

# Effect of pH, Ionic Strength, and Temperature on Uranyl Ion Adsorption by Poly(*N*-vinyl 2-pyrrolidone-*g*-tartaric Acid) Hydrogels

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**ABSTRACT:** Poly-electrolyte *N*-vinyl 2-pyrrolidone-*g*-tartaric acid (PVP-*g*-TA) hydrogels with varying compositions were prepared in the form of rods from ternary mixtures of *N*-vinyl 2-pyrrolidone/tartaric acid/water. The effect of external stimuli, such as the solution pH, ionic strength, and temperature, on uranyl adsorption by these hydrogels was investigated. Uranyl adsorption capacities of the hydrogels were determined to be 53.2–72.2 (mg UO<sub>2</sub><sup>2+</sup>/g dry gel) at pH 1.8, and 35.3–60.7 (mg UO<sub>2</sub><sup>2+</sup>/g dry gel) at pH 3.8, depending on the amount of TA in the hydrogel. The adsorption studies have shown that the temperature and the ionic strength of the swelling solution also influence uranyl ion adsorption by PVP-*g*-TA hydrogels. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2219–2226, 2000

**Key words:** hydrogel; poly(*N*-vinyl 2-pyrrolidone-*g*-tartaric acid); sorption; uranyl ions

## INTRODUCTION

Polymeric and copolymeric hydrogels continue to be developed and used to complex metal ions in both ion-exchange and selective adsorption purposes. Such polymeric ligands may be tailored to remove certain metal ions or groups from aqueous media heavy metal ions by bonding.

In view of the anticipated exhaustion of terrestrial uranium reserves in the near future, research has been directed toward the recovery of uranium from nonconventional sources, such as

coal and natural waters (0.1–10 mg U/m<sup>3</sup>), and especially from seawater (2.8–3.3 mg U/m<sup>3</sup>). The recovery of uranium from contaminated water of flooded mines (0.1–15 mg U/m<sup>3</sup>) also presents a very important environmental problem to be solved. The use of adsorbents is thought to be the most effective method for recovering uranium because of the high selectivity for uranium, the ease of handling, and safety to the environment.<sup>1–4</sup>

Crosslinked copolymers of the diethyl ester of vinyl phosphoric acid and acrylic acid, and crosslinked copolymers of natural polymers have been used for the adsorption of heavy metal ions.<sup>5,6</sup> Amidoxime derivatives of copolymeric hydrogels prepared from acrylonitrile and divinyl benzene have been used for the recovery of uranium from seawater.<sup>7–10</sup>

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In a series of articles published by Saraydin, Karadag, and Güven, new hydrogels were synthesized from copolymers of acrylamide and diprotic itaconic acid and maleic acid.<sup>11–13</sup> The authors noted that these hydrogels are potential adsorbents for biological agents and dyes and heavy metal ions from aqueous solution.<sup>14–16</sup>

Water uptake, and thereby metal ions uptake, increases as the hydrophilicity of the polymer is enhanced, because the diffusion of aqueous solutions into more hydrophilic polymers is faster than in less hydrophilic polymers. This is a rate-determining step for adsorption.<sup>17</sup>

We now report on the preparation of new hydrogel polymer adsorbents containing hydrophilic groups by grafting of tartaric acid during polymerization of *N*-vinyl 2-pyrrolidone with <sup>60</sup>Co  $\gamma$ -rays and the effect of external stimuli, such as pH, ionic strength, and temperature, on uranyl ion adsorption by these hydrogels.

## EXPERIMENTAL

### Chemicals

*N*-Vinyl 2-pyrrolidone (VP) was obtained from Aldrich, and tartaric acid (TA) from Carlo Erba. The uranyl nitrate (UN) used for adsorption studies and sodium salicylate used as a complexing agent were purchased from Fisher and Merck, respectively.

### Preparation of Hydrogels

Aqueous solutions of VP and TA were prepared in 1.0 mL of water at different compositions (VP/TA mole ratios of 98.4/1.6, 97.6/2.4, 96.8/3.2 for Gel 1, Gel 2, Gel 3, and Gel 4, respectively). The solutions were placed in PVC straws (4-mm diameter) and irradiated to 25 kGy in air at ambient temperature in a PX- $\gamma$ -30 Isslodovateji irradiator at a fixed dose rate of 3.87 kGy/h.

