

Electrochemical and Kinetic Studies of Micellization of Sodium Tetradecyl Sulfate in the Presence of Poly(vinylpyrrolidone)

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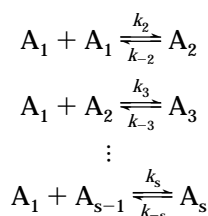
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In this work an attempt has been made to determine the interaction mechanism between sodium tetradecyl sulfate (STS) and poly(vinylpyrrolidone) (PVP). The binding of ionic surfactant to PVP is discussed, and results of surfactant electrode and pyrene fluorescence measurements are reported. The slow relaxation times of STS were determined in the presence of different concentrations of PVP at various temperatures. Data were gathered from equilibrium and kinetic experiments, which together indicated the mechanism of the STS/PVP interaction system.

Introduction

The slow relaxation process usually observed in the milisecond time range, determined by temperature-jump, pressure-jump, and stopped flow techniques,^{1–5} is attributed to a micellar dissolution process when the total concentration of micellar aggregates is perturbed. This process is identified with the stepwise buildup of micelles from monomer and the dispersion of micelles into monomers:



The slow relaxation time (τ_2) is associated with the dissociation–association process of the micelles. In previous studies, Bloor⁶ investigated the interaction of sodium dodecyl sulfate (SDS) with poly(vinyl pyrrolidone) (PVP). He also reported the variation of $1/\tau_2$ of SDS/PVP by varying the concentration of PVP at constant SDS concentration (0.04 mol dm⁻³). The reciprocal of τ_2 decreases at lower PVP concentration at 35 °C, and at 30 °C, $1/\tau_2$ reaches a shallow minimum and then increases with an increase in PVP concentration. The τ_2 of SDS in the presence of polyethylenglycol (PEG) has also been investigated by Bloor.^{6,7} He reported that at low polymer concentration there is a sharp minimum where $1/\tau_2$ was plotted as a function of PEG concentration. According to

Bloor's interpretation, the minimum in the plot of $1/\tau_2$ versus polymer concentration is associated with an increase in solution ionic strength at low polymer concentration resulting from a counterion effect in which it was thought that polymer-bound surfactant micelles bind less of their counterions than free surfactant micelles in solution. However, at that time, there was very little information available on qualitative measurement of the degree of counterion binding. Since then, Zana⁸ has reported that, for PVP/SDS and poly(ethylene oxide) PEO/SDS systems, the degree of dissociation of surfactant micelle increases in the presence of polymers. The degree of dissociation of SDS in the presence of PEO also has been measured by Francois⁹ who found only a slight increase from 0.22 to 0.28 in the absence and presence of PEO, respectively.

An alternative explanation will be sought and, in this regard we report our data of τ_2 STS in the presence of PVP. All the τ_2 measurements were carried out in the micellar region [i.e., at surfactant concentration $> T_2$ (the concentration at which the polymer probably becomes saturated with surfactant)]. All attempts to measure τ_2 in the $T_1 - T_2$ region (T_1 is the concentration at which interaction between the surfactant and the polymer first occurs) failed in the sense that no effect was observed experimentally. In this work we are concerned with an investigation of the behavior of τ_2 for STS in the presence of polymer (PVP).

Experimental Section

Materials. The PVP was of a special grade with a nominal molecular weight of 40 000 (supplied by Aldrich Chemical Company). The polymer was purified with an Amicon ultrafiltration cell with a type YM5 membrane that has a cutoff equivalent to a molecular weight of 5000. The PVP solution was diluted with fresh doubly distilled water that passed through the membrane taking with it ionic impurities and residual monomer. The purification continued until there was no further decrease in the conductivity of the water extracted from the ultrafiltration cell. The PVP was recovered from solution by the freeze-drying technique. Purified PVP was used to make up solutions (0.04, 0.2, and 0.5% w/v) with water that had been double distilled. Sodium tetradecyl sulfate (STS, 99% pure grade)

