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SHORT COMMUNICATION

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Decreased surfactant activity coefficients in polymer-surfactant mixtures

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Abstract The SDS unimer concentration in a series of mixed anionic/non-ionic surfactant solutions comprising sodium dodecylsulphate (SDS) and sugar-based dodecyl bis-*N*-methyl gluconamides (C_{12}BNMG) have been studied using an anionic surfactant selective electrode, both in the presence and absence of the polyampholyte gelatin. The activity of the SDS has been calculated at the critical micelle concentration (CMC) in the gelatin-free studies and at CMC(1) in the gelatin studies. From the known solution composition, the activity coefficients can be calculated; these show deviations from unity around a solution mole fraction (α_{SDS}) of 0.95 SDS in both cases. The deviation is significantly greater in the presence of gelatin, to an extent that the SDS activity versus α_{SDS} curve exhibits a maximum and a minimum in the region $\alpha_{SDS}=0.8$–1.0, consistent with the possibility of coexisting micelle types, in agreement with our earlier NMR study (Griffiths et al. (1998) J Chem Soc Chem Comm 1:53).

Keywords Surfactant activity · Micelles · Polymers · Adsorption · Surfactant selective electrodes

Introduction

Many technological applications utilise aqueous polymer solutions, often in conjunction with surfactants (see for example [1, 2, 3, 4, 5, 6, 7, 8]). The polymer serves as a rheology modifier and/or stabilising agent, whereas the surfactant can function as a wetting, dispersing or surface tension control agent. Understanding the behaviour of such mixtures is therefore crucial to their optimum performance, and many techniques are currently employed to this end; none however provide a complete picture [9]. One of the most common approaches is to interpret changes in the surface tension in terms of the bulk solution behaviour.

A typical surface tension study [10] would involve measuring the surface tension in a series of surfactant solutions encompassing a wide surfactant concentration range in which the polymer concentration is held constant, and comparing the measurements with those in the absence of polymer over the same concentration range. Simple surfactant solutions will show a decreasing surface tension with increasing surfactant concentration until a pronounced discontinuity is observed, indicating the critical micelle concentration (CMC). Above the CMC, a roughly constant limiting surface tension is observed. The situation is far more complex when a polymer is present. In this case, the surfactant is initially more efficient at reducing surface tension than when the polymer is absent. At some critical concentration, a discontinuity is observed, designated CMC(1), which is similar to the CMC in the simple surfactant case. However, relative to the CMC, CMC(1) typically occurs at a significantly lower surfactant concentration and a higher value of surface tension. CMC(1) corresponds to the formation of surfactant aggregates adsorbed to the polymer. Unlike the simple surfactant case, a second discontinuity in the surface tension versus surfactant concentration curve is also observed. This occurs at a higher concentration than the CMC, and is denoted CMC(2). Above CMC(2), a roughly constant limiting surface tension is observed. The latter discontinuity corresponds to the formation of free micelles in solution, and the unimeric surfactant concentration is comparable to its polymer-free CMC value [11]. Most polymer/surfactant studies use the anionic surfactant sodium dodecylsulphate, SDS, in conjunction with non-ionic, ionic and polyampholytic polymers, both natural and synthetic in origin [12, 13, 14, 15, 16, 17].

Often, however, surface tension measurements do not yield a reliable picture of the interface or the bulk solution behaviour. In a series of elegant experiments, Penfold et al. [18, 19, 20, 21] have used neutron reflection to probe the structure and composition of polymer/surfactant mixtures at interfaces, and have correlated this interfacial structure to the surface tension. Quite different behaviours are observed, depending on the nature of the polymer/surfactant interaction. For non-ionic polymers such as poly(ethylene oxide) (PEO) and poly(vinylpyrollidone) (PVP) interacting with SDS [22, 23], only the weak hydrophobic effect is present. In this case the surface tension behaviour is due to a competitive interaction for the surface between the surfactant and polymer, as well as some interaction between the polymer and surfactant at the interface. The polymer enhances the adsorption of the surfactant to the interface at low surfactant concentrations, but suppresses it at higher surfactant concentrations due to the preferential formation of bulk polymer/surfactant complexes. For gelatin/SDS [24] there is a stronger interaction between the polymer and surfactant, and whilst the surface tension behaviour is not dissimilar to the PEO/SDS and PVP/SDS cases, there is a substantial increase in the thickness of the interface between CMC(1) and CMC(2) due to the adsorption of polymer/surfactant complexes. For charged polymer/SDS mixtures [12, 20, 21, 25, 26, 27], the surface tension data initially decreases as in the classical experiment (PEO/SDS data), but subsequently increases at a well-defined surfactant concentration between the classical CMC(1) and CMC(2) discontinuities. For the poly(dimethyldiallylammonium chloride) polydmdaac/SDS [20, 21] and lysozyme/SDS systems [28], the polymer promotes surfactant adsorption at the interface in the form of polymer/surfactant complexes, which leads to the resultant decrease in surface tension.

