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Equilibrium swelling of poly(AAm-*co*-AMPS) gels in surfactant solutions

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Abstract

The interactions between poly(acrylamide-*co*-2-acrylamido-2-methyl-1-propane sulphonic acid) (poly(AAm-*co*-AMPS)) gel with low fraction of charges and four oppositely charged surfactants, differing in structure and hydrophobicity, were studied. The variation of the gel swelling profile with surfactant concentration and structure, amount of charges on the polymer gel network and temperature was determined.

The results showed that the surfactants induce profoundly different gel swelling profiles, and both the structure and hydrophobicity of the surfactants are determining factors. It was found that a change in the fraction of charges on the chains influences electrostatic interactions to a greater extent than hydrophobic gel–surfactant interactions. No significant effect of temperature in the range from 5 to 40°C on the gel swelling profiles in the surfactant solutions was found.

Keywords: Gel; Swelling; Surfactant

1. Introduction

A polymer gel network can respond to a number of external stimuli [1–4] by changing its volume and properties. Study of response of the polymer network to those stimuli is of interest not only for design of novel sensing, switching, drug delivery and other devices, but also for better understanding of interactions in polymer systems.

The interactions between surfactant molecules and a polymer gel network often result in a pronounced volume change of the gel [5–8], with the surfactants effectively absorbed by the gel. The binding of the surfactant molecules, which possess both hydrophilic and hydrophobic character, onto the polymer network, changes the properties of the network. Kokufuta and coworkers [6] showed that ionic surfactant molecules convert uncharged poly(*N*-isopropyl acrylamide) gel into an ionic gel due to binding through hydrophobic interactions. Osada and coworkers developed an electrically driven chemo-mechanical system that showed rapid response with motility [9–10]. Isogai and coworkers [5] converted a polyelectrolyte gel with no temperature sensitivity into a temperature sensitive gel by binding of a surfactant with bulky hydrophobic groups. Khokhlov and coworkers studied the interactions of polyampholyte gels with ionic surfactants which lead to pronounced collapse of the gel [11]. Formation of highly ordered nanoscale supramolecular structures in the polyelectrolyte–surfactant complex has been found and confirmed by small-angle X-ray scattering [12].

In this work the interactions of anionic polyelectrolyte (AAm-*co*-AMPS) gels with several cationic surfactants were studied: the work is part of an extensive study of this copolymer gel system. The effects of surfactant structure and surfactant concentration on the equilibrium swelling of gels with varying charge concentration were investigated at several temperatures.

2. Theoretical background

The binding of linear and crosslinked polyelectrolytes to oppositely charged surfactants has recently been theoretically re-analyzed by Gong and Osada [13,14]. In their theoretical approach the binding process is characterized by electrostatic salt formation of surfactant molecules with the network, which is considered as the initiation process, and the hydrophobic interaction between adjacently bound surfactant molecules, which stabilizes the aggregate.

It was shown [13,14] that the equilibrium value of the network volume fraction v_2, at the particular conditions, is obtained by setting $\partial F/\partial v_2 = 0$ (F being the free energy of the system), which gives the following

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equation:

$$\ln(1-v_2)+\chi v_2^2+\frac{v_2 v_e}{N}\left[\left(\frac{v_{2,o}}{v_2}\right)^{2/3}-\frac{1}{2}\right]+v_2(\beta-2\gamma)+2v\left[c_s+\frac{N(\alpha+\beta-\gamma)}{V-V_g}\right]=0 \quad (1)$$

χ is the Flory–Huggins interaction parameter, ν_e is the number of polymer chains, N is total number of moles of monomeric units of the polymer, $v_{2,0}$ is the volume fraction of the network in the reference state (defined as the state of the network at the preparation conditions), β is degree of binding defined as the ratio of the number of moles of bound surfactants to the total number of moles of monomeric units, $\gamma = S_g^-/N$ where S_g^- is the number of moles of surfactant counter-ions in the gel, $\alpha = S_g^+/N$ where S_g^+ is the number of moles of surfactant ions in the gel, V is volume of the surfactant solution at equilibrium and V_g is equilibrated volume of the network in the surfactant solution.

Eq. (1) indicates that the volume fraction of polymer network swollen to equilibrium in a surfactant solution depends on the usual molecular and structural network parameters, and also on surfactant concentration, degree of binding β, and the number of moles of surfactant ions and counter-ions in the gel.

It is to be expected that both the peculiarities of charged groups on the surfactant and the network, and the hydrophobicity of the surfactant tails will influence the equilibrium extent of gel swelling.

