Critical thickness of thin liquid films: comparison of theory and experiment

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Abstract

Values for the critical thickness of rupture (or ‘black spot formation’) of aqueous and non-aqueous (aniline and nitrobenzene) foam films were computed by the Vrij (1966) and Radoev–Scheludko–Manev (1983) theories. The ‘critical thickness versus film radius’ dependences were derived, using different formulae for the rate of film thinning. The theoretical values were compared to the available – from the literature, as well as the investigations conducted here – experimental data for the critical thickness determined in the thinnest domains of the investigated microscopic horizontal foam films. It has been established that in all cases the agreement between theory and experiment is largely enhanced when the formula of Manev et al. (1997) is employed to describe the rate of film thinning, instead of the classical Stefan–Reynolds equation.

Drainage of foam films stabilized with mixtures of non-ionic surfactants

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Abstract

The drainage of single foam films stabilized with a mixture of the non-ionic surfactants n-dodecyl-b-d-maltoside (C_{12}G_{2}) and hexaethyleneglycol monododecyl ether (C_{12}E_{6}) was studied at two different mixing ratios (b-C_{12}G_{2}:C_{12}E_{6} = 1:1 and 50:1) as a function of the electrolyte and the total surfactant concentration, respectively. The electrolyte concentration was varied from 10^{-3} to 10^{-1}M NaCl and the total surfactant concentration ranged from 0.01 to 10 CMC. Moreover, the influence which the film radius has on the drainage of the foam films was investigated. From the h (film thickness) versus t (time) dependence the values of the drainage coefficients (α) were determined for all films according to the equation derived by Manev et al. [E. Manev, R. Tsekov, B. Radoev, J. Disper. Sci. Tech. 18 (1997) 769]. It was found that the drainage of these foam films is generally in line with the theory. First, at concentrations below the CMC the value of α decreases with an increase in the total surfactant concentration and levels off at C_{surf} ≥ CMC in all cases except one. Second, increasing the ionic strength increases the rate of drainage at C_{surf} < CMC, while it does not significantly affect α at C_{surf} = CMC of the respective solution. Last but not least, films of smaller radius drain faster regardless of their composition. However, the results obtained for the 1:1 and the 50:1 mixture differ quantitatively. These differences are discussed and some of the results are compared with those obtained for the pure surfactants.
Drainage and critical thickness of foam films from aqueous solutions of mixed nonionic surfactants

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Abstract

The thinning and the critical thickness (of rupture or “black spots” formation) of foam films from aqueous solutions of mixed nonionic surfactants are studied under varied experimental conditions, as a function of film radius (0.05–0.15 mm), surfactant concentration (0.01–1.0 CMC) and ionic strength (0.001–0.1MNaCl). The experimental values of the drainage coefficient (α), determined from the film thickness versus time dependences, were used to calculate the theoretical values of the film critical thickness.

The real velocity of film thinning is a major factor in the process of reaching the state of kinetic instability when approaching the critical thickness (Scheludko’s criterion). The classical equation used to describe the film thinning rate, proposed and named by Scheludko (1955) “Reynolds Law”, is applicable for small film radii (r < 0.05 mm). At larger radii the velocity of thinning follows the equation of Manev et al. [E.D. Manev, R. Tsekov, B. Radoev, J. Colloid Interf. Sci. 18 (1997) 769], which takes into account the effect of the film thickness local nonhomogeneity. The studied stabilizing surfactants include n-dodecyl-β-d-maltoside (b-C12G2) and hexaethyleneglycol monododecyl ether (C12E6). Along with confirming the dependences following from the theories of the critical thickness [B. Radoev, A. Scheludko, E.D. Manev, J. Colloid Interf. Sci.95 (1983) 254] and film thinning [E.D. Manev, R. Tsekov, B. Radoev, J. Colloid Interf. Sci. 18 (1997) 769], the results of the present investigation established also certain deviations for films stabilized with mixed surfactants (b-C12G2 + C12E6). The effectiveness of the empirical equation, employing the drainage coefficient (α) to describe the film thinning, is emphatically proven here.

Comparative validation of the analytical models for the Marangoni effect on foam film drainage

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Abstract

The aim of this paper is to evaluate four of the well-known models for drainage of thin liquid films, containing non-ionic surfactants, by applying them to different types of draining foam films stabilized by either strong or weak non-ionic surfactants.

The effect of non-ionic surfactants on the drainage of foam films under different conditions was studied. The following series of surfactants were employed: (1) methylisobutyl carbinol (MIBC), (2) Dowfroth 200,
(3) pentaethyleneglycol monodecyl ether (C\textsubscript{10}E\textsubscript{5}), (4) pentaethyleneglycol monododecyl ether (C\textsubscript{12}E\textsubscript{5}), (5) hexaethyleneglycol monododecyl ether (C\textsubscript{12}E\textsubscript{6}), (6) octaethyleneglycol monododecyl ether (C\textsubscript{12}E\textsubscript{8}) and (7) tetraethyleneglycol monoocetyl ether (C\textsubscript{8}E\textsubscript{4}). The experimental ‘thickness’ vs ‘time’ dependences were processed with four kinetic models: (1) the model developed by Scheludko on the basis of the Stefan–Reynolds lubrication theory (Scheludko model); (2) the model of Radoev, Dimitrov and Ivanov for foam films confined between partially mobile planar gas–liquid surfaces (RDI model); (3) the model of Ruckenstein and Sharma for foam films with surfaces wrinkled by capillary waves (RSh model); (4) the model of Manev–Tsekov–Radoev for foam films with surfaces corrugated by quasi-stationary inhomogeneities (MTR model). A systematic validation based on the statistical level of uncertainty of the model predictions, as compared to the experimental results was performed. The test on the model kinetic equations confirmed their validations reported in the literature. In addition, cases in which none of the models is valid were identified as well. Ultimately, it was concluded that thin film drainage is a complex phenomenon, which should be studied further by different experimental techniques and modelling approaches.


№16 Foam films from mixed solutions of bovine serum albumin and n-dodecyl β-D-maltoside

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Abstract

New data for foam films from mixed aqueous solutions of important components non-ionic surfactant “n-dodecyl-β-D-maltoside” (C\textsubscript{12}G\textsubscript{2}) and globular protein “bovine serum albumin” (BSA) are presented.

