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SHORT COMMUNICATION

Wetting films on a hydrophilic silica surface obtained from aqueous solutions of hydrophobically modified inulin polymeric surfactant

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Abstract The thickness of wetting films on a hydrophilic silica surface was investigated using a microinterferometric technique. Aqueous solutions of hydrophobically modified inulin (INUTEC®SP1) at various concentrations, in the presence or absence of NaCl or Na_2SO_4, were studied. The equilibrium film thickness (h_{eq}) showed a complex dependence on INUTEC®SP1 concentration. At low electrolyte concentrations, h_{eq} decreased with an increase in INUTEC®SP1 concentration, reaching a minimum at 10^{-6} mol dm^{-3}. However, at high electrolyte concentrations, this dependence became less pronounced. At any given INUTEC®SP1 concentration, the equilibrium film thickness decreased with an increase in electrolyte concentration as a result of the compression of the electrical double layer reaching a minimum value. After that, the film thickness showed a small decrease with further increase in electrolyte concentration. This indicates that the electrostatic component of disjoining pressure can be neglected, and the steric repulsion of the loops and tails of INUTEC®SP1 determined the film thickness.

Keywords Wetting films · Equilibrium film thickness · INUTEC®SP1 · Polymeric surfactant

Introduction

The stabilization of dispersions of solid particles in an aqueous solution is very important for many technological applications, e.g., in paints, pigments, agrochemicals, pharmaceuticals, etc. Polymeric surfactants are widely used for stabilization of these dispersions [1, 2], particularly at a high volume fraction and in the presence of high electrolyte concentrations and temperatures. These polymeric surfactants are of the AB, ABA block, BA_n, or AB_n graft types. The block B to be referred to as the anchor chain is chosen to be strongly adsorbed on the surface (with multipoint attachment), and the A-block should be highly soluble in the medium and strongly solvated by its molecules to provide effective steric stabilization.

Recently, a novel graft AB_n copolymer has been designed with A consisting of inulin (linear polyfructose backbone) on which several alkyl groups are grafted [3]. This polymeric surfactant that is referred to as INUTEC®SP1 has been applied for stabilization of oil-in-water emulsions [4], latex dispersions [5], and other pigment dispersions. The high stability obtained by INUTEC®SP1 is due to the multipoint attachment to the solid surface or the oil by several alkyl chains leaving strongly hydrated loops and tails of linear polyfructose that provide enhanced steric stabilization. Evidence for the high repulsion obtained by this polymeric surfactant was obtained from measurements of emulsion films [6] as well as using atomic force microscopy [7].

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An alternative method for investigation of the stabilization of solid surfaces by this polymeric surfactant can also be obtained from the measurement of wetting films both on hydrophilic and hydrophobic surfaces. In this paper, we will only report the wetting films obtained on a hydrophilic silica surface from aqueous solutions of INUTEC®SP1. In a previous paper [8], we have reported experimental data of the contact angles at the three phase contact gas/liquid/solid for INUTEC®SP1 aqueous solutions, both on the hydrophilic solid silica surface as well as on a hydrophobic surface (obtained by treating the silica surface with dichlorodimethylsilane) [9]. These measurements could shed some light on the adsorption and conformation of the polymeric surfactant at the solid–liquid interface. The results obtained could be used for analysis of the results obtained on wetting films.

Experimental

Materials

The solid substrate used was a quartz glass smooth flat plate that was very carefully washed with acid mixtures and doubly distilled water; such a substrate had a hydrophilic surface. The quartz glass surface was not characterized using atomic force microscope or other similar techniques because the wetting films studied were relatively thick (25–70 nm) and the characteristic "macroscopically smooth" was enough for our experiments. The main characteristic of the solid surface was the contact angle θ of pure water on it. A drop of pure water put on this surface completely spread, and no contact angle could be measured ($\theta=0°$).

The polymeric surfactant was inulin on which several alkyl groups have been grafted (INUTEC®SP1, ORAFTI, Belgium). Its average molecular mass is approximately 4,500 g mol^{-1}. The inulin backbone (linear polyfructose) has a degree of polymerization greater than 23. The chemical structure of the polymeric surfactant has been given before [8]. The chemical composition of the modified polymer is not completely characterized there, as no such data have been provided by the producer ORAFTI. Aqueous INUTEC®SP1 solutions were prepared in the presence and absence of electrolytes: NaCl or Na_2SO_4 (from Merck) were heated for 2 h at 500 °C to remove any organic impurities. Doubly distilled water has been used for preparation of all solutions.

