Microencapsulating Properties of Sodium Caseinate

Sean A. Hogan, Brian F. McNamee,[†] E. Dolores O'Riordan,* and Michael O'Sullivan

Department of Food Science, Faculty of Agriculture, University College Dublin, Belfield, Dublin 4, Ireland

Emulsions were prepared with 5% (w/v) solutions of sodium caseinate (Na Cas) and soy oil at oil/protein ratios of 0.25–3.0 by homogenization at 10–50 MPa. Emulsions were spray-dried to yield powders with 20–75% oil (w/w). Emulsion oil droplet size and interfacial protein load were determined. Microencapsulation efficiency (ME), redispersion properties, and structure of the powders were analyzed. The size of emulsion oil droplets decreased with increasing homogenization pressure but was not influenced by oil/protein ratio. Emulsion protein load values were highest at low oil/protein ratios. ME of the dried emulsions was not affected by homogenization pressure but decreased from 89.2 to 18.8% when the oil/protein ratio was increased from 0.25 to 3.0, respectively. Mean particle sizes of reconstituted dried emulsions were greater than those of the original emulsions, particularly at high oil/protein ratios (>1.0), suggesting destabilization of high-oil emulsions during the spray-drying process.

Keywords: *Sodium caseinate; encapsulation; spray-drying; emulsion*

INTRODUCTION

Microencapsulation is a technology that allows sensitive ingredients to be physically enveloped in a protective matrix or "wall" material in order to protect these ingredients or "core" materials from adverse reactions, volatile loss, or nutritional deterioration. Spray-drying is the microencapsulation technique most commonly used in the food industry (*1*) and is employed to encapsulate a wide range of ingredients (*2, 3*). Carbohydrates such as maltodextrins, starches, corn syrup solids, and acacia gums have all been widely used as encapsulating agents. However, these wall materials, in general, have poor interfacial properties and must be modified or used in conjunction with a surface active agent to encapsulate oil-based materials (*4*). In contrast, the amphiphilic character and emulsification properties of proteins and, in particular, sodium caseinate (Na Cas) (*5, 6*) would appear to offer the physical and functional characteristics required to encapsulate lipid core materials. Much of the work on the surface activity and emulsifying properties of Na Cas relates to dilute protein solutions and high oil/protein ratios (*7, 8*). The use of Na Cas as an encapsulating agent involves drying emulsions of higher protein concentrations and lower oil phase volumes than those normally used in emulsion studies. Previous work has shown that Na Cas provides an effective wall material for the retention of orange peel oil (*9*). The effectiveness of Na Cas/lactose solutions as encapsulating agents for soybean oil (*10*) and fats of different melting points (*11*) has also been evaluated using electron spectroscopy for chemical analysis (ESCA). The effect of the oil/protein ratio on the emulsification and encapsulation properties of Na Cas, at levels consistent with potential applications in different microencapsulation systems, has not been fully investigated. The objectives of this study were to assess the potential of Na Cas as a wall material for the encapsulation of soy oil and to relate the properties of the spray-dried powders to those of the emulsions from which they were made.

EXPERIMENTAL PROCEDURES

Materials. Na Cas (protein content = 85%) was obtained from Avonmore plc., Kilkenny, Ireland. Soy oil was obtained from Anglia Oils Ltd., Kingston-Upon-Hull, North Humberside, England. All chemicals were of GPR grade and were purchased from BDH Laboratories Ltd., Poole, Dorset, England.

Emulsion Preparation. Soy oil was blended with aqueous solutions of Na Cas (5% w/v) using an Ultra-Turrax T25 high-shear probe mixer (Janke & Kunkel GmbH, Staufen, Germany) operated at 13500 rpm for 30 s to give pre-emulsions with oil/Na Cas ratios of 0.25–3.0 (w/w). In the remainder of the text this will be referred to as oil/protein ratio. The resultant emulsions were further homogenized at 10–50 MPa with four recirculations using a high-pressure laboratory valve homogenizer (Niro Soavi NS 1001 L, Parma, Italy) and subsequently spray-dried to yield powders with oil contents ranging from 20 to 75% (dry wt). Sodium azide (0.01%) was added to the emulsions as a preservative.