Based on the equilibrium surface tension isotherm of mixed aqueous solutions of BSA (10–6 M) with C\textsubscript{12}G\textsubscript{2}, obtained by Wilhelmy method it is found that protein–surfactant complexes are formed at concentration region from 3.10–6 to 1.5.10–5 M C\textsubscript{12}G\textsubscript{2}. Thinning of the films stabilized by mixtures with a composition corresponding to the special points of the isotherm is recorded and compared with this of the individual components. It is found that the films from mixed protein–surfactant solutions, exhibit irregular thinning behaviour and thickness nonhomogeneity. The critical and equilibrium thickness of stable films is measured interferometrically and discussed based on the specificity of interactions between the components. Films from pure BSA solutions are thinnest (11 nm) and their thickness corresponds to Newton black (NB). It is found that the thickness of mixed films is larger (17 nm) than that of films from pure BSA and corresponds to thickness of common black films, irrespectively that they visually look like Newton film (NF). The larger value of these thicknesses is explained with an increase in the thickness of adsorption layers due to the bigger hydrodynamic radius of complexes or reorientation of BSA molecule to the volume face during its displacement by C\textsubscript{12}G\textsubscript{2} domains.
Drainage of foam films stabilized by n-dodecyl-β-D-maltoside or dodecyl trimethylammonium bromide and their mixtures

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Abstract

The thinning of foam films from aqueous solutions of single non-ionic- [n-dodecyl-β-D-maltoside (β-C12G2)] and ionic-[dodecyl trimethylammonium bromide (C\textsubscript{12}TAB)] surfactants, as well as of their mixtures at C\textsubscript{i} = CMC, was studied at different molar ratios (50:1; 1:1; 1:50), with or without additional electrolyte (0.1M NaBr). The equilibrium surface tension isotherm of the mixture β -C\textsubscript{12}G\textsubscript{2}:C\textsubscript{12}TAB = 1:50 (+0.1M NaBr) was obtained by the Wilhelmy-plate method. Based on this isotherm and the isotherms of the individual surfactants, CMC of the other mixtures with electrolyte were determined theoretically, by the Ingram’s approach. The molar fractions of the surfactants in the mixed adsorption layers were estimated.

The ‘film thickness vs. time’ dependences were plotted for films with radii 0.05mm or 0.1mm. The results were compared to those obtained by different theoretical equations for the rate of film thinning. It was found that the small films from β-C12G2 or mixtures C\textsubscript{12}G\textsubscript{2}:C\textsubscript{12}TAB = 1:1; 50:1 (+0.1M NaBr) exhibit regular thinning which is almost in line with the classical Reynolds equation (Re). It was confirmed by the values of fractal dimension: α = 2. In contrast, the small films of β-C12TAB or mixture β-C\textsubscript{12}G\textsubscript{2}:C\textsubscript{12}TAB = 1:50 without NaBr drained at slower rate than that predicted by the Reynolds equation. We assume that it is due to the effect of electrokinetic streaming potential, which decreases the velocity of the film drainage because of the reverse fluxes from the periphery toward the center of the film. Films with radii 0.09mm thinned almost (or slower) according to Manev–Tsekov–Radoev (MTR) equation. The value of α obtained for these films was equal to 0.6–1.4 keeping in mind that α = 0.5 corresponds to MTR type of film drainage. This result confirms the influence of the film size on its nonhomogeneity.

Statistics of rupture in relation to the stability of thin liquid films with different size

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Abstract

We study the stability and the thinning behavior of foam films in the presence of ionic surfactant. Using the method of capillary cell at low pressures (20–50 Pa), combined with interference microscopy, we measured the film thickness vs. time, the critical thickness of rupture, and the lifetime of films with different sizes. The film behavior is characterized by two separate stages: at first, there is a hydrodynamic thinning without rupture; afterwards, film rupture occurs as a stochastic process. The measured lifetimes in an ensemble of films are scattered in a certain range. We found that this statistical behavior is well described by a specific distribution, with cumulative probability \(1 - \exp(-\beta t^2/2)\). By means of theoretical considerations, this distribution is derived from the time dependent differential probability for film rupture. Fitting of experimental data for the statistics of the film lifetimes is performed. This permits one to find the average transient lifetime at the stochastic stage; thus, thinning and rupture are distinguished.

The size dependence of the drainage time is shown to comply with theories which describe the behavior of films with irregular thickness. The time for thinning, and the inverse drainage rate coefficient, scale with the film radius as \(r_f^{4/5}\). This work may be relevant to understanding the stability of fluid dispersions in dependence of the particle size.

Drainage and critical thickness of foam films from mixed solutions of bovine serum albumin and \(n\)-dodecyl-\(\beta\)-D-maltoside

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Abstract

Data for the kinetic stability of foam films from “bovine serum albumin” (BSA) solution, or from its mixed solutions with non-ionic surfactant “\(n\)-dodecyl-\(\beta\)-D-maltoside” (\(C_{12}G_2\)) are presented and discussed based on the specificity of interactions between the components analyzed by tensiometry and fluorescence spectroscopy.

The thickness as a function of time in different areas of BSA or BSA/\(C12G2\) films formed at different experimental conditions (different molar ratios between protein and surfactant, film radius) is measured interferometrically from a video recording of the film evolution. The thinning velocity presented via drainage coefficient, \(\alpha\), in the areas where first, or other black spots appear, or in other film areas was determined from the \(\ln h(t)\) dependences up to the critical state (first black spot formation in the film). It is found that BSA film has the slowest thinning and the most regular thickness. The thinning velocity of the both BSA and BSA/surfactant films in the area where first spot appears decreases considerably with increasing of the film radius. The thinning velocity values in other film areas are close to those obtained in areas with spots, but only in the initial period of film drainage. The thinning in these places almost stops around the critical state. In above mentioned different film areas the thicknesses, corresponding to the critical state are measured and compared. It is found that the values of critical thickness in areas with spots are noticeably smaller, than critical thickness in other areas, irrespectively of the film radius and molar ratio of the stabilizers. It
means that the value of critical thickness for a protein film can not be obtained as an average value of the thickness values determined in different film areas just before the first black spot formation.


