Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Research 339 (2004) 1105–1111
Carbohydrate RESEARCH

Two-dimensional rotating-frame Overhauser spectroscopy (ROESY) and ^{13}C NMR study of the interactions between maltodextrin and an anionic surfactant

Apiradee Wangsakan,[a] David J. McClements,[a,*] Pavinee Chinachoti[a,†] and L. Charles Dickinson[b]

[a]*Biopolymers and Colloids Research Group, Department of Food Science, University of Massachusetts, Amherst, MA 01003, USA*
[b]*Conte National Center for Polymer Research, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA*

Received 12 June 2003; accepted 29 January 2004

Abstract—Rotational frame nuclear Overhauser effect spectroscopy (ROESY) and ^{13}C NMR measurements were carried out to study the molecular interaction between maltodextrin, a digestive byproduct of starch, and an anionic surfactant. Significant differences in chemical shifts were observed when sodium dodecyl sulfate (SDS) was introduced into the maltodextrin (DE 10) solutions. ^{13}C NMR measurement indicated that there were downfield shifts and broadening of peaks, especially in the region of 75–81 and 100–103 ppm, which were assigned to carbons 1 and 4 of the D-glucopyranose residues of maltodextrin, respectively. ROESY spectra indicated cross-peaks between the SDS and maltodextrin protons. These peaks can arise only in the case of the designated SDS protons and maltodextrin protons being less than 0.5 nm apart for a substantial period of time. The most intense cross-peaks are those between the central CH_2 protons of SDS near 1.2 ppm and the maltodextrin protons ranging from 3.5 to 3.9 ppm. The SDS-H3 CH_2 protons were resolved from the bulk of the SDS protons, with peaks and shoulders at 1.25 ppm, which indicated an especially strong interaction of the SDS hydrophobic tail with MD6 and some less intense interactions with MD2, 4, and 5.

Keywords: ROESY; ^{13}C NMR spectroscopy; Maltodextrin; Surfactant; Helical structure; Conformation

1. Introduction

It is well documented that biopolymers such as polysaccharides and proteins can interact with surfactants in aqueous solutions.[1–3] Maltodextrin, a digestive byproduct of starch, contains linear amylose and branched amylopectin degradation products[4] that can interact with several components such as water,[5–7] iodine,[8] fatty acids,[9–15] and anionic surfactants.[16] These complexes may influence the qualities and properties of natural starch itself,[17–20] as well as many food products.[21–23] Maltodextrin can also complex with certain enantiomeric compounds of pharmaceutical interest such as simendan, ibuprofen, and warfarin, which has been attributed to random coil-helix conformation transitions.[24]

It is possible to identify two types of polysaccharide–lipid interactions: (1) the molecular 'binding' of an individual lipid molecule to the polysaccharide, which is best exemplified with the well-known amylose–lipid complex; and (2) the interaction between a lipid phase (micelles) and the polysaccharide.[20] A number of studies have focused on the former case including molecular modeling,[12] thermal behavior by DSC,[9,17] X-ray diffraction,[25] and ^{13}C solid-state NMR measurement.[26,27] It is often assumed that the fatty acid tail is a 'stem' (planar zigzag) inside the helix whose inner surface is hydrophobic because of the carbon–hydrogen matrix provided

* Corresponding author. Tel.: +1-413-5451019; fax: +1-413-5451262; e-mail: mcclements@foodsci.umass.edu
† Present address: Science and Technology Center, PO Box 1658, Topeka, KS 66601-1658, USA.

0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.01.019

by the helically wound α-(1→4) glucan.[11] Given the pitch of the 6-fold helix and the planar zigzag geometry of the fatty acid tail, about 10% weight by weight of the polymers would suffice to create 100% complexation.