Emulsion Particle Size Measurements. Emulsion particle size distributions were determined by a laser diffraction technique (Malvern Mastersizer S, Malvern Instruments Ltd., Worcs., England). Calculation of the particle size distribution was based on a relative refractive index of 1.11 and absorption of 0.0001. Distilled water was used as the dispersing medium. Analysis of the size distribution also yielded specific fat surface area (square meters per gram of oil).

Viscosity. The apparent viscosities of emulsions at various oil/protein ratios were measured at 25 °C using a stress-controlled rheometer (Physica Rheolab MC 100, Paar Scientific Ltd., Raynes Park, London, England) fitted with a concentric cylinder geometry (MS-Z1 DIN) at a constant shear rate of 100 s^{-1}.

Protein Load Measurements. The amount of protein adsorbed onto the fat surfaces of the emulsions was determined by measuring the protein content of the aqueous subnatant phase following centrifugation at 17600g for 30 min at 4 °C

Microencapsulating Properties of Sodium Caseinate

J. Agric. Food Chem., Vol. 49, No. 4, 2001   **1935**

(Beckman J2-HS centrifuge, Beckman-RIIC Ltd., Bucks., England). An aliquot of the subnatant phase was removed by syringe and filtered through a 0.22 μm Millipore filter, and the protein content was determined by macro-Kjeldahl. The amount of protein adsorbed at fat surfaces was calculated from the difference between the protein concentration of the original emulsion and that of the subnatant following centrifugation and was expressed as protein load (Γ):

protein load (mg m^{-2}) =

total protein adsorbed (mg)/total fat surface area (m^2)

Spray-Drying. The emulsions were dried in a laboratory scale spray-drier equipped with a 0.5 mm, two-fluid, nozzle atomizer (LabPlant SD-04, Huddersfield, West Yorkshire, England). Emulsions were pumped to the spray-drier at room temperature at a flow rate of ~20 mL/min and dried at an inlet temperature of 180 °C and an outlet temperature of ~95 °C. The dried powder was collected and stored in airtight containers at 4 °C.

Microencapsulation Efficiency. Total oil content of the powder was determined according to the Röse−Gottlieb method (*12*). Extractable oil was determined by gently shaking 2.5 g of powder with 100 mL of petroleum ether in a sealed 250 mL glass bottle at 25 °C for 15 min. The solvent was filtered (Whatman No. 41), and extractable fat in the filtrate was determined gravimetrically on a 50 mL aliquot, following removal of the solvent by rotary evaporation (Resona Labo Rota 300) and subsequent oven-drying at 103 °C for 1 h. Microencapsulation efficiency (ME) was calculated as follows:

ME = [(total oil − extractable oil)/total oil] × 100

Powder Particle Size. Powder particle size was determined by laser diffraction, as described for the determination of emulsion particle size, following dispersion of the dried emulsion powder sample in propan-2-ol (*9*).

Redispersion Behavior. Redispersion characteristics of the powders were determined by mixing 0.5 g of powder in 150 mL of water or 150 mL of water containing 1% (w/v) Tween 20 [polyoxyethylene (20) sorbitan monolaurate]. The mixtures were stirred for 30 min at room temperature, and particle size distributions of the resulting dispersions were determined by laser diffraction as described for the determination of emulsion particle size.

Moisture Content. Moisture content of the powders was determined gravimetrically by oven-drying at 103 °C to constant weight.

Scanning Electron Microscopy. Scanning electron microscopy was used to study the surface and internal structures of the spray-dried powders. Powder particles were attached to a sample stub with double-sided sticky tape and fractured with a razor blade (*13*). The specimens were sputter coated with gold using a Polaron sputter coater E 500 (VG Microtech, East Sussex, England) and examined using a JEOL JSM-5410 LV scanning electron microscope (JEOL UK Ltd., Welwyn Garden City, Herts., England) at an accelerating voltage of 10 or 15 kV.

Statistical Analysis. All results represent the means of four replicates. PROC GLM of SAS (*14*) was used to determine differences between treatment means. Treatment means were considered significantly different at $P \leq 0.05$.

