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Collapse of a charged polymer gel induced by mixing ‘unfavorable’ counterions

Y. Nishiyama, M. Satoh*

Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-0033, Japan

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Abstract

Swelling behavior of alkali metal poly(acrylate) gels in aqueous ethanol was investigated in the mixed counterion systems. In the presence of Na^+ and K^+ counterions, both of which are favorable for the gel collapse in the relevant solvent system, no specific deswelling was observed. In the presence of Li^+ and Cs^+, both of which are relatively unfavorable for the gel collapse, however, the gel markedly deswelled in an ethanol composition that is lower than the critical compositions for the respective single counterion systems. This unexpected behavior seems to result from a subtle energy balance between the ion-pair formation (counterion binding) and dipolar aggregation of the formed ion-pairs. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali metal poly(acrylate) gels; Ion-pair formation; Collapse

1. Introduction

Counterion binding plays an essential role in charged gel collapse [1–7]. It is well known that cationic gels show significant counterion specificity for the collapse [2,5,7]. Starodoubtsev et al. [5] reported that a polycation gel having quaternary ammonium group sharply deswells in aqueous salt solution containing I^-, while only gradually for Br^- and Cl^- counterions. Recently, we have found that an anionic gel from alkali metal poly(acrylate)s (PAAM) also shows a remarkable counterion-specific collapse in aqueous organic solvents [8]; Na^+ and K^+ are more favorable for inducing the collapse than Li^+ and Cs^+. This ion-specificity was interpreted as resulted from a balance of two size effects, one on the charge neutralization due to counterion binding and the other on electrostatic (dipolar) aggregation of the formed ion-pairs. That is, for the former, smaller counterions are more effective and for the latter larger ones must be favorable. Then, it seems to be worthwhile to see how coexistence of counterions of different sizes affects the gel collapse. Here we report an unexpected effect of counterion mixing on the collapse of PAAM gels. A combination of ‘unfavorable’ counterions i.e. Cs^+ and Li^+, favors the collapse but not the other combinations.

2. Experimental

PAA gel was prepared by irradiating γ-rays to aqueous solution of PAA ($MW = 90,000$ (Polysciences, Inc.), 15 wt%, $pH = 2.0$) in a thin capillary ($\phi = 0.693$ mm). Four kinds of PAAM gels (M: Li, Na, K, Cs) were obtained by neutralization with the respective alkali solutions. The swelling degree was measured by microscope observation of the gel diameter, d (mm), after one day immersion. The details are given elsewhere [8].

Two kinds of swelling experiments were performed at 25 ± 0.5°C in aqueous ethanol (EtOH); composition of the organic solvent was increased by 10 vol% at a constant counterion ratio, or the counterion mole fraction was changed by 0.1 in a constant EtOH composition which was set just below or above the collapse point for the respective single-counterion systems. The change of the counterion mole fraction was carried out by immersing a gel sample for one day into a mixed solvent which contains two kinds of alkali hydroxides (total conc. = 0.01 N), e.g. LiOH and CsOH, in a desired mole fraction. Another aim of the alkali addition was to prevent protonation of the polymer carboxyl group due to carbon dioxide [9].

3. Results and discussion

Counterion mixing effect was investigated for PAAM gels swollen in EtOH. Fig. 1(a) shows plots of the gel

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* Corresponding author. Tel.: +81-3-5734-2133; fax: +81-3-5734-2888.
E-mail address: msatoh@polymer.titech.ac.jp (M. Satoh).

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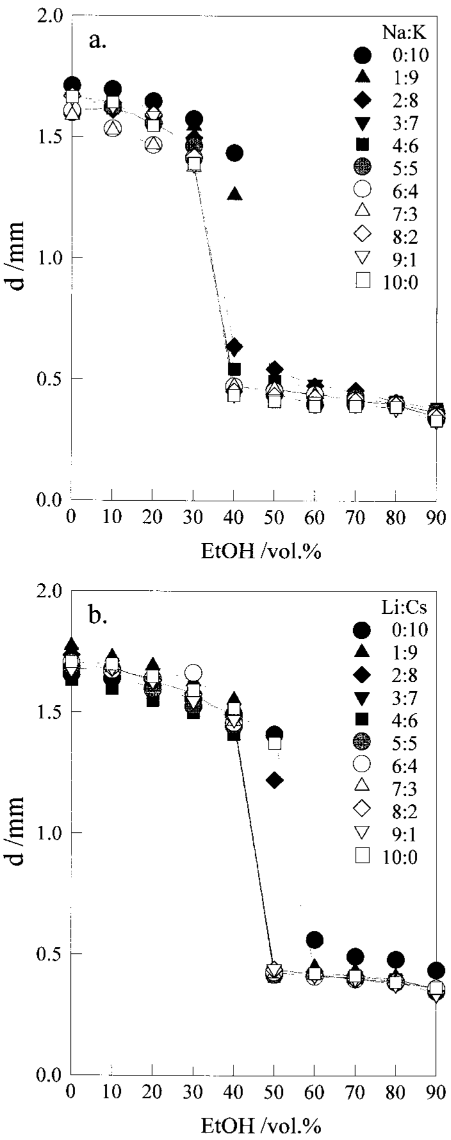

Fig. 1. Typical swelling behavior of PAAM gel in mixed counterion systems obtained by changing EtOH composition. (a) Mixing of two favorable counterions (Na^+ and K^+). (b) Two unfavorable counterions (Li^+ and Cs^+). Thin lines are guides for the eye.

