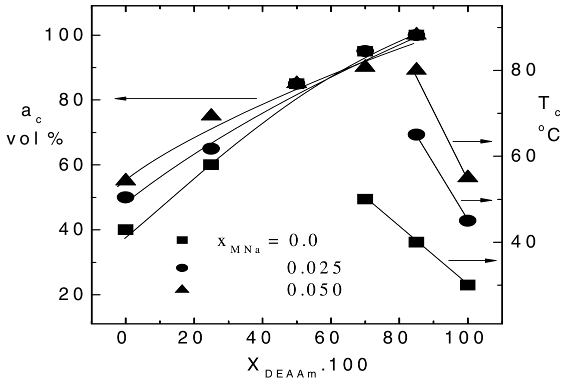


Figure 2. Dependence of the critical acetone concentrations, a_c, and transition temperature T_c, at which transition from expanded to collapsed state appeared on composition of copolymers

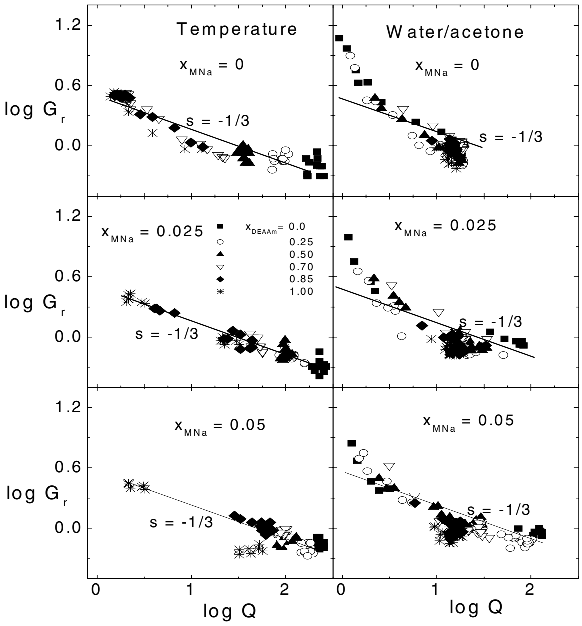


Figure 3. Dependence of reduced shear modulus log G_r on log Q for variously ionized gel with different fractions of DEAAm in copolymers measured in *w/a* mixtures at room temperature and in water at various temperatures

The dependences of log G_r on log Q of all three series copolymers measured in *w/a* mixtures are plotted in Fig. 3. For comparison, the predicted rubber elasticity slope [18] for the dependence of log G_r *vs.* log Q, $s = -0.33$, is also shown. Departures from the straight line in the region of low swelling (log $Q < 0.2$) are probably due to the influence of the main transition region (vitrification) at high acetone concentrations [5]. Stronger swelling dependence of the modulus with the slope $s = -5/6$ was suggested by the theory of Rubinstein *et. al.* [19] based on the scaling concept of the polyelectrolyte chain.

Swelling and Mechanical Behavior in Water at Various Temperatures: The dependences of swelling ratio in water, log Q, and reduced modulus log G_r, on temperature, T, are shown in Fig. 4. A continuous change in log Q from the expanded (low temperatures) to collapsed (high temperatures) state with increasing temperature can be seen for three uncharged networks with the highest contents of DEAAm (x_{DEAAm} = 1, 0.85 and 0.70). On the other hand only two charged networks with x_{DEAAm} = 1 and 0.85 exhibit jumpwise change in volume at temperature T_c. The copolymers with higher content of AAm exhibit log Q values practically independent of T. Incorporation of AAm, the more hydrophilic component, into copolymers results in pronounced shift of T_c to higher temperatures in all three series (Fig. 2); for uncharged networks the T_c values were determined as the temperatures where slope d(log Q)/dT has a maximum. From Fig. 2 it can be seen that both increasing x_{AAm} and x_{MNa} values shift the transition to higher temperatures very efficiently (more than 20 °C). This indicates that with increasing fraction of AAm as well as charge content in networks, the extent of hydrogen bonding increases and water becomes a better solvent for gels.

