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Short communication

Solubility of amylose/ionic surfactant complexes in dilute aqueous solutions: Dependence on surfactant concentration

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Abstract

The solubility in dilute aqueous solutions of amylose complexed with ionic surfactants has been investigated by turbidity measurements. The turbidity depended on both the amylose and the surfactant concentrations. Low and high surfactant concentrations resulted in macroscopic phase separation, while mixtures at intermediate surfactant concentrations remained monophasic for at least one month. The solubility of the complexes was sensitive to the addition of salt as well as to the surfactant charge and hydrophobic chain length. These results are interpreted in terms of an electrostatic stabilisation of soluble complexes. Complexes with a non-ionic surfactant were not soluble at any mixing ratio.

Keywords: Amylose; Surfactant; Inclusion complex; Starch; Solubilisation

1. Introduction

Amylose (AM) is the essentially unbranched fraction of starch, consisting of α-D-(1-4) glycosidic bonds. It is well known that AM can form inclusion complexes with amphiphilic compounds such as iodine (Barrett, Barrett, & Khan, 1998; Calabrese & Khan, 1999; Knutsson, 1999; Yamamoto, Sano, & Yasunaga, 1982) and surfactants (Bulpin, Cutler, & Lips, 1987; Bulpin, Welsh, & Morris, 1982; Egermayer, Norrman, & Piculell, 2003; Egermayer & Piculell, 2003; Eliasson, 1994; Gunning et al., 2003; Kowblansky, 1985; Lundqvist, Eliasson, & Olofsson, 2002a; Lundqvist, Eliasson, & Olofsson, 2002b; Svensson, Gudmundsson, & Eliasson, 1996; Takagi & Isemura, 1960; Yamamoto, Harada, Nakatsuka, & Sano, 1988; Yamamoto, Sano, Harada, & Yasunaga, 1983). In a complex, the hydrophobic part of a guest molecule is inserted into the central, hydrophobic cavity of an AM helix. Two types of inclusion complexes, differing in melting temperatures and crystallinity, have been observed, where the crystalline complexes have the higher melting temperature (Eliasson, 1994; Kowblansky, 1985; Tufvesson & Eliasson, 2000; Tufvesson, Wahlgren, & Eliasson, 2003a; Tufvesson, Wahlgren, & Eliasson, 2003b). Both crystalline and amorphous structures can be formed with non-ionic guest molecules, but only the amorphous form has been found with ionic guest molecules (Kowblansky, 1985). Whether crystalline or amorphous complexes are formed with non-ionic guest molecules is mainly determined by the thermal history of the sample. The crystalline form, referred to as amylose-V, has a lamellar-like organisation of the inclusion complexes where the amylose chains are folded in such a way that the chain axis is perpendicular to the surface of the lamella (Biliaderis & Galloway, 1989; Godet, Bouchet, Colonna, Gallant, & Buleon, 1996). The amorphous form is less well characterised and is generally found to be formed when the sample is subjected to rapid temperature changes. It is believed to contain V-type single helices, but the helices are not packed in crystals with long-range order. Gunning et al. (2003) have performed atomic force microscopy imaging of non-crystalline AM complexes containing

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iodine and a non-ionic surfactant. The images showed single chains, which were proposed to correspond to single-helical complexes including both iodine and surfactant.

AM is not soluble in water at room temperature, but dissolves on heating above 150 °C (Chronakis, Egermayer, & Piculell, 2002). On cooling to room temperature, it precipitates again. In the context of previous studies involving AM and surfactants in our laboratory (Egermayer et al., 2003; Egermayer & Piculell, 2003) it was noted, however, that AM cooled from hot dilute solutions in the presence of sodium dodecyl sulfate (SDS) did not precipitate out. Previous studies of the complexation between surfactants and AM in dilute solutions have been performed, with a primary aim to establish surfactant binding characteristics (Bulpin et al., 1987, 1982; Lundqvist et al., 2002a, 2002b; Svensson et al., 1996; Yamamoto et al., 1988, 1983). However, no systematic studies on the solubility of the formed complexes, nor of the dependence of the solubility on the surfactant concentration, seem to have been reported. This is the objective of the study reported here, where we have used turbidity measurements to systematically investigate the solubility of AM in dilute solutions (0.25–0.50%) in the presence of ionic surfactants. We find that the ionic surfactants that we have investigated can keep AM in solution, but the stabilizing ability is limited to an intermediate range of surfactant concentration, with precipitation occurring – sometimes only after prolonged storage – both at lower and at higher surfactant concentrations.

