

## Emulsification and Adsorption Properties of Hydrophobically Modified Potato and Barley Starch

LARS NILSSON\* AND BJÖRN BERGENSTÅHL

Division of Food Technology, Centre for Chemistry and Chemical Engineering, Lund University,  
 P.O. Box 124, S-22100 Lund, Sweden

In this paper, we studied the adsorption at emulsion droplets of potato starch, which was hydrophobically modified with octenyl succinate anhydride (OSA), a surface active macromolecule containing ultrahigh molar mass components. The results show that the substance works as an efficient emulsifier and that it can in some cases generate high surface loads (10 mg/m<sup>2</sup>). The results can be explained as an interplay between kinetic factors during the formation of the emulsion and the physical-chemical properties of the hydrophobically modified starch, such as the degree of substitution, molar mass, and radius. In turbulent flow fields, such as in a high-pressure homogenizer, the mass transport to the interface favors the adsorption of larger molecules as they are transported more rapidly to the interface. The larger molecules are also likely to have a higher substituent density and adsorption energy than smaller ones. This in turn is likely to give high surface loads and strengthen the effect of kinetic adsorption factors, as the large molecules will be overrepresented at the surface.

**KEYWORDS:** Hydrophobically modified starch; adsorption; emulsion; degree of substitution; oil–water interface

### INTRODUCTION

Hydrophobically modified polysaccharides are macromolecules that are of great interest in the formulation of dispersions. Through their amphiphilic character, the hydrophobically modified polysaccharides are surface active and can adsorb at interfaces and stabilize dispersions. The stabilization mechanism can either be of an electrostatic nature or of a steric nature with mainly entropic contributions. In the case of electrostatics, the ability to stabilize is of course dependent on the charge density of the macromolecule, and, in the case of steric stabilization, the size and solubility of the macromolecule in the continuous phase are important. In food applications, the number of surface active polysaccharides that are available is quite limited. Examples of natural surface active polysaccharides are gum arabic and demethoxylated pectin in which the surface activity is related to protein components closely associated with the polysaccharide (1, 2). Another amphiphilic macromolecule is starch that has been chemically modified with OSA (octenyl succinic anhydride) (3). The substitution with OSA can occur at carbons 2, 3, and 6 in the glucose molecule, and the typical degree of substitution (*DS*) for commercial samples is 0.01–0.03. It has been suggested by Shogren et al. that the substitution occurs preferentially in and around the amorphous branch points of the amylopectin, which is one of the two polymers present in starch (4). OSA-starch is able to adsorb at hydrophobic

interfaces, and due to its branched polymer structure and high molar mass it gives rise to steric stabilization in emulsions (5–7).

Emulsions are formed from two immiscible liquids by dispersing one of the phases in the other, which is commonly achieved by applying intense mechanical energy to the system (8). For an amphiphilic macromolecule to work as an effective emulsifier, it is vital that it is able to adsorb at the interface and cover it rapidly to prevent recoalescence of the newly formed droplets. The driving force for adsorption at the oil droplets is, in the case of hydrophobically modified polysaccharides, mainly hydrophobic interaction. Thus, the extent of modification, the number of hydrophobic groups grafted onto the macromolecule, is intuitively influencing the adsorption behavior at the interface. However, the relationship between the number of groups in a macromolecule with a high affinity for a surface and the adsorption behavior is often not trivial.

In a previous paper, we studied the adsorption of OSA-starch from barley at emulsion droplets (7). The results of that study showed that the adsorbed amount or surface load of OSA-starch could in some cases become quite high reaching, almost 16 mg m<sup>-2</sup>. The high surface loads were attributed to the relationship between the size of the surface created during emulsification and amount of OSA-starch available for adsorption. A small surface, that is, large droplets, and a high OSA-starch concentration in the bulk solution lead to high surface loads, and this was believed to be caused by close-packing and orientation of the macromolecules at the surface due to the kinetic factors

\* Author to whom correspondence should be addressed [telephone +46-46-222 9670; fax +46-46-222 4622; e-mail lars.nilsson@food.lth.se].

**Table 1.** OSA-Starch Samples<sup>a</sup>

sample	DS	DB	$Mw_i$ ( $10^6$ g/mol)	$Mw_f$ ( $10^6$ g/mol)	$r_{rms}$ (nm)
P23-14	0.014	0.035	18	8.8	32
P08-15	0.015	0.035	0.77	0.63	34 <sup>b</sup>
P34-076	0.0076	0.035	34	11	42

<sup>a</sup> DS is the degree of substitution, and DB is the degree of branching. The subscripts i and f denote initial and final average molar mass and refer to non-homogenized and homogenized samples, respectively.  $r_{rms}$  is the root-mean-square radius after homogenization. <sup>b</sup> From ref 22.

during the adsorption. We also showed by applying a collision model that the adsorption of larger molecules in a polydisperse sample is favored over that of smaller ones due to the convective mass transport. Furthermore, the adsorption times of the macromolecules were of the same order of magnitude as the droplet half-life, that is, the time it takes for all droplets to collide once. One important implication of this result is that the molar mass of an adsorbing macromolecule is as critical as the degree of substitution. However, we cannot expect the molar mass to remain constant during such a harsh treatment as high-pressure homogenization. In two previous studies by Modig et al. and Nilsson et al., we showed that the molar mass of OSA-starch is drastically reduced during a normal homogenization event (9, 10).