RESULTS AND DISCUSSION

Emulsification of Soy Oil/Protein. *Emulsion Particle Size.* The effect of homogenization pressure on emulsion oil droplet size (oil/protein ratio = 1.0) is shown in Table 1. Volume average diameter ($D_{4,3}$) of the pre-emulsion oil droplets was 10.4 μm and decreased significantly on subsequent homogenization at 20 MPa (0.87 μm). Increasing homogenization pressure up to 50 MPa did not result in further change in emulsion droplet

Table 1. Effect of Homogenization Pressure on Characteristics of Na Cas Stabilized Soy Oil Emulsions and Spray-Dried Emulsions[a]

	emulsion	powder	
homogenization pressure (MPa)	oil droplet size ($D_{4,3}$) (μm)	particle size ($D_{4,3}$) (μm)	ME (%)
pre-emulsion	10.39[a]	31.02[a]	27.41[a]
10	1.45[b]	18.96[ab]	54.70[b]
20	0.87[c]	16.33[c]	50.14[c]
30	0.58[d]	18.37[bc]	57.48[b]
40	0.47[d]	18.49[bc]	53.60[b]
50	0.41[d]	20.39[b]	51.09[c]

[a] Emulsions prepared at an oil/protein ratio of 1.0. Means within the same column with different superscript numbers differ significantly ($P < 0.05$).

Table 2. Effect of Oil/Protein Ratio on Characteristics of Na Cas Stabilized Soy Oil Emulsions and Spray-Dried Emulsions[a]

	emulsion		powder	
oil/ protein ratio	apparent viscosity (mPa s^{-1})	protein load (mg m^{-2})	particle size ($D_{4,3}$) (μm)	ME (%)
0.25	2.82[a]	3.10[a]	14.50[a]	89.15[a]
0.38	ND[b]	2.98[a]	ND	ND
0.50	3.15[a]	2.26[bc]	14.9[a]	74.51[b]
0.75	3.18[a]	2.40[b]	16.99[b]	64.29[c]
1.0	4.20[b]	2.14[bc]	19.89[c]	46.14[d]
1.5	4.30[b]	2.11[bc]	20.45[c]	35.60[e]
2.0	4.59[b]	2.04[c]	19.80[c]	23.70[f]
3.0	6.82[c]	2.04[c]	32.30[d]	18.80[g]

[a] Emulsions prepared at a homogenization pressure of 50 MPa. Means within the same column with different superscript numbers differ significantly ($P < 0.05$). [b] Not determined.

size. This initial decrease in oil droplet size may be related to the greater turbulence and shear forces associated with increased homogenization pressure. With sufficient Na Cas present to adsorb to newly exposed droplet interfaces, the homogenization pressure becomes the primary factor in the determination of the emulsion oil droplet size. $D_{4,3}$ values of oil droplets homogenized at 50 MPa were not influenced by the oil/protein ratio in the range from 0.25 to 3.0, and specific surface areas of these emulsions ranged from 17 to 18 m^2 g^{-1}. Unimodal particle size distributions showing normal distributions were observed for all emulsions (results not shown). The results indicated that fine oil/water emulsions, necessary for microencapsulation by spray-drying (*15*) were obtained in most cases.

Viscosity. Apparent viscosity of the emulsions increased significantly from 2.8 to 6.8 mPa s^{-1} when the oil/protein ratio was increased from 0.25 to 3.0 respectively (Table 2). The increase in apparent viscosity was most likely attributable to increases in the dispersed phase volume and emulsion total solids concentration. The viscosity of an emulsion is important as it is known to have implications for its behavior on subsequent drying and the rate of formation of a semipermeable membrane at the surface of drying particles, movement of core materials to the surface of powder particles during the spray-drying process, the size of dried powder particles, and the thickness of capsule walls (*16, 17*).