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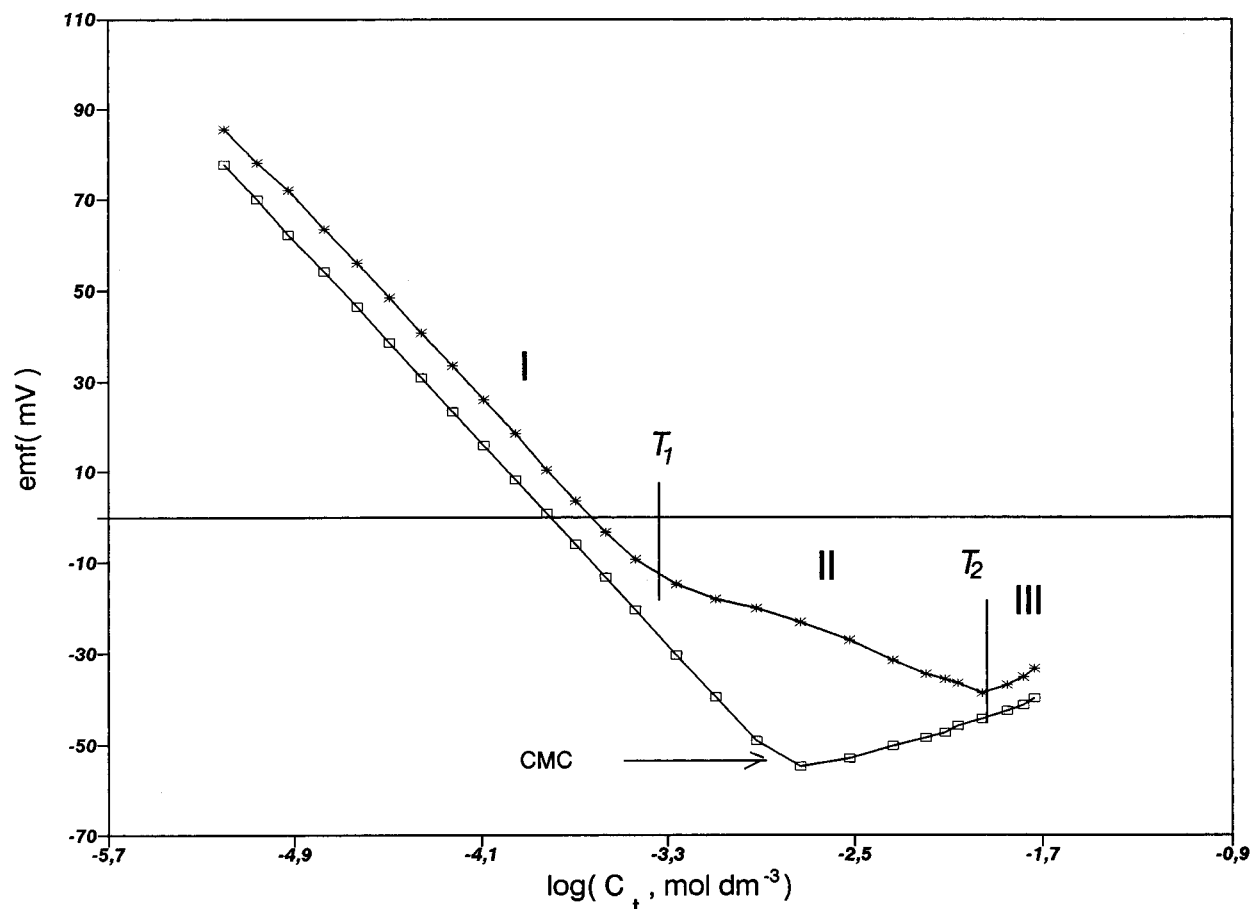


Figure 1. Plot of emf of $\log(C_t)$ for STS in the absence (\square) and presence (\star) of polymer, using Br electrode as a reference electrode. The salt (NaBr) concentration was $1 \times 10^{-4} \text{ mol dm}^{-3}$.

was from Lancaster. Pyrene (99% pure) was obtained from Aldrich Chemical.

