Heat inhibited reactions

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Acyl transfer from *p*-nitrophenyl trimethylacetate to hydrogen peroxide in millimolar aqueous solutions of an amphiphilic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer slows down as the temperature is raised due to partitioning of the hydrophobic ester into heat-induced micelles.

Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), **EPE**, triblock copolymers are commercially available surfactants with a highly temperature dependent critical micelle concentration (c.m.c.). Micelle formation is induced by raising the temperature, due to the pronounced decrease in solubility of the hydrophobic poly(propylene oxide) moiety.[1–3] The physical properties of dilute aqueous **EPE** solutions and of added probe molecules that partition into the micelle show an abrupt change as the temperature is increased, marking the onset of micelle formation at the critical micelle temperature (c.m.t.). There follows a transition region where the proportion of micellised surfactant increases with temperature until a second inflection occurs, above which virtually all the polymer is micellised.[1,2] The present communication is the first report that micelle formation in the transition region has a marked effect on the observed rate constants of bimolecular reactions involving species that partition between the micelles and the bulk aqueous phase. Moreover, the enthalpy and entropy of micellization are important thermodynamic parameters of solutions of **EPE** polymers and have previously been calculated from the temperature dependence of the c.m.c. or the concentration dependence of the c.m.t., obtained from measurements of physical properties over a range of both temperature and concentration. In this work self-consistent thermodynamic parameters are obtained from the temperature dependence of the observed rate constant for the reaction of hydrogen peroxide and *p*-nitrophenyl trimethylacetate at single **EPE** concentrations.

The Arrhenius equation, eqn. (1), gives the logarithmic dependence of the rate

$$\ln k_r = \ln A - \frac{E}{RT} \quad (1)$$

constant, k_r, of a reaction on the inverse temperature, T; where A is the pre-exponential factor, E the activation energy and R the gas constant. Fig. 1 shows that low concentrations of $E_{27}P_{61}E_{27}$

$$H\text{---}(OCH_2CH_2)_x\text{---}(\underset{\underset{CH_3}{|}}{OCHCH_2})_y\text{---}(OCH_2CH_2)_x\text{---}OH$$

$$E_xP_yE_x$$
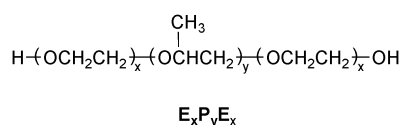
cause large deviations in the Arrhenius plot for the reaction of hydrogen peroxide and *p*-nitrophenyl trimethylacetate shown in eqn. (2).

$$(CH_3)_3C\text{---}CO\text{---}OC_6H_4NO_2 + {}^-OOH \rightarrow$$
$$(CH_3)_3C\text{---}CO\text{---}OOH + {}^-OC_6H_4NO_2 \quad (2)$$
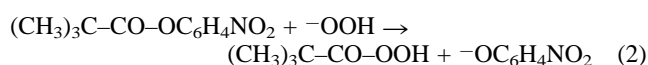
These deviations are caused by the heat-induced micellization of the triblock copolymer. The effects of surfactant micelles on the rates of chemical reactions are well-established.[4] In the present case the inhibition is consistent with the peroxide remaining in the bulk water whilst the ester increasingly partitions into the micelles with increasing polymer concentration. We have previously described the effect of surfactants on a range of chemical reactions involving peroxides,[5] and, in cases where only one of the reactants partitions into the micelle and there is insignificant reaction in the micellar pseudophase, the dependence of the observed rate constant, k_{obs} on the concentration of micellised surfactant, $[S]_{mic}$, is given by an equation of the form of eqn. (3).