In the conformational analysis of the molecular interaction, two-dimensional (2D) homonuclear NMR methods can provide valuable information. There have been 2D NMR studies on the complexes of maltose, maltoheptose, cyclodextrin,[28] the interaction between polysaccharides,[29] the linkages in polysaccharides,[30] the structure of amylose,[31] and the interaction of polysaccharides with surfactants.[32] Rotating frame nuclear Overhauser effect spectroscopy (ROESY) is one of the 2D NMR methods for correlating which signals arise from protons that are close in space.[33,34] A ROESY spectrum yields through-space correlations via the rotational nuclear Overhauser effect (ROE). ROESY is especially useful for cases where nuclear Overhauser effect spectroscopy (NOESY) signals are weak because they are near the transition between negative and positive. On the other hand, the ROE cross-relaxation rate is always positive.[30]

Our previous work[16] studied the interaction between maltodextrin and sodium dodecyl sulfate (SDS) by isothermal titration calorimetry (ITC) and surface tension measurement; however, these two methods cannot observe the conformational changes or molecular details of the interaction. Therefore, the objective of this work is to study the molecular interaction between maltodextrin and SDS as a model for the carbohydrate–lipid interaction by using NMR methods including ROESY, ^{13}C NMR spectroscopy, and T_1 relaxation.

2. Results and discussion

2.1. Chemical shifts

^{13}C NMR spectra were obtained on a 25.4 mM SDS solution, a 40.6 mM maltodextrin (DE 10) solution, and their mixture at these same concentrations, respectively, at 150 MHz with constant proton decoupling (Fig. 1). Note that the concentration of maltodextrin was calculated based on theoretical average molecular weight (= 1800) or about 10% SDS (w/w) of maltodextrin weight. This maltodextrin concentration was chosen so as to obtain an adequate signal-to-noise ratio and reasonable experimental time frame. Previous experiments using isothermal titration calorimetry (ITC) have shown that maltodextrin is only partially saturated with SDS at this concentration; hence, we expected the SDS–maltodextrin mixture to consists of free maltodextrin and

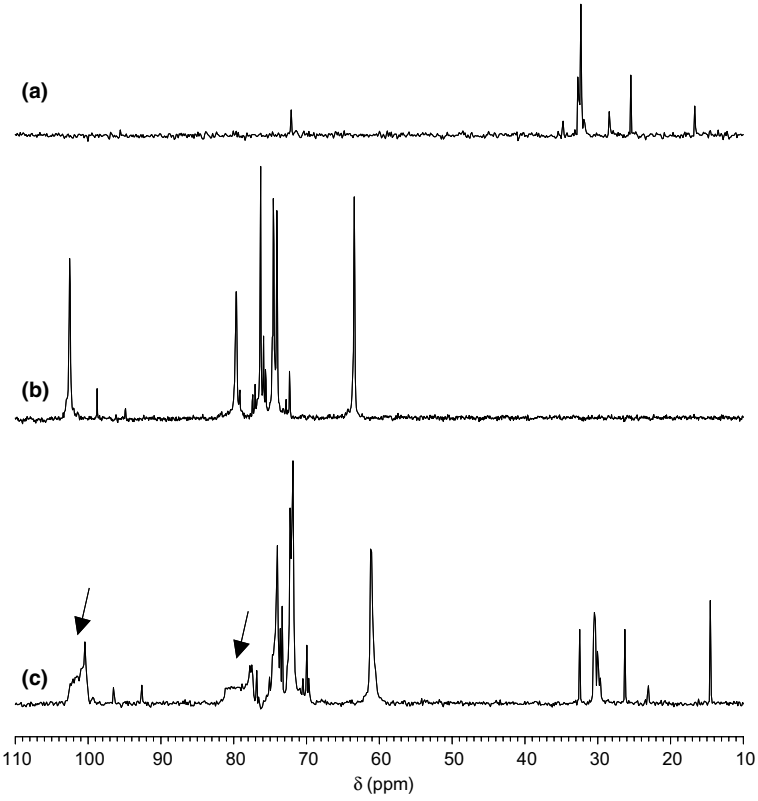

Figure 1. ^{13}C NMR spectra of (a) SDS, (b) maltodextrin DE10, and (c) maltodextrin–SDS mixture. All samples were in aqueous solution with 10% D_2O.