Two groups of aqueous solutions of INUTEC®SP1(in the range 2.5×10^{-8}–10^{-3} mol dm^{-3}) have been prepared at various NaCl concentrations (in the range 0 to 2 mol dm^{-3}) and at various Na_2SO_4 concentrations (in the range 0 to 1 mol dm^{-3}).

Methods

The experimental device for investigation of thin liquid-wetting films on solid surface [10–12] has been improved. A new experimental cell for the formation of the wetting films and their studying (Fig. 1) has been constructed. The films are formed between the horizontal surface of a smooth polished plate (*6* in the figure) of quartz glass (SiO_2) and the hemispherical gas bubble (*5* in the figure), which emerges from the orifice of a vertical capillary tube (*3* in the figure) forming a hemispherical meniscus. The meniscus is located very close to the solid surface, using a micrometric syringe, which creates a pressure difference between the gas phase in the bubble and the liquid phase (*4* in the figure) in the teflon vessel (*2* in the figure). The microscopic circular films are observed in reflected light through the transparent bottom of the cell using a vertical microscope (*1* in Fig. 1; Fig. 2). The light reflected from the film is measured using a photometric device with an amplifier, and the dependence photocurrent/time is recorded and further processed by a computer. The thickness h of the microscopic thin liquid films is calculated from the light intensity data, measured by the micro-interferometric method developed by Scheludko and Exerowa [13], using the following equation [14]:

$$h=\frac{\lambda}{2\pi n_2}\left(\frac{2m+1}{2}\pi-\frac{\delta}{2}-\arcsin\sqrt{\frac{\Delta}{1+4(1-\Delta)\frac{\sqrt{R_{12}R_{23}}}{\left(1-\sqrt{R_{12}R_{23}}\right)^2}}}\right),\tag{1}$$

$$\Delta=\frac{I-I_{\min}}{I_{\max}-I_{\min}},\tag{2}$$

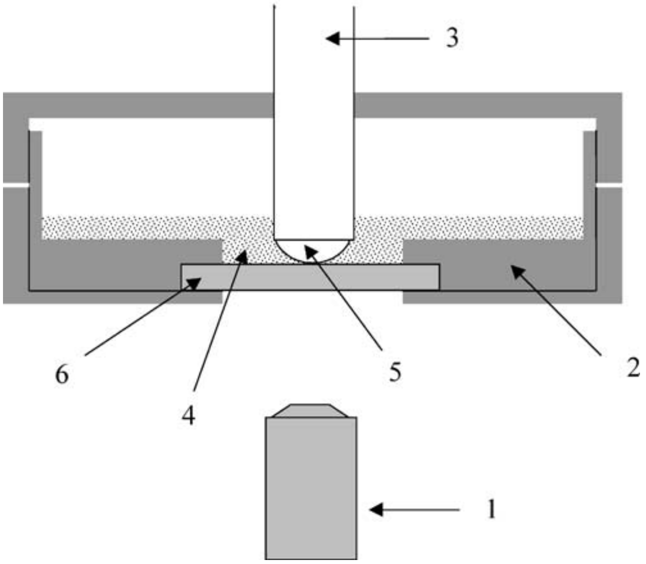

Fig. 1 Schematic presentation of experimental cell used for investigation of microscopic thin wetting films

