

Bulk and surface rheology of Aculyn™ 22 and Aculyn™ 33 polymeric solutions and kinetics of foam drainage

A. Bureiko¹, A. Trybala², J. Huang², N. Kovalchuk^{2,3}, V. Starov^{2*}

¹Procter & Gamble, USA

²Department of Chemical Engineering, Loughborough University, UK

³Institute of Biocolloid Chemistry, Kiev, Ukraine

Abstract

Experimental investigations of both bulk and surface rheology of solutions of commercially available polymers Aculyn™ 22 and Aculyn™ 33 in presence of sodium chloride are performed in a wide range of the polymer and salt concentrations. It is shown that the bulk viscosity and the surface viscoelastic modulus of solutions of both polymers increases with the increase of polymer concentration and the decrease of the salt concentration. Solutions of both polymers demonstrate very good foamability and form stable foams. Foam drainage is governed mainly by the bulk viscosity when the latter is in the range of 100-500 mPa·s.

Keywords: foam drainage, bulk viscosity, yield stress, surface visco-elasticity

*Corresponding author: V.M.Starov@lboro.ac.uk, tgel +44 (0)1509 222508,

fax +44 (0)1509 223923

Introduction

Foams are widely used in industry as well as in our everyday life. The well-known examples of industrial applications of foams are a froth flotation [1], a foam separation of surfactants [2], and various applications in petroleum and gas industries [2]. Everyday experiences include beer, cappuccino, ice cream, shaving foams etc. Foams become now more and more popular formulations in pharmacy and cosmetics owing to their good spreadability, lack of stickiness upon application, quick absorption of active components, ease of application to hair-bearing skin and to the desired place only (foams do not easily flow unlike usual liquids of low viscosity) [3-5]. According to [3], patients demonstrated preference for foams in topical drug formulations. According to [6], hair colouring products applied as foams demonstrated improved application and good colour delivery.

For many applications, including pharmaceutical and cosmetic, the rate of the liquid release from the foam, i.e. drainage kinetics, is of great importance because it determines the rate of delivery of active substances to the target place. The considerable efforts have been made in theoretical description of foam drainage [2,7-12] started by pioneering work of Leonard and Lemlich [13]. It was shown, that the drainage kinetics is different for the cases when dissipation occurs mainly in the Plateau borders or in nodes [14], for wet foams the contribution from lamellas can be also important [15]. The most important results on the foam drainage are presented in the recent review [16].

The characteristics of liquid flow inside the foam and therefore the drainage kinetics depend to a great extent on the boundary conditions on the liquid/air interfaces. Two limiting cases are Poiseuille flow if the interfaces are completely immobile in tangential direction (zero tangential velocity on the boundaries) and plug flow in the case of tangentially mobile interfaces [17]. The drainage is much slower in the first case of retarded interfaces. The surface retardation is determined by the amount and properties of substances adsorbed on the bubble interfaces. For example, experimental study involving flow visualization in the single Plateau border [18] has shown that the interface is tangentially immobile if a protein (bovine serum albumin) used as a foam stabilizer, whereas the interface is rather tangentially mobile if a low molecular weight surfactant (sodium dodecyl sulphate) is used.

It was assumed in [13] and many subsequent works that the surface shear viscosity is the parameter accounting for the surface retardation. On the other hand, according to [17] the dilational surface elasticity [19,20] is the acting parameter rather than the shear or surface viscosity. The latter is supposed to be true at least in foams stabilised by the low molecular weight surfactants, for which the shear viscosity is several orders of magnitude lower than the dilational viscoelastic modulus [19].

However, the contribution of surface viscoelasticity depends on other properties involved: the bubble size, liquid volume fraction and liquid bulk viscosity [11,13,17].

Unfortunately despite of the substantial progress in understanding of foam drainage processes the precise quantitative prediction of drainage behaviour based on the measurable properties of the substances involved is still impossible. That is why the experimental studies remain of great importance especially those involving new foaming agent, such as polymers.

During the last decade polymers (polyelectrolytes) have become frequently used additives to foaming solutions, most often together with surfactants [21]. Similarly to low-molecular surfactants polymers can adsorb at the interfaces and in that way stabilize foam films. Moreover, addition of polymers allows increasing the viscosity of foaming solutions and therefore slowing down the drainage and decreasing the gas permeability of foam films [21]. The use of polymers to replace significant portion of surfactants can be of benefit in industrial applications. For example, a US patent [22] describes polymer stabilised hair colouring foams which are essentially free of surfactants and provide improvements in colour delivery.

The large amount of comprehensive studies has been performed recently on the properties of thin liquid films stabilized by polymer-surfactant mixtures [23-25], and on foams stabilised by polymers or polymer/surfactant mixtures using both polyelectrolytes [26] and nonionic polymers, most common being poly(vinyl pyrrolidone) (PVP) [27] and polyoxyethylene (POE) [28].

Foaming properties of nonionic polymer poly(N-vinylformamide) and cationic polymer poly(vinylamine) in mixtures with different surfactants: anionic – sodium dodecyl sulphate (SDS), non-ionic – polyoxyethelene-23 dodecyl ether (Brij 35), and cationic – dodecyltrimethylamonium bromide (DTAB) were thoroughly studied in [29]. The foaming properties of most compositions have been explained in [29] considering the polymer surfactant interactions in bulk and at the interfaces. The most surprising result of this study, which still requires its explanation, is the increased (in comparison to pure surfactant solution) foamability and foam stability of mixture of cationic surfactant and cationic polymer.

Despite of intensive studies in this field, as to our knowledge there was no results published matching the bulk rheological properties of non-Newtonian foaming liquid, its surface rheology and foaming characteristics. The proposed results are aimed to fill the existing gap. For this study we have chosen the commercially available (from Dow) polymer emulsions Aculyn™ 22 and Aculyn™ 33 which are recommended for applications in cosmetics. Both polymers are soluble in water at high pH and are rheology modifiers, i.e. their solutions are highly viscous, shear thinning non-Newtonian liquids. The polymers are also expected to be surface active due to the presence of hydrophobic groups; however, the nature and distribution of these groups is expected to be quite different between the two polymers. One of the

polymers, Aculyn™ 22, is referred as a foam stabilizer in the Dow Technical Data Sheets [30].

