*Russian Chemical Reviews* **64** (3) 235–247 (1995) ©1995 Russian Academy of Sciences and Turpion Ltd

UDC 66.063.94.661.185.1

# Regularities in the concentration and separation of surfactants in a foam

T N Khaskova, P M Kruglyakov

## Contents


| | | |
|---|---|---|
| I. | Introduction | 235 |
| II. | Characteristic features of the adsorption concentration of surfactants in a highly expanded polyhedral foam and methods for determining its structural parameters | 236 |
| III. | Characteristics of the effectiveness of concentration, separation, and purification of solutions of surfactants | 238 |
| IV. | Experimental studies on the concentration of individual surfactants and mixtures | 242 |
| V. | Separation of components of a mixture of surfactants in a foam | 245 |
| VI. | Conclusion | 246 |


**Abstract. The theoretical and experimental studies devoted to the regularities of foam adsorption concentration and separation of substances occurring in the liquid phase in molecular, ionic, or micellar form are surveyed. The main characteristics of foam concentration and separation, their analytical dependences on the structural parameters of the foam, and their interdependences are analysed. Quantitative relationships for the characteristics of foam separation with due regard to the influence of foam destruction have been obtained. The dependences of the concentration coefficient on the expansion factor and dispersity of the foam and also on the capillary pressure in polyhedral (dry) foams prepared from solutions of individual surfactants and their mixtures are analysed. The reasons for concentration restrictions (upper and lower limits) of the foam concentration method are discussed. Examples of partial separation of surfactants in a foam and foam chromatography are considered. Brief information on equilibrium displacement and acceleration of chemical reactions in a foam is presented. The bibliography includes 77 references.**

## I. Introduction

Surface separation and concentration of substances comprise a group of related processes based on the regularities of adsorption and wetting. The longest used and best known among these processes is foam flotation. There exist several methods for the concentration of minerals based on flotation. According to one of these, mixtures of solid particles of various natures and degrees of dispersity are dispersed in an aqueous suspension by a gas. As this takes place, hydrophobic particles adhere to the rising bubbles, while hydrophilic particles remain in the bulk. Another method involves pumping of a suspension being separated onto a foam. This flotation process was called[1] foam separation. In the oil flotation process, drops of an emulsion to which ore particles adhere are used instead of gas bubbles. In the case of film flotation, the crushed ore is poured onto a constantly moving water surface; the easily wetted particles sink, while the poorly wettable ones remain at the surface and are then collected with the aid of a special device. A similar principle of flotation, but involving other properties of collecting agents, is also used for separation of drops of the organic phase from dilute emulsions, specifically, for the purification of waste water from oil impurities.

During the last two decades a large number of studies have been reported (see, for example, Refs. 2—6) on nonchromatographic methods of surface separation of dissolved substances (molecules and ions) and highly dispersed particles (colloids and other small particles), to which the regularities of normal flotation are inapplicable. Among these methods are isolation of ions, surfactants, proteins, dyes, and other organic compounds, colloidal particles, and microorganisms. Surfactants can be extracted from a solution or separated from each other (if in a mixture of surfactants) owing to different degrees of adsorption of components. In order to extract inactive components (in particular, ions), one should use collecting agents, which increase the ability of compounds to concentrate at the surface. The most frequently used collecting agents are diphilic compounds. Mechanisms of the action of these compounds are varied and depend on the type of species being extracted (ions, proteins, or colloidal particles). For example, ionogenic surfactants with high surface activities are typical collecting agents in the flotation of ions and molecules. As a result of ion exchange, the collecting agent attracts the substance being extracted (colligend) to the surface and forms an insoluble surface active compound with it (for example, iron ions can replace sodium ions in an anionic surfactant). This ion exchange reaction occurs most frequently in the bulk solution. In this case, the collecting agent acts as a precipitant that participates in the formation of a hydrophobised poorly soluble compound (sublate) in the bulk of the dispersive medium.

The processes of surface separation of dissolved compounds and particles of a colloidal degree of dispersion have been classified according to various criteria:[2–5] the substances being isolated (electrolyte ions, surfactants, organic compounds with high molecular weights, colloidal particles, microorganisms, etc.);[4] the type of particles in the composition of which the colligend is collected; the aggregative state of the phase in which the particles being flotated are collected; the type of interaction (binding) of the collecting agent with the compound being extracted, and according to other criteria.

**T N Khaskova, P M Kruglyakov** Department of Chemistry, Penza State Architectural and Building Institute, ul. Titova 28, 440028 Penza, Russian Federation, Fax (7-841) 262 04 10

Received 25 April 1993
*Uspekhi Khimii* **64** (3) 251–264 (1995); translated by Z P Bobkova

The methods of surface separation are named differently in various papers: in the case of extraction of surfactants they have been referred to as adsorption flotation,[2] foam flotation,[3] foam in fractionation, foam separation, or adsorption concentration,[5] and in the case of extraction of ions, the methods of ion flotation,[2] foam flotation of hydrophobic precipitates, etc. have been reported.

All these methods have many common features, but, at the same time, they are noticeably distinct. For example, in foam flotation of macroscopic particles (suspensions), separation is governed by wetting and adhesion and involves the step of the water–particle–gas three-phase contact; the concentration and separation of surfactants in a foam are determined by the adsorption ability, the rate of diffusion of the surfactant, and the properties of the foam (especially its stability). The principle of accumulation of substances at a surface and similarity of the equipment should be considered to be common features of these processes.

