



## Effects of additives on the foaming properties of Aculyn 22 and Aculyn 33 polymeric solutions



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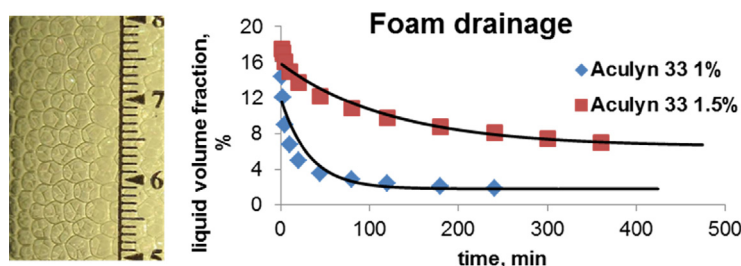
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### HIGHLIGHTS

- Aculyn 22 and Aculyn 33 have a high foamability and form stable foams.
- Addition of iso-propanol decreases viscosity of A22 but does not decrease the viscosity of A33.
- Aculyn 22 and Aculyn 33 solutions are non-Newtonian shear thinning liquids.
- Drainage kinetics of foams with addition of i-proH is faster.
- Addition of iso-propanol results in a faster foam coarsening.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 9 October 2013  
Received in revised form 21 February 2014  
Accepted 23 February 2014  
Available online 2 March 2014

#### Keywords:

Foaming polymer solutions  
Foam drainage  
Bulk viscosity  
Surface viscoelasticity

### ABSTRACT

Foam stability and foam drainage of aqueous solutions of Aculyn™ 22 and Aculyn™ 33 polymers are considered. Measurements of both bulk and surface rheology of A22 and A33 solutions in the presence of sodium chloride and iso-propanol are performed for the polymer concentrations 1–1.5%. Properties of mixtures of these polymers are investigated. Addition of iso-propanol does not change bulk properties of the A33 solutions but decreases their surface viscoelasticity. Addition of iso-propanol decreases bulk viscosity as well as the bulk and surface viscoelastic moduli of the A22 solutions and moves the region of pronouncing shear thinning behaviour to the smaller shear rates. The last effect depends on the salt concentration. Solutions of both polymers form foams, which are stable during several hours. Characteristic time of foam drainage increases with the polymer concentration and decreases with the salt concentration and iso-propanol content. The decrease in the surface viscoelastic modulus results in faster foam coarsening and lower foam stability.

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### 1. Introduction

Polymer emulsions Aculyn™ 22 and Aculyn™ 33 are rheology modifiers i.e. aqueous solutions of these polymers are highly viscous, shear thinning non-Newtonian liquids. They are compatible with many non-ionic and anionic surfactants and show synergistic

interaction with them [1,2]. Both polymers have a well-established toxicological profile [1,2], enabling their wide use in cosmetics. Aculyns are used in production of shampoos, bath foams, foaming facial cleansers, hair styling gels, liquid soaps, lotions, moisturizing creams and hair colourants [3]. In many of cosmetic and pharmaceutical applications foams are used as a carrying media for active agents and to attract customers' attention.

Traditionally, foams are stabilised by surfactants, but during the last decade polymers (polyelectrolytes) become frequently used additives in foaming solutions [4]. Polymers similar to

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low-molecular surfactants can adsorb on the interfaces and stabilize foam films. Polymers often increase viscosity of foaming liquids considerably, and in this way affect the foam drainage kinetics and gas permeability of the foam films [5]. Thin liquid films stabilized by polymer-surfactant mixtures, and foams stabilised by polymers or polymer/surfactant mixtures have been intensively investigated [6–8]. Most of common polyelectrolytes [8] and non-ionic polymers like poly(vinyl pyrrolidone) (PVP) [9] and polyoxyethylene (POE) [10] are used for foam stabilization. Polymers, surfactants and their mixtures are widely used not only in home and personal care products but in many industrial applications (e.g. paper industry) [11,12].

The rate of the liquid release from foam (drainage kinetics) is of great importance for the efficiency of the application (especially pharmaceutical and cosmetic). The rate of delivery of active substances to the target place is determined by the drainage kinetics.

There are two experimental methods to study foam drainage. In the ‘free-drainage’ situation, foam of initially uniform and constant wetness is allowed to drain: the foam dries first at the top, and the dry front propagates down through the foam, while the liquid emerges and accumulates at the bottom. Alternatively, in the ‘forced-drainage’ method, the foaming solution is poured onto the top of already dried foam, and the wet front propagates down through the foam. We used the free drainage method below.

Foam drainage has been investigated by a number of researchers [13–19], originating from the work of Leonard and Lemlich [20]. It was shown that the drainage kinetics is different for the cases when dissipation occurred mainly in the Plateau borders or in the nodes [21]; for wet foams, contribution from the lamellas can be also important [22]. The boundary conditions on the air/liquid interfaces in the foam determined mainly by surface viscoelastic properties of adsorption layers are also of great importance for the drainage kinetics. If the interfaces are retarded by the adsorbed surfactant, drainage slows down in comparison to the free interfaces [23].

In the previous paper [24] we presented the results of experimental study of influence of bulk and surface rheology of solutions of commercially available polymers Aculyn™ 22 and Aculyn™ 33 on foam drainage (we refer this paper as Part 1). Currently further investigations of properties modification (polymer, salt concentrations, mixtures) of Aculyn™ 22 (A22) and Aculyn™ 33 (A33) polymeric solutions for foaming applications are presented. In particular the foam coarsening was studied in details. Also influence of addition of iso-propanol alcohol on polymeric solutions properties (bulk and surface rheology) and relation to foaming (drainage kinetics, stability) are presented in this paper. Addition of iso-propanol is interesting from application point of view (this alcohol is often using as a solvent for active agents in cosmetics formulations).

