

FOAMS STABILIZED BY HYDROPHOBICALLY-MODIFIED INULIN POLYMERIC SURFACTANT

Khristo Khristov, Georgi Gotchew, Hristina Petkova,
Bart Levecke*, Tharwat Tadros**, Dotchi Exerowa

(Submitted on November 22, 2012)

Abstract

The foams and foam films stabilized by hydrophobically-modified inulin polymeric surfactant (INUTEC SP1) were investigated as a function of electrolyte concentrations. The Foam Pressure Drop Technique was applied to obtain the foam lifetime at constant capillary pressure. The Film Pressure Balance Technique was simultaneously applied to obtain the disjoining pressure as a function on film thickness. The results showed that at INUTEC SP1 concentration of 2×10^{-5} mol.dm⁻³ and constant capillary pressure of 5 kPa the foam lifetime τ_p was independent of electrolyte concentration in the range from 10^{-4} to 10^{-1} mol.dm⁻³ NaCl. Above 10^{-1} mol.dm⁻³ NaCl, the foam lifetime increased rapidly with the increase in NaCl concentration and the most stable foams were produced from solutions containing 1 and 2 mol.dm⁻³ NaCl. The critical pressure $P_{cr, foam}$ above which foam collapse (avalanche-like) occurred increased with the increasing of electrolyte concentration and this explained the higher stability of the foam at high NaCl concentrations. The disjoining pressure (Π)-thickness (h) isotherms showed a different behaviour at low and high electrolyte concentrations. At 10^{-3} mol.dm⁻³ NaCl, common thin films were obtained and the thickness decreased with increase in the pressure and rupture occurred at about 3 kPa. At 1 mol.dm⁻³ NaCl, black films were obtained with much smaller thickness that decreased slowly with the increase in Π and rupture occurred at about 2.7 kPa. These results indicated the transition from electrostatic to steric interaction as the electrolyte concentration was increased.

Key words: foam, foam films, inulin, polymeric surfactants

Introduction. The foam lifetime (foam stability) depends very much on the system, for example, in washing machines one would require a very short

lifetime and in this case anti-foaming agents are normally incorporated in the formulation. With personal care formulations, the lifetime of the foam must be adjusted to shampoo application and this lifetime should not be too long for ease of rinsing after application. In many other applications, a long lifetime is required as, for example, fire fighting foams, etc.

Several factors affect the foam lifetime, of which the following can be mentioned: (i) adsorption of surfactant at the air/water interface; (ii) formation of black film [1]. Both of these factors are affected by the nature of the surfactant and the electrolyte concentration.

As it has been shown in a previous study [2] on properties of foam films stabilized by INUTEK SP1, the dependence of film thickness vs electrolyte concentration below $5 \times 10^{-2} \text{ mol.dm}^{-3}$ NaCl a common thin films are formed, while above this concentration only black films are formed. This concentration has been named as $C_{\text{el, cr}}$ to denote the transition concentration from common thin films to black films, i.e. the transition from electrostatic to steric stabilization [1,2].

In this paper, we will report results on the foam lifetime and the Π/h isotherms for a single foam films stabilized by novel polymeric surfactant (INUTEK SP1, BENEIO Bio Based Chemicals ORAFTEI, Belgium) that is a graft-copolymer of the AB_n type, where A is inulin (linear polyfructose with a degree of polymerization greater than 23) and B are alkyl chains of C_{12} that are grafted on the inulin backbone. The effect of addition of electrolyte on the foam lifetime has been systematically investigated.

The above investigations provide fundamental information on the stabilization mechanism of foams produced using INUTEK SP1. Previous investigation in our laboratory showed that this graft-copolymer produced highly stable oil-in-water emulsions particularly in the presence of high electrolyte concentrations [3]. This high stability could be attributed to the strong adsorption of the polymeric surfactant (with multi-point attachment with several alkyl groups and the strong hydration of the linear polyfructose loops and tails) [3,4]. More evidence of this high stability has recently been obtained by investigation of emulsion films containing the polymeric surfactant [5].

