Int. J. Chem. Sci.: 11(1), 2013, 29-38
ISSN 0972-768X
www.sadgurupublications.com

EFFECT OF SOME SELECTIVE SURFACTANTS ON THE THERMOCHROMIC BEHAVIOR OF POLYVINYL ALCOHOL-BORAX GEL

NAOREM SHUBHASCHANDRA SINGH*

Department of Chemistry, Churachandpur Govt. College,
CHURACHANDPUR – 795128 (Manipur) INDIA

ABSTRACT

The phenomenon of changing colour intensity of PVA-Borax hydrogel in presence of surfactants like sodiumdodecyl sulfate (SDS), trimethyl triammonium bromide (TTAB) has been investigated in detail. The preparation of thermochromic Borax crosslinked PVA gel was performed by embedded with a pH sensitive dye (phenolphthalein) both in absence and presence of surfactant. The phenomenon of thermochromism in presence of surfactant was studied spectrophotometrically.

Key words: Thermochromism, PVA-Borax hydrogel, Surfactants, Spectrophotometer.

INTRODUCTION

The investigation on the thermochromism in a hydrogel system consisting of PVA/Borax/Surfactant was reported for the first time by Seeboth et al. in 1999[1]. Such hydrogels belong to the smart gel due to its reponses towards changes in temperature. The thermochromic property of polymer gel is perhaps very tricky and rather critical to better understandings and development of certain desired gel materials. The behaviour may occur due to the interaction of dye molecules with the microenvironment of the gel[2,3], in which a suitable chromophore or dye has been embedded. They embedded Reichardt's dye pyridinium N-phenolate betaine dye (DTPP) in the PVA/Borax gel using a suitable surfactant N,N-dimethyl-N-tetradecylammonioacetic acid bromide (N-DTB). The hydrogel used was obtained by addition of borax to a 20% aq. PVA solution. The behavior of thermochromic gels was found to be affected by the presence of the surfactant, which imparts turbid appearance in the gel. Precisely due to lack of detail understanding, a suitable surfactant has to be selected on heat and trial basis. These perhaps led to the preparation of surfactant free thermochromic PVA hydrogel system by Chung et al.[4] Butanol was used to

---

*Author for correspondence; E-mail: shubhasnaorem@yahoo.com; Ph.: +91-9862181905

replace a surfactant, where it can exhibit the same striking phenomenon of reversible thermochromic behaviour in the gel network. Thermochromism has also been observed in the hydrogel when embedded with other suitable pH indicator dyes viz. bromophenol blue[4], bromothymol blue, cresol red and Reichardt dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino) phenolate (DTPP)[5,6] with pK_a values between 7.0 and 9.4. Reichardt dyes are often used as optical sensors because of their marked solvatochromic properties[7,8] but in case of DTPP in the PVA/Borax/surfactant gels the observed thermochromic behaviour was attributed to temperature-induced pH changes in the gel network and not to solvatochromic effects. Obviously, the main reason for the observed reversible color changes is a temperature-induced increase of the pH of the polymer gel with rising temperature, which induces a higher amount of the colored phenolate form of the dye molecule. This behavior is in contrary to the normal behaviour of a buffer solution within the same pH range 7.4-8.5. It has been known that Seeboth et al.[5,6] advocated on the advantageous of water soluble thermochromic gel network for practical purposes.

In this paper, the effect of presence of a surfactant on the thermochromic PVA-Borax gel has been studied and reported with reference to the dependence of the thermochromic behaviour of the PVA/Borax gel on the type and the nature of the surfactant and also on the optical behavior of the thermochromic PVA gel.

EXPERIMENTAL

The polymer, PVA (MW 15,000) was procured from Fluka. Analytical reagent (AR) grade sample of sodium dodecyl sulfate (SDS) with purity greater than 99% was obtained from Loba Chemie, Bombay, while nonionic surfactant TX-100 [CH_3-$C(CH_3)_2$-CH_2-$C(CH_3)_2$-C_6H_5-O-$(Ch_2$-CH_2-$O)_x$-H, where x is 9.5 on an average] and the cationic surfactants cetyl trimethyl ammonium bromide (CTAB) and tetra doceyl trimethylammonium bromide (TTAB) were obtained from Sigma. The sample of SDS was purified following standard procedure[9]. It was re-crystallized several times from hot methanol, refluxed in diethyl ether nearly for 72 hours through Soxhlet extractor and finally dried under vacuum. The polymers and the surfactants were used as received, while the reagent grade sample of n-butanol was fractionally distilled prior to its use.