In the present review we shall restrict ourselves to the analysis of the foam method of concentration and separation of compounds that exist in solution as ions, molecules, or micelles (without formation of dispersions or precipitates). This method is based on the regularities of adsorption and the properties of a stable foam. The adsorption-bubble separation without foam formation, as well as flotation extraction and ion flotation with accumulation of a thin layer of the hydrophobic product at a surface, are outside the framework of our present review.

Depending on the purpose of foam separation, it will be referred to as adsorption foam concentration (separation of dissolved species from the solvent) or foam separation (in the case of partial or complete separation of dissolved species from one another).

## II. Characteristic features of the adsorption concentration of surfactants in a highly expanded polyhedral foam and methods for determining its structural parameters

Concentration of surfactants in a foam occurs due to their adsorption on the bubbles of the gas, which is passed through a layer of the solution, followed by the separation of the foam from the solution. This process can be either batch or continuous. The surface separation is mostly achieved due to the single-stage distribution of compounds between the bulk phase and the surface layers of foam bubbles. Transformation of a gas dispersion into foam is accompanied by segregation of the excess liquid from the latter (syneresis of the foam), which brings the composition of the foam product closer to that of the adsorption layers, by the change of the spherical shape of bubbles into polyhedral, by a partial internal destruction of the foam (a decrease in the liquid–gas interface due to coalescence of bubbles and diffusional transfer of gas from small bubbles into larger ones), and by distribution of the foam column as a whole. Desorption of the surfactant from the vanishing surfaces results in an increase in its concentration within the Plateau–Gibbs† channels and in three-dimensional parts of the films. Syneresis of a foam results in additional adsorption of the surfactant at the surface of bubbles lying below, and where several surfactants are present, because the desorption-adsorption event is repeated many times, some redistribution of the surfactants with height and in an increase in the lifetime of the foam occurs.

The return of the liquid phase partially enriched in the surfactant into subsequent portions of the foam is called internal dephlegmation. Its contribution to variations of the effectiveness of the concentration and separation becomes substantial at low concentrations of surfactants [below the critical concentration for micelle formation (CCM)].

The adsorption concentration is normally carried out under the conditions of the gravity separation of the liquid from the foam.[2–4,6] The equipment used in these processes has been described in detail in a number of monographs.[2–4,6] A method for the adsorption concentration of surfactants under the conditions of accelerated and more complete drying of foams by creating a pressure differential in the liquid phase of a foam and the corresponding high capillary pressure in the Plateau–Gibbs channels in the course of the liquid separation, has been suggested in a series of papers.[7–10]

The use of polyhedral foams for the processes of adsorption concentration and separation increases the effectiveness of the latter. The relative simplicity of the geometry of the Plateau–Gibbs channels and films (compared with a nonpolyhedral foam) allows one to obtain quantitative dependence of various characteristics of the adsorption concentration on structural parameters of a foam (expansion factor, dispersity, size of the channels).

Below we present technological features of concentration and separation of surfactants carried out under the conditions of capillary drying of a foam and also some characteristics of 'dry' foams.

For preparation of a highly expanded dry foam by the capillary method, a foam is brought into contact with a porous plate, beneath which a reduced pressure $P_0'$ is created (see Refs. 11 and 12). The pressure differential

$$\Delta P = P_0 - P_0',$$

($P_0'$ is the external pressure above the foam; usually, ambient pressure) should not exceed the capillary pressure in the pores of the filter

$$\Delta P_m = \frac{2\sigma \cos\theta}{r},$$

(where $\sigma$ is the surface tension of the solution; $\theta$ the contact angle of wetting of the material of the filter; $r$ the radius of a pore),‡ otherwise not only the liquid, but also the gas, would pass through the pores of the filter.

Under the action of the pressure differential in the liquid phase of the foam, the liquid quickly flows out until this differential is equilibrated by the capillary pressure in the foam. The porous partitions can be made of ceramics, metal ceramics, or glass, or be dense grids.

The increase in the expansion factor and in the capillary pressure in a dry foam is accompanied by the simultaneous decrease in the stability of the foam and increase in the time necessary for the equilibrium capillary pressure, corresponding to the pressure differential applied, to be established. Therefore, the optimum pressure differential, which will ensure the necessary expansion factor of the foam and a lifetime sufficient for its technological processing, should be selected experimentally.

The scheme of a laboratory unit for investigating the adsorption foam concentration in the continuous regime is presented in Fig. 1.

Separation column (*1*) is a vertical cylinder placed in a temperature-controlling jacket (*2*); in the bottom of the column there is a gas dispenser, viz. a removable glass filter (*3*), which allows gas dispensers of various porosities to be applied. In the lower section of the column there is also a cock (*4*), which serves for withdrawing samples of the solution subjected to separation. In the upper section of the column a number of holes are situated at various levels with respect to the solution surface (*5*–*7*) for the egress of the foam and for disposition of electrodes (*8*) and a capillary micromanometer (*9*), which measures pressure in the Plateau–Gibbs channels. The foam is dried with the aid of a cartridge filter (*10*), which is a metal frame covered with a

† Plateau borders in Western literature (Editor).

‡ If there are pores with different radii, the greatest one is meant.