Protein Load. The effect of increasing oil/protein ratio on protein load is shown in Table 2. Protein load values (Γ) at oil/protein ratios of 0.25 and 3.0 were significantly different ($P < 0.05$) with values of 3.1 and 2.0 mg m^{-2}, respectively. Increasing oil/protein ratios from 0.50 to 3.0 had no significant effect on protein load. Protein load
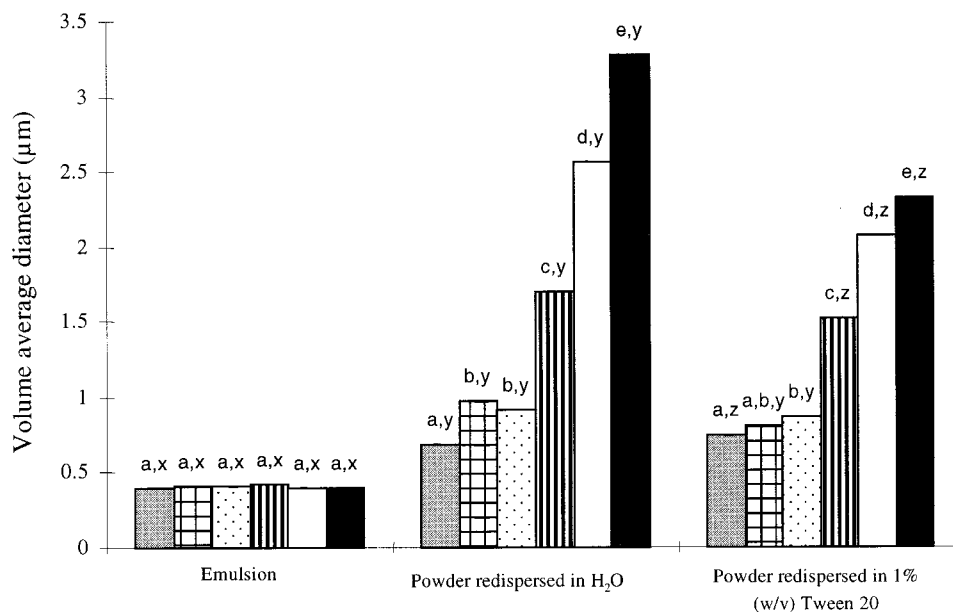
Figure 1. Effect of oil/protein ratio (0.25, gray bars; 0.5, windowpane bars; 0.75, dotted bars; 1.0, striped bars; 2.0, white bars; 3.0, black bars) on the volume average diameter of powders prepared by spray-drying Na Cas (5% w/v) stabilized soy oil emulsions homogenized at 50 MPa and redispersing in water or 1% (w/v) Tween 20. a–e refer to comparisons within treatments and between oil/protein ratios. x–z refer to comparisons within oil/protein ratios and between treatments. Data bearing similar superscripts are not significantly different ($P > 0.05$).

values at all oil/protein ratios were greater than the minimum limiting surface concentrations of Na Cas (1 mg m^{-2}) required to stabilize emulsions (*18*). Much of the previous work on protein adsorption focused on less concentrated protein solutions (*8, 19*) or on systems with much higher oil/protein ratios (*18, 20*) than those used in this study. The present findings are, however, similar to those reported by Sharma and Singh (*21*) at equivalent oil/protein ratios. Despite differences in emulsion compositions the decrease in Γ values with increasing oil/protein ratios observed here is in agreement with the findings of Hunt and Dalgleish (*18*) and Euston et al. (*22*), who showed that increasing protein concentration resulted in higher Γ values. The Γ values found in this study correspond mainly to saturated monolayer coverage with some evidence of multilayer adsorption at low oil/protein ratios. Graham and Phillips (*19*) showed that saturated monolayer coverage of β-casein occurred at a surface concentration of 2.6 mg m^{-2} and that further adsorption can continue as molecules form reversibly adsorbed multilayers.

Spray-Drying of Soy Oil/Protein Emulsions. *Moisture Content.* Moisture contents of spray-dried emulsions varied from 1.5 to 4% and were not affected by homogenization pressure or oil/protein ratio.

Powder Particle Size. The mean particle size ($D_{4,3}$) of powders prepared from emulsions that were homogenized prior to drying were significantly lower than that of the spray-dried pre-emulsion; however, powder particle size did not seem to be affected by homogenization pressure per se (Table 1). The particle size of the powders increased from 14.5 to 19.8 μm when the oil/protein ratio was increased from 0.25 to 2.0 (Table 2). Significantly larger powder particle sizes of 32.3 μm were observed at an oil/protein ratio of 3.0. Powder particle size increased as a function of total solids content of the emulsions and showed a high correlation ($R^2 = 0.98$) with the apparent viscosity of the emulsions. The large powder particle sizes observed at high oil/protein ratios may be attributed to inefficient atomiza-

tion of high-viscosity emulsions at the dryer nozzle combined with agglomeration or clumping of powder particles due to high surface fat levels (Figure 2B).