Estimations performed in [24] have shown that for foams prepared with polymeric solutions of Aculyn 22 and Aculyn 33 air/liquid interfaces should be fully retarded, therefore surface viscoelasticity does not influence the drainage of these foams and the bulk viscoelastic properties are of main importance. This conclusion was confirmed experimentally [24]. At the same time, surface viscoelastic properties should affect essentially foam stability [25,26]. The latter is proven below.

## 2. Materials and methods

Aculyn™ 22 (labelled as A22) is a hydrophobically-modified alkali soluble emulsion (HASE) [1]. Aculyn™ 33 (labelled as A33) is an anionic alkali polymer emulsion, water soluble, lightly crosslinked [2]. Polymer emulsions of Aculyn™ 22, 30%

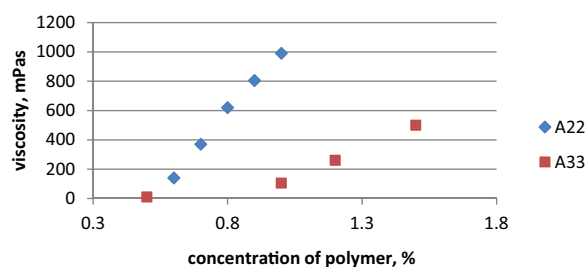


Fig. 1. Dependence of the viscosity of A22 and A33 solution on the polymers concentration (see text for details).

(A22) and Aculyn™ 33, 28% (A33) were supplied by Dow. For general formulas of A22 and A33 please see Fig. 1 in Part 1.

A22 and A33 are soluble in water in high pH (~12). Therefore aqueous solutions of polymers were prepared by neutralising the stock polymer emulsions with a 2% ammonia solution in ultra-pure water produced by Millipore Q, with ascorbic and citric acids added (0.2 mass % each). NaCl was added to solutions in the range of concentrations 0–1.5 M and iso-propanol was used at 0 or 1.67 M (10%) concentrations. The above compositions have been chosen to represent typical systems used in cosmetic applications where the polymers under investigation are utilized, for example in hair colourant applications. In such systems, salt is often used to control the ionic strength, and solvents like iso-propanol are added to control the solubility of actives.

Ammonia hydroxide solution 28–30%, sodium chloride >99.5%, citric acid >99.5%, (Sigma Aldrich); L-ascorbic acid, 99.8%, iso-propanol alcohol >99.5% (Fisher Scientific) were used as purchased.

The bulk rheology measurements have been made using the rheometer AR 1000-N, TA Instruments, with the cone geometry (4 cm diameter, cone of 1°59' and truncation of 56 μm). The temperature was kept constant using Peltier plate at 20 °C. In the oscillating mode the strain sweep measurements in the range 0.1–50 Pa have been performed, in the flow mode shear rate measurements in the range 1–20 s<sup>-1</sup> have been made. The experimental error at measuring probes taken from the same sample was below 5%, but the difference between individual samples of the same composition was larger, about 10%.

Surface rheology measurements have been performed at frequency 0.1 Hz by the Drop shape analyser DSA100, Kruss, Germany, using buoyant air bubble formed at the tip of the hooked capillary immersed in the cuvette containing a polymer solution. Bubble age for the presented results on surface viscoelasticity is 15 min.

Foaming experiments have been performed in a home-made set up consisting of glass cylinder with inner diameter of 43 mm and height of 380 mm and foaming head fitted in the base of cylinder [24]. The foaming head was equipped with 19 capillaries made of polyether ether ketone (PEEK) with inner diameter of 0.18 mm for gas supply. Inner diameter of the foaming head was 38 mm. The foaming gas was air. The flow rate was kept at 400 cm<sup>3</sup>/min.

The kinetics of foam drainage was studied according to the procedure described in Ref. [24]. A foaming liquid was poured into column to the height of 45 mm and bubbling was started with a constant flow rate. Bubbling was stopped after the foam reached the height of 250 mm. The height of the foam and the liquid under the foam were measured as functions of time. Each experimental run was repeated at least 3 times and the averages are reported below.

The average bubble size was found by analysing pictures taken after 5 min and 2 h after the foam formation, correspondingly; at least 20 bubbles were used to calculate the average size. Only size in vertical direction was analysed.

**Table 1**

Surface viscoelastic modulus,  $E$  (mN/m), for A33 and A22 solutions at various polymer concentrations (data presented in this table is summary of results presented in Part 1).

Polymer	Polymer concentration (%)	$E$ (mN/m)
Aculyn 33*	0.5	20
Aculyn 33	1	55
Aculyn 33*	1.2	63
Aculyn 33	1.5	85
Aculyn 22	0.6	20
Aculyn 22	0.7	32
Aculyn 22	0.8	49
Aculyn 22	1	65

### 3. Results and discussion

Concentration of the polymer, concentration of sodium chloride and addition of iso-propanol alcohol were selected as variable parameters to control properties of the A22 and A33 solutions. Mixtures of these polymers were also investigated to check their combined action, because mixtures of those polymers are of industrial relevance. Viscosity, bulk and surface viscoelastic moduli with relation to foam drainage kinetics and foam stability were measured. Characteristic time scales of foam drainage were calculated.

