Photosensitive gelatin†

Ana Vesperinas,[a] Julian Eastoe,*[a] Paul Wyatt,[a] Isabelle Grillo[b] and Richard K. Heenan[c]

Received (in Cambridge, UK) 30th June 2006, Accepted 3rd August 2006
First published as an Advance Article on the web 8th September 2006
DOI: 10.1039/b609267e

Employing photodestructible surfactants in gelatin-based aqueous gels presents novel possibilities for controlling colloidal and aggregation properties of surfactant gelatin complexes. Light-triggered breakdown of the gelatin-bound photosurfactant aggregates causes dramatic changes in viscosity and aggregation.

Gelatin is a commodity chemical, possessing gelling and film forming properties owing to its polyelectrolyte structure. Applications of gelatin span from foods to the photographic industry, and hence physico-chemical properties of gelatin-based systems have been well documented as a function of thermodynamic variables, electrolyte concentration, pH, *etc.*[1]

Addition of anionic surfactant, such as SDS (sodium dodecylsulfate), is also known to influence gelatin properties: the anionic headgroups are believed to bind on cationic residues along gelatin strands.[2–4] This interaction results in formation of micellar-type aggregates on the polyelectrolyte chains, which are thought to act as intra- and inter-chain cross-linking units. Therefore, rheological properties are a strong function of added SDS concentration for such surfactant–gelatin complexes (SGC's).[*e.g.* 2–4] As such these SGC's have received considerable attention because of their ability to impart significant changes to the interfacial, rheological and physicochemical properties of a common aqueous polyelectrolyte system such as gelatin. The formation of SGC's is particularly relevant in applications such as promotion of emulsification and control in surface tension during photographic film coating.

Photo-destructible surfactants offer the unique ability to control aggregation and interfacial properties through irradiation with light. Breakdown of photodegradable surfactant sodium 4-hexylphenylazosulfonate (C6PAS) *via* UV has been shown to affect surface tensions[5,6] and microemulsion stability/structure,[7,8] since a mixed population of the weakly surface-active alkylphenol and a surface inactive alkylbenzene are formed as the photoproducts (Scheme S1 of ESI).† This study explores photo-responsive viscosity and aggregation changes in SGC's by introducing a photodestructible surfactant. Viscometry and small-angle neutron scattering (SANS) analyses have been employed to study changes in rheological and aggregation properties of the photosensitive SGC's. This SGC system is distinctly different from those employed in other reports of triggered rheological changes: Sakai *et al.* used a viscoelastic phase generated by a cationic photosurfactant,[9] whereas Piculell *et al.*[10] used a pH cleavable zwitterionic surfactant in combination with hydrophobically modified hydroxyethyl cellulose polymer.

The gelatin (gift from Kodak) used was deionised photographic bone gelatin type IV which was alkali processed (nominal molecular weight of 1.07×10^5, density 1.4 g cm^{-3}). Surfactant sodium 4-hexylphenylazosulfonate (C6PAS) was synthesised and characterized as outlined elsewhere.[5,7] A series of solutions were prepared by dissolving the gelatin and surfactant in water at 50 °C for 1 h and then cooling to 25 °C. Samples were irradiated in a quartz vessel with an unfiltered 100 W high-pressure Hg lamp, the temperature during irradiation was kept at 40–42 °C. Total photobreakdown of C6PAS in the SGC's was confirmed by the disappearance of the UV-vis absorption peak at 308 nm, characteristic of C6PAS (ESI).†

Blank solutions, containing gelatin only, did not show any changes in appearance, rheology or SANS after identical UV irradiation over this temperature range. After UV irradiation the physical appearance of the C6PAS-containing SGC's changed. Samples turned from yellow to brown and a reduction in viscosity was noticeable at various surfactant concentrations (Fig. 1). The brown colouration is due to trace levels of the hexylphenyl diazonium salt formed, owing to incomplete photolysis (Scheme S1 of ESI).† Viscosity was measured on a controlled stress Bohlin (CVO) rheometer with C14 concentric cylinder geometry at 41 °C.

When anionic surfactants were added to aqueous gelatin solutions, large increases in viscosity were observed.[1] Viscosity measurements for 5 and 10 wt% C6PAS-SGC's, before (●) and after (○) irradiation, as a function of added surfactant are shown in Fig. 2. These curves trace the relative viscosity of the C6PAS-doped SGC's, where the SGC viscosity is normalized to that for the equivalent surfactant-free gelatin solution, having been subjected to the same UV exposure.