$$k_{obs} = \frac{k_w}{\left(1 + K^E_{mic}[S]_{mic}\right)} \quad (3)$$

Here k_w is the rate constant in water in the absence of surfactant and is equivalent to k_r in eqn. (1), and K^E_{mic} is (neglecting a small correction for the effective molar volume of the micellized surfactant) the micellar association constant of the ester. Now in the present work, $[S]_{mic}$ at different temperatures
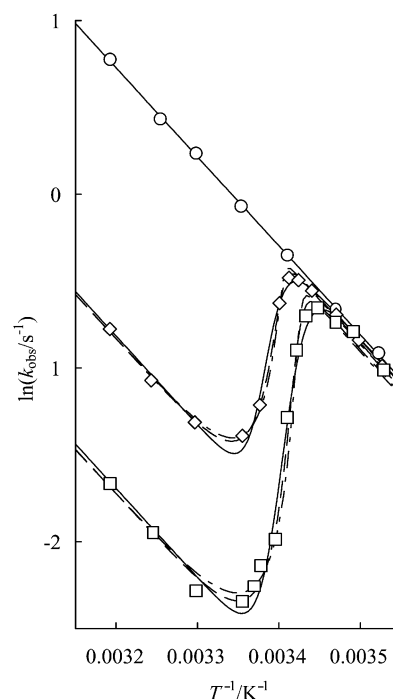

Fig. 1 Arrhenius plots for the reaction of $< 2.8 \times 10^{-5}$ mol dm^{-3} *p*-nitrophenyl trimethylacetate with 0.115 mol dm^{-3} hydrogen peroxide in the absence of triblock copolymer (circles) and the presence of 8.5×10^{-4} mol dm^{-3} (diamonds) and 2.55×10^{-3} mol dm^{-3} (squares) $E_{27}P_{61}E_{27}$. Reactions were carried out in water buffered with 0.0175 mol dm^{-3} sodium hydrogen carbonate and 0.0075 mol dm^{-3} sodium carbonate (pH 9.5 at 25 °C) containing 1×10^{-5} mol dm^{-3} ethylenediaminetetramethylenephosphonic acid to prevent decomposition of the working solution of hydrogen peroxide. Solid lines, dashed lines, and dot-dashed lines are best-fit curves for values of aggregation number, *n*, of 1, 5, and 15, respectively.

is calculated from the total surfactant concentration using a mass balance equation and the equilibrium constant, K_{mic}, for the process defined in eqn. (4), where n is the micellar aggregation number.

$$\textbf{EPE} = 1/n \ \textbf{EPE}_n \qquad (4)$$

The dependence of K_{mic} on temperature is given by eqn. (5) where ΔH^0_{mic} and

$$\ln K_{mic} = -\frac{\Delta H^o_{mic} - T\Delta S^o_{mic}}{RT} \qquad (5)$$

ΔS^0_{mic} are the enthalpy and entropy of micellisation. The curves in Fig. 1 are calculated from the best-fit values of K^E_{mic}, ΔH^0_{mic} and ΔS^0_{mic} (Table 1) obtained using non-linear regression of the data at 8.5×10^{-4} mol dm^{-3} and 2.55×10^{-3} mol dm^{-3} **EPE** at n values of 1, 5, and 15, respectively. (The value of $n = 1$ in eqn. (4) corresponds to unimolecular micelle formation where the poly(propylene oxide) converts from a loose hydrated random coil, where the **EPE** molecule has little surfactant property, to a more compressed, folded conformation.) It is notable that the choice of the micellar aggregation number, n, has only a small effect on the shape of the calculated curve and the best-fit parameters shown in Table 1. This will be discussed further in a later paragraph.

The present data treatment assumes that ΔH^0_{mic} and ΔS^0_{mic} are constant with temperature and this is in agreement with the reported linearity of plots of inverse c.m.t. *versus* the logarithm of **EPE** concentration.[2] The treatment also assumes that K^E_{mic} is constant with temperature and this is acceptable because, in fact, the dependence (results not shown) of k_{obs} on the total **EPE** concentration at temperatures above the c.m.t., where it essentially equals $[S]_{mic}$ and eqn. (3) applies, yields best-fit values of K^E_{mic} that vary by no more than 15% between 30 °C and 45 °C. Hence the concentration of ester remaining in the bulk aqueous phase and still able to react with peroxide remains constant within about 15% over this temperature range. This explains why the slopes of the Arrhenius plots in Fig. 1 at temperatures above the transition region are virtually identical to the slope in the absence of polymer.