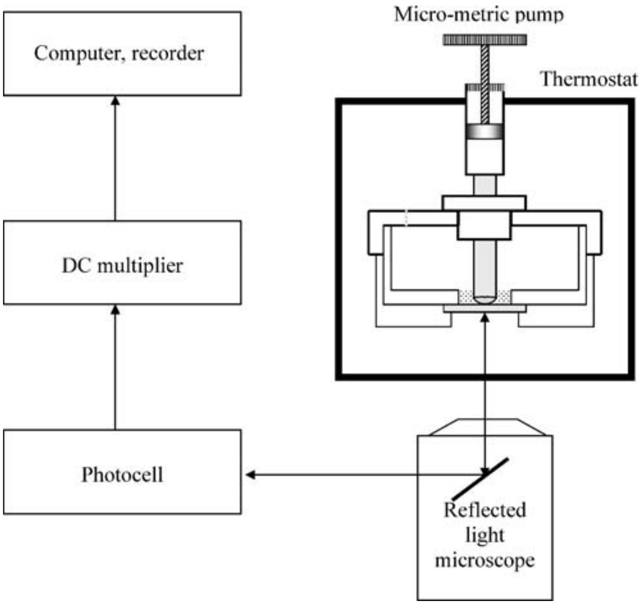

Fig. 2 Diagram arrangement of the microinterferometric apparatus

Here, m=0, 1, 2, 3,... determines the order of interference, $I_{\min}$ and $I_{\max}$ are the minimum and maximum intensities of interfered light, respectively, and

$$R_{12} = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \quad \text{and} \quad R_{23} = \frac{(n_2 - n_3)^2}{(n_2 + n_3)^2} \qquad (3)$$

The following values of the refractive indices have been used: n_1=1.00 for air, n_2=1.33 for aqueous solution, and n_3=1.46 for fused quartz (SiO$_2$); δ equals 0 because $n_3 > n_2 > n_1$. Because of the very low INUTEC®SP1 concentrations, the same n_2 value (1.3336) has been measured for all aqueous solutions.

The surface tension γ of all solutions studied has been measured using the Wilhelmy method [15]. The γ-log$C$ data have been used for evaluation of the critical association concentrations (CAC) of the INUTEC®SP1 aqueous solutions at different electrolyte concentrations. A summary of the measured surface tension γ as a function of surfactant and electrolyte concentration as well as the CAC values obtained at various NaCl concentrations is given in Table 1 of the study of Nedyalkov et al. [8]. The measured θ values for the solutions studied in the present work are also presented in the same paper [8].

All measurements have been performed at a temperature of 22 °C.

Results and discussion

Influence of equilibration time (t_{eq}) of the solid–liquid and liquid–gas interfaces on the film thickness

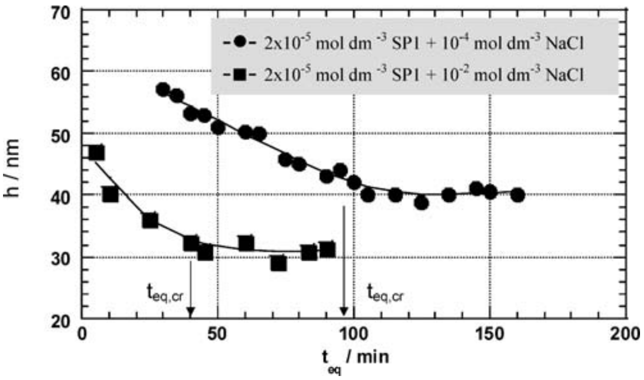

Fig. 3 Dependence of film thickness on the equilibration time (t_{eq}) for 2×10^{-5} mol dm^{-3} of INUTEC®SP1+10^{-4} mol dm^{-3} of NaCl and 2×10^{-5} mol dm^{-3} of INUTEC®SP1+10^{-2} mol dm^{-3} of NaCl aqueous solution

The variation of film thickness with equilibration time (t_{eq}) of the interfaces at the same INUTEC®SP1 concentration (2×10^{-5} mol dm^{-3}) and at two different electrolyte concentrations (10^{-4} and 10^{-2} mol dm^{-3}) is shown in Fig. 3. Each experimental point in this figure represents the film thickness obtained after equilibration of the two interfaces at the given times, and t_{eq} is the time elapsed between filling the cell with a solution and formation of a wetting film. Figure 3 shows that the film thickness decreases monotonically with the increase in the equilibration time of the interfaces, t_{eq}, reaching a constant value above a critical equilibration time ($t_{eq,cr}$). The latter depends on the electrolyte concentration, and $t_{eq,cr}$ is shorter at higher electrolyte concentrations. This behavior reflects the kinetics of adsorption of INUTEC®SP1 at the solid–liquid and air–liquid interfaces. One would expect adsorption to be faster at a higher electrolyte concentration because of the lower hydration of the molecule. $t_{eq,cr}$ may be identified with the time required for saturation of adsorption at both interfaces. The variation of $t_{eq,cr}$ with NaCl concentration is presented in Fig. 4. Figure 4 clearly shows that the critical time for saturation of both interfaces with INUTEC®SP1 decreases with increasing NaCl concentration, and a plateau value is reached between 10^{-2} and 10^{-1} mol dm^{-3}. This behavior reflects the increase in the adsorption rate of

