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Foam, emulsion and wetting films stabilized by polyoxyalkylated diethylenetriamine (DETA) polymeric surfactants

Khr. Khristov [a,*], H. Petkova [a], L. Alexandrova [a], M. Nedyalkov [b], D. Platikanov [b], D. Exerowa [a], J. Beetge [c]

[a] *Institute of Physical Chemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria*
[b] *Department of Physical Chemistry, University of Sofia, Sofia 1126, Bulgaria*
[c] *Champion Technology Inc., Fresno, Texas 77545, USA*

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ABSTRACT

This review explores three (A, B, C) polyoxyalkylated diethylenetriamine (DETA) polymeric surfactants belonging to the group of star-like polymers. They have a similar structure, differing only in the number of polymeric branches (4, 6 and 9 in the mentioned order). The differences in these surfactants' ability to stabilize foam, o/w/o and w/o/w emulsion and wetting films are evaluated by a number of methods summarized in Section 2. Results from the studies indicate that differences in polymeric surfactants' molecular structure affect the properties exhibited at air/water, oil/water and water/solid interfaces, such as the value of surface tension, interfacial tension, critical micelle concentration, degree of hydrophobicity of solid surface, etc. Foam, emulsion and wetting films stabilized by such surfactants also show different behavior regarding some specific parameters, such as critical electrolyte concentration, surfactant concentration for obtaining a stable film, film thickness value, etc. These observations give reasons to believe that model studies can support a comprehensive understanding of how the change in polymeric surfactant structure can impact thin liquid films properties. This may enable a targeted design of the macromolecular architecture depending on the polymeric surfactants application purpose.

1. Introduction

For several decades polymeric surfactants have been used to control the stability of colloids in conformity with their applications [1,2]. Lately, polymeric chemistry is capable to synthesize well defined macromolecules with controlled architecture [1,3,4]. Of a particular interest are those of a branch type, e.g. star-like polymers, grafted polymers, dendritic type polymers, etc. Star-like polymers are of a great interest as they can be designed to be biodegradable and with a minimal environmental impact. They are subject to extensive research as they have numerous industrial applications such as foaming/defoaming, emulsification/demulsification, solubilization, lubrication, in nanomaterial synthesis, etc. [1–4].

As it has been emphasized [5] the thin liquid films exist (and determine their properties) in all dispersion systems: symmetric—foam films, emulsion films, films between solid particles and asymmetric—wetting films. Thin liquid films are important study objects not only because of the corresponding disperse systems. The methods and the experimental techniques for thin liquid films research provide valuable information about the surface forces and different types of interactions, the properties of liquid interfaces, the self-assembly of amphiphilic molecules in solution, etc. [5–7]

To the authors' knowledge no studies on all thin liquid film types (foam, emulsion and wetting) stabilized by polymeric surfactant/s have been published. Moreover, articles dedicated to oil/water/oil (o/w/o), emulsion films stabilized by polymeric surfactants are scarce and their quantitative study is insufficient. This is even more valid for water/oil/water (w/o/w) emulsion films. In view of the large practical application enjoyed by polymeric surfactants in stabilizing disperse systems, mostly emulsions, such insufficiency comes as a surprise [5,8,9].

In this review article we summarize the results on foam, emulsion: oil/water/oil (o/w/o), water/oil/water (w/o/w) films and wetting films stabilized by star-like polyoxyalkylated diethylenetriamine (DETA) polymeric surfactants [10], named A, B, and C obtained in the past few years. A separate section is dedicated to the various methods used to study these films so that method evolution and applicability scope through the years may also be followed. Surfactant A is an industrially applied agent while surfactants B, C have been recently synthesized. They have a similar structure differing only by the number of polymeric branches: 4, 6 and 9 in the mentioned order. Systematic studies of thin liquid films stabilized by surfactant A (model studies) were performed to further characterize it through specific parameters which could be used as baseline to elicit the properties of the other polymeric surfactants. The aim was to establish a relationship between the surfactants' molecular structure and their

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* Corresponding author. Tel.: +359 2 8719206; fax: +359 2 9712688.
E-mail address: khristov@ipc.bas.bg (K. Khristov).

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respective physicochemical properties at different interfaces with the purpose to derive information pertinent to their practical application.

2. Materials and experimental methods

2.1. Materials

The polymeric surfactants reviewed in this paper were named A, B, and C and are products of Champion Technology, Inc, Fresno, Texas, USA. All of them belong to the class of branch type star-like diethylenetriamine based polymeric surfactants with a molecular weight of, respectively, 12,900, 16,700 and 13,800. Surfactant molecules consist of a diethylenetriamine (DETA) nucleus and a number of polymeric branches, containing polypropylene oxide blocks (PPO) and polyethylene oxide blocks (PEO). The molecule of each polymer is designed so as the polymer branches contain two parts: a more hydrophobic one, situated in the inner part of the molecule, closer to the DETA center (where PPO blocks are predominant) and a more hydrophilic one, situated in the outer part of the molecule (where PEO blocks are predominant). Thus, the surfactants are soluble in both water and organic solvents. Surfactants A, B, C have a similar structure differing only in the number of polymeric branches: 4, 6 and 9 in the mentioned order. A schematic of the polymeric surfactants is presented in Fig. 1. As mentioned above, surfactant A is an industrially applied agent and the concentration it is usually used is approximately 100 ppm [10]. For that reason the relevant experiments were carried out at this concentration. Emulsion films were prepared using toluene (analytical grade). The electrolyte used in the study was NaCl, Merck, roasted at 500 °C before use to remove all surface active impurities. All the water solutions were prepared using three distilled water with electro-conductivity $\kappa \leq 1\ \mu s\ cm^{-1}$ and surface tension $\sigma = 72 \pm 0.2$ mN m^{-1}.

