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Swelling and mechanical behavior of charged poly(*N*-iso-propylmethacrylamide) and poly(*N*-isopropylacrylamide) networks in water/ethanol mixtures. Cononsolvency effect

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Summary

Swelling and mechanical behavior of negatively (ionic comonomer-sodium methacrylate) and positively (ionic comonomer-(2-acrylamidoethyl)trimethyl ammonium chloride) charged networks of poly(*N*-isopropylmethacrylamide) (PIPMAm) and poly(*N*-isopropylacrylamide) (PIPAAm) was investigated in water/ethanol mixtures at room temperature. Strong cononsolvency effect was observed for uncharged and negatively charged gels of both systems; while for neat solvents high degree of swelling Q was observed, for solvent mixtures pronounced minima in swelling were found. Swelling minima are connected with the coil-to-globule transition of network chains and their characteristic parameters-concentration of ethanol at the minimum, $c_{eth,m}$, and corresponding swelling degree, Q_m, were determined. With increasing amount of negatively charged ionic comonomer the minimum in swelling shifts to higher $c_{eth,m}$ values and Q_m increase. On the other hand, positively charged networks of both systems exhibit roughly constant Q values practically independent of solvent mixtures compositions. For all four systems it was found that mechanical behavior is predominantly determined by the degree of swelling regardless of charge concentration.

Introduction

The transition from expanded to collapsed state of network chains in polyelectrolyte hydrogels, caused by a change of external conditions such as solvent composition or temperature, has received considerable attention in the literature [1-3]. SANS experiments showed that in the expanded state the chains have a coil shape, while in the collapsed state they are in globular form [4]. The change in volume is accompanied by a change in other physical properties, such as shear modulus, refractive index, dielectric permittivity, and the like [3]. Most experimental results were obtained with


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charged poly(acrylamide) (PAAm), poly(N-isopropylacrylamide) (PIPAAm), and poly(N,N-diethylacrylamide) (PDEAAm) hydrogels [2, 3, 5]. The extent of the transition and solvent composition or temperature at which transition takes place are affected by the charge concentration on the chain and structure of ionic comonomer.

The dimensions of network chains in mixed-solvent medium are dependent not only on polymer segments-solvents molecules interactions but are influenced by the interactions between the solvents themselves [6]. Cononsolvency phenomenon, i.e. the formation of nonsolvent by mixing two solvents, was found for some polymers [7-9]; typical example is PIPAAm in mixtures of water with polar organic solvents, such as methanol, tetrahydrofuran, dioxane and others. Smart PIPAAm hydrogels based on this phenomenon have been proposed [10].

Cononsolvency phenomenon can be qualitatively interpreted in terms of the interactions between polymer segments, polymer segments/solvents molecules and solvents molecules themselves. One can expect that introduction of charges on network chains and the change of structure of ionic comonomer will modify these interactions in water/organic solvents mixtures. In this work ionized poly(N-isopropyl-methacrylamide) and poly(N-isopropylacrylamide) networks were prepared with negative and positive charges bound on network chains and their swelling and mechanical behavior was investigated in water/ethanol mixtures.

Experimental

Poly(N-isopropylmethacrylamide) networks. Non-ionic monomer, N-isopropylmethacryl amide (IPMAm, Fluka) and a crosslinker, N,N′–methylene-bisacrylamide (MBAAm) (CR, Fluka), were used as received. While for a negatively charged networks ionic comonomer - sodium methacrylate (MNa) was used, for positively charged networks quaternary salt, N–(2-acrylamidoethyl)–N,N,N–trimethyl-ammonium chloride (QS) was used.

$$CH_2=CH-CO-NH-CH_2-CH_2-\overset{\oplus}{N}\overset{CH_3}{\underset{CH_3}{-CH_3}} \quad Cl^{\ominus}$$
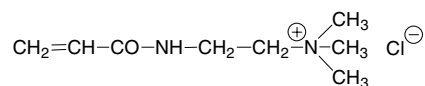
Negatively and positively charged PIPMAm networks, copolymers of IPMAm with various amounts of MNa or QS (mole fraction of sodium methacrylate $x_{MNa} = 0 - 0.1$ and mole fraction of quaternary salt $x_{QS} = 0 - 0.075$) and constant mole fraction of crosslinker ($x_{CR} = 0.04$) were prepared; 4,4′-azobis(4-cyanopentanoic acid) was used as initiator (mole fraction $x_I = 0.003$). Polymerisation was performed in glass ampoules, 10 mm in diameter (D^*), in ethanol/water (8/0.5 by vol.) mixture for 24 h at 70 °C; the volume fraction of all monomers in mixtures was $v_m = 0.15$.