#### 3.1. Concentration of polymer

Dependence of bulk viscosity on the polymer concentration for the polymeric solutions under study at a constant shear rate ( $12 \text{ s}^{-1}$ ) is shown in Fig. 1. It is extension of our previous results presented in Part 1 (see Figs. 3 and 4). In the case of Aculyn 22, 1% solution of A22 with 0.2 mol/l NaCl was subsequently diluted by pure water to get lower concentrations of the polymer (the concentrations of all other components were proportionally reduced). Dependence of the viscosity on the polymer concentration for Aculyn 33, presented in Fig. 1 is made for solutions without added salt, with polymer concentration at 0.5%, 1%, 1.2% and 1.5%.

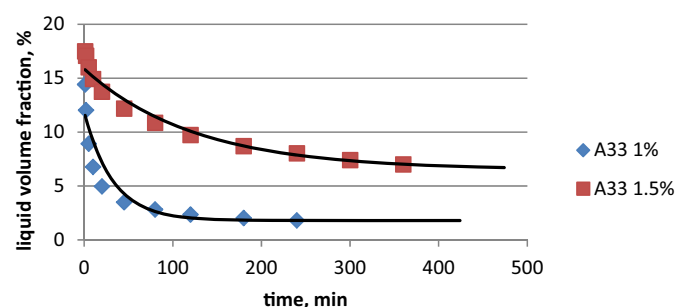
Fig. 1 shows that solution viscosity increases with the increase of the polymer concentration. Viscosity of the A22 solutions is much higher than that of the A33 solutions at the same polymer concentration. Bulk viscoelasticity measured for the same samples shows similar tendency, bulk viscoelastic modulus,  $G$  (Pa) increases with increasing of polymer concentration in solution. Presented results (for the particular components content) are in line with data described in Ref. [1,2]. Selected components (polymer, salt, ammonia, ascorbic and citric acids) content range was made because it is of industrial relevance.

Surface viscoelasticity was also measured, and the surface viscoelastic modulus,  $E$  (mN/m), was increasing with the polymer concentration in solution (see Table 1 which presents selected results obtained in Part 1 – Figs. 8–10 and new data labelled with\*).

All experimental results on foam drainage have been fitted exponentially as:

$$\varphi(t) = \varphi_{\infty} + (\varphi_0 - \varphi_{\infty}) \exp\left(\frac{-t}{t^*}\right) \quad (1)$$

where  $\varphi(t)$  is the liquid content at time  $t$ ,  $\varphi_0$  is the initial liquid content (%),  $\varphi_{\infty}$  is the liquid content in the equilibrium foam, estimated as an asymptotic value from the experimental time dependence of liquid volume fraction (%),  $t$  is time (min),  $t^*$  is a characteristic time scale of the drainage (min). It follows from Eq. (1) that  $t^*$  increases when the drainage slows down. Fig. 2 presents an example of fitting, all other drainage kinetic curves have been analysed in the same way and agree very well with dependency (1). To compare drainage kinetics, the characteristic time scale of drainage,  $t^*$ , was



**Fig. 2.** Drainage kinetics of foams produced using A33 1% and 1.5% polymeric solutions without NaCl (points) and exponential fitting (lines).

extracted in all cases under investigation. Characteristic drainage times for foams prepared with various solutions investigated in this study are presented in Table 2 together with bulk viscosity to simplify analysis (viscosity data for A33 1% and 1.5% and A22 1% 0.3 M and 1.3 M were presented earlier in Part 1).

Longer characteristic time is found for the foams formed with higher polymer content, due to higher viscosity of the solutions (see characteristic time for drainage kinetics of foam prepared from A33 solutions of 1% and 1.5% without NaCl, Table 2 and Fig. 2).

Strong influence of salt (NaCl) content on A22 and A33 solutions properties was presented in Part 1. Therefore concentration of sodium chloride was selected as a parameter to control viscosity of solutions for further investigations. For the both polymers viscosity decreases considerably with the increase of the salt concentration. Also surface viscoelastic modules essentially decrease with the increase of sodium chloride concentration. Similar tendency was found for the bulk viscoelastic modules.

#### 3.2. Mixtures of polymers

Properties of mixtures of A22 and A33 (1% polymer, 0.2 M NaCl) were investigated at 1:1, 1:3 and 3:1 A22:A33 ratios. The dependency of the bulk viscosity of the polymeric solutions on A22 concentration is presented in Fig. 3. The viscosity of mixture solution increases with the increase of A22 content.

The data presented in Fig. 4 show that the surface viscoelasticity for A33 is lower than for A22 and the surface viscoelasticity of mixture increases with the increase of A22 content. As both bulk and surface viscoelasticity depend rather smoothly on the content

**Table 2**

Characteristic time scale of drainage of foams prepared with investigated solutions.