PVA gel preparation

A stock solution of the PVA (7.5% w/v) was prepared by dissolving the polymer in double distilled water, the dissolution was carried out by standing the solutions for about 48 h at 25°C. A mixture containing 10 mL of 7.5% PVA solution and 0.5 mL of 3% borax aq. solution was prepared both in absence and presence of a surfactant. Concentrations of the surfactants i.e. for SDS, CTAB and TX-100 were chosen in the range of premicellar and post micellar region. The mixture was then made alkaline at a desired pH by adding different amounts of 1 N NaOH solution and thoroughly stirred. The gel was then embedded with 0.2 mL of 1% phenolphthalein and then warmed up to 50^{o}C for complete dissolution to give a uniform gel. The mixture was slowly cooled down to room temperature and allowed to remain at room temperature for 24 h in order to eliminate water bubble, when finally a reversible thermochromic PVA gel was obtained. UV-visible spectra for thermochromic PVA gel embedded with phenolphthalein dissolved in butanol were recorded in the wavelength range from 400 to 700 nm at different temperatures between 20-80^{o}C at an interval of 5^{o}C. In a similar manner pH measurements on the thermochromic gels with temperatures were carried out.

pH measurement

The pH of the thermochromic PVA gel was measured using the CyberScan Series PC 5500 (Eutech Instruments) bench meter, which operates with a state of art touch screen capable of measuring pH, conductivity and ions. The measurement was used to record the changes in the pH values of the thermochromic PVA gel with temperatures. The meter has a relative accuracy of ± 0.002. Temperature of the gel during measurement was maintained by circulating thermostated water from Haake thermostat.

UV-Visible Spectrophotometric measurement

The UV-visible absorption spectra of the thermochromic PVA gel both in aqueous and aqueous surfactant media were recorded against the polymer solution in the UV-visible scanning spectrophotometer (Shimadzu UV-2456) in the wavelength range from 400 to 700 nm at 303.15 K. The instrument has effective measuring wavelength range between 190-900 nm with variable spectral band width from 0.1 to 4 nm along with a resolution of 0.1 nm. The temperature of the gel was maintained constant by circulating thermostated water around the sample solution.

RESULTS AND DISCUSSION

The changes in the UV-visible absorption spectra in the wavelength region 400-700 nm of surfactant free thermochromic PVA gel at different temperature are shown in Figure 1. Maximum absorbance was observed around 550 nm (λ_{max}) throughout the investigated temperature ranges from 20-80^{o}C. Absorption of the gel at around 20^{o}C was very low, which present itself as almost coloureless. The colour in the gel develops gradually with raise in temperature thereby showing intense deep red colour at about 55^{o}C with a maximum absorbance value (Fig. 1 inset). The absorption maxima are, however, observed to start decreasing from 60°C onwards till 80°C. This typical change of optical behavior of the thermochromic PVA gel is unusual and has not been reported. Such a change in optical behavior at higher temperature range may be due to increasing amount of deeply coloured phenolate form of the dye molecule in the gel coupled with decreasing viscosity of the gel due to decreased cross link density at higher temperature[4,5,10,11]. This behaviour of changing pH in the range of investigated temperatures is in contrary to the normal behavior of a buffer solution within the same pH range 7.4-8.5[5].