Materials. The polymeric surfactant INUTEK[®]SP1 has been described before [3]. INUTEK[®]SP1 solutions were prepared with and without electrolyte. NaCl was a Merk product, with purity higher than 99.99% that was heated to 500 °C to remove any organic impurities. The electrical conductivity of the bi-distilled water used for the solutions was about $1 \mu\text{S.cm}^{-1}$.

Methods. A correlation between single foam films and real foams can be drawn only when the experimental conditions with respect to capillary pressure, film thickness and bubble radius, temperature, etc., are kept very close. Two techniques have been developed to meet this requirement: the Foam Pressure Drop Technique (FPDT) that allows one to apply specific (pre-determined) capillary pressure in the foam liquid phase to measure the foam lifetime at constant

pressure [1,6,7] and the Film Pressure Balance Technique (FPBT), that allows one to determine the disjoining pressure/film thickness isotherms [1,8-10]. This enables us to conduct comparisons between foam films and foams at equal capillary pressures [1,8-10].

An automated instrument developed on the principle of the Foam Pressure Drop Technique designated as the FA1 Foam Analyser [7] was used in these studies. The rationale behind this instrument is to measure foam drainage and foam lifetime under strictly defined value of the capillary pressure and to enable studying independently the drainage process and foam lifetime.

The single foam films were investigated with FPBT, which was described in detail in [1,2,8-10]. Briefly, with this technique a pressure can be applied to the film and the corresponding film thickness h is measured interferometrically, so that one obtains the disjoining pressure Π as a function of the film thickness h . From the resulting Π/h curves it is possible to estimate the stabilising surface forces acting in the film [1,2,6,10]. FPBT also enables to determine the critical pressure of single foam film rupture (the maximum pressure the films can resist). It was determined by smooth increase of pressure in the measuring cell up to film rupture [1,11].

Results and discussion. Figure 1 shows the dependence of foam lifetime τ_p vs electrolyte concentration (at $\Delta P = 5$ kPa) and INUTEC SP1 concentrations is $2 \times 10^{-5} \text{ mol.dm}^{-3}$. In the range of electrolyte concentrations from 10^{-4} to $10^{-1} \text{ mol.dm}^{-3}$, foam lifetime is about 2-3 min and almost independent of electrolyte concentration in this range. Above $10^{-1} \text{ mol.dm}^{-3}$ NaCl, the foam lifetime increases and the most stable foams are produced from solutions con-