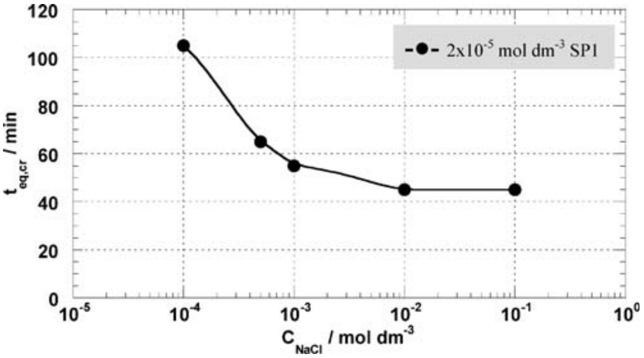

Fig. 4 Dependence of critical equilibration time ($t_{eq,cr}$) on the NaCl concentration for 2×10^{-5} mol dm^{-3} of INUTEC®SP1

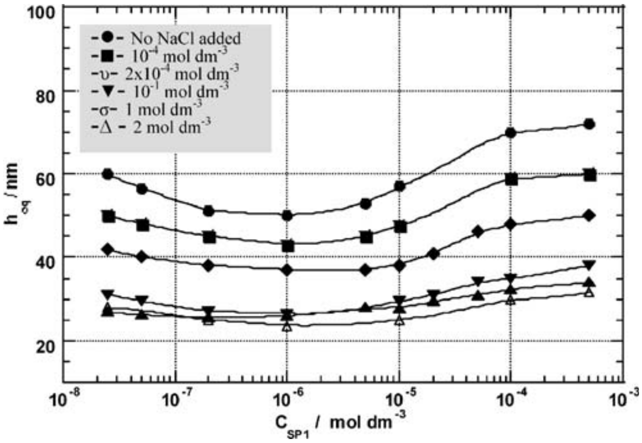

Fig. 5 Dependence of equilibrium film thickness (h_{eq}) on the INUTEC®SP1 concentration in the presence of different NaCl concentrations

INUTEC®SP1 with increase in NaCl concentration. To insure that an equilibrium thickness is reached, all measurements started 90 min after the solution was placed into the cell. For each solution studied, up to ten single *h* measurements have been performed, each of which outlasted about 10 min; that is, the duration of the *h* measurement procedure was about 90 min after the initial 90 min equilibration time.

Dependence of equilibrium film thickness (h_{eq}) on the INUTEC®SP1 concentration

The variation of the equilibrium film thickness (h_{eq}) with INUTEC®SP1 concentration, both in water and at various NaCl concentrations, is shown in Fig. 5. At C_{NaCl} below 10^{-1} mol dm^{-3}, the film thickness of h_{eq} decreases with an increase in INUTEC®SP1 concentration reaching a minimum at 10^{-6} mol dm^{-3}. After which, h_{eq} increases with further increase in polymeric surfactant concentration. However, at and above 10^{-1} mol dm^{-3} NaCl, this minimum at 10^{-6} mol dm^{-3} becomes less pronounced, and the increase in h_{eq} above 10^{-6} mol dm^{-3} of INUTEC®SP1 is slower. All the dependencies in Fig. 5 shift to smaller h_{eq} values as the concentration of NaCl increases. Similar results are obtained for Na_2SO_4 solutions; however, in this case, at 10^{-2} and 1 mol dm^{-3} Na_2SO_4, the minimum disappears all together (Fig. 6). In this case, the film thickness shows a weak dependence on INUTEC®SP1 concentration.