### Composition of Hydrogels

The hydrogels obtained as long cylinders were cut into 3–4 mm-long pieces. The pieces were dried in a vacuum oven at 315 K to constant weight, and subjected to Soxhlet extraction with water. The ungrafted TA and residual monomer were removed from the gel by this extraction. The extracted gel pieces were dried again in a vacuum oven at 315 K to constant weight. The amount of

unreacted TA in the aqueous extract was determined by titration with NaOH (0.05 M) to a phenolphthalein end point. The molar percentages of TA in the Gel 1, Gel 2, Gel 3, and Gel 4 were found to be 1.7, 2.0, 2.6, and 3.1%, respectively.

### Swelling Studies

The dried hydrogel was swollen in distilled water or aqueous UN solutions at 25°C. The swollen gel was removed from the water bath, dried with a filter paper, weighed, and replaced in the same bath. The mass percentage swelling was calculated from the following equation.<sup>18</sup>

$$S\% = [(m_t - m_0)/m_0] \cdot 100 \quad (1)$$

where  $m_t$  is the weight of swollen gel at time  $t$ , and  $m_0$  is the initial weight of the dried hydrogel.

### Adsorption of $\text{UO}_2^{2+}$ by PVP-*g*-TA Hydrogels

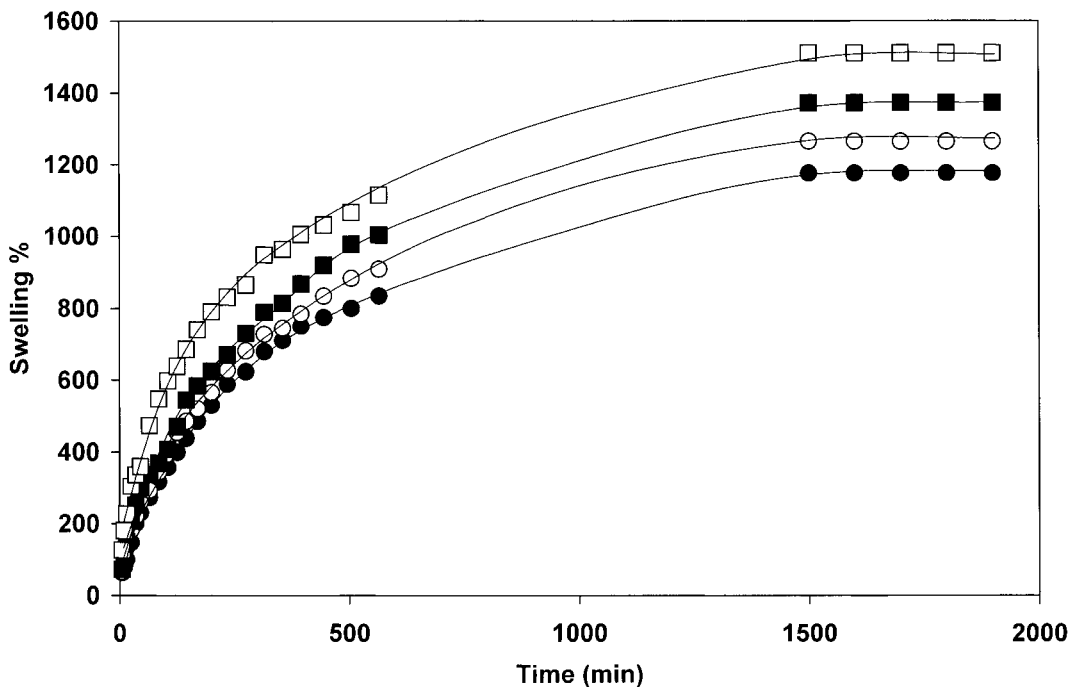
A weighed amount of the PVP-*g*-TA hydrogel (~0.1g) was added to 50 mL of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution (pH = 4.0) with a concentration range of 50–500 ppm, and allowed to equilibrate for 48 h at 25°C. The adsorbent was removed from the solution by decantation. The equilibrium concentration of the solution was determined by UV spectrometry. Sodium salicylate (10% w/w) with an absorption maximum at 466 nm wavelength was used as a complexing agent. The absorption measurements were performed with a Jenway 5105 UV visible spectrophotometer at 466 nm against a blank solution of deionized water.<sup>19</sup>

To investigate the effect of pH on the  $\text{UO}_2^{2+}$  adsorption capacity of the hydrogels, pH 2–10 solutions were prepared using HCl and NaOH. However, with addition of 500 ppm UN into these solutions the pH changed to 1.8–3.8. Therefore, the effect of pH on the  $\text{UO}_2^{2+}$  adsorption by the hydrogels was determined at pH 1.8, 3.0, and 3.8.