3. Experimental

3.1. Gel preparation

Gels were prepared by free radical solution polymerization of AAm (from Serva Feinbiochemica GmbH) and AMPS (Merck & Co., Inc.), together with *N*,*N*′-methylene-bis(acrylamide) (MBAAm) (Serva Feinbiochemica GmbH) as crosslinking agent. The total monomer concentration was 850 mM, and the MBAAm concentration was 12.75 mM (1.5 mol%). Glass capillaries with approximately 2.5 mm internal diameter were filled with the pre-gel solution. The gelation reaction, initiated by ammonium persulphate (0.001 mol l^{-1}), was carried out at 60°C for 1 h. The gels were cut into cylinders of approximately 3 mm length, and soaked in a large volume of water for 10 days to remove unreacted monomers and initiator.

The fraction of AMPS in the pre-gel solution was 2, 4, 6 or 20 mol%. The corresponding gels will be designated here as AMPS2, AMPS4, AMPS6 and AMPS20. It has been shown [15] that the fraction of AMPS in the polymerized gel is 0.875*F*, where *F* is the fraction of AMPS in the pre-gel solution.

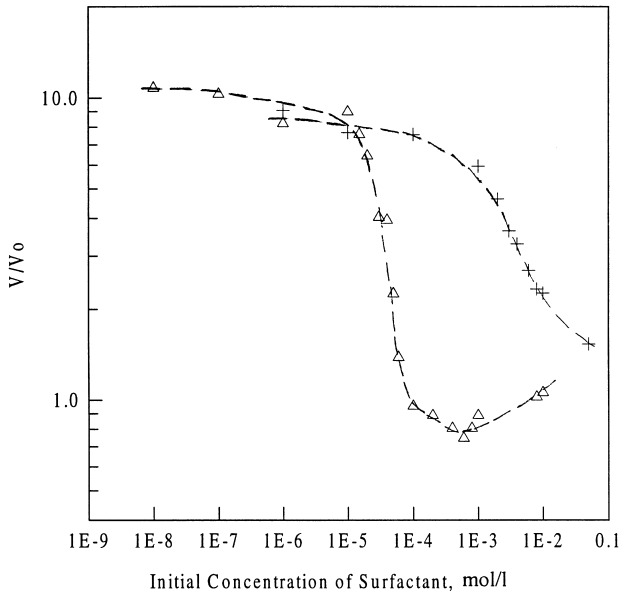

Fig. 1. Dependence of equilibrium swelling ratio, V/V_o of poly(AAm-*co*-AMPS) gel AMPS2, on the initial surfactant concentration: TPPC (+) and CTAB (△). Temperature of measurements: 23°C.

3.2. Equilibrium swelling

Cylindrical samples of poly(acrylamide-*co*-2-acrylamido-2-methyl-1-propane sulphonic acid) (poly(AAm-*co*-AMPS)) gels were immersed in 10 ml of aqueous surfactant solutions made up using Milli-Q water. For measurement of the equilibrium swelling in surfactant solution at least 10 days were allowed for equilibrium to be attained.

Equilibrium swelling of the gels was determined by measuring the gel diameter with a travelling microscope. The swelling ratio, (V/V_o), was calculated from the ratio of equilibrium gel diameter d to the original diameter d_o, i.e. $(V/V_o) = (d/d_o)^3$. The estimated relative error in V/V_o was ±2%.

Four cationic surfactants with strongly hydrophobic groups were used in a wide concentration range, namely cetyltrimethylammonium bromide (CTAB), (BDH Chemicals Ltd.), tetraphenyl phosphonium chloride (TPPC), (Lancaster Synthesis Ltd), cetylpyridinium chloride (C_{12}PyCl), (Lancaster Synthesis Ltd) and dodecylpyridinium chloride (C_{16}PyCl), (Aldrich Chemical Company, Inc.).

4. Results and discussion

4.1. The effects of surfactant concentration and surfactant structure

Figs. 1–3 show the dependence of equilibrium swelling of poly(AAm-*co*-AMPS) gels AMPS2, AMPS4 and AMPS6 on the initial concentration of surfactants. The