№22 Drainage and critical thickness of foam films stabilized by n-dodecyl-β-D-maltoside

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Abstract

The kinetic stability of foam films stabilized with n-dodecyl-β-D-maltoside (C12G2) in the presence of electrolyte (NaCl) has been investigated. The surface charge, type of the film and its electrostatic stabilisation were controlled by changing of the surfactant (from 0.01 to 1 CMC) and electrolyte (0.1 and 0.001 M) concentration. The drainage coefficient, critical thickness and life time to the critical state of films with different radii (0.05, 0.1 and 0.15 mm) were measured interferometrically using a new procedure suggested by us for determination of the reflected light intensity from a video recording of the film evolution. It was found that the films from solutions of C12G2 up to CMC (even at CMC) with 0.001 M NaCl are “common (CF) electrostatically stabilized films”, while at the same C12G2 concentrations they were unstable films (UF) or stable Newtonian black films (NBF), when the added electrolyte was 0.1 M. The values of film critical thickness obtained at a high electrolyte concentration were similar even when the concentration of C12G2 was varied from 0.1 to 1 CMC. It means that in a wide surfactant concentration range the electrostatic disjoining pressure is screened and the experimental data of critical thickness are appropriate for theoretical analysis. The disjoining pressure acting at different steps of the film evolution was evaluated based on experimental data of the film drainage. A non-DLVO attractive force for films with non-covered surfaces and Πel = 0 was detected. It was expressed by a power law in the same form as the van-der-Waals force, which makes it possible to directly compare these two forces by means of the force constant K232 and the Hamaker constant. The non-DLVO force was found to be considerably stronger than the Lifshitz – van-der-Waals forces. The obtained new experimental data for critical thickness were compared with those calculated by us with different equations (Radoev–Sheludko–Manev, Vrij, and Coons). In some of these cases we used the experimentally obtained value of the drainage coefficient instead of the velocity of the film thinning, calculated theoretically. It was found that the calculated hcr are noticeably lower than experimentally measured ones. Good agreement between measured and calculated her was achieved with a non-DLVO attraction force taken into account, when the films were obtained from solutions with low (C12G2) and high (NaCl) concentrations.

Competitive adsorption of bovine serum albumin and n-dodecyl-β-d-maltoside in foam films

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Abstract

The competitive adsorption of Bovine Serum Albumin (BSA) and n-dodecyl-β-d-maltoside (C_{12}G_{2}) on foam films surfaces formed from mixed solutions with a composition (BSA:C_{12}G_{2} = 1:7.5; 1:50; 1:100), corresponding to weak and strong binding of C12G2 molecules to BSA molecule was experimentally investigated. In order to answer the question which one of the surfactants or both of them is/are adsorbed on the film surfaces data for: (i) the kinetics of surface tension of the single surfactants and their mixtures; (ii) the AFM images of single BSA surface layer and its mixed layers with C_{12}G_{2}; (iii) the viscosity in the foam film determined from its thinning; (iv) the kinetics behavior and equilibrium properties of foam films from single and mixed solutions at pH = 4.9, 3.8; (v) the BSA concentration in the solution obtained by dissolving of a dried foam were obtained. Data for the surface activity of investigated solutions showed that in the mixed adsorption layers from solution with molar ratio BSA:C_{12}G_{2} = 1:7.5 BSA molecules predominate, while from BSA:C_{12}G_{2} = 1:50 and 1:100 C_{12}G_{2} molecules. This conclusion is supported by AFM images. The lower viscosity calculated from the thinning of foam films stabilized by these mixtures than this from the thinning of films from individual BSA solution is explained by the less aggregation between albumin molecules due to their hydrophilization by bind C12G2 molecules. The stable foams produced from the mixtures BSA:C_{12}G_{2} = 1:50 and 1:100 were dried to such an extent enough for black foam films formation in them. Quantitatively, it was found that the concentration of BSA in the solution obtained after dissolving of the dried foam is an order lower than the concentration of the solution drained from the foam during its drying. The thinning evolutions of the films from pure and mixed solutions, recorded at pH = 4.9 showed that C_{12}G_{2} films thin up to 90 nm, while the thinning of films from the mixture (1:100) depends on the time of film interfaces aging: the films with fresh interfaces have a similar drainage as the pure C12G2 films, but they thin to the thickness of 67 nm; the films with intermediate times of aging become unstable, or stable ones when black spots (mobile or frozen) are formed in them; the aged films thin fastest and they jump to NBF as the films from C12G2 solution but with pH = 3.8 or with 10^{-1} M NaBr. It means that the films electrostatic stabilization is screened which can be due to BSA adsorption. This suggestion was checked by an estimation based on the surface charge density of the following interfaces: air/water; air/C12G2 solution and air/BSA + C12G2 solution. It was found that the number of OH ions expelled by BSA is one order smaller that those by C12G2. Nevertheless, it is a proof for the presence of BSA in the film interfaces, as well as for its role on the film thinning. The values of films equilibrium thickness, surface potential and drainage in the case when pH of the mixed solution is 3.8 indicate that the films are common ones. This finding demonstrates again that BSA molecules adsorb on the film interfaces. At pH = 3.8 BSA molecule is charged positively that is why the film interfaces are recharged.
Abstract

Thinning rates of foam films, stabilized by surfactant mixtures of n-dodecyl- β-d-maltoside (C12G2 or G2) with hexaethyleneglycol monododecyl ether (C12E6 or E6), dodecanol (C12E0 or E0), and dodecyltrimethylammonium bromide (C12TAB or TAB) are studied and analysed. The influence on thinning of the film radius (0.05–0.15 mm), surfactant concentration (0.01–1.0 CMC), ionic strength (0.001 or 0.1 M NaCl) and mixture composition is investigated. It is found that: (i) the thinning rate falls with the increase in film radius and surfactant concentration in accord with the MTR-equation; (ii) for films from mixtures of 50:1 ratio the thinning rate correlates with that for films stabilized by pure C12G2 at all studied surfactant concentrations, additives and ionic strength levels; (iii) for films from mixed solutions of C12G2 with C12TAB the thinning rate depends on the ratio of the components in the adsorption layers; (iv) for films from mixtures of 1:1 ratio it is controlled by the component dominating in the adsorption layer. For the mixture of C12G2 + C12E6 the thinning rate is determined primarily by C12E6, while for the C12G2 + C12TAB mixtures – by both components. The accelerated film thinning at low surfactant concentration and high ionic strength is associated with the potential effect of an additional non-DLVO force.
EMULSION FILMS STABILIZED BY SODIUM CASEINATE

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ABSTRACT In this study, the influence of the electrolyte on the Na-caseinate emulsion film properties was investigated by: visual observation of the film drainage; measurement of the film life-time; determination of the equilibrium or critical film thickness; measurement of the contact angle.