Methods. An ion-selective electrode sensitive to surfactant ion was used for the measurement of m_1 (the monomer surfactant concentration) and α (degree of dissociation of counterion), and to obtain the binding isotherms [graphs that plot r versus $\log(m_1)$, where r is defined as $(C_t - m_1)/C_p$, and where C_t and C_p are total surfactant and polymer concentrations, respectively]. The electrode was constructed as described previously.^{10,11} The following cell comprised of surfactant membrane electrode and sodium or bromide electrode was used:

Ag | AgBr | internal solution | PVC membrane | test solution | reference electrode

Test solutions were saturated with pyrene at a concentration of $2.0 \times 10^{-6} \text{ mol dm}^{-3}$. These solutions were then purged with nitrogen to prevent oxygen from quenching the fluorescence emission. Fluorescence intensity measurements were obtained with a Perkin-Elmer fluorescence spectrometer at 25 °C. Using a pressure-jump apparatus with conductivity detection (Dialogue), and incorporating a rapid data capture and analysis system as described by Strehlow,¹² relaxation times were measured over the time range 10^{-4} –10 s. In addition, the temperature dependence of the relaxation time over the temperature range of 20 to 35 °C was also determined.

Results and Discussion

Potentiometry. The electromotive force (emf) data for the electrode is plotted in Figure 1. The total concentration of STS was plotted against emf referenced

to a bromide electrode and three different regions were found: (I) The first region shows the Nernstian slope that indicates there is no binding and hence no measurable interaction between polymer and surfactant, which is present in the form of free monomer. (II) In the second region, a break was found in the linear line which is shown as T_1 in many articles,^{13–15} where the interaction between PVP and STS begins. In this region, the concentration of both bound and free monomer of STS varies. (III) T_2 is the beginning of third region where the monomer concentration has reached a maximum. Above this point, the monomer concentration gradually decreased as the total concentration of STS increased. This result is normally considered to reflect the appearance of proper micelles, presumably occurring on the chain of polymer.^{14,16,17}

A summary of the characteristics of the electrode is given in Table 1. In the forthcoming analysis of the various relaxation time equations, we took the electrode data directly from the experiment. The degree of micellar dissociation (α) was found by measuring the electrode characteristics and analyzing the results by the method proposed by Hall.^{18–19} In these circumstances, α is the

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Table 1. The cmc, Slope, Intercept, and Degree of Dissociation for STS Using a Potentiometric Technique ($T = 297\text{ K}$)

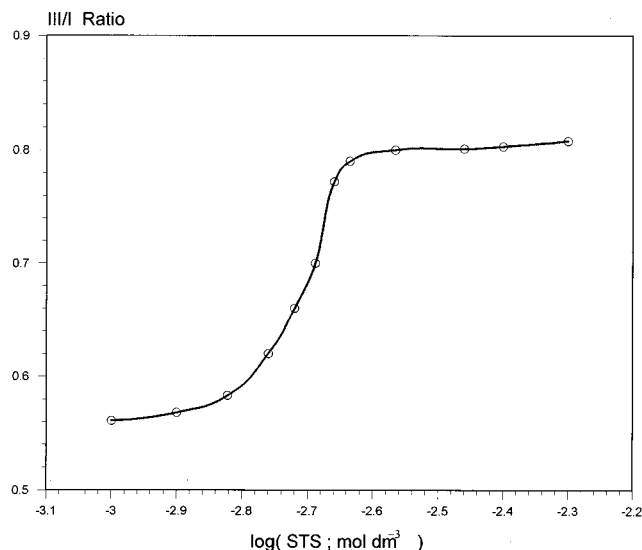
slope, $\text{mV dm}^3 \text{ mol}^{-1}$	intercept, $\text{mV } (\pm 0.2)$	linear range ($\times 10^{-4}$)	cmc, mol dm^{-3}	α^a
58.5	-142	0.5–20	0.0021	0.26

^a By use of expression: $\log(m_1\gamma_{\pm}) = K - (1 - \alpha) \log(m_2\gamma_{\pm})$ (ref 18).

Table 2. The Degree of Dissociation for STS Between T_1 and T_2^a

r	α
0.023	0.73
0.100	0.54
0.200	0.49
0.290	0.46
0.430	0.41
0.570	0.34
0.720	0.30
0.860	0.25

^a Concentrations of salt and PVP were $1 \times 10^{-4} \text{ mol dm}^{-3}$ and 0.2% w/v, respectively, and temperature was 297.15 K.