Materials and methods

Aculyn™ 22 (A22 below) is a hydrophobically-modified alkali soluble emulsion (HASE) with general structure shown in Fig. 1a [30]. Aculyn™ 33 (A33 below) is an anionic alkali soluble polymer emulsion, lightly crosslinked, with general structure shown in Fig. 1b [31]. All substances (polymer emulsions Aculyn™ 22, 30 % (A22) and Aculyn™ 33, 28 % (A33), Dow; ammonia hydroxide solution 28-30 %, sodium chloride >99.5 %, citric acid >99.5 %, Sigma Aldrich; L-ascorbic acid, 99.8 %, Fisher Scientific) were used as purchased. Aqueous solutions of polymers were prepared by dilution of stock emulsions with 2 % ammonia solution in ultra-pure water produced by Millipore Q, containing additionally ascorbic and citric acids (0.2 mass % each). Solutions had pH12 providing good solubility of polymers. Solutions with lower pH values were not studied because of essential decrease of polymers solubility with decrease of pH. NaCl was added to solutions in the range of concentrations 0-1.5 M to regulate the bulk viscosity.

Foaming experiments have been performed in a home-made column consisting of glass cylinder with inner diameter of 43 mm and height of 380 mm and foaming head fitted in the base of cylinder. The foaming head is equipped with capillaries with inner diameter of 0.18 mm made of polyether ether ketone (PEEK) for gas supply. The foaming gas was air. The equipment allows varying the flow rate in the range of 200-1000 cm³/min. In this study the flow rate has been kept at 400 cm³/min.

The kinetics of foam drainage was studied as follows. A foaming liquid was poured into column to the height of 45 mm and bubbling was started keeping the flow rate constant. Bubbling was stopped after the foam reached the height of 250 mm. The height of foam and the liquid under the foam were measured as functions of time.

The measurements of bulk rheology have been performed on the rheometer AR 1000-N, TA Instruments using a cone and plate geometry with a steel cone of 4 cm diameter, cone of 1°59' and truncation of 56 μm. The temperature was kept constant at 20 °C using Peltier plate. The yield stress was estimated as the stress value at which the storage modulus becomes equal to the loss modulus [32,33]. The strain sweep measurements in the range 0.1-10 have been performed at frequency 1 Hz. The experimental error at measuring probes taken from the same sample was below 5 %, but the difference between different samples of the same composition was larger, about 10 %

The measurements on the surface rheology have been performed in the range 0.02-0.5 Hz by the Drop shape analyser DSA100, Kruss using buoyant air bubble formed at the tip of hooked capillary immersed in the cuvette containing a polymer solution.

Results and discussion

Bulk rheology

Bulk rheology determines to a great extent the foam drainage behaviour. The velocity of drainage, v , can be estimated as [11]:

$$v = \frac{K\rho gR^2 f(\varphi)}{\mu} \quad (1)$$

where K is a geometrical coefficient, ρ is the liquid density, g is the acceleration due to gravity, R is the bubble radius, φ is the liquid volume fraction, with $f(\varphi)=\varphi$ for the rigid surface of Plateau border and $f(\varphi)=\varphi^{1/2}$ for the mobile surface, μ is the dynamic viscosity. According to Eq (1) the drainage velocity is inversely proportional to the bulk viscosity. In the case of shear thinning liquids viscosity itself depends on the velocity, increasing with the decrease of velocity, what further slows down the drainage.

If the foaming liquid demonstrates a noticeable yield stress it can also affect the drainage. Liquid drains from the foam under the gravity opposed by the gradient of the capillary pressure. If the resulting driving force is smaller than the yield stress the drainage stops. The yield stress is considered sometimes currently as a rather controversial concept and it is claimed sometimes that the non-Newtonian liquids can flow under any stress whatever low it is [34,35]. However, on the time scale of the practical interest of foams drainage below such flow can be neglected.

Both A22 and A33 solutions demonstrate well pronounced shear thinning behaviour (Fig.2). To display the dependence of the viscosity on the concentrations of salt and polymer, the viscosity data for one chosen shear rate, 12 s^{-1} are presented in Figs. 3 and 4. Fig. 2 shows that this viscosity is close to the high shear rate limit. Fig. 3 shows that for both polymers viscosity decreases considerably with the increase of the salt concentration. Viscosity of A22 solutions is much higher than that of A33 solutions at the same composition. Viscosity increases essentially with the increase of the polymer concentration as it is seen from Fig. 3 for A33 and from Fig. 4 for A22. For the data presented in Fig. 4 the solution of A22 1%, NaCl 0.2 mol/l was chosen as the basic one and then was diluted by pure water to get lower concentrations of the polymer (the concentrations all other solutes became also lower). The similar samples have been used for measurements on the yield stress presented in Fig. 6.

Solutions of A22 polymer demonstrate noticeable yield stress, decreasing with the increase of NaCl concentration (Fig. 5) and increasing with the increase of polymer concentration (Fig. 6). Solutions of A33 polymer are predominantly viscous, the only measurable values of yield stress have been found for 1.5 % solutions of A33 at low salt concentration 0.05 M NaCl (about 1.4 Pa) and without NaCl (about 3.1 Pa).

Surface rheology

The surface rheology is another important factor affecting the foam drainage, because it determines the mobility of the Plateau border surfaces. The drainage slows down by the decrease of the surface mobility. Leonard and Lemlich [13] first introduced the dimensionless parameter

$$M_s = \frac{\mu r}{\mu_s} \quad (2)$$

defining the surface mobility, where r is the radius of a Plateau border, μ_s is the surface shear viscosity. The surface is assumed to be rigid at $M \ll 1$ and mobile at $M \gg 1$. This assumption was confirmed by the direct numerical simulations of the liquid flow through the single Plateau border taking into account the surface shear rheology and neglecting dilational surface rheology [36]

Later Durand and Langevin [17] introduced a similar parameter for the case when dilational viscoelasticity comes into play. For the insoluble monolayer

$$M_{di} = \frac{\mu D_s}{E r} \quad (3)$$

and for adsorption monolayer

$$M_{da} = \frac{\mu D \Gamma_{eq}}{E r c_{eq}} \left(\frac{dc}{d\Gamma} \right)_{eq}, \quad (4)$$

where D_s is the surface diffusion coefficient, D is the bulk diffusion coefficient $E = \left(\frac{d\Gamma}{d(\ln\Gamma)} \right)_{eq}$ is the limiting elasticity, Γ is the adsorption, c is the bulk concentration of surfactant.

