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## The interaction between triton X series surfactants and poly (ethylene glycol) in aqueous solutions

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**Abstract** A series of Triton X surfactants with different ethylene oxide chain length and poly(ethylene glycols) with different molecular weight were used, to find the effects of polymer chain length and size of the micelles on the cloud point of the surfactants. Two possible models are considered on the basis of cloud point changes of the solutions, to describe the polymer–surfactant interactions. One model considers that intra-chain micelles of polysoap are formed among the surfactant monomers and long polymer chains. The bridging attraction between two intra-chain micelles in such structures can enhance the collisions among the micelles, due to the exchange of amphiphilic monomers among the neighboring micelles. The other model suggests

that flocculation depletion for the polymer chains exists between two regular micelles. This provides the driving force for the neighboring micelles to approach each other and destabilize the colloidal system. The flocculation effect is more significant for polymer with a long chain. Polymers with a shorter chain block the approach of the micelles, since there is no typical polymer–surfactant association formed but just simple small molecule associations in which the steric and solvation effects of the polymer chains make the inter-micelle interactions repulsive.

**Key words** Cloud point – polymer – nonionic surfactant – poly(ethylene glycol)

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### Introduction

Understanding the nature of surfactant–polymer interactions both in bulk aqueous solutions and at the air–solution interface is relevant to the manufacture of many products including detergents, cosmetics, paints and coatings, adhesives and glues, lubricants, photographic films, food and pharmaceutical products [1–6]. Usually, the simultaneous presence of surfactants and polymers is required to achieve ideal dispersion effects in which surfactants provide emulsification capacity, interfacial tension control and colloidal stability. Polymers impart colloidal stability and special rheological features.

The practical importance of surfactant–polymer systems has motivated many studies of these systems, in which techniques such as viscosity and conductivity measurement, dialysis, fluorescence spectroscopy, NMR and neutron scattering have been used [7]. The most investigated model systems are aqueous solutions of nonionic polymers and ionic surfactants, because of their simple structures and interactions e.g. poly(ethylene oxide)-sodium dodecylsulfate [8–11], polyvinylpyrrolidone-SDS [12–15], and PEO-cetyltrimethylammonium bromide [16, 17].

For these systems, two important models were developed to describe the interactions. The first model [18] considers that polymer segments present at the micellar

surface penetrate into the region occupied by the surfactant ionic heads, and partially shield the contact area between the micellar hydrocarbon core and water. This effect is thought to constitute the main driving force for complexation. On the other hand, the increased steric repulsion between surfactant head groups and segments at the micellar surface induced by the polymer shielding will oppose complexation.

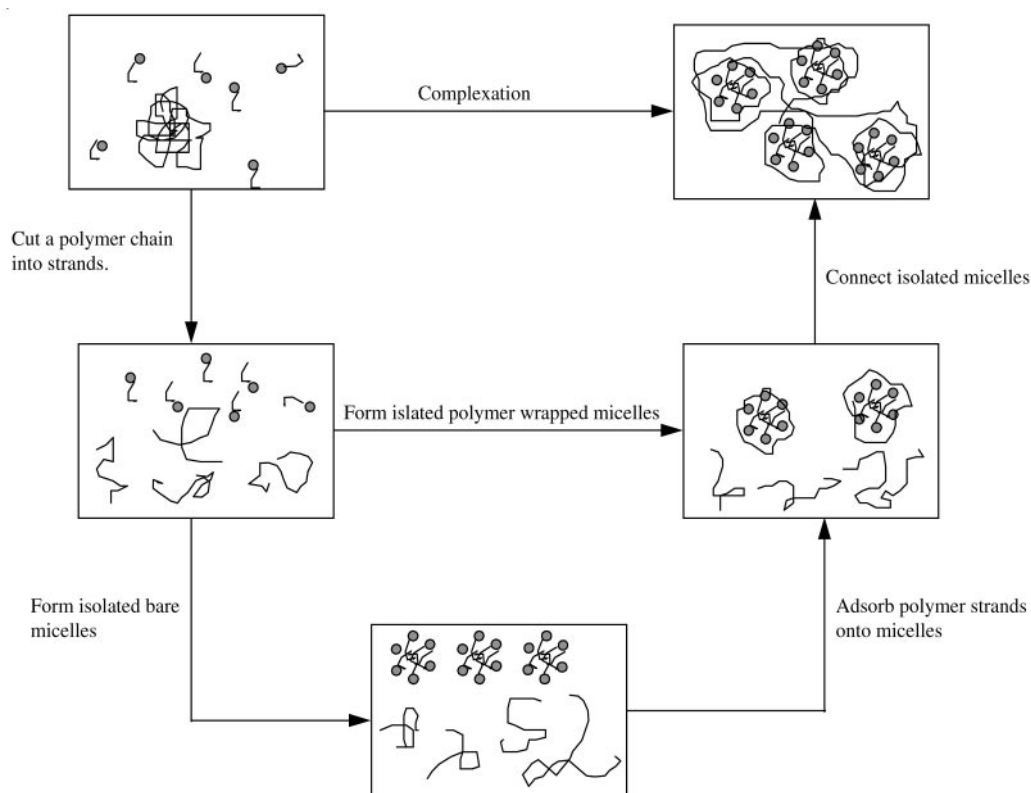
The second model [19] assumes that the adsorption of polymer on the micellar surface will induce a change in the microenvironment surrounding the micelles (from pure water to an aqueous polymer solution), since the polymer segment is less hydrophilic than water. The change will bring about a decrease in the interfacial free energy between the micellar hydrocarbon core and the solvent, and this will be the primary driving force for polymer binding to the surfactant micelles. Since the surfactant heads are hydrated and highly hydrophilic, the change of solvent from pure water to an aqueous polymer solution is assumed to result in an increase of the interfacial free energy between surfactant hydrophilic chains and the solvent, thus opposing polymer-surfactant complexation.