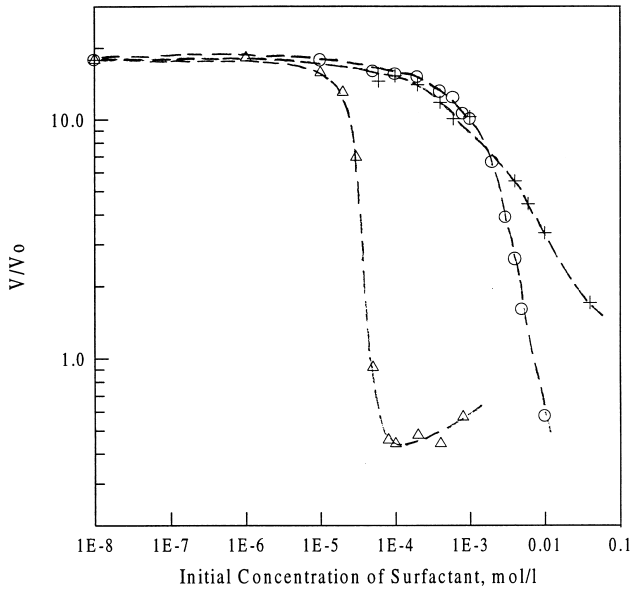

Fig. 2. Dependence of equilibrium swelling ratio, V/V_o of poly(AAm-*co*-AMPS) gel AMPS4, on the initial surfactant concentration: C_{16}PyCl (△), C_{12}PyCl (○), and TPPC (+). Temperature of measurements: 22°C.

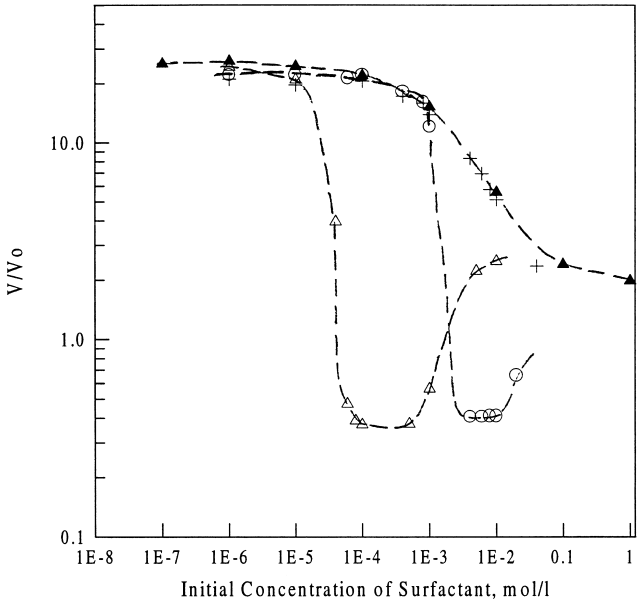

Fig. 3. Dependence of equilibrium swelling ratio, V/V_o of poly(AAm-*co*-AMPS) gel AMPS6, on the initial surfactant concentration: C_{16}PyCl (△), C_{12}PyCl (○), TPPC (+). The swelling of the same gel in NaCl solutions (▲) is given for comparison. Temperature of measurements: 24°C.

corresponding equilibrium degrees of swelling $Q = 1/v_2$ in water were 233, 364 and 483.

Increase in the surfactant concentration leads to a profound volume change of the gel sample. Increasing concentration of TPPC induces a relatively gradual decrease of the gel volume, whereas the other surfactants effect a drastic change in the volume of the gel over a narrow range of surfactant concentrations. Such a transition resembles the conformational transitions observed for the volume phase transition in a poor solvent [15].

Figs. 1–3 show that the concentration range where collapse of the gel occurs depends significantly on the surfactant. Such surfactant structure related concentration dependence of gel collapse confirms that formation of the surfactant–gel network is not purely an ion exchange reaction; the hydrophobicity of the surfactant molecules, and surfactant structure also play a role.

Fig. 1 shows the swelling of gel AMPS2 in solutions of TPPC and CTAB. Although both surfactants possess strongly hydrophobic tails, there is an obvious difference in the gel swelling profiles. That difference can be attributed to the significantly different structures of the two surfactants. CTAB, as well as C_{12}PyCl and C_{16}PyCl, have long hydrophobic alkyl tails, while TPPC has bulky aromatic hydrophobic groups. It seems that hydrophobic interactions between the bulky groups of the TPPC molecules bound to adjacent sites on the poly(AAm-*co*-AMPS) gel network, are not strong enough to induce cooperativity. Possible reasons may be a stereochemical effect of large TPPC molecules [5], or a sufficiently low density of charges on the polymer gel to keep the short hydrophobic tails of TPPC at a distance large enough to suppress hydrophobic interactions between them.

The effect of hydrophobicity of the surfactant tail on the swelling equilibrium of poly(AAm-*co*-AMPS) gels is clearly demonstrated by comparing the gel swelling profiles in solutions of C_{12}PyCl and C_{16}PyCl (Figs. 2 and 3). It is known [16] that increase in the length of the alkyl chain gives stronger hydrophobic interactions; i.e. the free energy of transfer of hydrocarbon molecules from water to a purely hydrocarbon solvent significantly increases. Hence C_{16}PyCl is more hydrophobic than C_{12}PyCl since its hydrophobic tail contains four more CH_2 groups than C_{12}PyCl. Figs. 2 and 3 show that increasing the hydrophobicity of the alkyl chains shifts the position of the abrupt volume change of the gel to lower surfactant concentration. The concentration difference for the beginning of the poly(AAm-*co*-AMPS) gel collapse with C_{12}PyCl and C_{16}PyCl is as large as two orders of magnitude. The transition is also somewhat sharper in the case of gel swelling in C_{16}PyCl solutions.