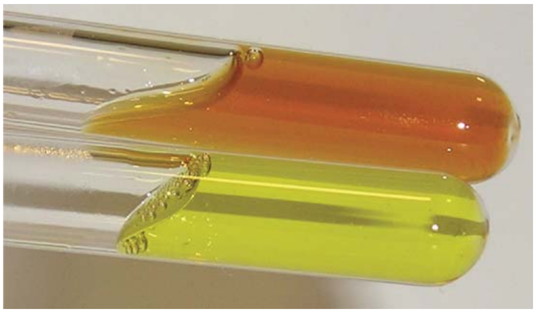

Fig. 1 Physical appearance of 10 wt% gelatin 0.03 M C6PAS sample at 41 °C before (lower sample) and after irradiation (top).

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[a] School of Chemistry, University of Bristol, Bristol, UK BS8 1TS. E-mail: julian.eastoe@bristol.ac.uk; Fax: +44 117 9250612; Tel: +44 117 9289180
[b] Institut Max-von-Laue-Paul-Langevin, BP 156-X, F-38042, Grenoble, Cedex, France
[c] ISIS Rutherford Appleton Laboratory, Chilton, Oxon, UK OX11 0QX

† Electronic supplementary information (ESI) available: C6PAS photochemistry, UV-Vis spectra, small-angle scattering analysis. See DOI: 10.1039/b609267e

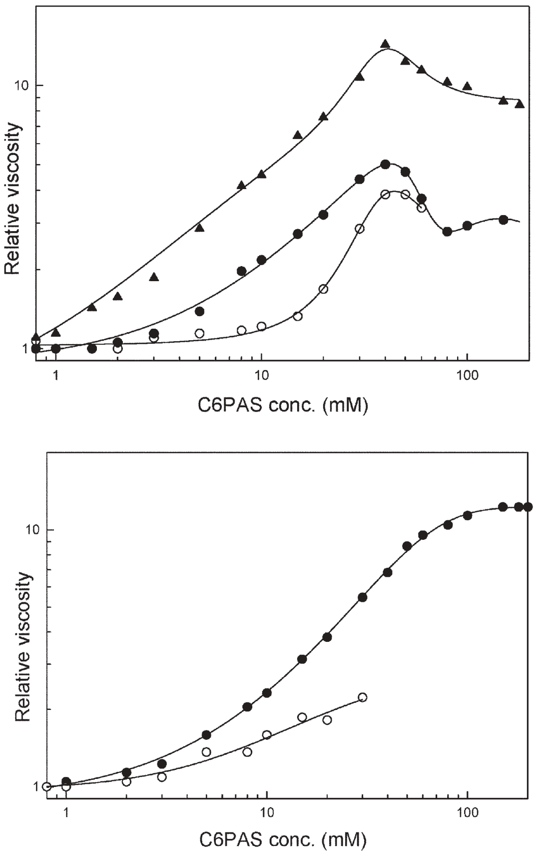

Fig. 2 Relative viscosity *versus* C6PAS concentration for 5% (top) and 10% (bottom) gelatin solutions at 41 °C. Effect of irradiation: before (●) and after (○). For comparison (▲) SDS-SGC.

Increasing surfactant concentration initially results in a sharp increase in viscosity. For mixtures of SDS/gelatin[2] a maximum in the viscosity was also observed at a characteristic SDS concentration (around 40 mM): after this point, a drop in viscosity was observed. This may be caused by partial collapse of the gelatin network, since the cooperative binding sites are saturated around 40 mM SDS. These significant viscosity enhancements have been attributed to micelle mediated cross-linking of gelatin strands, induced by favourable interactions between anionic surfactants and cationic patches on gelatin strands.[*e.g.*2–4]

A similar viscosity–concentration profile is seen when inert SDS is replaced by the photolabile surfactant C6PAS (Fig. 2). Irradiation of C6PAS/gelatin complexes resulted in a reduction in relative viscosity for both gelatin concentrations. Similar light treatment of the inert SDS-SGC's did not result in any relaxation of viscosity. Therefore, the UV-induced decrease in viscosity for C6PAS-SGC's could be ascribed to breakdown of the micelle cross-links as the surfactant loses its anionic headgroup in the photodegradation. A maximum decrease in viscosity of 7.1×10^{-2} Pa s was observed for the 10% gelatin sample after irradiation. For 5% gelatin/C6PAS mixtures the maximum difference in viscosity (1.1×10^{-2} Pa s) occurred at C6PAS concentrations 20–30 mM. Viscosity of irradiated samples at high surfactant concentrations was difficult to determine reliably, perhaps owing to the higher background level of photoproducts.