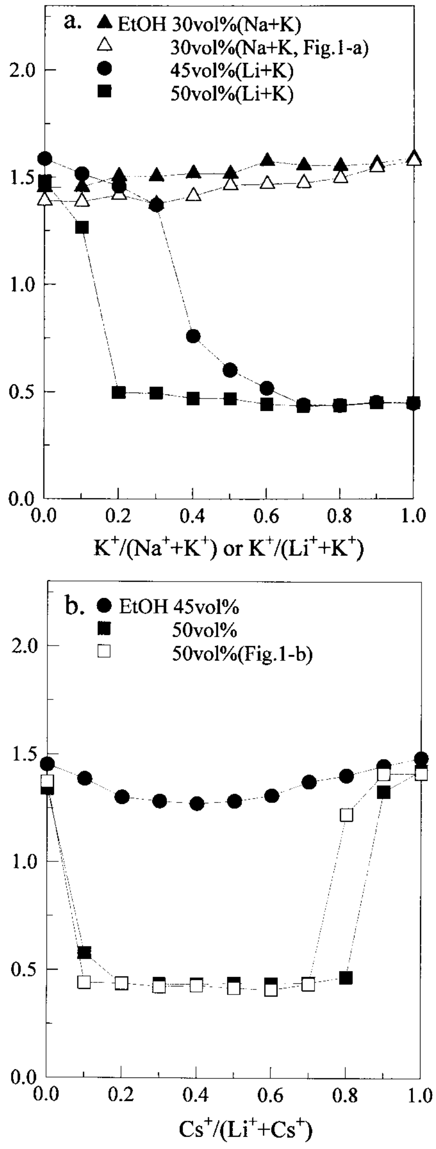

Fig. 2. Typical swelling behavior of PAAM gel in mixed counterion systems obtained by changing counterion mole fractions. (a) Two favorable counterions (Na^+ and K^+), and one favorable (K^+) and one unfavorable (Li^+). (b) Two unfavorable counterions (Li^+ and Cs^+). Thin lines are guides for the eye.

diameter, *d*, as a function of EtOH composition for a combination of 'favorable' counterions, Na^+ and K^+. No specific swelling or deswelling was observed.

For example, at 40 vol% EtOH, *d* smoothly decreases with increasing Na^+ fraction. On the other hand, one can see an unusual deswelling for unfavorable Li^+ and Cs^+ combination in Fig. 1(b). Namely, at 50 vol% EtOH, PAALi and PAACs gels are swollen while those of mixed counterion systems are collapsed.

In order to observe the counterion mixing effect more clearly, swelling behavior in a solvent of a fixed composition was investigated by changing the counterion mixing ratio i.e. mole fraction of two counterions in the immersing solvent. The results are shown in Fig. 2. For $Na^+ + K^+$ system, almost the same result as that shown in Fig. 1(a) was obtained for 30 vol% EtOH. For a combination of unfavorable Li^+ and favorable K^+ too, no specific behavior was observed. A gradual deswelling occurs with increasing favorable K^+ fraction at 45 vol% EtOH. At 50 vol%, the collapse occurs more sharply at the lower K^+ fraction, which seems rather natural because the solvent composition (50 vol% EtOH) is very close to the collapse region of PAALi (see Fig. 1(b)).

Fig. 2(b) clearly shows that the mixing system of Li^+ and Cs^+ is more favorable for the gel collapse than the respective single counterion systems. The deswelling–swelling course is almost similar to that obtained by changing EtOH composition at the respective counterion fractions (Fig. 1(b)). Although one may note small differences between the plots from the two experiments (open and filled squares), they may be ascribed to insufficient increase in Cs^+ mole fraction within the gel by increasing Cs^+ fraction in the immersing solvent. To be noted here is that an appreciable deswelling, though much less significant than that in 50 vol% EtOH, was also induced by mixing the two counterions in 45 vol% EtOH, a less favorable solvent for gel collapse of the respective single counterion systems.

The counterion mixing effect observed must be closely related with the mechanism of the charged gel collapse. According to Philippova et al. [10], collapse of charged gels is accompanied by ion-cluster formation, in which ion-pairs like $-COO^-M^+$ aggregate by dipolar attraction. Therefore, an optimum condition for the collapse should be obtained when counterion binding occurs with a moderate degree of charge neutralization that can reserve a sufficient dipolar attraction. If too small counterions formed ion-pairs with polymer charges, the dipolar attraction among them may be insufficient for ion-cluster formation. Judged from the ion-specificity known for the counterion binding of poly(carboxylate)s [9,11,12] i.e. $Cs^+ < K^+ < Li^+ < Na^+$ or $Cs^+ < K^+ < Na^+ < Li^+$, Li^+ can effectively neutralize the polymer charge by counterion binding, probably also in the present PAA gel systems. Thus, the reason why Li^+ as counterion is unfavorable for the gel collapse seems to be the small dipole moment of the ion-pair. On the other hand, counterion binding of the other unfavorable ion, Cs^+, should result in ion-pairs of a large dipole moment, although the degree of counterion binding may be insufficient for ion-cluster formation. Once these unfavorable counterions are mixed, the respective weak points may be compensated. For example, presence of a small amount of $-COO^-Li^+$ ion pairs in PLGCs system may contribute to induce a nucleus for the ion-cluster formation by complementing the number of ion-pairs, which is otherwise insufficient in the single Cs system. On the other hand, addition of small amount of Cs^+ into the PLGLi system may induce a nucleus for the ion-cluster formation by slightly enhancing the attractive force among the mixed ion-pairs than the single Li system.

The present ‘unexpected’ counterion mixing effect for PAA gel collapse seems to come from the inherent high cooperativity of the phenomenon, where only a subtle change in the energy balance would give rise to quite a different output. In order to demonstrate the above speculation, microscopic observation of the ion-pair formation e.g. by NMR, would be necessary. Such an investigation, as well as extension of the solvent and polymer systems, is now being undertaken.

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