Recently, Holzwarth and Wyn-Jones et al. [29, 30] have reported the interaction between SDS and ethoxylated poly(ethylene imine) polymers using small-angle neutron scattering, isothermal titration and surfactant specific electrodes. The SDS and polymer interact strongly, and the electrode response is used to quantify their binding isotherms; the electrode response is proportional to the unimer concentration (in other words the activity of SDS in solution). Therefore, the difference between the total surfactant and unimer concentration represents the amount of bound surfactant. At surfactant concentrations comparable to the onset of binding, their data suggest the absence of "proper micellar aggregates". All of these studies, taken together, illustrate the variety of behaviours exhibited by different polymer/surfactant systems at surfactant concentrations close to and just above that required for an interaction to occur.

Previously, we reported [31] critical micelle concentrations derived from surface tension studies for a range of binary surfactant mixtures in the absence and presence of gelatin, based on SDS and a series of sugar-based *n*-alkyl bis-*N*-methyl gluconamides (C_nBNMG, where $n = 10$, 12 and 14). In the absence of gelatin, the CMCs of the mixed surfactants show monotonic behaviour as a function of solution mole fraction, with the magnitudes of the CMCs indicating a synergistic interaction between SDS and C_nBNMG for $n = 10$ and 12, as well as for $n = 14$ for SDS-rich solutions (CMCs lower than the ideal [32] prediction). For non-ionic rich compositions with $n = 14$, antagonistic interactions are observed. Indeed, the nonionic unimer concentration appears to exceed pure nonionic CMC, implying a significant reduction in the surfactant activity coefficient.

In the presence of gelatin, the CMCs of the mixed surfactants exhibit a peak as a function of solution mole fraction for all three non-ionic surfactant tail lengths (*n*); the magnitude and location of the peak depends on *n*. Here, we report studies attempting to elucidate the basis of this peak in the CMC behaviour, using the SDS/C_{12}BNMG system and utilising a dodecyl anion selective electrode to probe the surfactant activity.

Experimental

Materials

The gelatin used here is a deionised, polydispersed, alkali-processed bone gelatin (Kodak Ltd) which has had its pH raised from its isoelectric point of 5.0 to pH = 5.8 by addition of NaOH during manufacture. The precise ionic strength of the gelatin is unknown, but is thought to be approximately 1–2 mM for a 5 wt% solution. SDS (98% purity, Aldrich Chemical Co. Ltd.) was purified by no fewer than four recrystallisations from absolute alcohol until the surface tension showed no "dip" around the CMC. The non-ionic surfactant C_{12}BNMG (U.S. patent 5,298,191, Kodak Limited) was extensively purified by reverse-phase HPLC prior to use, as described previously [31].

Equipment

A "High Sense" surfactant electrode (Methrohm Ltd.) was used here, which consists of a PVC membrane developed and optimised for the titrimetric determination of ionic surfactants. The electrode was used in conjunction with a silver/silver chloride reference electrode. All measurements were made at 20 °C. The response of the electrode to changes in SDS concentration in gelatin-free solutions is shown in Fig. 1 and was found to be linear over four decades of concentration, with a gradient (−61.3 mV per decade) in reasonably good agreement with the Nernstian prediction, (−58.1 mV per decade). Above the CMC, the electrode response increases slightly concomitant with the decrease in SDS unimer concentration. Further, the electrode showed a Nernstian response in the presence of gelatin under conditions where no interaction occurs (in other words pre-CMC(1)) and with the non-interacting octyl sulphate $CH_3(CH_2)_7OSO_3Na$ [11, 33, 34]. These linear responses have been used to validate and calibrate the performance of the electrode, and thereby determine the SDS unimer concentration in the SDS/C_{12}BNMG mixtures with and without gelatin. No phase separation – an obvious cause of reduced surfactant activity – was observed in any of these systems.