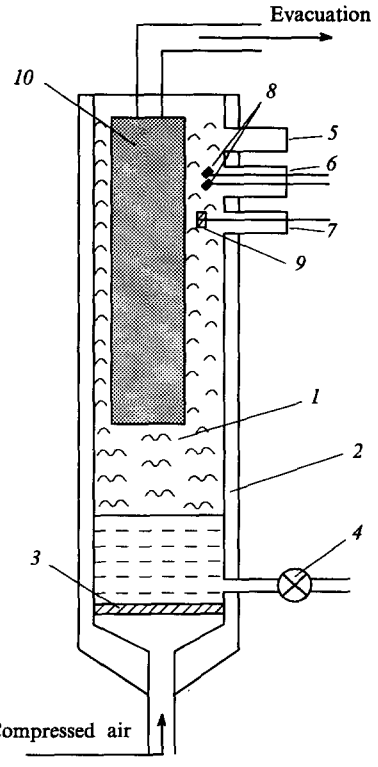



**Figure 1.** The scheme of a laboratory unit for adsorption concentration in 'dry' foams. (*1*) A separation column; (*2*) a temperature-controlling jacket; (*3*) a removable glass filter; (*4*) a cock for withdrawing samples of the liquid; (*5–7*) holes for the egress of the foam; (*8*) platinum electrodes; (*9*) a micromanometer; (*10*) a cartridge filter.

metallic grid having a mesh of 60 μm. A cylinder smaller in diameter than the column acts as the cartridge. It occupies 1/3 of the height of the column and is located 5–15 cm above the level of the liquid. A reduced pressure ($\Delta P_L$ = 1.0 – 2.0 kPa) of no more than the capillary pressure in the pores of the filter (grid) is produced within the cartridge. Under the action of the pressure differential, the liquid from the foam is drawn off into the cartridge. The liquid that finds its way into the cartridge is collected in a glass sampler, which makes it possible to determine the surfactant concentration and to evaluate the losses. Hereafter this liquid will be referred to as 'filtrate'.

It should also be noted that a dry polyhedral foam is very sensitive to external factors, including the rate of its movement and the diameter of vessels and tubes in which it moves. Special rheological studies§ have shown that intense destruction of a foam occurs at expansion factors of more than 300 even when the foam moves in the sliding mode (piston mode). For this reason, in the case of continuous drying of a moving foam the coefficient of the concentration of a surfactant is lower than in the case of a stationary foam in a batch-operating unit, the pressure in the Plateau–Gibbs channels being the same.[7,8]

A major part of the physicochemical characteristics of foam concentration correlates quantitatively with the expansion factor and dispersity of the foam. The expansion factor of a foam ($n$) characterises the volume proportion of liquid in the foam:

$$n = \frac{V_F}{V_{L,F}}, \tag{1}$$

where $V_F$ is the volume of the foam and $V_{L,F}$ is the volume of liquid in it.

§ See, for example, P M Kruglyakov, T V Meshkova *Kolloidn. Zh.* **52** 487 (1990).

To determine the expansion factor, especially of dry foams, the conductometric method is most commonly used,[1,8,9] as

$$n = \frac{\kappa_F}{\kappa_L B}, \tag{2}$$

where $\kappa_F$ and $\kappa_L$ are the specific electric conductivities of the foam and the solution of a foam-forming agent respectively, $B$ (= 1.5 to 3) is a coefficient depending on the distribution of the liquid between the channels and films.[13–15] For a polyhedral foam with a purely channel conduction mechanism, where the liquid in films may be neglected, $B = 3$, and for a foam with a film conduction mechanism, where the contribution of channels may be neglected, $B = 1.5$ (see Ref. 14).

Analysis of experimental data carried out by Lemlich[14] has shown that the coefficient $B$ increases monotonically from 1.5 to 3 as the expansion factor increases from 4 to 200, and that the experimental data obtained for bubbling foams are well approximated by the relationship

$$B = 3 - 2.5\left(\frac{\kappa_F}{\kappa_L}\right)^{1/3} + 0.5\left(\frac{\kappa_F}{\kappa_L}\right). \tag{3}$$

Characteristics of foam concentration depend substantially on the dispersity of the foam,[2–6] for which a variety of methods exist for its determination, for example, microphotography, an optical method, a method based on the measurement of the gauge pressure after destruction of the foam, and others (for details, see Refs. 5, 16, and 7).

A method based on the simultaneous measurement of the local expansion factor and the pressure in the Plateau–Gibbs channels at the same level in a foam[18] is very convenient for kinetic studies of the variation of the dispersity in highly expanded foams. The expression used is

$$a = (0.46\sqrt{n} - 1.8)\frac{\sigma}{\Delta P_L}, \tag{4}$$

where $a$ is the size of the edge of a polyhedron (from here on, a dodecahedron), $n$ the expansion factor of the foam at a given instant $\tau$, $\sigma$ the surface tension of the foam-forming solution, and $\Delta P_L$ the gauge pressure measured by a micromanometer at time $\tau$.