The emulsion films were formed from solutions with constant Na-caseinate concentration (0.1 wt.%), and constant pH equal to 6.2. At low salt (≤0.02 M), Na-caseinate forms unstable Newton Black emulsion films (NBF). Addition of NaCl causes a thickness transition, from unstable Newton black to stable (gray) common black films (CBF). At 0.15 M NaCl, aggregation of Na-caseinate is favored and inhomogeneous films are observed.

Ageing of the film surfaces (for 30 minutes) leads to an essential increase of the film thickness and stability (at low electrolyte concentrations, up to 0.02 mol/l). This is likely to be due to continuing adsorption. With NaCl over 0.05 mol/l, the adsorption is faster, so the addition of more salt does not essentially change the film type and the stability (the latter levels off). The obtained dependence of the film thickness vs. the salt in the gray films seems to correlate with the DLVO theory (screening of the electrostatics).

KEY WORDS: sodium caseinate, emulsion films, film (critical or equilibrium) thickness, contact angles
Foam Films Aqueous Dowfax and Dynakoll Solutions

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Summary: The properties of foam films formed from “paper surfactants” solutions were studied. The influence of the Dowfax and Dynakoll concentration as well as electrolyte concentration on the films drainage and stability was investigated.

The aim of this study was to find the experimental conditions at which the films became unstable. For this purpose visual observation of the film drainage, measurement of the film life-time, determination of the equilibrium or critical film thickness under varied surfactant and electrolyte concentration, and different film radius were performed. It was found that up to 0.001% Dowfax and Dynakoll concentration without addition of NaCl films were thick, stable they drain slowly. The films became stable up to $1 \times 10^{-2}$ M NaCl added to solutions with the lowest surfactant concentration (0.001%). Based on the Dowfax composition and dissociation the concentration of Na’ counter ions ($1.52 \times 10^{-5}$ to $1.52 \times 10^{-2}$ M) in solutions without electrolyte was estimated. This result confirms experimentally determined values of the equilibrium film thicknesses decreasing from 93 to 26 nm. Contrary, under the same experimental conditions Dynakoll films were thick and non-homogeneous. One can conclude that the stability and thinning of Dowfax films are electrostatically controlled. The data for equilibrium film thickness, experimentally obtained, were fitted by DLVO theory. The dependences of the critical thickness and life time on the film radius, experimentally obtained, are in accord with the theoretical predictions: the value of the critical thickness increases for the bigger films and they rupture faster.

Keywords: Dynakoll; Dowfax; foam films; equilibrium and critical thicknesses, film life time.
Изтъняване на пени фили
стабилизирани от смеси на нейнени
повърхностно активни вещества

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Summary: The drainage of single foam films stabilized with a mixture of the non-ionic surfactants n-dodecyl-β-D-maltoside (β-C_{12}G_{2}) and hexaethyleneglycol monododecyl ether (C_{12}E_{6}) was studied at two different mixing ratios (C_{12}G_{2} : C_{12}E_{6} = 1:1 and 50:1) as a function of the electrolyte and the total surfactant concentration, respectively. The electrolyte concentration was varied from \(10^{-4}\) to \(10^{-1}\) M NaCl and the total surfactant concentration ranged from 0.01 to 1 CMC. Moreover, the influence the film radius has on the drainage of the foam films was investigated. From the \(h\) (film thickness) vs. \(t\) (time) dependence the values of the drainage coefficients (\(\alpha\)) were determined.

It was found that the drainage of these foam films is generally in line with the theory. First, at concentrations below the CMC the value of \(\alpha\) decreases with an increase in the total surfactant concentration. Second, increasing the ionic strength increases the rate of drainage at \(C_{\text{surf}} < \text{CMC}\), while it does not significantly affect \(\alpha\) at CMC. Last but not least, films of smaller radius drain faster regardless of their composition. The differences obtained for the 1:1 and the 50:1 mixture are discussed and some of the results are compared with those obtained for the pure surfactants.

Keywords: n-dodecyl-β-D-maltoside; hexaethyleneglycolmonododecyl-ether; foam films; drainage coefficient.
Composition and Properties of Adsorption Layers of n-Dodecyl-β-D-maltoside and Hexaethyleneglycol Dodecyl Ether on the Interface Solution/air

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Abstract: The nonionic surfactants of the type C\textsubscript{n}H\textsubscript{2n+1}(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{n}OH are intensively studied because of ecological, technological and commercial reasons (low foamability, insensibility to water hardness, low critical micelle concentration, CMC). They are used as foam and emulsion stabilizers, or as additives to ionic surfactants in detergent mixtures to attain positive synergism. Their physical condition and their temperature sensitivity limit their use. During the last years particular interest was paid to alkylglycoside (carbohydrate) surfactants which are a special group of nonionic surfactants. Due to their nontoxicity, easy biodegradability and insensitivity to the temperature changes they are a good alternative of used so far nonionic surfactants. The alkyl-glycoside surfactant most frequently used in foam and foam films studies is n-dodecyl-β-D-maltoside. The investigation of its mixtures with other surfactants is topical because in detergent mixtures the stabilizer is always mixed (at least with another surfactant).

In the presented study the equilibrium surface tension isotherms of solutions of n-dodecyl-β-D-maltoside (C\textsubscript{12}G\textsubscript{2}), hexaethyleneglycol dodecyl ether (C\textsubscript{12}E\textsubscript{6}) and their 1:1 and 50:1 mixtures were analysed in van der Waals approximation and by Ingram method. Data for the adsorption, the interface saturation and the Gibbs elasticity of the adsorption layers on the solution/air interface as a function of the surfactant concentration and ratio of the two surfactants in the mixture were obtained. The composition of the adsorption layers was estimated. From the foam film equilibrium thickness and capillary pressure the surface potential was calculated.

The obtained values of equilibrium surface parameters, composition of the adsorption layer and surface potential on the film surfaces were used to interpret the thinning behavior of the studied foam films from mixed (C\textsubscript{12}G\textsubscript{2} + C\textsubscript{12}E\textsubscript{6}) solutions.