2. Experimental

Materials. Potato amylose (AM) with a molecular weight of about 800,000 g/mol was obtained from Sigma Chemical Co. Prior to use, the AM was placed in an oven at 80 °C for 1 h to minimise solvent impurities such as butanol. (Butanol is used as a precipitant in the extraction of AM from starch.) Sodium dodecyl sulphate (SDS) obtained from BDH, sodium octyl sulphate (SOS) from ACROS, dodecyl trimethylammonium chloride (C_{12}TAC) obtained from TCI and sodium chloride from Prolabo were used without further purification. Water of Millipore quality (resistivity $\sim$18 MΩ cm^{-1}), which was degassed using a water suction pump, was used to prepare all samples.

Sample preparation. Samples were prepared using the same protocol as was previously used in our laboratory to prepare AM inclusion complexes (Egermayer et al., 2003). Stock surfactant solutions were prepared at room temperature. AM samples were prepared at concentrations twice the final AM concentration, heated to 150 °C for approximately 20 min in a Pierce Reacti-Therm heating/stirring module, and cooled down to 90 °C . To each 90 °C AM solution, an equal total volume of room-temperature (25 °C) surfactant solution + water was then immediately added to yield a final mixed solution with the desired surfactant content. The mixture thus prepared was then allowed to cool to room temperature.

Spectroscopy. The turbidity was measured using a Perkin–Elmer UV/VIS spectrometer. Reported turbidity values correspond to the absorbance at 220 nm at room temperature. The measurements were performed two days after preparation of the samples. No measurements were performed on samples which had separated into two macroscopic phases.

3. Results and discussion

After cooling to room temperature, the samples displayed one of the following types of behaviour. Some samples were clear and others homogeneously translucent one day after cooling. Some of these samples remained clear or translucent, respectively, during one month, whereas others became visibly more turbid or phase-separated macroscopically into a precipitate and a clear supernatant after some time. A 0.25 wt% solution of AM alone belonged to the latter category, being visibly clear after one day and macroscopically phase separated after one month. Finally, samples containing high concentrations of SDS and/or salt had developed precipitation already one day after cooling.

Turbidity measurements were performed two days after sample preparation in order to investigate how the concentration of surfactant affected the homogeneity of the samples. The turbidity of samples which contained 0.25 wt% AM and SDS is shown in Fig. 1. The lowest SDS concentration investigated was 0.01 mM. As the surfactant concentration increased, the turbidity decreased and went through a minimum plateau in the range 0.2–30 mM SDS, after which the turbidity gradually increased.

Dynamic light scattering measurements (not shown), gave broad relaxation time distributions, corresponding to average hydrodynamic radii of around 80 nm, for all visibly clear samples in the series of mixtures with SDS, regardless of the surfactant concentration. This size is compatible with loosely packed entities containing single AM

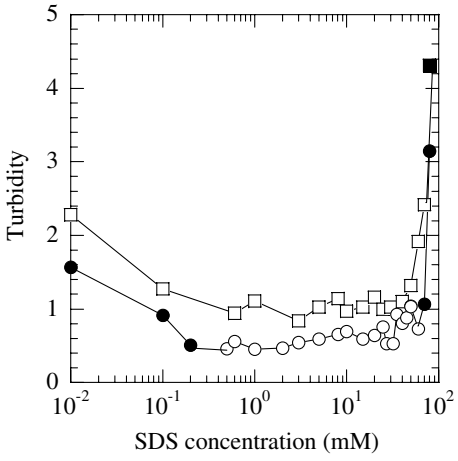

Fig. 1. Turbidity with increasing SDS concentration for 0.25 wt% AM (circles) and 0.5 wt% AM (squares). Data recorded after storage at room temperature for two days after sample preparation. Open symbols indicate samples that remained visibly clear also one month after preparation.

