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The interfacial, emulsification and encapsulation properties of hydrophobically modified inulin

S. Kokubun, I. Ratcliffe, P.A. Williams*

Centre for Water Soluble Polymers, Wrexham Glyndwr University, Plas Coch, Mold Road, Wrexham, LL11 2AW, United Kingdom

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ABSTRACT

Octenyl- and dodecenyl succinic anhydride derivatives (OSA- and DDSA-) of inulin have been synthesised and their solution and interfacial properties have been determined and compared to a commercially available alkylated inulin, Inutec SP1. All samples formed micellar aggregates in solution above a critical concentration (critical aggregation concentration) and were able to 'dissolve' a hydrophobic dye. They were also able to form stable oil-in-water (O/W) emulsions as assessed by measurements of their droplet size as a function of time. DDSA-inulin with a high degree of substitution was found to be effective at encapsulating beta carotene using the solvent evaporation method which yielded a solid which dissolved readily in simulated gastric fluid. The results confirm the potential application of these materials in a number of areas including, drug delivery, pharmaceuticals, neutraceuticals, cosmetics and personal care.

1. Introduction

Inulin is a polyfructan and is obtained commercially from chicory. It consists of β 2,1 fructose chains, with degrees of polymerisation ranging between 2 and 60, which terminate with a glucose residue. It is classed as a type of dietary fibre because it is not absorbed in the stomach or small intestine but is degraded by bacteria in the colon to form short-chain fatty acids which have health benefits. There has been considerable interest in recent years in the derivatisation of inulin to form a range of speciality chemicals (Stevens, Merigii & Booten, 2001). Inutec SP1 is a hydrophobically modified inulin derivative which is produced commercially by reaction of inulin with dodecyl isocyanate in an aprotic solvent to yield inulin dodecyl carbamate (Gotchev, Kolarov, Levecke, Khristov, & Exerowa, 2007; Nestor et al., 2007; Stevens et al., 2001; Exerowa et al., 2007, 2009a, 2009b). It has a molar mass of about 5000 g/mol (Exerowa et al., 2009b; Nestor et al., 2005, 2007, 2008) and is used in a variety of industrial sectors for the stabilisation of emulsions and dispersions.

A number of other hydrophobic derivatives have been synthesised by reaction of inulin in organic solvents with fatty acid chlorides, methyl esters, alkyl epoxides, and alkyl isocyanates (Exerowa et al., 2009a, 2009b; Gotchev et al., 2011; Khristov & Czarnecki, 2010; Stevens, Merigii & Booten, 2001). A 'green' approach to modification has been developed by Morros, Levecke, and Infante (2010), Morros, Levecke, and Infante (2011), Kokubun, Ratcliffe & Williams (2013), Kokubun, Ratcliffe & Williams (2015) and Han, Ratcliffe and Williams (2015) who have recently reported the modification of inulin using alkenyl succinic anhydrides in water under mild alkaline conditions to produce inulin derivatives with varying alkenyl chain length and varying degrees of substitution. It was confirmed that these surfactants adsorbed at the air-water interface and that they formed micellar-like aggregates in solution above a critical concentration.

The ability of hydrophobically modified inulin derivatives to form micellar aggregates has attracted much interest in recent years. Muley, Kumar, El Kourati, Kecharwani, and Tummala (2016), for example, used Inutec SP1 for the encapsulation and controlled release of the anti-cancer drug, paclitaxel. Encapsulation was achieved using both the 'thin film hydration' and 'solvent evaporation' methods and they demonstrated through dynamic light scattering and transmission electron microscopy studies that near spherical drug-loaded micellar aggregates of ~250 nm were produced. Other groups have also used hydrophobic derivatives for encapsulation of active compounds within micellar-like structures. For example, Di Prima et al. (2017) synthesised an amine derivative which was further modified to incorporate retinoic acid to yield mucoadhesive micelles with enhanced transcorneal permeation properties while Mandracchia et al. (2017) produced derivatives containing both vitamin E and biotin capable of forming micelles for potential application as long-circulating carriers for receptor-mediated targeted drug delivery. In another approach, Lopez-Molina et al. (2015) synthesised a cinnamoylated inulin derivative by reaction with cinnamic acid chloride in pyridine and produced microspheres for the targeted delivery of drugs to the colon.

* Corresponding author.
E-mail address: williamspa@glyndwr.ac.uk (P.A. Williams).

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The purpose of the present study was to synthesise octenyl and dodecenyl succinic anhydride derivatives of inulin and to investigate their solution and interfacial properties in comparison with Inutec SP1 and to evaluate their ability to encapsulate water insoluble beta carotene. It is our hypothesis that encapsulation using the anionic succinylated derivatives could have significant benefits in the controlled release of the beta carotene compared to the commercial non-ionic Inutec SP1.

2. Materials and methods

2.1. Materials

Inulin coded Fibruline® DS2 was supplied by Cosucra and was dried at 70 °C for 24 h before use. It was found to have a weight average and number average molar mass of 3760 and 3000 g/mol respectively (Kokubun et al., 2013). Inutec SP1 was obtained by Beneo Biobased Chemicals and was used as supplied.

2-octen-1-yl-succinic anhydride (OSA) and 2-dodecen-1-yl-succinic anhydride (DDSA) were obtained from Aldrich Chemical Co. and were used as received. Medium Chain Triglyceride (MCT) gold oil was obtained from Trec Nutrition UK and was used as supplied. Sudan IV was obtained from the Eastman Kodak Company. Beta carotene Type I synthetic ≥93% (UV) powder was obtained from Sigma-Aldrich Chemie GmbH., and was used as supplied.