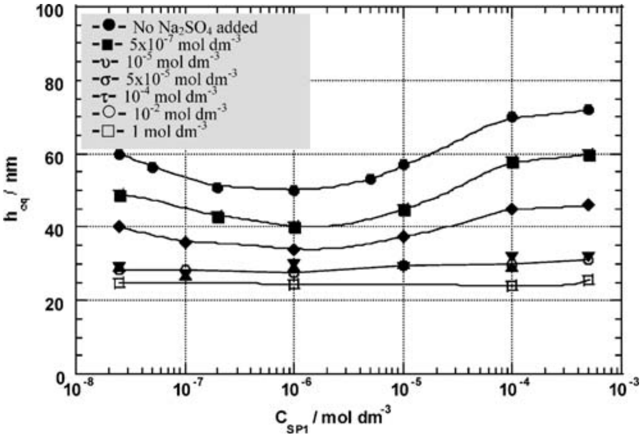

Fig. 6 Dependence of equilibrium film thickness (h_{eq}) on the INUTEC®SP1 concentration in the presence of different Na_2 SO_4 concentrations

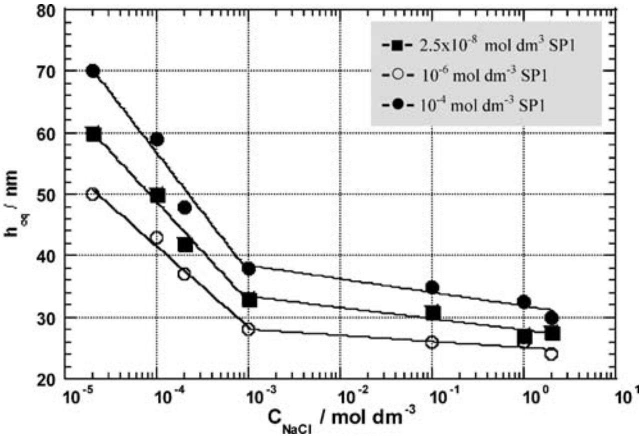

Fig. 7 Dependence of equilibrium film thickness (h_{eq}) on the NaCl concentration for 2.5×10^{-8}, 10^{-6}, and 10^{-4} mol dm^{-3} of INUTEC®SP1

The general trend of the variation of film thickness with INUTEC®SP1 concentration is difficult to be explained. Although not too large, the change of the film thickness is significant and reliable. The following qualitative picture could be drawn up on the basis of these data. It may be rationalized in terms of the adsorption and orientation of the polymeric surfactant at the solid–liquid and liquid–air interface. At low INUTEC®SP1 concentration, the INUTEC®SP1 molecules adsorb with the hydrophilic polyfructose loops and tails pointing toward the silica substrate

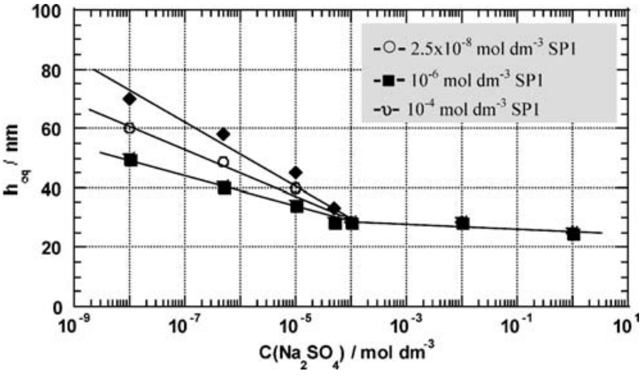

Fig. 8 Dependence of equilibrium film thickness (h_{eq}) on the Na_2SO_4 concentration for 2.5 × 10^{-8},10^{-6}, and 10^{-4} mol dm^{-3} of INUTEC®SP1

leaving the alkyl chains in solution. In contrast, at the air–water interface, the alkyl chains are in the air leaving the hydrophilic polyfructose loops and tails in the solution [16]. Contact angle measurements [8] showed a presence of a maximum in the contact angle on a hydrophilic silica surface at 10^{-6} mol dm^{-3} INUTEC®SP1 [8]. This maximum coincides with the minimum in film thickness. However, it is difficult to visualize why the film thickness should reach a minimum at this concentration. At a high INUTEC®SP1 concentration, the INUTEC®SP1 molecules form a bilayer with the hydrophilic polyfructose loops and tails now pointing to the aqueous phase, and this was illustrated schematically earlier (Fig. 7 in [8]). This bilayer formation can explain the increase in film thickness with an increase in INUTEC®SP1 concentration, which is also accompanied by the decrease in the contact angle [8].