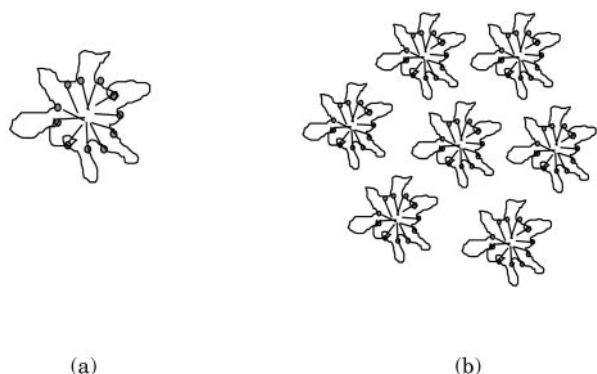
Competition between opposing tendencies in the two models will decide whether cooperative complexation process actually occurs. The weakness of the models is that

penetration of polymer segments into the micelles will change the size and shape of the micelles, and it is quite hard to find the change. Also the length of polymer chain and size of the micelles should be taken into account.

Other models have been proposed on the basis of different points of views. Nikas and Blankshtein [20] proposed the necklace model to describe the interaction in bulk aqueous solutions and a set of conceptual steps in the calculation of the free energy has been worked out (see Fig. 1). However, usually it is difficult to use this model in practice because of its idealization. Piculell et al. [21] suggested employing "spaghetti-and-meat balls" character for the polymer/surfactant aqueous solution systems. Recently, Borisov and Halperin [22] used the concept of polysoap micelles (a possible structure is shown in Fig. 2) to describe the effect of bridging interactions in polymer surfactant solutions. They provided a new structure of the solutions and suggested that the formation of the corona-shaped intra-chain micelles can significantly affect the properties of polymer-surfactant solutions. In these theories the micellar size, and length of flexible polymer chain are the main factors taken into consideration. However, so far only theoretical discussions have been given and few experimental observations have been explained with the theories.

**Fig. 1** A conceptual model for surfactant-polymer interactions





**Fig. 2** The possible structure of intra-chain micelle of surfactant-polymer polysoap (a) a single intra-chain micelle (b) several intra-chain micelles in polysoap solutions

For the interactions between nonionic surfactant and nonionic polymer, the problem becomes more difficult since the interaction is weaker, the CMC is smaller than those of the ionic counterparts, and the micellar interface is not as clear as that for ionic surfactant micelles. One of the most convenient ways to study the interaction in nonionic surfactant aqueous systems is to find the changes of cloud point of the aqueous solutions, because the cloud point is a measure of the association of the surfactant with water, the solvent, and can be affected by the addition of a third component, such as polymers to the systems. There are a few previous studies concerning the cloud point of aqueous Triton X solutions in the presence of additives which include surfactants, inorganic salts, and organic solvents [23–28]. It has been shown that the so-called cloud point transition in the nonionic micellar solutions is a phase separation which results in a water-rich phase and a surfactant micelle-rich phase. The changes of cloud point of the solutions are due to the changes in hydration of the micelles which can be affected by additives. For water-soluble polymer additives it was suggested that their chains penetrate into the cores of the surfactant micelles and increase the solubility of the micelles in water which induces the increase of cloud point. But the studies did not consider the size and shape of the micelles and the possibility of other structures for the solutions. Therefore, they failed to explain the experimental facts reasonably. For example, according to the above explanation the addition of polymer will increase cloud points, while in practice the cloud point sometimes decreases.