Keywords: surface tension; adsorption layer; n-dodecyl-β-D-maltoside; hexaethyleneglycol dodecyl ether; foam films; drainage; surface potential.

Introduction

The stability of the thin liquid films determines the stability of colloid systems. Frequently, the thermodynamic and the kinetic stability of thin films are discussed although a rigorous discrimination between them is not possible. The mechanic condition \( P_0 = \Pi \) of thin film is considered as a condition for thermodynamic equilibrium. It depends on the nature and the concentration of the stabilizer, on the type and concentration of the electrolyte and on the pH of the solution. However, thin liquid films not always successfully achieve the thermodynamic equilibrium despite of the presence of necessary conditions. They can rupture during the thinning course because of hydrodynamic disturbances. The factors which prevent the film rupture during the draining determine their kinetic stability. There are hypotheses according to which the kinetic stability of the films is decisive insofar as in the absence of kinetic stability the film would never reach thermodynamic equilibrium even if the conditions of the thermodynamic equilibrium are fulfilled. The kinetic stability depends on the rheological properties of the adsorption layers formed on the film interfaces which in turn depend not only on the solution composition but also on some specific interactions at the film interfaces. These interactions are characterized through the Gibbs elasticity (\( \mathcal{E}_0 \)), the surface viscosity (\( \eta_0 \)) and the adsorption relaxation time (\( \tau \)). On one hand the increase in the nonionic surfactant concentration leads to an increase of the Gibbs elasticity and the surface viscosity but on the other hand it causes lowering of the surface charge of the interfaces, i.e., changing the thermodynamic
Kinetic Stability of Foam Films from Aqueous Solutions of Single and Mixed Surfactants

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Abstract: The kinetic stability of microscopic foam films from aqueous solutions of the nonionic surfactant β-C\textsubscript{12}G\textsubscript{3}, and its mixtures with other non-ions: C\textsubscript{12}E\textsubscript{6}, C\textsubscript{12}E\textsubscript{o}, as well as the ionic C\textsubscript{12}TAB is studied as a function of surfactant concentration (0.1 - 10.0 CMC), ionic strength (10\textsuperscript{-3} - 10\textsuperscript{-1} M NaCl) and film size. The values of the drainage coefficient (α) are determined for each film from its kinetic ‘thickness vs. time’ dependence. The experimentally obtained values of the critical thickness (of rupture or “black spots formation”) are compared to those computed by means of different formulae for the rate of film thinning (the classical ‘Reynolds law’, equation of Manev et al., 1997, experimental ‘α’) vs. radius dependence. The results of the study show that the actual velocity of film determines the state of reaching kinetic instability when approaching the critical thickness, in accord with the Scheludko’s criterion.

Keywords: foam film; critical thickness; non-ionic surfactants; surfactant mixtures

Background

The disperse system stability is a central topic in surface and colloid science. Studying the hydrodynamic and thermodynamic characteristics of the thin liquid films, which build the disperse systems, is an efficient tool for this task. The destruction of the thinning film occurs when it reaches the state of kinetic instability at its critical thickness. There the film either ruptures, or undergoes an abrupt transformation to a new state of a thinner ‘black film’. The critical thickness of thin liquid films and the factors that govern this phenomenon have been the subject of many theoretical and experimental investigations during the decades [1-15]. Essential knowledge on the subject of kinetic stability and the role of the drainage behaviour of thin liquid films one can obtain from the recent reviews of Manev & Nguyen [16,17], as well as from preceding comprehensive publications, like these of Scheludko [18], Ivanov et al [19], Exerowa and Kruglyakov [20] and other.

A necessary condition for the existence of foam films is the presence of surfactants, whose concentration and molecular structure substantially influence the film stability. In practice, single (individual) surfactants are seldom used as stabilizers of colloidal systems. Hence, investigations of films stabilized by surfactant mixtures are of primary importance to the subject [21].

The focus in this investigation is on the mixtures of n-dodecyl-β-D-maltoside (β-C\textsubscript{12}G\textsubscript{3}) with other nonionics: hexaethyleneglycol monododecyl ether (C\textsubscript{12}E\textsubscript{6}), as well as dodecanol (C\textsubscript{12}E\textsubscript{o}) and the cationic dodecyltrimethylammonium bromide (C\textsubscript{12}TAB). The reason for studying mixtures of ethyleneoxide- and sugar-based surfactants is that, in spite of being non-ionic, these surfactants exhibit significant differences in their surface properties [22-25]. One can deduce, therefore, that films stabilized by mixture of these surfactants shall behave differently, depending on the surfactant composition.

The aim of the presented study is to establish the common and different kinetic characteristics of films stabilized by individual surfactants and their mixtures. The evolution and critical thickness of the films were studied as a function of the electrolyte (0.001-0.1 M NaCl) and the total surfactant concentration (0.1-10.0 CMC).
Влияние на нейонно повърхностноактивно вещество върху изтягването на пеници филми от n-додецил-β-D-малтозид

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Abstract: The present study is dealing with mixture of non-ionic surfactants n-dodecyl-β-D-maltoside (β-C12E2) and dodecanol (C12E0). The aim of the study is to investigate how do small traces of C12E0 in the solution will influence the drainage coefficient and critical thickness of foam films obtained from mixture of β-C12E2:C12E0 = 50:1. These films parameters were studied as a function of the total surfactant (0.1–10 CMC) concentration and film radius (0.05, 0.1 and 0.15 mm) at constant electrolyte concentration (10^3 M NaCl). In order to evaluate the C12E0 influence the data for films from mixed solutions were compared with those for films of pure β-C12E2. It was found that the drainage coefficient decelerates with increasing C_{ref} irrespectively of solution (mixture or pure) and film radius. This trend is more pronounce for films from mixture. The values of measured critical thicknesses of the films from β-C12E2 + C12E0 increase with increasing of C_{i} (up to 5 CMC).

Keywords: n-dodecyl-β-D-maltoside; dodecanol; foam films; drainage coefficient; critical thickness; composition of adsorption layer.

