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Thin liquid films from aqueous solutions of non-ionic polymeric surfactants

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ABSTRACT

The conditions of formation and stability of foam, emulsion, and wetting films from aqueous solutions of non-ionic polymeric surfactants have been established. Two types of polymeric surfactants – PEO–PPO–PEO three-block copolymers (A–B–A type) and hydrophobically modified inulin graft polymer (AB_n type) – have been explored. Information about surface forces and nanoscale phenomena in aqueous films containing polymeric surfactants was obtained using the micro-interferometric technique and the Thin Liquid Film–Pressure Balance Technique. Two types of surface forces, which determine the stability of the foam and emulsion films, have been distinguished, namely: DLVO-forces at low electrolyte concentrations and non-DLVO-forces at high electrolyte concentrations. Non-DLVO-forces are steric surface forces of the brush-to-brush and loop-to-loop interaction type according to De Gennes. A substantial difference in the behavior of these two film types has been established and in the case of O/W emulsion films transitions to Newton black film (NBF) have been observed. These films are very stable and so are the respective emulsions. In contrast the wetting films are relatively thicker compared to emulsion films, and their thickness depends on the concentration of the AB_n polymeric surfactant. The steric repulsion of the loops and tails of the polymeric surfactant determine the film thickness of wetting films on a hydrophilic solid surface. For solid surfaces with different degrees of hydrophobicity the wetting films are stable only at high polymer concentrations and low degree of hydrophobicity. Otherwise the films are unstable and rupture. Two types of bilayer emulsion films have been distinguished for the first time. One type is related to the brush-to-brush or loop-to-loop interactions according to De Gennes. The other type is a NBF where the forces are also steric between strongly hydrated brush and loops but they are short-range forces acting in a two-dimensional ordered system. They determine the high NBF stability.

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1. Introduction

Thin liquid films are formed when two particles of the disperse phase (solid particles, liquid drops or gas bubbles) come close to each other in liquid disperse media. A more detailed introduction of thin liquid films is hardly necessary since the studies in this area now represent an independent field in colloid and interface science which is developing rapidly. Thin liquid films obtained from solutions of common surfactants have proven their advantages in both the study of interaction forces in them [1,2] and in the elucidation of the main reasons for their formation and stability. Most of the results on thin liquid films refer to emulsion, foam and colloid stability. However thin liquid films have also independent importance regarding the study of, for instance, bio-membranes [3–5]. Many studies [1,4,6,7] have been dedicated to the role of thin liquid films in the understanding of disperse systems stability when the latter are stabilized by common surfactants, phospholipids, etc. During the last decades a number of authors have reported results of model experiments with thin liquid films (foam, emulsion and wetting films) stabilized by polymers. In most of the papers polyelectrolytes have been used [8–16].

Amphiphilic diblock copolymers have also been used for thin liquid film studies [17,18]. Liquid films between hydrophobic solid surfaces have been studied in Ref. [17]. Interesting results about foam films from aqueous solutions of PEO–PBO diblock and PEO–PBO–PEO triblock copolymers have been reported [18] (PEO = polyethyleneoxide, PBO = polybutyleneoxide). The diblock copolymers produced more stable foam films than the triblock copolymers. A pronounced steric disjoining pressure dominated the interaction at small film thickness. Foam films formed from mixed solutions of PEO–PBO copolymers and CTAB showed a more dominating electrostatic component of the disjoining pressure with increasing CTAB content [18].

Emulsion films stabilized by natural polymeric surfactants from bitumen [19] and thin liquid films from protein (bio-polymer) aqueous solutions [20] should also be noted. Papers dedicated to the stabilizing properties of various non-ionic polymeric surfactants have appeared only recently [21–32]. However, reference data on thin liquid films from aqueous solutions of non-ionic polymeric surfactants are scarce and their quantitative study — insufficient.