The current explanation [29] of cloud point is that when the cloud point is approached the increased intermicellar interaction is the result of strong entropy dominance. The ethylene oxide chains of the surfactants are highly hydrated and well structured (less entropy). When two micelles approach each other, there is an overlap of

hydration spheres and some water molecules are freed, thereby increasing the entropy. At the cloud point this increase in entropy is larger and the corresponding  $\Delta G$  is much more negative than that arising from the repulsive forces. Hence, the total free energy is negative and the cloud point appears. The influence of an additive on the cloud point depends on how it affects the intermicellar interactions. One possibility is that the additive stays in the medium or at the interface of the micelles. In this case the additive does not change the original micelles, but makes the environment of the micelles different, and the intermicellar interaction may be changed. Another possibility is that the additive molecules penetrate into or mix with the micelles to form new micelles which consist of additives and surfactant, and have different size and aggregation from the regular micelles. The intermicellar interactions will be different in this case as well, and the cloud points change. So far, however, there is no clear description of the mixed micellar structures and the intermicellar interactions. How the properties of the solutions are affected by the intermicellar interactions has not been elucidated either.

In the present work, the changes of cloud points of the aqueous Triton X solutions were determined, and used to reveal polymer-surfactant interactions in the bulk solutions. In our discussion the size of micelles and length of polymer chains play major roles in the intermicellar interactions of the solutions and are paid much attention.

## Experimental

### Materials

PEG200, PEG1000, PEG6000, and PEG20000 (with average molar mass 200, 1000, 6000 and 20 000  $\text{g mol}^{-1}$ ) from BDH Chemicals Ltd. were used without further purification.

Triton X-114, Triton X-100 and Triton X-102 (with average number of EO units 7.5, 9.5 and 12.5, respectively) from Union Carbide Corporation were used after molecular sieve (0.3  $\mu\text{m}$ ) treatment for a few days to remove residual water in the products.

Deionized water with conductivity 0.2  $\mu\text{S}$  was used as the solvent.

### Measurements

Cloud points were determined visually by noting the temperature at which turbidity is observed. The average of the temperatures of appearance and disappearance of turbidity was taken as the cloud point. Heating and cooling

rates were controlled at  $0.5\text{ }^{\circ}\text{C min}^{-1}$  and three determinations for each point were conducted to achieve  $\pm 2\%$  uncertainty of the results.

## Results and discussion

In the aqueous polymer solutions, the added surfactant molecules initially accumulate in the surface until a critical concentration (different in magnitude from the CMC of the surfactant aqueous solution without any polymer) is reached. At the surface, the hydrophilic chains of the surfactant make contact with the chains of PEG and an equilibrium may be set up in the formation of some kind of complex:

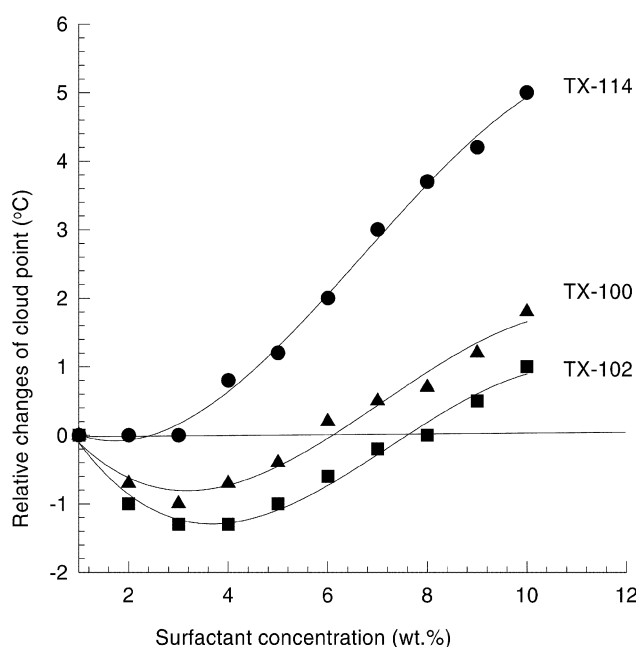
Free surfactant monomers + Polymer

$\rightleftharpoons$  Surfactant-polymer complex

Chari and Lenhart [30] found the CAC (critical aggregation concentration) of SDS surfactant/PVP polymer system from the turning points of the surface tension-concentration curves, and suggested that at the air-solution interface surfactant must reach a critical concentration (namely the CAC), then start to associate with the polymer chains. They suggested that CAC of the solutions can be determined from the change of surface tension of the solutions.

This complex should be different from its counterpart in the bulk solution where the surfactant molecules form micelle-like particles which are associated with polymer chains, although there is no direct structural comparison between them yet, due to the different circumstances (in the surface the hydrophobic tails of the surfactant molecules are pulled vertically to avoid contact with water which can make the energy of the whole system higher, but in the bulk solution there is no such limit for the surfactant molecules and they can form a spherical or a rod-like micelle). The formation of the complex will change the solution structure and affect the physical properties of solution. One such property is the cloud point of the solutions.