Microencapsulation Efficiency. In a preliminary study Na Cas at a concentration of 5 or 10% (w/v) was used to encapsulate soy oil at oil/protein ratios of 0.25–0.75. The ME values of powders prepared using 5 or 10% (w/v) Na Cas were similar at comparable oil/protein ratios; consequently, all further work was carried out at the 5% (w/v) concentration. The ME of spray-dried powders (oil/protein ratio = 1.0) increased significantly from 27.7%, in the case of those prepared from a pre-emulsion, to ∼50% for those manufactured from emulsions homogenized at 10 MPa. Increasing homogenization pressure from 10 to 50 MPa had no significant effect on the ME of powders (Table 1), suggesting that a stable emulsion of sufficiently small particle size (1.45 μm) was achieved at a homogenization pressure of 10 MPa. Increasing the oil/protein ratio from 0.25 to 3.0 resulted in a progressive decrease in ME from 89.2 to 18.8% (Table 2). Solvent extraction of spray-dried powders recovers both surface fat and fat originating from the interior of the powder, which is accessible to the solvent (*23*). ME values, therefore, reflect both the presence of oil on the surface of powder particles and the degree of protection afforded by the wall material to fat droplets internal to the powder particles. As emulsion particle size was not affected by oil/protein ratio, it would appear that the low ME values observed at high oil/protein ratios may be related to the larger oil phase volume, coupled with higher apparent viscosities, in the emulsion being atomized. This may have resulted in a decrease in atomization efficiency during spray-drying. Relatively lower levels of bulk protein at high oil/protein ratios may also have resulted in an increase in the time required for crust formation during the drying process. As a result greater disruption of emulsion droplets prior to complete formation of powder particles may have occurred, causing a decrease in ME values (*17*). Destabilization of emulsion droplets during the drying process
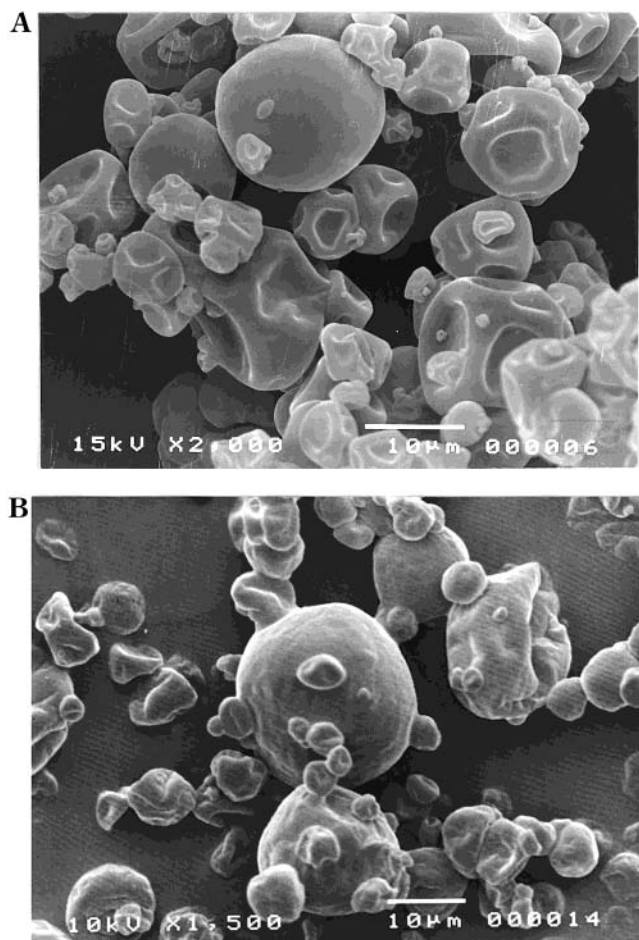
Microencapsulating Properties of Sodium Caseinate

J. Agric. Food Chem., Vol. 49, No. 4, 2001 **1937**

Figure 2. SEM micrographs of spray-dried Na Cas (5% w/v) stabilized soy oil emulsions prepared at oil/protein ratios of (A) 0.25 (×2000) and (B) 3.0 (×1500). Homogenization pressure = 50 MPa. (Figure is reproduced here at 50% of its original size.)

