Insights on polymer surfactant complex structures during the binding of surfactants to polymers as measured by equilibrium and structural techniques

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This *tutorial review* provides new insights into the binding interactions between anionic surfactant molecules and various macromolecules in solution. The systems are of inherent scientific interest because synergistic mixing between these two components leads to complexes commonly found in applications such as detergency, cosmetic products, rheology control, paint and pharmaceutical formulations. We describe how the basic foundations, which are prerequisite to characterize a given polymer/surfactant system are evaluated together with information on the binding mechanism and structure derived from several methodologies.

Introduction

The basic surface active components of many detergents, cosmetic and pharmaceutical products is usually a blend containing ionic surfactant and polymers very often mixed with other additives and a non-ionic surfactant. These mixtures form a class of materials which have direct impact

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Michael K. C. Tam (1959) is professor in the School of Mechanical & Aerospace Engineering and the School of Chemical & Biomedical Engineering at Nanyang Technological University, Singapore. He received his PhD degree from the Department of Chemical Engineering, Monash University in 1991, and was awarded the Harold Jan Shoemaker Award by the International Association for Hydraulic Research for the best paper published in the Journal of Hydraulic Research between 1990 and 1992. Following an eighteen months post-doctoral fellowship at McMaster University (Canada), he joined Nanyang Technological University in 1992 as a Lecturer and was promoted to professor in 2004. He is currently a fellow in the Chemical and Pharmaceutical Engineering programme under the Singapore–MIT Alliance. His research interest focuses on the microscopic and macroscopic properties of self-assembly systems such as surfactants, block copolymers, and associative polymers. The scope of his research includes polymer synthesis using ATRP, physical characterization using light scattering (static and dynamic), rheometry, and calorimetry (ITC and DSC). The objectives are to correlate the polymer architecture to the microscopic and macroscopic properties of novel self assembly systems. The potential applications of his research are in enhanced drug release, gene therapy, bio and chemical separations, and environmentally friendly coating systems.

Evan Wyn-Jones

Professor Wyn-Jones was born in 1939 and educated at Ysgol y Moelwyn, Ffestiniog, University of Wales, Aberystwyth and St. John's College, Oxford. He was awarded the degree of DSc in 1976 by the University of Wales. He started his academic career in 1965 as a Lecturer in Physical Chemisty at Sir John Cass College, London. In 1966 he joined the University of Salford as Lecturer and was promoted to Senior Lecturer (1971), Reader (1974) and Professor of Physical Chemistry in 1977. From 1982 to 1993 he was the Chairman of the Chemistry Department. His early research interest involved the use of ultrasonic relaxation and infra-red studies on the dynamics of conformational changes in small molecules. In the early 1970's he was involved in the development of the studies on the kinetics of micelle formation in surfactants. The work was then extended to study the kinetics of surfactant solutions containing additives which led to his interest in polymer surfactant interactions. From 1999 to 2005 he was a visiting Professor at the Fritz Haber Institute of the Max Planck Society, Berlin where he coordinated a successful collaboration between Salford, Berlin and the Rutherford Appleton Laboratory. During his time at the Max Planck Institute in Berlin he found out that his DPhil supervisor at Oxford, the late Professor Sir H. W. Thompson of football fame, actually carried out his PhD studies with Max Planck in the early 1930's.

on phase separation, rheological and interfacial properties.[1,2] The behaviour of ionic surfactant/polymer mixtures can be quite different from individual polymer or surfactant solution due to an attractive interaction often resulting in surfactant micelles binding to polymers below their normal critical micellar concentration (*cmc*). It is often necessary to optimize the formulation of these blends so that a product emerges which satisfies stringent criteria for processing, appearance and marketing. In the absence of a theory to predict the behaviour of such mixtures, the formulation of products has traditionally relied on trial and error approaches based on trends and rules many of which are deduced on an empirical basis from fundamental studies on model polymer/surfactant mixtures. Nowadays, largely as a result of health, safety, energy conservation and issues involving the environment, more and more surfactant/polymer mixtures are being tested as potential products. These studies have been carried out using a diverse range of physiochemical techniques and have led to new insights on the binding characteristics of many different polymer/surfactant mixtures.[1–4] In many of these systems, most of the useful information has emerged by complementing data from more than one experimental method—this is extremely important in these systems since different experiments probe different aspects of these macromolecular/aggregating systems.[1–4] In most studies, the choice of surfactant has remained more or less the same since the pioneering work—the anionic sodium dodecyl sulfate has been used in the majority of publications, there is a small body of studies with cationics and finally non-ionic surfactants feature in very few experiments. On the other hand, the use of different polymers has mushroomed mainly because of the emergence of new methodologies in polymer synthesis with particular emphasis on the addition of functional groups at the end or along the polymeric backbones. Although the field of polymer/surfactant interactions has been well reviewed with two books[1,2] and various review articles,[3,4] some of the fundamental methodologies and new results have yet to be considered in a single treatment.

Since surfactant micelles feature in most of this study, we shall briefly consider this aggregating phenomenon. The onset of micelle formation in surfactants usually occurs at a well-defined concentration that is denoted as the critical micellar concentration. It is now recognized that the dominant controlling force for micellization is driven by the gain in entropy. This positive gain can be attributed to the tendency of the hydrophobic group of the surfactant to remove itself from the solvent environment to aggregate at the interior of the micellar hydrophobic core. The large entropy increase can be further elaborated as follows. The first explanation relates to the extensive hydrogen-bonding environment in water. As water does not hydrogen bond with the surfactant hydrocarbon chains, the water molecules would form a structure surrounding the hydrophobic groups, which produces cavities in the water structure. The resulting water molecules become more ordered, which caused a noticeable decrease in entropy. When there is sufficient surfactant in the aqueous solution, micellization begins when the surfactant hydrophobic groups are removed from the water and they form a micellar hydrophobic core with their hydrophilic parts directed towards the water. The cavities formerly occupied by the hydrocarbon chains are returned to the bulk water. That is the highly organized water structure, formerly involved in the cavities, returns to the normal hydrogen-bonded water causing an increase in entropy that drives the micellization process.

The thermodynamic analysis of micelle formation process has been treated using a mass action model and phase separation model[2] where the standard free energy of micellization ΔG_{mic} is described by eqn (1):

$$\Delta G^{\mathrm{o}}_{\mathrm{mic}} = RT\ln x_{cmc} \tag{1}$$

where x_{cmc} is the surfactant mole fraction at *cmc*.

The interaction of polymers with surfactants, unlike with other small molecules such as salt, is complicated by the micellization of the surfactants and sometimes, the self-aggregation of certain associating polymers. Polymer–surfactant interaction involves a surfactant aggregation process that is akin to micellization. As an analogy with free surfactant micellization, the onset of surfactant molecules binding on the polymers is denoted as the critical aggregation concentration, *cac*. By making assumptions that the driving force for surfactants aggregating onto polymers is similar to that for a normal free surfactant micellization process, the standard free energy of surfactant in terms of *cac* can be used. From eqn (1), the free energy per mole of surfactant aggregation to a polymer can be represented by;

$$\Delta G^{\mathrm{o}}_{\mathrm{b}} = RT\ln cac \tag{2}$$

and the surfactants involved in the transformation of free micelles to polymer-bound mixed micelles are shown in the reaction, *i.e.*: free micelles ⇔ polymer bound micelles. The free energy per mole of surfactant involved in this reaction is then described by;

$$\Delta G^{\mathrm{o}}_{\mathrm{PS}} = \Delta G^{\mathrm{o}}_{\mathrm{b}} - \Delta G^{\mathrm{o}}_{\mathrm{mic}} = RT\ln\frac{cac}{cmc} \tag{3}$$

This free energy is a quantitative measure of the strength of interaction between the polymer and the surfactant. It is argued that the ratio *cac*/*cmc* should be less than one because if *cac* is greater than *cmc*, the situation would suggest that the surfactant molecules would prefer to micellize with themselves instead of forming mixed micelles, which would otherwise indicate that no polymer–surfactant interactions exist at all.

In the following discussion we have presented a general overview of the type of data which can yield the basic information required to underpin a reasonable knowledge of the binding behaviour of a typical non-ionic polymer–surfactant system, namely polyvinylpyrrolidone (PVP)/SDS. We have chosen three methodologies, namely the surfactant selective electrode, isothermal titration calorimetry and small angle neutron scattering, which we consider are fundamental in these studies in the sense that they monitor the binding process, determine binding isotherms and also give direct information on the structure of the complex. The results as discussed here were not published in chronological order, rather they have been chosen to illustrate how various pertinent information evolve from the experiments. In many

cases, the substantial contributions of other standard physical chemical techniques will be mentioned.

Surfactant selective electrode

The surfactant selective electrode has been used extensively to study the binding of ionic surfactants to charged and neutral macromolecules.[5a] In general the binding of surfactants to polymers are conducted on the same basis as classical ligand/macromolecule studies in that the concentration of the polymer is kept constant and the concentration of the surfactant is varied. The electrode is the only device which can directly measure and monitor the concentration of unassociated surfactant monomers in the presence or absence of additives. Thus when a known amount of surfactant is added to a polymer solution, the amount bound equals the total added less its monomer concentration. Most of the early studies, mainly carried out and reviewed by Kwak[2] involved cationic surfactants interacting with polyanions. Although surfactant selective electrodes are available commercially, those that have been used to study polymer/surfactant systems have been constructed in various laboratories.[5a] Many different procedures are available and by far the most successful ones are those which incorporate a solid modified polyvinyl chloride (PVC) membrane. The biggest drawback with the use of surfactant electrodes for polymer binding studies is their reliability as robust and routine devices. The main problems arise from the choice of membranes, which can be temperamental, unstable and often breakdown in the presence of surfactant micelles. The most successful membrane we have encountered is modified polyvinyl chloride, PVC, covalently grafted with cationic or anionic groups. In principle the charged PVC is neutralized with the oppositely charged surfactant under investigation. A polymeric plasticizer which is miscible with PVC is used to condition the surfactant neutralized PVC to introduce pliability and facilitate ion transport across the membrane. The negatively charged PVC for use with cationic surfactants is available commercially. On the other hand the positively charged PVC which is used in SDS electrodes has to be synthesized and modified in the laboratory. Although recipes are available[5] for the synthetic procedure, health and safety and other issues have acted as barriers to the use of these devices for many investigators. Despite the limitations and idiosyncrasies of these surfactant selective electrodes it is true to say that in the hands of a competent operator they can provide accurate measurements in an almost routine fashion. Provided they are maintained well, they can have a reasonable lifetime (~few months). The electrodes are used to measure the monomer concentration of surfactant and a reference electrode preferably solid state and not using a salt bridge is required. The electrode is calibrated by injecting a known amount of surfactant into a cell containing the surfactant and reference electrode. The EMF is measured after each titration and plotted against surfactant concentration[5] (see Fig. 1). The following checks are made to test the quality of the electrode: Does the EMF–concentration plot obey Nernstian behaviour below the *cmc*, and in the absence of added salt does the monomer concentration decrease after the *cmc* is reached?

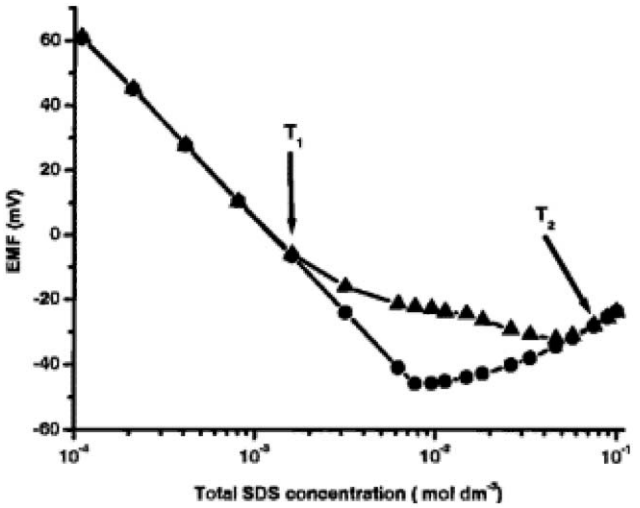

Fig. 1 Graph of the emf of an SDS electrode (reference silver/Br^- electrode) as a function of total SDS concentration with and without 1% (w/v) PVP at 25 °C: (●) pure SDS; (▲) SDS + 1% (w/v) PVP. (Reprinted with permission from ref. 5*b*, Copyright (2000) American Chemical Society.)