the SDS–maltodextrin complex. All samples contained 10% D_2O for field-frequency lock, and the experiments were carried out at 298 K. The spectrum of SDS (Fig. 1a) in aqueous solution was similar to that reported previously.[35] The SDS spectrum showed a clear resolution of each of the 12 carbons of the chain. These peaks were readily assignable based on the standard spectra (Sadtler Index),[36] ACD (Advanced Chemistry Development, Toronto, Canada) calculated spectrum at 298 K as shown in the molecular structure of SDS (Fig. 3) and Table 1.

In addition, the maltodextrin spectrum showed six major peaks at 102.5, 79.4, 76.4, 74.6, 74.1, and 63.48 ppm and a series of peaks in the vicinity of the six main peaks at approximately 15% of the intensity of the major peak (Fig. 1b). These peaks were also assignable based on the standard spectra (Sadtler Index),[36] ACD (Advanced Chemistry Development, Toronto, Canada) calculated spectrum at 298 K as shown in the molecular structure of glucose polymers (Fig. 3) and Table 1. The spectrum was similar to those of degraded starches reported by Gidley. [37] Extensively degraded starches contain significant amounts of glucose as well as higher *gluco*-oligosaccharides. The Gidley[37] study suggested that even in significantly degraded starches, the resonance (67–68 ppm.) of C-6 in the branching residue was very broad.[37] Jane et al.[38] showed that the chemical shift of C-6 was around 60 ppm. They also suggested that the minor signals that appear in the region of 68–74 ppm, specifically 69, 72, and 72.5 ppm, corresponded to a small amount of α-(1 → 6)-branch linkages.[38]

Figure 1c shows the spectrum of the maltodextrin–SDS mixture. Significant differences in chemical shifts were observed when SDS was present in the maltodextrin solution. There were downfield shifts and a dramatic broadening of peaks, especially in the region of 75–81 and 100–103 ppm, which was also observed in the studies where triiodine was added to amylodextrin[38] and to *malto*-oligosaccharides.[8] They suggested that the changes involved carbon 1 and 4 (the carbons involved in glucosidic bonds) of the D-glucopyranose residues of the amylodextrin. These changes have been interpreted as the changes in the torsion angles (ϕ and ψ) of the α-(1 → 4) glucosidic linkage, due to formation of a helical structure.[38] Interestingly the minor peaks in the carbon spectrum do not show any change. The SDS peaks remain observable in the mixture with some loss of resolution.

It would be interesting to theoretically assign these changed maltodextrin lineshapes. It seems that it is most likely a distribution of chemical-shift values due to variability in the helix—a range of strain values or bond angles either due to the range of helix lengths, or over the range of a typical helix. The cause of this range of strain values is not known specifically.

Table 1. The maltodextrin and SDS spectrum at 298 K and the relaxation values (T_1) of maltodextrin (MD), SDS, and maltodextrin–SDS mixture

Assign carbon[a]	Chemical shift observed (ppm)	T_1[c], C (s) of separated components	T_1[c], C (s) of a mixture
MD-C1	102.50	0.35	0.29–0.41
MD-C4	79.40	0.41	0.25–0.53
MD-C2, 3, 5[b]	76.40, 74.60, 74.10	0.40, 0.40, 0.40	0.43, 0.43, 0.43
MD-C6	63.48	0.22	0.28
SDS-C1	72.30	1.07	0.41
SDS-C2	34.68	1.82	0.99
SDS-C3	32.44	1.05	0.70
SDS-C4	32.44	1.05	0.70
SDS-C5	32.44	1.05	0.70
SDS-C6	32.28	0.99	0.65
SDS-C7	32.12	1.33	0.75
SDS-C8	31.20	1.03	0.72
SDS-C9	31.79	1.20	0.72
SDS-C10	28.26	1.39	0.68
SDS-C11	25.40	2.53	1.00
SDS-C12	16.65	3.64	2.49

[a] Assignment based on the standard spectra (Sadtler Index), ACD (Advanced Chemistry Development, Toronto, Canada).