Note, that the Plateau border radius is a function of the bubble radius and the liquid volume fraction. For dry foam with the Kelvin structure [7]

$$r \cong 1.737R\sqrt{\varphi}. \quad (5)$$

Below the dilational surface viscoelasticity [19,20] and its effect on the foam drainage is investigated. The data are presented in the terms of surface viscoelastic modulus

$$E = \sqrt{(E')^2 + (E'')^2}, \quad (6)$$

where E' is the real part of surface viscoelasticity (storage modulus) and E'' is the imaginary part (loss modulus). The effect of surface shear viscosity was not considered in this study.

Both polymers studied are surface active, as expected. The values of equilibrium surface tension for chosen solutions are given in Table 1. The viscoelastic modulus of both solutions increases with frequency as it is shown in Fig. 7 for A33 solutions. The results presented in Fig. 7 were obtained on 30 min old surface. Similarly to the bulk viscosity the surface viscoelastic modulus increases with the increase of polymer concentration and decreases with the increase of salt concentration (Figs. 7-9). For compositions with similar bulk viscosity the surface viscoelastic modulus of A33 solutions is considerably higher than that of A22 solutions.

The measurements in the whole frequency range are impossible for the samples with a high bulk viscosity because the bubble do not retain the Laplasian shape [37,38]. The analysis of the data obtained for solutions of relatively low bulk viscosity in the full range of frequencies has shown that diffusion model [39] cannot be used for these solutions in order to find the limiting elasticity. That is why, to compare the surface viscoelastic properties of different solutions we performed the measurements on the one fixed frequency of 0.1 Hz. For this frequency on all samples the measured oscillations of the surface area and surface tension had no noticeable deviations from the sinusoidal shape and the average value of surface tension measured during oscillations was similar to that measured in the static regime before and after oscillations. Therefore it can be expected that the deviations of the bubble shape from the Laplasian one were negligible at this frequency.

Let us estimate the velocity gradient during the drainage determining the characteristic time scale for the dilational deformation of the surface. The fastest drainage occurs in the first few minutes after the foam formation. According to the data on foam drainage (see the next paragraph below) the drainage velocity is in the range $v_d \sim 1-5$ mm/min (depending on the bulk viscosity) during the first 10 minutes. During this time the foam height remained practically constant, therefore the liquid volume fraction on the top of the foam exceeded considerably the critical value at which foam collapses. Our estimation of the liquid volume fraction at the top of the foam give about $\varphi_t \sim 0.5$ %. On the bottom of the foam, in contact with liquid the liquid fraction can be estimated as $\varphi_b \sim 26$ % (close packing spheres). Therefore the difference in the velocity of the liquid in the Plateau border between the top and the bottom of foam can be estimated as $dv = \frac{v_d}{\varphi_t} - \frac{v_d}{\varphi_b} \sim 3-15$ mm/s. The foam height in our drainage experiments was 250 mm, therefore the velocity gradient can be estimated as $0.01-0.06$ s⁻¹. This estimation is very rough, however, it gives the time scale for the measurements on the surface rheology (0.1 s⁻¹). The latter should be comparable (by the order of magnitude) to the characteristic time of surface deformation during the foam drainage.

For the dynamic processes like foaming and foam collapse it is important to know how the surface viscoelasticity depends on the surface age. For A22 solutions there was a rather weak increase in the surface viscoelastic modulus during the first 15-20

minutes as shown in Fig. 8 and then viscoelastic modulus remained nearly constant during two hours of measurement. The behaviour of A33 solutions was more complicated. Fig. 10 presents the results for A33 solutions used in the drainage experiments. These results are most typical from 5-8 measurements made on different samples. For A33 1.5 % solution without NaCl we always obtained a curve with a weak maximum (curve 2 in Fig. 10). For A33 1 % solution without NaCl the presented shape of the curve (curve 1 in Fig. 10) was obtained for 7 samples, whereas 3 samples demonstrated transition to the higher surface viscoelastic modulus similar to curve 3 in Fig. 10. This transition to the higher surface viscoelastic modulus was more typical for A33 1.5 % solution with 0.2 M NaCl (about 70 % samples have shown the transition, 30 % did not).

Foam drainage

To study the drainage of foams produced from A22 and A33 polymer solutions and the effect of surface rheology on the drainage kinetics five compositions of polymer solutions have been chosen as shown in the Table 1. All studied samples had high foamability and foam remained stable during several hours: the decrease in the foam height was less than 10 % during first two hours for all samples. This high stability of foams can be related to the high enough surface viscoelasticity of all solutions used (see the last column in Table 1).

Table 1. Properties of solutions used in foam drainage experiments.

N	Composition	Bulk viscosity at shear rate 12 s^{-1} , mPa·s	Equilibrium surface tension, mN/m	Surface dilational viscoelastic modulus at frequency 0.1 Hz, mN/m
1	A22 1 % NaCl 0.3 M	500 ± 50	42 ± 1	40 ± 7
2	A33 1.5 % without NaCl	500 ± 50	27 ± 1	110 ± 20
3	A22 1 % NaCl 1.3 M	110 ± 10	38 ± 1	20 ± 5
4	A33 1.5 % NaCl 0.2 M	110 ± 10	26 ± 1	$40 \pm 8 / 100 \pm 10$
5	A33 1 % without NaCl	110 ± 10	30 ± 1	60 ± 10

The bubble size was practically the same for the solutions of similar viscosity, namely in the range of 2.5-3 mm for less viscous solutions and in the range 4-5 mm for the more viscous solutions. The foams formed from the more viscous solutions have larger bubbles as it is shown in Fig. 11 and, as expected, the drainage of those foams occurs slower despite of larger bubbles size (compare Figs. 12 and 13). The foams produced from the less viscous solutions during the first 10 minutes released

about 50 % and after 20 minutes more than 60 % of liquid, whereas the foams produced from the more viscous solutions released less than 15 % and about 20 % correspondingly. There was no considerable increase in the bubble size during the first two hours after foam formation.