In the present study, we investigated the influence of the degree of substitution (DS) of the OSA-starch on the adsorption and the DS interplay with other physical parameters such as molar mass and molecular size in the adsorption behavior.

## MATERIALS AND METHODS

The three OSA-starch samples were provided by Lyckeby Stärkelsen (Kristianstad, Sweden) and were of native potato origin containing 20% amylose and 80% amylopectin. The molar degree of branching and the molar degree of substitution (DS) were determined via <sup>1</sup>H NMR spectroscopy. The samples for NMR were prepared by dispersing 100 mg of OSA-starch in 10 mL of D<sub>2</sub>O and placing it in a boiling water bath for 10 min.

The samples were freeze-dried, and approximately 80 mg of the freeze-dried sample was redissolved in 5 mL of DMSO-*d*<sub>6</sub>. The samples were placed in a boiling water bath for 10 min after which the NMR measurements were performed. The NMR spectrometer (ARX 500, Bruker Fällanden, Switzerland) operated at 500 MHz, and the experimental method has been described in greater detail elsewhere (11, 12). The molar mass distribution, average molar mass, and the root-mean-square radius ( $r_{rms}$ ) of the OSA-starch samples was determined before and after homogenization by asymmetrical flow field-flow fractionation (AsFIFFF-MALS-RI) and are described by Modig et al. (9) and Nilsson et al. (10). The properties of the various OSA-starch samples are given in **Table 1**. OSA-starch solutions of 1% (w/v) were prepared by dispersing 1.0 g of OSA-starch in a phosphate buffer (10 mM, pH = 6.0) containing 20 ppm NaN<sub>3</sub>, which was then diluted to 100 mL. The samples were placed in a boiling water bath under stirring for 10 min, after which they were left overnight at room temperature.

Emulsions were prepared with 5% (w/w) of medium chain triglyceride oil Miglyol 812 F (Sasol, Witten, Germany) in a buffer solution as above. Emulsions with different OSA-starch concentrations were then prepared by mixing for 3 min using a high shear mixer, Ystral X10/25 (Ystral, Ballrechten-Dottingen, Germany), followed by high-pressure homogenization in a lab-scale valve homogenizer at 15 MPa. All experiments were performed at room temperature. The average droplet size ( $d_{32}$ ) in the emulsions was determined by light diffraction using a Coulter LS130 (Beckman Coulter, High Wycombe, U.K.), and from this the emulsion surface area could be calculated. The adsorbed amount was determined through serum depletion, and the emulsions were separated in two steps by mild centrifugation to avoid coalescence

until a clear supernatant was obtained. The first separation step was carried out at 3400 RCF for 10 min and the second step at 7000 RCF for 15 min.

The total OSA-starch content was determined by enzymatic degradation according to the method of Åman et al. (13). The determination was carried out in the supernatant of the separated emulsion sample and in a reference sample containing the same initial OSA-starch concentration. The reference sample was treated in the same way as the emulsion sample and thus went through the same steps of homogenization and centrifugation.

As the method of Åman et al. was developed for nonmodified starches, the recovery was slightly lower for the OSA-starch, which was probably due to incomplete hydrolysis. The recovery varied between 85% and 89%. However, by assuming that the recovery is equal in the emulsion sample and in the reference sample, this error can be minimized.

**Calculation of the Surface Load of OSA-Starch.** The adsorbed amount of OSA-starch is obtained from the difference between the amount in the reference sample containing no disperse phase and the amount in the supernatant after separation of the emulsion.

$$c_{ads} = c_{reference} - c_{sub} \quad (1)$$

The surface load ( $\Gamma$ ) is obtained by relating the adsorbed amount to the specific surface area of the emulsion

$$\Gamma = \frac{c_{adsorbed} \cdot d_{32}}{\varphi \cdot 6} \quad (2)$$

where  $d_{32}$  is the Sauter mean droplet diameter and  $\varphi$  is the dispersed phase volume fraction.

**Surface Tension Measurements.** The surface pressure of OSA-starch solutions was determined at the air/water interface and the oil/water interface according to axis symmetrical drop shape analysis (ADSA) (14) using the Tracker instrument (Teclis, Longessaigne, France).