[b] C-2, -3, and -5 are too close to resolve.

[c] Error on the broadened C-1 and C-4 peaks range from ±10% to ±25% for 50% probability of being in that range based on standard deviation of observed points from the fitted curve. Other values are ±5% or better.

2.2. Relaxation measurement

Relaxation times of the carbon resonances were measured by the simple inversion recovery technique for delay times ranging from 0.01 to 8 s. Intensity data was analyzed by using the relaxation fitting module of XWINNMR (Bruker–Biospin Inc., Billerica, MA). The results show a dramatic effect on SDS in a maltodextrin–SDS mixture (Table 1). The resonances in maltodextrin most affected by the formation of the helix show some significant changes in relaxation rates with the mixing. Curiously, the T_1 for the broadened lineshapes shows a range over the shape. For example, C-1 shows a lowering to 0.2 s at 103 ppm and rising to 0.4 s at 100 ppm. This would mean that the part of the peak at the original C-1 position, 102 ppm, shows a lengthening of relaxation time, whereas the most shifted C-1 part of the lineshape shows a shortening of the T_1. If we speculate that the most shifted is the most strained carbon, and thus has a longer correlation time, then the relaxation mode must be below the extreme narrowing limit. However, it seems strange that some carbons then have longer T_1's and shorter correlation times than those observed for free maltodextrin. The simplest interpretation of this would be that some helical C-1's are more mobile than those in the conformation of maltodextrin alone, and some C-1's are less mobile.

2.3. ROESY experiments

Rotational frame Overhauser NMR spectroscopy (ROESY) was carried out to study the molecular interactions in the maltodextrin–SDS complex (Figs. 2 and 3). These experiments utilize the dipolar interaction between protons at distances less than 5 Å. The overall ROE effect also depends on how rapidly the molecule tumbles in solution, and thus on the molecular mass and the organization of the molecules.[33,34] A ROESY spectrum was obtained from a mixture of 13.5 mM maltodextrin and 19.5 mM SDS in 9:1 H_2O–D_2O. These concentrations were the concentrations at which maltodextrin was saturated with SDS as determined in a previous study.[16]

Maltodextrin and SDS peaks were assigned based on their standard spectra (Sadtler Index),[36] ACD spectral simulations from libraries of like compounds, and comparison with authentic spectra of separate maltodextrin and SDS samples. The molecular structures of SDS and glucose polymers in Figure 3 show the numbering of the atoms for each molecule.

The ROESY cross-peaks between SDS and maltodextrin are shown in the sectional spectrum (Fig. 2). Other internal cross-peaks for maltodextrin interactions are observed, but are not of direct interest in this study. The ROESY peaks (Figs. 2 and 3) can arise only in the case of the designated SDS protons, and maltodextrin protons being less than 0.5 nm apart for a substantial period of time. The molecules may manifest a variety of conformations in their geometric relationship and interconvert between those configurations. The expanded 2D NMR spectrum (Fig. 3) is displayed so that mainly the SDS proton chemical shift region is on the vertical axis and the maltodextrin (and SDS-H1) chemical shift region is along the horizontal axis.