Estimations made in [17] for the surface mobility (Eqs. 3 and 4) in foams stabilized by common surfactants (bulk viscosity 1 mPa·s, bubble radius about 1 mm, limiting elasticity 10 mN/m, liquid volume fraction 1 %) has given the values $M_{di} \sim 10^{-8}$ for an insoluble surfactant and $M_{da} \sim 10^{-5}$ for a soluble surfactant. The diffusion coefficient of polymers is at least about 1 order of magnitude lower than that of low molecular weight surfactants. According to the data given in the last column of Table 1 the surface viscoelastic modulus is about 1 order of magnitude higher than the value used in [17] for the limiting elasticity, whereas the bulk viscosity (column 2 in Table 1) is two order of magnitude higher than the water viscosity used in [17]. The bubble radius in our study was 1-3 mm (Fig. 11). Aculyn polymers are soluble in water at pH used in this study. Therefore according to Eq. (4) and taking into account estimations made in [17], for all compositions presented in Table 1 $M_{da} \sim 10^{-4}-10^{-5}$, i.e. $M_{da} \ll 1$. Thus the retarded surface of Plateau borders and Poiseuille-like flow is expected in all cases with the drainage rate being determined by the bulk viscosity and practically independent of the surface properties.

Indeed, all samples with the bulk viscosity around 100 mPa·s demonstrate the very similar drainage kinetics as shown in Fig. 12. Therefore we can conclude that in this case not only the dilational but also the shear surface rheology is of the minor importance. The foams produced from more viscous solutions have some difference in the initial liquid content, but as it is seen from Fig. 13 initial drainage kinetics is very similar for both samples. However after 20 minutes the sample of A22 polymer surprisingly drains more quickly than that of A33 polymer. Taking into account larger yield stress and larger viscosity at small shear rates of A22 sample (Fig. 2) the opposite trend could be expected. It can be only speculated that this is the result of different structure of polymers under consideration. Possibly in the confined geometry of Plateau borders and foam films cross-linked polymer A33 forms structured network which slows down the drainage. At least the very high value of surface viscoelastic modulus for this sample points out on the formation of a rather rigid structure at the liquid/air interface. Therefore the results presented in Fig. 13 demonstrate that for highly viscose non-Newtonian polymer solutions the foam drainage can be influenced also by some structural features. This is the question that has to be addressed in the future studies.

Conclusions

Performed study of solutions of commercially available polymers Aculyn™ 22 and Aculyn™ 33:

1. The solutions of both polymers demonstrate shear thinning behaviour. The bulk viscosity of solutions can be varied in a very broad range by the variations of concentrations of polymers and added salt (NaCl in this study). Viscosity increases with the increase of polymer concentration and decreases with the increase of salt concentration. At the same composition, viscosity of A22 solutions is much higher than that of A33 solutions. A22 solutions demonstrate noticeable yield stress, whereas for A33 solutions non-zero yield stress observed only for the most viscous samples.

2. Both polymers are surface active at the water/air interface and their solutions demonstrate a high surface viscoelasticity. The surface viscoelasticity has the same trend as the bulk viscosity: it increases with the increase of polymer concentration and decreases with the increase of salt concentration. For the similar bulk viscosity the surface viscoelastic modulus of A33 solutions is several times higher than that of A22 solutions.

3. Both polymers have a high foamability and form stable foams. Drainage kinetics is determined by the bulk viscosity rather than the surface viscoelasticity, what is in line with theoretical estimations for the measured values of these parameters. However for the highly viscous (high shear rate viscosity about 500 mPa·s) A33 solution the drainage after 20 min slows down in comparison to A22 solution of the similar viscosity.

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Figures captions

Fig. 1. Structure of Aculyn™ 22 (a) and Aculyn™ 33 (b).

Fig. 2. Viscosity of solutions A33 1.5 % without salt added (1) and A22 1 % with 0.3 M NaCl depending on the shear rate imposed.

Fig. 3. Viscosity of A33 1 % (1), A33 1.5 % (2) and A22 1 % (3) solutions at the shear rate of 12 s⁻¹ vs concentration of NaCl.

Fig. 4. Viscosity of A22 solution depending on polymer concentration (see text for details).

Fig. 5. Yield stress of A22 1% solution vs NaCl concentration.

Fig.6. Yield stress of A22 1% solution depending on polymer concentration (see text for details).

Fig. 7. Viscoelastic modulus of A33 solutions vs frequency: 1 – 1 % A33 1.5 mol/l NaCl, 2 – 1 % A33 0.2 mol/l NaCl, 3 – 1 % A33 0.1 mol/l NaCl, 3 – 1.5 % A33 0.1 mol/l NaCl.

Fig. 8. Dependence of viscoelastic modulus of 1 % A22 solutions on the surface age: 1 – 1.5 mol/l NaCl, 2 – 1 mol/l NaCl, 3 – 0.3 mol/l NaCl. Frequency 0.1 Hz.

Fig. 9. Dependence of surface viscoelastic modulus on concentration of A22 polymer. Frequency 0.1 Hz, samples similar to Figs. 4 and 6.