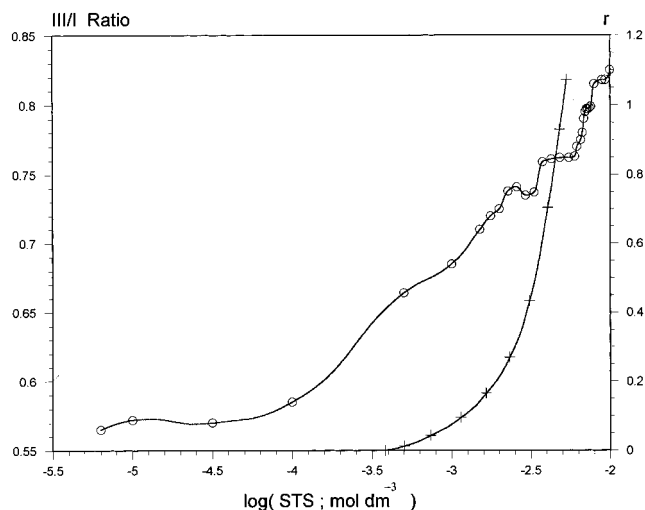
**Figure 2.** Plot of pyrene III/I fluorescence ratio versus logarithm concentration of STS.

slope of the plot $\log m_1 + 2\log \gamma_{\pm}$ vs $\log m_2$, where m_2 is free counterion concentration and γ_{\pm} is the activity coefficient.

The result shows that as r (binding value) increases, the degree of dissociation (α) decreases between T_1 and T_2 (see Table 2), and above T_2 , α is approximately constant.

Fluorescence Spectroscopy. The principle of this method is measurement of the ratio of the fluorescence intensity of the third vibronic band (at 383 nm) of a pyrene probe relative to the fluorescence intensity of the first vibronic band (at 372.5 nm). The ratio of these two intensities is termed the (III/I) ratio and it can be used to probe the hydrophobic environment of the pyrene molecule when it is placed in different solutions (Figure 2). Thus, using this technique, the critical micelle concentration (cmc) of a surfactant may be evaluated and a cmc value of $2 \times 10^{-3} \text{ mol dm}^{-3}$ for STS was obtained. This result is in good agreement with the result determined with an ion-selective electrode that was obtained by our group ($2.1 \times 10^{-3} \text{ mol dm}^{-3}$) and the accepted value of $2.1 \times 10^{-3} \text{ mol dm}^{-3}$ reported by other workers.^{20–23}

Above the cmc, pyrene penetrates inside the micelles where it is almost entirely in a nonpolar environment

**Figure 3.** Plot of pyrene III/I fluorescence ratio relative peak height of vibronic band fluorescence versus total STS concentration (○) and binding isotherm of STS/PVP interaction (+).

compared with tetradecane. Consequently, the III/I ratio increases dramatically above the cmc and can be used to probe the hydrophobic environment in which the pyrene probe exists. The interaction between PVP (0.04% w/v) and STS was investigated as a function of STS concentration. At low concentrations (namely, $[\text{STS}] < T_1$), the III/I ratio intensity value is very similar to the value of saturated pyrene in water. That is, at low concentration of PVP (0.04%) there is no interaction between surfactant and polymer leading to aggregation. Figure 3 shows that around the T_1 concentration ($3.8 \times 10^{-4} \text{ mol dm}^{-3}$), the III/I ratio intensity is increased because of the binding of small aggregates of STS to PVP and the increased hydrophobicity of the environment. Above T_2 (the concentration at which the polymer probably becomes saturated with surfactant), presumably with the formation of proper micelles and an increase in the hydrophobicity of the environment, the III/I ratio increases as STS concentration increases. In the present case, it is not possible to carry out experiments at higher concentrations because of precipitation problems.

Slow Relaxation for the STS/PVP System. The STS/PVP system was investigated at constant STS (5×10^{-3} and $2.5 \times 10^{-2} \text{ mol dm}^{-3}$) and varying PVP concentration. It should be noted that the data that are presented for the $5 \times 10^{-3} \text{ mol dm}^{-3}$ STS in different concentrations of PVP in the range 0.0–0.07% w/v are above the T_2 concentration (i.e., in the micellar region). Figure 4 shows that when the polymer (PVP) was initially added to $5 \times 10^{-3} \text{ mol dm}^{-3}$ STS, $1/\tau_2$ remains fairly constant. Further addition of polymer decreases $1/\tau_2$ until it reaches a minimum at $\sim 0.05\%$ (PVP), after which the $1/\tau_2$ values increase rapidly with increasing polymer concentrations. As stated in the Introduction, the explanation for the minimum in terms of counterion bonding is probably not correct because that explanation is very different for the degree of dissociation of 'free' and 'polymer bonded' micelles. As a result, we considered an alternative way