The swelling of poly(AAm-*co*-AMPS) gel in sodium chloride solutions is shown in Fig. 3 together with swelling curves for the same gel in surfactant solutions. The shielding of electrostatic interactions is responsible for volume change of the gel when swelling occurs in the salt solution [17–18]. There is a similarity of the swelling curves of the gels swollen in the TPPC solutions and NaCl solution, while those obtained for C_{12}PyCl and C_{16}PyCl are markedly different. It should be noted that there is not only a difference in the position and sharpness of the transition: in addition the amplitude of the transition from swollen to the collapsed state is much larger for the gel swollen in the surfactant solutions.

Again, it is apparent that the mechanism for the abrupt volume change of the gels swollen in C_{12}PyCl and C_{16}PyCl

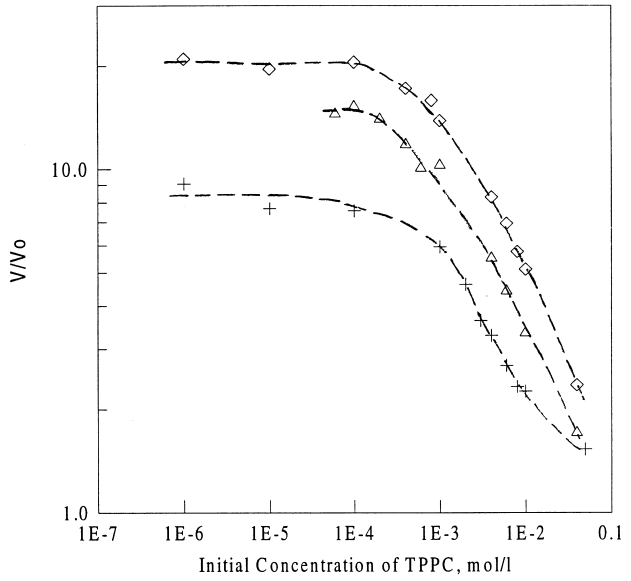

Fig. 4. Dependence of equilibrium swelling ratio, V/V_0 of poly(AAm-*co*-AMPS) gels AMPS2 (+), AMPS4 (△) and AMPS6 (◇) mol% of AMPS, on the initial concentration of TPPC, at room temperature.

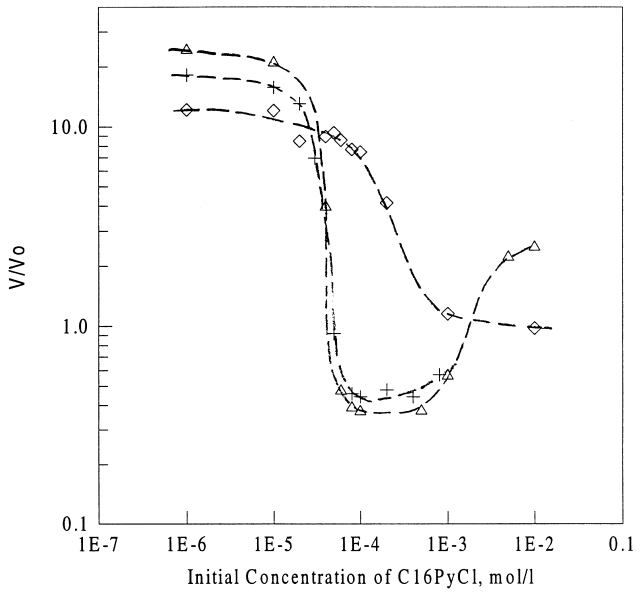

Fig. 6. Dependence of equilibrium swelling ratio, V/V_0 of poly(AAm-*co*-AMPS) gels AMPS4 (+), AMPS6 (△) and AMPS20 (◇) mol% of AMPS, on the initial concentration of C_{16}PyCl, at room temperature.

is not simply electrostatic shielding; hydrophobic interactions must also play a role.

Another interesting feature of the poly(AAm-*co*-AMPS) gel swollen in the solutions of CTAB, C_{12}PyCl and C_{16}PyCl can be observed from Figs. 1–3, in that the curves show a slight increase in the volume ratio after reaching minimum swelling at a certain surfactant concentration. Similar findings have been reported for poly(sodium methacrylate-*co*-acrylamide) gels swollen in cetylpyridinium bromide solutions [7]. The authors assumed that the effect is a result of the introduction of bulky surfactant ions into the gel, most of which participate in the formation of micelles or aggregates.