## RESULTS AND DISCUSSION

### Swelling behavior of PVP-*g*-TA Hydrogels in Water and $\text{UO}_2^{2+}$ Solutions

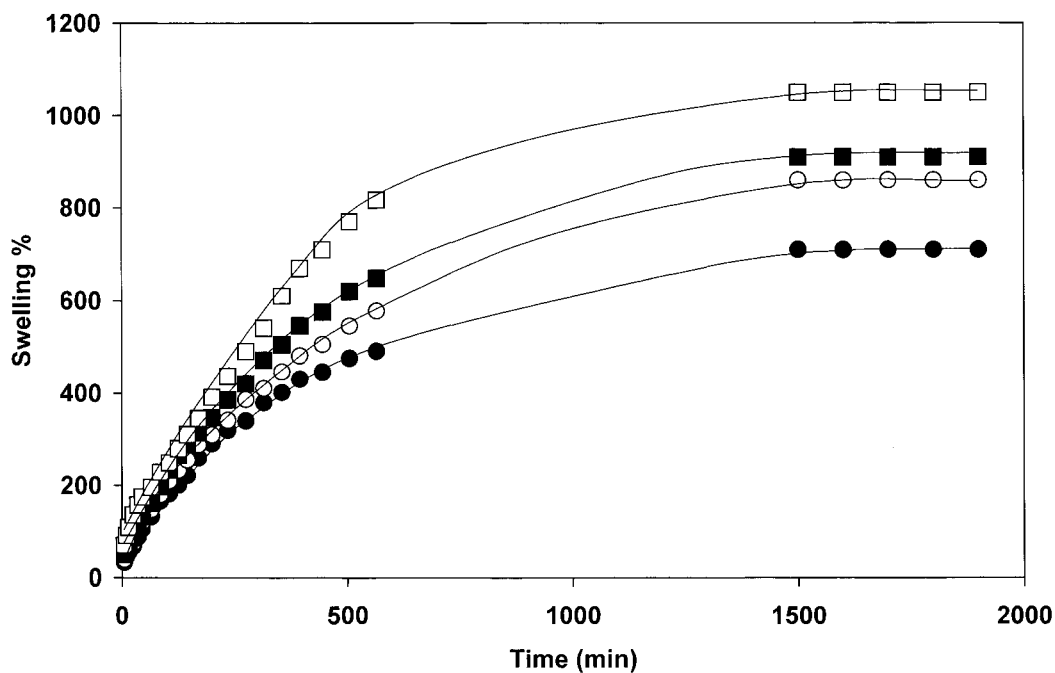
Water uptake of initially dry hydrogels containing various amounts of TA was followed gravimetrically. The dynamic swelling curves of PVP-*g*-TA hydrogels in water and uranyl nitrate solution are given in Figures 1 and 2, respectively. As can