Relationship (4) is obtained by simultaneous solution of the equation that relates the expansion factor to the size of the edge of a polyhedral bubble and to the radius of curvature of the Plateau–Gibbs channels and the dependence of the capillary pressure on the surface tension of the solution and the gauge (reduced) pressure in the channels.[5] Eqn (4) is valid for a monodisperse foam. A real foam is a polydisperse system. The dispersity of such a system can be expressed quantitatively via average values for size, surface area, and volume of particles. These average values can be determined from the known function of size distribution of bubbles. Then the average linear ($a_L$), average surface ($a_S$), and average volume ($a_V$) magnitudes of the parameter $a$ will be expressed by the relationships

$$a_L = \int_0^\infty F(a)a\,da, \tag{5}$$

$$a_S^2 = \int_0^\infty F(a)a^2 da, \tag{6}$$

$$a_V^3 = \int_0^\infty F(a)a^3 da, \tag{7}$$

where $F(a)$ is the size distribution function for bubbles.

From Eqns (5)–(7) the volume–surface averaged parameter $a$ may be written as follows[19]

$$a_{VS} = \frac{a_V^3}{a_S^2} = (0.46\sqrt{n} f_a' - 1.8)\frac{\sigma}{\Delta P_L} , \quad (8)$$

where

$$f_a' = \frac{a_V^{3/2} a_L^{1/2}}{a_S^2} .$$

To calculate the coefficient $f_a'$, taking into account polydispersity of the system, we used various functions suggested as distribution functions for foams.[5] It turned out that the resulting values of the parameter differ from each other by no more than 5%. For example, when the de Vries[20] function,

$$F(R) = \frac{6\alpha R}{(1+\alpha R^2)^4} \quad (9)$$

($\alpha$ is the distribution parameter), or the $\gamma$-function,

$$F(R) = cR^{\alpha-1}\exp(-\lambda R) , \quad (10)$$

($\alpha$ and $\lambda$ are distribution parameters selected from normalisation conditions

$$\int_0^\infty F(R)\mathrm{d}R = 1) ,$$

was taken as the distribution function, the resulting values of the coefficient $f_a'$ were 1.15 and 1.14 (at $\alpha = 2$ and 3, respectively) for the $\gamma$-function and 1.16 for the de Vries function.

In the discussion of experimental data throughout the subsequent sections of the review we have used the volume–surface averaging of the parameter $a$ based on the de Vries distribution function.

## III. Characteristics of the effectiveness of concentration, separation, and purification of solutions of surfactants

The process of foam separation of surfactants is used for solving various problems: the concentration of surfactants in a foam aimed at their extraction or at purification of the solution from the surface active impurities; complete or partial extraction of one of the components or fractionation of surfactants for the purpose of separating them from each other; displacement of a chemical equilibrium in the foam with respect to the initial solution, for example, to increase the degree of hydrolysis of a soap.

To evaluate the effectiveness of foam separation processes, various physicochemical characteristics are used, for example, the degree of extraction, concentration coefficients, selectivity coefficient, carry-over of the liquid, etc.[2, 21, 22]

Distribution of a surfactant between a foam and a solution is characterised by the coefficient (constant) of concentration ($R^f$). The small ($R_{min}^f$) and large ($R_{max}^f$) coefficients of concentration are distinguished:[2,4,5,26]

$$R_{min}^f = \frac{c_F}{c_{L,0}} , \quad (11a)$$

$$R_{max}^f = \frac{c_F}{c_{L,R}} , \quad (11b)$$

where $c_F$ is the surfactant concentration in the foam including the substance of the adsorption layers; $c_{L,0}$ and $c_{L,R}$ are surfactant concentrations in the solution prior to and after the process. Equations connecting the coefficient of concentration to parameters of the foam structure (dispersity, expansion factor, and the radius of curvature of the Plateau–Gibbs channels) can be derived from the balance equations for the surfactant and the liquid phase, and data on the foam structure.

The total amount of a surfactant in a foam ($G_F$) is given by

$$G_F = G_L + G_S = V_{L,F}\, c_{L,F} + \Gamma_S , \quad (12)$$

where $G_L$ is the amount of the surfactant in the liquid phase of the foam (channels and films) without considering adsorption layers, $G_S$ is the amount of the surfactant in adsorption layers, $V_{L,F}$ the volume of the liquid phase of the foam, $c_{L,F}$ the concentration of the surfactant in the liquid phase of the foam, $S$ the total interfacial area in the foam, and $\Gamma$ the degree of adsorption.

The total concentration of the surfactant in the foam is

$$c_F = \frac{G_F}{V_{L,F}} = c_{L,F} + \frac{\Gamma S}{V_{L,F}} . \quad (13)$$

On the one hand, if one considers a unit volume of the foam containing $\upsilon$ bubbles of radius $R$, then the total interfacial area in this foam is $S = \upsilon 4\pi R^2$, and the volume of gas bubbles is

$$V_g = \upsilon\frac{4}{3}\pi R^3 .$$

On the other hand, $V_g = 1 - V_{L,F}$, therefore

$$\upsilon = \frac{3(1 - V_{L,F})}{4\pi R^3} .$$

Taking into account the number of bubbles, we have

$$\frac{S}{V_{L,F}} = \frac{3(1 - V_{L,F})}{RV_{L,F}} = \frac{3(n-1)}{R} . \quad (14)$$

From Eqn (11a) with allowance for (13) and (14) we obtain

$$R_{min}^f = \frac{c_{L,F}}{c_{L,0}} + \frac{3\Gamma(n-1)}{c_{L,0}R} . \quad (15)$$