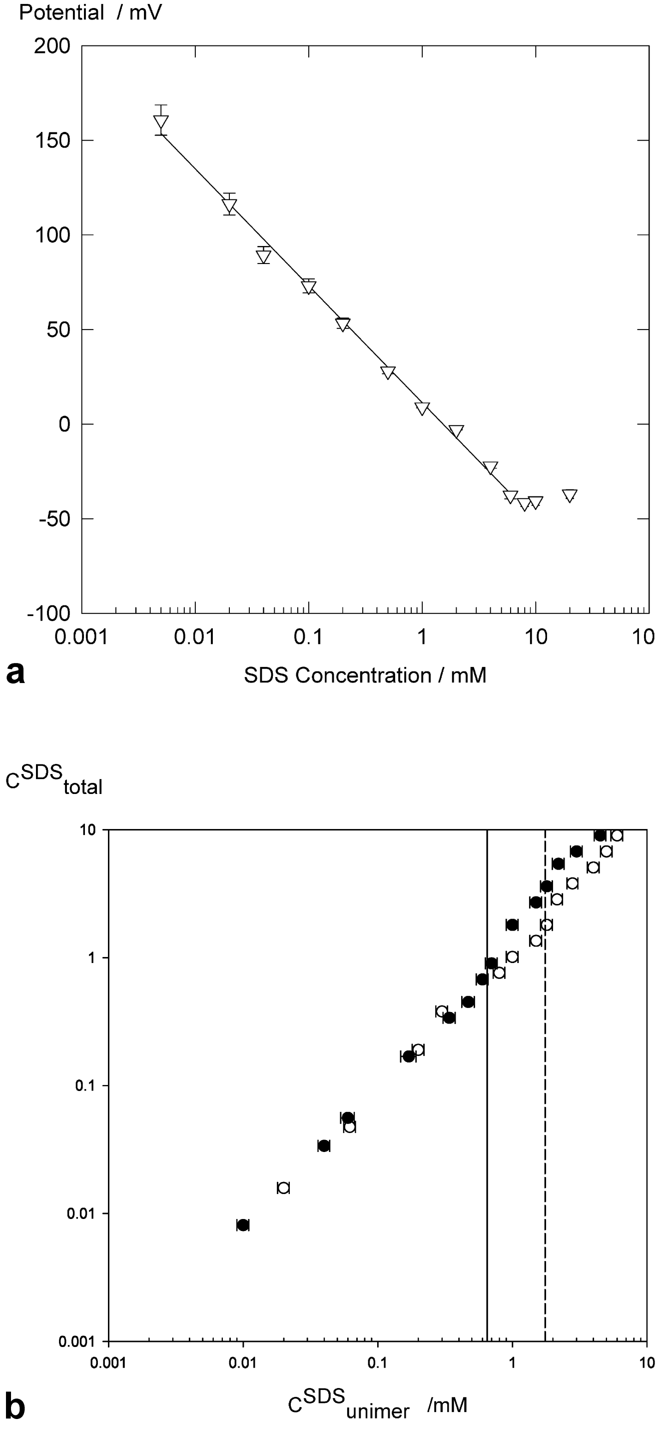

Fig. 1 a Response of the SDS selective electrode to changes in SDS concentration. **b** SDS unimer concentration as a function of total SDS concentration for SDS/C_{12}BNMG mixtures, when $\alpha_{SDS} = 0.9$: surfactants only (unfilled circles) and surfactants plus 0.25 wt% gelatin (filled circles). The CMC(1) (solid line) and CMC (broken line) for this binary surfactant combination is shown

Results and discussion

A parallel series of SDS/C_{12}BNMG solutions were prepared, one without gelatin, and the second with $C_{gelatin} = 0.25$ wt% that spanned the surface tension derived critical micelle concentration. The electrode response was measured in each solution and the corresponding SDS unimer concentration was calculated from the Nernstian EMF versus surfactant concentration calibration plot [31]. Accordingly, an effective SDS unimer concentration C_{unimer}^{SDS}, which corresponds to the activity of SDS in solution, is obtained as a function of the total surfactant concentration and (for instance) the total SDS concentration; the latter is related to the former by the mole ratio of the two surfactants. From the critical micelle concentration versus solution mole fraction plot [31], it is then possible to measure directly, or interpolate, the SDS unimer concentration immediately prior to the CMC, $C_{unimer}^{SDS(CMC)}$. Therefore $C_{unimer}^{SDS(CMC)}$ is the solution activity of the SDS at the CMC. The activity coefficient of SDS at the CMC is then defined as $f_{SDS} = \frac{C_{unimer}^{SDS(CMC)}}{C_{total}^{SDS(CMC)}}$ where $C_{total}^{SDS(CMC)}$ is the total amount of SDS in the system at the CMC. If there is no SDS unimer adsorption to the polymer [35] and $f_{SDS} = 1.0$, $C_{unimer}^{SDS(CMC)} = C_{total}^{SDS(CMC)}$.