The water solutions contained 100 ppm of OSA-starch, and all measurements were performed at 25 °C. The interfacial pressure ( $\Pi$ ) is obtained from eq 3, where  $\gamma_0$  is the interfacial tension of the pure interface and  $\gamma$  is the interfacial tension of the interface with adsorbed OSA-starch.

$$\Pi = \gamma_0 - \gamma \quad (3)$$

**Statistical Analysis.** The adsorption experiments were evaluated with linear regression and ANOVA.

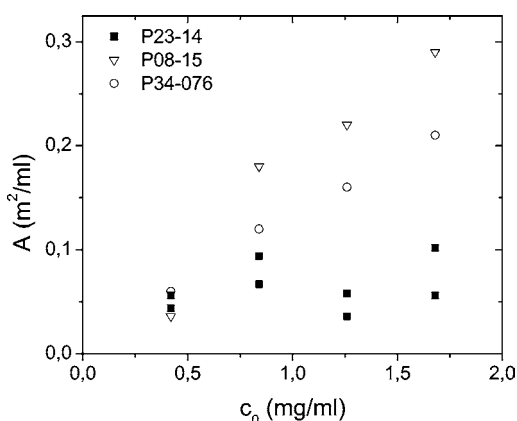
## RESULTS

The emulsions were formed with different levels of the three OSA-starch samples, and the particle size of the emulsions was determined with light diffraction. The emulsions were separated, and the amount of non-adsorbed OSA-starch was determined. The results of the emulsification experiments are shown in **Table 2**. The emulsification performance is shown in **Figure 1** as emulsion surface area created versus initial OSA-starch concentration ( $c_0$ ). The results show that the emulsion surface area increases with increasing OSA-starch concentration and thus that OSA-starch is functional as an emulsifier. The Sauter mean diameter of the oil droplets was between 0.4 and 11  $\mu$ m, which corresponds to an emulsion surface of approximately 0.03–0.72 m<sup>2</sup> mL<sup>-1</sup>. For samples P08-15 and P34-076, the amount of surface area created during emulsification increases almost linearly with increasing initial OSA-starch concentration, but for sample P23-14 the surface area seems to be independent of the initial OSA-starch concentration. Replicates of sample P23-14 also exhibit a rather large variation in the surface area created. **Table 3** shows the slope obtained from the linear regression with the corresponding *p*-value for the dependence. Samples P08-15 and P34-076 show a significant linearity for  $A = f(c_0)$

**Table 2.** Results from the Adsorption Experiments with the Different OSA-Starch Samples<sup>a</sup>

sample	$c_0$ (mg/mL)	$d$ ( $\mu\text{m}$ )	$A$ ( $\text{m}^2/\text{mL}$ )	apparent $c_{\text{eq}}$ (mg/mL)	$\Gamma$ ( $\text{mg}/\text{m}^2$ )	$c_{\text{adsorbed}}/c_0$
P23-14	0.42	5.4	0.056	0.24	2.0	0.27
	0.42	6.8	0.044	0.27	1.9	0.20
	0.84	4.5	0.067	0.54	3.1	0.25
	0.84	3.2	0.094	0.46	2.6	0.30
	1.26	8.3	0.036	0.84	10.3	0.30
	1.26	5.2	0.058	0.78	4.8	0.22
	1.68	5.3	0.056	1.15	7.0	0.23
	1.68	3.0	0.102	0.97	3.7	0.22
P08-15	0.42	8.3	0.036	0.23	3.1	0.27
	0.84	1.7	0.18	0.46	1.5	0.32
	1.26	1.3	0.22	0.76	1.4	0.25
	1.68	1.0	0.29	1.03	1.2	0.21
P34-76	0.42	5.3	0.06	0.26	1.4	0.20
	0.84	2.5	0.12	0.56	1.2	0.18
	1.26	1.9	0.16	0.83	1.6	0.20
	1.68	1.4	0.21	1.13	1.2	0.16

<sup>a</sup>  $c_0$  is the initial OSA-starch concentration,  $d$  is the Sauter mean diameter of the emulsion droplets,  $A$  is the emulsion surface area,  $c_{\text{eq}}$  is the apparent OSA-starch equilibrium concentration,  $\Gamma$  is the surface load of OSA-starch, and  $c_{\text{adsorbed}}/c_0$  is the adsorption yield.

**Figure 1.** Emulsion surface area created by emulsification with different OSA-starches. The emulsions contained 5% (w/w) of MCT-oil.

and  $c_{\text{ads}} = f(A)$  as expected when the interfacial area is determined by the available emulsifier. However, for sample P23-14, this relationship is absent.

