Specific volume phase transition of 2-acryloyloxyethyl acid phosphate gels in various solvent mixtures at a particular transition point

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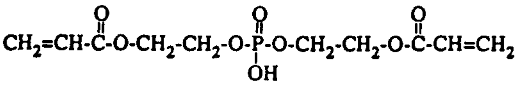
Volume behaviours of 2-acryloyloxyethyl acid phosphate monopolymer gels immersed in methanol–water, acetonitrile–water, tetrahydrofuran–water, dioxane–water and dimethylsulfoxide–water mixtures were examined. Polymer gel samples of the same composition but differing in overall concentration all exhibited a discontinuous volume change at an appropriate solvent composition, regardless of change in gel concentration. This could be accounted for by an unchanged interaction between the polymer gel at various concentrations and a solvent mixture at each transition point.

(Keywords: volume phase transition; polymer gel; solvents)

Introduction

Polyelectrolyte gels undergo a discontinuous volume change with change in solvent composition, temperature, pH and ionic strength[1–16]. This behaviour is a volume phase transition between a swollen gel and a shrunken gel and is generalized as a typical first-order phase transition. The typical volume phase transition observed for a sodium acrylate gel immersed in acetone–water mixtures has been characterized by the following volume behaviour[7,8]. As acetone composition increases, the gel undergoes volume change from a shrunken to a swollen state via discontinuous volume change. Volume change at the transition point increases with ionic density of the gel and the transition point shifts to a higher acetone composition. This suggests that discontinuous volume change may be considerably dependent on crosslinking, ionizing and polymerizing in the polymer gel. According to conventional experimental results[1,7], popular crosslinked gels with an ionizable group generally exhibit discontinuous volume change at different transition points. In contrast to this, a new type of volume phase transition was recently observed for 2-acryloyloxyethyl acid phosphate (AEAP) monopolymer gels[9,10].



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2$$

2-Acryloyloxyethyl acid phosphate (AEAP)

The gels all underwent discontinuous volume change depending on acetone composition. This new type of volume phase transition may be explained based on characteristic properties of the gel of the same composition but different overall concentration. This type of gel has the same chemical composition regardless of change in gel concentration. An intermolecular interaction between the polymer gel and acetone–water mixture (or miscibility of the polymer gel to an acetone–water mixture) would appear to remain almost unchanged regardless of gel concentration. The above specific volume phase transition has been clarified only by experimental data on AEAP monopolymer gels in acetone–water mixtures. Thus, whether specific transition behaviour can generally be observed for AEAP monopolymer gels, even in other solvent mixtures, is a point that should be clarified. This experiment was thus conducted to examine comprehensively the specific transition behaviour of AEAP monopolymer gels immersed in methanol–water, acetonitrile–water, tetrahydrofuran (THF)–water, dioxane–water and dimethylsulfoxide (DMSO)–water mixtures.

Experimental

AEAP was obtained from Daihachi Co. Ltd and used as a monomer reagent for preparing AEAP monopolymer gel samples. The sample preparation procedure was the same as that previously reported[9–11]. The concentrated mother liquor was first prepared and aqueous solutions of various concentrations were made by successive dilutions of the mother liquor with distilled water. Gel samples having various AEAP concentrations (A, 0.75 M; B, 0.65 M; C, 0.55 M; D, 0.45 M; and E, 0.40 M) were prepared by the polymerization of each aqueous solution in micropipettes at 50°C for 1 h following the addition of ammonium persulfate (initiator, 40 mg). The prepared gel samples were washed in flowing water for a few days and immersed in methanol–water, acetonitrile–water, THF–water, dioxane–water and DMSO–water mixtures. After equilibrium had been reached, the diameter of each cylindrical gel sample was measured. Gel volume (V) was estimated by cubing the diameter.

Results and discussion

Figure 1 shows the volume behaviour of AEAP monopolymer gels immersed in methanol–water mixtures. The equilibrium volume of each AEAP monopolymer gel sample (A–E) in distilled water or mixtures of high methanol composition decreased with an increase in AEAP concentration. This volume behaviour is in marked contrast to that observed for conventional crosslinked gels with an ionizable group, because the

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equilibrium volume of the gels was observed to increase with an increase in ionic density. Thus, the present experimental results could be explained as follows. AEAP is a bifunctional monomer with an ionizable group. Since a bifunctional group such as a crosslinker causes the gel to shrink and the ionizable group causes the gel to swell, the AEAP monopolymer gel should be influenced by the two competing effects at the same time. In this case, the former effect dominates the latter, because an increase in gel concentration (AEAP) actually resulted in a decrease in gel volume. In this manner, the increase in AEAP could ultimately be responsible for the decrease in gel volume[9-11]. A similar volume decrease was observed for the AEAP gels immersed in other solvent mixtures, as shown in *Figures 2–5*.