Usually cloud point (CP) of surfactant aqueous solutions can show hydrogen bonding between the hydrophilic parts of the surfactant and water molecules. At the same molar concentration the longer the ethylene oxide chains of the surfactant molecules, the higher the cloud points of their aqueous solutions. The reason for this is that the EO units of the surfactant molecules form hydrogen bonds to water, and when the EO chain is longer, more hydrogen bonds may be formed and more energy is needed to break them up. For each Triton X surfactant, the relative changes of CP with concentration are shown in Fig. 3 and



**Fig. 3** The influence of concentration on the cloud point of Triton X surfactant aqueous solutions

**Table 1** The relative cloud point changes of Triton X surfactant aqueous solutions

| Concentration<br>[% w/w] | Triton X-114 | Triton X-100 | Triton X-102 |
|--------------------------|--------------|--------------|--------------|
| 1.0                      | 0            | 0            | 0            |
| 2.0                      | 0            | -0.7         | -1.0         |
| 3.0                      | 0            | -1.0         | -1.3         |
| 4.0                      | 0.8          | -0.7         | -1.3         |
| 5.0                      | 1.2          | -0.4         | -1           |
| 6.0                      | 2.0          | 0.2          | -0.6         |
| 7.0                      | 3.0          | 0.5          | -0.2         |
| 8.0                      | 3.7          | 0.7          | 0            |
| 9.0                      | 4.2          | 1.2          | 0.5          |
| 10.0                     | 5.0          | 1.8          | 1            |

Table 1. With increasing surfactant concentration CPs decrease initially and then increase monotonically. Koshy and co-workers [28] suggested that the minimum in the CP-concentration curve is the result of "floating" water barriers which stay between the micelles and prevent them from colliding with each other at a higher surfactant concentration. Hence, more energy is needed to remove the barriers. But there has not been any evidence showing the existence of such special water molecules, and this model cannot explain why Triton X-114 does not have a valley like the other two surfactants. However, if we consider the problem from the point of view of the shape variation of micelles in the solutions, we can explain this fact quite

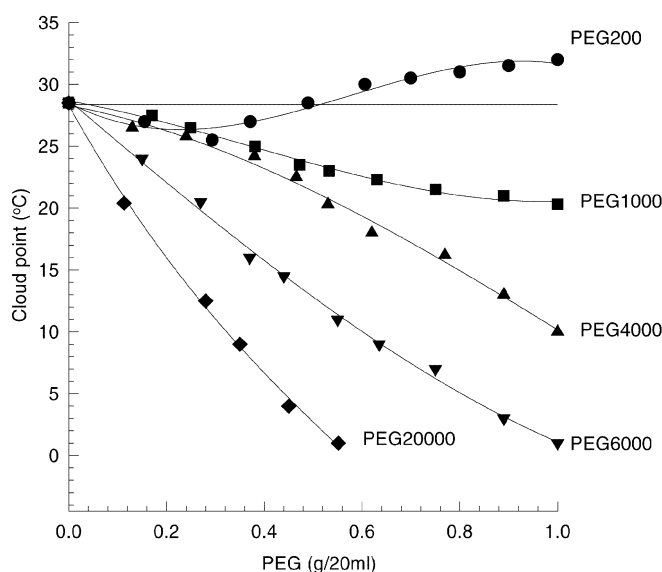


Fig. 4 The effect of PEG on the cloud point for Triton X-114 aqueous solutions

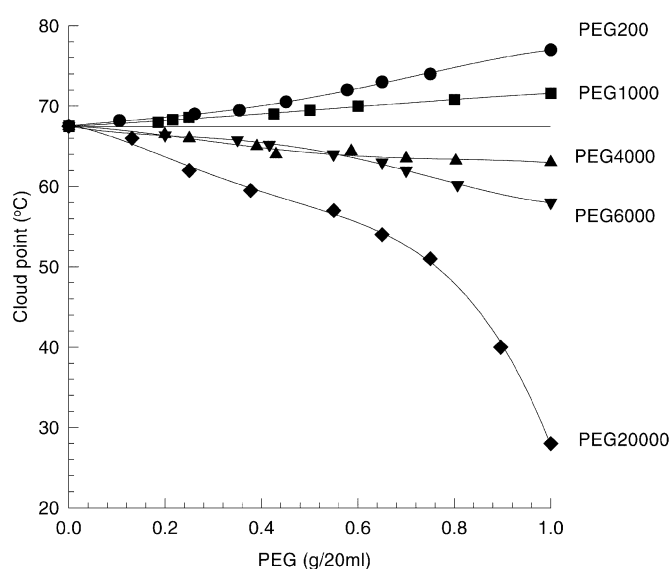


Fig. 5 The effect of PEG on the cloud point for Triton X-100 aqueous solutions

easily. Before the minimum point, initially, the micelles increase in number without changing their original shape, and the greater the number of the micelles in the solution, the higher the probability of collisions, so the cloud point decreases. This tendency cannot be maintained for long however. At the minimum point the micelles begin to change their shapes from spherical to cylindrical, especially for Triton X-100, and Triton X-102 (Triton X-114 forms cylindrical micelles from its CMC and only the size of the micelles increases with the concentration increase, so that the concentration effect is not significant for Triton X-114, and its minimum point is very shallow) [31–33]. The changes in micellar shapes result in a very large increase in the viscosity of the surfactant solutions due to the increase of the gyration radii of the particles [34]. In such viscous fluids, collision among the micelles becomes more difficult and more energy is needed to reach the cloud point.