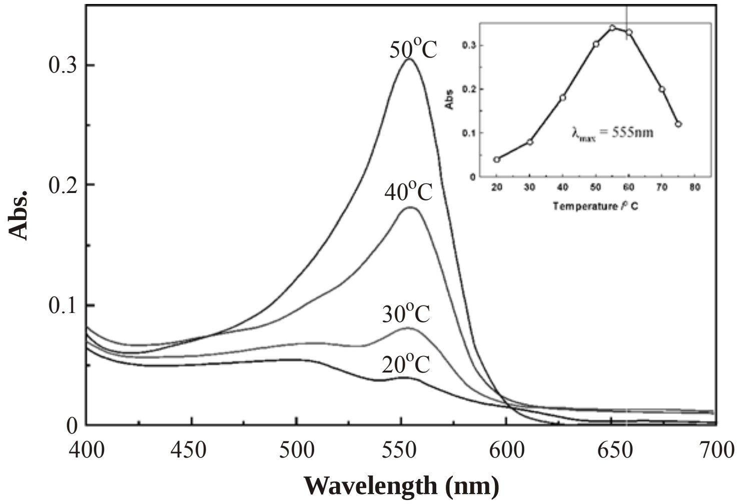


Fig. 1: Variation of absorption spectra of thermochromic PVA gel with temperature

It has been reported that in the microenvironment of the dye molecule in the PVA gel network at lower temperature, the phenol form of the dye molecule is stabilized over cooperative linkage amongst other by hydrogen bond formation through the OH groups of PVA[1-3]. At higher temperature the cooperative linkages are cleaved gradually again and the dye molecule is preferentially present in (the deeply colored) phenolate form by shifting the equilibrium (between the phenolate and the phenol form of the dye) towards forward direction[4,5] as shown in proposed reaction Scheme 1.

Figure 2 represents the changes in the absorption spectra, while Figure 3 shows the changes in the pH values of the PVA gel as a function of temperature both in absence and presence of SDS. In a similar pattern, effect of presence of cationic, CTAB or nonionic surfactant, TX-100 on the absorption spectra of the thermochromic PVA gel as a function of temperature are shown in Figures 4 and 5 and the changes in pH of the gel with temperature are shown in Figures 6 and 7, respectively.

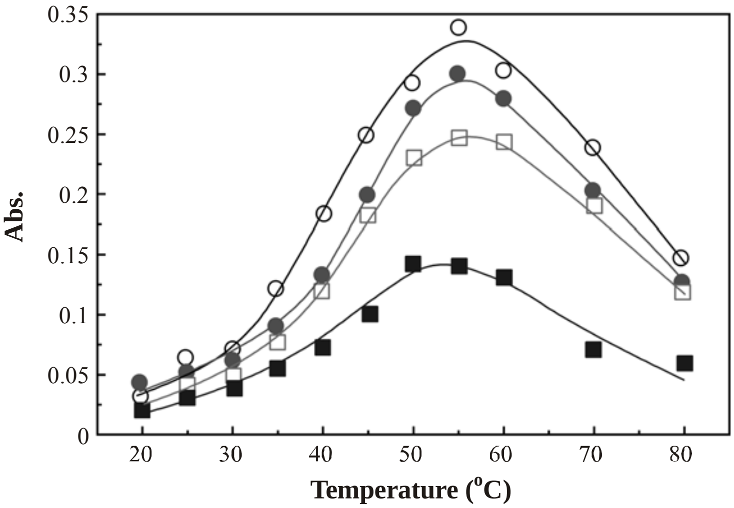


Fig. 2: Plot of absorbance (550 nm) against temperature of thermochromic PVA-gel in presence of SDS: ○ -0; ● -2; □ -6; ■ -12 mM SDS