Обща част

Много са теоретичните и експериментални изследвания [1,2], изучаващи кинетичното поведение на тънките течни филми (ТТФ). Повечето от тях, обаче, се отнасят до филми, стабилизирани от еднородни повърхностноактивни вещества (ПАВ). Приложимостта на тези изследвания директно в
Effect of Afranil wax on the drainage and stability of foam films from mixed solutions of Dynakoll and Solvitose at different temperatures

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Abstract: The present study is dealing with a complex system of paper surfactants (Dynakoll and Solvitose) in foam film. The properties of foam films (via life time, critical thickness) under: low capillary pressure; varied concentrations of Dynakoll, Solvitose, Afranil, (changing the concentration ratios); different concentration of NaCl at room temperature and 40°C were studied in order to check the influence of Afranil on their drainage and stability.

The observed behavior of the foam films from solutions of Dynakoll and Solvitose with or without NaCl imply that the film stability is dependent by a number of factors. The changes of the film stability, the drainage rate and the critical thickness of the film rupture as a function of the Dynakoll proportion or of Solvitose and electrolyte concentration were assumed to be due to the interactions of Solvitose with both Dynakoll and NaCl. These interactions can include electrostatic (screening) effects, intermolecular associations or forming of inclusion complexes between Dynakoll and Solvitose. The intermolecular interactions can cause conformational changes and, respectively, changes of the volume part of Solvitose which would influence dramatically the film drainage and stability.

It is found that the film stability is higher at the elevated temperature (40°C), compared to the room temperature, and the effect is well pronounced with more Afranil (more than 0.05%). This is an indication for release of surface active species from the wax, which play a stabilizing role. The filtration of the solutions leads to increase of the surface tension. This means that surfactant is removed together with the particles. The films from filtered solutions are unstable.

Keywords: surfactant mixture of Dynakoll and Solvitose; surface tension isotherm; Afranil wax; foam films; life time; critical thickness.
Влияние на Дафакс върху изтъняването и критичната дебелина на пени филми, стабилизирани от смес на Динакол и Солвитоза

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Резюме: Изследвана е кинетичната стабилност на пени филми (c радиуси 0.005, 0.01, 0.015 cm), получени от смесени разтвори на на Динакол и Солвитоза (1:10) и Динакол, Солвитоза и Дафакс при 40°C. Тя е състоявана с тази на филмите от разтвори на Дафакс и смесените разтвори на Динакол, Солвитоза и Афранил.

Установено е, че вида и стабилността на пеница филм зависи от количеството на Дафакса (0.005, 0.05%) в смесения разтвор. С повишаване на концентрацията на Дафакс, филмите от късици се в момента на получаване на черно петно, стават стабилни мутонови.


Keywords: paper surfactants; foam films; drainage; critical thickness.
Пенни филми от разтвори на \( n \)-додецил-\( \beta \)-D-
малтозид с додецил триметиламониев бромид

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Резюме: Изследвано е изтъняването на пени филми, образувани от смесени разтвори на \( n \)-додецил-\( \beta \)-D-
малтозид \( (C_{12}G_{2}) \) и додецил триметиламониев бромид \( (C_{12}TAB) \) с молни съотношения 1:0, 50:1, 1:1, 1:50, 0:1 в отсъствието и в присъствието на NaBr. Интерферометрично са определени критичната и равновесна дебелина на филмите. Тоталната концентрация на ПАВ за всяка от смесите е равна на критичната й концентрация на мицелообразуване (ККМ). Чрез молното съотношение на сместа са контролирани повърхностния товар, типа и електростатиката във филма.

Филмите от разтвори с молни съотношения 1:0, 50:1, 1:1 (без NaBr) не изтичат с времето и са с дебелина около 100 нм, докато при 1:50 е намерен скок в дебелината им.

За филмите при йонна сила \( (0.1 \text{ mol/l}) \) е намерена разлика в типа на филма \( (\text{NBF или CBF}) \) в зависимост от молното съотношение на компонентите в сместа, но е установено, че прийдането на ПАВ не влияе върху стойността на коефицентата на изтъняване. Влиянието на радиуса на филма върху скоростта на изтъняване и критичната дебелина е в съответствие с теорията на Манев и съвт.[5], което е доказателство, че тя е валидна и за филми от смесени разтвори.

Keywords: \( n \)-dodecyl-\( \beta \)-D-maltoside; foam films; drainage constant; equilibrium thickness; surface charge.
Гибсова еластичност на адсорбционни слоеве от смесени разтвори на n-додецил-β-D-малтозид с додеканол

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Резюме: Систематично е изследвана повърхностната активност на разтвори от n додецил β-D-малтозид и неговата смес с додеканол чрез метод, основаващ се на анализ на профила на мехурче или капка. Анализът на кинетиките на повърхностното напрежение при ниски, средни и високи концентрации на тези повърхностно активни вещества показа, че процесът на адсорбция до концентрации 1×10^{-2} мол/l е бариерно-лимитиран, докато при по-високи концентрации е дифузионно-лимитиран.

Чрез оценените равновесни стойности на повърхностното напрежение е построена изотермата на смеса и от нея в приближение на ван-дер Ваалс са изчислени Гибсовите еластичности. Получени са и експериментални данни за повърхностното напрежение и Гибсовата еластичност на разтвори на додеканол, където са в пълно съответствие с литературните данни в [8,9]. Показва се, че стойностите на Гибсовата еластичност на слоета от n додецил β-D-малтозид и додеканол са по-ниски от тези за разтворите с n додецил β-D-малтозид.

Ключови думи: n-додецил-β-D-малтозид, додеканол, повърхностно напрежение, Гибсова еластичност.
Abstract: The critical thickness of foam films from solutions of n-dodecyl-β-D-maltoside, dodecyl trimethylammonium bromide and their mixtures (50:1; 1:1; 1:50) was measured interferometrically. The obtained values were compared with those calculated by formula of Radeev, Sheludko, Manev using experimental data for the velocity of film thinning. It is found a good correlation between measured and calculated values for critical thickness of foam films from investigated solutions.

Keywords: n-dodecyl-β-D-maltoside; dodecyl trimethylammonium bromide; foam films; drainage coefficient; critical thickness.