In polymer binding studies the EMF of the electrode is first measured when the surfactant is titrated into a cell containing water and then the experiment repeated in the cell containing a constant concentration of polymer. The first titration is a control and calibration experiment. In these studies binding is taking place when the EMF of the electrode in solutions with and without the polymer is different. This is illustrated for the system SDS/polyvinyl pyrrolidone (PVP)[5b] in Fig. 1 and the data clearly show where binding starts and finishes. Historically the surfactant concentrations corresponding to the onset and end of binding were denoted T_1 and T_2 respectively by Jones[6] in his pioneering studies using surface tension. From the electrode data the amount of surfactant bound ($C_1 - m_1$) at each surfactant concentration, C_1 can be evaluated, where m_1 is the measured monomer surfactant concentration. The binding isotherm is then plotted, in line with classical ligand/macromolecule studies as the amount bound *versus* monomer concentration shown in Fig. 2. T_2 is often referred to as the concentration at which the polymer is saturated with bound surfactant and the quantity ($T_2 - m_1$) represents the binding capacity of the polymer.

Once T_2 is reached any further surfactant that is added is used up to form micelles in solution. This is clearly reflected in the electrode measurements when the monomer surfactant concentration, m_1, decreases with increasing C_1. Indeed the dependence of m_1 and C_1 can be informative. For example m_1 always increases with C_1 when binding is exclusive. However, in some instances m_1 reaches a maximum during the binding process. When this occurs it is a signal that free micelles are formed before the binding is completed at T_2. Finally it is worth pointing out that the amount of Na^+ counterions bound to the micelles in the polymer surfactant complex can also be measured using the electrode. This is achieved by measuring the EMF of the electrode relative to a sodium electrode. In favourable circumstances the degree of counterion binding to the bound micelles can also be estimated from conductivity

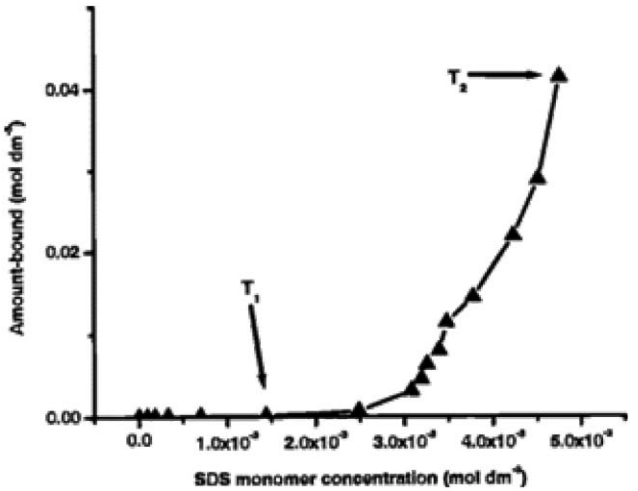

Fig. 2 Binding isotherm at 25 °C showing the amount of polymer-bound SDS plotted as a function of monomer SDS concentration m_1. Binding data were terminated at T_2 where free SDS micelles start to form. (▲) SDS + 1% (w/v) PVP. (Reprinted with permission from ref. 5*b*, Copyright (2000) American Chemical Society.)

measurements.[1] Surfactant electrodes are selective to the chosen surfactant but normally respond to other surfactants as well, in particular those surfactants which belong to the same homologous series. It is now generally accepted that for neutral polymer–sodium dodecyl sulfate systems the sharp break observed at T_1 as shown in Fig. 1 is associated with the formation of bound micelles on the polymer chain. This sharp break was observed in many other different experiments[1,2] and it was also found that T_1, behaved like the *cmc* of the surfactant in that it decreased with added salt and also as the chain length of the surfactant increased. T_1 was also found to be independent of the polymer concentration. These experiments together with the binding isotherm Fig. 2, confirmed the cooperative nature of the surfactant binding process. Further experiments with spectroscopic probes confirmed the existence of a hydrophobic environment at SDS concentration exceeding T_1.[1–4] These probes, typically pyrene and dyes were solubilized with the solution or covalently bonded to the polymer chain. Finally the existence of micelles was directly confirmed by small angle neutron scattering (SANS) measurements,[5b,7] which also demonstrated conclusively that for linear polymers the structure of the polymer–surfactant complex involved the flexible polymer chain wrapped around the bound micellar surface (Fig. 3). It is therefore not surprising that the multitude of techniques that have been used to study micellization in pure surfactants have also been used successfully to study polymer–surfactant mixtures. Indeed even more techniques can be adapted for these latter systems because of the presence of the polymer. These large assemblies also facilitate the use of separation technique such as gel filtration and ultracentrifugation.[1] In general most of the methods to study polymer–surfactant systems involve techniques which either measure the macroscopic properties of the solution or which focus on microscopic moieties. Examples of the former include conductivity, surface tension, viscosity, light scattering and calorimetry. The latter techniques include the electrode which

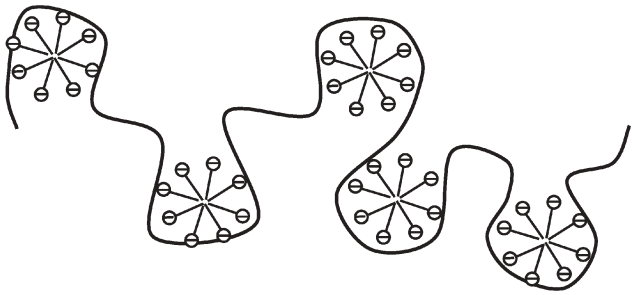

Fig. 3 Typical polymer–micellar surfactant complex.

focuses on the surfactant monomer and spectroscopic probes for absorption, fluorescence and election spin resonance detect surfactant aggregates. At present we cannot over emphasize the contributions made by these techniques not only in the early stages laying the foundation for the development of the subject but also in current research. The use of these techniques to study polymer–surfactant interactions are described in review articles[1–4,22] and also in the examples described in this review, specifically surface tension;[6,8,20,25,33] viscosity;[18,22–24,33] light scattering;[8,20,28] ESR;[30,33,34] fluorescence[25,30,36] and fast reaction techniques.[18,36] With the exception of fast reactions all these techniques measure the equilibrium properties[1–4] of the system and information on the microscopic level is inferred from these data. Very often it is the case that speculation from the use of one technique has been reinforced by speculation from other techniques to build up a conventional wisdom about the mechanisms and overall general structures. However, the only handle on direct structural data and aggregates dimensions can be obtained from SANS. The use of SANS with contrast matching also enables different components of these complexes to be probed.[5b,7] In practice however, the most successful applications of SANS in this field have relied on *a priori* knowledge of the structures inferred from equilibrium data.

Small angle neutron scattering

In the present work, there are excellent references[5b,7,8,16,31,33] describing the application of SANS to study the structure of polymer–surfactant complexes. Briefly, in ordinary Bragg diffraction (Fig. 4) intense elastic coherent maxima are observed when the Bragg condition is satisfied, as described by eqn (4).

$$\lambda = 2d \sin\left(\frac{\theta}{2}\right) \tag{4}$$

where λ is the wavelength, d is a distance, θ is the scattered angle, also known as the Bragg angle, which is related to the value of the scattering vector, given the symbol Q:

$$Q = \mathrm{K_s K_i} = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{5}$$

where Q the scattering vector, also known as the wave vector, describes the relationship between the incident ($\mathrm{K_i}$) and scattered ($\mathrm{K_s}$) beams. Q quantifies length in reciprocal space, possessing the dimensions of $(\text{length})^{-1}$, normally quoted in

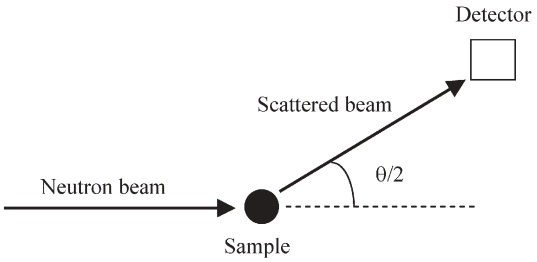

Fig. 4 Schematic set-up of a small angle neutron scattering experiment.

units of nm^{-1} or $Å^{-1}n$ where n is the neutron reflective index of a material, ($n \approx 1$ in neutron scattering). The Bragg condition can be also expressed by the combination of eqn (4) and (5) to yield eqn (6):

$$d = \frac{2\pi}{Q} \tag{6}$$

where Q is the wave vector at the Bragg resonance. The term Small Angle refers to low Q values, $0 < Q < \pi/d$ where individual atoms are not resolved and in the UK SANS measurements were performed on the LOQ (low Q) diffractometer at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. The measurements were performed using the white-beam time-of-flight method with a limited wavelength range at a source frequency of 50 Hz (giving a Q range of 0.02 to 0.15 $Å^{-1}$), which allows the structure of polymers and surfactant micelles with dimensions in the range 2–150 nm to be studied. The data were corrected for background scattering and detector response, and converted to the scattering cross-section (in absolute units of cm^{-1}) using standard procedures. The SANS data were analysed using established models for SDS micelles and also polymer bound micelles. For a solution of globular polydisperse interacting micelles, the coherent scattering cross-section can be written by the so-called ''decoupling approximation'' (assuming that there are no correlations between position, orientation and size in eqn (7):

$$\frac{d\sigma}{d\Omega}(Q) = N_p\left[S(Q)\left|\langle F(Q)\rangle_Q\right|^2 + \langle|F(Q)|^2\rangle_Q - \left|\langle F(Q)\rangle_Q\right|^2\right] \tag{7}$$

Here the averages denoted by <> are averages over particle size and orientation, N_p is the particle number density, $S(Q)$ the structure factor and $F(Q)$ the particle form factor. The micelles are modelled as a ''core + shell'' and hence the form factor is given by eqn (8):

$$F(Q) = V_1(\rho_1 - \rho_2)F_o(QR_1) + V_2(\rho_2 - \rho_s)F_o(QR_2) \tag{8}$$

where $V_i = (4\pi R_i^3)/3$, $F_o(QR) = 3j_1(QR)/(QR)$, ρ_1, ρ_2 and ρ_s are the scattering length densities of the micelle core and shell, and of the solvent, and $j_1(x)$ is the first order spherical Bessel function. For example, for simple surfactant micelles, such as SDS, the model comprizes an inner core made up of the alkyl chains, constrained to space fill a volume limited by a radius R_1, and defined by the fully extended chain length of the surfactant. Remaining alkyl chains, and head groups with the corresponding hydration define the radius of the outer shell, R_2. The inter-particle interactions are included using the rescaled mean spherical approximation, RMSA, calculation for a repulsive (or attractive) Yukawa potential: where the surface potential is defined by the surface charge and the Debye screening length, κ^{-1}. κ is represented in the usual form in eqn (9),

$$\kappa = \left(\frac{8\pi n e^2}{\varepsilon k_B T}\right)^{1/2} \tag{9}$$

and n is taken as the surfactant monomer concentration. The main adjustable model parameters are then the aggregation number, (v), surface charge (z), and polydispersity (σ). For polymer–micellar surfactant complexes where the SANS data indicate predominantly SDS micelles with bound polymer an additional parameter, f_p, which accounts for the polymer in the outer shell of the SDS micelles (as a fraction of the polymer chain), is included.