Figure 3. SEM micrographs showing internal structure of spray-dried Na Cas (5% w/v) stabilized soy oil emulsions prepared at oil/protein ratios of (A) 3.0 (×2000) and (B) 0.25 (×7500). Homogenization pressure = 50 MPa. (Figure is reproduced here at 50% of its original size.)

may also be related to the protein load. Previous conclusions regarding the relationship between protein load and emulsion droplet stability have varied. Graham (*24*) showed that the coalescence stability of protein-stabilized emulsions is at a maximum when interfacial protein layers are thickest and also highly charged. In contrast, Tornberg and Ediriweera (*20*) found that emulsion stability was enhanced with lower protein load as more extensive unfolding of proteins provided a higher energy barrier to desorption of surface protein. The results of this study suggest that the higher protein load values observed at low oil/protein ratios may have conferred enhanced stability on emulsion oil droplets during atomization. It would appear also that the ability of Na Cas to effectively encapsulate soy oil at oil/protein ratios >0.75 is limited.

Redispersion. Droplet sizes observed following redispersion of the dried emulsions in water were significantly higher ($P < 0.05$) than those of the original emulsion (Figure 1). This increase in particle size, which reflects destabilization of fat droplets and resultant flocculation and/or coalescence, was more pronounced at higher oil/protein ratios. A similar effect was reported by McNamee et al. (*25*) for the redispersion behavior of gum arabic stabilized spray-dried emulsions. Addition of Tween 20 (1% w/v) to the redispersion medium resulted in significant decreases in particle size compared to powders redispersed in water alone, at oil/protein ratios >0.75, although the mean size of the
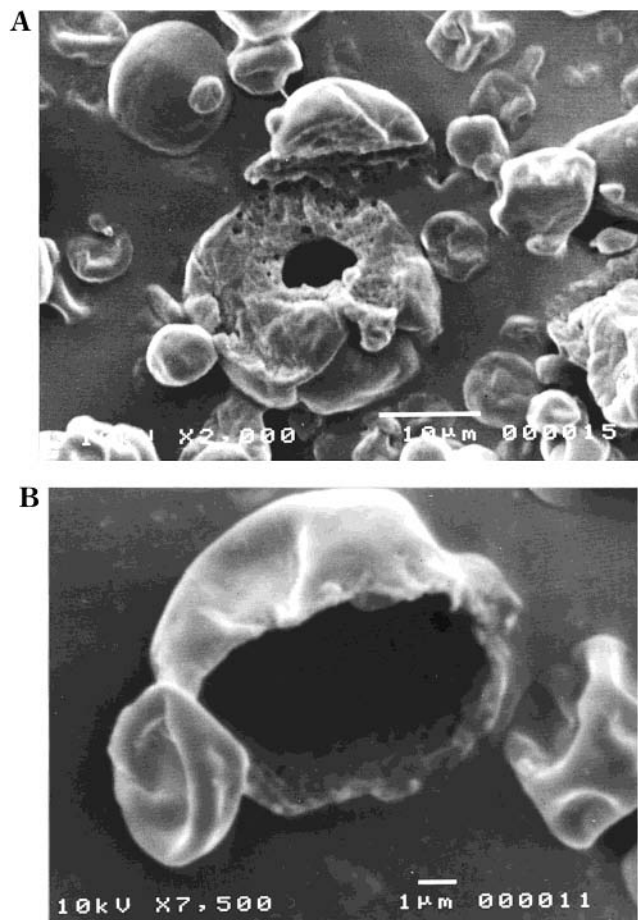
redispersed droplets at all oil/protein ratios remained greater than those of the corresponding original emulsions despite this treatment. The observed decrease in droplet size, at high oil/protein ratios, was possibly due to displacement of Na Cas from fat droplet surfaces by Tween 20, resulting in dissociation of flocculated droplets (*26*). The fact that emulsion droplet sizes remained greater than those of the original emulsions, despite treatment with Tween 20, may also indicate some level of coalescence. Examination of redispersed powders by light microscopy confirmed that changes in particle sizes following redispersion were due to both flocculation and coalescence of destabilized emulsion droplets, with these effects most pronounced at oil/protein ratios of 2.0 and 3.0.