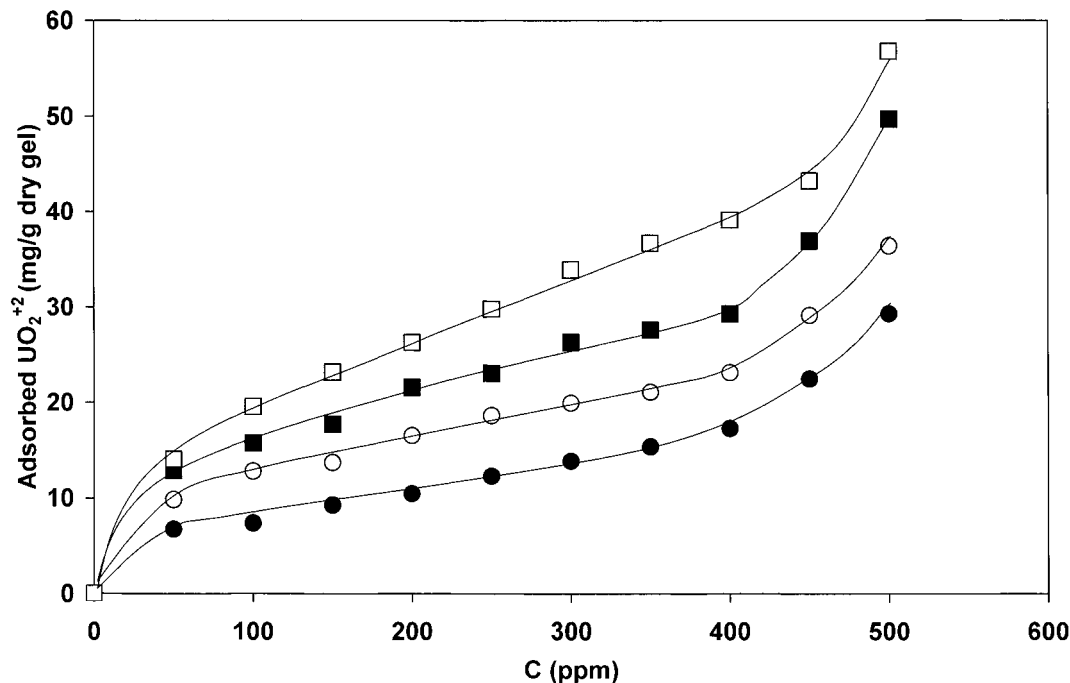
**Figure 1** Swelling curves for hydrogels in water: (●) Gel 1, (○) Gel 2, (■) Gel 3, (□) Gel 4.

be seen from these figures, the percentage equilibrium swelling of the hydrogels is lower (710–1050%) in uranyl solutions than (1180–1510%) in

water. This decrease is attributed to the adsorption of uranyl ions in the gel system with exclusion of water molecules at the expense of ad-



**Figure 2** Swelling curves for hydrogels in  $UO_2^{2+}$  solutions: (●) Gel 1, (○) Gel 2, (■) Gel 3, (□) Gel 4.



**Figure 3** Adsorption isotherms for uranyl ion from uranyl nitrate solutions onto PVP-g-TA hydrogels: (●) Gel 1, (○) Gel 2, (■) Gel 3, (□) Gel 4.

sorbed ions, and to an increase of the ionic strength of the swelling solution. It has been determined that the equilibrium swelling value of PVP-g-TA hydrogels is very sensitive to the ionic strength of the swelling solutions.<sup>20</sup>

#### Adsorption of $\text{UO}_2^{2+}$ on PVP-g-TA Hydrogels

To observe the adsorption of  $\text{UO}_2^{2+}$  ions, the PVP-g-TA hydrogel was placed in aqueous solutions of uranyl nitrate and allowed to equilibrate for 2 days. At the end of this time, the colors of  $\text{UO}_2^{2+}$  ion-adsorbed PVP-g-TA had changed from light yellow to dark brown. However, a PVP hydrogel did not sorb any  $\text{UO}_2^{2+}$  ions from the solution. The mass of uptake of  $\text{UO}_2^{2+}$  ions per unit mass of adsorbent was calculated from the following relation:

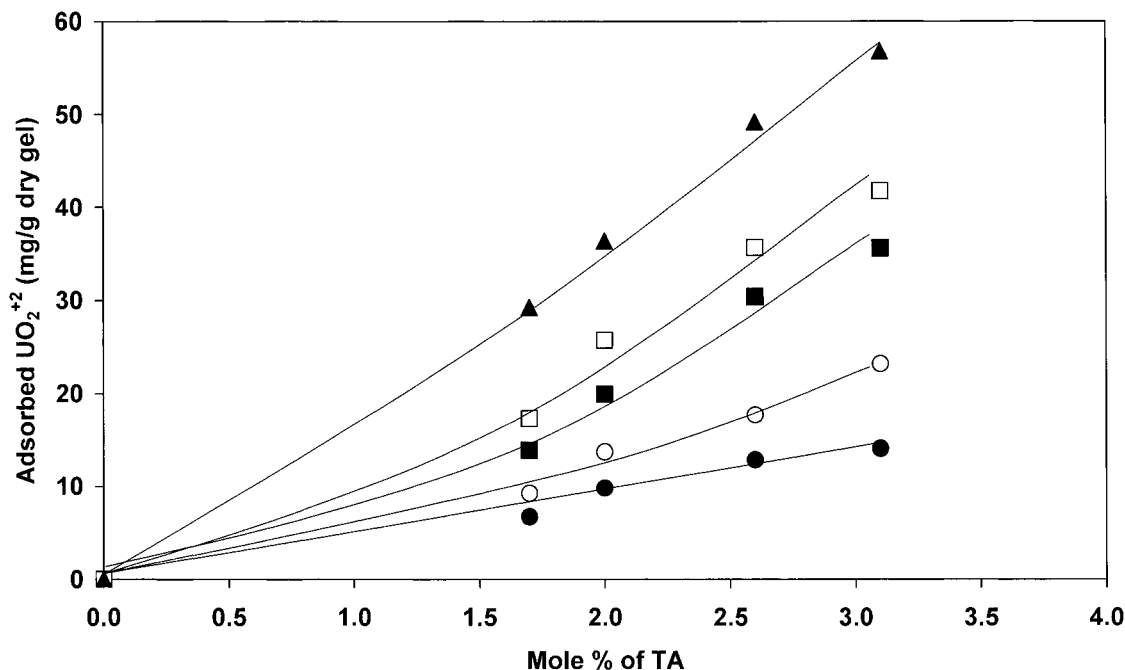
$$\text{Adsorbed } \text{UO}_2^{2+} \text{ (mg/g dry gel)} = \frac{C_i - C}{m} V_t \quad (2)$$

where  $C_i$  and  $C$  are the initial and equilibrium concentrations of solution of adsorbate,  $V_t$  is the total volume of solution of adsorbate, and  $m$  is the mass of dry adsorbent.

Graphs of adsorbed  $\text{UO}_2^{2+}$  against the equilibrium concentrations of  $\text{UO}_2^{2+}$  ions,  $C$ , are plotted in Figure 3.

Adsorption of  $\text{UO}_2^{2+}$  ions from solution of uranyl nitrate onto PVP-g-TA hydrogels corresponds to Type II isotherms.<sup>21</sup> In the vast majority of cases, physical adsorption gives rise to a Type II isotherm. The model is controlled by the forces between the adsorbent and the adsorbate molecules (vertical interactions), and neglects the forces between an adsorbate molecule and its neighbors in the same layer (horizontal interactions). From the nature of the intermolecular forces, it is certain that adsorbate-adsorbate interactions must be far from negligible when a layer is approaching completion and the average separation of molecules is, therefore, small in relation to their size.<sup>21</sup>

The amount of adsorbed  $\text{UO}_2^{2+}$  ions depends on the concentration of the uranyl solution and mole percentage of TA in the gel system, as shown in Figure 4. As can be seen from the figure, the uranyl adsorption capacity of these hydrogels is in the range of 7–57 mg  $\text{UO}_2^{2+}$ /g dry gel for the uranyl nitrate solution. Increasing the amount of TA in the hydrogel from 1.7 to 3.1 mol % causes a



**Figure 4** Effect of the mol % of TA in the gel system on the uranyl ion adsorption from uranyl nitrate solutions: (●) 50 ppm, (○) 150 ppm, (■) 300 ppm, (□) 400 ppm, (▲) 500 ppm.

significant increase in the amount of adsorbed  $\text{UO}_2^{2+}$  ions. This is attributed to an increase in specific interactions between positively charged  $\text{UO}_2^{2+}$  ions and ionized TA in the hydrogel, as well as an increase of free volume of gel available for diffusion.