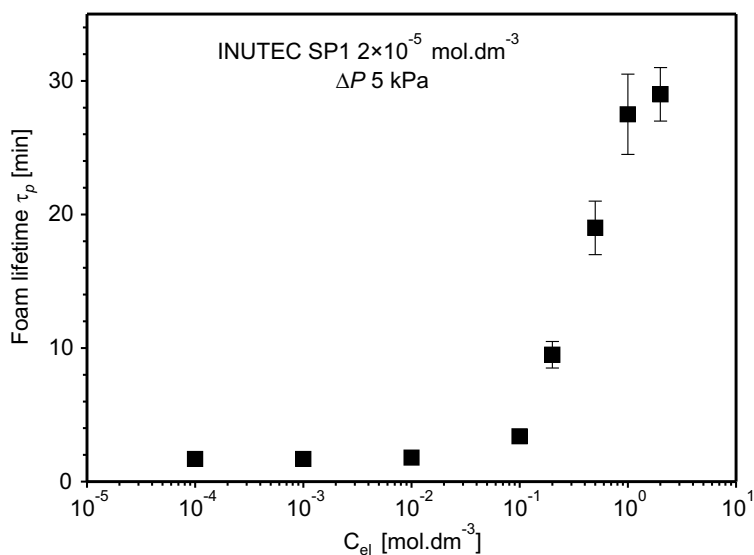


Fig. 1. Dependence of foam lifetime τ_p vs electrolyte concentration

taining 1 and 2 mol.dm⁻³ NaCl. The dependence of film thickness on electrolyte concentration (C_{el}) has been described before [2] and this indicates that up to 5×10^{-2} mol.dm⁻³ NaCl concentrations common thin films (CTF) are formed, above which only black films are formed. This electrolyte concentration has been referred to as $C_{el, cr}$ and it indicates the transition from electrostatic to steric interaction in this case [2]. These different types of foam films have been explained in detail before [1,6,10]. The results in Fig. 1 indicate that above this critical electrolyte concentration the foam lifetime rapidly increases with the increase of electrolyte concentration as a result of black film formation. As it is seen in Fig. 1, the range of electrolyte concentrations in which foam lifetime increases coincides with the one after which black foam films are formed [2].

It should be mentioned that the dispersity of the foam also showed a big change as the electrolyte concentration was increased. Below the critical electrolyte concentration, the foam had a low dispersity, giving large bubbles in the region of 2 mm diameter. Above $C_{el, cr}$ the dispersity of the foam increased and ultimately bubbles, in the region of 100 μ m, were produced at high electrolyte concentration. This change in dispersity could be explained in terms of the effect of the electrolyte concentration on the conformation of the loops and tails of polyfructose. Below $C_{el, cr}$ these loops and tails were well-extended, giving thick hydrated layers and under these conditions only large air bubbles could be produced. Above $C_{el, cr}$ the loops and tails became significantly collapsed, giving thinner layers and this could produce small foam bubbles. Evidence of the collapse of the tails and loops on addition of electrolyte has recently been obtained using Atomic Force Microscopy [4].

Figure 2A, B shows the foam lifetime τ_p dependence on applied pressure ΔP at two different INUTEK SP1 concentrations of 2×10^{-5} and 1×10^{-4} mol.dm⁻³. In both sub-figures, three different electrolyte concentrations, namely 10^{-3} , 0.5 and 1 mol.dm⁻³ NaCl, were used. The critical pressure [11] above which foam collapse (avalanche-like) occurred is indicated by arrows in the sub-figures. It can be seen that $P_{cr, foam}$ increased with increase in electrolyte concentration and it was almost independent of INUTEK SP1 concentration. Only at 10^{-3} mol.dm⁻³ NaCl (foam with CTF), the $P_{cr, foam}$ increases slightly. This clearly shows that the most stable foams are produced at high electrolyte concentrations.

Figure 3 shows the Π/h isotherms for black films (curve 1) and CTF (curve 2). Increasing the pressure led to thinning of black films from 15 nm at 50 Pa to 9 nm at 1500 Pa then they did not change in thickness with further increase in pressure up to 2.75 kPa, which was their critical pressure of rupture. With CTF the change in film thickness with pressure increase was significantly larger, from 62 nm at 50 Pa to 14 nm at 3 kPa. In this case, the critical pressure of film rupture is 3.5 kPa. Detailed description of Π/h isotherms of films stabilized with INUTEK SP1 has been presented in [2] and for this reason we will only point out here that the critical pressures of rupture for both film types are very close. The