The adsorption isotherms for the three OSA-starches, as obtained from the emulsification experiments, are shown in **Figure 2**. The surface load ( $\Gamma$ ) varies between 1 and 10  $\text{mg}/\text{m}^2$ . The surface load of sample P34-076 shows no concentration dependence and remains at a level of 1–2  $\text{mg}/\text{m}^2$ , which is a surface load that can normally be expected from an adsorbing macromolecule. Sample P08-15 has a behavior similar to that of sample P34-076 except at the lowest equilibrium concentration where the surface load becomes slightly higher. The adsorption isotherm for sample P23-14 generally shows higher surface loads at most concentrations. The surface load is increasing with increasing apparent equilibrium concentration, although at higher concentrations the variation becomes large between replicates. At these higher equilibrium concentrations, the surface loads obtained can become quite high, reaching 10  $\text{mg}/\text{m}^2$ . On the other hand, it is interesting to note the difference between the potato OSA-starch in this study and the barley OSA-starch previously studied (7). With potato OSA-starch, we observe constant surface loads or surface loads increasing with increasing apparent equilibrium concentration, while with the barley OSA-starch, we observed a surface load that was declining with increasing apparent equilibrium concentration. A way of rationalizing these observations is to assume that

the adsorption during homogenization is a nonequilibrium process (hence the use of “apparent equilibrium concentration” in the adsorption isotherm). In our previous paper with barley OSA-starch, we observed that the adsorption process was controlled by the relation between surface area and initial OSA-starch in the bulk solution rather than the equilibrium concentration of the latter (7). The relationship between the emulsion surface area and initial OSA-starch concentration is hereafter referred to as the dynamic surface load ( $\Gamma_{\text{dyn}} = c_0/A$ ). In **Figure 3**, the surface load,  $\Gamma$ , is plotted versus the dynamic surface load, and the results show a clear relationship between the two parameters for sample P23-14 where  $\Gamma$  increases with increasing  $\Gamma_{\text{dyn}}$ . The other two samples show a more ideal emulsifying behavior; that is, the added amount of OSA-starch gives a larger surface area in the emulsion instead of adsorbing in higher amounts. The adsorption yield in the experiments (i.e., the concentration of adsorbed OSA-starch  $c_{\text{ads}}$  divided by the initially added concentration  $c_0$ ) ranged between 16% and 32%.

**Table 3** shows the slope of the linear regression and the corresponding  $p$ -value for  $A = f(c_0)$ ,  $c_{\text{ads}} = f(A)$ , and  $c_{\text{ads}} = f(c_0/A)$ . It is clearly seen that for sample P23-14,  $A = f(c_0)$  is not a satisfactory model while  $c_{\text{ads}} = f(c_0/A)$  (i.e., dynamic surface load) gives a much increased satisfaction in the description. This improvement is, however, not true for the other two samples for which the transition to  $c_{\text{ads}} = f(c_0/A)$  does not yield any improvement.

The surface activity of the OSA-starch was also characterized in terms of the surface pressure generated during adsorption, and the results of the interfacial tension measurements at the air/water interface and the oil/water interface can be seen in **Table 4**. The results show that the surface pressure in all cases is quite low but still significant. It is interesting to note that the surface pressures of the three OSA-starches are higher at the oil/water interface than at the air/water interface.

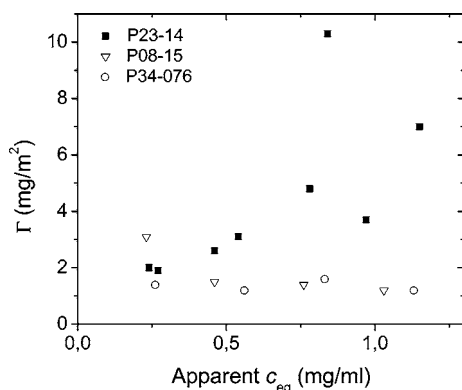
## DISCUSSION

The results in this study strengthen the evidence that starch that has been hydrophobically modified with OSA can act as an emulsifier and generate colloidal stability in emulsions. The results of the interfacial tension measurements show that the interfacial pressure is higher at the oil/water interface than at the air/water interface, which indicates that the adsorption at the oil/water interface is driven by stronger interactions than

**Table 3.** Statistical Analysis of the Experimental Results

sample	linear regression slope $\pm$ standard error			slope $p$ -value <sup>a</sup>		
	$A = f(c_0)$	$c_{\text{ads}} = f(A)$	$c_{\text{ads}} = f(c_0/A)$	$A = f(c_0)$	$c_{\text{ads}} = f(A)$	$c_{\text{ads}} = f(c_0/A)$
P23-14	$0.013 \pm 0.018$	$1.2 \pm 2.1$	$0.0092 \pm 0.0029$	0.50	0.60	0.019
P08-15	$4.9 \pm 0.92$	$0.96 \pm 0.092$	$-0.029 \pm 0.010$	0.033	0.0092	0.11
P34-076	$0.12 \pm 0.0063$	$1.2 \pm 0.34$	$0.15 \pm 0.034$	0.0029	0.067	0.049