The model is finally convoluted with the known instrument resolution and compared with the data on an absolute intensity scale on a least squares basis. Acceptable model fits require not only that the shape of the scattering is reproduced, but that the absolute value of the scattering cross-section is reproduced; this is reflected in the value of the scale factor, f, (data/theory), where an acceptable variation is (plus or minus) 10%. The neutron scattering length density, δ, of a molecule of i atoms may be readily calculated using eqn (10):

$$\delta = \sum\nolimits_i b_i \frac{DN_A}{M_w} \tag{10}$$

where D is the bulk density of the scattering body and M_w is the molecular weight, N_A is Avogardro's number, b_i is the neutron scattering length for i atom. The contrast is the difference in values between the parts of the sample of interest, δ_p and the rest of the matrix, δ_m. This value is squared as follows (eqn (11)):

$$(\Delta\delta)^2 = (\delta_p - \delta_m)^2 \tag{11}$$

If $(\Delta\delta)^2$ is zero, then there is no scattering. When this condition is reached, the scattering bodies are said to be at contrast match. Since the scattering from the scattering bodies is essentially a contrast-weighted summation of the SANS from the individual components, the technique of contrast matching can be used to simplify the scattering patterns. For example, hydrogen and deuterium have scattering lengths of opposite sign, that is, they can influence the contrast, and hence there will be different scattering patterns of the SANS. One of the beneficial outcomes stemming from this scattering behaviour in relation to SANS experiments on surfactant aggregates is to substitute the hydrogenated surfactant by its fully deuterated derivative. For example we compared SANS scattering data for aggregates of SDS-h_{25} ($CH_3(CH_2)_{11}SO_4$) by its deuterated analogue SDS-d_{25} ($CD_3(CD_2)_{11}SO_4$), then in these circumstances the aggregates of the deuterated surfactant are to a first approximation transparent in the SANS experiment (a small allowance is required for the head groups). By carrying out systematic experiments of this kind as well as substituting H_2O by D_2O and D_2O–H_2O mixtures as solvent, it

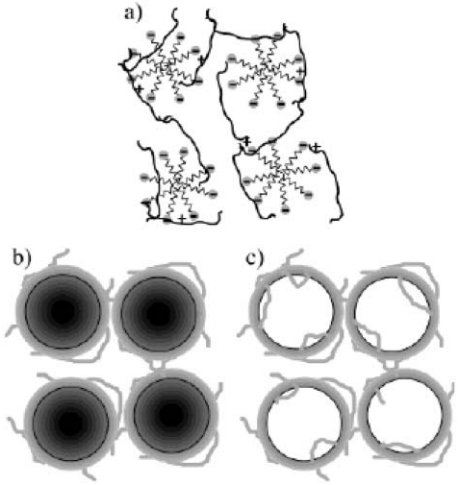

Fig. 5 Schematic representation of surfactant micelles structuring the polymer. (a) The polymer induces micellization of the surfactant, and the surfactant micelles "structure" the polymer. (b) Schematic representation of the scattering from the polymer with hydrogenated surfactant in D_2O; the scattering is dominated by the contributions from the surfactant micelles. (c) Schematic representation of the scattering from the polymer with deuterated surfactant in D_2O; the surfactant is "matched out" and therefore does not scatter. (Reprinted with permission from ref. 16*b*, Copyright (2002) American Chemical Society.)

is possible to study different component of a macromolecular complex *in situ* (Fig. 5).[16b]

Isothermal titration calorimetry

It could be argued that the most successful experimental technique to emerge in the last ten years for studying polymer–surfactant interactions is isothermal titration calorimetry (ITC). The measurement principle of ITC is based on both titration and power compensation techniques. Titration calorimetry is a technique that combines thermochemical and analytical applications and it measures the enthalpy change of a chemically reacting system as a function of the amount of added reactant. In a compensation calorimeter, the effect of the heat to be measured (in this case the change in temperature) is suppressed by means of an electric signal. The advantage of this kind of calorimeter lies in their quasi-isothermal conditions during the measurement, which signifies that heat leaks do not contribute large error sources and therefore precise measurement of the electric compensation energy is possible. The mode of operation of an ITC is isothermal and the principle of construction is based on a differential calorimeter that measures raw heat signal from the electrical power required to maintain a constant temperature difference between the sample and reference cells. It measures the enthalpy per titration ($-\Delta H_i$) as surfactant is titrated into a polymer solution. Thermodynamic functions such as ΔH, ΔS, ΔG and C_p are determined, which are useful for understanding the energetics behind polymer–surfactant interactions. A detailed classification of calorimetric methods can be found in a recent monograph.[9] A typical schematic of a commercial isothermal titration calorimeter (ITC) is shown in Fig. 6a. This power compensation, differential instrument was previously described in detail by Wiseman *et al.*[10] It has a reference cell and a sample cell of approximately 1.35 ml and the cells are both insulated by an adiabatic shield. The titration is carried out by injecting concentrated surfactant solution (in aliquots of 0.1–10 μl) from a 250 μl injection syringe into the sample cell filled with a known concentration of sample polymer solution. The syringe is tailored-made such that the tip acts as a blade-type stirrer to ensure continuous mixing efficiency at 400 rpm. An injection schedule is automatically carried out using interactive software after setting up the number of injections, volume of each injection and time between each injection. The principles and basic thermodynamic convention of ITC were discussed recently by Jelesarov and Bosshard.[11] The data are reproducible to within $\pm 5\%$. The raw heat signals for the

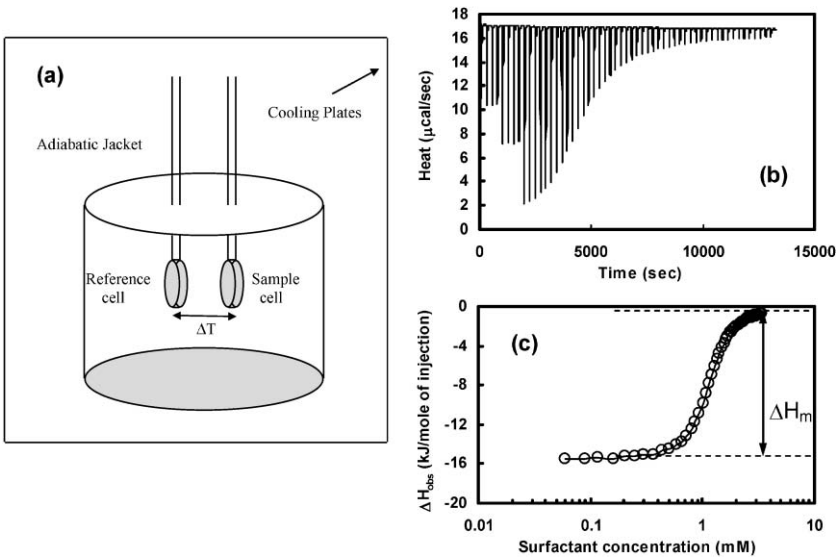

Fig. 6 (a) Schematic of a commercial isothermal titration calorimeter (ITC); (b) raw heat signals for the titration of a non-ionic surfactant into water; (c) integrated heat corresponding to the enthalpy for each titration as shown in (b).

titration of a non-ionic surfactant into water are shown in Fig. 6b, and integration for each titration yields a typical isothermal titration thermogram giving an enthalpy profile shown in Fig. 6c). An obvious exothermic heat produced from the titration where the difference in the enthalpy between the two horizontal parts of the S-shaped curve as marked is equal to ΔH_m, while the *cmc* value was determined from the first-order differential curve of the ITC thermogram. Useful thermodynamic information can be derived from the ITC data.

The ITC technique is versatile, extremely sensitive and is non selective as far as polymers and surfactants are concerned—the only requirement is that an enthalpy change is generated during the binding process. When a surfactant is titrated into a polymer solution some of the processes which give rise to measurable enthalpy changes as shown in Fig. 7 are:

(1) Demicellization—in order to attain a significant concentration range during an experiment the surfactant is titrated in micellar form. Following the initial titrations these surfactant micelles dissociate into monomers.

(2) Dilution effects as a result of titration (can be subtracted by conducting a blank titration run).

(3) Conformational changes in the polymer (usually small).

(4) Binding interaction between surfactant monomer–micelles and polymers.

Although it is not possible to resolve all these different processes, the most significant and measurable $-\Delta H_i$'s come from the binding process (4). The commercial ITC techniques were built to study the binding of ligands to macromolecules in biological systems. In these cases the binding is dominated by specific binding sites and from the enthalpy data it is possible to evaluate a binding isotherm similar to that shown in Fig. 2. In practice the development and interpretation of experimental data for surfactant polymer systems has not reached this stage. On the other hand, because of its extreme sensitivity the ITC technique has made significant progress and contribution in understanding many aspects of polymer–surfactant interactions. In practice the enthalpy profile is recorded for titrations of surfactant into solutions with and without the polymer. As in EMF studies, binding is taking place over the regions where the enthalpies with and without the polymer are different (see Fig. 7). This technique is ideal for monitoring binding processes and because of its sensitivity it can identify binding in systems which many others techniques are unable to detect.

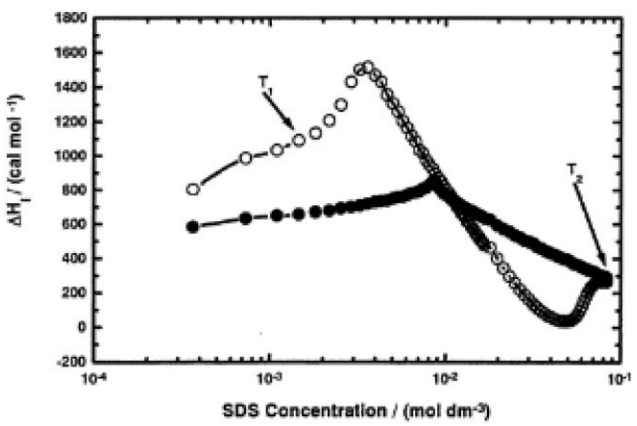

Fig. 7 Graph of ΔH_i in the ITC experiment as a function of total SDS concentration for (●) SDS alone; (○) SDS + 1% (w/v) PVP, measurements carried out at 25 °C. (Reprinted with permission from ref. 5*b*, Copyright (2000) American Chemical Society.)

The application of ITC as a technique to study the thermodynamics of binding between surfactant molecules and polymers has gained popularity in the last 10 years. For example, there were about 22 publications for the period 1996 to 2000, and the number has increased to 103 for the last 5 years (2001 to 2005), pointing to the increasing use of this technique for the study of polymer–surfactant interactions. Illustration of some of the recent results using ITC for the thermodynamic quantification of polymer–surfactant interactions will be discussed in subsequent sections.

Binding below the *cac*

One of the advantages of ITC experiments on neutral polymer–surfactant systems has been the observation that at SDS concentrations below T_1 or the *cac* as measured by other independent techniques the enthalpies with and without the polymer were different (compare Fig. 1 and 7). This implies that a prebound micellar binding process takes place. At first it was difficult to reconcile this observation with the conventional wisdom that the onset of binding occurred when micelles start forming on the polymer. In the PVP–SDS system, further confirmation that binding takes place below the *cac* was provided by neutron reflection and an automated continuous mixing technique which simultaneously measured light scattering and viscosity.[8] The reason why a prebound micellar bonding process is detected by some techniques and not others is associated with their sensitivity. For example the absence of observable binding below the *cac* in Fig. 1 on SDS–PVP is associated with the fact that the emf can be measured to ± 1 mV. This means that a PVP molecule of MW 15,000 can bind up to 3 or 4 monomers of SDS without being detected. This type of binding has now been detected by many different techniques including emf experiments[12*b*] and is regarded as a non cooperative process involving a few surfactant monomers binding to the polymer probably through an ion–dipole attraction.

As a result of the study of a diverse range of polymers with surfactants it has been possible to obtain detailed information on the trends and behaviour of $-\Delta H_i$ values during the binding process. The polymers involved include neutral polymers, as well as high and low charge density polyions. For these systems it has been possible to link trends and subtle changes in $-\Delta H_i$ with specific interactions that occur during binding. Examples of how ITC complemented by other techniques can lead to a better understanding of the binding process and also new insights on binding mechanisms are given below.