Table 1 Best-fit values ± their standard deviations of the micellar association constant of *p*-nitrophenyl trimethyl acetate and the enthalpy and entropy of micellization of the triblock copolymer, **E$_{27}$P$_{61}$E$_{27}$**, for various micellar aggregation numbers at two polymer concentrations.

[E$_{27}$P$_{61}$E$_{27}$]/ 10^{-3} mol dm^{-3}	n	$K^E_{mic}/10^3$ dm^3 mol^{-1}	$\Delta S^0_{mic}/10^3$ J mol^{-1} K^{-1}	$\Delta H^0_{mic}/10^5$ J mol^{-1}
0.85	1	4.18 ± 0.17	2.34 ± 0.15	6.94 ± 0.04
2.55	1	3.93 ± 0.31	2.11 ± 0.17	6.23 ± 0.05
0.85	3	—	—	—
2.55	3^a	3.91 ± 0.17	1.13 ± 0.04	3.24 ± 0.12
0.85	4^a	4.18 ± 0.05	1.14 ± 0.003	3.25 ± 0.008
2.55	4	—	—	—
0.85	5	4.18 ± 0.06	1.07 ± 0.001	3.02 ± 0.04
2.55	5	3.80 ± 0.15	0.97 ± 0.002	2.74 ± 0.004
0.85	15	4.14 ± 0.11	0.87 ± 0.006	2.41 ± 0.002
2.55	15	3.76 ± 0.25	0.73 ± 0.013	1.99 ± 0.003

^{a} Best-fit integer value of n at this concentration of polymer.

The micellar aggregation number, n, is temperature dependent and decreases from 121 to 32 between 45 °C and 25 °C, according to static light scattering measurements,[3] and presumably decreases further as the temperature is further decreased. A temperature dependence of n is not included in the present data treatment because the value of n itself has only a small effect on the calculated curves shown in Fig. 1 and it would be futile to include another fitting parameter to account for its temperature dependence. Notwithstanding this, careful examination of the curves shows that the cooperativity in micelle formation at larger n should be reflected in a sharper break at the c.m.t., whereas the best fit integer values of n are only 3 or 4 at the concentrations of **EPE** used (Table 1). However, like the changes in $\ln k_{obs}$ in Fig. 1, changes in dye solubilisation used to determine c.m.t. values do not show the abrupt break expected of a highly cooperative aggregation process with large n.[2] Neither does the temperature dependence of the molar excess heat capacity obtained from differential scanning calorimetry. A recent paper on the latter shows that the size of the cooperative unit of **E$_{28}$P$_{48}$E$_{28}$** is about 2, much lower than the value around 37 for n from static light scattering at 40 °C.[6] It is therefore safe to assert that the low value of n obtained in this study is not an artefact of the kinetic method of the present work, but an actual property of the polymer solution. This may possibly reflect a low n value at the onset of micellisation, just after the c.m.t., and is related to the polydispersity of the polymer, as discussed in Ref. 6.

Table 1 shows that the best-fit values of K^E_{mic} are almost identical for the different chosen values of n, and, moreover, are independent of the concentration of **EPE** within experimental error. Best-fit values of ΔH^0_{mic} and ΔS^0_{mic} show a systematic drop with increasing n, but this is not particularly large and diminishes with increasing n. The best-fit values of ΔH^0_{mic} and ΔS^0_{mic} at different concentrations of **EPE** are in perfectly satisfactory agreement. The seemingly 'too small to be true' standard deviations in ΔH^0_{mic} and ΔS^0_{mic} translate into reasonable experimental errors in K_{mic} after application of eqn. (5). The values of ΔH^0_{mic} and ΔS^0_{mic} for the best-fit integer values of $n = 3$ and 4 shown in Table 1 at the two different concentrations of **EPE**, respectively, are in excellent agreement with each other and close to the values, 2.96×10^5 J mol^{-1} and 1.09×10^3 J mol^{-1} K^{-1} of Hatton and co-workers obtained from the concentration dependence of the c.m.t.[2]

Notes and references

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