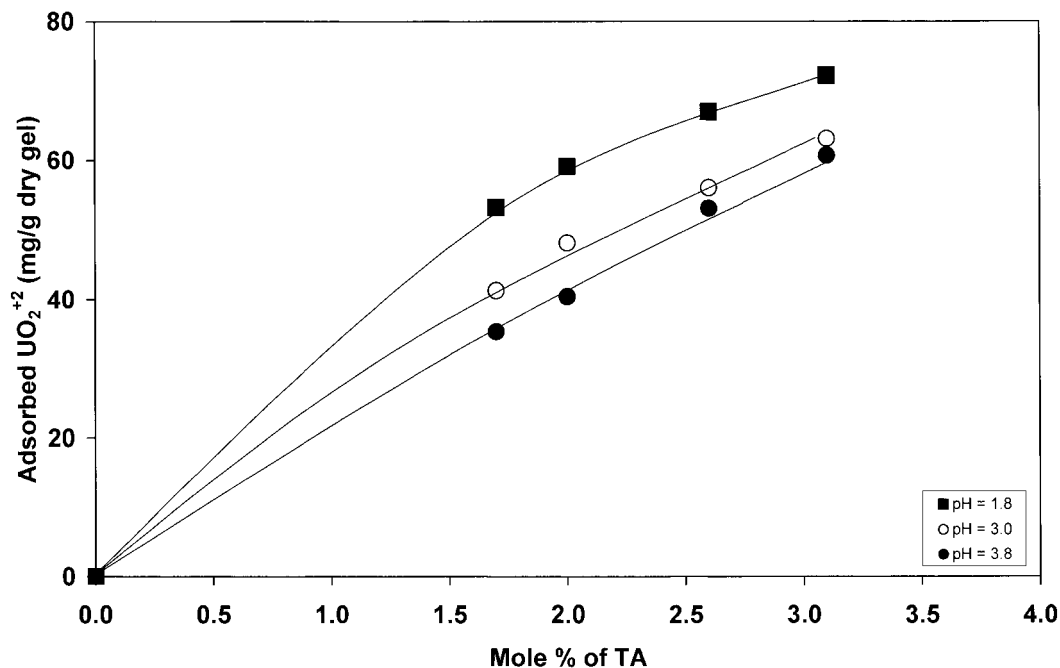
#### The Effect of pH on the $\text{UO}_2^{2+}$ Adsorption

To investigate the effect of pH on the  $\text{UO}_2^{2+}$  adsorption capacities of the hydrogels, adsorption experiments were conducted at varying pH with a fixed temperature ( $T = 25^\circ\text{C}$ ). Figure 5 shows the change in the adsorbed  $\text{UO}_2^{2+}$  ions by PVP-g-TA hydrogels containing various mol ratios of TA with changing pH values. Consistent with polyelectrolyte systems, adsorption of  $\text{UO}_2^{2+}$  ions in the gels is strongly dependent on the pH. A decrease in pH from 3.8 to 1.8 caused a significant increase in the amount of  $\text{UO}_2^{2+}$  ions adsorbed by the gel. Equilibrium swelling of PVP-g-TA hydrogels is very sensitive to pH changes of the swelling solution. Hydrogels swell at high pH values due to ionization and subsequent electrostatic repulsions of ionized groups, and shrink at low pH values with protonation.<sup>20</sup> The 20–50% increase

in adsorption capacity of hydrogels with changing pH from 3.8 to 1.8 is the result of this shrinking and reduction in the proximity of chains, providing increasing intermolecular contacts. A similar effect on the adsorption of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions by poly(acrylic acid) based hydrogels was observed by Khara and Peppas.<sup>22</sup>