The behaviour of $C_{total}^{SDS(CMC)}$, $C_{unimer}^{SDS(CMC)}$ and f_{SDS} for the gelatin-free case is plotted in Fig. 2 as a function of the solution mole fraction, α_{SDS}. Remember that for these relatively few points, each one corresponds to the intersection of the appropriate C_{unimer}^{SDS} versus C_{total}^{SDS} and CMC (or CMC(1)) versus composition plots, as shown in the insert to the figure. Each of these values are therefore extracted from a much wider concentration study [31]. Clearly, the values $C_{unimer}^{SDS(CMC)}$ and $C_{total}^{SDS(CMC)}$ are essentially the same over the range $\alpha_{SDS} = 0$–0.8 and at $\alpha_{SDS} = 1.0$. However, at solution mole fractions in the vicinity of $\alpha_{SDS} \approx 0.95$, the SDS activity ($C_{unimer}^{SDS(CMC)}$) is significantly less than $C_{total}^{SDS(CMC)}$; this mole fraction corresponds to approximately 2–4 C_{12}BNMG molecules per micelle ($N_{agg} \approx 60 \pm 5$). Therefore, there is a marked decrease in the SDS activity coefficient (f_{SDS}) from unity in the region around $\alpha_{SDS} = 0.95$, which means that there is a minimum in f_{SDS} in this region. This signifies that

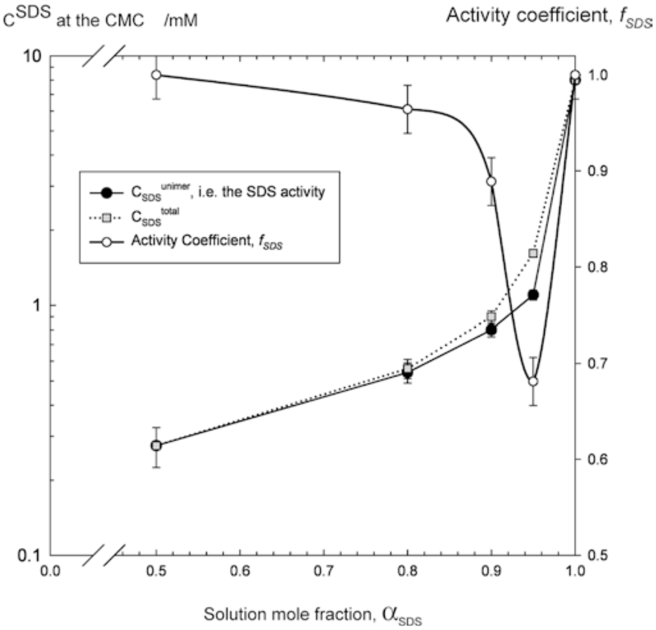

Fig. 2 SDS unimer concentration, SDS activity coefficient f_{SDS} and the derived SDS activity behaviour at CMC(1), as a function of solution mole fraction α_{SDS} in binary SDS and C_{12}BNMG mixtures

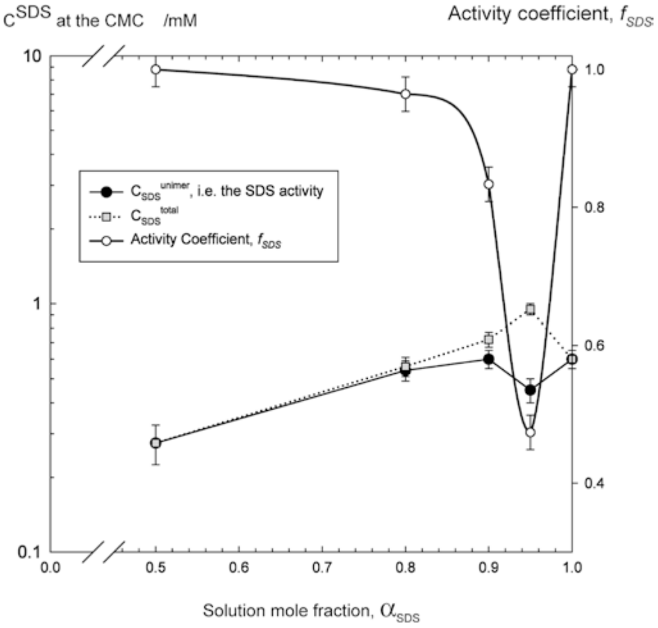

Fig. 3 SDS unimer concentration, SDS activity coefficient f_{SDS} and the derived SDS activity behaviour at CMC(1), as a function of solution mole fraction α_{SDS} in binary SDS and C_{12}BNMG mixtures in the presence of 25 wt% gelatin

something different is happening here relative to the regions of lower α_{SDS} or $\alpha_{SDS} = 1.0$ where activity coefficients are unity. Unfortunately, however, the curve described by f_{SDS} between $\alpha_{SDS} = 0.9$–1.0, and so the position and value of the minimum in activity coefficient, are not known with any precision since there is only a single datum point in this range ($\alpha_{SDS} = 0.95$). There is however, a clear maximum in the CMC and a corresponding minimum in f_{SDS}.