The most intense cross-peaks are those between the central CH_2 protons of SDS near 1.2 ppm and the whole 3.5–3.9 ppm range of maltodextrin protons. The single most intense peak is between MD2, 5, and those central SDS CH_2 protons (Fig. 3). (Note that MD stands for maltodextrin.) As the SDS-H3 CH_2 protons are resolved from the bulk of the SDS protons, the peaks, and shoulders at 1.25 ppm are evident, indicating an especially strong interaction with MD6 and some lesser intense interactions with MD2, 4, and 5. These peaks conclusively show that all of the CH_2 protons of SDS form a complex of some definite structure of longer

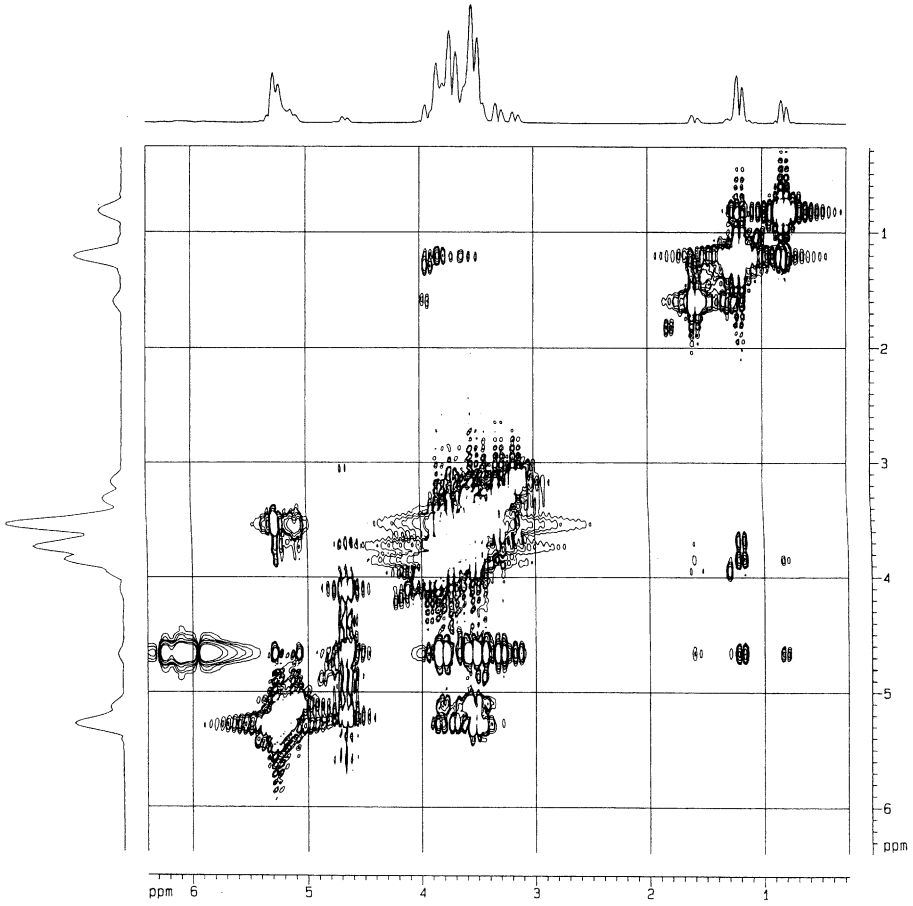

Figure 2. Proton–ROESY experiment of a maltodextrin–SDS mixture.