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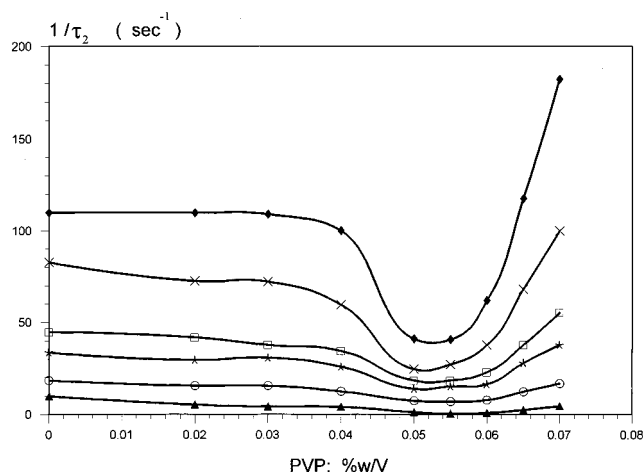


Figure 4. Inverse of relaxation time as a function of PVP% at constant STS concentration (5×10^{-3} mol dm $^{-3}$). Key: (▲)-20; (○)-25; (★)-27.5; (□)-30; (×)-32.5; (◆)-35 °C.

to account for the data. Initially, when the polymer concentration is small (0.04% w/v), it is very likely that all the polymer molecules will be saturated with micelles with a structure similar to a bead-type model. Moreover, the majority of the aggregate surfactant will exist as free micelles in solution. In theory, one would expect that the free micelles and the micelles bound to the polymer should have two separate slow relaxation times, $1/\tau_2$ and $1/\tau'_2$, respectively. In the range between 0 and 0.04% w/v PVP, only one relaxation time was observed experimentally. In the solution containing free and polymer-bound micelles, there is a dynamic equilibrium between free and bound micelles. This result means that either or both of the following is true: (a) if this exchange rate is fast, then only one relaxation time can be observed; and/or (b) if this exchange is slower than the measured slow relaxation time, then in theory, two separate relaxation times should be observed.

In practice it is very likely that the exchange between free and bound micelles is slower than the measured slow relaxation time. Because only one relaxation has been observed experimentally, the chances are that the separate relaxation times associated with the free and bound micelles are close in value and that an average relaxation time (τ_0) is measured. In these circumstances, τ_0 is given by eq 1:

$$1/\tau_0 = (\beta_2/\tau_2 + \beta'_2/\tau'_2)/(\beta_2 + \beta'_2) \quad (1)$$

where β_2 and β'_2 are weight factors associated with a rise in the individual slow relaxation times of the free and bound micelles, respectively. These conclusions, therefore, lead to the proposition of the model illustrated in Figure 5. (I) In the region 0.0–0.04% w/v PVP, the polymer molecules are saturated with micelles in a bead-like structure and free micelles also exist in solution (Figure 5, II). (II) As the polymer concentration increases, the balance between the number of free and bound micelles will shift in favor of polymer-bound micelles. As the concentration of polymer is further increased, more free micelles are taken up until a situation will arise when all the free micelles will be incorporated as bound micelles with the polymer (Figure 5, III). We believe that this situation corresponds to the minimum in $1/\tau_2$ at $\sim 0.05\%$ w/v PVP. (III) When the polymer concentration exceeds this critical value, then there are more sites available on the polymer than free micelles to fill these sites. When this occurs, there are no more free micelles present in the

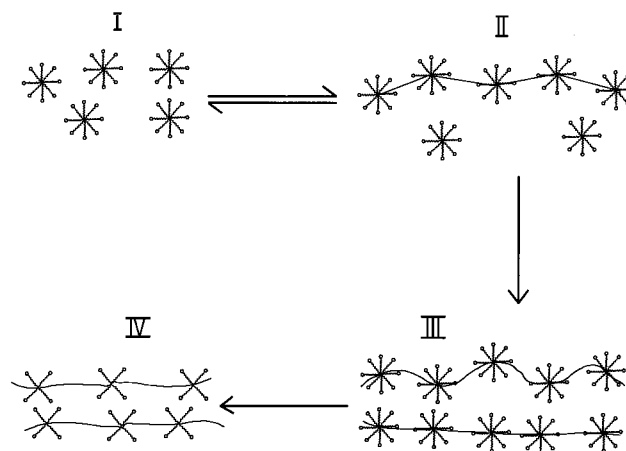


Figure 5. Schematic representation of surfactant interaction with PVP chains.