Poly(N-isopropylacrylamide) networks. As in previous case non-ionic monomer, N-isopropylacrylamide (IPMAm, Fluka) and a MBAAm crosslinker, were used as received. The same ionic comonomers - MNa and QS were used for preparation of charged PIPAAm networks. Negatively and positively charged PIPAAm networks, copolymers of IPAAm with MNa and QS ($x_{MNa} = 0 - 0.1$ and $x_{QS} = 0 - 0.075$) and constant mole fraction of MBAAm ($x_{CR} = 0.006$), were prepared by radiation polymerization in water (dose $\gamma = 2$ kGy at room temperature). The volume fraction of all monomers in mixtures was $v_m = 0.10$.

Swelling Measurements. After extraction, the samples (~ 1 cm^3 in volume) were immersed in 200 ml water/ethanol (w/eth) mixtures at room temperature; swelling proceeded for one month. Then the inverse swelling ratio X, relative to the network formation state, was calculated from

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

where D^* and D, respectively, are sample diameters after preparation and swelling in w/eth mixtures, V^* and V are the corresponding sample volumes. The diameters were measured with a travelling microscope (Abbe comparator). From X values, the volume fraction of dry polymer in the swollen state $v_2 = v^1 X$, where $v^1 = v_m/\rho$ is the volume fraction of dry polymer at network formation, ρ is the dry density (1.10 g.cm^{-3} for PIPMAm and 1.06 g.cm^{-3} for PIPAAm) or the swelling degree relative to the dry state, $Q = 1/v_2$, were determined (Figs 1a and 1b). The values Q_w in water at room temperature are shown in Table 1.

Mechanical Measurements. The mechanical experiments at given w/eth concentration were done at room temperature in uniaxial compression. The specimen (~ 10 mm high) was compressed to a ratio λ ($\lambda = l/l_o$ where l and l_o, respectively, are compressed and initial heights) and force f was measured after 30-s relaxation. Usually ten values of λ and f were determined ($0.8 < \lambda < 1$); the shear modulus G was calculated from [2]

$$G=f/[S_o(\lambda^2-\lambda^{-1})] \tag{2}$$

where S_o is the initial cross-section of the specimen (Table 1).
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 v_d was determined from [2]

$$v_d=G_1/(Rv^1T^1) \tag{3}$$

where R is the gas constant and $T^1 = 298$ K is temperature of measurement (Table 1). From moduli G and G_1, the reduced modulus

$$G_r=G/G_1 \tag{4}$$

was also calculated (Figs 2 and 3).

Results and discussion

Effect of network formation conditions on the network structure. Both, PIPAAm and PIPMAm polymers with amphiphilic structure exhibit LCST in water (LCST~30 ºC for PIPAAm and ~40 ºC for PIPMAm [11]). Due to that the synthesis of PIPMAm networks was carried out in ethanol/water mixture (8/0.5 by vol.) at low initial volume fractions of monomers, $v_m = 0.15$. As follows from Table 1, the initial modulus of PIPMAm gels after preparation, G_1, at constant amount of crosslinker, MBAAm, slightly decreases with increasing amount of charged comonomers regardless of the sign of the charge. On the other hand, the values of G_1 of negatively charged gels are more than two times larger than those of positively charged ones. This finding means that efficiency of crosslinking reaction is lower for ammonium salt than sodium methacrylate comonomer. No such effect was observed for PIPAAm gels (prepared by radiation crosslinking polymerisation in water in presence of a constant amount of

MBAAm) for which G_1 values are virtually constant for both series (Table 1). In this case the efficiency of radiation crosslinking in PIPAAm gels is roughly independent of amount and structure of ionic comonomer. In such a way the decrease in the efficiency of crosslinking found for salt is probably connected with specific interactions of α-methyl group of IPMAm and long side chain of quaternary salt.