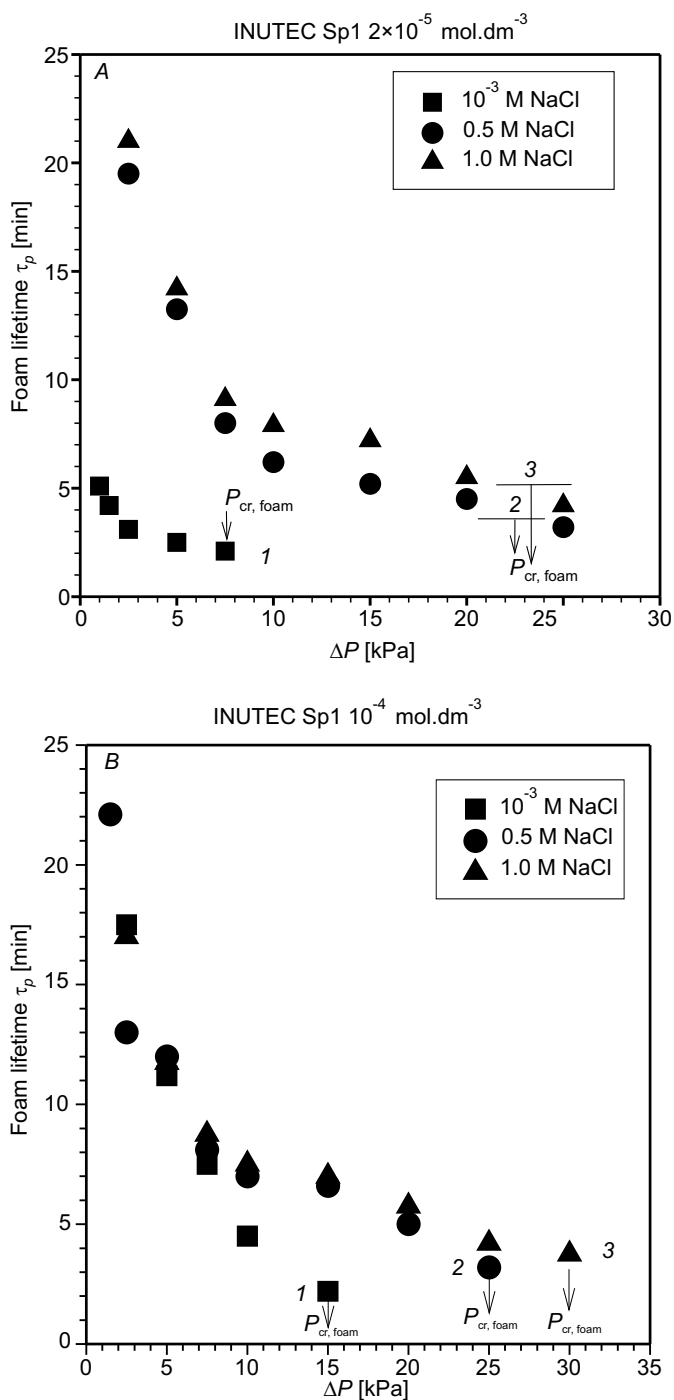


Fig. 2. Foam lifetime τ_p dependence vs applied pressure ΔP
 A – INUTEC SP1, 2×10^{-5} mol.dm⁻³; B – INUTEC SP1,
 10^{-4} mol.dm⁻³

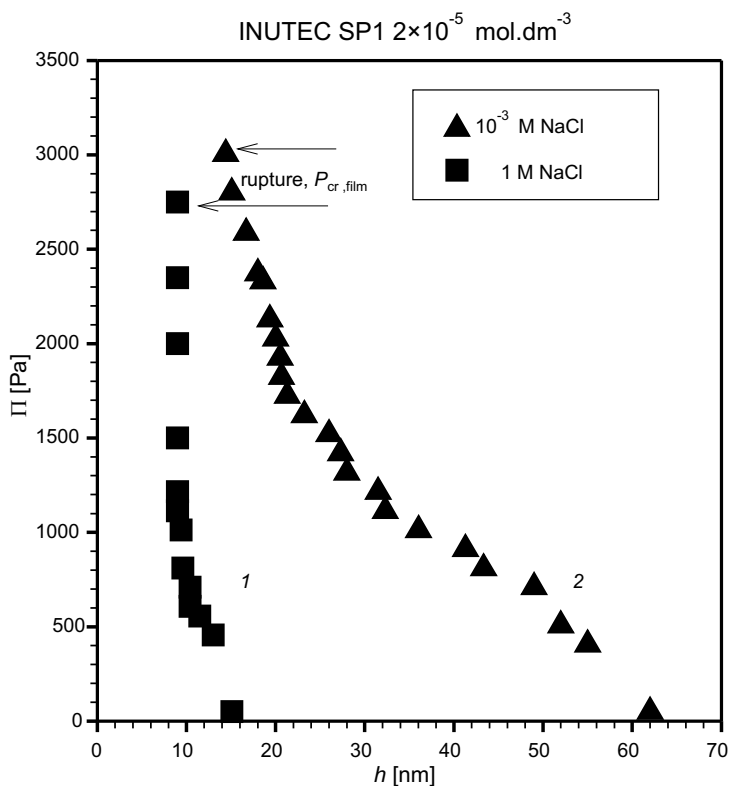


Fig. 3. Disjoining pressure (Π) vs film thickness (h) isotherms: curve 1 for black films and curve 2 for common thin films