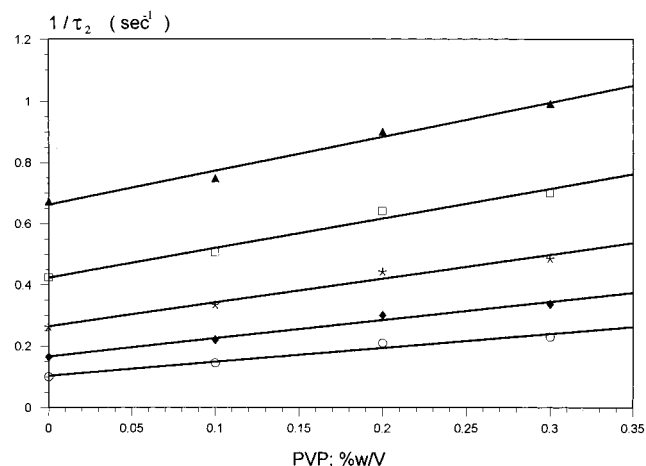


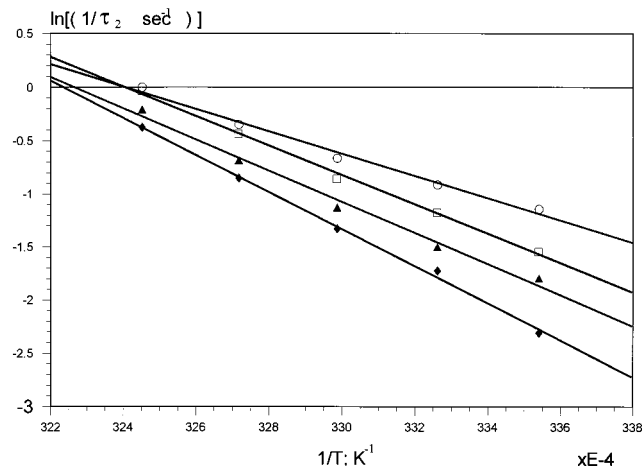
Figure 6. Inverse of relaxation time versus PVP% at constant STS concentration (2.5×10^{-2} mol dm $^{-3}$). Key: (○) 25; (◆) 27.5; (★) 30; (□) 32.5; and (▲) 35 °C.

solution to take up extra binding site. To accommodate the available binding sites, we believe that the micelles break up into smaller aggregates, which in turn leads to an increase in $1/\tau_2$ as observed experimentally. Eventually however, the micelles will get smaller and smaller with the addition of polymer until there are no longer "micelle proper" but the small aggregate equivalent to those found in the T_1 – T_2 region of the binding isotherm (Figure 3). When this occurs, we are unable to observe the slow relaxation process. In addition, of course, the relaxation time may also be too fast for the pressure-jump apparatus to measure it. This result is very similar to Zana's measurements²⁴ for the SDS/PEO system by the time-dependence fluorescence technique in which the aggregation numbers are measured.

At the higher polymer concentration, these data showed that $1/\tau_2$ starts to increase with increasing polymer concentration. Unfortunately it was not possible to extend the measurements to higher polymer concentration because the amplitude of the relaxation becomes too small to make meaningful measurements. To investigate the behavior of the relaxation in this region, we carried out additional measurements of $1/\tau_2$ in a larger and constant amount of micellar STS (2.5×10^{-2} mol dm $^{-3}$) and with increasing the polymer concentration over a wide range from 0 to 0.3% w/v. Figure 6 shows the variation of the reciprocal of slow relaxation time as a function of PVP

Table 3. Enthalpy of Activation in Different Concentrations of STS and PVP ($T = 297$ K)