Swelling and mechanical behaviour. As can be seen from Figures 1a and 1b all uncharged and negatively charged PIPAAm and PIPMAm gels exhibit the "reentrant" swelling behavior in the water/ethanol (w/eth) mixtures; after abrupt deswelling, swelling minimum and reswelling with increase of ethanol content in mixture is observed. Ethanol can interact with polymer segments through the polar and unpolar groups, while water lacks the nonpolar group. A drastic shrinkage of gels at low ethanol concentrations is caused dehydration of chains due to stronger hydrophobic interactions between alcohol and polymer. The steepness of transition is indicative of cooperative effects; once alcohol molecules destroy a part of hydration shell, the damage quickly propagates through entire hydration structure and dehydrated chains associate to form a collapsed structure. In this state, ethanol molecules are adsorbed on collapsed structure. On further increase of ethanol content, the solvent power of the mixture overcomes polymer cohesion and gels begin to swell again.

Table 1. Composition, mechanical, and swelling parameters of hydrogels

x_S	G_1 g cm^{-2}	$v_d \times 0^{-5}$ mol cm^{-3}	Q_w	Q_m	$c_{eth, m}$	ϕ
poly(N-isopropylacrylamide)						
0	54.3	2.34	17.0	1.5	30	-
0.025[a]	61.5	2.65	28.8	1.9	33	0.19
0.050[a]	65.7	2.83	85.1	2.6	38	0.23
0.075[a]	63.2	2.72	112.0	11.3	60	0.18
0.100[a]	67.4	2.90	123.0	14.8	60	0.15
0.025[b]	60.8	2.62	95.5	-	-	0.46
0.050[b]	53.0	2.28	154.9	-	-	0.28
0.075[b]	62.2	2.68	199.5	-	-	0.25
poly(N-isopropylmethacrylamide)						
0	146.7	4.38	13.2	2.6	36	-
0.025[a]	145.3	4.34	21.8	2.6	36	0.47
0.050[a]	134.4	4.01	37.5	3.9	37	0.46
0.075[a]	124.6	3.72	41.8	5.8	40	0.28
0.100[a]	120.2	3.59	50.1	7.7	44	0.13
0.025[b]	57.4	1.71	75.9	-	-	0.29
0.050[b]	47.2	1.41	128.8	-	-	0.18
0.075[b]	40.0	1.19	148.9	-	-	0.11

[a] $x_S = x_{MNa}$; [b] $x_S = x_{QS}$

For uncharged PIPAAm and PIPMAm networks the swelling minima are observed at $c_{eth,m} \sim 33$ vol. % of ethanol (Table 1). It is important to mention that the swelling minima roughly coincide with maximum of the mixing enthalpy, ΔH, of w/eth

mixtures (c_{eth}=35 vol. %, ΔH=-180 cal/mol, ref. [12]); this $c_{eth,m}$ value corresponds also to the maximum of w/eth interactions. From Figs 1a and 1b it further follows that the swelling degree Q of PIPAAm and PIPMAm gels in water and ethanol are roughly the same, which means that swelling power of both neat solvents is similar.