Общая часть

Тънките течни филми (ТТФ) са обект на много изследвания [1]. Пенният филм е най-лесния модел за теоретично и експериментално изследване на силите, определящи стабилността на колоидно – дисперсната система пана. Стабилността на пенния филм може да бъде контролирана чрез регулиране на повърхностния зарад на фазовите му граници, което се реализира чрез промяна на типа и концентрацията на повърхностно - активните вещества (ПАВ). Адсорбцията на нейоните ПАВ на междуджезовата граница понижава
Foam Films from Mixed Solutions of Bovine Serum Albumin and n-Dodecyl-β-D-maltoside

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Abstract: New data for foam films from mixed aqueous solutions of important components non-ionic surfactant n-dodecyl-β-D-maltoside (C₁₂G₂) and globular protein, bovine serum albumin (BSA) are presented. Based on the equilibrium surface tension isotherm of mixed aqueous solutions of BSA (10⁻⁶ M) with C₁₂G₂, obtained by Wilhelmy method it is found that protein-surfactant complexes are formed at concentration region from 3 × 10⁻⁶ to 1.5 × 10⁻⁵ M β-C₁₂G₂. Thinning of the films stabilized by mixtures with a composition corresponding to the special points of the isotherm is recorded and compared with this of BSA. It is found that the films from mixed protein-surfactant solutions, exhibit irregular thinning behaviour and thickness nonhomogeneity. Films from pure BSA solutions are thinnest and their thickness corresponds to Newtonian films. It is found that the thickness of mixed films is larger than that of films from pure BSA and corresponds to thickness of common black films, irrespectively that they visually look like Newtonian. The larger value of these thicknesses is explained with an increase in the thickness of adsorption layers due to the bigger hydrodynamic radius of complexes or reorientation of BSA molecule to the volume face curing its displacement by C₁₂G₂ domains.

Keywords: bovine serum albumin (BSA); n-dodecyl-β-D-maltoside (β-C₁₂G₂); surface tension; film drainage.

1. Introduction

The model foam film study is an ideal tool to learn about the films and foam stability. Usually, ionic [1-2], nonionic surfactants [3-4] or their mixtures [5] are used as stabilizers of foam because they
DETERMINATION OF THE CRITICAL THICKNESS OF THIN LIQUID FILM BASED ON A VIDEO RECORD OF ITS THINNING

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ABSTRACT: A new procedure for the determination of the foam film critical thickness is proposed. Films produced from n-dodecyl-β-D-maltoside aqueous solutions, of concentration equal to CMC, were used in the presence of 0.1 mol/l NaBr. The new element in the procedure is the determination of the reflected light intensity from a video recording of the film evolution. The values of the critical thickness, calculated via the reflected light intensity measured in places where black spots have appeared "h<sub>cr in the spot</sub>" are compared to the values estimated for other thinner segment of the same films "h<sub>cr in other places</sub>". It is found that "h<sub>cr in the spot</sub>" are noticeably smaller, than "h<sub>cr in other places</sub>" - especially for films of radii larger than 0.05 mm. Furthermore, it is shown that the h<sub>cr bi</sub> does not depend on the film radius. These findings made us conclude that the value of the film critical thickness should be averaged from the thickness values determined in many different places of the film during its critical phase.

KEYWORDS: foam film; n-dodecyl-β-D-maltoside; video record of film thinning; critical thickness, Hamaker constant (A<sub>μ</sub>);

ТЕОРЕТИЧНА ЧАСТ

Стабилността на колоидно-дисперсните системи (КДС) е основан проблем в различни области на науката и технологията. Подходящ и много продуктивен модел за теоретично и експериментално изследване на стабилността на КДС е тънкият течен филм (ТТФ) като основен течен градивен елемент. Стабилността на КДС пяна се определя от свойствата на пленния филм (ПФ), което позволява тя да бъде контролирана чрез промяна на кинетичните му свойства [1].

Процесът на образуване и изтъняване на един пленен филм удобно се моделира чрез динамичния метод на Шелудко и Ексерова [1]. Главните етапи от еволюцията на такъв филм са обсъждани и представени в литературата [2].

Разглежданити ПФ е образуван в центъра на двойно вдънбната капка. При изсмукване на течността повърхностите ѝ се деформират и възниква „димплът”. Първоначално той нараства, след което или се изтласква, или постепенно се сплесква и се образува ПФ. Повърхностните на филма са нагънати...
INTERACTION OF BOVINE SERUM ALBUMIN WITH n-DODECYL-β-D-MALTOSIDE IN AQUEOUS SOLUTIONS

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ABSTRACT: The interaction between Bovine serum albumin (BSA) and nonionic surfactant n-dodecyl-β-D-maltoside (C\textsubscript{12}G\textsubscript{2}) in the mixed aqueous solutions with constant BSA concentration (1×10\textsuperscript{-6}M) and varied surfactant concentration (from 1×10\textsuperscript{-7} to 3×10\textsuperscript{-4}M) was investigated by tensiometry and fluorescence spectroscopy. Based on surface tension and fluorescence data the average number of bound C\textsubscript{12}G\textsubscript{2} molecules per protein molecule (\(v\)) and fractional occupation of the hydrophobic areas of BSA by C\textsubscript{12}G\textsubscript{2} (\(\theta\)) were determined. It was found that up to 1.5×10\textsuperscript{-3}M C\textsubscript{12}G\textsubscript{2} non-cooperative binding occurs and BSA keeps its native conformation and surface activity. At higher C\textsubscript{12}G\textsubscript{2} concentrations especially around CMC the fluorescence intensity decreases significantly and shifts of the emission maximum of 2+9.5 nm are observed. These data indicate that at these conditions a cooperative binding of C\textsubscript{12}G\textsubscript{2} takes place and leads to unfolding of BSA molecule.

KEYWORDS: bovine serum albumin (BSA), n-dodecyl-β-D-maltoside (C\textsubscript{12}G\textsubscript{2}), surface tension, fluorescence and absorption spectra
Experimental data for the velocity of thinning and critical thickness of foam films stabilized by hexaethyleneglycol monododecyl ether

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Disjoining pressure isotherms obtained by the dynamic method for foam films stabilized by nonionic surfactants

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Abstract: The present study is an attempt to explain by an additional non-DLVO force the accelerated thinning of foam films at low concentrations of n-dodecyl-β-D-maltoside and hexaethylene glycol monododecyl ether in the presence of 0.1M NaCl, than that predicted by the Reynolds law. For its evaluation Π(h) isotherms were obtained based on experimental dynamic thinning curves.

Keywords: foam film, disjoining pressure, film thinning

Introduction

The behaviour of the thin liquid films of the dispersion medium are crucial for the stability of the respective colloidal disperse system which they constitute, such as foam or emulsion. The film behaviour is in its turn governed by the presence and properties of surfactants in the system.