molecules, but more compact species containing many chains would also be compatible with these results; no detailed information on the aggregate shape or density is provided by dynamic light scattering. However, based on information available from previous studies, we conclude that the soluble complexes formed under our experimental conditions are inclusion complexes with SDS (Takagi & Isemura, 1960; Eliasson, 1994; Kowblansky, 1985; Lundqvist et al., 2002a, 2002b; Svensson et al., 1996; Yamamoto et al., 1988, 1983).

Samples with a surfactant concentration higher than 80 mM separated into two macroscopic phases already one day after preparation. The amylose-containing precipitate in these samples had a white, "fluffy" appearance. Samples with SDS concentrations between ~0.2 and 50 mM were visibly clear one month after preparation. Samples with higher or lower SDS concentration separated into two macroscopic phases within one month after preparation.

We interpret the above findings as follows. As SDS molecules were bound, the AM molecule gained properties similar to a traditional polyelectrolyte. An electrostatic repulsion developed between AM molecules complexed with surfactant, giving rise to soluble complexes. As more and more SDS molecules were complexed with AM, the turbidity correspondingly decreased. When the AM molecules were saturated with surfactant molecules, additional surfactant served mainly as an added electrolyte, which decreased the repulsion between the AM molecules. The SDS concentration at the onset of the low turbidity plateau in Fig. 1 corresponds well to the concentration range (0.2–0.5 mM) where two previous investigations have found that the AM molecules, at a concentration of 0.25 wt% were saturated with SDS (Svensson et al., 1996; Yamamoto et al., 1983).

Similar turbidity measurements were also performed on samples which contained 0.5 wt% AM, Fig. 1. The turbidity of these samples followed the same trends as for the 0.25 wt% AM samples, but shifted to higher turbidity values. The plateau value was roughly twice that obtained for 0.25 wt% AM, which agrees with an expected doubling of the concentration of soluble complexes. As expected, more SDS was required to reach the plateau of minimum turbidity for the higher AM concentration.

In order to test the hypothesis of electrostatic stabilisation of the soluble AM complexes, the effect of various constant levels of added simple salt (NaCl) was tested with increasing SDS concentration, Fig. 2. Indeed, the effect of adding a simple salt was similar to that of increasing the surfactant concentration, that is, a decreased homogeneity of the samples. All samples containing 10 mM NaCl or more separated into two phases within one month after mixing; only the samples in 5 mM NaCl containing less than 40 mM SDS remained clear after one month. One day after mixing, however, many samples prepared with added salt were still visibly clear or homogeneously translucent, and displayed a minimum turbidity at intermediate

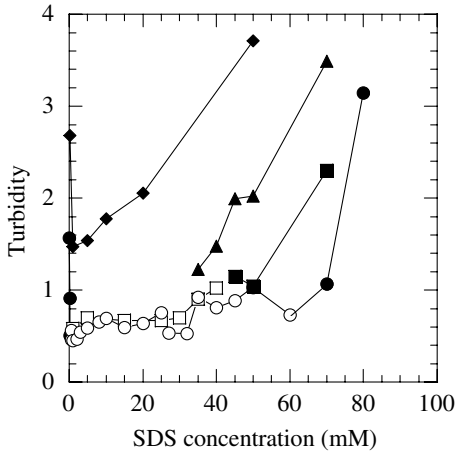

Fig. 2. Turbidity with increasing SDS concentration for 0.25 wt% AM without NaCl (circles) with 5 mM (squares), 10 mM (triangles) and 20 mM NaCl (diamonds). Data recorded after storage at room temperature for two days after sample preparation. Open symbols indicate samples that remained visibly clear also one month after preparation.

surfactant concentrations, as confirmed by the measurements displayed in Fig. 2.