Neutral polymer–surfactant systems

The system of polyethylene glycol (PEG or PEO) and SDS has been extensively studied in the past two decades by many different techniques.[1,2] Recently however it has received detailed attention from ITC studies.[12–15] At low molecular

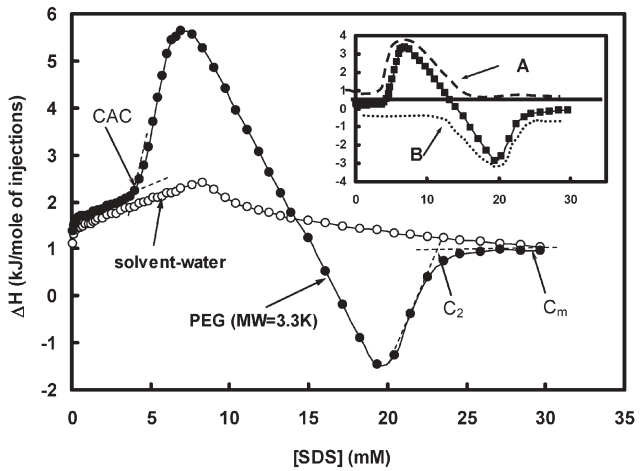

Fig. 8 ITC thermograms of 0.2 M SDS titrating into water (○) and 0.2 M SDS titrating into 0.1 wt% PEG-3.3 K (●) at 298 K. (Reprinted with permission from ref. 12*a*, Copyright (2001) American Chemical Society.)

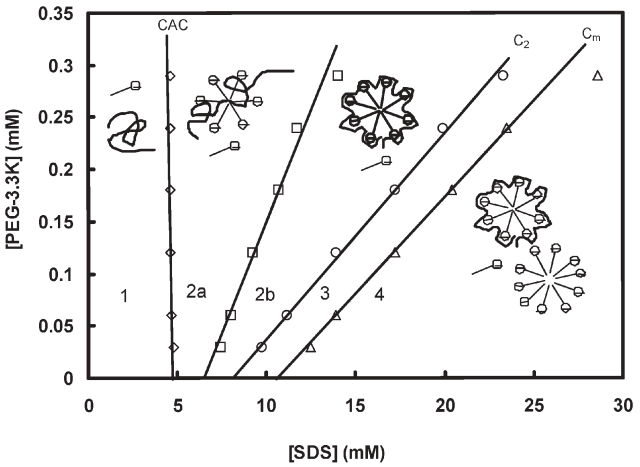

Fig. 9 Phase diagram for the interaction between the SDS and PEG-3.3 K system at 298 K. (Reprinted with permission from ref. 12*a*, Copyright (2001) American Chemical Society.)

weight (MW $<$ 400 Daltons), SDS does not bind to PEG chains. As PEG molecular weight increases from 900 to 1450 Daltons, an endothermic peak, which is attributed to the formation of an SDS–PEG aggregation complex by the polymer induced surfactant micellization process is observed. SDS micelles of lower aggregation number adsorb on the PEG backbones and some PEG segments are solubilized in the hydrophobic core of SDS micelles. When the molecular weight exceeds 3350 Daltons, an endothermic peak followed by an exothermic peak is observed (Fig. 8).[12*a*]

The existence of endothermic and exothermic peaks in the ITC curves suggests that the interaction between the surfactant and polymer is controlled by the balance of two binding mechanisms: the polymer-induced micellization at low SDS concentrations (endothermic process) and the re-hydration of PEG chains to form the ion–dipole aggregation at high SDS concentrations (exothermic process). At low surfactant concentrations, the endothermic process corresponds to the co-operative binding of SDS micelles to dehydrated PEG segments. The dominant interaction at high SDS concentration is the binding between ionic charged surfaces of SDS micelles and PEG segments driven by PEG–SDS ion–dipole aggregation. In this process, PEG chains re-hydrate from the core of SDS micelles to the water phase (an exothermic process shown by dotted line marked "B"), hence is the direct opposite to the ΔH for dehydration of PEG from water phase to SDS hydrophobic core groups (an endothermic process shown by dotted line marked "A") (see inset of Fig. 8). The binding behaviour is controlled by the equilibrium between polymer-induced micellization at low SDS concentrations and ion–dipole association at high SDS concentrations. When binding is complete, free micelles are formed at T_2. Increasing the polymer concentrations causes T_2 to increase, however, the critical aggregation concentration (*cac*) is independent of polymer concentrations. Polymer molecular weights strongly influence T_2 (T_2 and C_2 are used interchangeably in this review article), but only marginally on *cac*. In the absence of emf data, the value of (T_2 − *cac*) can be used to estimate the amount of SDS bound to polymer chains and this value increases with increasing polymer concentrations. From these ITC results a 'phase' diagram (Fig. 9) shows the proposed structures for the PEO–SDS complexes during the binding process. The PEO can either be solubilized in the hydrophobic core of SDS micelles or absorbed on the surface of SDS micelles to form a necklace-like structure.[7] Indeed the necklace structure was also proposed as a result of a SANS study on SDS with 'star' PEO.[16*a*] Star polymers are molecules where several linear polymer arms are attached to a small central core. The star PEGs used in this work were star PEG 130 and star PEG 170 with molecular weights of 130 000 and 170 000 respectively and together with 15 and 19–20 arms. The star molecules were able to bind several micelles and the structure of the resulting complex is shown in Fig. 10.

For uncharged water-soluble polymers, temperature plays an important role in controlling the solubility of polymer in aqueous solution. At temperature exceeding the lower critical

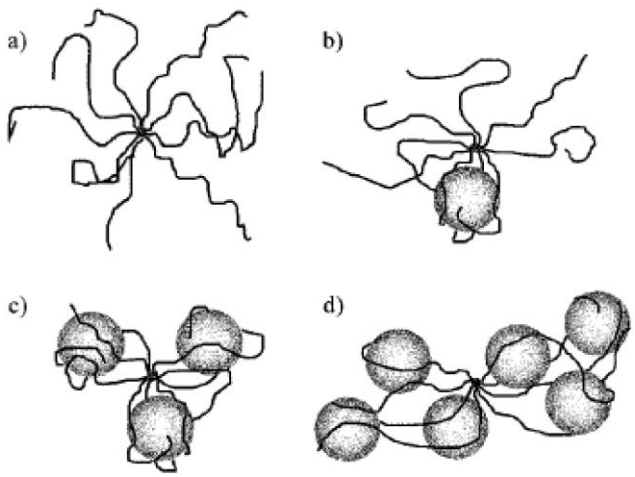

Fig. 10 Schematic of the star polymer as a function of SDS concentration: (a) In the absence of surfactant; (b) at a surfactant concentration just above T_1; (c) at the surfactant's normal *cmc*; (d) on saturation with surfactant. (Reprinted with permission from ref. 16*a*, Copyright (1999) American Chemical Society.)

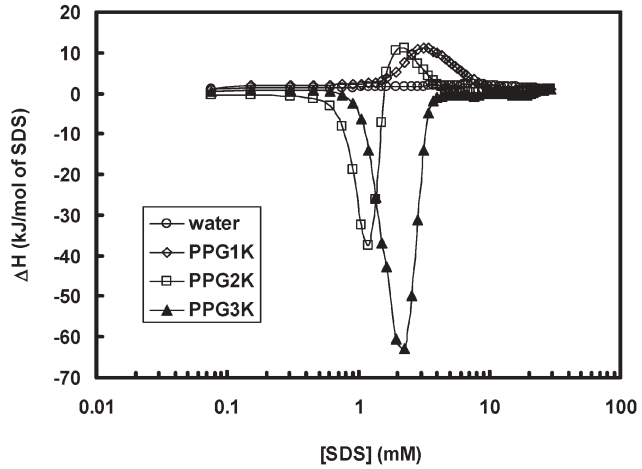

Fig. 11 ITC thermograms for titrating 0.2 M SDS into 0.1 wt% of different molecular weights PPG aqueous solutions at 25 °C and 1 atm. (Reprinted with permission from ref. 15, Copyright (2004) American Chemical Society.)

solution temperature (LCST), the polymer precipitates from solution. The polymer–surfactant binding interactions at temperatures greater than the LCST should be different from those lower than the LCST. PEG is one of the widely used water-soluble polymers with LCST greater than 80 °C. As a result of the methyl group, the LCST of polypropylene glycol (PPG) in aqueous solution is significantly lower than that of PEG. Although polymer–surfactant interactions between SDS and PEG at room temperatures have been extensively studied and the binding mechanisms are better understood, there are only a few reported studies on the interactions between SDS and PPG.[17,18] In previous studies, only PPG with molecular weight of 1,000 Da was reported and these studies were conducted at temperatures lower than the LCST of PPG. Polypropylene glycol (PPG) exhibits a lower critical solution temperature (LCST) ranging from 15 to 42 °C, depending on the molecular weights. The binding mechanisms between sodium dodecyl sulfate (SDS) and different molecular weight PPGs depend on temperatures. At temperature lower than the LCST, the binding interactions are similar to those of SDS and low molecular weight PEGs (MW $<$ 3500 Da), while at temperatures greater than the LCST, the binding interactions are dominated by direct solubilization of PPG chains into mixed micellar cores. At temperatures near the LCST, the binding interactions are controlled by the balance of the PPG solubilization at low SDS concentrations and polymer-induced micellization at high SDS concentrations (Fig. 11).[15]

Polyelectrolyte–surfactant systems

Part of the motivation for the substantial amount of effort invested in the study of the interaction between polyions and oppositely charged surfactants over the last three decades has stemmed from the knowledge in the 1930's that proteins interacted strongly with cationic surfactants. As we shall note later in this review, the interaction between anionic surfactants and skin protein causing skin irritation is an issue in the formulation of personal care product. The interactions between surfactants and polyelectrolytes have been well reviewed[1,2] and the dominating factor which influences binding is the electrostatic charged neutralization of the polyion by oppositely charged surfactants. Recent ITC studies have, however, revealed other details concerning binding.[19]

For example interaction between a mono-dispersed poly (acrylic acid) (PAA) (M_w = 5,670 g mol^{-1}, M_w/M_n = 1.02) with sodium dodecyl sulfate (SDS) was investigated using isothermal titration calorimetry (ITC), ion-selective electrode (ISE), surface tension and dynamic light scattering measurements.[20] Contrary to previous studies, evidence of interaction between SDS and PAA when the degree of neutralization (α) of PAA is lower than 0.2 was observed. Hydrocarbon chains of SDS cooperatively bind to apolar segments of PAA, driven by hydrophobic interaction. The interaction is enthalpically and entropically favored since ΔH is negative and ΔS is positive. The SDS concentration corresponding to the onset of binding (*i.e. cac*) is $\sim$2.4 mM and the saturation concentration (*i.e.* T_2) is $\sim$13.3 mM at $\alpha = 0$. When PAA is neutralized and ionized, the binding is hindered by the enhanced electrostatic repulsion between negatively charged SDS and PAA chains and improved solubility of the polymer. With increasing α to 0.2, *cac* increases to $\sim$6.2 mM, T_2 drops to 8.6 mM, and the interaction is significantly weakened and the amount of bound SDS on PAA is reduced considerably. The values of *cac* and T_2 derived from different techniques are in good agreement. The binding results in the formation of mixed micelles on apolar PAA coils, which then expand and dissociate into single PAA chains. Following T_2 the majority of unneutralized PAA molecules exist in solution as single polymer chains stabilized by bound SDS micelles.