Figures 4–6 and Table 2 show the influence of PEG with different chain length on the CP of Triton X aqueous solutions, for a constant surfactant concentration ( $100 \text{ g l}^{-1}$ ). The changes seem much more complex than can be accounted for by the explanations that have been proposed by some researchers [21, 23]. It has been suggested that the polarity of the solubilizes, the additives, determine the CP changes, such that additives with a high polarity can lower CP while those with low polarity can raise CP. As to the effect of polymer additives on CP, there are few papers that can elucidate the polymer–surfactant interactions and its relation with CP since some opposite and confusing effects may be found when the surfactant

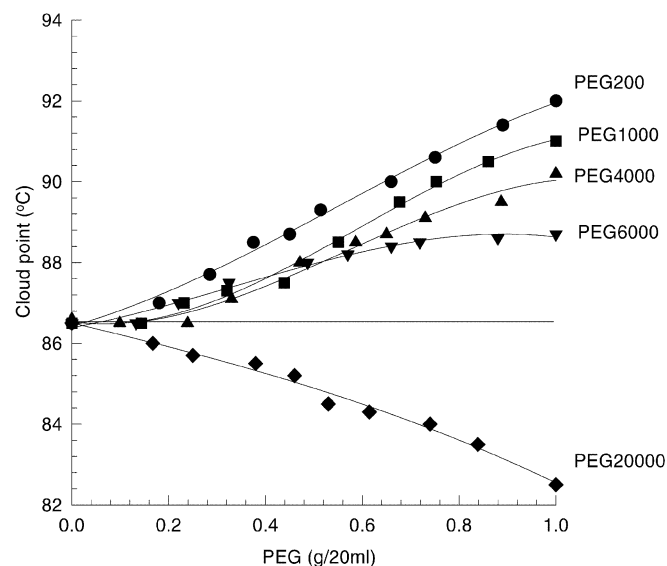


Fig. 6 The effect of PEG on the cloud point for Triton X-102 aqueous solutions

tail and the polymer chain change their lengths [26]. In the present work, we analyze the structures of the solutions and the functions of each part, and provide two possible models for the change of cloud point.

#### Model 1

When PEG is added to the surfactant aqueous solution there are two kinds of interactions between the polymer

**Table 2(a)** Effect of PEG on the cloud point of Triton X-114 surfactant aqueous solution ( $C_{\text{Triton X-114}}$  is  $100\text{ g l}^{-1}$ )

| PEG200           |      | PEG1000          |      | PEG4000          |      | PEG6000          |      | PEG20 000        |      |
|------------------|------|------------------|------|------------------|------|------------------|------|------------------|------|
| $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   |
| 0                | 28.5 | 0                | 28.5 | 0                | 28.5 | 0                | 28.5 | 0                | 28.5 |
| 0.1552           | 27.0 | 0.1703           | 27.5 | 0.1300           | 26.5 | 0.1512           | 24.1 | 0.1132           | 20.4 |
| 0.2934           | 25.1 | 0.2485           | 26.0 | 0.2412           | 25.8 | 0.2697           | 20.5 | 0.2803           | 12.5 |
| 0.3713           | 27.0 | 0.3813           | 24.9 | 0.3803           | 24.2 | 0.3710           | 16.0 | 0.3514           | 8.9  |
| 0.4899           | 28.5 | 0.4721           | 23.5 | 0.4656           | 22.5 | 0.4412           | 14.5 | 0.4498           | 4.1  |
| 0.6056           | 30.1 | 0.5327           | 22.9 | 0.5302           | 20.3 | 0.5488           | 10.9 | 0.5516           | 1.0  |
| 0.7000           | 30.5 | 0.6300           | 22.2 | 0.6200           | 18.0 | 0.6351           | 9.0  | –                | –    |
| 0.8013           | 31.2 | 0.7503           | 21.5 | 0.7694           | 16.2 | 0.7502           | 7.1  | –                | –    |
| 0.8997           | 31.5 | 0.8911           | 21.1 | 0.8911           | 13.0 | 0.8900           | 3.2  | –                | –    |
| 0.9968           | 32.0 | 0.9962           | 20.3 | 1.023            | 10.0 | 1.059            | 1.0  | –                | –    |

$C_{\text{PEG}}$  is the concentration of PEG (g/20 ml).  
CP is cloud point of the solutions ( $^{\circ}\text{C}$ ).