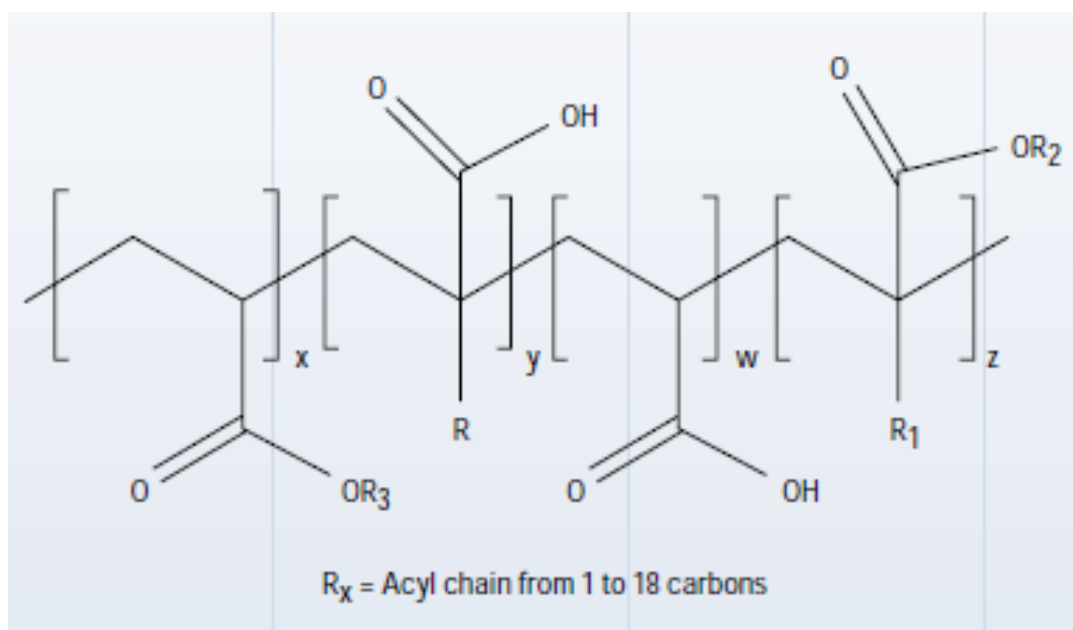
Fig. 10. Dependence of viscoelastic modulus of A33 solutions on the surface age: 1 – 1 % A33 without NaCl, 2 – 1.5 % A33 without NaCl, 3 – 1.5 % A33 0.2 mol/l NaCl. Frequency 0.1 Hz.

Fig. 11. Foams produced from A33 1 % (1) and A33 1.5 % solutions without NaCl after 80 min drainage.

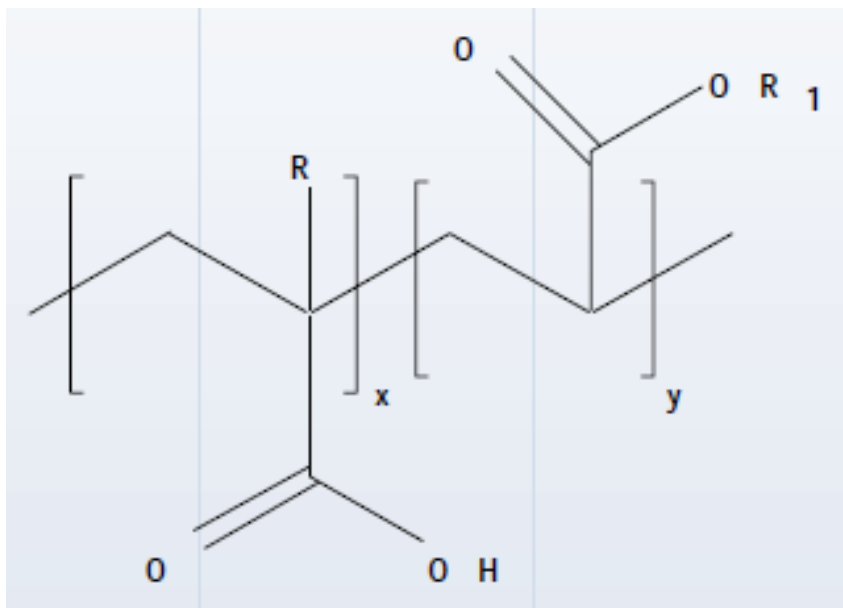
Fig. 12. Drainage of foams produced from polymeric solutions with the high shear rate bulk viscosity 110 mPa·s: -■- – A22 1 % NaCl 1.3 mol/l, -●- – A33 1 % without NaCl, -▲- – A33 1.5 % NaCl 0.2 mol/l.

Fig. 13. Drainage of foams produced from polymeric solutions with the high shear rate bulk viscosity 550 mPa·s: 1 – A22 1 % NaCl 0.3 mol/l, 2 – A33 1.5 % without NaCl.

Figures



a



b

Fig. 1. Structure of Aculyn™ 22 (a) and Aculyn™ 33 (b).

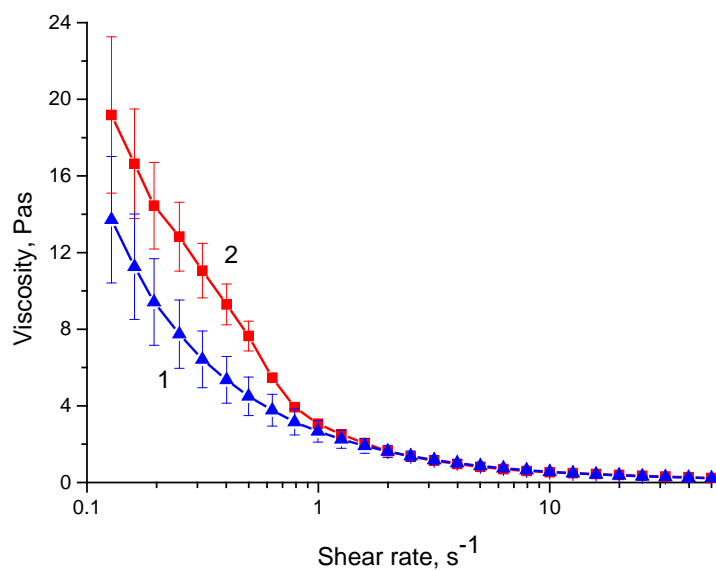


Fig. 2. Viscosity of solutions A33 1.5 % without salt added (1) and A22 1 % with 0.3 M NaCl depending on the shear rate imposed.