The current understanding on the interaction between fully ionized polyelectrolyte such as polyacrylic acid and cationic surfactant is that the polymer chains induce the formation of bound micelles. The surfactant binds to the polymer at all α, however the mechanism varies. When α is lower than a critical value (α_C), the hydrocarbon chains of dodecyltrimethylammonium bromide (DTAB) cooperatively bind to the apolar segments of PAA driven by hydrophobic interaction at very low DTAB concentration ($C_{DTAB} \leqslant 0.2$ mM). In this binding region, the ITC profile exhibits a significant exothermic peak and the mixture precipitates, which is attributed to the inter-chain complexation *via* hydrogen bonding induced by the binding. The precipitate is soon resolubilized with further addition of surfactant as more DTAB micelles are bound on the polymer backbones with their ionic head groups extending outwards. When $\alpha > \alpha_C$, the hydrophobic binding ceases as the polymer is progressively ionized and DTAB binds to the charged polymer chains driven by electrostatic attraction. The counterions condensed on the charged polymer chains are released *via* the ion exchange process, resulting in an endothermic maximum on the ITC profile. The value of α_C determined from ITC is approximately 0.3, which is reasonably close to the theoretical value derived from the Manning's counterion condensation theory (approximately 0.35). The thermodynamic parameters derived from ITC measurements suggest that the electrostatic binding is an endothermic process driven by entropy. The positive entropy is attributed to the recovery of translational entropy of released counterions by

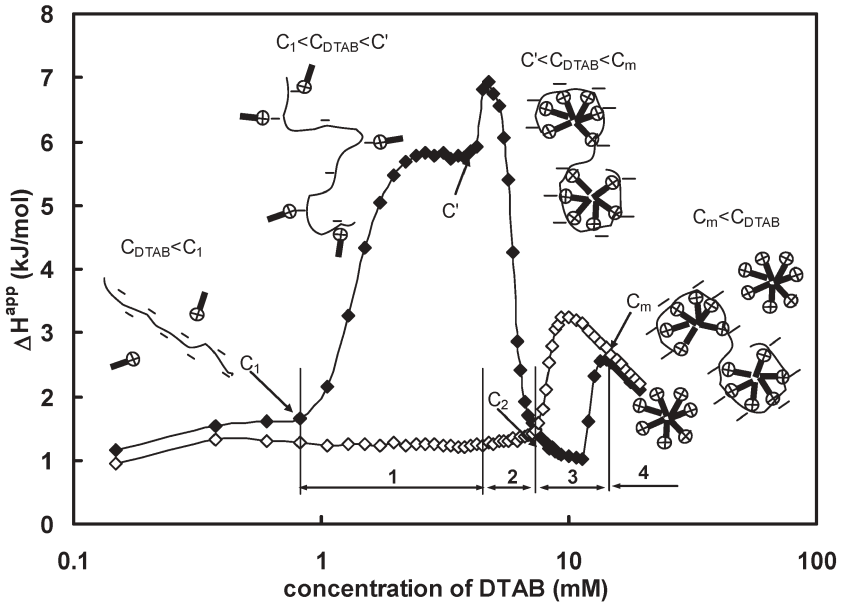

Fig. 12 Classification of binding regimes and schematic binding mechanism of the PAA–DTAB system: (♦) binding isotherm in 0.1 M NaCl solution; (◇) dilution curve in 0.1 M NaCl solution. (Reprinted with permission from ref. 20*a*, Copyright (2002) American Chemical Society.)

the bound surfactant. The ITC curves for titrations performed in different salt conditions show that addition of salt screens the electrostatic repulsion between surfactant head groups and attraction between oppositely charged polymer chains and surfactant molecules. This favors the formation of free micelles, which weakens the binding of surfactant onto the polymers. The ITC thermogram and proposed structures during the binding interaction are shown in Fig. 12.

The interactions between (DTAB) and methacrylic acid–ethyl acrylate copolymers involved the initial electrostatic binding of cationic surfactant molecules to negative charged carboxylate groups on the polymer chains.[21] In this regime, a pronounced endothermic peak is detected in the enthalpy curve and a slight reduction in the particle size is observed. Beyond a critical concentration, the micellization of electrostatic bound surfactant commences and the particle size increases by several orders of magnitude corresponding to the formation of large hydrophobic polymer–surfactant complex that precipitates. Further addition of surfactant, induces the formation of free micelles, and the precipitates either resolubilize (for the polymers with lower charge density) or form gels (for the polymers with higher charge density).

Hydrophobically modified polymer–surfactant systems

Hydrophobically modified water-soluble polymers consist of long hydrophilic chains to which small amounts of hydrophobic substituents are covalently incorporated as pendant chains, blocks or terminal (end capped) groups. The hydrophilic chain can either be a non-ionic polymer or a polyelectrolyte. The degree of modification of the polymer is expressed in mol%. Sometimes these polymers are called polymeric surfactants but it is their interaction with surfactants that has prompted interest. In reality surfactants can control and manipulate the viscous properties of these systems and therefore an understanding of their interactions is desirable, especially with so many potential applications. As these systems have been well reviewed a brief resume of their binding characteristics is given below.[2,22–24]

The types of structures that are claimed to occur at various stages in hydrophobic polymer–SDS systems are illustrated in Fig. 13.

It must be emphasized that this is a simplistic representation and that the evidence is based on a number of complementary experiments, notably steady state shear viscosity. When these polymers are dissolved in water as dilute solutions and their concentration is increased there is strong evidence of both intra **(I)** and intermolecular **(II)** association of the hydrophobic tails. These conclusions are based on both zero and steady shear viscosities which are useful indication for the state of aggregation and shape of macromolecules. It is also inferred from these studies that the intramolecular association is increased when the backbone of the parent polymer is flexible. A rigid backbone can be provided by a high charge density polyelectrolyte. When SDS is added to these systems, a *cac* is reached whereby SDS micelles are hydrophobically attached to the pendant alkyl groups **(III)**. As more SDS is added, the solution becomes viscous as a result of intermolecular association caused by the cross-linking **(IV)** of the alkyl chains *via* the bound micelles. Depending on the polymer and surfactant concentrations, this cross-linking can lead to a three dimensional structure showing high viscosity and gel-like behaviour. At the maximum viscosity, the ratio of surfactant micelles to bound hydrophobic tails is at its lowest optimal value to enable the formation of the largest polymer micellar complex. As binding proceeds, more SDS micelles become available for binding and the ratio of bound micelle to pendant chains increases leading to the breakdown of the network structure. This breakdown and subsequent deaggregation

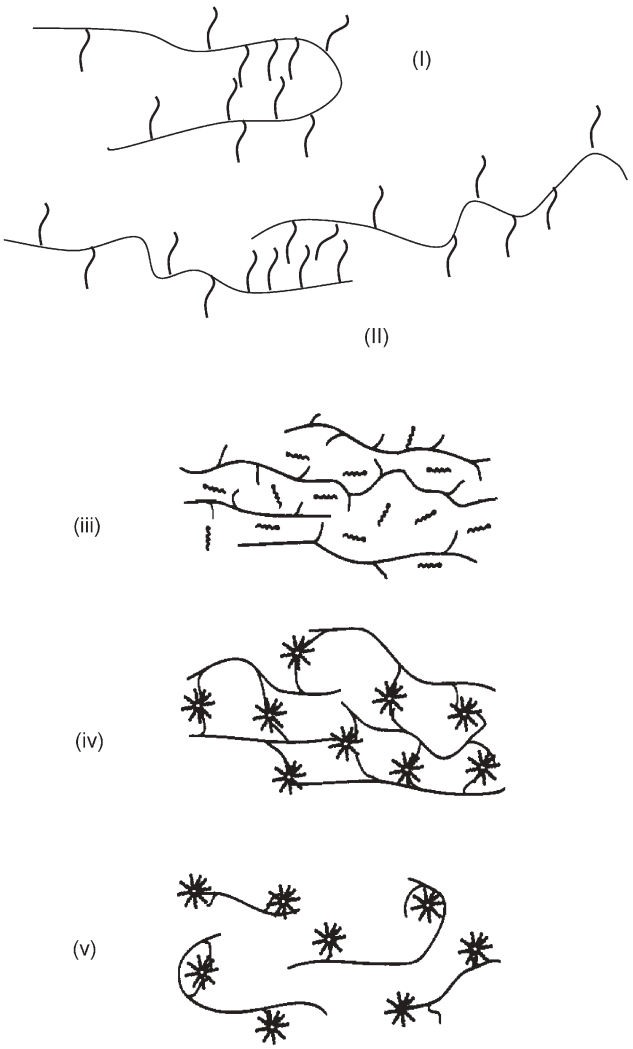

Fig. 13 Types of structures occurring at various stages for hydrophobically modified polymer–SDS systems.

of the polymer leads to a dissociated polymer–micellar surfactant complex **(V)** which is fully saturated with bound micelles and when the overall micelle–bound alkyl chain ratio is highest.

For these hydrophobically modified polymers Somasundaran and his collaborators[25] have recently reported some unusual binding involving the hydrophobically modified anionic polymer poly(maleic acid–octyl vinyl ether) PMAOVE with both the non-ionic surfactant $C_{12}EO_5$ and also the anionic SDS. For both surfactants the onset of binding involves the surfactants being incorporated into the hydrophobic microdomains of the polymer. Two critical concentrations were identified—the onset of binding involving mixed micelles with the octyl chains of the polymer and the saturation of the polymer with bound surfactant micelles (Fig. 14).

Although it is the exception rather than the rule that a non-ionic surfactant interacts with polymer, the interaction involving anionic surfactant and anionic polymer is highly unusual and clearly demonstrates the effectiveness of the hydrophobic effect.

Finally, the interactions between hydrophobic ethoxylated urethane (HEUR) and sodium dodecyl sulfate (SDS) results in the formation of SDS–HEUR complexes *via* the polymer-induced micellization process at the critical aggregation concentration (*cac*).[12b] With increasing SDS concentrations, the SDS aggregation number continues to increase and the SDS–HEUR complexes re-organize to form a necklace-like structure through the ion–dipole association. At the saturation concentration C_2, all the binding interactions between SDS and HEUR are completed. Due to the increase in the hydrophobicity of polymer chains, the *cac* value of SDS–HEUR is lower than that of SDS–PEO. The *cac* is independent of HEUR concentrations, but C_2 shifts to higher SDS concentrations when the polymer concentration is increased. The values of *cac* and T_2 are not affected by polymer molecular masses (for MM $\geqslant$ 17500 g mol^{-1}) and size of end-capped hydrophobes. The electromotive force measurements revealed the existence of non-cooperative prebound micellar binding prior to the cooperative binding at *cac* for the $C_{16}H_{33}$ end-capped alkyl hydrophobic chains (Fig. 15).

Both the *cac* and T_2 obtained from ITC and emf are identical, and the free SDS monomer concentrations during the binding process could be determined from the emf measurements.