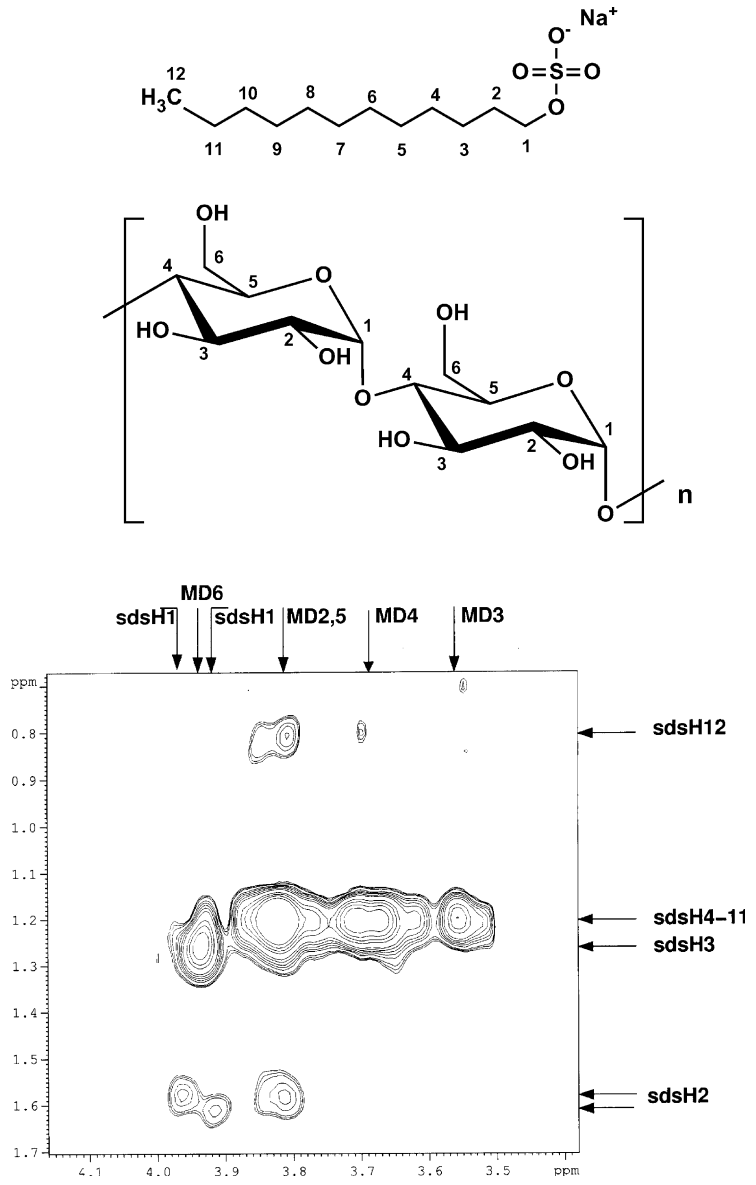

Figure 3. The molecular structures of sodium dodecyl sulfate (SDS) and two molecules of glucose polymers as a part of maltodextrin molecules; and numbered of each atom. ROESY cross-peak, expanded and amplified from Figure 2, of maltodextrin–SDS mixture. MD = maltodextrin and SDS = sodium dodecyl sulfate. The number after MD and SDS stands for the position assignment of each proton.

lifetime than the inverse of the line width, for example, 0.1 s.

The outlying peaks due the SDS CH_3 protons at 0.8 ppm and the SDS penultimate CH_2 from the SO_3 group are interesting. Clearly the CH_3 interacts preferably with MD4 and MD5 and not nearly as strongly with the rest of the MD protons. There are several much weaker peaks (figure not shown) near the noise floor, which indicates interactions less than 10% of the intensity of the largest SDS-H12 and MD2, 5 interactions. These multiple peaks could arise from a population of different structures or from the varying dipolar distances of the CH_3 protons to the various MD protons in some average structure. This can only be sorted out by a specific model calculation and comparison via quantitative interpretation of the ROESY data. In either case, the SDS CH_3 and MD2, 5 interactions are preferred or stronger.

The SDS-H2 peaks show a preference for MD2, 5, and 6 interactions; however, there are no weak peaks to other MD protons as was the SDS CH_3 case. It is curious that there seem to be two SDS-H2 and SDS-H1 cross-peaks, but one of these peaks could arise from some alternate geometry of the SDS in the maltodextrin, for example, an all *trans* and a *trans–gauche* conformation.

The weak cross-peak at (1.62, 3.92 ppm) arises due to the internal proximity of the SDS-H1 and SDS-H2

protons and could be used as an internal ROESY distance standard for quantity of the intensities to calculate explicit distances.

