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Discontinous volume changes of sodium acrylate-acrylamide-*N,N'*-methylenebisacrylamide copolymer gels in various solvent mixtures

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Summery

Volume behaviors of sodium acrylate-acrylamide-N,N'-methylenebisacrylamide copolymer gels in various solvent mixtures were examined. The gel samples having the same composition but different overall concentrations exhibited a discontinuous volume change at an appropriate solvent composition when immersed in methanol-water and tetrahydrofuran-water mixtures, but at some different solvent compositions when immersed in dioxane-water and acetonitrile-water mixtures because of significant flucutuation of the gel polymer-solvent mixture interaction.

Introduction

In previous works,[1-3] we have referred to the specific discontinuous volume phase transitions that 2-acryloyloxyethyl acid phosphate mono polymer gels of various concentrations all undergo at an appropriate solvent composition when immersed not only in acetone-water mixtures but also in other solvent mixtures. The above behavior is essentially different from the typical volume phase transition observed when conventional cross-linked gels with an ionizable group are immersed in some solvent mixtures,because the ionic gels undergo a discontinuous volume change from a shrunken to swollen state and the volume change at the transition point increases with an increase in ionic density of the gel and the transition point shifts to a higher acetone composition.[4-11] Such specific volume behavior has also been observed for sodium acrylate(SAc)-acrylamide(Am)-N,N'-methylenebisacrylamide(Bis) copolymer gels having the same composition but different overall concentrations, when they were immersed in acetone-water mixtures.[2] Accordingly, the remaining problem is whether the SAc-Am-Bis copolymer gels immersed in solvent mixtures other than acetone-water mixtures all undergo discontinuous volume changes at an appropriate solvent

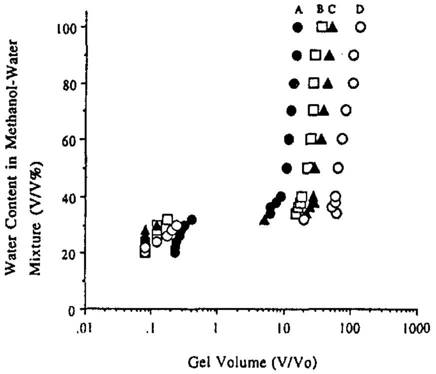

Figure 1. The volume phase transition of sodium acrylate(SAc) - acrylamide(Am) - N,N'-methylene-bisacrylamide(Bis) copolymer gels immersed in methanol-water mixtures.

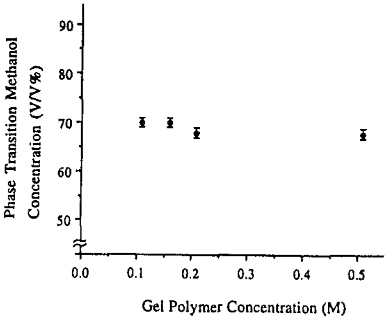

Figure 2. A plot of the phase transition methanol concentration (v/v%) versus the SAc-Am-Bis copolymer gel concentration.

composition or not. The purpose of the present experiment is thus to examine the volume behaviors of SAc-Am-Bis copolymer gels immersed in methanol-water, tetrahydrofuran-water, dioxane-water, acetonitrile-water and dimethylsulfoxide-water mixtures and generalize the specific transition behavior depending on an appropriate solvent composition.

Experimental Section

Acrylic acid(Ac), acrylamide(Am) and N,N'-methylenebis-acrylamide(Bis) were commercially obtained and used as monomer reagents for preparations of the gel samples. Methanol, tetrahydrofuran, dioxane, acetonitrile and dimetylsulfoxide were also commercially obtained and used for preparations of various types of solvent mixtures. Sodium acrylate(SAc), which was previously prepared by reacting acrylic acid to sodium carbonate before preparation of gel samples, was actually incorporated into the gel polymers. A concentrated mother liquor containing SAc, Am and Bis was first prepared and then aqueous solutions of various concentrations were prepared by successive dilution of the mother liquor with distilled water. Thus, the gel samples (A-D) were prepared by copolymerization of each aqueous solution at 50°C for 1hr. after adding ammonium persulfate(initiator;40mg), where the SAc contents in each gel sample(A, B,C and D) were 0.5, 0.2, 0.15 and 0.1 M in each case and the molar ratio of each composition(SAc/Am/Bis) remained constant at 1/ 5.5/ 0.05. The prepared gel samples were washed in distilled water for a few days and then immersed in methanol-water, acetonitrile-water, tetrahydrofuran-water, dioxane-water and dimethylsulfoxide-water mixtures.

Results and Discussion

Figure 1 shows the volume behaviors of SAc/Am/Bis copolymer

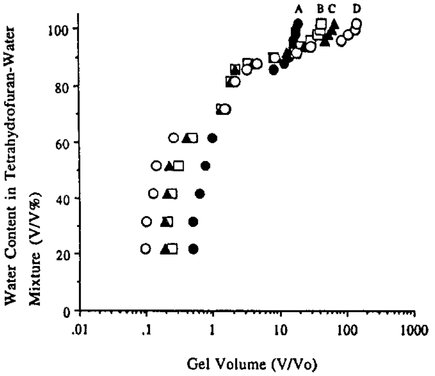

Figure 3. The volume phase transition of SAc-Am-Bis copolymer gels immersed in tetrahydrofuran-water mixtures.

