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Effect of the degree of grafting in hydrophobically modified inulin polymeric surfactants on the steric forces in foam and oil-in-water emulsion films

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ABSTRACT

The interaction forces in foam and oil-in-water emulsion films stabilized by four inulin based graft copolymers with different degree of grafting of the dodecyl chains onto the inulin backbone were investigated. The adsorbing copolymers were found to form inulin-loops at the oil (air)/water interface, as the inulin-loop size decreased with increasing degree of grafting. Disjoining pressure isotherms (disjoining pressure, Π vs. equivalent film thickness, h_w) were measured for the foam and emulsion films at sufficiently high NaCl concentration, whereby there is no electrostatic interaction in the films. Under these conditions, the stabilization of the films is due to interaction between the two layers of inulin-loops at oil (air)/water film interfaces. Transition to a stable Newton black film in the disjoining pressure isotherm for the emulsion films was observed for all the copolymers and the transition pressure significantly decreased for the films from the copolymer with the smallest inulin-loops. The stability against rupture of the foam films decreased with reducing inulin-loop size. The *de Gennes*' scaling theory for interaction between polymer 'brushes' was fitted to the experimental data for the foam films with the inulin-loops layer thickness as a fitting parameter. The results were interpreted on the basis of inulin-loop size induced changes of the steric forces in the foam and emulsion films.

1. Introduction

Foam and emulsion stability has been described on the basis of the interaction forces that prevent the coalescence of bubbles and drops. The interactions resulting from combination of electrostatic repulsion and van der Waals interactions have been described by the theory of colloid stability due to Deryaguin–Landau–Verwey–Overbeek (DLVO theory) [1,2]. In addition, the stabilization of colloid systems in the presence of adsorbing polymers has been attributed to steric forces between the colloid particles covered with polymer adsorption layers, e.g. [3–6].

Recently, in our laboratory, we have studied the interaction forces in foam [7,8] and oil-in-water emulsion [7,9] films obtained from aqueous solutions of a hydrophobically modified inulin (HMI) graft copolymer, namely INUTEC SP1 at various electrolytes concentrations (C_{el}). A transition from electrostatic to steric stabilization of the films has been found at a certain critical C_{el}-value ($C_{el,cr}$). At $C_{el} \geq C_{el,cr}$, the main driving force for film stabilization is due to steric interaction between the copolymer adsorption layers at film surfaces. A loop-tail like conformation of the adsorbed INUTEC SP1 macromolecules at oil (air)/water interface has been considered and the action of steric forces in the films has been attributed to the interaction of the layers of strongly hydrated inulin loops and tails at film surfaces. Evidence for the strong hydration of the inulin chains at both high temperature and high C_{el} has been derived from cloud point measurements [10] and AFM (Atomic Force Microscopy) experiments [11]. Similar loop-tail like conformation has been considered by Millet et al. [12] for the case of adsorbed hydrophobically modified poly(acrylic acid) graft copolymers at the air/water interface. In order to confirm the 'loop-to-loop' steric interaction, we have investigated the effect of a change in the degree of grafting, i.e. inulin-loop size in HMI-surfactants on the surface forces in foam [13] and oil-in-water emulsion [14] films. In the present paper we summarize these results and present complementary ones, all of them confirming the steric nature of the repulsive force in the foam and emulsion films studied.

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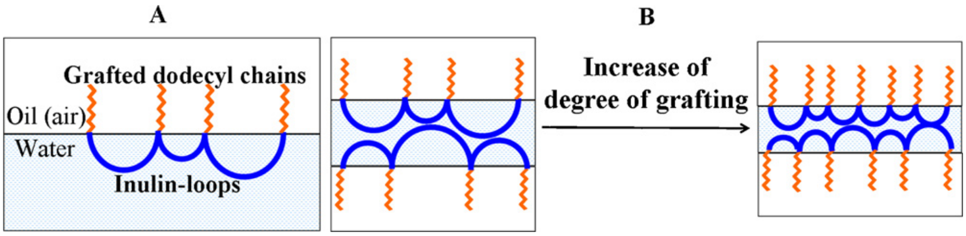

Fig. 1. (A) Schematic representation of an adsorbed HMI-macromolecule at oil (air)/water interface; the number of dodecyl chains is arbitrary. (B) An illustration of emulsion (foam) films and the change in the inulin-loop size with increasing the degree of grafting in HMI-surfactants.