A shorter chain length of the alkyl chain of the hydrophobic ligand is known to decrease the tendency for complexation with AM (Yamamoto et al., 1983). To investigate whether this had any effect on the homogeneity of the AM/surfactant solutions comparative measurements were performed with SOS, Fig. 3. Although the data for SOS scatter somewhat, especially at low surfactant concentration, the overall non-monotonic trend with increasing surfactant concentration is the same as for SDS. Moreover, the samples with SOS concentration higher than 10 mM separated immediately into two macroscopic phases. The poorer stability of the SOS complexes against phase

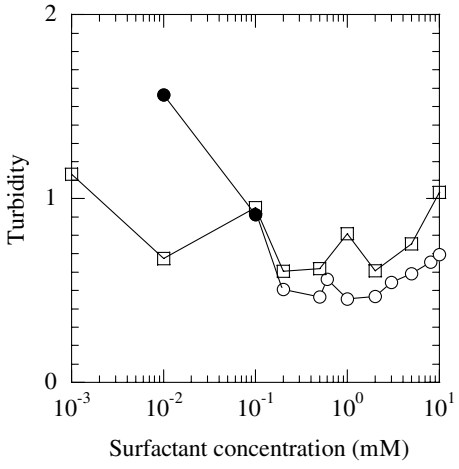

Fig. 3. Turbidity with increasing surfactant concentration for 0.25 wt% AM with SDS (circles) and SOS (squares). Data recorded after storage at room temperature for two days after sample preparation. Open symbols indicate samples that remained visibly clear also one month after preparation.

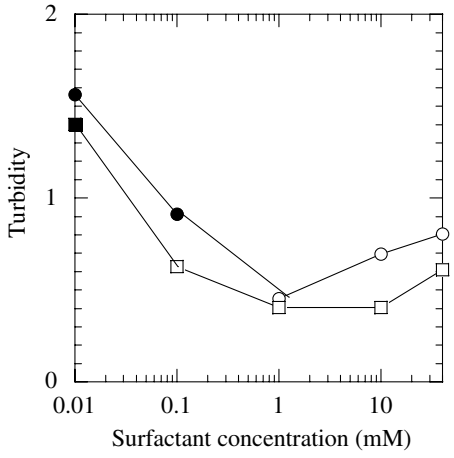

Fig. 4. Turbidity with increasing surfactant concentration for 0.25 wt% AM with SDS (circles) and C_{12}TAC (squares). Data recorded after storage at room temperature for two days after sample preparation. Open symbols indicate samples that remained visibly clear also one month after preparation.

separation, compared to the SDS complexes, may be attributed to less surfactant binding, which results in both a less charged complex and a higher concentration of non-complexed surfactant, acting as a screening electrolyte.

In order to investigate the effect of the sign of the charge of the surfactant, measurements were performed with 0.25 wt% AM and cationic C_{12}TAC, Fig. 4. The turbidity of the mixture with the cationic surfactant was slightly lower than the turbidity with the anionic surfactant. All samples, except the sample with the lowest C_{12}TAC concentration (0.01 mM) were clear also one month after mixing.

Mixtures with 0.25 wt% AM and 0.005–100 mM non-ionic surfactant penta-ethylene glycol mono *n*-dodecyl ether ($C_{12}E_5$) were also investigated (results not shown) and only samples with a surfactant concentration below 0.05 mM $C_{12}E_5$ did not separate into two macroscopic phases within two days after preparation. These results further confirm the notion that the solubility of the AM complexes with ionic surfactants is due to the polyelectrolyte properties of the latter complexes.

4. Conclusions

The complexation of ionic surfactant molecules can stabilise AM molecules against precipitation in dilute aqueous solutions at room temperature. However, the stability of the solutions decreases at an increased level of external electrolyte, present either as excess non-bound surfactant or as added simple salt. In some cases the stabilisation is clearly only kinetic, since the solutions eventually phase separate (after days or weeks). At high degrees of surfactant binding and low levels of excess electrolyte the situation is less clear, since for such samples no tendency of phase separation could be detected during the entire time of observation (one month) in this work.

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