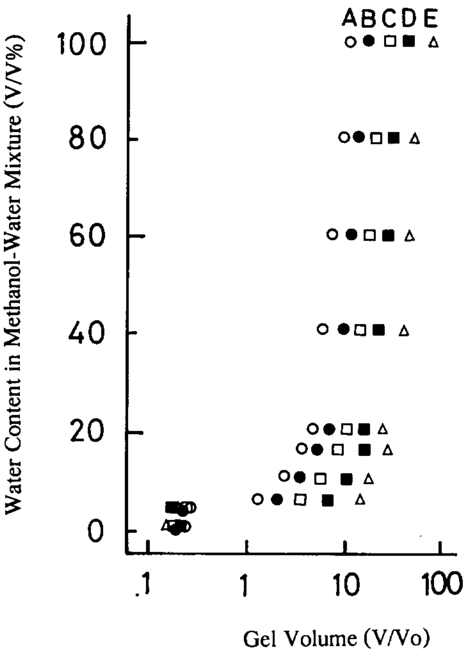

Figure 1 Volume behaviour of AEAP monopolymer gels immersed in methanol–water mixtures. AEAP content of the gel samples: A, 0.75 M; B, 0.65 M; C, 0.55 M; D, 0.45 M; E, 0.40 M

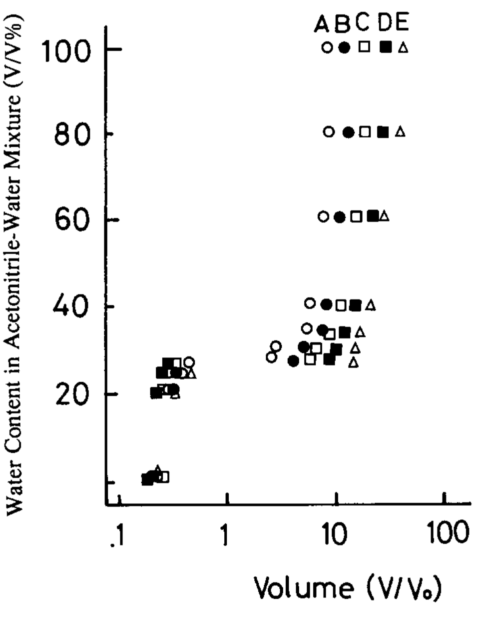

Figure 2 Volume behaviour of AEAP monopolymer gels immersed in acetonitrile–water mixtures. A–E as in *Figure 1*

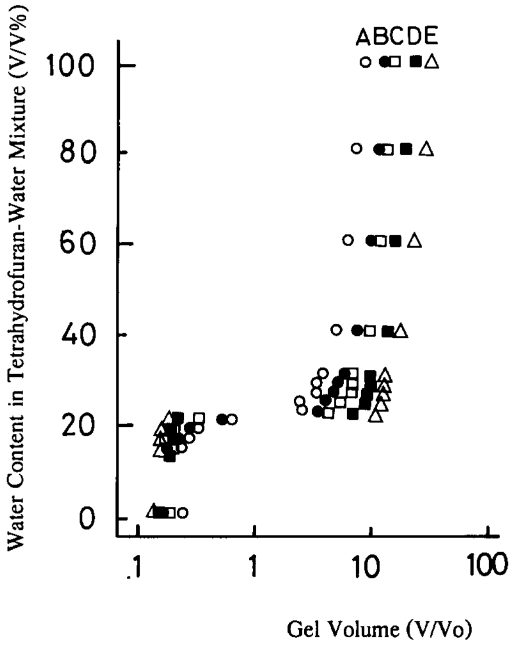

Figure 3 Volume behaviour of AEAP monopolymer gels immersed in tetrahydrofuran–water mixtures. A–E as in *Figure 1*

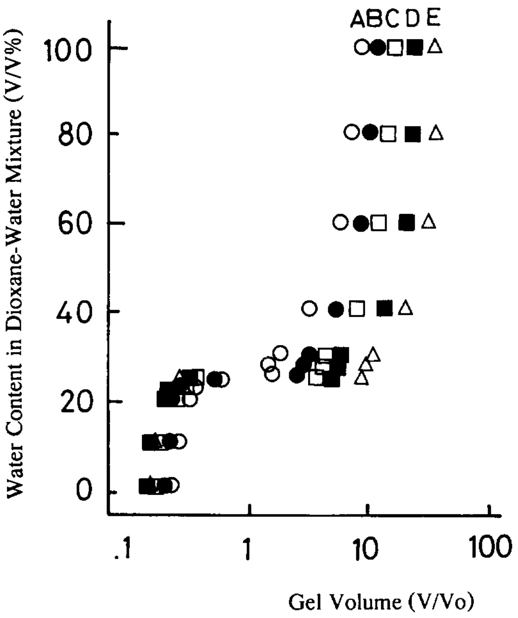

Figure 4 Volume behaviour of AEAP monopolymer gels mmersed in dioxane–water mixtures. A–E as in *Figure 1*