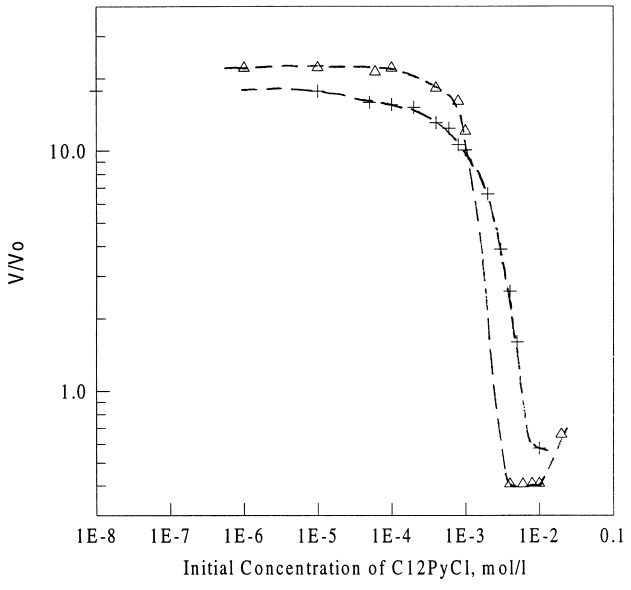

Fig. 5. Dependence of equilibrium swelling ratio, V/V_0 of poly(AAm-*co*-AMPS) gels AMPS4 (+) and AMPS6 (△) mol% of AMPS, on the initial concentration of C_{12}PyCl, at room temperature.

4.2. The effect of the amount of charges on the poly(AAm-co-AMPS) gel

It is well known that the amount of charges influences gel swelling equilibrium and the volume phase transition [15]. It is to be expected, therefore, that the amount of charges on the polyelectrolyte network will also affect the amount of surfactant bound to the network, and hence the swelling equilibrium of the gel in surfactant solutions.

Fig. 4 compares the swelling profiles for poly(AAm-*co*-AMPS) gels with varying amounts of AMPS, swollen in solutions of TPPC. As expected, the swelling curves resemble the swelling of poly(AAm-*co*-AMPS) gels in a salt solution [15], since there is no apparent hydrophobic interaction between the TPPC molecules, as discussed above. Increase in the amount of AMPS in the copolymer gel shifts the transition region to higher TPPC concentrations, and the transition is sharper.

Figs. 5 and 6 show equilibrium swelling curves for poly(AAm-*co*-AMPS) gels with varying fractions of AMPS in solutions of C_{12}PyCl and C_{16}PyCl. In both cases, there is no significant effect of changing the amount of AMPS in pre-gel solution from 4 to 6 mol%. However, the transition is slightly sharper and the extent of the volume change is slightly larger for gel AMPS6. Such a small difference in swelling curves of AMPS4 and AMPS6 can be explained by