The solid substrate used for contact angle and wetting film measurement was a smooth, flat, plane-parallel SiO_2-glass plate, which was rigorously prewashed with acid mixtures and doubly distilled water. Such a plate had a fully hydrophilic surface: contact angle $\theta_{aq} = 0°$ for pure water.

2.2. Experimental methods

2.2.1. Foam and emulsion film studies

The foam and emulsion film experiments were carried out using the microinterferometric method of Sheludko–Exerowa and Thin Liquid Film-Pressure Balance Technique (TLF-PBT) described in detail elsewhere [11–13]. Two variants of the measuring cell of Sheludko–Exerowa were used. For foam films studies a cell with glass film holder (radius R = 2 mm) where the film forms in the middle of a biconcave drop under constant capillary pressure was used [11,12]. For o/w/o emulsion films a cell with a porous plate film holder where the film forms in a hole drilled in the porous plate was used [11–13]. A third type of measuring cell representing an adaptation of porous plate method of Exerowa–Sheludko was used for w/o/w emulsion films. A number of modifications have been made to the porous plate technique in order to study w/o/w films [8,9] so as to account for the special requirements of these films. Among them the most important is the hole radius. It is drilled down to 1 mm or less to prevent the less dense oil phase from floating out of the hole and up to the air/water surface. Next, special preparation methods have been developed to ensure the hydrophobicity of the porous plate holder so that it functions properly [8,14,15].

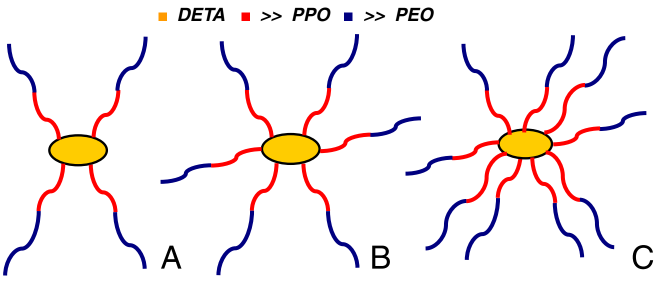

Fig. 1. Schematic presentation of polyoxyalkylated diethylenetriamine (DETA) polymeric surfactants: surfactant A (4 polymer chains); surfactant B (6 polymer chains) and surfactant C (9 polymer chains).

Recently two new intriguing techniques have been developed for assessing w/o/w emulsion film stability by applying an electrical field across the film. In article [16], the authors present an upgrading of TLF-PBT that combines AC or/and DC polarization with optical microinterferometry. The main advantage of this new method is that it is possible to measure film size and thickness by optical methods and critical voltage of film rupture and film capacitance from electrical impedance measurements within a single experiment and on the same film specimen. A microfluidic device to measure w/o/w emulsion films stability (critical voltage of film rupture) at micron size scale allows studying emulsion films under conditions close to real pressures as well as film areas observed in many real emulsion systems [17,18].

Electroconductivity of solutions investigated was monitored by Ino LAB Cond 730 conductometer (accuracy ± 0.5%) and surface and interfacial tension were measured using a Digital-Tensiometer K 10T, KRUSS, Hamburg by ring and Wilhelmy-plate methods.

2.2.2. Contact angle measurement

The contact angle θ was measured using the sessile drop technique [19] that is suitable for a flat solid surface. The experimental device has been described in our previous paper [20]. A 0.5 µl drop of water or aqueous solution, set on the solid surface was illuminated using white diffuse light. This drop was observed through the optical cuvette walls using a tele-microscope. The powerful objective lens used, produced a clear image of the drop which was directly transferred through a CCD-camera to project the drop profile, that can be used to determine the contact angle at the three phase contact line solid/liquid/gas. The accuracy of the contact angle measurements was increased using a special computer program (IMAQ Vision Builder) for image analysis. The accuracy of the contact angle measurements was ± 0.3° in the range of 1°–5° and ± 1.0° in the range of 5°–40°. Only the receding contact angle θ_r was measured in all experiments.

2.2.3. Wetting film thickness measurement

The experimental technique for studying thin wetting films [21–23] and for interferometrical measurement [11] of their thickness h has been upgraded and described in our previous paper [24]. The central part of the apparatus is the new experimental cell for formation of the microscopic thin wetting films. They are formed in the tetrafluoroethylene cell by slow approach of an air semi-bubble (blown out of a capillary tube) to the glass substrate. The microscopic circular film is observed in reflected light through the transparent bottom of the cell. Software for the computer treatment of the interferometrical data has been developed as well. We used an algorithm for calculating the thickness according to the equations derived in Ref. [25] with the following values of the optical constants: $\lambda = 575$ nm (wavelength of monochromatic light) and refractive indices $n_1 = 1.00$ (air), $n_2 = 1.33$ (aqueous solution), $n_3 = 1.46$ (fused SiO_2). The film thickness h obtained using this procedure is referred to as "water-equivalent film thickness" [11]. It is the thickness, which the wetting film would have provided that it was homogeneous and had a refractive index equal to that of the aqueous bulk solution.

3. Foam films

3.1. Surface tension measurements and critical association concentration (CAC) determination

It is a well known fact that for low molecular surfactants stable foam films in foam are formed when surface tension is reduced and