**Table 2(b)** Effect of PEG on the cloud point of Triton X-100 aqueous solution ( $C_{\text{Triton X-100}}$  is  $100\text{ g l}^{-1}$ )

| PEG200           |      | PEG1000          |      | PEG4000          |      | PEG6000          |      | PEG20 000        |      |
|------------------|------|------------------|------|------------------|------|------------------|------|------------------|------|
| $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   |
| 0                | 67.5 | 0                | 67.5 | 0                | 67.5 | 0                | 67.5 | 0                | 67.5 |
| 0.1050           | 68.2 | 0.1854           | 68.0 | 0.19095          | 66.5 | 0.2035           | 66.5 | 0.1312           | 66.0 |
| 0.2610           | 69.0 | 0.2158           | 68.3 | 0.2503           | 66.0 | 0.3512           | 65.8 | 0.2510           | 62.1 |
| 0.3541           | 69.5 | 0.2492           | 68.6 | 0.3912           | 65.1 | 0.4162           | 65.2 | 0.3773           | 59.6 |
| 0.4511           | 70.5 | 0.4255           | 68.9 | 0.4300           | 64.0 | 0.5493           | 64.1 | 0.5499           | 57.1 |
| 0.5776           | 72.0 | 0.5120           | 69.5 | 0.5858           | 64.4 | 0.6512           | 63.1 | 0.6511           | 53.9 |
| 0.6503           | 73.2 | 0.5983           | 70.1 | 0.7070           | 63.5 | 0.7030           | 62.1 | 0.7498           | 51.1 |
| 0.7497           | 74.0 | 0.8011           | 70.9 | 0.8031           | 63.2 | 0.8066           | 60.2 | 0.8963           | 40.2 |
| 1.031            | 77.1 | 0.9994           | 71.6 | 1.121            | 62.9 | 1.056            | 58.1 | 1.017            | 27.9 |

See footnotes to Table 2(a).

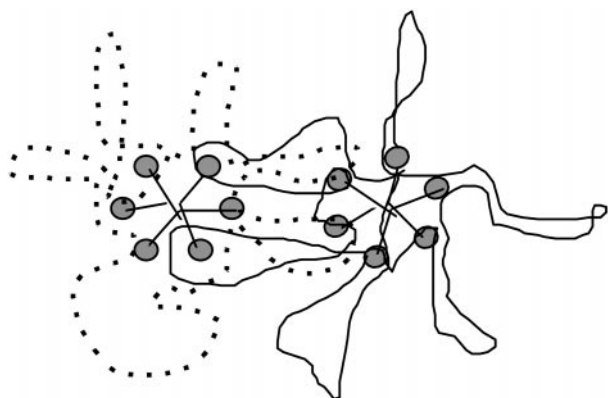
**Table 2(c)** Effect of PEG on the cloud point of Triton X-102 aqueous solution ( $C_{\text{Triton X-102}}$  is  $100\text{ g l}^{-1}$ )

| PEG200           |      | PEG1000          |      | PEG4000          |      | PEG6000          |      | PEG20 000        |      |
|------------------|------|------------------|------|------------------|------|------------------|------|------------------|------|
| $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   | $C_{\text{PEG}}$ | CP   |
| 0                | 86.5 | 0                | 86.5 | 0                | 86.5 | 0                | 86.5 | 0                | 86.5 |
| 0.1802           | 87.0 | 0.1438           | 86.5 | 0.0988           | 86.5 | 0.1327           | 86.6 | 0.1672           | 86.1 |
| 0.2854           | 87.7 | 0.2314           | 87.1 | 0.2390           | 86.6 | 0.2202           | 87.1 | 0.2503           | 85.8 |
| 0.3749           | 88.5 | 0.3203           | 87.3 | 0.3301           | 87.1 | 0.3246           | 87.6 | 0.3796           | 85.5 |
| 0.4501           | 88.8 | 0.4388           | 87.5 | 0.4711           | 88.0 | 0.4873           | 88.1 | 0.4600           | 85.2 |
| 0.5141           | 89.3 | 0.5501           | 88.5 | 0.5863           | 88.6 | 0.5705           | 88.2 | 0.5305           | 84.5 |
| 0.6595           | 90.1 | 0.6766           | 89.4 | 0.6500           | 88.7 | 0.6612           | 88.4 | 0.6146           | 84.3 |
| 0.7488           | 90.6 | 0.7524           | 90.1 | 0.7313           | 89.1 | 0.7188           | 88.5 | 0.7414           | 84.0 |
| 0.8902           | 91.4 | 0.8600           | 90.5 | 0.8871           | 89.5 | 0.8795           | 88.6 | 0.8387           | 83.5 |
| 0.9987           | 92.0 | 1.105            | 91.1 | 1.012            | 90.2 | 1.033            | 88.7 | 0.9964           | 82.5 |

See footnotes to Table 2(a).