Rubin and Gaden,[22] who assumed that $c_{L,F} = c_{L,0}$ and that the liquid volume in the foam can be neglected in relation to the total volume of the foam, derived a relationship for the concentration coefficient:

$$R_{min}^f = 1 + \frac{k\Gamma n}{Rc_{L,0}} , \quad (15a)$$

where $k$ is a geometric coefficient for the shape of bubbles ($k = 3$ for a spherical foam and $k = 3.3$ for a polyhedral foam of the pentagonal dodecahedron type). However, the $V_{L,F}$ value for a spherical foam is substantial and amounts to 48% of the total foam volume for simple cubic packing and 26% for hexagonal close packing; the expansion factor varies at these packings from 2.01 to 3.85, which may introduce large errors into the calculations of the numerical value for $R_{min}^f$. In a polyhedral foam the volume of liquid may be neglected in comparison with the foam volume, but for determination of $R_{min}^f(n)$ more detailed information on the structure of the foam is required.

The ratio of the interfacial area to the volume of liquid in a foam can be expressed via unit cell parameters of the foam. If a pentagonal dodecahedron is taken as the unit cell, this ratio will be[5]

$$\frac{S}{V_{L,S}} = \frac{20.7a^2}{6 \times 1.725\, a^2h + 10 \times 0.16\, r^2a} = \frac{20.7a^2}{10.35\, a^2h + 1.6\, r^2a} , \quad (16)$$

where $20.7a^2$ is the area of the dodecahedron surface, 6 and 10 are the numbers of films and channels that belong to one polyhedron, $1.725a^2$ is the area of a dodecahedron face (a film), $h$ the thickness of the film, $0.16r^2$ the cross-section area of a channel of curvature radius $r$.

From Eqn (11a) and relationships (13) and (16), formulae can be derived for calculating concentration coefficients at various distributions of liquid between the channels and the films.

For the film model of foam (where all the liquid is located in the films, $10.35a^2h \gg 1.16r^2a$) the concentration coefficient $R^f_{min}$ is

$$R^f_{min} = \frac{c_{L,F}}{c_{L,0}} + \frac{2\Gamma}{hc_{L,0}} . \quad (17)$$

For the channel model of foam (where all the liquid is located in the channels, $10.35a^2h \ll 1.16r^2a$), with allowance for the fact that the foam expansion factor for this model is

$$n = \frac{7.66\,a^3}{1.6\,ar^2} = 4.8\frac{a^2}{r^2} ,$$

the concentration coefficient is given by

$$R^f_{min} = \frac{c_{L,F}}{c_{L,0}} + \frac{\Gamma n}{0.37\,c_{L,0}a} . \quad (18)$$

If the radius of curvature of the Plateau–Gibbs channels is expressed in terms of the capillary pressure $R = P_\sigma/\sigma$, then the equation for the concentration coefficient assumes the form

$$R^f_{min} = \frac{c_{L,F}}{c_{L,0}} + \frac{\Gamma a}{0.77\,c_{L,0}} \left(\frac{P_\sigma}{\sigma}\right)^2 . \quad (18a)$$

Relationship (18) indicates that when $\Gamma = \text{const}$ and $n = \text{const}$, the concentration coefficient is determined by the dispersity of the foam, and when $\Gamma = \text{const}$ and $a = \text{const}$, it is determined by the expansion factor of the foam and the capillary pressure.

The parameter $a$ can be expressed in terms of the radius of a sphere whose volume is equivalent to that of the dodecahedron ($7.66a^3 = \frac{4}{3}\pi R^3$), that is

$$a = 0.816R.$$

By substituting this dependence into Eqn (18) we obtain

$$R^f_{min} = \frac{c_{L,F}}{c_{L,0}} + \frac{\Gamma n}{0.302\,c_{L,0}R} . \quad (18b)$$

The resulting expression is analogous to relationship (15a). In the absence of internal disruption when the surfactant concentration in the bulk parts of the foam $c_{L,F}$ is equal to its concentration in the solution from which the surfactant is extracted, the first term in Eqns (18) and (18b) is equal to unity.

When internal disruption occurs, i.e. diffusion of the gas between the bubbles and coalescence or destruction of the foam column, the liquid phase is enriched in the surfactant that is desorbed from the surfaces of vanishing films. The more intense the destruction process, the larger the quantity of the substance desorbed returning into the bulk of the foam. The increase in the concentration of the substance in the liquid phase of the foam occurring in the course of destruction is expressed by the dependence[23]

$$c_{L,F} = c_{L,0} + \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n\,d\varepsilon . \quad (19)$$

where $c_{L,F}$ is the surfactant concentration in the liquid phase of the foam at a given instant, $c_{L,0}$ the initial surfactant concentration in the liquid phase of the foam, $\varepsilon_\tau$ and $\varepsilon_0$ are specific surface areas of the foam at time $\tau$ and at the initial instant, respectively, $n$ the expansion factor of the foam corresponding to the given specific surface area at a given instant. Thus, if the destruction proceeded at a constant expansion factor and a constant adsorption, the increase in the substance concentration in the foam bulk ($\Delta c = -\Gamma n \Delta\varepsilon$) would correspond exactly to the diminution of the substance due to desorption from the surface layers.