The gel samples became swollen in mixtures below 95% methanol and collapsed in mixtures above 95% methanol. All underwent discontinuous volume change at 95% methanol. It is noteworthy that AEAP monopolymer gel samples in methanol–water mixtures, as well as those in acetone–water mixtures, exhibited discontinuous volume change at the same transition point, regardless of gel concentration. The characteristic properties of gels of the same composition but different in overall concentration may be the reason for the above results.

Figure 2 shows the volume behaviour of AEAP monopolymer gels immersed in an acetonitrile–water mixture. Each became swollen in mixtures below 72% acetonitrile and collapsed in mixtures above 72% acetonitrile. At 72% acetonitrile, all gels underwent

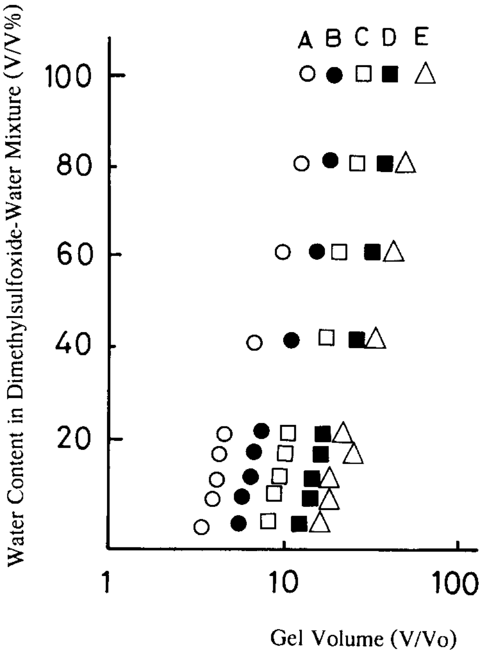

Figure 5 Volume behaviour of AEAP monopolymer gels immersed in dimethylsulfoxide–water mixtures. A–E as in *Figure 1*

discontinuous volume change. It should be pointed out that the AEAP monopolymer gels all exhibit discontinuous volume change at the same transition point, regardless of change in gel concentration.

Similar volume behaviour was observed for AEAP monopolymer gel samples immersed in THF–water (*Figure 3*) and dioxane–water mixtures (*Figure 4*). In the former case, the gels underwent discontinuous volume change at 77% THF, became swollen in mixtures below 77% THF and collapsed in mixtures above 77% THF. In the latter case, they were swollen in mixtures below 74% dioxane and collapsed in mixtures above 74% dioxane. All underwent discontinuous volume change at 74% dioxane. Thus, concentrations of the mixtures at the transition point could all be determined with errors of less than 2% v/v in the same manner as previously reported[10]. However, the AEAP monopolymer gel samples immersed in DMSO–water mixtures underwent gradual volume change with a change in DMSO concentration; that is, no discontinuous volume change could be observed (*Figure 5*).

It is evident from the present results that the AEAP monopolymer gel samples immersed in methanol–water, acetonitrile–water, THF–water and dioxane–water mixtures exhibit discontinuous volume change at an appropriate solvent composition regardless of gel concentration. Such specific transition behaviour, depending on an appropriate transition point, was previously shown to be due to characteristic properties of gels of the same composition but differing in overall concentration[10,11]. Thus, this type of gel always has the same chemical composition regardless of change in gel concentration. It then follows that an intermolecular interaction between a polymer gel and a solvent mixture (or miscibility of a polymer gel with a solvent mixture) remains almost unchanged although gel concentration may change. According to the general rule for volume phase transition[2,12], the transition point from a swollen to a collapsed gel should generally be equivalent to the phase transition from one phase to two phases in a polymer–solvent binary system. Alternatively, it should correspond to conversion from a good to a poor solvent. The phase transition point may thus be governed primarily by an intermolecular interaction (or miscibility). If the chemical compositions of AEAP monopolymer gel samples remain unchanged regardless of change in gel concentration, an intermolecular interaction between the polymer gel at various concentrations and a solvent mixture at each transition point should also remain unchanged. If this is the case, critical conditions at the transition point may be determined primarily by an appropriate solvent composition. This is a reason for the discontinuous volume change depending on an appropriate transition point.

Consequently, such discontinuous volume change may be observed for AEAP monopolymer gels even in solvent mixtures other than acetone–water mixtures. The specific transition behaviour observed for polymer gels of the same composition but differing in overall concentration should be considered as a general phenomenon.

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