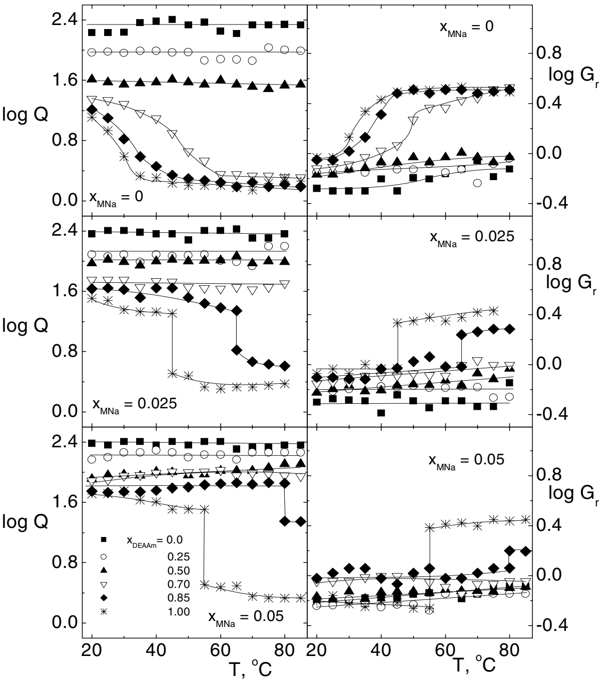


Figure 4. Dependence of the swelling degree in water, log Q, and reduced modulus log G_r on temperature T for gels with indicated mole fractions of DEAAm, x_{DEAAm} and for indicated mole ratios of sodium methacrylate, x_{MNa}

These results can be helpful in practical applications of hydrogels as they show the possibility of adjusting T_c by composition of copolymer to the required values.

The dependences of the reduced shear modulus, G_r (Eq. 4) on temperature are also shown in Figure 4. As expected, a decrease in the volume of the gel is reflected in an increase of the G_r and continuous or jumpwise dependences of log G_r on T are observed for networks with continuous or jumpwise dependences of log Q on T. The dependences of the log G_r on log Q for three series of copolymers with various ratios x_{MNa} are plotted in Fig. 3. As in previous case, the predicted rubber elasticity slope [18] for the dependence of log G_r vs log Q, $s = -0.33$, is also shown; one can see that theory describes quite well experimental data for all network. For hydrogels measured in water at various temperatures no vitrification effect is seen in Fig. 3 at low swelling (log $Q < 0.2$) as in the case in *w/a* mixtures; we believe that high temperatures compensate low swelling so that all copolymers are deeply in the rubbery region. Since good correlation exists between log G_r and log Q we can conclude that mechanical behavior of all hydrogels is predominantly determined by the swelling degree.

Comparison of Swelling Data with the Theory of Polyelectrolyte Networks: Several models have been suggested for describing the swelling degree of charged gels [1,2,5,6]. For comparison of swelling results with theory, we will use our generalized model in which the effects of repulsion of charges on the chain and finite chain extensibility were included [2]; in this model, all molecular parameters are independently accessible. This theory semiquantitatively described the collapse phenomenon of various charged gels in *w/a* mixtures and at various temperatures [5, 20, 21]. The theory predicts the swelling pressure P as a sum of four terms [2]

$$P = \mu_1/V_1 = P_m + P_{el} + P_{os} + P_{els} \qquad \mathbf{(5)}$$

where μ_1 is the chemical potential of the solvent, V_1 is the molar volume of the solvent, P_m is the Flory-Huggins (FH) mixing term given by mixing solvent molecules with chain segments (in this approach monomer/water and hydrophilic/hydrophobic interactions are included in the apparent FH χ parameter), P_{el} is the elastic term given by the change in elastic energy with swelling in which finite chain extensibility was included, P_{os} is the osmotic term given by mixing network ions with the solvent and P_{els} is the electrostatic term determined by the interaction (repulsion) of charges on the chain.