comparison of the critical pressure of rupture for CTF (curve 2, Fig. 3) with the critical pressure of destruction for foams with CTF, curve 1, Fig. 2A indicates that they are very close, but still $P_{cr, foam}$ is higher (3.5 kPa for single foam films and 5–7 kPa for foams). With black films, however, the difference is more substantial. The critical pressure of film rupture is about 2.75 kPa, (curve 1, Fig. 3), while the critical pressure for foams is within the interval of 20–25 kPa, i.e. higher by an order, curves 2 and 3, Fig. 2A, B. Similar results have been obtained with other surfactants too [1, 6, 10–12]. A possible explanation is that films of a freshly-generated foam need time to thin to the respective thickness and thus to rupture. Under low applied pressures (like in our case), this process might be relatively slow [13] so that it is mainly the drainage and not the stability of the films that determines the foam lifetime (see Fig. 4). As an isolated film drains fast compared to a three-dimensional network of interrelated films, that may be a reason for higher value of $P_{cr, foam}$. The other reasons for the differences between $P_{cr, foam}$ and $P_{cr, film}$ have been discussed in detail in [11].

Figure 4 also indicates that the initial volume content of foam with CTF (curve 1) is much less than that of foam with black films (curve 2). This is at-

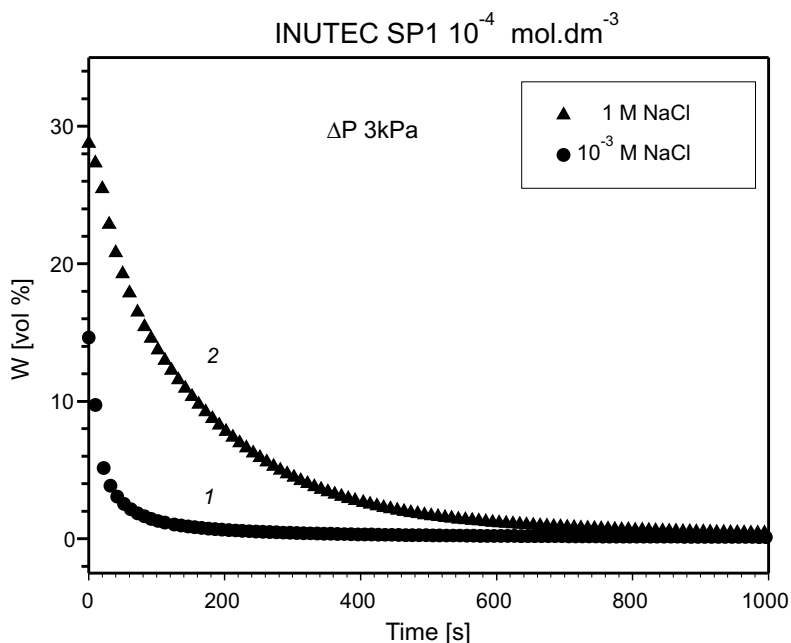


Fig. 4. Drainage rate for foam with common thin films (curve 1) and black films (curve 2)

tributed to the more coarse dispersity of the foam in the former case, even though experimental conditions, such as gas flow rate, pore size, surface tension, surfactant concentration, etc., were maintained equal and only the electrolyte concentration was different. Similar behaviour was observed in the foam lifetime vs electrolyte concentration dependence (Fig. 1), where after electrolyte concentration of 10^{-1} mol.dm $^{-3}$, the initial bubble size decreased, i.e. the foam became more finely dispersed and respectively foam lifetime increased [1]. The question why foam dispersity changes within electrolyte concentrations over 10^{-1} mol.dm $^{-3}$ is not clear yet. A probable explanation could be that the conformation of the loops and tails of polyfructose of the surfactant changes within this electrolyte concentration range [3,4]. This, however, deserves additional study and experimental corroboration.