Foaming solution	Bulk viscosity of foaming solution (mPas)	Characteristic time of drainage (min)
A33 1% 0 M NaCl	100 ± 10	32
A33 1% 0 M NaCl	100 ± 10	29
10% i-prOH		
A33 1.5% 0 M NaCl	500 ± 50	125
A33 1.5% 0 M NaCl	500 ± 50	100
10% i-prOH		
A22 1% 0.3 M NaCl	550 ± 10	100
A22 1% 0.3 M NaCl	400 ± 7	37
10% i-prOH		
A22 1% 1.3 M NaCl	100 ± 5	36
A22 1% 1.3 M NaCl	40 ± 5	2
10% i-prOH		
A22 1% 0.5 M NaCl	100 ± 10	12
10% i-prOH		
A22:A33 1:1	90 ± 10	6
A22:A33 1:3	40 ± 10	4
A22:A33 3:1	300 ± 15	70

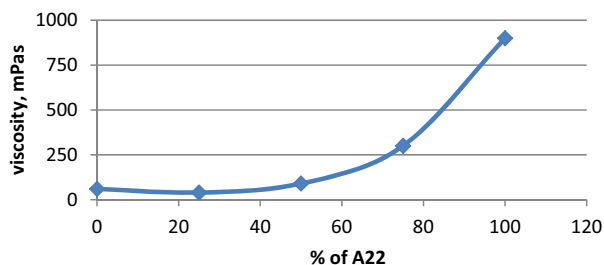


Fig. 3. Dependence of viscosity of mixtures of polymers solution on content of A22 (%) at shear rate  $12 \text{ s}^{-1}$ .

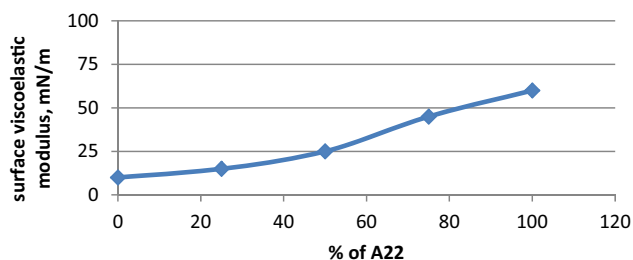


Fig. 4. Dependence of the surface viscoelastic modulus of mixtures of polymers solution on content of A22 (%); frequency 0.1 Hz, surface age 15 min.

of A22, i.e. no synergetic effect has been observed, it can be concluded that there is no essential interactions between two polymers in solution.

The characteristic drainage time scales (see Eq. (1)) for mixture of A22 and A33 are presented in Table 2. These data confirm that the drainage process is governed mainly by the viscosity of the liquid. Drainage of foam containing 75% of A22 is much slower than two others. However, the foam produced with the 1:1 mixture, which has nearly the same viscosity (90 mPa·s) as samples A33 1% 0 M NaCl and A22 1% 1.3 M NaCl (100 mPa·s), drains much more quickly. For the 1:1 sample the drainage was practically completed already in 20 min with 1% liquid left inside the foam, whereas in the samples of individual polymers with viscosity of 100 mPa·s there was about 5% liquid left after 20 min and about 2% after 2 h. The dependence of the viscosity on shear rate for this solution was very similar to that of A33 1% 0 M NaCl (Fig. 5), that is, taking into account faster drainage and shear thinning, the real viscosity during the drainage for the 1:1 mixture is expected to be even higher than for corresponding solutions of individual polymers. The surface viscoelastic modulus of 1:1 mixture is about two times lower than that of A33 1% 0 M NaCl but more than 2 times higher than that of A22 1% 1.3 M NaCl (see Table 3), therefore it cannot be the reason of the accelerated drainage. Thus, at the moment we cannot explain such fast drainage of 1:1 mixture.

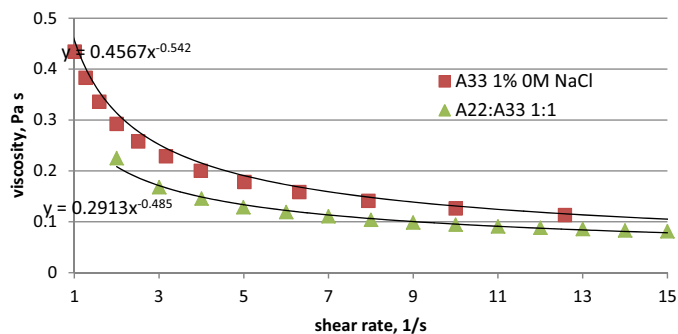


Fig. 5. Dependence of viscosity on shear rate for A22:A33 1:1 mixture and A33 1% 0 M NaCl polymeric solutions. Both dependences are fitted according to Eq. (2). The fitted parameters are:  $\mu_{\infty} = 0$  in both cases; for A33 1% 0 M NaCl  $K = 0.4567$ ,  $n = 0.458$ ; for A22:A33 1:1  $K = 0.2913$ ,  $n = 0.515$ .

Table 3

Comparison of properties of the A33 and A22 solutions containing 10% i-prOH.

Solution	Bulk viscosity (mPa·s)	$\gamma$ (mN/m)	E (mN/m)
A33 1% 0 M NaCl	$100 \pm 10$	$30 \pm 1$	$55 \pm 5$
A33 1% 0 M NaCl 10% i-prOH	$100 \pm 10$	$33 \pm 1$	$20 \pm 3$
A33 1.5% 0 M NaCl	$500 \pm 50$	$27 \pm 1$	$85 \pm 5$
A33 1.5% 0 M NaCl 10% i-prOH	$500 \pm 50$	$30 \pm 1$	$55 \pm 2$
A22 1% 0.3 M NaCl	$550 \pm 10$	$42 \pm 1$	$37 \pm 5$
A22 1% 0.3 M NaCl 10% i-prOH	$400 \pm 7$	$36 \pm 1$	$7 \pm 1$
A22 1% 0.5 M NaCl	$100 \pm 10$	$35 \pm 1$	$3 \pm 1$
A22 1% 0.5 M NaCl 10% i-prOH	$100 \pm 5$	$38 \pm 1$	$10 \pm 1$
A22 1% 1.3 M NaCl	$40 \pm 5$	$32 \pm 1$	$1.5 \pm 1$
A22 1% 1.3 M NaCl 10% i-prOH			

### 3.3. Addition of 10% iso-propanol (i-prOH) to polymers solutions

Polymer solutions of the viscosity 100 mPa·s and 500 mPa·s were selected to study influence of iso-propanol on their properties.