In view of Eqn (19) expression (18) assumes the form

$$R_{min} = 1 + \frac{1}{c_{L,0}} \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n\,d\varepsilon + \frac{\Gamma n_\tau}{0.37 c_{L,0} a_\tau} , \quad (20)$$

where $n_\tau$ is the expansion factor of the foam at time $\tau$, $a_\tau$ the size of the edge of a polyhedron at time $\tau$, $n$ a variable expansion factor which varies from $n(\varepsilon_0)$ to $n(\varepsilon_\tau)$ in the course of concentration.

In the case where the foam is stable and the duration of the process is low, the concentration caused by the internal breakdown is not very great. For unstable foams and prolonged processes the concentration resulting from the internal disruption and destruction of the column is comparable with that occurring in the adsorption layers. In addition, if concentration is carried out with increase in the expansion factor in the course of gravity syneresis or by the method of the capillary drying of the foam, then the excess of the substance that accumulates in the bulk sections of the foam owing to its destruction would be removed with the liquid being drawn off from the foam and would result in a diminution of the effectiveness of the concentration processes.

When the concentration of a mixture of surfactants is carried out, the selectivity of foam separation is evaluated from the selectivity coefficients, which are generally represented by the ratios between the coefficients of concentration of the $i$th ($R^f_i$) and $j$th ($R^f_j$) components:[2,5]

$$K_{ij} = \frac{R^f_i}{R^f_j} . \quad (21)$$

It should be noted that the selectivity coefficient like the concentration coefficient is a relative value depending not only on the nature of substance but also on the initial concentration of the surfactant in the solution.[3, 24–26]

In order to evaluate the effectiveness of isolation of surfactants in the course of foam separation, especially in a foam being destroyed, it is expedient to introduce a parameter $\gamma$ characterising the quantity of the substance extracted with the foam ($G_F$) per unit volume of the gas consumed ($V_g$):

$$\gamma = \frac{G_F}{V_g} . \quad (22)$$

If we assume that adsorption reaches a constant equilibrium value during foam concentration, the foam is not destroyed, and the whole bulk of the gas remains in the foam, then using Eqn (22) and taking into account the balance of the substance in the foam (12) we obtain the following dependence

$$\gamma = \frac{c_{L,F}V_{L,F} + \Gamma S}{V_g} = \frac{c_{L,F}}{n-1} + \Gamma\varepsilon \simeq \frac{c_{L,F}}{n} + \Gamma\varepsilon , \quad (23)$$

where $(n-1) \approx n$ for highly expanded foams.

It follows from Eqn (23) that with the expansion factor of the foam being constant the effectiveness of the extraction is mostly determined by the degree of its dispersity, since normally $c_{L,F}/n \ll \Gamma\varepsilon$.

The coefficient of the effectiveness of extraction is related to the concentration coefficient by the following relationship

$$\gamma = R^f_{min} \frac{c_{L,0}V_{L,F}}{V_g} = R^f_{min} \frac{c_{L,0}}{n} . \quad (24)$$

Thus, the greater $R^f_{min}$, the greater the coefficient of extraction effectiveness at $c_{L,F} = \text{const}$ and $n = \text{const}$. Eqn (24) also shows that when the extraction is carried out from solutions with different initial concentrations of surfactants (at $R = \text{const}$), to achieve equal effectivenesses of the process different amounts of the gas are required.

With allowance for the internal destruction [Eqn (19)] the dependence (23) assumes the form

$$\gamma = \frac{c_{L,0}}{n_\tau} + \frac{1}{n_\tau}\int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n \, d\varepsilon + \Gamma\varepsilon_\tau \ , \tag{25}$$

where $n_\tau$ is the expansion factor of the foam at time $\tau$, and $\varepsilon_\tau$ the specific surface area of the foam at time $\tau$.

Carry-over of a liquid with a foam during foam separation is reflected by the volume factor $R_V$ [21,22] and the water flooding coefficient $\beta_V$.[28]

$$R_V = \frac{V_{L,F}}{V_{L,0} - V_{L,F}}, \tag{26a}$$

$$\beta = \frac{V_{L,F}}{V_{L,0}} \ , \tag{26b}$$

where $V_{L,F}$ is the volume of the liquid in the foam product and $V_{L,0}$ is the initial volume of the liquid at the beginning of separation.

The same parameters can be expressed in terms of the expansion factor of a foam

$$R_V = \frac{n_0}{n - n_0} \ , \tag{27a}$$

$$\beta = \frac{n_0}{n} \ , \tag{27b}$$

where $n$ is the expansion factor of the foam as it leaves the separation column, $n_0$ the foam expansion factor on the assumption that the whole liquid has been converted into the foam.

The influences of various factors on the carry-over of liquid with the foam have been studied by many authors.[21,29–33] In particular, empirical equations relating the reciprocal of the expansion coefficient to the viscosity and density of the foam-forming solution, the diameter of foam bubbles, and the rate of its movement were obtained.[32,33]

In the general case, it is rather difficult to predict quantitatively the carry-over of a liquid with a foam. Analytical equations describing the distribution of liquid with height have been obtained only for a hydrostatically equilibriated foam.[34–36]

The distribution of liquid throughout the height of the column of a moving foam can be calculated only for the simplest (steady-state) regime.[36] This calculation is possible only for the channel variant of foam with stationary surfaces of the channels if the rate of the foam movement is lower than the rate of gravity syneresis in a spherical foam $V$ ($V = 1$ cm s$^{-1}$).[36]

Some results on the distribution of liquid with height for a foam being continuously generated have also been obtained by numerical methods on a computer with the aid of various hydrodynamic models.[37–41]

The volume of liquid carried away with a foam is determined, on the one hand, by the rate at which the liquid is incorporated into the foam (which is proportional to the rate of bubbling of the gas) and, on the other hand, by the rate at which this liquid flows out of the foam (the rate of syneresis). In fact, when the consumption of the gas is low and the whole excess liquid has time to flow out from the foam, then a foam with an expansion factor close to the hydrostatically equilibriated distribution of liquid with height should be formed at the outlet from a foam generator. Conversely, when the consumption of the gas is high, the expansion factor should diminish and approach asymptotically that of a spherical foam.