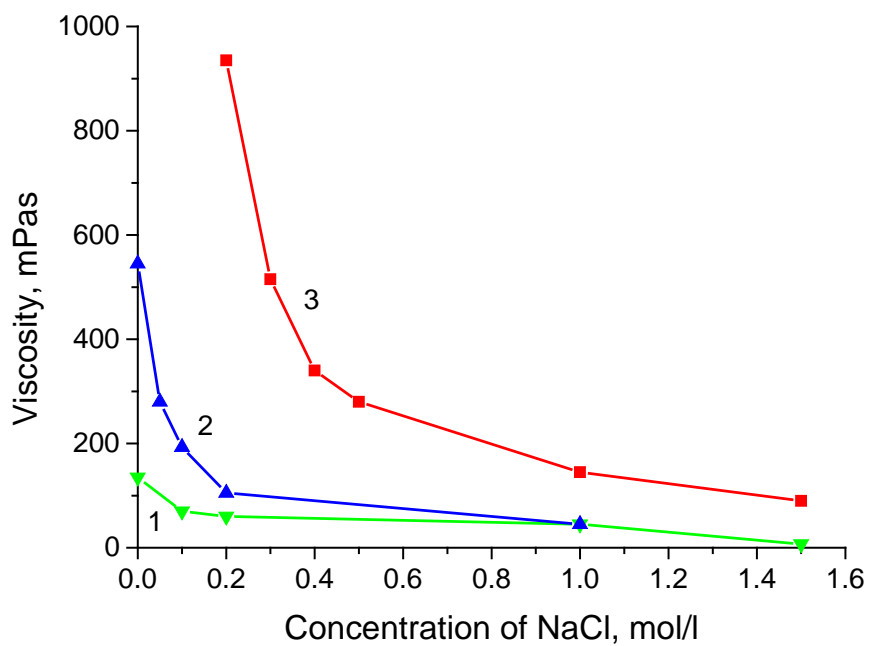


Fig. 3. Viscosity of A33 1 % (1), A33 1.5 % (2) and A22 (3) 1 % solutions at the shear rate of 12 s^{-1} vs concentration of NaCl.

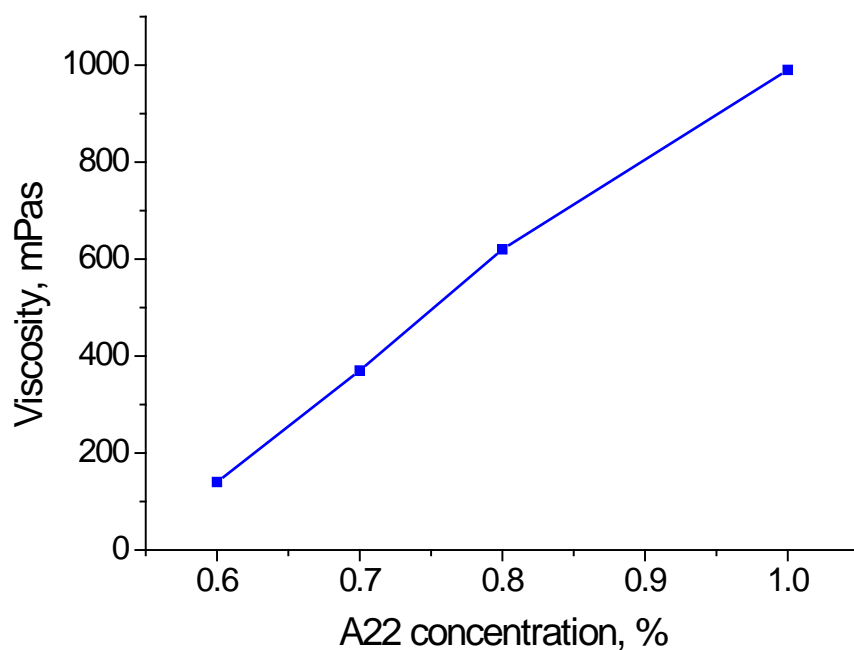


Fig. 4. Viscosity of A22 solution depending on polymer concentration (see text for details).

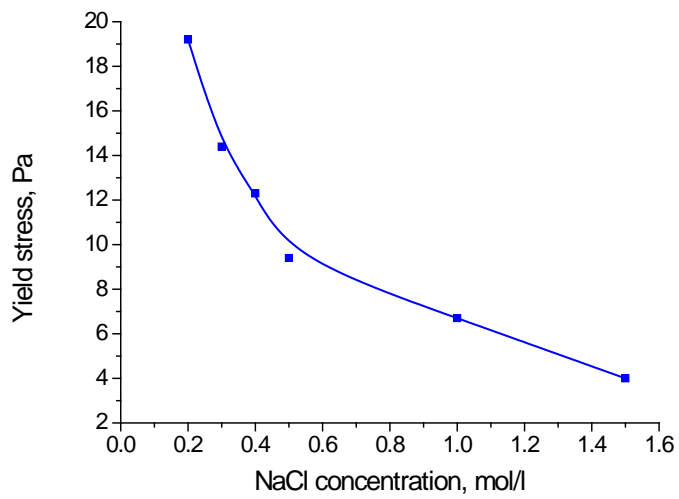


Fig. 5. Yield stress of A22 1% solution vs NaCl concentration.

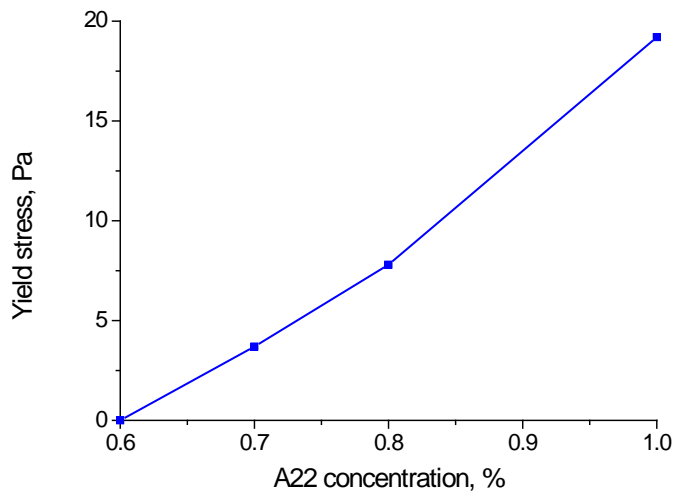


Fig.6. Yield stress of A22 1% solution depending on polymer concentration (see text for details).