#### Effect of Ionic Strength and Temperature on $\text{UO}_2^{2+}$ Adsorption

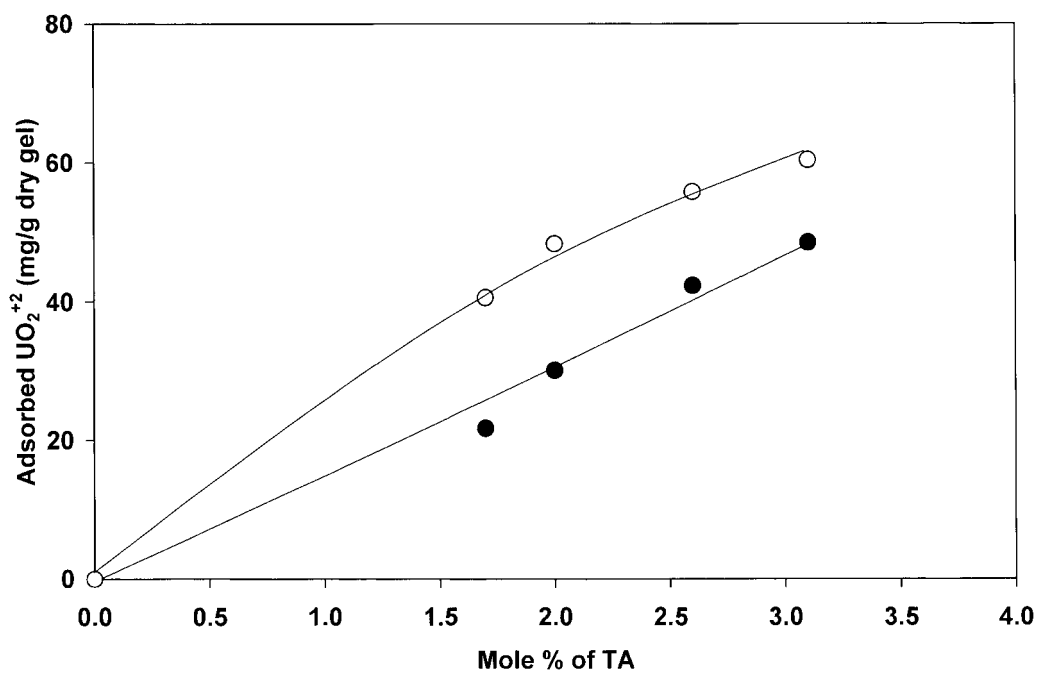
The effects of temperature and ionic strength on the  $\text{UO}_2^{2+}$  adsorption capacities of PVP-g-TA hydrogels were investigated at 15, 25, and  $35^\circ\text{C}$  in water and 0.1 M NaCl solutions. Variation of adsorbed  $\text{UO}_2^{2+}$  ions in water and NaCl solution with TA content, as a function of temperature, is presented in Figures 6–8. As can be seen, an increase in the TA content of the gel system caused an increase in the amount of adsorbed  $\text{UO}_2^{2+}$  ions. However, it is noted that the ionic strength or presence of NaCl ions also has a pronounced effect on the adsorption properties of hydrogels. An increase in ionic strength generally decreases the swelling, because the difference in concentration of mobile ions between the gel and



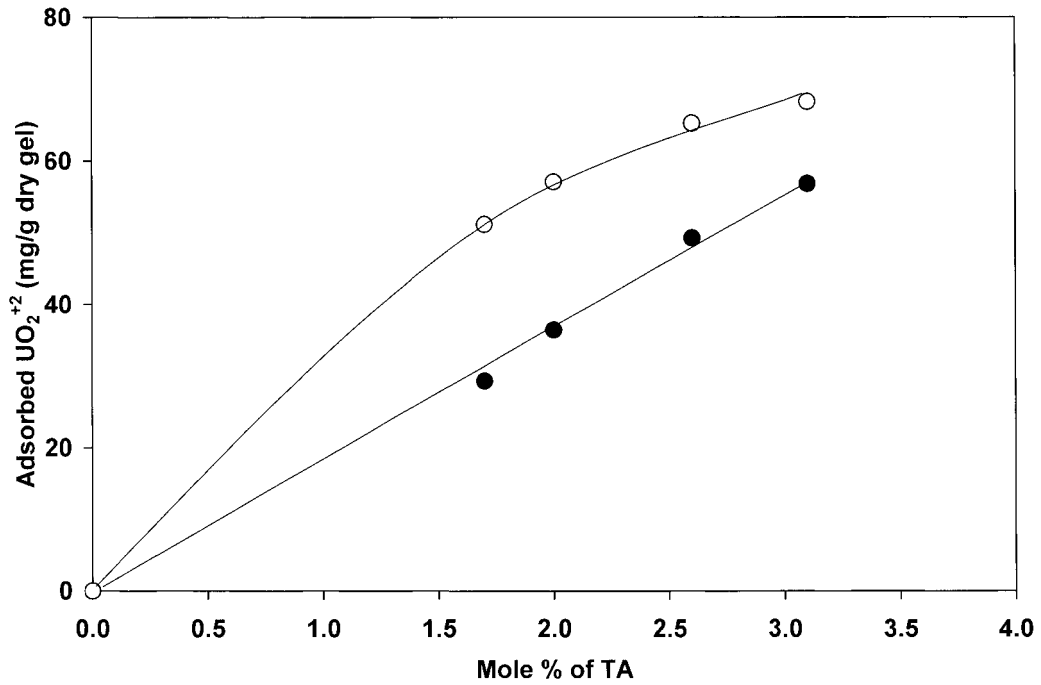
**Figure 5** Effect of mol % of TA in the gel system on uranyl ions adsorption at various pH.