and the surfactant. Low molecular weight PEGs (degree of polymerisation <10–15) are believed to form micelle–glycol complexes in which the glycol is adsorbed on the surface of the micelle in a manner similar to that by which small polar compounds combine with the micelles, since the short chains can just cover or attach to part of the micelle [35]. Higher molecular weight glycols are believed to form another kind of polymer–surfactant complex (the

typical polymer–surfactant complexes) in which the glycol is in the form of a random coil bound to the surfactant with its hydrophilic groups oriented toward the aqueous phase [36]. In the latter case, the polysoaps, hydrophilic PEG polymers incorporating Triton X monomers, may form intra-chain micelles (a possible structure is shown in Fig. 2b). Such a structure indicates that the micelle–micelle interaction is attractive, and can be expected to facilitate



**Fig. 7** Surfactant monomer exchange between adjacent intra-chain micelles

collisions among the micelles. In this case the micellar attraction is due to the bridging resulting from the exchange of Triton X amphiphiles between the neighboring micelles (see Fig. 7). When the chain is longer and more loops can be made for each micelle, there are more opportunities for the exchange and micellar collisions, leading to a lower CP. This gives a reasonable explanation for the trends in Figs. 4–6 in which the higher-molecular-weight PEGs reduce cloud point to a greater extent. On the other hand, the lower molecular weight PEGs cannot form intra-chain micelles because of their short EO chains, and merely wrap or cover the surface of the regular micelles partially. A repulsion will be produced between the wrapped micelles due to steric and solvation effects of the polymer chains. This prevents the micelles from colliding with each other, so that more energy is needed for the solutions to reach their CP.

It should be noted that the concepts of lower molecular weight and higher molecular weight PEGs are relative to the sizes of the micelles with which they will interact. Since the hydration of EO chains of Triton X molecules is weakened heavily by the PEG chain cover, the size of the micelle should be proportional to the size of the surfactant molecule (in contrast to the situation in Triton X aqueous solution with no added PEG). Therefore, for some intermediate cases, such as PEG1000 in Triton X-114 and Triton X-100 aqueous solutions, the size of Triton X-100 micelles is larger than that of Triton X-114 micelles, so PEG1000 reduces the CP of Triton X-114 aqueous solutions but increases the CP of Triton X-100 solutions.

The interpretation advanced above depends on the following conditions being fulfilled: the systems formed by Triton X and PEG are dilute solutions of noninteracting polysoaps; the intra-chain micelles are spherical; free Triton X monomers do not adsorb on the spacer chains.

As the real Triton X/PEG aqueous solutions can only partially fulfil the above conditions (there are interactions in the polysoap solutions, for example), and some intermediate situations are also possible, such as that PEG with shorter chains may be able to give a partial coverage of the surface of a micelle but to be absorbed on more than two different micelles. This enhances rather than counteracts the aggregate formation. Consequently the bridging flocculation produced by PEG with shorter ethylene oxide chains should be taken into account.

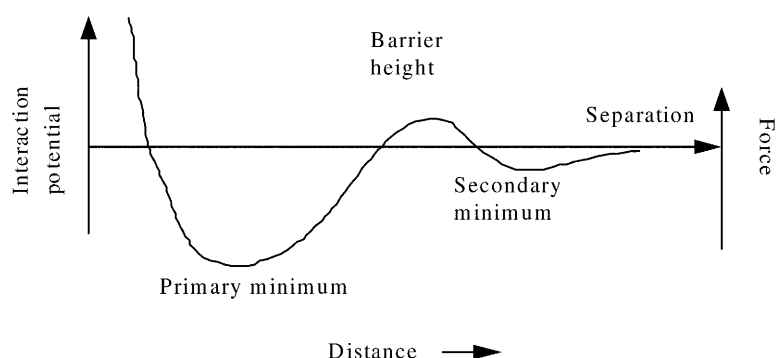
## Model 2

If we consider the problem from the point of view of stabilization of the colloidal systems, we find that polymers can have either stabilization or destabilization effects on the dispersed surfactant micelle systems, which means that their addition can raise or lower the energy valley of the potential energy curves showing two minima as depicted in Fig. 8. The primary minimum represents coagulation which is an irreversible association among the colloidal particles, while the second is flocculation, a reversible association. Generally PEG as a hydrophilic polymer is thought to provide a protective shield which prevents the micelles concerned from approaching each other. Such protection can be due either to strong bonds between the hydrophilic EO chains with water, the medium, or to the tendency of the chains to assume a large number of configurations when in the congenial water medium. The former effect is enthalpic and the latter is entropic. Therefore PEG will stabilise the colloid solutions by the above two effects although it is not clear yet which effect is dominant.

When the length of PEG chains changes, however, another factor – destabilization of the Triton X colloidal solution by depletion flocculation – should be considered. When PEG dissolves in the aqueous Triton X solutions, parts of the PEG chains associate with the exterior of Triton X regular micelles, and the other parts of the PEG chains may straddle the media between two dispersed micelles, where the configuration of the chain may be restrained by the space between the neighboring two micelles. The less the space or the longer the chain, the greater the restraint, and the more significant depletion to PEG becomes. As a result of the depletion, the increasing osmotic pressure difference between the solutions inside and outside the space makes the two micelles approach each other and aggregation can occur more readily.