As all experimental swelling data were collected for free swelling $P = 0$ in Eq. 5 will be used in further analysis. The individual terms P_i of Eq. 5 were expressed in network molecular parameters [2,5] - the concentration of elastically active network chains υ_d (Table I), density of dry networks ρ_d, average molecular weight of monomer unit M (= $x_{AAm}M_{AAm} + x_{DEAAm}M_{DEAAm}$), molar volumes of *w/a* mixtures V_1 (determined earlier [22]) or water V_1 18.1 cm^3/mol, volume fractions of dry polymer at network formation v_1, the dielectric constants of mixed solvents or water D ($D = 80$ for water and 21 for acetone; for *w/a* mixtures the linear dependence of D on a was used).; as low fractions of MNa were used and pH of external solvents were higher than pK$_0$ of methacrylic acid we assumed, in the first approximation, that the degree of ionization $\alpha = x_{MNa}$. Using Eq. 5 with $P = 0$, the dependence of the apparent interaction parameter χ on the volume fraction of dry polymer in the swollen state, $v_2 = 1/Q$, can be calculated from experimental equilibrium Q values measured in *w/a* mixtures or in water at various temperatures by employing the same procedure described in detail earlier [2,5].

The application of Eq. 5 (with $P = 0$) for the uncharged series ($\alpha = x_{MNa} = 0$, $P_{os} = P_{els} = 0$, classical Flory-Huggins equation is restored) and using the Q_w values measured at room temperature (expanded state of gels, Table 1), leads to the values of the apparent interaction parameters χ shown in Table I. As expected with increasing x_{DEAAm} the χ values slightly increase due to a decrease in Q_w; for all copolymers these values are higher than 0.5. The increase of χ means that increasing content of hydrophobic DEAAm component in copolymers slightly decreases the overall hydration of P(AAm/DEAAm) chains in neat water. Finally, from Q_w data of uncharged networks measured at various *w/a* compositions and temperatures (Fig. 5), the universal increase of χ with increasing v_2 shown in Fig. 5, independent of composition of hydrogels was obtained. Such universal dependences were observed earlier [5].

As expected, the swelling degree in water Q_w measured at room temperature increases with increasing content of charged groups on the chain x_{MNa} (Table 1). Similarly to previous cases [5, 20, 21], the use of Eq. 5 for ionic networks with the degree of ionization $\alpha = x_{MNa} > 0$ gives unrealistic high χ values calculated from Q_w (for networks of various compositions with x_{MNa} = 0.025, 0.05, χ values in the region 0.65–0.85 were obtained). Since, as mentioned in the used theory, χ is a measure of polymer–water interactions when all charges are screened (the effect of charges is included in P_{os} and P_{els} terms), χ values shown in Table 1 for uncharged networks may be, in the first approximation, required also for corresponding ionic hydrogels swollen

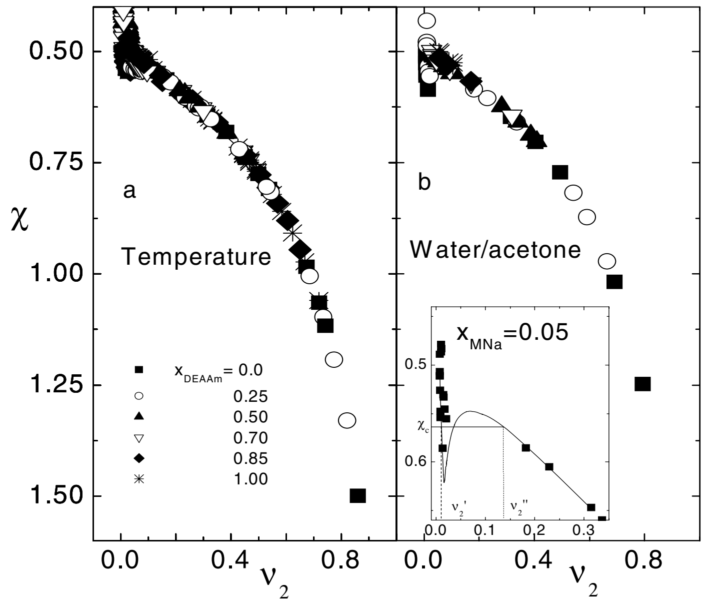


Figure 5. Dependence of the apparent interaction parameter, χ, on the volume fraction of dry network in the swollen state, v_2, measured in water on heating (a) and in *w/a* mixtures at room temperature (b) for gels with indicated x_{DEAAm} mole fractions and various ionic comonomer concentrations

in water at room temperature. With this requirement, the Q_w data shown in Table 1 can be described by Eq. 5 assuming that the "effective degree of ionization α*" is lower than the x_{MNa}, *i.e.*, $\alpha^* = \Phi x_{\mathrm{MNa}}$, where Φ is the correction (fitting) factor. This factor can be related to the fact that not full dissociation of MNa was achieved, to low activity coefficient of counter-ions, to clustering of counter-ions due to possible heterogeneity of highly dilute networks and can accounts for the effects which were not considered in used theory. The Φ values thus calculated lie in the range 0.1 – 0.4 (Table 1) and are dependent on the content of charges and composition of hydrogels (with increasing x_{MNa} and x_{DEAAm} the Φ values decrease). Higher Φ values were found earlier [23] for charged poly(N,N'-isopropylacrylamide) hydrogels with MNa (Φ = 0.67 - 0.20 for x_{MNa} = 0.01 – 0.10).