2.2. Methods

2.2.1. Synthesis of hydrophobically modified inulin

Hydrophobically modified inulin samples were synthesised in aqueous solution under alkaline conditions using OSA and DDSA and were characterised by nuclear magnetic resonance (NMR) spectroscopy as previously reported (Kokubun et al., 2013). The samples obtained, namely OSA(1), OSA(2) and DDSA(1) had approximately 1–2 alkenyl chains per molecule and a further sample, DDSA(2), had ~5 alkenyl chains per molecule.

2.2.2. Critical aggregation concentration

The CAC was determined by the dye solubilisation technique using Sudan IV. 10 mg of the dye was added to 10 mL of the OSA-, DDSA-inulins or Inutec SP1 at varying concentrations in deionised water. The samples were mixed at 40 °C overnight and filtered using a Millex-GP 0.22 µm filter (Millipore Ireland Ltd.) into disposable UV-grade 10 mm path length cuvettes (CXA-110-0053 from Fisher Scientific Ltd.). The absorbance of the solutions was measured at 510 nm using a Lambda 25 UV/vis Spectrometer PerkinElmer. The CAC was determined as the point at which the absorbance increased.

2.2.3. Surface and interfacial tension

The surface tension at the air/water interface and the interfacial tension at ASA-inulin or Inutec SP1 aqueous solution/MCT oil interface were measured at varying concentration at 25 °C ± 1 °C using the Du Nouy ring method with a Tensiometer K8 and a 4 cm circumference platinum ring RI 01 from Krüss GmbH. The equilibrium surface and interfacial tensions were plotted as a function of the sample concentration and the CAC was estimated from the change in slope of the plots.

2.2.4. Zeta potential

The zeta potential of inulin-coated emulsion droplets was determined at various pH at 25 °C using a Zetasizer Nano ZS (Malvem Instrument Lab, Malvern, UK) equipped with a 5 mw He-Ne laser (λ_0 633 nm) and a digital correlator. Measurements were carried out using a folded capillary cell DTS1060 (Malvern Instrument Lab, Malvern, UK). The cell was washed with ethanol and deionised water several times and dried before measurements. Oil-in-water (O/W) emulsions were prepared by mixing 1.5 g MCT oil with 8.5 g of 2.5% OSA-, DDSA-inulin or Inutec SP1 solution for 3 min at 24 000 rpm, using an IKA T25 digital Ultra-Turrax mixer. Two drops of the emulsion were added into 10 mL 0.01 M NaCl which was filtered with a type GN 0.2 µm filter (Millipore Ireland Ltd) before use. The system was mixed for 30 s and the pH was adjusted using 0.1 M HCl and 0.1 M NaOH. Ten runs were performed for each sample. The data was analysed using the Zetasizer Software 6.20 © 2002–2010 from Malvern Instruments Ltd and the zeta potential was determined from the electrophoretic mobility using the Smoluchowski equation.

2.2.5. Emulsification properties

O/W emulsions were prepared as above and droplet size measurements were made immediately after emulsion preparation and over a period of 21 days for samples stored at room temperature (25 °C) and at 50 °C using the Mastersizer 2000 (Malvern Panalytical Ltd Malvern, UK). Before measuring the samples, background readings for the instrument were carried out to subtract the ambient light signals from the total scattering received from samples. Two or three drops of the sample were introduced into the dispersion unit containing distilled water. The dispersion unit pump speed was 2000 rpm. The obscuration was between 10% and 30%. The refractive index of the dispersing medium and the dispersed particles were 1.33 and 1.45 respectively. Measurements were performed in duplicate.

2.2.6. Encapsulation

Encapsulation of beta carotene using hydrophobically modified inulin was facilitated using the solvent evaporation method. Approximately 1.0 g of the beta carotene and 5.0 g of the ASA-inulin or Inutec SP1 were added to 70 mL of chloroform and the system was stirred with a magnetic stirrer and then left overnight at room temperature inside a fume cupboard to enable the chloroform to evaporate completely. The solubility of the beta carotene in the resulting solid matrix was determined by preparing a number of samples containing 0.02 g of the solid in 10 mL deionised water or simulated gastric fluid and mixing at 37 °C. The simulated gastric fluid was prepared by adding 500 mL 1 M HCl and 10.22 g sodium chloride to 5 L deionised water and stirring with a magnetic stirrer overnight at room temperature to fully dissolve. 3 mL of each of the dispersions was taken at various time intervals and filtered using a Millex-GP 0.22 µm filter (Millipore Ireland Ltd.) into disposable UV-grade 10 mm path length cuvettes (CXA-110-0053 from Fisher Scientific Ltd.). The absorbance of the solutions was measured at 455 nm using a Lambda 25 UV/vis Spectrometer PerkinElmer.

3. Results and discussion

3.1. Critical aggregation concentration and interfacial properties

The results obtained for the dye solubilisation studies are presented in Fig. 1. It is seen that the absorbance increased at values of 0.70% ± 0.1%, 0.02% ± 005% and 0.002% ± 0.001% for the OSA(1)-inulin, DDSA(1)-inulin and Inutec SP1 respectively.

The increase is attributed to the formation of micellar-like aggregates through hydrophobic association of the inulin molecules and the dissolution of the dye in the hydrophobic core as discussed previously (Kokubun et al., 2013). The CAC values for the succinylated samples are expected to be higher than those for Inutec SP1 since the former have an anionic carboxylate group in the linkage between the alkenyl chains and the inulin molecule which will tend to inhibit molecular aggregation due to intermolecular electrostatic repulsions. The CAC is significantly higher for OSA-inulin compared to DDSA-inulin which is consistent with our previous studies (Kokubun et al., 2013, 2015; Han et al., 2015) and the work of Van Kempen, Maas, Schols, Linden, and Sagis (2013), Van Kempen, Boeriu et al. (2013), Van Kempen, Schols, Linden, and Sagis (2014) who studied the CAC of a