In the medium region of gas consumption the expansion factor of the foam at the outlet from the foam generator depends substantially not only on the rate of bubbling but also on physicochemical properties of the solution of a foam-forming agent (viscosity, surface tension) and the structural parameters of the foam (dispersity). To analyse the experimental data obtained for this region one can use the equation of syneresis in a gravitation field[42] which contains two empirical constants, the value for one of which ($V'_{L,0}$) is known:

$$\Delta V'_L = V'_{L,0}\frac{\tau}{\tau + V_{L,0}/w_0} \ , \tag{28}$$

where $V'_L$ is the volume of liquid that has flowed out of the foam by time $\tau$ (referred to unit cross-sectional area of the foam), $V'_{L,0}$ is the initial volume of liquid in the foam referred to unit surface area, and $w_0$ is the initial volumetric rate of syneresis.

The analytical dependence of $w_0$ on the structural parameters of a foam is unknown. Therefore, to carry out a semiquantitative estimation of the influence of the structural parameters of a foam and the properties of a foam-forming solution, one may use the equation for the flow rate of homogeneous polyhedral foam for the channel variant[36]

$$\begin{aligned} w_0 &= 3.6 \times 10^{-4}\frac{r^4}{\eta R^2}\left[\rho g - \left(\frac{\partial p}{\partial H}\right)_0\right] \\ &= 3.3 \times 10^{-3}\frac{R^2}{\eta n^2}\left[\rho g - \left(\frac{\partial p}{\partial H}\right)_0\right] \ , \end{aligned} \tag{29}$$

where $3.6 \times 10^{-4}$ and $3.3 \times 10^{-4}$ are hydrodynamic coefficients, $R$ the average radius of a bubble, $\eta$ the dynamic viscosity, $r$ the radius of curvature of Plateau–Gibbs channels, $\rho$ the density of the foam-forming solution, $g$ the acceleration due to gravity, and $(\partial p/\partial H)$ the gradient of the capillary pressure with the height of the foam column at the beginning of syneresis.

It has been found[29,30] that at low specific gas consumptions ($< 0.8$ cm min$^{-1}$) a foam with a distribution of liquid hydrostatically equilibriated with height leaves the foam generator regardless of the type of surfactant. At high specific gas consumptions ($> 20$ cm min$^{-1}$) a foam with an expansion factor of 10–12 comes out of the foam generator. The authors did not manage to achieve further decrease in the expansion factor owing to the very high rates of syneresis in slightly expanded foams and the 'break-down' of the foam formation on further increase in the gas consumption.

When the rate of gas consumption falls within the limits $0.8 < W_g < 20$ cm min$^{-1}$ the carry-over of a liquid with a foam depends considerably on the rate of syneresis. All the factors that decrease the rate of syneresis [diminution of bubble size and of the surface tension, increase in the surface and dynamic viscosities, and lowering of the foam column [see Eqn (29)] resulted in increase in the carry-over of the liquid with the foam. Conversely, all the factors increasing the rate of syneresis diminished the carry-over of the liquid with the foam.

A detailed study of Eqns (25a)–(25b) and identification of the relationship of characteristics of foam separation to structural parameters of the foam and to each other are possible on the basis of the material balance equations for the substance in the foam and in the solution, including those taking into account destruction of the foam.

The material balance for a substance involved in foam separation is given by the formula

$$G_0 = G_F + G_R \ , \tag{30}$$

where $G_0$ is the amount of the substance in the original solution, $G_F$ is the amount of the substance in the foam, and $G_R$ is the amount of the substance in the solution after the separation.

In view of Eqn (12) the material balance may be written as follows:

$$G_0 = G_L + G_S + G_R \ . \tag{31}$$

The total volume of the liquid involved in foam separation is given as:

$$V_{L,0} = V_{L,F} + V_{L,R} , \quad (32)$$

where $V_{L,0}$ is the volume of the solution subjected to foam separation, $V_{L,F}$ is the volume of the liquid phase in the foam, and $V_{L,R}$ is the residual volume of the solution after foam separation.

If we express the substance amounts by means of the corresponding concentrations and volumes, we obtain

$$c_{L,0}V_{L,0} = c_{L,F}V_{L,F} + \Gamma S + c_{L,R}V_{L,R} , \quad (33)$$

where $c_{L,0}$ is the surfactant concentration in the solution subjected to separation, $c_{L,F}$ the surfactant concentration in the liquid phase of the foam, $c_{L,R}$ the surfactant concentration in the solution after separation, and $S$ the total interfacial area in the foam. All these parameters are values averaged through the whole period of foam separation.