Triblock copolymers–surfactant systems

Water soluble poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymers are essentially non-ionic polymers. They are also surface active and behave like non-ionic surfactants in the sense that they form micelles above their *cmc*. SANS structural studies have shown that these micelles form a hydrophobic core consisting of propylene oxide (PO) blocks which are surrounded by an outer shell of hydrated ethylene oxide blocks.[26] The difference in water solubility of the EO and PO blocks renders the micellization process thermally reversible. This results in the formation of pluronic micelles, an extremely temperature dependent process, which causes a reduction in the *cmc* of several orders of magnitude upon a small increase in temperature. This latter behaviour has led to the widespread use of the critical micellar temperature (cmt) as a very useful and practical micellar parameter.[27]

In polymer–surfactant studies, the most widely used pluronics are the BASF code named F127, EO_{97}–PO_{69}–EO_{97} (MW 12,500 g mol^{-1}) and L64, EO_{13}–PO_{30}–EO13 (MW 2900 g mol^{-1}). These pluronics bind strongly to anionic, cationic and non-ionic surfactants.[16,28,29] We will focus initially on their behaviour with SDS because this is the most widely used surfactant. At temperatures below the cmt the pluronics exist predominantly as unassociated nonionic polymers and form what is regarded as normal micellar complexes with SDS. In the binding region, the EMF data show that the L64 and F127 monomer have a high affinity for SDS micelles. In the SANS analysis for L64/SDS over the binding region a parameter which accounts for the extent of copolymer coverage on the SDS micellar surface is estimated from the scattering data.[8b] For L64–SDS this parameter decreases significantly from the early stages of binding to the binding

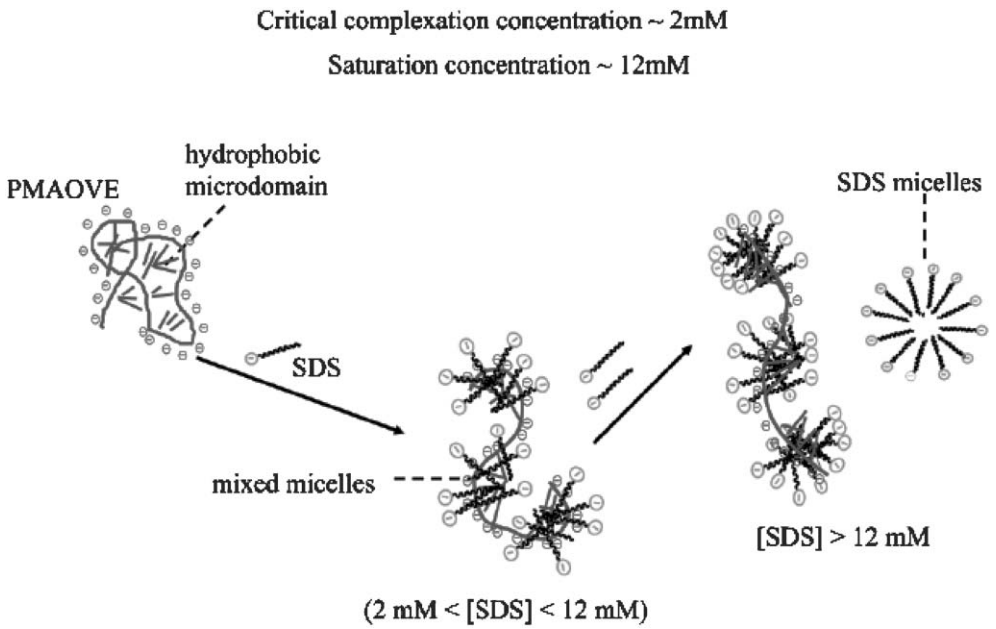

Fig. 14 Binding involving hydrophobically modified anionic polymer poly(maleic acid–octyl vinyl ether) PMAOVE with both the non-ionic surfactant $C_{12}EO_5$ and also the anionic SDS. (Reprinted with permission from ref. 25*a*, Copyright (2003) American Chemical Society.)

limit. At the binding limit (T_2) the complex contains on average two copolymer molecules per micelle. On the basis of the SANS data, it is quite likely that at the initial stage of binding, several L64 copolymer monomer ($\sim$10) are associated with each SDS micelle.

Above the cmt the pluronics exist in micellar form and their interaction with SDS is more dramatic. When SDS is first added to micellar F127 or L64 mixed SDS/pluronic micelles are formed in which the hydrophobic chain of the SDS penetrates the PPO core of the pluronic micelle and with the anionic SO_4^- headgroup at the surface of the PPO core as shown in Fig. 16.

As the SDS content of the mixed micelle increases, the electrostatic repulsion caused by these anionic head groups results in a breakdown of the mixed micelle into smaller mixed aggregates. This gradual deaggregation of L64 in the mixed micelles takes place over the SDS concentration region 1–20 mM SDS for 1% L64. During this process, SDS still binds to the pluronics, which results in the mixed micelles getting richer in SDS. Eventually a stage is reached when the amount

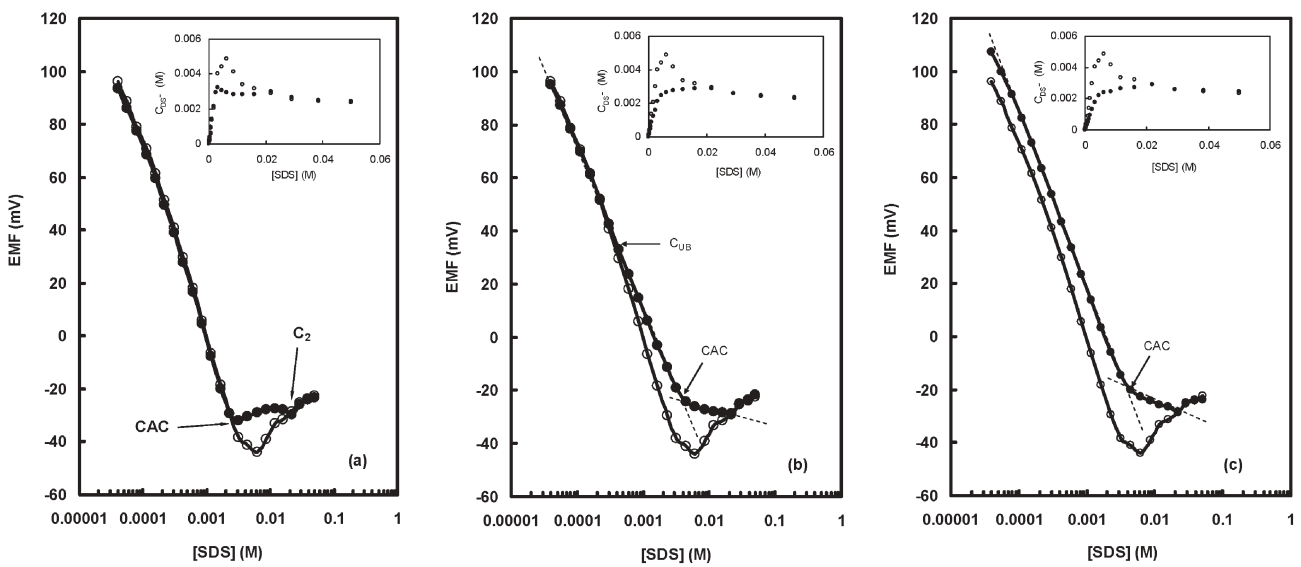

Fig. 15 SDS concentration dependence of emf values on total SDS concentrations at 298 K and 1 atm. Open circles are for SDS in water, and filled circles are for SDS in 0.1 wt% (a) HEUR–$C_1$51K, (b) HEUR–C_{12}51K, and (c) HEUR–C_{16}51K. The insets plot monomeric SDS concentration *versus* total SDS concentration. (Reprinted with permission from ref. 12*b*, Copyright (2004) American Chemical Society.)

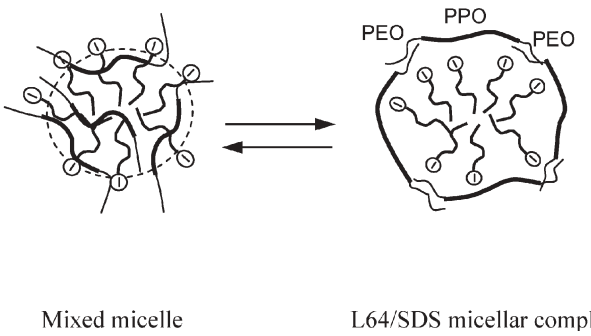

Fig. 16 Schematic of the mixed micelle to L64 bound SDS micelle transition in SDS–L64 mixed system.

of SDS monomers in the mixed micelles increases to the extent that they self aggregate to form SDS micelles and this signals the final stage of the intramolecular rearrangement involving the deaggregation of L64 in the mixed micelle and their transfer to the surface of the SDS micelle as bound polymers. As the binding proceeds, more SDS micelles are formed and the ratio of bound polymer per micelle decreases to a value of 2 at the end of binding. Thus the gradual addition of SDS to micellar L64 causes a transformation in the mixed aggregate structure from a mixed L64–SDS micelle to copolymer bound SDS micelles. The most sensitive method to monitor this transformation is using ITC. Recently a systematic study using SANS of the mixed aggregate structures over the transformation region was carried out for 1% w/v L64 and 1–20 mM SDS in approximately 1 mM intervals and using contrast matching with h-SDS and d-SDS.[8b] This study showed that the transformation is a fairly sharp process and is intramolecular in the sense that there is no obvious experimental evidence for substantial gain or loss of free monomers of L64 nor SDS taking place. Rather, the transformation (Fig. 16) seems to be fairly smooth and occurs at $\sim$6 mM SDS. In contrast, the earlier data involving equilibrium technique implied that over a limited concentration region both mixed pluronic–SDS micelles and polymer bound SDS micelles coexisted in solution.[28,29]

The pluronics F127 and L64 also interact strongly with the non-ionic surfactant $C_{12}EO_6$ both above and below the cmt of the pluronics. In all cases mixed pluronic–$C_{12}EO_6$ micelles are formed and from the *cmc* of the mixed micelles determined using ITC, the mixing of both surfactants is synergistic. SANS studies have further shown that the structure of the mixed micelles involves the C_{12} alkyl group incorporated into the PPO core with the EO_6 chains and the EO blocks of the pluronics making out the outer hydrophilic shell of the mixed micelles.[16]

Dendrimer–surfactant systems

As we have mentioned, progress in polymer synthesis has been developed to the extent that new polymers can be readily synthesized or known polymers synthetically modified. Many of the synthetic procedures are targeted towards the polymers exhibiting functional groups. Such polymers which are water-soluble can interact with surfactants to produce polymer–surfactant complexes. In general, however, most of these polymers tend to possess some degree of non-uniformity, *e.g.* chain length, molecular weight range, *etc*. On the other hand, dendrimers can be regarded as macromolecular but possessing precise molecular weights and structures. Starburst dendrimers are a class of highly branched polymers synthesized from various initiator cores *via* covalently bonded layers generation by generation resulting in macromolecules with well-defined radial branches, very specific molecular masses and uniform size. The polymer terminates in a radially templated surface, which can accommodate a high number of accessible reactive groups, and can be chosen to give specific functionality. The most commonly available dendrimers are the poly(amidoamines), (PAMAM), whose chemical structure for generation G0, G1 and G2 as in Fig. 17.

The dendrimers possess three distinguishing architectural features:

1. The interior core which is the initial monomeric unit that has a layer of building blocks connected to it *via* the core ethylenediamine.

2. The interior layer which consists of repeating units that are covalently bonded to the central core. In theory, these need not be alike.

3. The external layer or periphery which is formed by the addition of new repeat units which possess the surface functionalities.

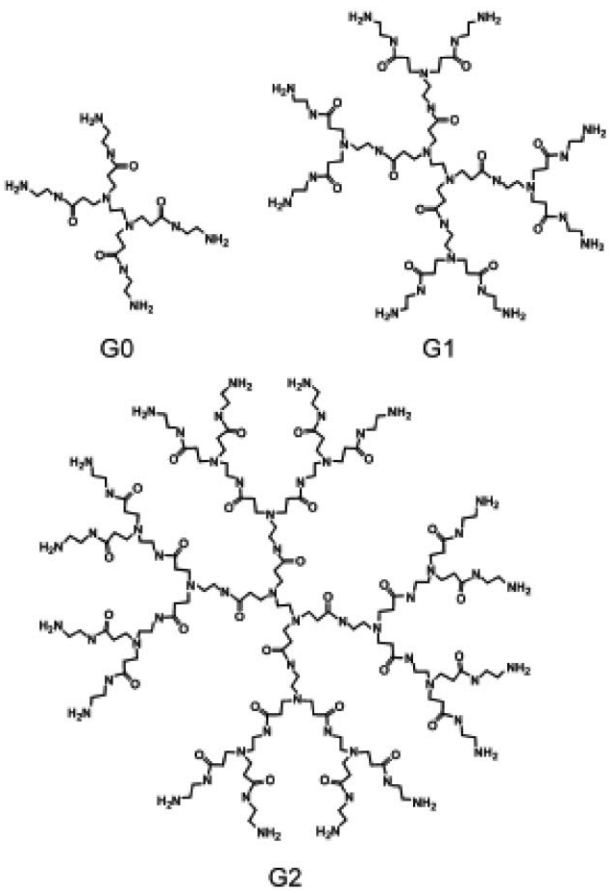

Fig. 17 Chemical structure of the poly(amidoamine) (PAMAM) dendrimers for generations G0, G1, and G2.