The bulk viscosity at shear rate  $12 \text{ s}^{-1}$ , the equilibrium surface tension and the surface viscoelastic modulus of investigated solutions are presented in Table 3.

Addition of 10% i-prOH does not change substantially both the viscosity and the bulk viscoelasticity of A33 solutions. The equilibrium surface tension,  $\gamma$  (mN/m), slightly increases and the surface viscoelasticity decreases for solutions with i-prOH (Table 3). According to Ref. [2] addition of 10% i-prOH to the solution of A33 1.5% decrease viscosity, but do not change viscosity of 3% and 0.75% of polymer (for pH 8). Comparison of this data [2] and our results presented in Table 3 confirms that properties of solutions of A22 and A33 polymers strongly depend of composition of and even small change in components/amounts/conditions could results in significant changes in properties.

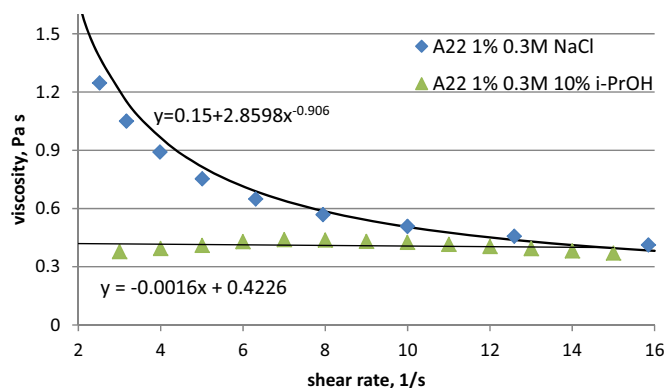
In the case of the foams prepared with A33 solutions and 10% i-prOH the drainage is only slightly faster (Table 2) in comparison to solutions without alcohol. The foams are stable for at least 2 h. This lack of influence of iso-propanol on A33 polymer solutions viscosity probably could be related to the polymer structure (A33 is cross-linked). In the case of A22 solutions addition of 10% i-prOH decreases the viscosity and the surface viscoelastic modulus (Table 3).

In the case of A22 addition of both NaCl and i-prOH influences bulk and surface properties of the solutions in rather similar way. However in the case of A33 addition of NaCl influence bulk viscosity of the solutions, whereas addition of i-prOH does not. Iso-propanol alcohol influence only surface viscoelasticity of A33 solutions.

The drainage is much faster than that of the sample without iso-propanol (Table 2) and the foam is stable for at least 2 h in the case of the foams prepared with A22 1%, 0.3 M NaCl, 10% i-prOH (by addition of iso-propanol solution viscosity decreases from 500 mPa·s to 400 mPa·s).

For the foams prepared with A22 1%, 1.3 M NaCl addition of 10% i-prOH results in the decrease of solution viscosity from 100 mPa·s to 40 mPa·s, considerable decrease of surface viscoelasticity and much faster drainage (Table 2). The foam with iso-propanol is stable for only 20 min.

Much faster drainage of foams prepared with solutions containing iso-propanol can be easily explained by consideration of the shear rate dependence of viscosity. As it is seen in Fig. 6, solution of A22 1% 0.3 M NaCl with 10% i-prOH at shear rates above  $2 \text{ s}^{-1}$  can be considered as Newtonian ones with viscosity independent of shear



**Fig. 6.** Dependence of viscosity on shear rate for A22 1% 1.3 M NaCl polymeric solutions with and without iso-propanol. Both dependences are fitted according to Eq. (2). The fitted parameters are: for A22 1% 0.3 M NaCl  $\mu_\infty = 0.15$ ,  $K = 2.8598$ ,  $n = 0.094$ ; for A22 1% 0.3 M NaCl 10% i-prOH dependence is almost constant.

rate, that is at low shear rates viscosity of this solution is much smaller than that without iso-propanol. From the data on drainage kinetics we estimated, that in the first 10 min of drainage of solutions without iso-propanol having viscosity 100 mPas at shear rate  $12 \text{ s}^{-1}$  (A33 1% 0 M NaCl and A22 1% 1.3 M NaCl) the shear rate in the Plateau borders is of the order of  $1 \text{ s}^{-1}$ . According to Fig. 5 viscosity corresponding to this shear rate is around 400 mPas, i.e. very close to that of A22 1% 0.3 M NaCl with isopropanol (Fig. 6) at any shear rate above  $2 \text{ s}^{-1}$ . It is seen from Table 2 that indeed characteristic time of foam drainage is rather close for solutions of A33 1% 0 M NaCl and A22 1% 1.3 M NaCl without iso-propanol and A22 1% 0.3 M NaCl with 10% i-prOH.

Solution of A22 1% 1.3 M NaCl with 10% i-prOH displays the shear thinning behaviour at shear rates below  $10 \text{ s}^{-1}$ , with viscosity about 100 mPas at shear rate  $2 \text{ s}^{-1}$ . If we accept that the drainage rate of foam produced with A22 1% 1.3 M NaCl solution corresponds to initial viscosity about 400 mPas as discussed above, then it is clear that drainage should be much faster for the sample of A22 1% 1.3 M NaCl with 10% i-prOH.