Non-ionic polymeric surfactants have widely been used in practice to stabilize disperse systems, mostly emulsions. For instance, using novel graft AB_n copolymers (A being inulin, a linear polyfructose backbone, that has been modified by introducing several alkyl groups B) [33] some very stable oil in water (O/W) emulsions have been obtained [34,35]. These emulsions were stable for more than one year up to 50 °C and NaCl concentration up to 2 mol dm^{-3} or 1 mol dm^{-3} $MgSO_4$. This high emulsion stability was attributed to the nature of the hydrophilic polyfructose chain [34]. It is believed that the sign of the Flory–Huggins interaction parameter χ (related to the chain solubility in a medium [36]) changes. In aqueous solution both inulin and PEO are strongly hydrated by the water molecules, hence $\chi < 1/2$ under these conditions. It seems that the inulin stabilizing chain can retain its hydration to much higher temperatures and electrolyte concentrations and this is probably the reason for the high stability obtained when using such polymeric surfactants based on inulin as emulsifier. Their steric stabilization is unique and it is most interesting to understand which are the interaction forces acting in the single emulsion film and if they lead to film stabilization.

The use of non-ionic polymeric surfactants as stabilizers of foam, emulsion and wetting films is an interesting topic. A–B–A block copolymers and novel graft polymers AB_n based on inulin have been used by us as representatives of non-ionic polymeric surfactants. The hydrophobic chains B penetrate the oil/water interface, leaving the hydrophilic chains A strongly hydrated in the aqueous solution. We have performed systematic studies of foam, emulsion and wetting films, published recently. The aqueous solution/air, aqueous solution/oil, and aqueous solution/solid interfaces play a significant role in the film's properties and stability. DLVO and non-DLVO interaction forces stabilizing the film have also been studied and the film thickness ranges where they act have also been found.

This article is an overview of our results [29–32,37,38] as well as unpublished results, obtained on foam, emulsion and wetting films, stabilized by the above mentioned non-ionic polymeric surfactants. A particularly interesting result is the formation of Newton black films (NBF) in the O/W emulsion films. It will be demonstrated that these NBF are believed to be decisive for the high stability of the real emulsion. What proved to be very successful was the use of a microscopic thin liquid film (radius of about 100 µm) as a model for the studies. It permits to work at very low polymeric surfactant concentrations thus making it possible to follow film formation and stability. Foam, emulsion and wetting films will be considered separately and it will be demonstrated that mainly steric forces are the interaction forces responsible for their stability.

2. Experimental section

2.1. Materials

The A–B–A block copolymers from the Pluronic series: $EO_{128}PO_{54}$-EO_{128} (F108), $M = 14{,}000$ Da and $EO_{31}PO_{54}EO_{31}$ (P104), $M = 5900$ Da have been used as received from BASF, Germany. The AB_n graft copolymer surfactant INUTEC SP1 is based on inulin and it has been prepared by ORAFTI Bio Based Chemicals, Belgium. The inulin linear polyfructose backbone having degree of polymerization greater than 23 had been hydrophobically modified by grafting of C_{12}-alkyl chains [39], the molecular mass being about 4500 Da. Three other hydrophobically modified inulin polymeric surfactants (HMI), namely HMI-A, HMI-B, and HMI-C with different degrees of substitution, have also been prepared by ORAFTI Bio Based Chemicals, Belgium.. In these polymeric surfactants the degree of substitution (DS) increases by a factor 2–3, the INUTEC SP1 being between HMI-A and HMI-B according to its DS. Isoparafinic oil Izopar M from Exxon Mobil Chemicals, Belgium, has been used as an oil phase for the emulsions and the emulsion films.

2.2. Experimental methods for investigating different types of thin liquid films

The formation, the film thickness, the life time, and the stability of all types thin liquid films have been studied by the *micro-interferometric method* of Scheludko–Exerowa. This method has widely been used by many authors for investigation of both symmetric thin liquid films (foam and emulsion films) and asymmetric ones (wetting films). The so-called *Thin Liquid Film–Pressure Balance Technique* allows direct measurement of the disjoining pressure, respectively the interaction forces in the film. These methods have been described in several papers e.g. [2,40–43] as well as in a book [1]. Here we shall describe them only cursorily.

The measuring cell, in which the microscopic thin liquid films are formed and studied, is the basic part of the micro-interferometric apparatus. Fig. 1 presents the main details of three measuring cells. In the Scheludko–Exerowa cell (Fig. 1a) the film is formed in the middle of