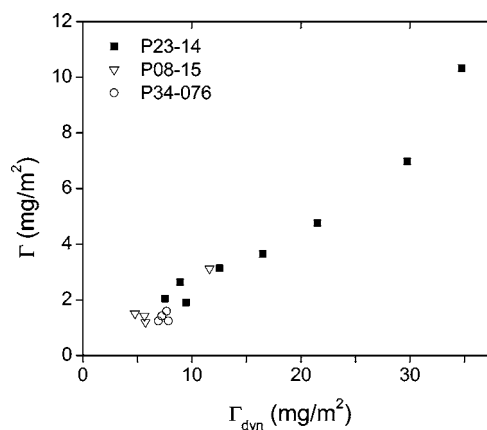
<sup>a</sup> Versus regression coefficient equal to zero.

**Figure 2.** Adsorption isotherms for the OSA-starches at the oil/water interface.

poor aqueous solubility. This interaction is likely to be a contribution of van der Waals attraction as it would be stronger for oil than for air. Under conditions with a small emulsion surface area and high concentrations of OSA-starch, the surface loads obtained can indeed become very high, reaching 10 mg/m<sup>2</sup>. Other studies of amphiphilic polysaccharides adsorbing to emulsion droplets have also shown that the surface loads can become high (2, 7). From the results in the present study, it seems that  $\Gamma$  is related to the starch derivatives ability to generate small oil droplets, and thus a high surface area, during homogenization. The specific emulsion surface area was not constant in the experiments, and the emulsification performance (**Figure 1**) shows large variations in the amount of surface area that is created by P23-14. This variation can become large when using emulsifiers that give a low decrease in interfacial tension such as OSA-starch (**Table 4**).

When the surface area becomes small, kinetic factors are likely to become important as macromolecules compete for available adsorption sites at the interface. This in turn can cause jamming (random close packing) at the interface, as the macromolecules are unable to optimize their conformation to the most thermodynamically favorable; that is, spreading and reorientation is inhibited. In a previous paper (7), we have shown with a collision model that in the turbulent flow conditions that occur during high-pressure homogenization the flux to the interface from the bulk solution is likely to be dominated by convection rather than diffusion. This will favor the adsorption of large macromolecules over small ones. Furthermore, we showed that the adsorption times of large macromolecules at the interface are of the same order of magnitude as the emulsion droplets half-life, that is, the time it takes for all droplets to have collided once. To prevent re-coalescence after the disruption of the oil droplets, it is vital that the emulsifier is able to cover a large extent of the interface rapidly, and as the adsorption times and the droplet half-life are similar, it further shows how kinetics and jamming at the interface can become important.

In the present study, the possibility that multilayer adsorption contributes to the high surface loads cannot be ruled out, as the

**Figure 3.** The emulsion surface load ( $\Gamma$ ) vs. the dynamic surface load ( $\Gamma_{\text{pot}}$ ), that is, amount of OSA-starch available per specific emulsion surface area.**Table 4.** Interfacial Pressure ( $\Pi$ ) for the Different OSA-Starch Solutions (100 mg L<sup>-1</sup>) at the Air/Water and Oil/Water Interfaces

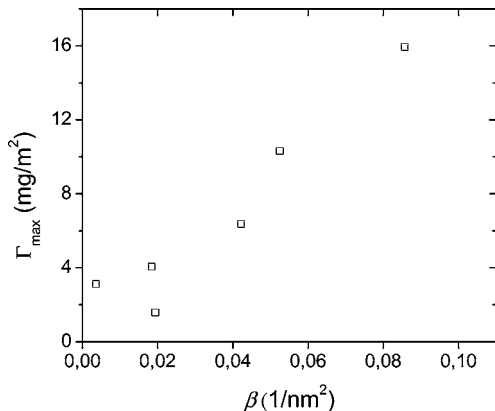
sample	$\Pi_{\text{air/water}}$ (mN/m)	$\Pi_{\text{oil/water}}$ (mN/m)
P23-14	0.66	2.74
P08-15	0.45	2.07
P34-076	1.31	2.26

surface load can increase with increasing apparent equilibrium concentration for sample P23-14. Multilayer adsorption could be caused by the formation of inclusion complexes between adsorbed and non-adsorbed OSA-starch. The inclusion complex occurs when a hydrocarbon chain enters the hydrophobic cavity of amylose (15). This would also be more likely to occur for potato OSA-starch, as it contains approximately 20% amylose.