ΔH^\ddagger (kJ/mol)	PVP % (w/v)										
	0	0.02	0.03	0.04	0.045	0.05	0.06	0.07	0.1	0.2	0.3
5×10^{-3} mol dm $^{-3}$ STS	124	154	152	154	168	141	153	174			
2.5×10^{-2} mol dm $^{-3}$ STS	144								122	116.5	85

**Figure 7.** Reciprocal of slow relaxation time versus inverse of temperature at different concentration of PVP and 5×10^{-3} mol dm $^{-3}$ STS. Key: (◆) 0.0; (▲) 0.1; (□) 0.2; (○) 0.3% w/v PVP.

concentration at constant STS concentration (2.5×10^{-2} mol dm $^{-3}$). In this experiment, the addition of PVP to a micellar STS solution causes an increase in the value of $1/\tau_2$ in comparison with pure micellar solution (i.e., the relaxation process became faster). As we have said previously, it is very likely that all the micelles are bound on the polymer. In relation to the experiments just described, all the present measurements are taken at polymer concentrations that are higher than that corresponding to the minimum in $1/\tau_2$. As a result, there are more micellar binding sites available on the polymer than micelles to fill these sites. To compensate for this situation, we propose that the micelles break down into smaller micelles so as to accommodate the binding site. As the polymer concentration is further increased, we further propose that the micelles get smaller and smaller. The increase in $1/\tau_2$ as the PVP concentration is increased is consistent with the formation of smaller micelles that are known to have faster relaxation times. Figure 6 shows that as the concentration of PVP is increased, the inverse of relaxation time increases. These results are consistent with Bloor's data.⁷

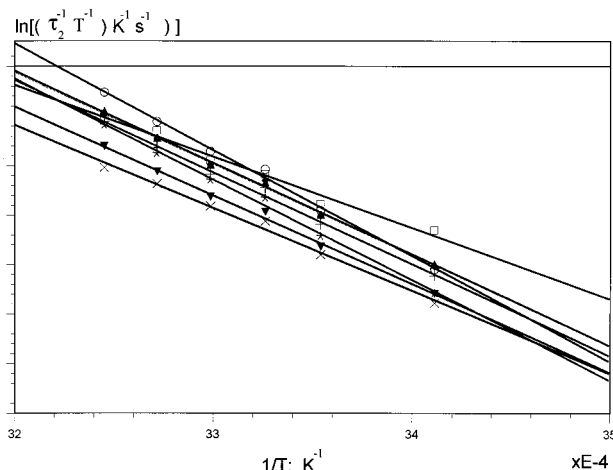
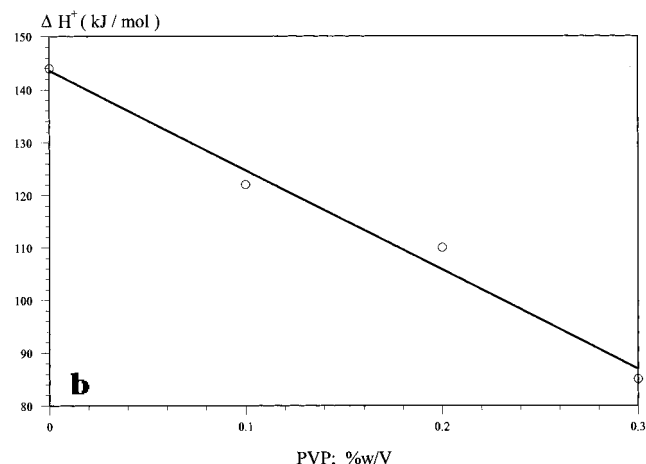
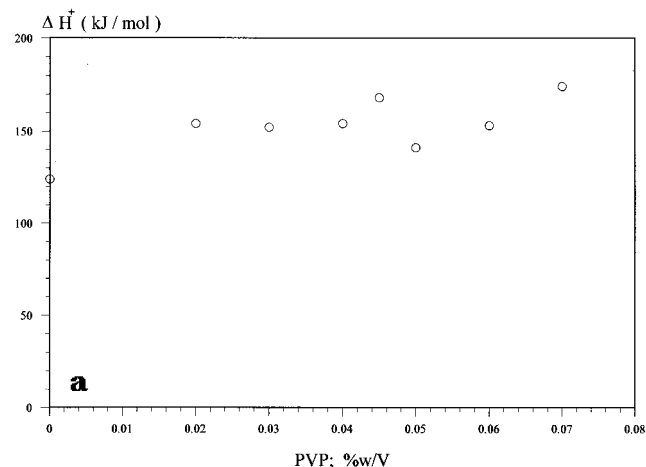
Effect of Temperature on Slow Relaxation Time and Calculation of ΔH^\ddagger Parameter. The slow relaxation time of the STS/PVP system was measured at various temperatures and PVP concentrations. A plot of $\ln(1/\tau_2)$ versus the inverse of temperature ($1/T$) (Figure 7) gives a straight line and obeys the Arrhenius rate equation:

$$1/\tau_2 = A e^{(-E/RT)} \quad (2)$$

where R , E , and A are the gas constant, activation energy, and Arrhenius "A" factor, respectively. In the application of the Arrhenius equation, $\ln(1/\tau_2)$ is plotted against $1/T$, which gives a straight line of intercept A and slope $-E/R$.

The enthalpy of activation, ΔH^\ddagger , associated with the slow processes can be obtained from the Eyring rate equation:

$$1/(\tau_2 T) = (kK/h) e^{(-\Delta H^\ddagger/RT)} e^{(\Delta S^\ddagger/R)} \quad (3)$$

**Figure 8.** The $\ln [1/(\tau_2 T)]$ was plotted as a function of inverse temperature at 5×10^{-3} mol dm $^{-3}$ STS and different concentrations of PVP. Key: (□) 0.0; (▲) 0.02; (◆) 0.03; (+) 0.04; (★) 0.045; (×) 0.05; (▼) 0.06; and (○) 0.07% w/v PVP.**Figure 9.** The value of ΔH^\ddagger was plotted versus PVP% at STS concentrations of (a) 5×10^{-3} mol dm $^{-3}$ and (b) 2.5×10^{-2} mol dm $^{-3}$.

where K is the transmission coefficient, k is the Boltzman constant, h is the Planck constant, ΔH^\ddagger is the enthalpy of activation, and ΔS^\ddagger is the entropy of activation.

At very low concentration of PVP, $1/\tau_2$ for micellar STS remain fairly constant and very close to the value observed for pure STS micelles. In these circumstances, the polymer molecule is saturated with STS micelle, which has a structure similar to a bead-type model. Furthermore, in this region the separate relaxation time of the 'free' and 'bound' micelle cannot be resolved. Addition of further polymer results in an uptake of more free micelles with the polymer until a situation is reached when all the polymer molecules are saturated with STS micelles. This situation corresponds to the minimum in the $1/\tau_2$ values.

As shown in Figure 8, the temperature dependence of $\ln(1/\tau_2 T)$ yields a value of ΔH^\ddagger (see Table 3) for the average enthalpy of activation associated with the micellar association/dissociation process. In this case, the dissociation of the micelle, for example, takes place via all the intermediate aggregates in the stepwise mechanism described in the Introduction. As we have said previously, in a monomer, micelle is present but the concentration of the intermediate aggregates are assumed to be so much smaller that they are neglected.

In the measurement of $1/\tau_2$ for $5 \times 10^{-3} \text{ mol dm}^{-3}$ STS in the presence of 0.0–0.07% w/v PVP, the value of ΔH^\ddagger remains fairly constant with polymer concentration (see

Figure 9a). This result means that the overall enthalpy process just depicted remains almost unaltered as we move from pure STS micelle to a solution micelle. Presumably this result means that the free micelles are not that much different from those micelles incorporated on the polymer. On the other hand the measurement for $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ STS in the presence of 0.0–0.3% w/v PVP shows that ΔH^\ddagger decreases with increasing polymer concentration (see Figure 9b). As we have said previously, this result corresponds to a situation in which the micelles get smaller and the overall actual enthalpy also gets smaller. This situation is also considered with the pyrene III/I fluorescence ratio, where the packing of the surfactant monomers is thought to be lower as the size of the micelle decreases. In these circumstances, the concentrations of the intermediate species are also more stabilized relative to pure STS and the pure STS in the presence of a small amount of PVP.

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