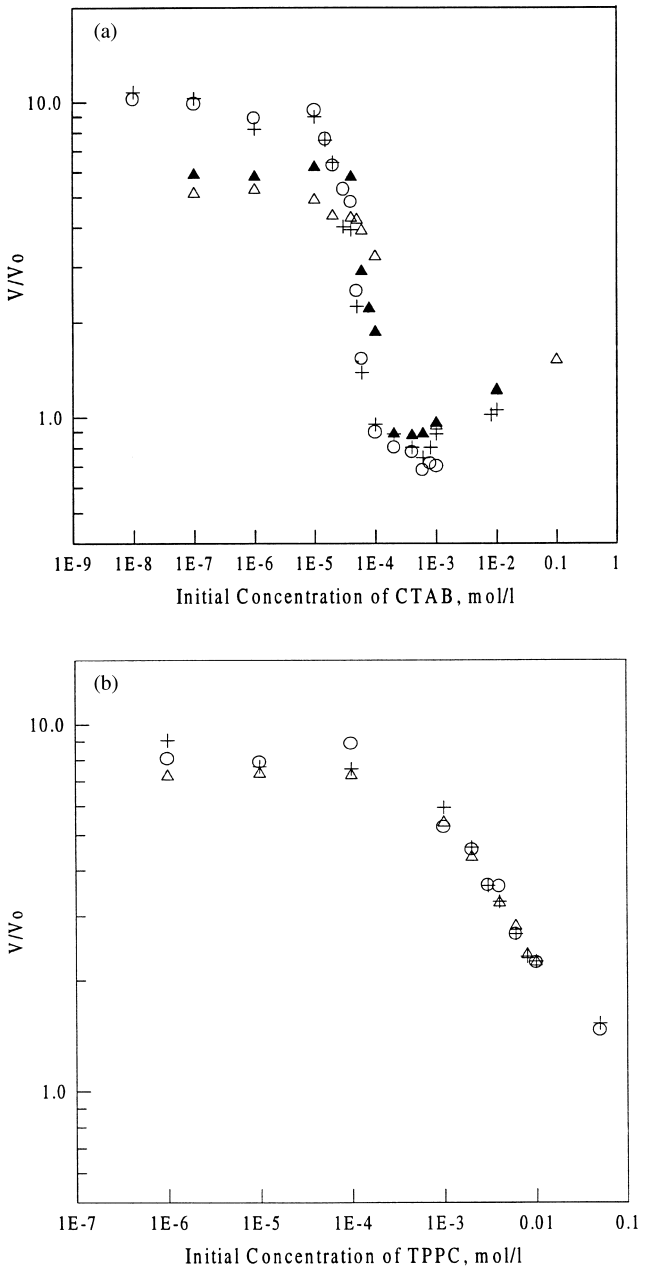

Fig. 7. Swelling isotherms of poly(AAm-*co*-AMPS) gel AMPS2, in dependence of concentration of: (a) CTAB; and (b) TPPC; obtained at 10°C (○), 23°C (+), and 40°C (△ and ▲).

the fact that both AMPS4 and AMPS6 are weakly charged polyelectrolyte gels, and the difference in the charge density is not large enough to observe more pronounced differences in swelling behavior. The equilibrium swelling curve for poly(AAm-*co*-AMPS) gel AMPS20 is included in the graph in Fig. 6. It should be noted that the latter gel was prepared with a significantly higher amount of crosslinking agent MBAAm (3 mol% in comparison with the other gels studied which were prepared with 1.5 mol% of MBAAm) in order to partially suppress its enormous swelling capacity. The resulting increased crosslink density interferes with the effect of charges, so that the extent of swelling and volume change cannot be directly compared with those of the other gels. However, it is apparent that increase of the amount of charged co-monomer shifts the transition to higher surfactant concentrations.

4.3. The effect of temperature

When poly(AAm-*co*-AMPS) gel swells in cationic surfactant solutions, electrostatic complex formation occurs due to electrostatic interaction between the charges on the polyelectrolyte network and surfactant ions. The polyelectrolyte hydrophilic network is thereby transformed into a neutral or at least less ionic network with a certain extent of hydrophobic domains caused by the hydrophobic surfactant tails. Since, in a complex relationship, both enthalpy and entropy changes are involved in determining hydrophobic interactions [16], changing the temperature at which swelling experiments are performed is likely to affect the swelling equilibrium through the effect on hydrophobic interactions.

Isogai and coworkers [5] reported a transformation of poly(AMPS) gel into a thermosensitive gel by binding of TPPC onto it. The TPPC binding made the polyelectrolyte gel strongly hydrophobic, leading to thermosensitive behavior, and it was found that the concentration at which collapse of the gel occurred depends on the temperature.

The swelling isotherms of poly(AAm-*co*-AMPS) gels AMPS2, AMPS4 and AMPS6, as a function of the concentration of CTAB, TPPC, C_{12}PyCl, and C_{16}PyCl, obtained at several temperatures in the range from 5 to 40°C, are presented in Figs. 7–9.

The general observation from Figs. 7–9 is that there is no significant effect of temperature on the position of the abrupt change in gel volume, regardless of the surfactant. This behavior is contrary to that found for binding of TPPC to poly(AMPS) gel [5]. The low fractions of AMPS in poly(AAm-*co*-AMPS) gels studied here, causing a relatively low density of surfactant molecules bound to the poly(AAm-*co*-AMPS) gels, can be considered as responsible for the difference observed.

Increase in the temperature at which the equilibrium swelling experiments were performed was found to decrease the extent of the abrupt volume change, mostly due to the smaller swelling ratios found at low surfactant concentrations for gels swollen at higher temperatures. An increase in the experimental temperature makes the aqueous solution of the surfactant a poorer solvent for the gels.

The swelling profiles of the poly(AAm-*co*-AMPS) gels show slight temperature sensitivity in the region of low surfactant concentrations (except for the case of C_{16}PyCl binding to the gel AMPS4).