Conclusion. The application of the two mutually complementing techniques – Film Pressure Balance Technique (FPBT), for the study of single foam films, and Foam Pressure Drop Technique (FPDT), for the study of foams, provides a possibility to make a correlation between foam film and foam stability. These methods were applied to study foam films and foams obtained using hydrophobically-modified inulin polymeric surfactant INUTEC SP1. The results obtained showed that the foam lifetime could be regulated by electrolyte concentration and this could find application in personal care formulations such as shampoos, hand wash, etc.

REFERENCES

- [1] EXEROWA D., P. M. KRUGLYAKOV. In: Foam and Foam Films (eds D. Möbius, R. Miller), Elsevier, Amsterdam, 1998, 773 pp.
- [2] EXEROWA D., T. KOLAROV, I. PIGOV, B. LEVECKE, TH. TADROS. *Langmuir*, **22**, 2006, No 11, 5013–5017.
- [3] TADROS TH., A. VANDAMME, B. LEVECKE, K. BOOTEN, C. V. STEVENS. *Adv. Colloid Interface Sci.*, **108–109**, 2004, 207–226.
- [4] NESTOR J., J. ESKUENA, P. F. LUCKHAM, M. MUSOKO, B. LEVECKE, TH. TADROS. *J. Coll. Interface Sci.*, **311**, 2007, No 2, 430–437.
- [5] EXEROWA D., G. GOTCHEV, T. KOLAROV, KHR. KHRISTOV, B. LEVECKE, TH. TADROS. *Langmuir*, **23**, 2007, 1711–1715.
- [6] STUBENRAUCH C., A. V. MAKIEVSKI, KHR. KHRISTOV, D. EXEROWA, R. MILLER. *Tenside, Surfactant, Detergents*, **40**, 2003, No 4, 196–201.
- [7] KHRISTOV KHR., D. EXEROWA, L. CHRISTOV, A. M. MAKIEVSKI, R. MILER. *Review of Scientific Instruments*, **75**, 2004, No 11, 4797–4803.
- [8] EXEROWA D., T. KOLAROV, KHR. KHRISTOV. *Colloids and Surfaces*, **22**, 1987, Nos 2–4, 171–185.
- [9] KHRISTOV KHR., D. EXEROWA, P. M. KRUGLYAKOV. *Coll. Polymer Sci.*, **261**, 1983, No 3, 265–270.
- [10] KHRISTOV KHR., D. EXEROWA, K. MALYSA. *Surfactant Foaming: New Concepts and Perspectives on the Basis of Model Studies*, Proc. Eurofoam 2000, Delft, the Netherlands, 2000, 21.
- [11] KHRISTOV KHR., B. JACHIMSKA, K. MALYSA, D. EXEROWA. *Coll. and Surfaces A*, **186**, 2001, Nos 1–2, 93–101.
- [12] KHRISTOV KHR., D. EXEROWA, G. MINKOV. *Colloids and Surfaces A*, **210**, 2002, Nos 2–3, 159–166.
- [13] KHRISTOV KHR., D. EXEROWA. *Colloids and Surfaces*, **94**, 1995, Nos 2–3, 303–309.

*Institute of Physical Chemistry
Bulgarian Academy of Sciences
Acad. G. Bonchev Str., Bl. 11
1113 Sofia, Bulgaria
e-mail: khristov@ipc.bas.bg*

**BENEO Bio Based Chemicals
Remylaan 4
3018 Wijgmaal, Belgium*

***89 Nash Grove Lane
Wokingham
Berkshire RG40 4HE, UK*