2. Experimental

2.1. Materials

The HMI graft copolymers (INUTEC®SP1) used were based on inulin and were prepared at BENEO BIO Based Chemicals labs (Belgium). INUTEC SP1 was the same material used in our previous studies [7–9,13,14]. It has a weight-average molar mass of about 5000 Da and a number average molar mass of about 4000 Da, i.e. a polydispersity of about 1.25. The inulin backbone consisted of linear poly-fructose chains having degree of polymerization greater than 23 [15]. The same poly-fructose chains were hydrophobically modified by random grafting by dodecyl chains. A schematic representation of HMI-macromolecule conformation at oil (air)/water interface is shown in Fig. 1A. The degree of grafting was related to the number of dodecyl chains per single inulin chain. Three other HMI-derivatives were synthesized, namely 0.5HMI, 2HMI and 3HMI by changing the degree of grafting relative to that of INUTEC SP1; 0.5HMI contained half degree of grafting compared to INUTEC SP1 and hence it formed the largest inulin-loops; 2HMI and 3HMI contained double and triple degree of grafting, respectively, compared to INUTEC SP1, hence they progressively lowered the loop size. Thus, one would expect the inulin-loop size to decrease as follows: 0.5HMI > INUTEC SP1 > 2HMI > 3HMI (illustrated in Fig. 1B).

2.2. Methods

The Thin Liquid Film – Pressure Balance Technique was used involving a porous plate cell whereby the capillary pressure (equal at equilibrium to the disjoining pressure, Π, in the film) could be altered, e.g. [7,16]. The film thickness was measured interferometrically, e.g. [16,17]. Thus, Π vs. h_w plots (disjoining pressure isotherms) for the foam and emulsion films were obtained.

3. Results and discussion

The equivalent film thickness vs. C_{el} measurements at constant capillary pressure for foam [7,8,13] and oil-in-water emulsion [7,9,14] films from HMI-surfactants obtained previously have clearly indicated a transition from electrostatic to steric interaction in the films at $C_{el,cr}$ (around 20 mM NaCl for the foam films and 50 mM NaCl for the emulsion films). The steric forces in the films has been attributed to the interaction between the layers of inulin-loops at the oil (air)/water film interfaces (illustrated in Fig. 1B). One can obtain more detailed information about these steric forces by measuring Π vs. h_w dependence for films obtained at $C_{el} \geq C_{el,cr}$. Below we summarize the disjoining pressure isotherm results to date for the foam and emulsion films from the four HMI-surfactants used [13,14] and present complementary ones for foam films from the same polymeric surfactants.

3.1. Oil-in-water emulsion films

Fig. 2 shows disjoining pressure isotherms for oil-in-water emulsion films from 20 μM aqueous HMI-surfactants at $C_{NaCl} > C_{el,cr}$. The thickness of the films from the first three HMI-surfactants (with increase of degree of grafting) slightly decreased at higher disjoining pressure of around 500 Pa and subsequently a transition to a Newton black film (NBF) was observed. The formation of a NBF was due to overcoming the transition barrier in the disjoining pressure isotherm, e.g. [16–18]. In the lack of electrostatic interaction in the emulsion films studied at and above $C_{el,cr}$, one can consider that the transition barrier was due to the action of steric forces. Obviously, the behavior of the emulsion films from these three HMI-surfactants was similar and no effect of the reduction in the inulin-loop size on film properties was detected. However, the emulsion films from 3HMI (having the highest degree of grafting) followed the same trend, but in this case the transition to a NBF occurred at significantly lower disjoining pressure of 36 Pa. It seemed not unreasonable to assume that the lower transition pressure would imply weaker steric barrier in the disjoining pressure isotherm due to the smallest inulin-loop size for 3HMI. All the NBF obtained had the same thickness of about 7 nm and remained stable, not showing rupture or thickness change up to the highest measurable pressure of 45 kPa. Such highly stable NBF could account for the observed high stability of oil-in-water emulsions stabilized by INUTEC SP1 [10].

At a given disjoining pressure (before the transition to a NBF), the equivalent film thickness for the four HMI-surfactants with dif-

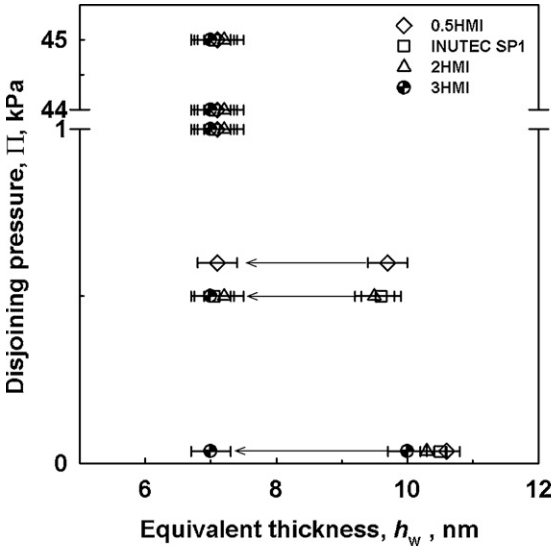

Fig. 2. Disjoining pressure isotherms for oil-in-water emulsion films obtained from aqueous solutions of 20 μM HMI-surfactants at $C_{NaCl} > C_{el,cr}$; arrows indicate transition to a NBF.

Redrawn from Ref. [14].