Another parameter, except the size of the macromolecule, which is likely to influence the adsorption, is the  $DS$ , which should influence the adsorption energy of the macromolecule. Other authors have shown that the  $DS$  can influence the adsorption of polysaccharides (16–18). Demé and Lee studied the adsorption of cholesterylpullulan at the air/water interface and found that  $\Gamma$  decreases with an increasing  $DS$  (17). This was attributed to a higher amount of loops and tails in the adsorbed macromolecule, which in turn was due to the lower amount of anchoring points in the samples with a lower  $DS$ . Paris and Cohen Stuart studied the adsorption of hydrophobically modified 6-carboxypullulan from water to polystyrene particles (16). The authors found a strong effect of  $DS$  of hydrophobic groups on both the  $\Gamma$  and the adsorption rate, where a higher  $DS$  gave a higher  $\Gamma$  and a higher adsorption rate. Simon et al. studied the adsorption of hydrophobically modified carboxymethylpullulans and found that the plateau value of  $\Gamma$  increased with increasing hydrophobic  $DS$  up to a  $DS$  value of about 0.25, after which the plateau value became somewhat lower (18). The behavior was attributed to an initial regime with an increase in affinity for the surface when the  $DS$  increases, which is then followed by a second regime where the decrease in  $\Gamma$  is due to

**Table 5.** Surface Substituent Density for the Various Samples As Estimated from Eq 4

sample	$\beta$ (nm <sup>-2</sup> )	sample	$\beta$ (nm <sup>-2</sup> )
B39-22 <sup>a</sup>	0.086	P23-14	0.053
B27-21 <sup>a</sup>	0.042	P08-15	0.004
B86-10 <sup>a</sup>	0.018	P34-076	0.019

<sup>a</sup> From ref 7.**Figure 4.** The maximum surface load ( $\Gamma_{\max}$ ) obtained in the experiments increases with the surface substituent density ( $\beta$ ) of the OSA-starch.

a change in conformation of the adsorbed polysaccharides causing a decrease in the number of loop and tails at the interface. Similar evidence, which is more pronounced, was found experimentally by Poncet et al. for hydrophobically modified polyacrylates (19) adsorbing at hydrophobic surfaces and theoretically in a mean-field study by Linse (20).

Considering these different results described in the literature, it is clear that no general relationship between  $DS$  and  $\Gamma$  exists but that their relationship is rather system dependent. In the present study, the results do not show a simple correlation between  $\Gamma$  and  $DS$  (see **Table 1** and **Figures 1–3**). Rather, the results suggest that the surface load is determined by a combination of  $DS$  and molecular size (i.e., molar mass and rms radius). An explanation taking these parameters into account is that the affinity to the interface may be controlled by the surface density of substituents, if we imagine the OSA-starch molecules as particles in the aqueous phase. It would thus be interesting to estimate the density of substituents on the surface of the macromolecule assuming spherical geometry and that all substituents are situated close to the surface. This can be described by

$$\beta = N \frac{DS}{4\pi r_p^2} \quad (4)$$

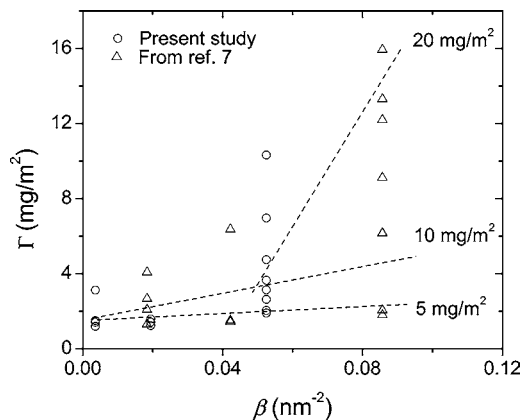
where  $\beta$  is the surface substituent density,  $N$  is the average number of glucose units in the OSA-starch sample, and  $r_p$  is the polymer radius. The values of  $\beta$  are given in **Table 5**. **Figure 4** shows that the maximum surface load obtained in the experiments ( $\Gamma_{\max}$ ) depends on  $\beta$  and that a higher value of  $\beta$  allows for higher surface loads. In **Figure 4** and **Table 5**, three samples from a previous study are included (7), which are also shown to follow a similar relationship. The characteristics of these samples are given in **Table 6**.