The dendrimers are claimed to possess dual functionality in connection with their ability to interact with small molecules and ions. Firstly, the internal surface of the dendrimer which encompasses the core plus the interior surface layers can act as a host for guest molecules. Secondly the periphery groups at the surface can be chosen for specific purposes. Another interesting feature concerning the PAMAM dendrimer is that the primary N atom at the surface and the tertiary amines in the interior can be selectively protonated by pH changes: for example at pH > 10, only a small amount, if any, of the amine groups are protonated, at pH $\sim$ 7–8 the surface periphery groups are protonated and at pH < 2, all the amine groups are protonated.

There have been several studies of the interactions between dendrimers and surfactants. Turro, Tomalia and coworkers[30] have used spectroscopic and ESR probes to study the interactions of cationic surfactants with anionic dendrimers having a carboxyl groups on the surface. The binding is dominated by charge neutralization and some of the structures postulated are shown in Fig. 18. Wyn-Jones *et al.*[31] have studied the neutral PAMAM dendrimers having $-NH_2$, –OH and sugar groups at the surface.

In all cases micellar bound complexes were observed and it was noticeable that both T_2 and the aggregation number of the bound SDS micelles increase as the generation of the dendrimers increases. It was found from a combination of SANS and emf data that on average one dendrimer binds two SDS micelles at the binding limit with a structure illustrated in Fig. 19.

Moderation of polymer surfactant interactions

In the formulation of products involving polymer and surfactant mixtures, it is often necessary to manipulate and optimize the polymer and surfactant interactions.[5b] An inspection of the binding isotherm in Fig. 2 shows clearly that it is the magnitude of the monomer SDS concentration that controls the binding. In other words, binding in the form of bound micelles can only start once the monomer concentration of surfactant has reached a value T_1 (= *cac*). It is also known

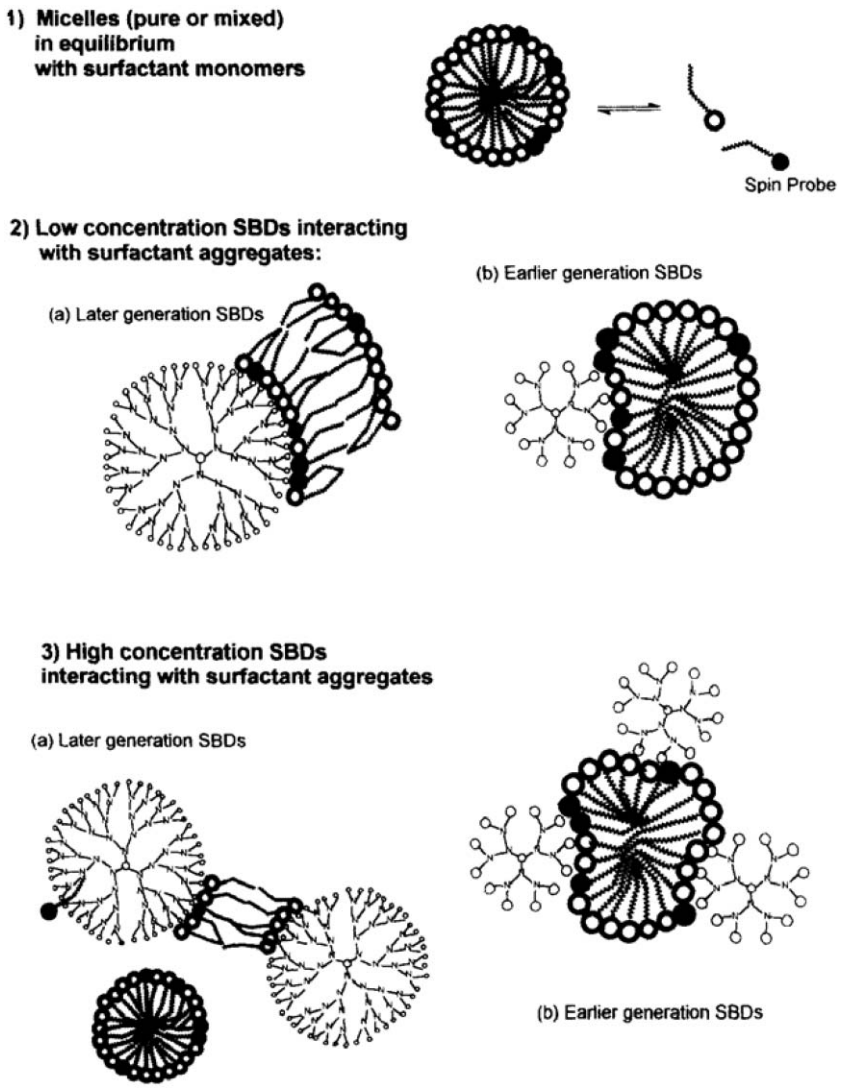

Fig. 18 Schematic diagram of various surfactant complexes with different generations of starburst (SBD) dendrimers. (Reprinted with permission from ref. 30*b*, Copyright (1997) Springer Wien.)

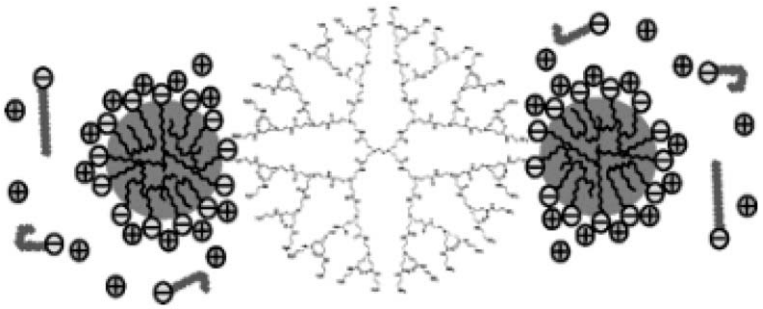

Fig. 19 Microstructure for the binding of SDS to dendrimers. (Reprinted with permission from ref. 31, Copyright (2004) American Chemical Society.)

that the monomer concentration of SDS in the presence of micelles can be reduced by the addition of salt and/or non-ionic surfactant.[1,2] Indeed Dubin[32] demonstrated that the electrostatic interactions between SDS micelles and polycations could be reduced by the addition of a non-ionic surfactant. Wyn-Jones *et al.* also showed[5] that bound SDS micelles can be stripped from a labelled non-ionic polymer by adding the non-ionic surfactant hexaethylene glycolmono-n-dodecyl ether $C_{12}EO_6$. In an attempt to experimentally monitor the desorption of SDS micelles from a non-ionic polymer, the ITC technique was adapted for this purpose. The principle of the method relies on previous observations that the enthalpies per titration, $-\Delta H_i$, with and without polymer are different when binding is taking place and merge when no binding occurs. We first demonstrated that the non-ionic $C_{12}EO_6$ does not bind to PVP as shown by the overlap of the two curves in Fig. 20.

The ITC procedure to monitor desorption of SDS from PVP was as follows:

1. A 'sample' solution of micellar SDS is initially chosen in the presence of 1% w/v PVP (Fig. 2).

2. A control solution of micellar SDS having the same concentration as **1** is also chosen.

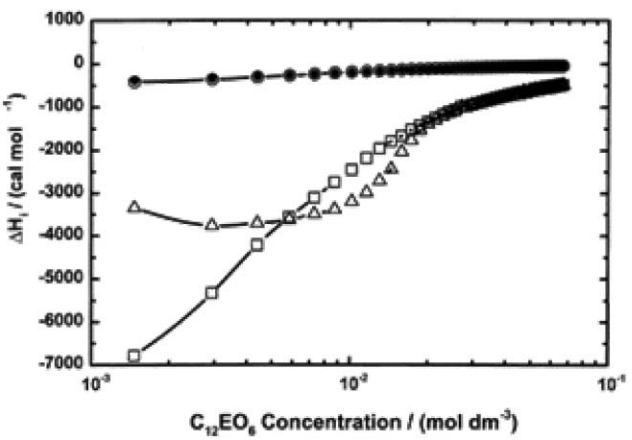

Fig. 20 Graph of ΔH_i in the ITC experiment as a function of total $C_{12}EO_6$ concentration for (●) $C_{12}EO_6$ alone; (○) $C_{12}EO_6$ + 1% (w/v) PVP; (□) $C_{12}EO_6$ + 16 mM SDS; (△) $C_{12}EO_6$ + 16 mM SDS + 1% (w/v), PVP measurements carried out at 25 °C. (Reprinted with permission from ref. 5*b*, Copyright (2000) American Chemical Society.)

In two separate ITC experiments $C_{12}EO_6$ was injected by titration into solutions **1** and **2** under exactly the same conditions. The results are in Fig. 20. The noteworthy feature here is that the corresponding enthalpies per injection are different when similar amounts of $C_{12}EO_6$ were first added. This is not an unexpected result because the aggregated SDS in solution **1** exists as polymer bound micelles whereas solution **2** contains normal free micelles. Eventually as more $C_{12}EO_6$ is added the enthalpy curves first cross over, start merging then become closer together before finally merging at 20 mM $C_{12}EO_6$. When the enthalpies merge, further addition of $C_{12}EO_6$ has exactly the same effect on the SDS whether the polymer is present or not. At this merger point all the SDS has been removed from the polymer and consequently behaves as free SDS in solution. The driving force in this desorption process is the formation of mixed $C_{12}EO_6$–SDS micelles initially both on the polymer chain and in the bulk solution. As the titration proceeds, the $C_{12}EO_6$ content of the bound mixed micelles increases to the extent that the $-EO_6$ head groups sterically hinder the ability of the DS^- anion to bind to the polymer. As a result all the SDS bound to the polymer is desorbed to form mixed micelles in solution.

Using a different approach Griffith *et al.*[33] have demonstrated that the strong binding between SDS and gelatin can be controlled by the addition of the non-ionic surfactant dodecylmalono-bis-*N*-methylglycamide (C_{12}BNMG). Using ESR, viscosity, surface tension and SANS they found that when gelatin is in the presence of both SDS and C_{12}BNMG a critical mole fraction of SDS occurs above which gelatin binds the mixed surfactant micelle. This critical solution mole fraction corresponds to a micellar surface that has no displaceable water. They also found similar results for the system SDS–PVP–ethanol where a competition between ethanol and PVP to occupy the head group of the SDS micelle exists. At low ethanol concentration the PVP displaces the ethanol and the PVP–SDS micellar complex resembles that formed in the absence of ethanol. At higher ethanol content the polymer does not bind to the ethanol rich micellar surface.

Indeed most practical applications of surfactants invariably utilize mixtures containing ionic and non-ionic blends because of their improved performance in comparison to the single component.[1,22] The presence of the non-ionic surfactant also provides an additional bonus in domestic washing because it allows non-ionic polymers to be introduced as additives to soak up any free dye leached from coloured garments. As

described above, any competitive binding from the ionic surfactant in the detergent is avoided because of the presence of the non-ionic surfactant. Ionic surfactants, whose presence is required in many cosmetic formulations to achieve a phase with a smooth creamy texture can often cause skin irritation. This harshness is related to surfactant interaction with proteins and lipids in the upper layers of the skin—the stratum corneum. This has prompted experimental studies of mixing SDS with zein protein and lipid bilayers. The harshness can be considerably reduced and probably avoided by reducing the activity of the ionic surfactant in the personal care product by addition of a non-ionic surfactant.

Mechanisms

One of the major objectives in all the research work carried out on surfactant–polymer systems is to determine the nature of the attractive forces between polymer and surfactant. A brief summary of the factors which have been identified is given below. When a polymer resides on the micellar surface, several factors have been identified which contribute to a lowering of the free energy of micelle. *e.g.*

(1) There can be electrostatic attraction between polar moieties of the surfactant and polymer.

(2) A hydrophobic contribution involving the removal or protection of hydrophobic parts of the polymer from contact with water.