Scanning Electron Microscopy (SEM). SEM micrographs of the dried powders having highest and lowest oil/protein ratios, that is, 0.25 and 3.0, respectively (Figure 2A,B), showed considerable differences in particle structure. Wide particle size distributions ranging from 2 to 40 μm were observed in all powders and may be attributed to the drying process (*27*). No visible pores or cracks were detected in the outer surfaces of the particles at any oil/protein ratio. The smooth powder particles observed at an oil/protein ratio of 3.0 (Figure 2B) appear to be agglomerated, which may indicate high surface fat levels and helps to explain the large powder particle sizes observed by Malvern analysis. Low-oil powders (Figure 2A) exhibited a higher level of surface

1938 *J. Agric. Food Chem.*, Vol. 49, No. 4, 2001

Hogan et al.

indentation than high-oil powders. The presence of surface dents has been attributed to shrinkage of casein and uneven drying of powder particles (*28*) and the presence of high levels of protein (*29*). The internal structure of the dried powders revealed increased wall thickness and decreased central vacuole size at an oil/protein ratio of 3.0 (Figure 3A) compared to powders at an oil/protein ratio of 0.25 (Figure 3B). Despite increased wall thickness, resulting from increased apparent viscosities and total solids levels, the presence of high surface fat levels at high oil/protein ratios resulted in poor core retention at these levels.

Conclusion. Decreasing the average droplet size of emulsions to ≤ 1.45 μm did not improve the encapsulating properties of Na Cas. Emulsions prepared at an oil/protein ratio of 0.25 had the highest protein load values and encapsulation efficiency despite low powder particle size. The oil/protein ratio had a greater effect on the properties of powders such as ME ($R^2 = 0.985$) and the size of droplets redispersed in water ($R^2 = 0.91$) than on the physical properties of the emulsions. As emulsion oil droplet size was not dependent on the oil/protein ratio, within the range examined, it would appear that excess Na Cas is required primarily to fulfill a "matrix forming" rather than a surfactant role. The effect of combining Na Cas with carbohydrate-based wall materials is the subject of continuing research in this laboratory.

LITERATURE CITED

(1) Gibbs, B. F.; Kermasha, S.; Alli, I.; Mulligan, N. Encapsulation in the food industry: a review. *Int. J. Food Sci. Nutr.* **1999**, *50*, 213−224.

(2) Jackson, L. S.; Lee, K. Microencapsulation and the food industry. *Lebensm. -Wiss. -Technol.* **1991**, *24*, 289−297.

(3) Shahidi, F.; Han, X. Encapsulation of food ingredients. *Crit. Rev. Food Sci. Nutr.* **1993**, *33*, 501−547.

(4) Bangs, W. E.; Reineccius, G. A. Corn starch derivatives. In *Flavor Encapsulation*; ACS Symposium Series 370; Risch, S. J., Reineccius, G. A., Eds.; American Chemical Society: Washington, DC, 1988; pp 12−28.

(5) Kinsella, J. E. Milk proteins: physicochemical and functional properties. *Crit. Rev. Food Sci. Nutr.* **1984**, *21*, 197−262.

(6) Leman, J.; Kinsella, J. E. Surface activity, film formation and emulsifying properties of milk proteins. *Crit. Rev. Food Sci. Nutr.* **1989**, *28*, 115−138.

(7) Tornberg, E. Functional characterisation of protein stabilized emulsions: emulsifying behavior of proteins in a valve homogenizer. *J. Sci. Food Agric.* **1978**, *29*, 867−879.

(8) Britten, M.; Giroux H. J. Interfacial properties of milk protein-stabilized emulsions as influenced by protein concentration. *J. Agric. Food Chem.* **1993**, *41*, 1187−1191.

(9) Kim, Y. D.; Morr, C. V. Microencapsulation properties of gum arabic and several food proteins: spray-dried orange oil emulsion particles. *J. Agric. Food Chem.* **1996**, *44*, 1314−1320.