The swelling degree in water Q_w increases with increasing content of charged groups on chains for all four networks series (Figs 1a and 1b, Table 1); generally higher swelling values are observed for more hydrophilic PIPAAm than for PIPMAm gels and for positively charged gels in comparison with negatively charged ones. Pronounced swelling minima in dependence on w/eth compositions are observed for gels with negative charge; with increasing ionic comonomer content the ethanol concentration in the minimum, $c_{eth,m}$ as well as degree of swelling in the minimum, Q_m, increase (Table 1). The shift of minimum to higher ethanol content indicates that charges stabilize the hydrogen bonding between water molecules and chains segments and make alcohol molecules to destroy the hydration shell more difficult. Increasing Q_m values with MNa content mean that amount of mixed solvent in collapsed structures increases with increasing ionisation. Generally, higher changes in $c_{eth,m}$ and Q_m with x_{MNa} are observed for more polar PIPAAm gels in comparison with PIPMAm ones. For charged gels of both network series water is better solvent than neat ethanol.
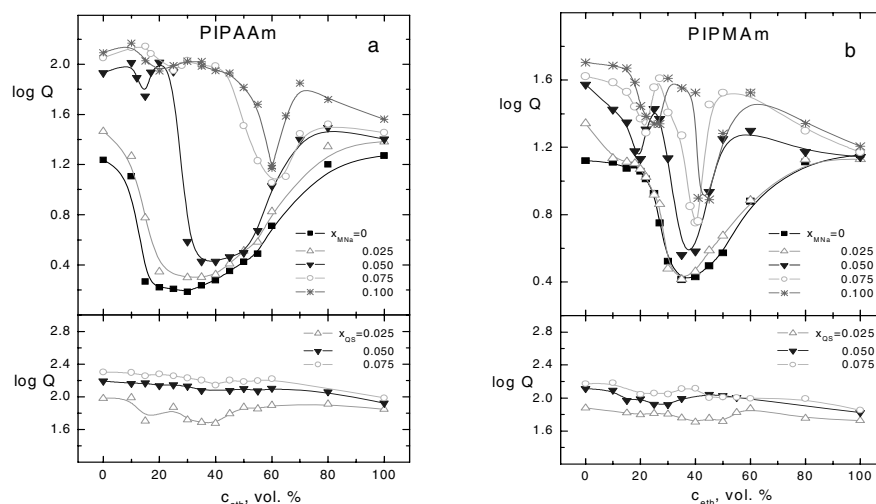

Figure 1. Dependence of the swelling ratio Q on ethanol concentration c_{eth} in water/ethanol mixtures for PIPAAm (a) and PIPMAm (b) gels with different content of ionic comonomers.

From Figs 1a and 1b also follows that at low ethanol concentrations second, less pronounced, swelling minimum exists on w/eth composition for negatively charged gels of both series; the increase in ethanol concentration and swelling degree in the minimum with charge content can be seen as in previous case of the main minimum. As larger changes in Q values are observed for less polar PIPMAm gels (with α-methyl group), we believe that this minimum is connected with interactions of alkyl groups of ethanol with nonpolar groups of polymer main chain.

Unexpected swelling results were found for positively charged gels of both network series (Figs 1a and 1b). In this case roughly no minima on Q vs. w/eth dependences

were found. This means that 2.5 mol% of quaternary ammonium salt is sufficient for stabilization of hydration of polymer chains. We believe that this behavior is caused by the presence of alkyl groups in side chain of ammonium salt. In such a case the structure of ionic comonomer plays an important role in cononsolvency behavior of charged gels in mixed solvents.

An example of the measured dependences of the reduced modulus, $G_r = G/G_1$ (Eq. (4) on ethanol concentration in w/eth mixtures is shown in Fig. 2 for PIPAAm gels.
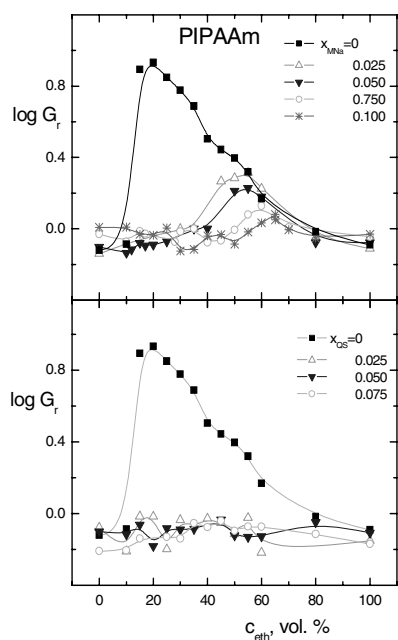