Finally, we can use Eq. 5 (with $P = 0$) with known molecular parameters and with the $\alpha^* = \Phi x_{\mathrm{MNa}}$, and calculate theoretical dependence of the apparent χ parameter on v_2; at the same time we can apply the same equation and calculate experimental χ on v_2 dependence from Q values measured in various *w/a* mixtures and temperatures (Figs 1 and 4) for all copolymers. As was discussed previously [2,5], the van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump in the gel volume (collapse). If the van der Waals loop in the dependence of χ on v_2 is experimentally found then the critical interaction parameter χ_c and compositions of coexisting phases (the values v_2' and v_2'') at the transition are given by the condition [2,5]

$$\int_{v_2'}^{v_2''}(\chi-\chi_c)dv_2 = 0 \qquad \textbf{(6)}$$

In the inset of Fig. 5b an example of such procedure is shown for neat PAAm network with $x_{\mathrm{MNa}} = 0.05$ measured in *w/a* mixtures together with the application of Eq. (6) Maxwell construction is applied to the theoretical χ *vs* v_2 dependence (full line), the critical value χ_c is determined by the requirement that the areas above and below the line are equal. In such way, the values χ_c and the extents of the collapse, $\Delta v_2 = v_2'' - v_2'$ can be determined for measured data. As expected, the experimental χ points lie on full line (Fig 5b). As the v_2 vs. a dependences for non-ionic networks are known, the dependences of χ vs. v_2 can be transformed to the dependences of χ vs. a and the critical acetone compositions a_c can be determined from χ_c values.

The phase state of P(AAm/DEAAm) gels in water and *w/a* mixtures is determined by interactions of polar and non-polar groups on the chain with water and/or acetone molecules. Since $\chi = 0.49$ and $\chi = 0.51$ were found for the PAAm and PDEAAm uncharged networks in water (Table 1), the presence of ethyl side groups in DEAAm has decreased the overall hydration of the P(AAm/DEAAm) chains as the number of hydrophobic groups in the side chain of the DEAAm monomer increased. In P(DEAAm) networks swollen in water the SAXS measurements have revealed [24] that network chains adopt more or less dense conformations with hydrophobic micelle-like structure near LCST.

Conclusions

From the swelling and mechanical measurements carried out on ionized networks of AAm/DEAAm copolymers swollen in water/acetone mixtures at room temperature and in water at various temperatures the following conclusions can be drawn:

(a) The degree of swelling of P(AAm/DEAAm) gels in water is strongly influenced by the amount of charges on the chain and composition of networks. A comparison of experimental swelling results with theory of polyelectrolyte networks has shown that qualitative agreement can be achieved only if "the effective degree of ionization α*" (= Φx_{MNa}) is introduced. The correction (fitting) factor Φ has had very low values ranging between 0.1- 0.4.

(b) For AAm rich copolymers increasing content of DEAAm component shifts the transition from expanded to collapse state to higher acetone concentrations in *w/a* mixtures. Charged gels prepared with MNa undergo a first-order phase transition; the critical acetone concentration a_c increases with increasing x_{MNa}.

(c) Neat PDEAAm and copolymers with the highest DEAAm content exhibit transition from expanded to collapse state with increasing temperature. Both increasing x_{AAm} and x_{MNa} values in copolymers shift the transition to higher temperatures very efficiently (more than 20 °C).

(d) The moduli G, measured in *w/a* mixtures as well as in water at various temperatures, correlate reasonable well with the swelling degrees Q; the dependences of log G on log Q are roughly the same regardless of x_{MNa} and x_{DEAAm}. This means that the mechanical behavior is predominantly determined by the degree of swelling of gels.

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