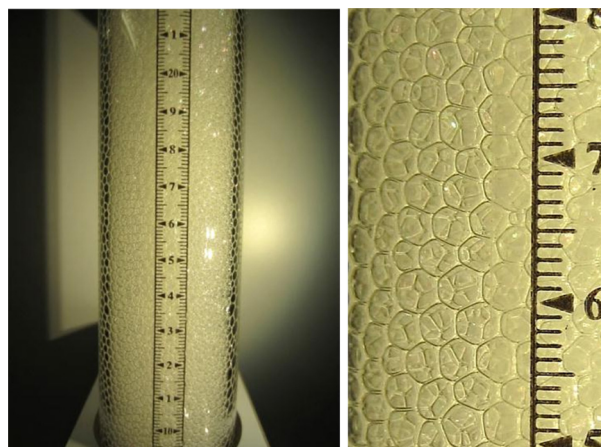
To understand in more details the influence of iso-propanol on the foam drainage kinetics, one more sample, A22 1% 0.5 M NaCl 10% i-prOH, having viscosity 100 mPas at  $12 \text{ s}^{-1}$  was studied. This solution demonstrated the shear thinning behaviour at shear rates below  $4 \text{ s}^{-1}$  and at shear rate  $2 \text{ s}^{-1}$  had viscosity about 180 mPas, i.e. much smaller than the sample of A33 1% 0 M NaCl (Fig. 5) having the same viscosity, 100 mPas, at  $12 \text{ s}^{-1}$ . It is seen from Table 2 that the drainage kinetics of foam produced with this sample is faster than that of sample with A33 1% 0 M NaCl.

The discussion above is in line with results presented in Ref. [27] where forced-drainage of foams made from Newtonian and non-Newtonian solutions of different viscosities has been compared. It was concluded that performance of both type of solutions is identical, provided one considers the actual viscosity corresponding to the shear rate found inside the foam. To summarise, it should be stressed that if we consider as a characteristic viscosity of shear thinning liquid the value  $\mu_c$  taken at certain shear rate,  $\dot{\gamma}_c$ , the dependence of the drainage rate on this characteristic viscosity will be stronger than just inverse proportionality. Accepting the commonly used power-law relationship for the viscosity of shear thinning liquid [28]

$$\mu = \mu_\infty + K\dot{\gamma}^{n-1} \quad (2)$$

where  $\mu_\infty$  high shear rate viscosity. In our case (Fig. 5)  $n < 1$  ( $1/n > 1$ ). It is easy to show that at  $\mu_\infty = 0$

$$\dot{\gamma} \sim \mu_c^{-1/n} \cdot \dot{\gamma}_c^{1-1/n} \quad (3)$$



**Fig. 7.** The snapshots of the foam produced from mixture of A22 and A33 (1:1) solution; the foam age is 5 min.

It is also noticeable that effect of iso-propanol on the bulk viscosity of A22 solutions depends on the salt concentration. Decrease in the salt concentration moves the region of pronouncing shear thinning behaviour to the smaller shear rates.

### 3.4. Bubble size distribution and foam stability

During the foaming experiments the snapshots (Fig. 7) were taken after 5 min and 2 h. The average bubble size  $D$  (mm) was measured and the bubble coarsening parameter  $C$  (%) was calculated as:

$$C = \frac{D_{2 \text{ h}} - D_{5 \text{ min}}}{2D_{5 \text{ min}}} \times 100\% \quad (4)$$

The average bubble size (mm), the coarsening parameter (%) and the percentage of changes in foam height after 2 h are presented in Table 4. The bubble size distribution was measured in vertical direction only, in horizontal direction photos do not show real bubble size due to deformation caused by lens effect of glass cylinder used in experiments. For convenience of analysis an extra column with surface viscoelastic modulus is included.

Foams formed using more viscous solutions (higher polymer concentration) have larger bubbles and are more stable, that is, they display smaller changes in the foam height (see Table 4). Foams form smaller bubbles if they were prepared using solutions containing higher NaCl concentration and with iso-propanol addition. The results given in Table 4 demonstrate also that there is no substantial change in the bubble size during first 2 h for samples without iso-propanol added, whereas in the samples with iso-propanol the bubbles grow faster.

The increase of value of the coarsening parameter with the decrease of surface viscoelasticity was found for solutions of each polymer. The only exceptions from that is A33 1% without NaCl and A33 1.5% without NaCl with 10% i-prOH solutions ( $E = 55 \text{ mN/m}$ ). The lower value of the coarsening parameter in the case of the foam prepared using A33 1.5% without NaCl and 10% i-prOH solution can be explained taking into consideration higher viscosity of those solutions (see Table 3) and, as a result, a slower drainage (see Table 2) and thicker liquid films.

If drainage range is the same (similar characteristic time scale of drainage) then coarsening is determined by surface viscoelasticity. For example for the solutions of A33 1% 0 M NaCl without and with 10% of i-prOH bulk viscosity is the same (100 mPas), characteristic time scale of drainage is similar (32 and 29 min), but surface viscoelasticity is much different – higher for solution without alcohol 55 mN/m and lower for solution with alcohol 20 mN/m. Coarsening

**Table 4**  
The average bubble size (mm), the bubble coarsening per hour (%) and the decrease in the foam height for foams produced from solutions of A33, A22 and their mixtures.