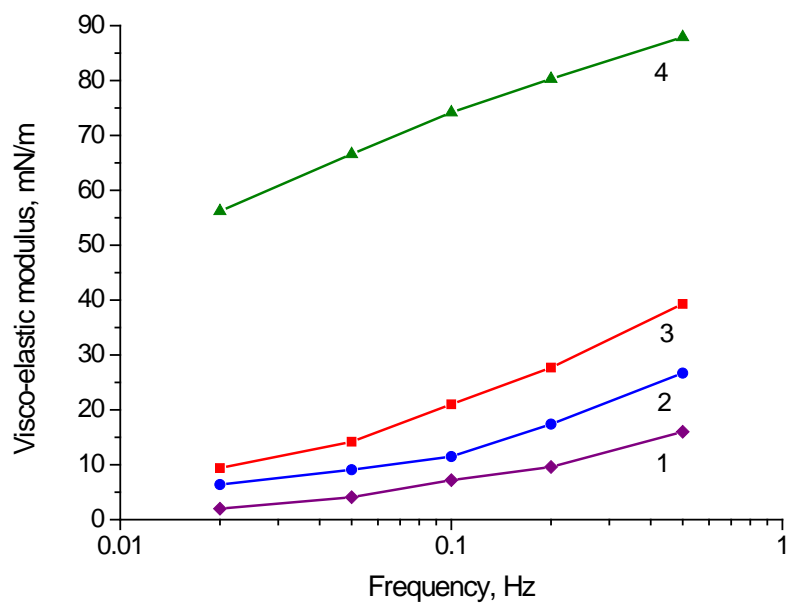


Fig. 7. Viscoelastic modulus of A33 solutions vs frequency: 1 – 1 % A33 1.5 mol/l NaCl, 2 – 1 % A33 0.2 mol/l NaCl, 3 – 1 % A33 0.1 mol/l NaCl, 4 – 1.5 % A33 0.1 mol/l NaCl.

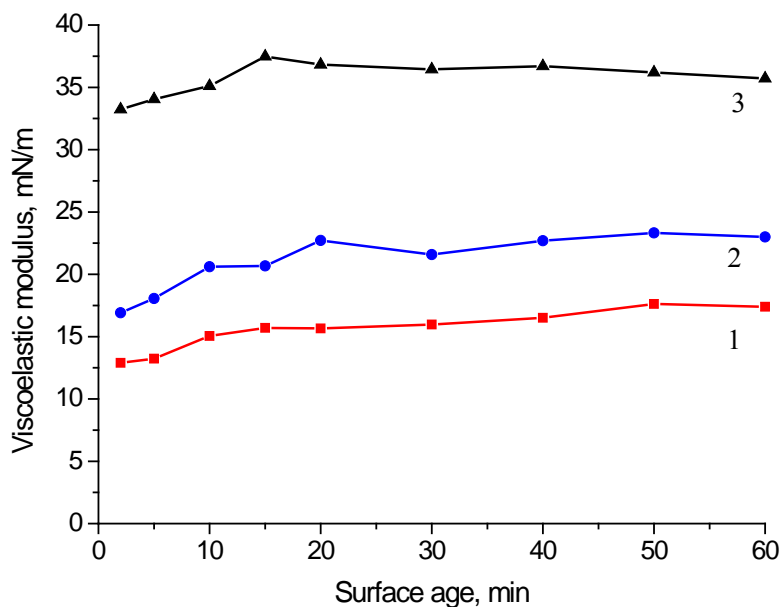


Fig. 8. Dependence of viscoelastic modulus of 1 % A22 solutions on the surface age: 1 – 1.5 mol/l NaCl, 2 – 1 mol/l NaCl, 3 – 0.3 mol/l NaCl. Frequency 0.1 Hz.

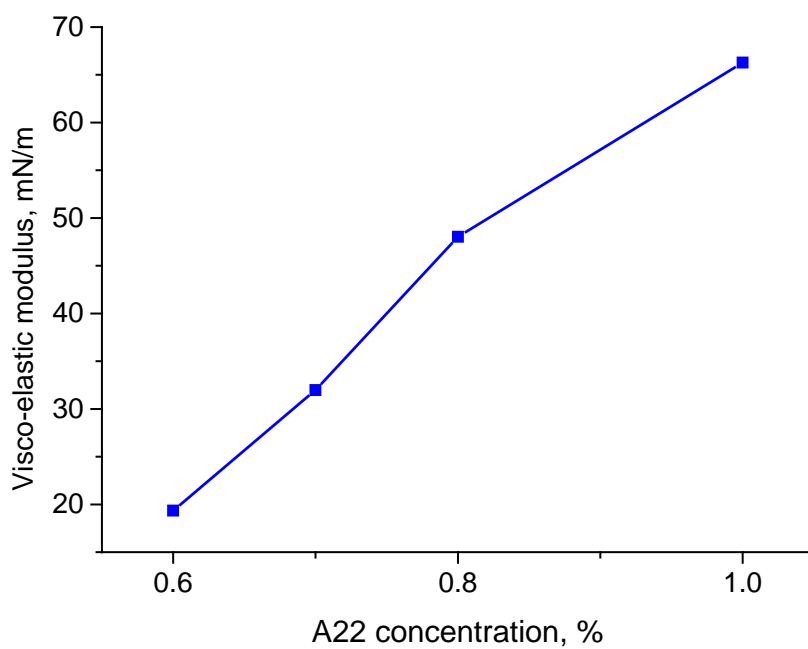


Fig. 9. Dependence of surface viscoelastic modulus on concentration of A22 polymer. Frequency 0.1 Hz, samples similar to Figs. 4 and 6.