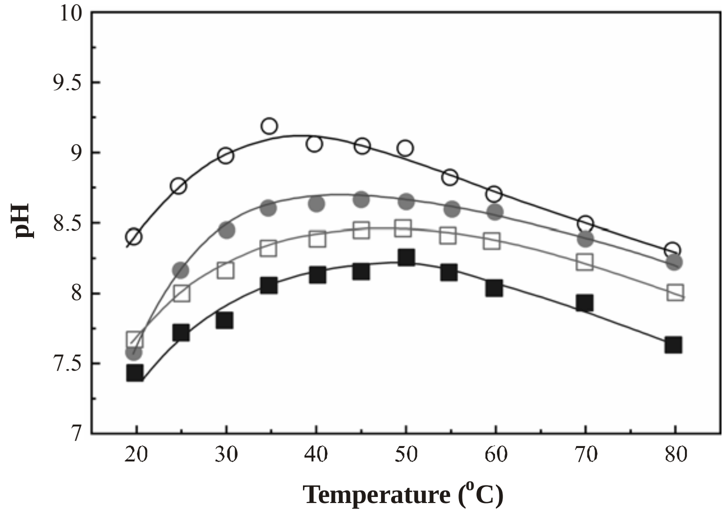
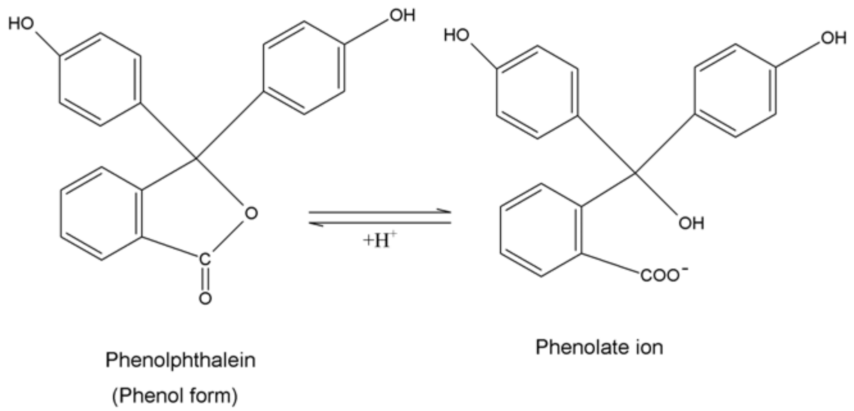
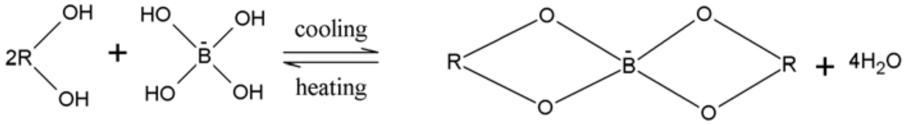


Fig. 3: Plot of pH against temperature of thermochromic PVA-gel in presence of SDS: ○ -0; ● -2; □ -6; ■ -12 mM SDS

It was observed from Figure 2 that presence of anionic surfactant, SDS in the thermochromic PVA gel lead to decreasing the adsorption and hence intensity of the gel colour. This would imply that presence of negatively charged SDS molecules inhibits formation of phenolate ions nor does it facilitate the di-diol formation[4,12] as shown in Scheme 2.



Scheme 1: Formation of phenolate ion



Scheme 2: Formation for the di-diol complex between borate ion and PVA polymer

In the pH measurement, the pH of the thermochromic PVA gel initially increased with temperature upto a maximum value around 40°C and then it gradually decreased with further increase in temperature as shown in Figure 3. This is in conformity with the earlier finding from spectrophotometric studies (Figure 1). The decrease in pH values of the PVA gel beyond a certain temperature is due to formation of more and more the di-diol complex (Scheme 2). While the presence of SDS in thermochromic PVA gel have favoured di-diol complexation at higher temperature, there is shifting in the transition temperature from 45 to 50°C in presence of micelles of the anionic surfactant. From the Figure 4, it was observed that the presence of monomers of CTAB, PVA gel network showed an enhanced absorption indicating promotion of phenolate ion by the presence of positively charged CTAB. A similar behavior has also been observed in case of non-ionic surfactant TX-100 as is evident from Figure 5. The presence of monomer of TX-100 also led to stabilizing of the phenolate ions but it subsequently starts decreasing with increasing concentration of the surfactant (Figure 5). The transition temperature of the thermochromic PVA gel, determined as the temperature at which the maximum absorption occurrs was observed around 55°C. This temperature appears to remain unchanged in the spectrosphotometric study (as shown in Figure 3) in presence of SDS while there is shifting towards lower temperature in presence of CTAB or TX-100. The transition temperature of the thermochromic PVA gel is shifted to about 40°C in presence of TX-100 monomer. In a similar pattern, the transition temperatures of thermochromic PVA gel are also determined from the temperature around which a change in pH values is observed. The changes of pH values would support the explanation given in case of the optical behavior.