Comparison of Fig. 7(b) with Figs. 8(a) and 9(a), and Fig. 8(c) with Fig. 9(c), reveals that increase in the amount of

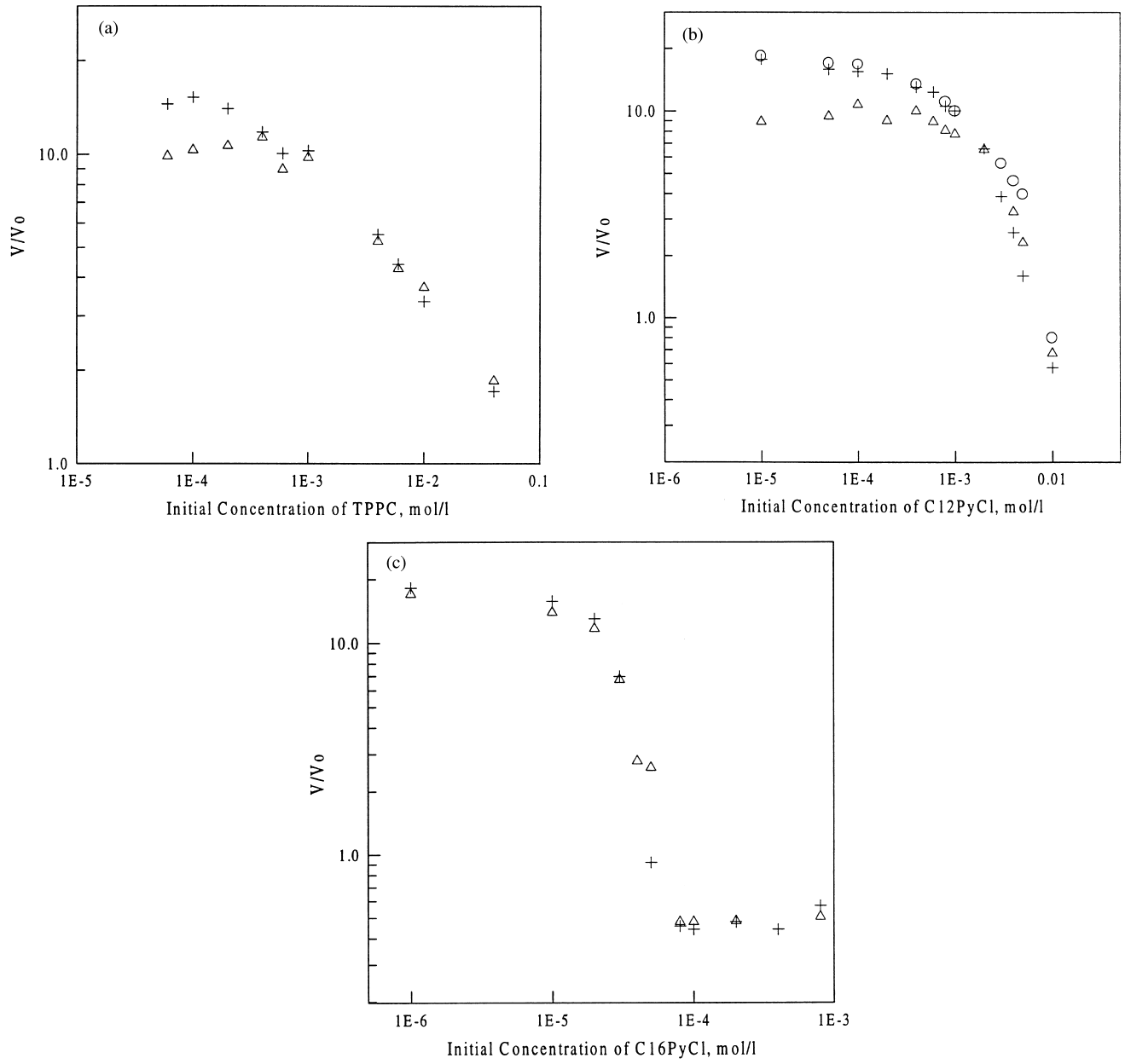

Fig. 8. Swelling isotherms of poly(AAm-*co*-AMPS) gel AMPS4, as a function of the concentration of: (a) TPPC; (b) C_{12}PyCl; and (c) C_{16}PyCl, obtained at 5°C (○), 22°C (+), and 40°C (△).

charges leads to higher temperature sensitivity for the gels swollen in TPPC and C_{16}PyCl.

5. Conclusions

The swelling profiles of polyelectrolyte poly(AAm-*co*-AMPS) gels with low fraction of charges swollen in the surfactants solutions were investigated. The surfactants CTAB, C_{12}PyCL and C_{16}PyCl induce abrupt change in the gel volume. The major effect of surfactant structure and surfactant hydrophobicity on the position and extent of the gel collapse was revealed. Such gel sensitivity on the surfactant structure can serve as a mechanism for adsorption of organic compounds.