In conclusion, our data are consistent with previous studies, which suggest that the surfactant tail is present in a helical maltodextrin structure, and the surfactant promotes a coil-to-helix transition.

3. Experimental

3.1. Materials

Maltodextrin DE 10 (MALTRIN M 100) was obtained from Grain Processing Corporation (Muscatin, IA). Sodium dodecyl sulfate (SDS, L-4509) was purchased from Sigma Chemical Co. (St. Louis, MO). Deuterium oxide (D_2O) was purchased from Cambridge Isotope Laboratories (Andover, MA). Double-distilled water was used for the preparation of all solutions.

3.2. NMR spectroscopy

A Bruker–Biospin AVANCE 600 spectrometer (Billerica, MA) operating at a proton frequency of 600.03 MHz and using a 5.0-mm TXI Z-gradient probe was used to determine ^{13}C NMR spectra of the maltodextrin (DE 10) solution, the SDS solution, and the maltodextrin–SDS mixture solution. For all samples, double-distilled water was used as solvent with 10% D_2O added for frequency lock. ^{13}C chemical shifts, quoted in ppm from tetramethylsilane, were measured by reference to internal TMS or internal resonances. In addition to ^{13}C NMR measurement, the 2D ROESY experiments were performed. Mixing times were varied for optimization and in an effort to produce integrable off-diagonal peaks. Generally, 16 scans and 128 or 256 F1 slices were obtained. The ROESY pulse program was run with 6.78 μs, 90° pulses and a 150 ms spinlock at 2.9 kHz rf level. Temperature was stabilized at 289 K. States-TPPI quadrature detection as used in the F1 dimension so that the diagonal and off-diagonal peaks both had absorption lineshapes, but with opposite phase. Any spin diffusion (TOCSY) breakthrough would have the same phase as the diagonal peaks. Water signals were suppressed with the 'double watergate' technique.[39] Further analysis is required to demonstrate whether quantitation will yield more detailed structural information on the complex.