**Figure 5** shows that  $\Gamma$  can increase substantially when  $\beta$  increases. The three lines are the corresponding dynamic surface loads that demonstrate that at higher values of  $\beta$  the dynamical surface load can, but does not necessarily, become higher. This

**Table 6.** Barley OSA-Starch Samples<sup>a</sup>

sample	$DS$	$DB$	$Mw_i$ (10 <sup>6</sup> g/mol) <sup>b</sup>	$Mw_f$ (10 <sup>6</sup> g/mol) <sup>b</sup>	$r_{rms}$ (nm) <sup>b</sup>
B39-22	0.022	0.055	39	12	38
B27-21	0.021	0.050	27	8.6	44
B86-10	0.010	0.053	86	6.7	41

<sup>a</sup>  $DS$  is the degree of substitution, and  $DB$  is the degree of branching. The subscripts  $i$  and  $f$  denote initial and final average molar mass and refer to non-homogenized and homogenized samples, respectively.  $r_{rms}$  is the root-mean-square radius after homogenization. <sup>b</sup> From ref 10.

**Figure 5.** The relationship between the surface substituent density ( $\beta$ ) and the surface load ( $\Gamma$ ). The lines indicate the approximate corresponding dynamic surface loads.

is again an indication of the influence of kinetics during the adsorption, which will ultimately influence the surface load obtained.

For a macromolecule to adsorb and remain adsorbed at an interface, it is necessary that the adsorption energy is substantially larger than  $kT$  (21), for instance,  $30kT$ . Even though the adsorption energy per monomer unit is quite low, the total adsorption energy for a macromolecule can become high. The adsorption energy is thus related to the number of monomer units with a high affinity for the interface, which in our case corresponds to the  $DS$ . As the  $DS$  of the OSA samples must be considered low (on average every 50th to 100th glucose unit is substituted), it is likely that the lower molar mass components in the samples will have a lower probability of adsorbing at the interface. It is possible to estimate the limiting number of monomer units in a macromolecule for adsorption to occur with the following expression:

$$N_{\min} = \frac{U}{A_{\text{subst}} \cdot \gamma_{o/w} \cdot DS} \quad (5)$$

where  $N_{\min}$  is the minimum number of monomer units,  $U$  is the adsorption energy per macromolecule,  $A_{\text{subst}}$  is the surface area of the hydrophobic substituents, and  $\gamma_{o/w}$  is the surface tension of the corresponding hydrocarbon of the substituents. By estimating  $A_{\text{subst}}$  to  $3.7 \times 10^{-19} \text{ m}^2$ ,  $\gamma_{o/w}$  to  $50 \text{ mN m}^{-1}$ , and assuming an adsorption energy of  $30kT$  and that one-half of the substituents are in contact with the interface upon impact, we obtain a limit of about 1680 monomer units for an OSA-starch with a  $DS$  of 0.8%. This corresponds to a limiting molar mass for adsorption of about  $3 \times 10^5 \text{ g/mol}$ , and this estimation suggests that the adsorption of larger molecules in the sample is favored due to their higher adsorption energy. It also gives a possible explanation to the poor adsorption yield of the OSA-

starch samples with a comparably low molar mass ( $c_{\text{ads}}/c_0 = 16\text{--}32\%$ ), that is, samples with a high fraction of low molar mass material, as these molecules are unable to achieve a sufficient adsorption energy. This effect is obviously also related to the amylose content (about 20% in potato starch) as amylose has a comparatively low molar mass.

Thus, we conclude that the results in this study showed that two of the three OSA-starch samples were efficient emulsifiers, as the surface area increased with initial bulk concentration and gave surface loads of approximately  $1\text{--}2\text{ mg m}^{-2}$ . The third sample (P23-14) was a less efficient emulsifier, and the surface area did not depend on the initial concentration. The surface loads for this sample could become high and reached  $10\text{ mg m}^{-2}$ . We believe that this behavior is due to kinetic factors during the adsorption and the interplay between the degree of substitution and other physical parameters such as the molar mass and molecular size of the OSA-starch. The surface substituent density ( $\beta$ ) describes the relationship between these parameters, and the results show that the surface loads that can be obtained become higher when  $\beta$  increases. When the surface of the emulsion is small in relation to the concentration of the OSA-starch in the solution, a competition for adsorption sites is likely to occur, and as adsorption occurs, rapidly little time is available for optimization of the OSA-starch at the interface. This can make kinetic factors important and cause jamming and close-packing of the macromolecules at the surface. In turbulent flow fields, such as in a high-pressure homogenizer, the mass transport to the interface favors the adsorption of larger molecules, as they will be transported more rapidly to the interface. The larger molecules will also have a higher substituent density and adsorption energy than smaller ones, assuming that the hydrophobic substituents are homogeneously distributed in the samples. This is likely to increase the surface loads and strengthen the effect of kinetic adsorption factors as the large molecules will overrepresented at the surface.

#### NOTE ADDED AFTER ASAP PUBLICATION

The original posting of January 23, 2007, has been corrected. There was a minor revision to the second to last paragraph of the Discussion section in the revised ASAP posting of January 24, 2007.