solution is reduced with a decrease in the osmotic swelling pressure of these ions inside the gel. Due to the decrease in swelling and collapsing of

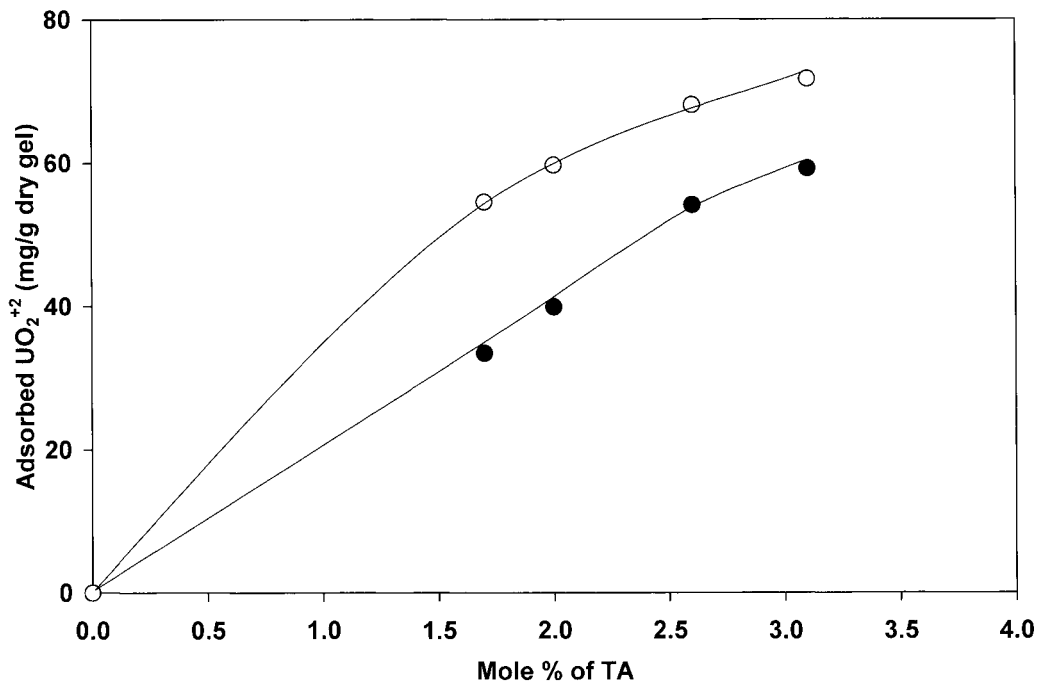
chains in the gel system, the possible interaction between the  $\text{UO}_2^{2+}$  ions and polymer chain increases. Figures 6–8 also show the effect of tem-



**Figure 6** Variation of adsorbed  $\text{UO}_2^{+2}$  ions from water and NaCl solution with mol % of TA at 15°C: (●) Water, (○) 0.1 M NaCl.



**Figure 7** Variation of adsorbed  $\text{UO}_2^{+2}$  ions from water and NaCl solution with mol % of TA at 25°C: (●) Water, (○) 0.1 M NaCl.



**Figure 8** Variation of adsorbed  $\text{UO}_2^{+2}$  ions from water and NaCl solution with mol % of TA at 35°C: (●) Water, (○) 0.1 M NaCl.

perature on the  $\text{UO}_2^{2+}$  adsorption. An increase of the temperature from 15 to 35°C caused an increase in the amount of adsorbed  $\text{UO}_2^{2+}$  ions. This increase was attributed again to shrinking of the hydrogel systems with increasing temperature.

## CONCLUSION

In this study, we have studied the effect of gel composition, pH, ionic strength, and temperature on the  $\text{UO}_2^{2+}$  ions adsorption capacity of PVP-g-TA hydrogels. It was found that not only the gel composition but also external stimuli, such as the pH, ionic strength, and temperature, play an important role in the adsorption behavior of PVA-g-TA hydrogels. These hydrogels are potential sorbents for the removal of  $\text{UO}_2^{2+}$  ions from wastewater and aqueous effluents.

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