In some respects, the situation in the presence of gelatin is not that dissimilar to the gelatin-free case, but it appears rather different with $C_{\text{total}}^{\text{SDS(CMC)}}$ passing through a maximum and $C_{\text{unimer}}^{\text{SDS(CMC)}}$ passing through a maximum and minimum, as a function of α_{SDS} (Fig. 3). This latter observation has an important significance: with the SDS activity ($C_{\text{unimer}}^{\text{SDS(CMC)}}$) passing through a maximum and minimum there is the possibility that different micellar compositions can coexist at the same SDS activity – in other words at the same chemical potential. Indeed, this situation should be a prerequisite for the coexistence of two types of micelle. Therefore, two micelle types could coexist in principle, subject to mass balance constraints and comparable activity of the non-ionic co-surfactant. The simplest interpretation would be an SDS-rich micelle bound to the gelatin and a nonionic-rich micelle free in solution, a conclusion consistent with our diffusion data for this system [36]. Further confirmation of two micellar environments could be obtained from small-angle neutron scattering, but for this system, the scattering from bound and free micelles is virtually impossible to distinguish due to their composition-independent size and shape [37].

As implied above, there is some similarity between the gelatin and gelatin-free cases in that both systems show significant depressions in the activity coefficient of SDS at high α_{SDS}. This may be indicative that there are also two micelle types coexisting in the gelatin-free case in this region. Unfortunately, the differential seen between $C_{\text{total}}^{\text{SDS(CMC)}}$ and $C_{\text{unimer}}^{\text{SDS(CMC)}}$ at $\alpha_{SDS} = 0.95$ is much less in the gelatin-free case and there is insufficient data in this region to make this inference. However, it is possible that there could be a greater differential either side of $\alpha_{SDS} = 0.95$ which would lead to a maximum and minimum in the SDS activity ($C_{\text{unimer}}^{\text{SDS(CMC)}}$) curve for the gelatin-free case in the range $\alpha_{SDS} = 0.9$–1.0, and that it has simply been missed due to insufficient frequency of data at high α_{SDS}. If this were the case, it could be that the presence of the gelatin enhances the tendency of the gelatin-free system to form two coexisting micellar types at high α_{SDS} because of favourable electrostatic and hydrophobic interactions between the SDS-rich micelles and gelatin. On the other hand, the reduction in f_{SDS} at high α_{SDS} for the gelatin-free case could be due to some form of pre-micellar aggregation, though the authors have no hypothesis as to why this should particularly be so. Ideally, more data is required at high α_{SDS} to test these hypotheses but since the aggregation number is ~60 [38], such experiments would be at the limit of what is physically meaningful (the micellar composition would be varying by as little as a single non-ionic molecule). Nevertheless, the main point remains that activity coefficients at the CMC are significantly reduced at high α_{SDS} in these mixed surfactant systems in the absence of gelatin, indicating a different behaviour in this region, and that the behaviour parallels that found in the presence of gelatin in this respect.

Conclusions

An anionic surfactant selective electrode has been used to measure the SDS unimer concentrations, and therefore SDS activity, in a series of mixed surfactant solutions comprising SDS/C_{12}BNMG in water or aqueous gelatin; measurements were determined at the CMC in the gelatin-free studies and at CMC(1) in the gelatin studies. Activity coefficients of SDS are essentially equal to unity over a wide range of solution mole fractions, including pure SDS, for both types of system; however, significant deviations from unity are observed around a solution mole fraction of 0.95 SDS in both cases. The deviation of the SDS activity coefficient from unity at $\alpha_{SDS} = 0.95$ is significantly greater in the presence of gelatin and the SDS activity versus α_{SDS} curve exhibits a maximum and minimum in the region $\alpha_{SDS} = 0.8$–1.0. Accordingly, the variation in activity behaviour in the presence of gelatin is consistent with the possibility of coexisting micelle types at high solution mole fractions of SDS. In the gelatin-free case, the divergence between the SDS activity and actual SDS concentration at $\alpha_{SDS} = 0.95$ is less; given this weaker effect, there is insufficient frequency of data at high α_{SDS} to ascertain whether or not a corresponding (albeit less distinct) situation exists, giving the possibility of coexisting micelle types.

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