Figure 2. Dependence of the reduced modulus G_r on the ethanol concentration c_{eth} in w/eth mixtures for PIPAAm gels.
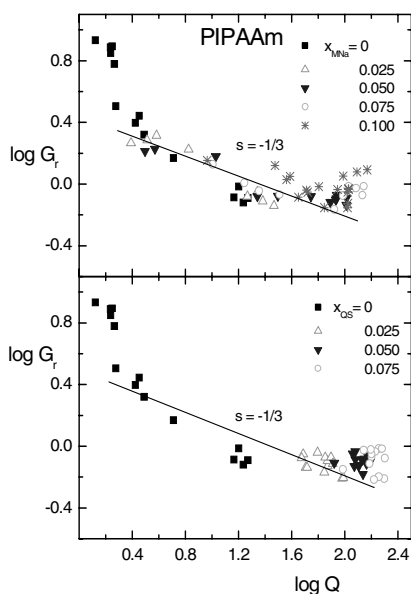
Figure 3. Dependence of the reduced modulus G_r on the swelling degree Q for PIPAAm gels.

As expected, minima found in Q vs. c_{eth} dependences (Fig. 1a) for uncharged and negatively charged gels are reflected in maxima in dependences of G_r vs. c_{eth}. For positively charged PIPAAm gels G_r values roughly independent of c_{eth} were observed. The dependences of the log G_r on log Q of PIPAAm gels are plotted in Fig. 3. For comparison, the predicted rubber elasticity slope [13] for the dependence of log G_r vs. log Q, $s = -0.33$, is also shown. In the range of high swelling (log $Q > 2$), the increase in modulus G_r from expected dependence with increasing swelling can be seen for all gels; this increase is probably due to the finite extensibility of the chains. Departures from the straight line in the region of low swelling (log $Q < 0.3$) are probably due to the influence of the main transition region (vitrification) at low swelling degrees [3]. The value of $s = 0.33$ independent of charge concentration was found [14] for poly(1-vinyl-2-pyrrolidone) networks. On the other hand, a high value of $s = 0.7$ independent of charge concentration, was found [15] for charged polyacrylamide (PAAm) networks in water/acetone mixtures. The swelling dependence of the modulus with the

slope $s = 5/6$ was recently suggested by the theory of Rubinstein et al. [16] based on the scaling concept of the polyelectrolyte chain. Qualitatively similar results were obtained also for PIPMAm gels. Universal correlation between log G_r and log Q means that mechanical behavior is predominantly determined by the degree of swelling regardless of charge concentration and its polarity for both network systems.

Comparison of the theory of swelling equilibria and experiment. Several models for interpretation of thermodynamic properties of charged gels have been suggested [2, 5, 17] in which also the effect of repulsion of charges on the chain and finite chain extensibility were included. For comparison of experimental swelling data with theoretical prediction, we use the theory discussed in Refs [2, 3] based on single liquid approximation. This theory predicts the swelling pressure P as a sum of four terms

$$P = \mu_1/V_1 = P_m + P_{os} + P_{el} + P_{els} \tag{5}$$

where μ_1 is the chemical potential of the solvent, V_1 is the molar volume of the solvent, P_m is the mixing term given by mixing of solvent with chain segments (Flory-Huggins equation with interaction parameter χ), P_{el} is the elastic term given by the change in elastic energy with swelling in which the finite chain extensibility was included, P_{os} is the osmotic term given by mixing of network ions with the solvent, P_{els} is the electrostatic term determined by the interactions (repulsion) of charges on the chain. For the uncharged gel, only two first terms in Eq. 5 remain as the degree of ionization $\alpha = 0 = x_S$, i.e., $P_{os} = P_{els} = 0$. From the knowledge of network parameters (ν_d, ρ, v^1, determined independently), and using reduced Eq. 5, the dependence of the interaction parameter χ on the volume fraction of dry polymer in the swollen state, v_2, could be calculated from experimental v_2 (or Q) values of the uncharged networks measured in w/eth mixtures (Fig. 4). As swelling data were collected for free swelling, $P = 0$ in Eq. 5. In such way, the values of $\chi = 0.497$ and 0.515 were found for PIPAAm and PIPMAm gels in water. As expected, with increasing v_2 (increasing ethanol concentration), χ values of uncharged networks first increase (deswelling region) and after that they decrease (reswelling region). It is interesting to note that χ values determined from all w/eth mixtures lay on the same χ on v_2 dependence for both PIPAAm and PIPMAm gels, regardless of cononsolvency effect (Fig. 4).