(10) Fäldt, P.; Bergenståhl, B. Changes in surface composition of spray-dried food powders due to lactose crystallization. *Int. J. Food Sci. Technol.* **1996**, *29*, 438−446.

(11) Fäldt, P.; Bergenståhl, B. Fat encapsulation in spray-dried food powders. *J. Am. Oil Chem. Soc.* **1995**, *72*, 171−176.

(12) Richardson, G. H., Ed. *Standard Methods for the Examination of Dairy Products*, 15th ed.; American Public Health Association: Washington, DC, 1985.

(13) Young, S. L.; Sarda, X.; Rosenberg, M. Microencapsulating properties of whey proteins 1. Microencapsulation of anhydrous milk fat. *J. Dairy Sci.* **1993**, *76*, 2868−2877.

(14) *SAS User's Guide: Statistics*, version 5 ed.; SAS Institute: Cary, NC, 1985.

(15) Risch, S. J.; Reineccius, G. A. Spray-dried orange oil: effect of emulsion size on flavour retention and shelf stability. In *Flavor Encapsulation*; ACS Symposium Series 370; Risch, S. J., Reineccius, G. A., Eds.; American Chemical Society: Washington, DC, 1988; pp 67−77.

(16) Reineccius, G. A. Spray-drying of food flavours. In *Flavor Encapsulation*; ACS Symposium Series 370; Risch, S. J., Reineccius, G. A., Eds.; American Chemical Society: Washington, DC, 1988; pp 55−66.

(17) Rosenberg, M.; Kopelman, I. J.; Talmon, Y. Factors affecting retention in spray-drying microencapsulation of volatile materials. *J. Agric. Food Chem.* **1990**, *38*, 1288−1294.

(18) Hunt, J.; Dalgleish D. G. Adsorption behavior of whey protein isolate and caseinate in soy oil-in-water emulsions. *Food Hydrocolloids* **1994**, *8*, 175−187.

(19) Graham, D. E.; Phillips, M. C. Protein at liquid interfaces II. Adsorption isotherms. *J. Colloid Interface Sci.* **1979**, *70*, 415−426.

(20) Tornberg, E.; Ediriweera, N. Factors that influence the coalescence stability of protein-stabilised emulsions, estimated from the proportion of oil extracted by hexane. *J. Sci. Food Agric.* **1988**, *46*, 93−113.

(21) Sharma, R.; Singh, H. Adsorption behaviour of commercial milk protein and milk powder products in low-fat emulsions. *Milchwissenschaft* **1998**, *53*, 373−377.

(22) Euston, S. E.; Harjinder, S.; Munro, P. A.; Dalgleish, D. G. Competitive adsorption between sodium caseinate and oil-soluble and water-soluble surfactants in oil-in-water emulsions. *J. Food Sci.* **1995**, *60*, 1124−1131.

(23) Buma, T. J. Free fat in spray-dried whole milk. 10. A final report with a physical model for free fat in spray-dried milk. *Neth. Milk Dairy J.* **1971**, *25*, 159−174.

(24) Graham, D. E. Structure of adsorbed protein films and stability of foams and emulsions. Ph.D. Thesis, Council for National Academic Awards, London, U.K., 1976.

(25) McNamee, B. F.; O'Riordan, E. D.; O'Sullivan, M. Emulsification and microencapsulation properties of gum arabic. *J. Agric. Food Chem.* **1998**, *46*, 4551−4555.

(26) Dickinson, E. Proteins at liquid interfaces. In *An Introduction to Food Colloids*; Oxford University Press: New York, 1992; pp 140−173.

(27) Rosenberg, M.; Young, S. L. Whey proteins as microencapsulating agents. Microencapsulation of anhydrous milkfat-structure evaluation. *Food Struct.* **1993**, *12*, 31−41.

(28) Buma, T. J. Free fat in spray-dried whole milk 8. The relationship between free-fat content and particle porosity of spray-dried milk. *Neth. Milk Dairy J.* **1971**, *25*, 123−140.

(29) Fäldt, P.; Bergenståhl, B. The surface composition of spray-dried protein-lactose powders. *Colloids Surf.* **1994**, *90*, 183−190.