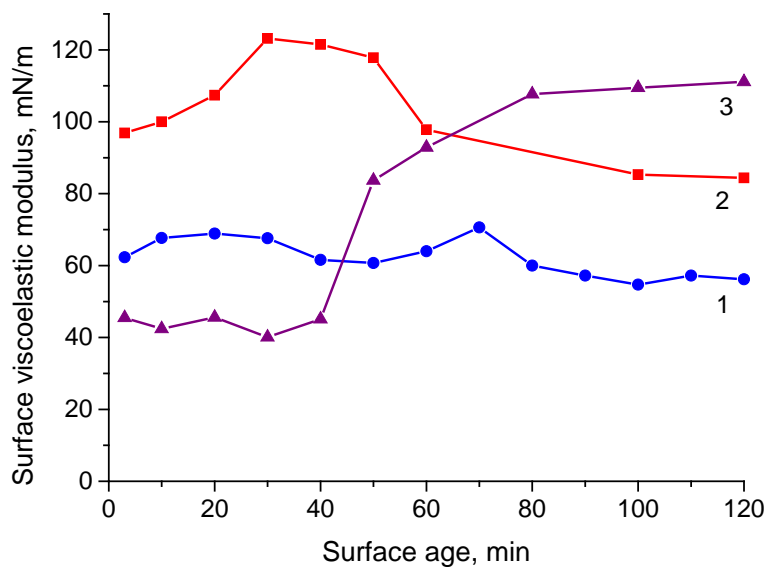


Fig. 10. Dependence of viscoelastic modulus of A33 solutions on the surface age: 1 – 1 % A33 without NaCl, 2 – 1.5 % A33 without NaCl, 3 – 1.5 % A33 0.2 mol/l NaCl. Frequency 0.1 Hz.

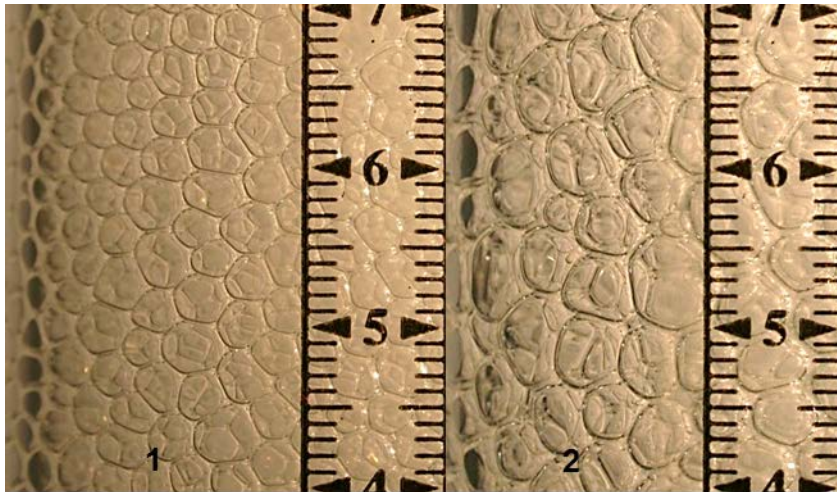


Fig. 11. Foams produced from A33 1 % (1) and A33 1.5 % solutions without NaCl after 80 min drainage.

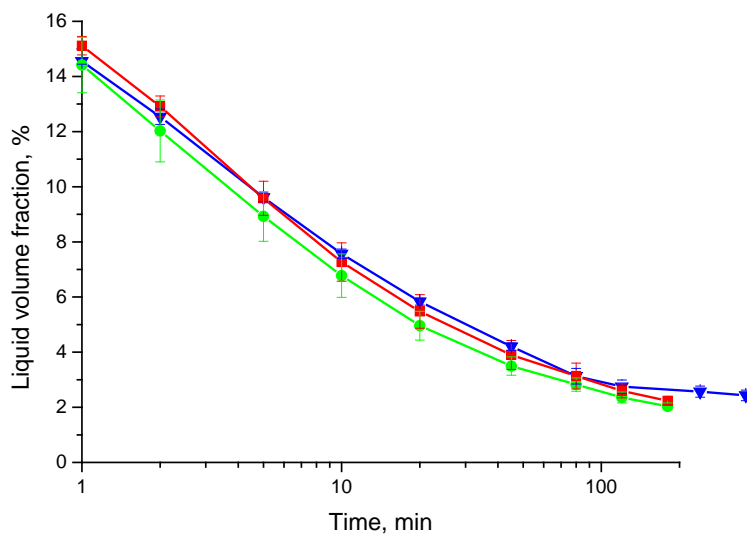


Fig. 12. Drainage of foams produced from polymeric solutions with the high shear rate bulk viscosity 110 mPa·s: -■- – A22 1 % NaCl 1.3 mol/l, -●- – A33 1 % without NaCl, -▲- – A33 1.5 % NaCl 0.2 mol/l.

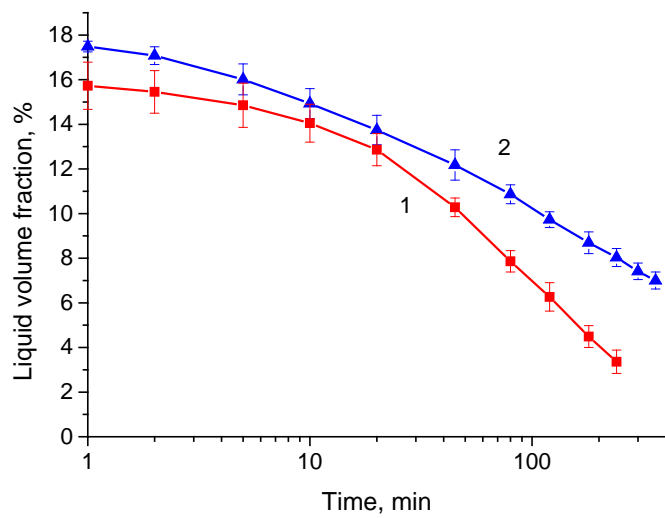


Fig. 13. Drainage of foams produced from polymeric solutions with the high shear rate bulk viscosity 500 mPa·s: 1 – A22 1 % NaCl 0.3 mol/l, 2 – A33 1.5 % without NaCl.