References

1. Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36–42.
2. Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255–300.
3. Goddard, E. D. Polymer-Surfactant Interaction. In *The Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC: Boca Raton, Ho, 1993; pp 123–201.
4. Chronakis, I. S. *Crit. Rev. Food Sci.* **1998**, *38*, 599–637.
5. Radosta, S.; Schierbaum, F.; Yuriev, W. P. *Starch/Stärke* **1989**, *41*, 428–430.
6. Radosta, S.; Schierbaum, F.; Yuriev, W. P. *Starch/Stärke* **1990**, *42*, 142–147.
7. Gutierrez, A. M.; Baianu, I. C. *J. Food Sci.* **1990**, *55*, 462–465.
8. Vetter, D.; Thorn, W. *Starch/Stärke* **1992**, *44*, 271–274.
9. Biliaderis, C. G.; Page, C. M.; Slade, L.; Sirett, R. R. *Carbohydr. Polym.* **1985**, *5*, 367–389.
10. Eliasson, A.-C.; Krog, N. *J. Cereal Sci.* **1985**, *3*, 239–248.
11. Godet, M. C.; Buléon, A.; Tran, V.; Colonna, P. *Carbohydr. Polym.* **1993**, *21*, 91–95.
12. Godet, M. C.; Tran, V.; Delage, M. M.; Buléon, A. *Int. J. Biol. Macromol.* **1993**, *15*, 11–16.
13. Godet, M. C.; Bizot, H.; Buléon, A. *Carbohydr. Polym.* **1995**, *27*, 47–52.
14. Jovanovich, G.; Añón, M. C. *Lebensm.–Wiss. Technol.* **1999**, *32*, 95–101.
15. Tufvesson, F.; Eliasson, A.-C. *Carbohydr. Polym.* **2000**, *43*, 359–365.
16. Wangsakan, A.; Chinachoti, P.; McClements, D. J. *J. Agric. Food Chem.* **2001**, *49*, 5039–5045.
17. Eliasson, A.-C. *Thermochim. Acta* **1994**, *246*, 343–356.
18. Eerlingen, R. C.; Cillen, G.; Delcour, J. A. *Cereal Chem.* **1994**, *71*, 170–177.
19. Svensson, E.; Autio, K.; Eliasson, A.-C. *Food Hydrocolloids* **1998**, *12*, 151–158.
20. Eliasson, A.-C. Lipid–Carbohydrate Interactions. In *Interactions: The Keys to Cereal Quality*; Hamer, R. J., Hoseney, R. C., Eds.; American Association of Cereal Chemists: St. Paul, MN, 1998; pp 47–79.
21. Baines, Z. V.; Morris, E. R. Suppression of Perceived Flavor and Taste by Hydrocolloids. In *Food Colloids*; Bee, R. D., Richmond, P., Mingins, J., Eds.; Royal Society of Chemistry: Cambridge, UK, 1989; p 184.
22. Bakker, J. Flavor Interactions with the Food Matrix and their Effects on Perception. In *Ingredient Interactions: Effects on Food Quality*; Gaonkar, A. G., Ed.; Marcel Dekker: New York, 1995.
23. Gaonkar, A. G. *Ingredient Interactions: Effects on Food Quality*; Marcel Dekker: New York, 1995.
24. Soini, H.; Stefansson, M.; Riekkola, M.; Novotny, M. V. *Anal. Chem.* **1994**, *66*, 3477–3484.
25. Biliaderis, C. G.; Seneviratne, H. D. *Carbohydr. Polym.* **1990**, *13*, 185–206.
26. Snape, C. E.; Morrison, W. R.; Maroto-Valer, M. M.; Karkalas, J.; Pethrick, R. A. *Carbohydr. Polym.* **1998**, *36*, 225–237.
27. Lebail, P.; Buléon, A.; Shiftan, D.; Marchessault, R. H. *Carbohydr. Polym.* **2000**, *43*, 317–326.
28. Bekiroglu, S.; Kenne, L.; Sandstrom, C. *J. Org. Chem.* **2003**, *68*, 1671–1678.
29. Tezuka, Y. *Biopolymers* **1994**, *34*, 1477–1482.
30. Cipollo, J. F.; Trimble, R. B.; Rance, M.; Cavanagh, J. *Anal. Biochem.* **2000**, *278*, 52–58.
31. Yamamoto, C.; Yashima, E.; Okamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12583–12589.
32. Gjerde, M. I.; Nerdal, W.; Hoiland, H. J. *Colloid Interface Sci.* **1996**, *183*, 285–288.
33. Sanders, J.; Hunter, B. K. *The Modern NMR Spectroscopy—A Guide for Chemists*. 2nd ed.; Oxford University Press: New York, 1993; pp 160–176.
34. Hull, W. E. Experimental Aspects of Two-Dimensional NMR. In *The Two-Dimensional NMR Spectroscopy—*

Applications for Chemists and Biochemists; Croasmun, W. R., Carlson, R. M. K., Eds., 2nd ed.; VCH: New York, 1994; pp 337–343.
35. Varshney, M. *Colloids Surf.* **1995**, *96*, 273–275.
36. *The Sadtler Standard Spectra: Carbon-13 NMR Spectra*; Sadtler Research Laboratory: Philadelphia, PA.
37. Gidley, M. J. *Carbohydr. Res.* **1985**, *139*, 85–93.
38. Jane, J. L.; Robyt, J. F.; Huang, D. H. *Carbohydr. Res.* **1985**, *140*, 21–35.
39. Liu, M.; Mao, X.; Ye, C.; Huang, H.; Nicholson, J. K.; Lindon, J. C. *J. Magn. Reson.* **1998**, *132*, 125–129.