As can be seen from Table 1, the swelling degree in water at room temperature, Q_w, increases with charge concentrations; the Q_w values are always higher for ammonium salt in comparison with MNa. As we know all network parameters ((ν_d, ρ, v^1), and if we further assume that the degree of ionization $\alpha = x_S$ ($x_S = x_{Mna}$ or $x_S = x_{QS}$), we can use Eq. 5 for the description of dependence of Q_w on x_S. We obtain unrealistic high χ values (ranging from 0.6 to 10). As it was introduced into the used theory [2, 3] χ is a measure of polymer–solvent interactions when all charges are screened. It is therefore reasonable to require the same value of $\chi = 0.497$ for all PIPAAm and $\chi = 0.515$ for all PIPMAm charged networks in water. This requirement is possible to fulfill by the assumption that the effective degree of ionization α^* is lower than the ammonium salt concentration x_S, i.e., $\alpha^* = \phi\alpha = \phi x_S$, where ϕ is the correction factor; the values ϕ in the range $\sim$ 0.47–0.11 were found (Table 1). Due to higher Q_w values found for gels with ammonium salt their ϕ vales are always higher than those of gels with MNa. The ϕ factor is related to the osmotic coefficient of counter-ions and to the clustering of counter-ions due to possible heterogeneity of highly dilute networks and accounts for

the effects, which were not considered in the used theory. Similar ϕ values were found earlier [3] for charged poly(N,N-diethylacrylamide) hydrogels with sodium methacrylate (MNa) ($\phi = 0.56$–0.28 for $x_{MNa} = 0.005$–0.07).
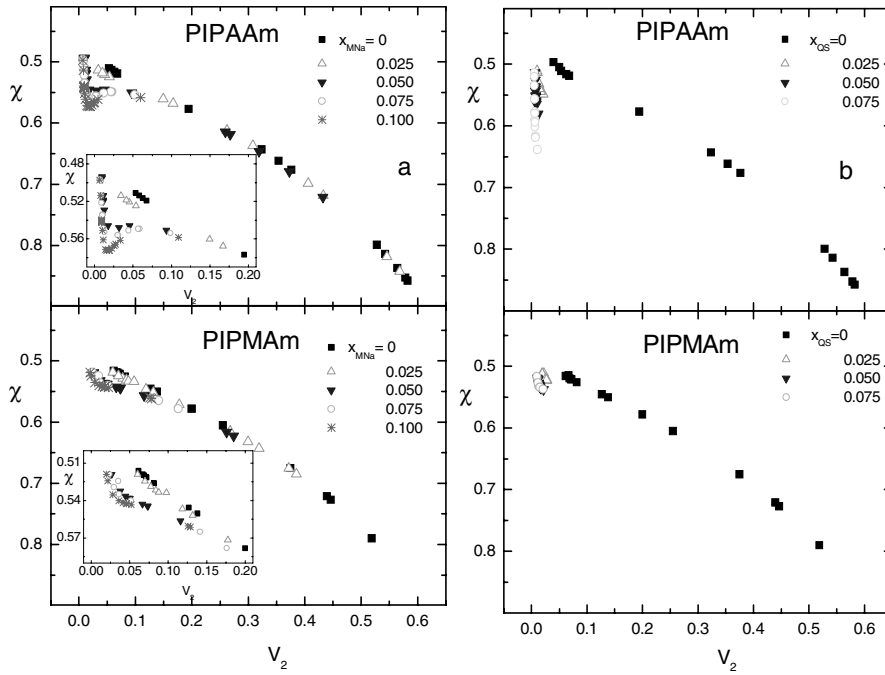

Figure 4. Dependence of interaction parameter, χ, on volume fraction of dry network in the swollen state, v_2, measured in water/ethanol mixtures with indicated ionic comonomers (a) negatively charged gels and (b) positively charged gels.