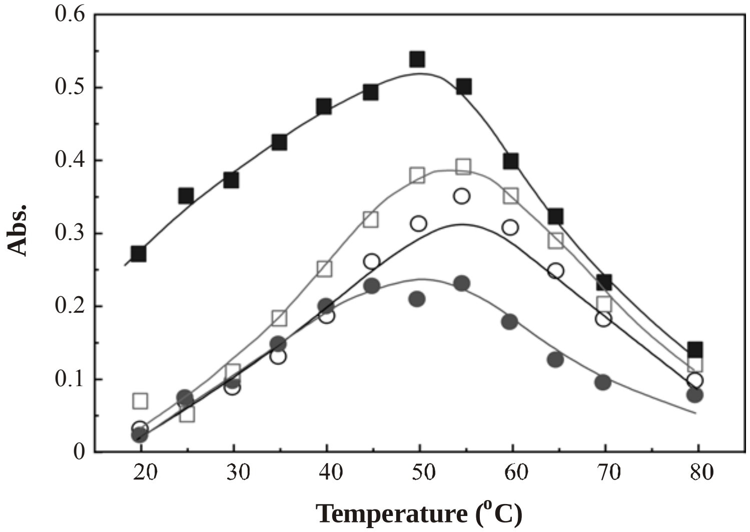


Fig. 4: Plot of absorbance (550 nm) against temperature of thermochromic PVA-gel in presence of CTAB: ○-0; ●-0.2; □-0.5; ■ -1.1 mM CTAB

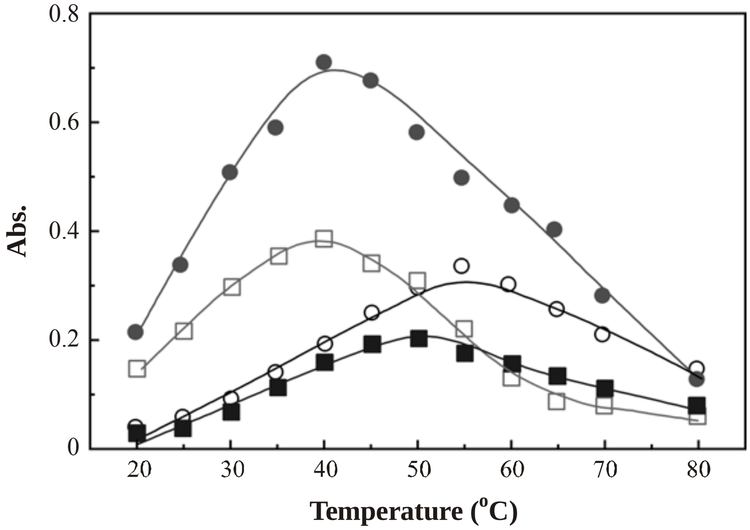


Fig. 5: Plot of absorbance (550 nm) against temperature of thermochromic PVA-gel in presence of TX-100: ○-0; ●-0.07; □-0.25; ■ -0.5 mM TX-100

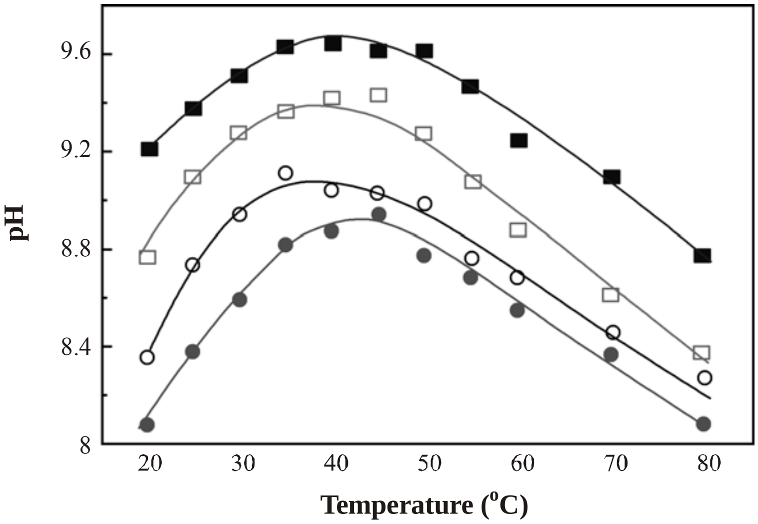


Fig. 6: Plot of pH against temperature of thermochromic PVA-gel in presence of CTAB: ○-0; ●-0.2; □-0.5; ■ -1.1 mM CTAB