(3) The counterions can play a role.

(4) The polymer chain can reduce head group repulsion in the micelle.

(5) The polymer can protect the hydrophobic interior of the micelle from bulk water.

For any of these non covalent binding mechanisms to be facilitated, the respective 'sites' on the polymer and micelle must be available to make contact. This can only occur provided steric constraints are met and that hydrated sites involved in the binding must lose their bound water.

Clearly the affinity between the polymer and the surfactant micelle depends on the above conditions being favourable. In some cases there are no moieties on certain polymers to achieve favourable interactions. In other cases steric constraints can occur, *e.g.* there is only little affinity between cationic surfactants and polymers and this is attributed to the bulky cationic head group preventing any close contact with the polymer. Recently two very interesting publications have emerged[35] where it was shown that sodium dodecyl sulfate had a high affinity for PVP whereas sodium dodecyl sulfonate showed only a small tendency to bind to the same polymer. The differences were attributed to the different distribution of charges on the head group. This is an interesting example of how small changes in head group structure of the surfactants can lead to substantial binding selectivity. It has already been stated that non-ionic surfactants have little affinity for polymers except under unusual circumstances. The formation of micelles at the *cac* may be associated with two possibilities: (i) It was suggested[16] that a redistribution of monomeric surfactant takes place with preference for the polymer coil regions over the bulk solution. This is not an unreasonable assumption because of the affinity between SDS monomers and the polymer. As a result the local surfactant concentration close to the coil region of the polymer reaches values of the normal *cmc* of the surfactant long before the bulk concentration and micelles are formed. Alternatively small aggregates are formed as a consequence of time dependent concentration gradients in the vicinity of the interface with the polymer. In aggregating systems which exhibit phase behaviour or critical points (*e.g. cac*) these concentration fluctuations can couple with the aggregating system leading to the formation of short lived surfactant aggregates. When these micelles/aggregates bind to the polymer, their free energy is reduced to the extent that they become stable; (ii) In the premicellar binding which has been recently being reported in many systems the bound surfactant monomers on the polymer chain could act as nuclei to promote the formation of bound micelles.

Kinetics associated with polymer bound micelles

The kinetics of micelle formation in surfactants was explained by the seminal theoretical work of Aniansson and Wall[35] These authors considered that micelles A_m are formed from monomers A_1, *via* a sequence of successive bimolecular steps of the kind:

$$A_1 + A_{n-1} \leftrightarrows A_n \; n = 2,3,4\ldots.. \; etc. \qquad (12)$$

In such a micellar system the monomers and micelles are present in measurable quantities whereas the concentrations of the intermediate species are negligibly small. The presence of these intermediate species are however required in the mechanism. It was known from experimental studies that the kinetics of micellar solutions were amenable for studies using chemical relaxation techniques. Aniansson and Wall showed that the kinetics of eqn (12) is characterized by two well-defined relaxation times, a short time which is associated with the formation–dissolution of the micelles and a fast time associated with the monomer–micelle exchange process. These fast and slow relaxation times were observed experimentally and their dependence on surfactant concentration were also successfully predicted. These results confirmed that the above mechanism describes the formation of micelles in pure surfactants. Fast and slow relaxation times have also been observed in polymer bound SDS micelles in the PVP–SDS system. The chemical relaxation techniques[36] used were the pressure jump and ultrasonic relaxation techniques. These measured relaxation times are of the same order of magnitude as those found for pure micellar SDS respectively, *i.e.* $\sim 10^{-4}$s and $\sim 10^{-8}$s.[36] The observation of these two relaxation times shows that the mechanism depicted by eqn (12) also describes the formation of polymer bound micelles. The slow relaxation time of the bound micelle which is a measure of the lifetime of the micelle on the polymer is slightly faster and has lower activation energy compared to the free micelle at comparable concentrations. This suggests that the polymer plays an important role not only in determining the stability of the bound micelles but also the intermediate species between monomers and micelles in the above schemes. In the kinetic analysis of the fast relaxation time, measured by ultrasonic

methods,[36] the association of a surfactant monomer to a bound micelle is an almost diffusion controlled step.

Concluding remarks

We have reviewed recent developments on studies of polymer–surfactant interactions with particular focus on charged surfactants with various types of polymeric systems. By combining the experimental findings from various physical characterization techniques, new information on the binding of surfactant molecules to polymeric chains were obtained. We have focused particularly on three specific techniques, namely surfactant selective electrodes, titration calorimetry and neutron scattering because each respective method provides specific information on the binding isotherm, thermodynamics of binding and microstructure that allow us to understand the specific nature of binding between surfactant molecules and polymers. It is clear from the discussions that many other equilibrium techniques have made notable contributions to the developments in this field. Finally studies using fast reaction techniques have shown that the sequential bimolecular mechanism describing the formation of micelles from monomers also applies to polymer bound micelles.

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References

1 *Interactions of Surfactants with Polymer and Proteins*, ed., E. D. Goddard and K. P. Ananthapadmanaban, CRC Press, Boca Raton, FL, 1993.
2 *Polymer-Surfactant Systems, Surfactant Science Series*, ed., J. C. T. Kwak, Marcel Dekker, New York, 1998, vol. 77.
3 P. Somasundran and S. Chakraborty, *J. Cosmet. Sci.*, 2004, **55**, S1.
4 P. C. Griffiths and A. Y. F. Cheung, *Mater. Sci. Technol.*, 2002, **18**, 591.
5 (*a*) R. Xu and D. M. Bloor, *Langmuir*, 2000, **16**, 9556; (*b*) Y. Li, D. M. Bloor, J. Penfold, J. F. Holzwarth and E. Wyn-Jones, *Langmuir*, 2000, **16**, 8677.
6 M. N. Jones, *J. Colloid Interface Sci.*, 1967, **23**, 36.
7 (*a*) B. Cabane and R. Duplessix, *J. Phys. (Paris)*, 1982, **43**, 1529; (*b*) B. Cabane and R. Duplessix, *J. Physique*, 1987, **48**, 651.
8 (*a*) S. Couderc-Azouani, J. Sidhu, T. Thurn, R. Xu, D. M. Bloor, J. Penfold, J. F. Holzwarth and E. Wyn-Jones, *Langmuir*, 2005, **22**, 10197; (*b*) J. Sidhu, S. Couderc-Azouani, J. Penfold, J. F. Holzwarth and E. Wyn-Jones, *Langmuir* (Submitted).
9 *Calorimetry and Thermal Analysis of Polymers*, ed., V.B.F. Mathot, Hanser Publishers, New York, 1994.
10 T. Wiseman, S. Williston, J. F. Brandts and L. N. Lin, *Anal. Biochem.*, 1989, **179**, 131.
11 I. Jelesarov and H. R. Bosshard, *J. Mol. Recognit.*, 1999, **12**, 3.
12 (*a*) S. Dai and K. C. Tam, *J. Phys. Chem. B*, 2001, **105**, 10759; (*b*) S. Dai, K. C. Tam, E. Wyn-Jones and R. D. Jenkins, *J. Phys. Chem. B*, 2004, **108**, 4979.
13 L. Bernazzani and S. Borsacchi, *J. Phys. Chem. B*, 2004, **18**, 8960.
14 R. C. daSilva and W. Loh, *Thermochim. Acta*, 2004, **417**, 295.
15 S. Dai and K. C. Tam, *Langmuir*, 2004, **20**, 2177.
16 (*a*) R. D. Wesley, T. Cosgrove and L. Thompson, *Langmuir*, 1999, **15**, 8376; (*b*) R. D. Wesley, T. Cosgrove, L. Thompson, S. P. Armes and F. L. Baines, *Langmuir*, 2002, **18**, 5704.
17 (*a*) G. Olofsson and G. Wang, *Pure Appl. Chem.*, 1994, **66**, 527; (*b*) G. Wang and G. Olofsson, *J. Phys. Chem.*, 1995, **99**, 5588.
18 D. M. Bloor, W. M. Z. Wan Yunus, W. A. Wanbadhi, Y. Li, J. F. Holzwarth and E. Wyn-Jones, *Langmuir*, 1995, **9**, 3395.
19 J. Fundin, P. Hansson, W. Brown and I. Lidegran, *Macromolecules*, 1997, **30**, 1118.
20 (*a*) C. Wang and K. C. Tam, *Langmuir*, 2002, **18**, 6484; (*b*) C. Wang and K. C. Tam, *J. Phys. Chem. B*, 2005, **109**, 5156.
21 C. Wang, K. C. Tam, R. D. Jenkins and C. B. Tan, *J. Phys. Chem. B*, 2003, **107**, 4667.
22 E. D. Goddard, *J. Am. Oil Chem. Soc.*, 1994, **71**, 1.
23 (*a*) P. Hansson and B. Lindman, *Curr. Opin. Colloid Interface Sci.*, 1996, **1**, 604; (*b*) I. Iliopoulos, *Curr. Opin. Colloid Interface Sci.*, 1998, **3**, 493.
24 M. Tsianou and P. Alexandridis, in *Mixed Surfactant Systems*, Surfactant Science Series 112, ed. M. Abe and J. F. Scamehorn, 2nd edn, 2005, p. 657.
25 (*a*) P. Deo, S. Jockusch, S. Jockusch, M. F. Ottaviani, A. Moscatelli, N. J. Turro and P. Somasundaran, *Langmuir*, 2003, **19**, 10747; (*b*) P. Deo and P. Somasundaran, *Langmuir*, 2005, **21**, 3950.
26 I. Goldmints, G. E. Yu, C. Booth, K. A. Smith and T. A. Hatton, *Langmuir*, 1999, **15**, 1651.
27 P. Alexandridis, J. F. Holzwarth and T. A. Hatton, *Macromolecules*, 1994, **27**, 2414.
28 (*a*) E. H. Hecht, K. Mortensen, M. Gradzielski and H. J. Hoffmann, *J. Phys. Chem.*, 1995, **99**, 4866; (*b*) E. H. Hecht and H. J. Hoffmann, *Colloids Surf., A*, 1995, **96**, 1.
29 R. C. daSilva, G. Olofsson, K. Schillen and W. Loh, *J. Phys. Chem. B*, 2002, **106**, 1239.
30 (*a*) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Callos, S. Martin, J. Roeck, J. Ryder and P. Smith, *Polym. J. (Tokyo, Jpn.)*, 1985, **17**, 117; (*b*) M. F. Ottaviani, R. Daddi, M. Brustolon, N. J. Turro and D. A. Tomalia, *Appl. Magn. Reson.*, 1997, **13**, 347; (*c*) M. F. Ottaviani, P. Andechaga, N. J. Turro and D. A. Tomalia, *J. Phys. Chem. B*, 1997, **101**, 6057.
31 J. Sidhu, D. M. Bloor, S. Courdec-Azouani, J. Penfold, J. F. Holzwarth and E. Wyn-Jones, *Langmuir*, 2004, **20**, 9320.
32 H. Zhang, Y. Li, P. L. Dubin and T. Kato, *J. Colloid Interface Sci.*, 1996, **183**, 546 and references quoted therein.
33 (*a*) P. C. Griffith and A. Y. F. Cheung, *Langmuir*, 2004, **20**, 7313; (*b*) P. C. Griffiths, N. Hirst, A. Paul, S. M. King, R. K. Heenan and R. Farley, *Langmuir*, 2004, **20**, 6904.
34 (*a*) P. Yao and J. X. Xiao, *Colloids Surf., A*, 2004, **244**, 39; (*b*) A. M. Tedeschi, E. Busi, L. Paduamo, R. Basori and G. D'Ernico, *Phys. Chem. Chem. Phys.*, 2003, **5**, 5077.
35 E. A. G. Aniansson and S. N. Wall, *J. Phys. Chem.*, 1974, **78**, 10421975, **79**, 857.
36 (*a*) D. M. Bloor and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 657; (*b*) W. A. Wanbadhi, W. M. Z. Wan Yunus, D. M. Bloor, D. G. Hall and E. Wyn-Jones, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2737.