Using known molecular parameters and the effective degree of ionization $\alpha^* = \phi x_S$, the dependences of χ on v_2 were calculated from Q values measured at various w/eth compositions (Fig. 1) for all ionized networks (Fig. 4). As follows from Fig. 4a for negatively charged PIPAAm and PIPMAm gels universal χ vs. v_2 dependences, independent of charge concentration, were found in region of lower swelling ($v_2 > 0.1$). Such universal dependences were observed earlier for variously charged gels of different systems [3]. As follows from the insets in Fig. 4a, in the region of high swelling ($v_2 < 0.1$), χ vs. v_2 dependences depend on amount of charges; such results were not earlier observed. Also for positively charged networks χ vs. v_2 dependences are different from those of uncharged ones (Fig. 4b). Both two latest facts mean that Eq. 5 gives only qualitative description of the swelling results. It is worthwhile to mention that a van der Waals loop in the dependence of χ on v_2 is a necessary condition for the appearance of a jump-change in the gel volume (1st-order phase transition [3, 18]). Only negatively charged PIPAAm gels with $x_S \geq 0.075$ show the tendency to exhibit such type behavior (Fig. 4a). From Fig. 1 it follows that all negatively charged gels exhibit similar swelling behavior on w/eth composition.

Conclusions

From our investigation following conclusions can be made: a) For uncharged and negatively charged PIPAAm and PIPMAm gels strong cononsolvency effect, connected with coil/globule transition, was observed in water/ethanol mixtures; increasing charge concentration shifts the minimum in swelling to higher ethanol concentrations and higher swelling degree. b) Positively charged gels of both systems exhibit roughly constant degree of swelling, independent of solvent composition. c) As expected, swelling degree increases with increasing charge concentration in whole w/eth region in all four investigated systems.

References

1. De Rossi D, Kajiwara K, Osada Y, Yamauchi A (Eds) (1991) Polymer Gels. Fundamentals and Biomedical Applications. Plenum Press, New York
2. Dušek K (ed) (1993) Responsive Gels: Volume Transition I and II. Adv Polym Sci 109, 110
3. Ilavský M (1993) Adv Polym Sci 109:173
4. Pleštil J, Ostanevich Yu, Borbely S, Stejskal J, Ilavský M (1987) Polym Bull 17:465
5. Shibayama M, Tanaka T (1993) Adv Polym Sci 109:1
6. Dondos A, Patterson DJ (1969) Polym Sci A-2 7:209
7. Schild HG, Muthukumar M, Tirrell DA (1991) Macromolecules 24:948
8. Mukae K, Sakurai M, Sawamura S, Makino K, Kim S-W, Ueda I, Shirabama K (1993) J Phys Chem 97:737
9. Pagonis K, Bokias G (2004) Polymer 45:2149
10. Zhang X-Z, Yang Y-Y, Chung T-S (2002) Langmuir 18:2538
11. Fomenko A, Pospíšil H, Sedláková Y, Pleštil J, Ilavský M (2002) Phys Chem Chem Phys 4:4360
12. Belousov VP, Morachevskij AG (1970) Mixing Heats of Liquids. Khimia, Leningrad
13. Dušek K, Prins W (1969) Adv Polym Sci 6:1
14. Mamytbekov G, Bouchal K, Ilavský M, Bekturov E (1998) Polymer J 30:713
15. Ilavský, K. Bouchal (1988) Phase transition in swollen gels 10. Effect of the positive charge and its position in the side chain on the collapse and mechanical behaviour of poly(acrylamide) networks. In: Kramer O (Ed) Biological and Synthetic Polymer Networks. Elsevier, New York, p. 435
16. Rubinstein M, Colby HR, Dobrynin VA, Joanny J-F (1996) Macromolecules 29:398
17. Onuki A (1993) Adv Polym Sci 109:63
18. Ilavský M (1981) Polymer 22:1687