The kinetic stability of thin foam films (TFF) stabilized with nonionic surfactants n-dodecyl-β-D-maltoside (C₁₂G₃) [1] and with hexaethylene glycol monododecyl ether (C₁₂E₆) [2] were investigated. The foam films were obtained from solutions with concentration of surfactants from 0.01 to 1.0 CMC (CMC₈C₁₂G₂ = 1.5 × 10⁻⁴M; CMC₈C₁₂E₆ = 7.3 × 10⁻⁵M) in the presence of 0.1M NaCl (enough to suppress the electrostatics in the film). It was found that experimental
Effect of bovine serum albumin adsorption on the thinning of foam films stabilized by n-dodecyl\(\beta\)-D maltoside

Abstract
The kinetic behavior and equilibrium properties of foam films from individual n-dodecyl\(\beta\)-D maltoside, \(C_{12}H_{25}O\) (1\(\times\)10\(^6\) M) or from its mixed solutions with bovine serum albumin, BSA (1\(\times\)10\(^6\) M) with molar ratio 100:1 at pH = 4.9, 3.8 were studied. A difference between evolutions of single and mixed film thinning was found. It was shown that the drainage of films from the mixture depends on the time of film interfaces aging. The values of surface charge density of the air/C\(_{12}\)G\(_2\) solution and air/C\(_{12}\)G\(_2\)-BSA solution interfaces at pH = 4.9 and 3.8 were estimated based on the films equilibrium thicknesses. It was found that at pH = 4.9 the number of OH ions expelled from air/C\(_{12}\)G\(_2\)-BSA film interfaces by adsorbed BSA molecules is an order smaller than those by C\(_{12}\)G\(_2\). At pH=3.8 the co-adsorption of positively charged BSA molecules in the C\(_{12}\)G\(_2\) adsorption layer recharges the film interfaces which explains why the obtained films are common black ones.

Увод
Стремежът към използването на високомолекулярните повърхностно-активни вещества ВМПАВ (белъци) като стабилизатори на пенни емулсии е обоснован от желанието на хората за запазване на екологично чисти храни, лекарства и нетоксични детергентни смеси, както и от способността на белъците, добавени към високомолекулярни ПАВ, да променят живота на пината или емулсията, като повлияват кинетичните и равновесни свойства на тънкия филм в тях. Това се свързва с коформацията и особените адсорбционни свойства на ВМПАВ, които водят до промени на високотемпературните филми, реологичните свойства и конформация на висококонцентрационните филми и фазови граници.

Основна цел на настоящето изследване бе да се установи дали адсорбицията на BSA молекули, от смесени разтвори на C\(_{12}\)G\(_2\) (1\(\times\)10\(^4\) M) c BSA (1\(\times\)10\(^4\) M) с pH=4.9 и 3.8, повлиява кинетичното поведение и равновесниите свойства на пенни филми (ПФ), образувани от тях.
Determination of the viscosity in foam films from Bovine Serum Albumin and from its mixtures with n-dodecyl-β-D-maltoside

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Abstract: The thinning of foam films from pure Bovine Serum Albumin (BSA) and its mixed solutions with a composition BSA : C₁₂G₂ = 1:7.5; 1:50; 1:100, was recorded and analyzed with appropriate equations in order to calculate the viscosity. It was found that the thinning of films formed from pure BSA solution and from mixed BSA:C₁₂G₂ = 1:7.5 one is slower than that predicted by Reynolds (Re) equation. The thinning of films from 1:50 mixed solution follows Re law, while the thinning of films from 1:100 mixed solution is in accord with Manev-Tsekov-Radoev (MTR) equation which points out that the film interfaces in the case of 1:100 are most mobile which is due to a low content of BSA molecules in the adsorption layers. h(t) depends before 100 and after 100 nm for single and mixed films were plotted in coordinates h²(t) or h⁻²(t) respectively and from their slopes the viscosities in the films were calculated. The values obtained for pure BSA and mixed (1:7.5) films are 50% higher than the values of measured bulk viscosity. In the same time the viscosity obtained from h⁻²(t) dependence for film from 1:100 is in accordance with the bulk viscosity of native protein (1.04×10⁻³ Pa.s). Based on viscosity data and Einstein equation the radius of BSA molecule in pure and mixed solutions was estimated. According to the obtained data it was concluded that in the mixed solution 1:50; 1:100 there is not an aggregation between BSA and these molecules bound per BSA molecule. The difference found between viscosity values measured by Ostwald method and those obtained from the film thinning gives a possibility for using of TTF as a precise viscometer.

Keywords: Bovine Serum Albumin (BSA); n - dodecyl - β -D-maltoside (C₁₂G₂); mixed BSA/C₁₂G₂ solutions; viscosity from film drainage.

Introduction

Foamability and foam stability are old but still actual problems. The obtained of dried foam is an important problem for the flotation, which is used during the separating of mixtures of natural physiologically - active surfactants. The kinetic stability of the foams is important for the food, pharmaceutical and cosmetic industries. In these cases it is important to find conditions for obtaining of the quickly drying and stable foams. It can be realized, if the foam is stabilized with low molecular surfactants, at the following conditions: a surfactant concentration close to the CMC or by an addition of electrolyte equal to the concentration of transition to Newtonian black films (NBF), according to DLVO – theory. If the addition of the electrolyte is not desirable in the system, for example in the case with proteins, then it can be get by an addition of second surfactant, which acts as a booster and a positive synergism or decreasing in the surface charge on the surface is realized. Moreover the second surfactant should be led to the fast thinning, foam stability but does not change significant the protein native structure. It follows that the right combination between a protein and low molecular surfactant is an important moment for the practice. According to the literature [1,2] mixtures of bovine serum albumin (BSA) and non-ionic sugar surfactant n-dodecyl-β-D-maltoside (C₁₂G₂) are more suitable, because: the first - non-ionic surfactants have lower CMC and decrease the surface charge; the second - in a wide concentration range the interaction between them does not lead to substantial changes in the conformation of protein molecule; the third - C₁₂G₂ is temperature and pH insensitivity and the fourthly certain sugar surfactants are nontoxic and biodegradable, which is important for the human health and environmental. In [1, 2] solutions with different molar ratio BSA:C₁₂G₂ (1:7.5; 1:50 and 1:100) at pH = 4.9 have been