Solution	Average bubble size (mm) after 5 min	Average bubble size (mm) after 120 min	Coarsening (%)	% of changes in foam high after 2 h	E (mN/m)
A33 1% 0 M NaCl	2.12	2.52	9.0	6.9	55
A33 1% 0 M NaCl 10% i-prOH	2.81	3.74	16.5	6.9	20
A33 1.5% 0 M NaCl	5.41	5.54	1.2	1.9	85
A33 1.5% 0 M NaCl 10% i-prOH	3.85	4.12	3.5	3.9	55
A22 1% 0.3 M NaCl	5.46	5.74	2.5	0.77	37
A22 1% 0.3 M NaCl 10% i-prOH	2.79	3.41	11.1	3.5	7
A22 1% 0.4 M NaCl 10% i-prOH	2.62	3.30	12.9	3.6	4
A22 1% 0.5 M NaCl 10% i-prOH	2.60	3.77	22.5	3.3	3
A22 1% 0.7 M NaCl 10% i-prOH	2.45	3.67	24.9	3.9	2.5
A22 1% 0.8 M NaCl 10% i-prOH	2.31	3.49	25.5	4.7	2
A22 1% 1.3 M NaCl	3.15	3.49	5.4	4.3	10
A22 1% 1.3 M NaCl 10% i-prOH	1.98	3.04 <sup>a</sup>	160	79.7	1.5
A22:A33 1:3	2.80	3.17	6.6	10.6	15
A22:A33 1:1	2.15	3.72	3.6	7.5	25
A22:A33 3:1	4.10	4.35	3.0	3.0	45

<sup>a</sup> At the foam age of 20 min.

parameter is much higher for solution with i-prOH. Similar tendency is observed in the case of solutions of A33 1.5% 0 M NaCl without and with 10% of i-prOH. Also for the solutions of A22 1% 1.3 M NaCl and A22 1% 0.3 M NaCl despite the differences in bulk viscosity, characteristic time scale of drainage is almost identical and coarsening is determined by surface viscoelasticity (higher value of E and lower coarsening for solution A22 1% 1.3 M NaCl).

Therefore, it can be concluded that the decrease in the surface viscoelastic modulus results in faster foam coarsening and lower stability. The less stable sample A22 1%, 1.3 M NaCl, 10% i-prOH (the highest percentage of changes in the foam height) is characterized by the lowest surface viscoelasticity modulus.

Similar findings were presented in Ref. [29]. Authors demonstrate that rate of bubble Ostwald ripening in the foams, that is foam time of living (stability), depends on surface modulus of used surfactants solution. Higher surface modulus results in slower rate of Ostwald ripening. Adsorption layers in foams made of solutions with higher surface viscoelastic modulus are less permeable for gas.

At the same surface viscoelasticity bubbles in foam stabilised by A33 grow faster. This can be concluded by comparison of samples A33 1% 0 M NaCl and A22 1% 1.3 M NaCl. Those samples have very similar drainage kinetics [27] therefore the liquid films between bubbles are expected to be similar. However the coarsening in sample A33 1% 0 M NaCl is bigger than that in A22 1% 1.3 M NaCl despite the fact that the first sample displays much higher surface viscoelasticity (55 vs. 10 mN/m).

For the mixtures of polymers the surface viscoelasticity increases with the increase of A22 percentage, correspondingly the stability of foam increases and the coarsening decreases.

#### 4. Conclusions

Solutions of both studied polymers, Aculyn 22 and Aculyn 33, have a high foamability and form stable foams. Drainage kinetic is determined by bulk viscosity. The foams stability and coarsening at given drainage kinetics are determined mainly by the surface viscoelasticity.

Concentrations of polymers, sodium chloride and iso-propanol alcohol are useful parameters to control properties of A22 and A33 solutions and, hence, kinetics of foam drainage and foam stability.

The bulk viscosity of A22 solutions is much higher than that of A33 solutions at the same composition. Viscosity of mixture solution increases with increase of the A22 content. Addition of iso-propanol results in a decrease of the bulk viscosity of A22 solution whereas the viscosity of A33 remains unchanged. It is important to take into account that polymeric solutions used are non-Newtonian shear thinning liquids for which the changes of viscosity with the shear rate can depend strongly on the composition. For A22 solutions containing iso-propanol the region of pronouncing shear thinning behaviour is moved to the smaller shear rates. The last effect depends on the salt concentration.

The bulk viscoelastic modulus,  $G$  (Pa), and the surface viscoelastic modulus,  $E$  (mN/m), increase with the increase of polymer concentration in solutions and with the decrease of the salt concentration.

Addition of iso-propanol lowers the surface viscoelasticity of both polymeric solutions, but effect is much more pronouncing for those of A22. The drainage kinetics of foams prepared using solutions with addition of 10% i-prOH is faster than that of foams without iso-propanol, especially for A22 solutions.

The considerable decrease in the surface viscoelastic modulus due to addition of iso-propanol results in a faster foam coarsening. The considerable decrease in the foam stability was noticed for sample with the lowest value of the surface viscoelastic modulus.

### Acknowledgements

This research was supported by Procter & Gamble, USA; PASTA project, European Space Agency; COST projects CM1101 and MP1106 and EPSRC, UK.

### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.02.052>.