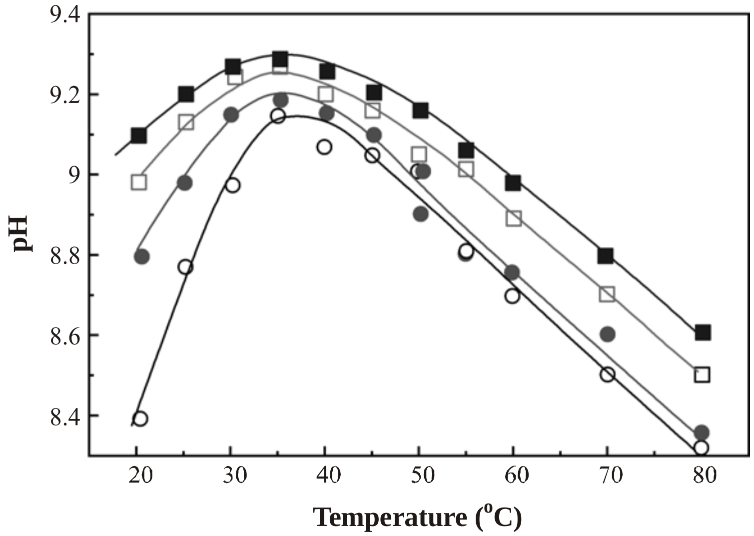


Fig. 7: Plot of pH against temperature of thermochromic PVA-gel in presence of TX-100: ○-0; ●-0.07; □-0.25; ■ -0.5mM TX-100

CONCLUSION

The PVA-based gels thermochromism with a change of colour from colourless to deep red at about 30^{o}C and the red colour gradually disappears above 60^{o}C. The gels showed a maximum absorption at 550 nm, which is not affected by the change in temperature. While the transition temperature of the PVA-Borax gel was not significantly affected by SDS or CTAB, presence of TX-100 was observed to bring about a decrease in the transition temperature. The presence of SDS in the thermochromic gel leads to reduction of the phenolate ions, which resulted into a decrease in the intensity of the color. The presence of CTAB or TX-100, on the other hand, was generally found to enhance the phenolate ions and hence an increase in the intensity of the color.

ACKNOWLEDGEMENT

The author thankfully acknowledges Prof. Homendra Naorem of Chemistry Department, Manipur University, Canchipur for his help in providing research facility, while taking the measurements of UV-visible spectrophotometer. His valuable advice during preparing manuscript was also commendable and highly appreciated.

REFERENCES

1. A. Seeboth, J. Kriwanek and R. Vetter, J. Mater. Chem., **9**, 2277 (1999).
2. A. Seeboth, J. Schneider and A. Patzak, Sol. Energy Mater. Sol. Cells, **60(3)**, 263 (2000).
3. H. Fujimatsu, S. Ogasawara, H. Ihara, T. Takashima and K. Toyaba, Colloid Polym. Sci., **266(8)**, 688 (1988).
4. W. Y. Chung, S. Minlee, S. M. Koo and D. H. Suh, J. Appl. Polym. Sci., **91**, 890 (2004).
5. A. Seeboth, J. Kriwanek, D. Lötzsch and A. Patzak, Polym. Adv. Technol., **13(7)**, 507 (2002).
6. J. Kriwanek, D. Lötzsch, R. Vetter and A. Seeboth, Polym. Adv. Technol., **14(2)**, 79 (2003).
7. C. Reichardt, Chem. Rev., **94(8)**, 2319 (1994).
8. P. Blum, G. J. Mohr, K. Matern, J. Reichardt and U. E. Spichiger-Keller, Anal. Chem. Acta., **432(2)**, 269 (2000).
9. J. H. Fendler and E. J. Fendler, Catalysis in Micellar and Macromolecular System, Academic Press, New York (1975).

10. E. Pezron, A. Leibler, A. Ricard and R. Audebert, Macromolecules, **21**, 1126 (1988).

11. K. Koga, A. Takada and N. Nemoto, Macromolecules, **32**, 8872 (1999).

12. H-L. Lien, W-H. Liu, K-S. Shen, T. L. Yu and C. H. Cheng, J. Polym. Res., **10**, 171 (2003).

Revised : 08.10.2012 *Accepted : 12.10.2012*