Dependence of the film thickness on the electrolyte concentration

The variation of equilibrium film thickness with NaCl concentration at three different INUTEC®SP1 concentrations is presented in Fig. 7. The corresponding results for Na_2SO_4 are shown in Fig. 8. The general trend in both cases is similarly a decrease in the film thickness with an increase in electrolyte concentration reaching a minimum value at a critical electrolyte concentration $C_{el,cr}$. Above that concentration, the h_{eq} dependency shows only a slow decrease with an increase in electrolyte concentration. The critical concentration at which a minimum of h_{eq} is reached is lower for the Na_2SO_4 solution (10^{-4} mol dm^{-3}) as compared with the NaCl solution (10^{-3} mol dm^{-3}). This behavior (decrease in a film thickness with electrolyte concentration) reflects the compression of the electrical double layer at a higher electrolyte concentration as described in the DLVO theory [17, 18]. It is interesting that according to Figs 7 and 8, the ratio of the critical electrolyte concentrations $C_{el,cr}$ for NaCl and Na_2SO_4 is $C_{NaCl}/C_{Na2SO4} \approx 20$. This value is close to the value 2^6 predicted by the Schulze–Hardy rule [15], which, however, was derived for 1–1 and 2–2 electrolytes, while Na_2SO_4 is a 1–2 electrolyte.

A similar behavior has been observed earlier with emulsion films [19]. However, above a critical electrolyte concentration, the significant compression of the double layer means that the steric repulsion of the loops and tails of the INUTEC®SP1 determines the film thickness. The slow decrease in film thickness with increase in electrolyte concentration above $C_{el,cr}$ may be caused by some dehydration of the polyfructose loops and tails.

Conclusion

Wetting films from aqueous solutions of hydrophobically modified inulin polymeric surfactant (INUTEC®SP1) on hydrophilic silica surfaces were studied using a micro-interferometric technique. These wetting films showed a significant reduction in equilibrium film thickness with an increase in electrolyte concentration as a result of the compression of the electrical double layer. The film thickness reached a minimum value above a critical electrolyte concentration that depends on the nature of the electrolyte. The film thickness shows a small decrease with further increase in electrolyte concentration. The film thickness at high electrolyte concentrations is determined by the steric repulsion of the hydrophobically modified inulin surfactant. These results explain the stabilizing mechanism of solid particles in liquid dispersions stabilized using INUTEC®SP1.

References

1. Tadros ThF (1999) In: Goddard ED, Gruber JV (eds) Principles of science and technology in cosmetics and personal care. Marsel Dekker, New York
2. Napper DH (1983) Polymeric stabilization of colloidal dispersions. Academic, New York
3. Stevens CV, Merigg A, Peristoupoulo M, Christov P, Booten K, Levecke B, Vandamme A, Pittevils N, Tadros ThF (2001) Biomacromolecules 2:1256
4. Tadros ThF, Vandamme A, Levecke B, Booten K, Stevens CV (2004) Adv Colloid Interface Sci 108–109:207
5. Esquena J, Dominiguez FJ, Solans C, Levecke B, Tadros ThF (2003) Langmuir 19:10463
6. Exerowa D, Gotchev G, Kolarov T, Khristov Kh, Levecke B, Tadros ThF (2007) Langmuir 23:1711
7. Nestor J, Esquena J, Solans C, Luckham PF, Musoke M, Levecke B, Booten K, Tadros ThF (2007) J Colloid Interface Sci 311:430
8. Nedyalkov M., Alexandrova L, Platikanov D, Levecke B, Tadros ThF (2007) Colloid Polym Sci (in press)
9. Cecil R (1967) Nature 214:369
10. Platikanov D (1964) J Phys Chem 68:3619
11. Zorin Z, Platikanov D, Kolarov T (1987) Colloids Surf A 22:147
12. Diakova B, Filiatre C, Platikanov D, Foissy A, Kaisheva M (2002) Adv Colloid Interface Sci 96:193
13. Exerowa D, Kruglyakov PM (1998) Foam and foam films. Elsevier, Amsterdam
14. Scheludko A, Platikanov D (1961) Kolloid-Z 175:150
15. Lyklema J (2000) Fundamentals of interface and colloid science, vol III, liquid–fluid interfaces. Academic, London, p 1.39
16. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, NewYork
17. Derjagiun BV, Landau LD (1941) Acta Physicochim URSS 14:633
18. Verwey EJV, Overbeek TG (1948) The theory of the stability of liophobic colloids. Elsevier, Amsterdam
19. Exerowa D, Kolarov T, Pigov I, Levecke B, Tadros ThF (2006) Langmuir 22:5013