### References

- [1] <http://www.dow.com/assets/attachments/business/pcare/aculyn/aculyn.22/tds/aculyn22.pdf>
- [2] <http://www.dow.com/assets/attachments/business/pcare/aculyn/aculyn.33/tds/aculyn33.pdf>
- [3] Patent Number: RD478008-A; Patent Assignee Name(s) and Code(s): KEENAN A(KEEN-Individual) HAAS R A(HAAS-Individual); Hair gel formulations, useful for hair styling and as e.g. mousses, sprays and aerosols, contains Acudyne 180 hair fixative polymer thickened with combinations of Aculyn 22, 28, or 33 rheology modifiers to give improved formulation.
- [4] N. Kristen, R. Von Klitzing, Effect of polyelectrolyte/surfactant combinations on the stability of foam films, *Soft Matter* 6 (2010) 849–861.
- [5] R. Von Klitzing, H.J. Muller, Film stability control, *Curr. Opin. Colloid Interface Sci.* 7 (2002) 42–49.
- [6] D. Langevin, Polyelectrolyte and surfactant mixed solutions. Behavior at surfaces and in thin films, *Adv. Coll. Int. Sci.* 89–90 (2001) 467–484.
- [7] C. Uzum, N. Kristen, R. Von Klitzing, Polyelectrolytes in thin liquid films, *Curr. Opin. Colloid Interface Sci.* 15 (2010) 303–314.
- [8] A. Bhattacharyya, F. Monroy, D. Langevin, J.F. Argillier, Surface rheology and foam stability of mixed surfactant-polyelectrolyte solutions, *Langmuir* 16 (2000) 8727–8732.
- [9] B.M. Folmer, B. Kronberg, Effect of surfactant-polymer association on the stabilities of foams and thin films: sodium dodecyl sulphate and poly(vinyl pyrrolidone), *Langmuir* 16 (2000) 5987–5992.
- [10] A. Cervantes-Martinez, A. Maldonado, Foaming behaviour of polymer-surfactant solutions, *J. Phys. Condens. Matter* 19 (2007) 246101.
- [11] E.D. Goddard, K.P. Ananthapadmanabhan (Eds.), *Application of Surfactants with Polymers and Proteins*, CRC Press, Boca Raton, FL, 1993.
- [12] E.D. Goddard, K.P. Ananthapadmanabhan (Eds.), *Application of Polymer-Surfactant Systems*, Surfactant Science Series, vol. 77, Marcel Dekker, New York, 1998.
- [13] D. Exerova, P.M. Kruglyakov, Foam and foam films, in: D. Mobius, R. Miller (Eds.), *Theory, Experiment, Application. Studies in Interface Science*, vol. 5, Elsevier, Amsterdam, 1998.
- [14] D.L. Weaire, S. Hutzler, *The Physics of Foams*, Oxford University Press, Oxford, 2001.
- [15] D. Desai, R. Kumar, Flow through a plateau border of cellular foam, *Chem. Eng. Sci.* 37 (1982) 1361–1370.
- [16] A. Saint-Jalmes, D. Langevin, Time evolution of aqueous foams: drainage and coarsening, *J. Phys. Condens. Matter* 14 (2002) 9397–9412.
- [17] H.A. Stone, S.A. Koehler, S. Hilgenfeldt, M. Durand, Perspectives on foam drainage and the influence of interfacial rheology, *J. Phys. Condens. Matter* 15 (2003) S283–S290.
- [18] A. Saint-Jalmes, Physical chemistry in foam drainage and coarsening, *Soft Matter* 2 (2006) 836–849.
- [19] P.M. Kruglyakov, S.I. Karakashev, A.V. Nguyen, N.G. Vilkova, Foam drainage, *Curr. Opin. Colloid Interface Sci.* 13 (2008) 163–170.
- [20] R.A. Leonard, R. Lemlich, A study on interstitial liquid flow in foam. Part. 1. Theoretical model and application to foam fractionation, *AIChE J.* 11 (1965) 18–25.
- [21] S.A. Koehler, S. Hilgenfeldt, H.A. Stone, A generalized view on foam drainage: experiment and theory, *Langmuir* 16 (2000) 6327–6341.
- [22] V. Carrier, S. Destouesse, A. Colin, Foam drainage: a film contribution? *Phys. Rev. E* 65 (2002) 061404.
- [23] M. Durand, D. Langevin, Physicochemical approach to the theory of foam drainage, *Eur. Phys. J. E* 7 (2002) 35–44.
- [24] A. Bureiko, A. Trybala, J. Huang, N. Kovalchuk, V.M. Starov, Bulk and surface rheology of Aculyn™ 22 and Aculyn™ 33 polymeric solutions and kinetics of foam drainage, *Colloid Surface A* 434 (2013) 268–275.
- [25] H. Fruhner, K.D. Wantke, K. Lunkenheimer, Relationship between surface dilational properties and foam stability, *Colloid Surface A* 162 (1999) 193–202.
- [26] D. Langevin, Influence of interfacial rheology on foam and emulsion properties, *Adv. Coll. Int. Sci.* 88 (2000) 209–222.
- [27] M. Safouane, A. Saint-Jalmes, V. Bergeron, D. Langevin, Viscosity effects in foam drainage: Newtonian and non-Newtonian foaming fluids, *Eur. Phys. J. E* 19 (2006) 195–202.
- [28] R.G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford University, New York, 1999.
- [29] S. Tcholakova, Z. Mitrinova, K. Golemanov, N.D. Denkov, M. Vethamuthu, K.P. Ananthapadmanabhan, Control of Ostwald ripening by using surfactants with high surface modulus, *Langmuir* 27 (2011) 14807–14819.