The increase in the charge density on the poly(AAm-*co*-AMPS) gel network from AMPS4 to AMPS6 has stronger effect on the gel swelling in the solutions of TTPC than in the solutions of C_{12}PyCl and C_{16}PyCl. Since C_{12}PyCl and C_{16}PyCl bind cooperatively onto poly(AAm-*co*-AMPS) gel network, and TPPC does not, this indicates that a small increase in the amount of charges affects electrostatic interactions to a greater extent than hydrophobic interactions.

The poly(AAm-*co*-AMPS) gels with low charge density,

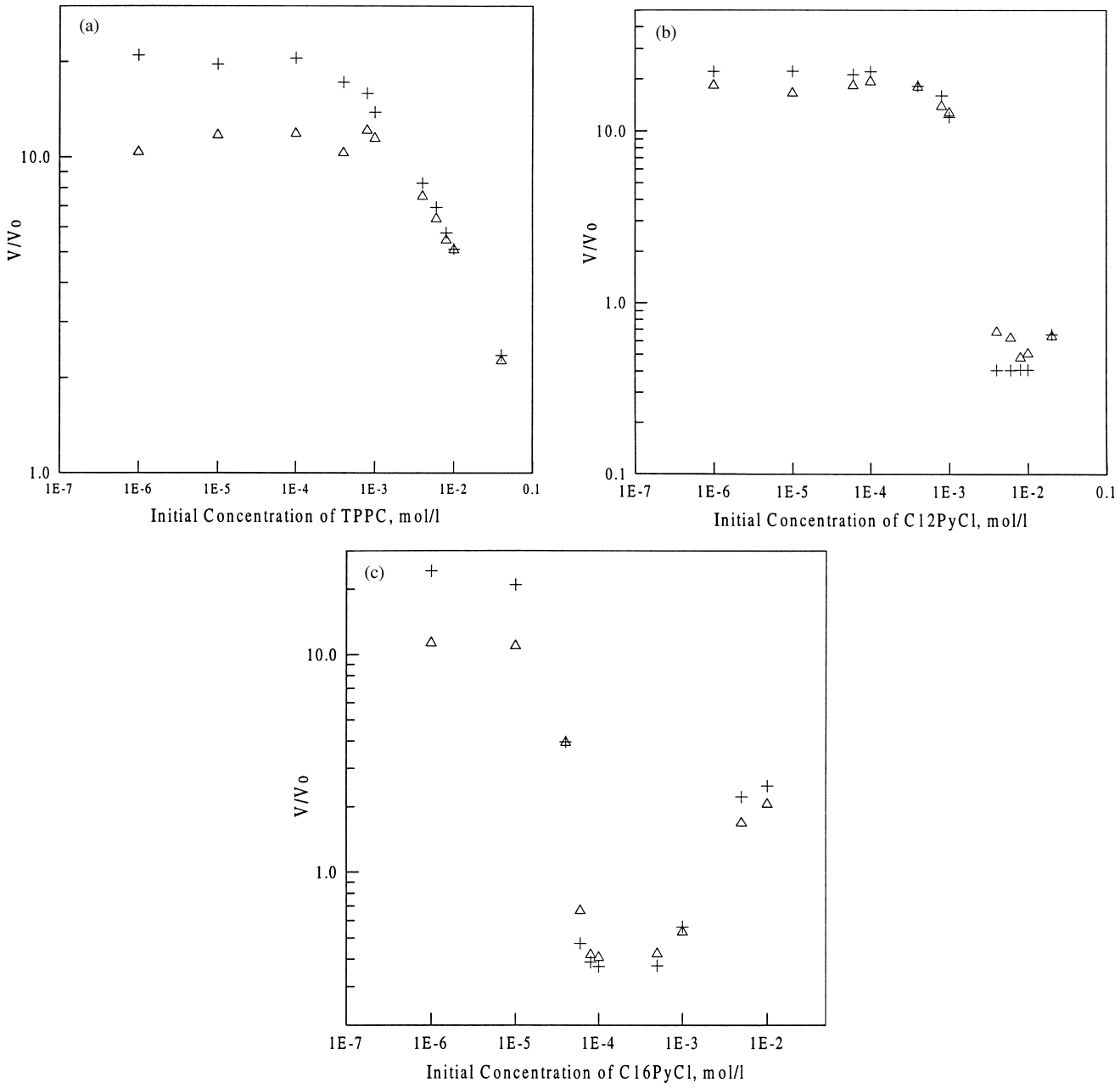

Fig. 9. Swelling isotherms of poly(AAm-*co*-AMPS) gel AMPS6, as a function of the concentration of: (a) TPPC; (b) C_{12}PyCl; and (c) C_{16}PyCl, obtained at 24°C (+), and 40°C (△).

swollen in the surfactant solutions showed only a slight temperature sensitivity in the region of low surfactant concentrations.

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