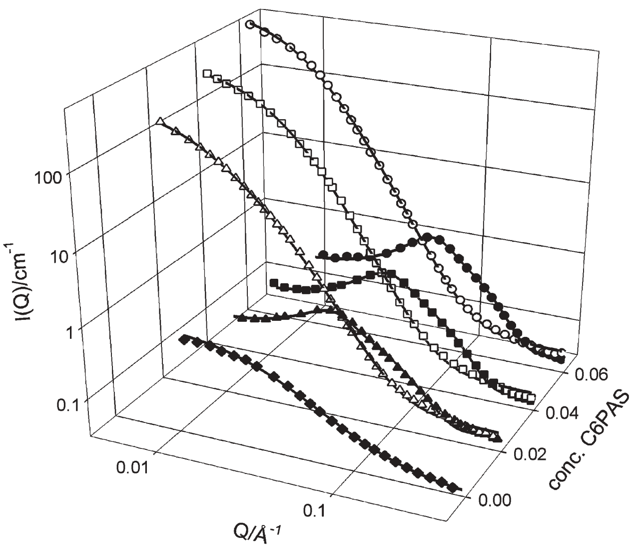

Fig. 3 SANS data and model fitting analyses for 5% gelatin C6PAS-SGC's in D_2O. Before irradiation filled, and after irradiation empty markers.

Small-angle neutron scattering (SANS) was used to follow changes in aggregation (Fig. 3). Samples for SANS were prepared using D_2O at different concentrations of C6PAS and gelatin, as described before (h-C6PAS/h-gelatin/D_2O). The SANS data were analyzed using the FISH model fitting program.[11]

Pure gelatin solution scattering was fitted to a Lorentzian plus Debye–Bueche model, resulting in a mesh size ξ = 34.4 Å and an inhomogeneity domain size a = 154 Å, dimensions which are very similar to those reported by Pezron[12] (ESI).†

In the presence of C6PAS the gelatin scattering at low Q disappeared, which suggests that gelatin has undergone a dramatic change in configuration on complexation with C6PAS. Prior to irradiation the scattering profile changes progressively with increasing surfactant concentration: these $I(Q)$ profiles exhibit the classic repulsive $S(Q)$ peak, characteristic of charged micelles.[11] The pre-UV data could be fitted by the celebrated Hayter–Penfold charged ellipsoidal micelle scattering model.[13] The ellipsoidal micelles apparently become smaller and less charged with increasing surfactant concentration (Table 1). With SGC's micellar clusters are believed to decorate the gelatin strands,[4,14] as depicted in Scheme S2 of the ESI.† Hence, the gelatin-adsorbed micelles are

Table 1 Fitted parameters of 5 wt% gelatin/C6PAS mixtures

Non irradiated			
[C6PAS]/mM	R_1/Å	R_2/Å	Charge α
20	16.5	82.4	30
40	15.8	62.1	17
60	15.3	54.5	16
UV irradiated			
[C6PAS]/mM			t/Å
20			110
40			184
60			289

[a] R_1 and R_2 are the radii of an ellipsoid and t is the sheet thickness.

thought of as independent clusters, which interact through a screened Coulomb-type potential.[4,14]

The SANS intensities with C6PAS pre-irradiation are similar to those seen for SDS-SGC's.[4,14] The apparent increase in micelle size with decreasing surfactant concentration has been tentatively accounted for by other authors.[4,14] In principle, contrast variation could be employed to generate individual C6PAS and gelatin partial structure factors, as performed with SDS-SGC's.[4] However deuterated C6PAS would be needed, and this is not easy to synthesize from commonly available deuterated reagents. The arrangement studied here (h-C6PAS/h-gelatin/D_2O) highlights the neutron contrast step from D_2O to the entire h-SGC surfactant–gelatin mixed aggregate. With this contrast only the composition is difficult to discern, and the relative contributions will depend on the C6PAS/gelatin concentration ratio. Hence, it is likely that the apparent change in size of the aggregates as a function of [C6PAS] (Table 1) is a reflection of this locally varying aggregate composition. (Scheme S2 of the ESI).†

After irradiation the aggregation increases and the changes are consistent with a transition from ellipsoidal charged micelles to extended sheet-like aggregates. For the post–irradiated C6PAS-SGC's strong logarithmic scattering is observed, which can be interpreted using the Kotlarchyk–Ritzau model,[15] accounting for monodisperse, randomly-oriented lamellar stacks. As shown in Table 1 there is apparently a growth in stack thickness with concentration. In truth, these post-irradiated SANS curves are difficult to model with certainty, and this proposed structure should be considered as a plausible approximation. However, the large differences between the pre- and post-irradiated SANS signals are consistent with a dramatic UV-induced change in aggregation, from charged ellipsoidal micelles to much larger aggregates. Similar SANS data were recorded for 10% Gelatin/C6PAS mixtures (ESI).†

A novel approach to control rheological and aggregation properties of aqueous gelatin-containing systems has been presented. The use of UV as a rheo-structural trigger means the transitions can be induced externally, without need for gross changes in thermodynamic or internal composition variables. Photodegradation of C6PAS in gelatin presents a novel approach to controlling aqueous gel properties with possible applications requiring rheological switches.

A.V. thanks Syngenta and the University of Bristol for a studentship. CCLRC are thanked for allocation of beam time at ISIS and ILL. Roy Hughes and Cheryl Flynn (Bristol Colloid Centre) are thanked for assistance with rheological measurements.

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