The stabilizing and destabilizing effects will influence the solutions simultaneously. The circumstances of the solutions decide which is the dominant effect. For PEG with a longer chain, such as PEG6000 and

**Fig. 8** A schematic energy/force-distance diagram showing the interaction between two particles in the solutions



PEG20000, the destabilising effect becomes dominant, while for the PEG with a shorter chain, such as PEG200, the stabilising effect is dominant since the depletion is more significant for the polymer molecules with a long chain. Consequently, PEG200 and PEG20000 can have the opposite influence on phase separation in the surfactant solutions.

The different effects on the CP of Triton X-114 and Triton X-100, may be due to the sizes of their regular micelles. Triton X-114 has more micelles than Triton X-100 at the same molar concentration in water because it has a shorter hydrophilic chain and a smaller aggregation

number. Hence the space between two neighbouring Triton X-114 micelles is less, on average, than that between two Triton X-100 micelles. The smaller space makes Triton X-114 colloid solutions more sensitive to the increase of polymer chain length which leads to the depletion effect for the polymer. That is why PEG1000 can reduce the CP of Triton X-114 solution, but increase the CP of Triton X-100 solution.

At present, both explanations are possible; there is no clear evidence favouring one over the other. They provide an understanding of the same phenomenon from two different points of view.

## References

- Napper DH (1987) In: Polymeric Stabilisation of Colloidal Dispersions. Marcel Dekker, New York, p 19
- Saito S (1987) In: Nonionic Surfactants – Physical Chemistry. Schick MJ (ed) Marcel Dekker, New York, p 881
- Goddard ED (1993) In: Interactions of Surfactants with Polymers and Proteins. Goddard ED, Ananthapadmanabhan KP (eds) CRC, Boca Raton, FL, p 395
- Robb ID (1981) In: Lucassen-Reynolds EJ (ed) Anionic Surfactants – Physical Chemistry. Marcel Dekker, New York, p 109
- Hayakawa K, Kwak JC (1991) In: Rubingh DN, Holland PM (eds) Cationic Surfactants – Physical Chemistry. Marcel Dekker, New York, p 189
- Breuer MM, Robb ID (1972) Chem Ind 13:531
- Lindman B, Thalberg K (1993) In: Goddard ED, Ananthapadmanabhan KP (eds), Interactions of surfactants with polymers and Proteins. CRC, Boca Raton FL, p 203
- Dubin K, Graber JH, Xia J, Zhang H (1992) J Colloid Interface Sci 148:35
- Jones MN (1967) J Colloid Interface Sci 23:26
- Cabane B (1977) J Phys Chem 81:1639
- Brackman JC, Engberts JBFN (1989) J Colloid Interface Sci 132:250
- Chari KJ, Lenhart WC (1990) J Colloid Interface Sci 137:204
- Chari KJ (1992) J Colloid Interface Sci 151:294
- Fishman ML, Eirich FR (1971) J Phys Chem 75:3135
- Murata M, Arai H (1972) J Colloid Interface Sci 44:475
- Witte FM, Engberts JBFN (1987) J Org Chem 52:4767
- Brackman JC, Engberts JBFN (1992) Langmuir 8:424
- Nagarajan R, Harold MP (1980) In: Mittal KL, Fendler EJ (eds) Solution Behaviour of Surfactants. Vol 2, Plenum, New York, p 1391
- Ruckenstein E, Huber G, Hoffmann H, (1987) Langmuir 3:382
- Nikas YJ, Blankschtein D (1994) Langmuir 10:3512
- Piculell L, Bergfeldt K, Gerdes S (1996) J Phys Chem 100:3675
- Borisov OV, Halperin A (1996) Macromolecules 29:2612
- Maclay WN (1956) J Colloid Sci 11:272
- Sadaghiania AS, Khan A (1991) J Colloid Interface Sci 144:191
- Goldstein RE (1986) J Chem Phys 84:3367
- Nilsson PG, Lindman B (1984) J Phys Chem 88:539
- Rathman JF, Scamehorn JF (1986) Langmuir 2:354
- Koshy L, Saiyad AH, Rakshit AK (1986) Colloid – Polym Sci 274(6):582–587
- Kjellander R, Floriu E (1981) J Chem Soc Faraday Trans 77:2053
- Chari K, Lenhart WC (1990) J Colloid Interface Sci 137:204
- Robson RJ, Dennis EA (1977) J Phys Chem 81:1075
- Kushner LM, Hubbard WD (1954) J Phys Chem 58:1163
- Ribeiro AA, Dennis EA (1975) Biochemistry 14:3746
- Lomax EG (1996) In: Lomax EG (ed) Amphoteric Surfactants, 2nd edn. Marcel Dekker, New York, p 27
- Rosen MJ (1989) In: Surfactants and Interfacial Phenomena, 2nd edn. Wiley, New York, p 181
- Shinoda K (1967) In: Solvent Properties of Surfactant Solutions. Marcel Dekker, New York