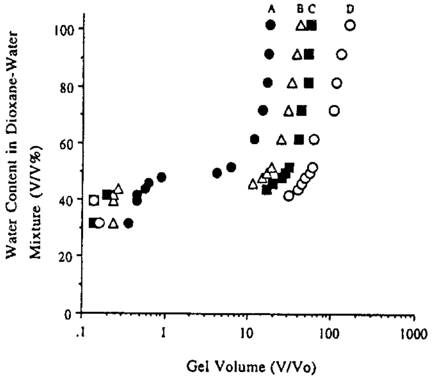

Figure 4. The volume phase transition of SAc-Am-Bis copolymer gels immersed in dioxane-water mixtures.

gels immersed in methanol-water mixtures. An equilibrium volume of the gel samples(A-D) in distilled water or in mixtures of high methanol composition decreased with an increase in gel concentration, where the gel concentration varied with the SAc concentration. The same tendency in volume behavior was also observed for the SAc/Am/Bis copolymer gels immersed in tetrahydrofuran-water, dioxane-water, acetonitrile-water and dimethylsulfoxide-water mixtures, as shown in Figures 3,4,5 and 6. These volume behaviors are in marked contrast to those observed for conventional polymer gels, because an equilibrium volume of the gels is generally observed to increase with an increase in ionic density. As a result of previous work,[2,3] the above result can be accounted for by a characteristic volume behavior of polymer gels having the same composition but different overall concentrations.

The copolymer gel samples all exhibited swollen states in the mixtures below 68% methanol and collapsed states in the mixtures above 68% methanol. It is noteworthy that the gels all undergo a discontinuous volume change at the same composition of 68% methanol. In order to estimate the accuracy of methanol concentration to justify the observation at the transition point, the methanol composition at the transition point is plotted against the gel polymer concentration in Figure 2. Since observations near the transition point were carefully performed using solvent mixtures at 2 V/V% intervals, the above finding that the gels all underwent a discontinuous volume change at 68% methanol could be determined within an error of 2 V/V%. Thus, the present copolymer gels in methanol-water mixtures, as well as those in acetone-water mixtures previously reported,[4-11] exhibit discontinuous volume changes at an appropriate transition point, although the gel concentration changes.

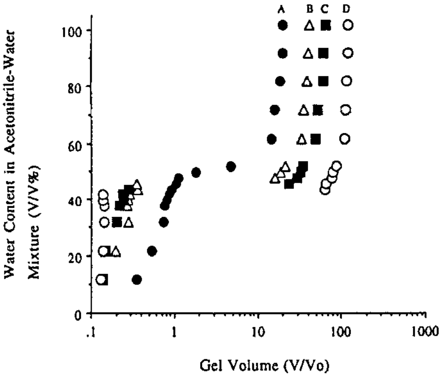

Figure 5. The volume phase transition of SAc-Am-Bis copolymer gels immersed in acetonitrile-water mixtures.

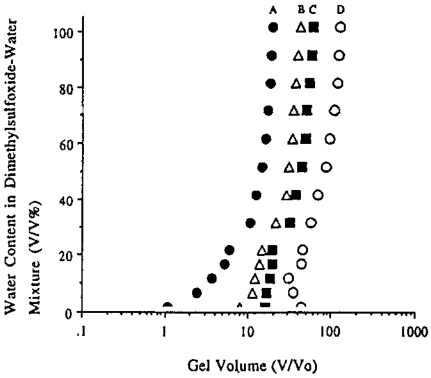

Figure 6. The volume phase transition of SAc-Am-Bis copolymer gels immersed in dimethylsulfoxide-water mixtures.

Figure 3 shows the volume behaviors of the SAc-Am-Bis copolymer gels immersed in THF-water mixtures. As the THF concentration decreases, the gel samples of A and B underwent a gradual volume change from a swollen to collapsed state via a slight discontinuous volume change at 13 and 11% THF. On the other hand, the gel samples of C and D underwent gradual volume changes with an inflection point at about 10% THF. These results suggest that the discontinuous volume changes and the inflection points occur at a particular transition point within an accuracy of 3%. The accuracy of THF concentration to justify the observation was also estimated by examining the phase transition of THF concentration vs. the polymer concentration.

Volume behaviors of the copolymer gels immersed in dioxane-water and acetonitrile-water mixtures are shown in Figures 4 and 5. Transition points in Figure 4 were somewhat scattered over 51% to 57% dioxane, and those in Figure 5 were also scattered over 50% to 57%. This suggests that the copolymer gels immersed in dioxane-water and acetonitrile-water mixtures no longer underwent discontinuous volume changes at an appropriate solvent composition. On the basis of the previous discussion,[2] the specific volume behavior whereby the copolymer gels having the same composition but different overall concentration undergo a discontinuous volume change at an appropriate acetone composition has been successfully considered consistent with an inter-molecular interaction between the gel polymer and the solvent mixture(or miscibility of the gel polymer to the solvent mixture), because the interaction (or the miscibility) at the transition point remains almost unchanged even though the polymer concentration changes. In contrast to this, the present result could be accounted for by the fact that the interaction (or miscibility) near the transition point fluctuates slightly upon changes in polymer concentration against a solvent mixture and no longer remains unchanged.

The SAc-Am-Bis copolymer gel samples immersed in dimethylsulfoxide(DMSO)-water mixtures exhibited gradual volume changes from a swollen to collapsed state with an increase in DMSO concentration, but neither any inflection points nor discontinuous volume changes could be detected (Figure 6).

Consequently, the SAc-Am-Bis copolymer gels immersed in methanol-water and THF-water mixtures almost exhibited discontinuous volume changes at appropriate solvent compositions, but those in dioxane-water and acetonitrile-water mixtures exhibited some scattered transition points because of a significant fluctuation in the interaction between the gel polymer and the solvent mixtures. These results could also be accounted for by considering that the miscibility of the gel polymer to the solvent mixtures is dependent upon changes in gel concentration.

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