#### LITERATURE CITED

- Dickinson, E. Hydrocolloids at interfaces and the influence on the properties of dispersed systems. *Food Hydrocolloids* **2003**, *17*, 25–39.
- Akhtar, M.; Dickinson, E.; Mazoyer, J.; Langendorff, V. Emulsion stabilizing properties of depolymerized pectin. *Food Hydrocolloids* **2002**, *16*, 249–256.
- Caldwell, C. G.; Wurzburg, O. B. Polysaccharide derivatives of substituted dicarboxylic acids. U.S. Patent 2,661,349, 1953.
- Shogren, R. L.; Viswanathan, A.; Felker, F.; Gross, R. A. Distribution of octenyl succinate groups in octenyl succinic anhydride modified waxy maize starch. *Starch/Stärke* **2000**, *52*, 196–204.
- Viswanathan, A. Effect of degree of substitution of octenyl succinate starch on the emulsification activity on different oil phases. *J. Environ. Polym. Degrad.* **1999**, *7*, 191–196.
- Tesch, S.; Gerhards, C.; Schubert, H. Stabilization of emulsions by OSA starches. *J. Food Eng.* **2002**, *54*, 167–174.
- Nilsson, L.; Bergenståhl, B. Adsorption of hydrophobically modified starch at the oil/water interface during emulsification. *Langmuir* **2006**, *22*, 8770–8776.
- Walstra, P. Formation of emulsions. In *Encyclopedia of Emulsion Technology Volume I: Basic Theory*; Becher, P., Ed.; Marcel Dekker Inc.: New York, 1983; pp 57–127.
- Modig, G.; Nilsson, L.; Bergenståhl, B.; Wahlund, K. G. Homogenization induced disruption of hydrophobically modified starch as measured by FFF-MALS. *Food Hydrocolloids* **2006**, *20*, 1087–1095.
- Nilsson, L.; Leeman, M.; Wahlund, K. G.; Bergenståhl, B. Mechanical degradation and changes in conformation of hydrophobically modified starch. *Biomacromolecules* **2006**, *7*, 2671–2679.
- Nilsson, G. S.; Bergquist, K.-E.; Nilsson, U.; Gorton, L. Determination of the degree of branching in normal and amylopectin type potato starch with  $^1\text{H-NMR}$  spectroscopy. *Starch/Stärke* **1996**, *48*, 352–357.
- Richardson, S.; Nilsson, G. S.; Bergquist, K.-E.; Gorton, L.; Minschnik, P. Characterisation of the substituent distribution in hydroxypropylated potato amylopectin starch. *Carbohydr. Res.* **2000**, *328*, 365–373.
- Åman, P.; Westerlund, E.; Theander, O. Determination of starch using a thermostable alpha-amylase. In *Methods in Carbohydrate Chemistry Volume 10*; BeMiller, J. N., Manners, D. J., Sturgeon, R. J., Eds.; John Wiley & Sons Inc.: New York, 1994; pp 111–115.
- Rotenberg, Y.; Boruvka, L.; Neumann, A. W. Determination of surface tension and contact angle from the shapes of axisymmetric fluid interfaces. *J. Colloid Interface Sci.* **1983**, *93*, 169–83.
- Thompson, J. C.; Hamori, E. A kinetic investigation of the amylose-iodine reaction. *J. Phys. Chem.* **1971**, *75*, 272–280.
- Paris, E.; Cohen Stuart, M. A. Adsorption of hydrophobically modified 6-carboxypullulan on hydrophobic surface. *Macromolecules* **1999**, *32*, 462–470.
- Demé, B.; Lee, L.-T. Adsorption of a hydrophobically modified polysaccharide at the air/water interface: Kinetics and structure. *J. Phys. Chem. B* **1997**, *101*, 8250–8258.
- Simon, S.; Picton, L.; Le Cerf, D.; Muller, G. Adsorption of amphiphilic polysaccharides onto polystyrene latex particles. *Polymer* **2005**, *46*, 3700–3707.
- Poncet, C.; Tiberg, F.; Audebert, R. Ellipsometric study of the adsorption of hydrophobically modified polyacrylates at hydrophobic surfaces. *Langmuir* **1998**, *14*, 1697–1704.
- Linse, P. Adsorption of weakly charged polyelectrolytes at oppositely charged surfaces. *Macromolecules* **1996**, *29*, 326–336.
- Evans, D. F.; Wennerström, H. *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet*, 2nd ed.; Wiley-VCH: New York, 1999.
- Modig, G., personal communication.

---

Received for review July 24, 2006. Revised manuscript received November 27, 2006. Accepted December 1, 2006. Financial support from the Center for Amphiphilic Polymers from Renewable Resources (CAP), Lund, Sweden, is gratefully acknowledged.

JF062087Z