If there is no internal disruption in the foam or destruction of the foam column, then $c_{L,F}$ varies from $c_{L,0}$ to $c_{L,n}$ in the course of separation. On the assumption that the specific interfacial area in the foam is constant and the concentration in the liquid phase of the foam is close to the initial value, Eqn (33) with account taken of Eqn (31) can be represented as follows:

$$c_{L,0}V_{L,0} = c_{L,0}V_{L,F} + \Gamma S + c_{L,R}(V_{L,0} - V_{L,F}) . \quad (34)$$

Taking into account that $n = V_F/V_{L,F}$, $S/V_F = \varepsilon$, and $c_{L,0} = c_{L,F}$, we obtain from Eqns (34) and (26b)

$$\frac{\Delta c}{\beta} = \Delta c + \Gamma \varepsilon n . \quad (35)$$

Here $\beta$ is the water flooding coefficient

$$\beta = \frac{\Delta c}{\Delta c + \Gamma \varepsilon n}, \quad (36)$$

where $\Delta c = c_{L,0} - c_{L,n}$, $\varepsilon$ and $n$ are the specific surface area and the expansion factor of the foam (average values throughout the process).

The water flooding coefficient is related to the volume factor ($R_V$) by the relationship[27]

$$R_V = \frac{\beta}{1-\beta} \quad (37)$$

The combination of Eqns (36) and (37) gives

$$R_V = \frac{\Delta c}{\Gamma \varepsilon n} . \quad (38)$$

For the process of foam separation in which the foam is dried through the action of a pressure differential in the Plateau–Gibbs channels Eqns (31), (32), and (34) assume the form

$$G_0 = G_L + G_S + G_D + G_R , \quad (39)$$

$$V_{L,0} = V_{L,F} + V_{L,D} + V_{L,R} , \quad (40)$$

$$c_{L,0}V_{L,0} = c_{L,F}V_{L,F} + \Gamma S + c_{L,D}V_{L,D} + c_{L,R}V_{L,0} - c_{L,R}V_{L,F} - c_{L,R}V_{L,D} . \quad (41)$$

The index D designates the corresponding values in the 'filtrate'. Considering that $c_{L,D} = c_{L,F}$, $S = V_F\varepsilon$, $n = V_F/V_{L,F}$, and $\beta = V_{L,F}/V_{L,0}$, we obtain from Eqn (41)

$$\beta_F = \frac{\Delta c_{max}}{(c_{L,F} - c_{L,R})(1+\delta) + \Gamma \varepsilon n} \quad (42)$$

where $\Delta c_{max} = c_{L,0} - c_{L,R}$, $\beta_F$ is the flooding coefficient of the foam that emerges from the column (irrespective of the liquid carried away with the 'filtrate'), $\delta = \beta_D/\beta_F$ is the constant of drying, and $\beta_D = V_{L,D}/V_{L,0}$ is the coefficient of carry-over of the liquid with the 'filtrate'.

As the process is carried out, the concentration of the substance in the liquid phase of the foam varies within the range $c_{L,R} \leqslant c_{L,F} \leqslant c_{L,0}$.

At the start, $c_{L,0} = c_{L,F} = c_{L,D}$, and the water flooding coefficient is given by

$$\beta_{F(0)} = \frac{\Delta c_{max}}{\Delta c_{max}(1+\delta) + \Gamma \varepsilon_0 n_0} . \quad (43)$$

At the end of the process $c_{L,F} = c_{L,R}$, and

$$\beta_{F(R)} = \frac{\Delta c_{max}}{\Gamma \varepsilon_R n_R} . \quad (44)$$

The overall flooding coefficient of the foam, $\beta_\Sigma$, with allowance for the liquid extracted during drying ('filtrate'), is found from the equation

$$\beta_\Sigma = \beta_F + \beta_D = \frac{\Delta c_{max}}{(c_{L,F} - c_{L,R})(1+\delta) + \Gamma \varepsilon n}(1+\delta) . \quad (45)$$

From Eqn (34), taking into account (19), one can obtain the following expression for the foams destroyed during the foam separation:

$$c_{L,0}V_{L,0} = \left(c_{L,F} + \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n \, d\varepsilon\right) V_{L,F} + \Gamma S_\tau + c_{L,R}V_{L,R} , \quad (46)$$

where $S_\tau$ is the surface area of bubbles in the foam at time $\tau$.

From Eqn (36), the general expression for the carry-over of the liquid phase with a foam, which undergoes destruction, can be obtained from

$$\beta = \frac{\Delta c_{max}}{\Delta c_{max} + \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n \, d\varepsilon + \Gamma \varepsilon_{min} n_\tau}, \quad (47)$$

where $\Delta c = c_{L,0} - c_{L,R}$, and $\varepsilon_{min}$ is the specific surface area of the foam at the outlet from the column at time $\tau$.

For the process of foam concentration involving capillary drying, an equation can be obtained which relates the water flooding coefficient to the structural parameters of the foam.[43]

The mass ($\alpha_m$) and concentration ($\alpha_c$) degrees of extraction are characteristics of the completeness of the extraction of a substance:

$$\alpha_m = 100 \frac{G_0 - G_R}{G_0}, \quad (48)$$

$$\alpha_c = 100 \frac{c_{L,0} - c_{L,R}}{c_{L,0}} \quad (49)$$

The equations of the material balance during the foam separation and dependence (48) make it possible to obtain an equation relating $R^f_{min}$, $\beta$ to $\alpha$

$$\alpha = 100\frac{G_0 - G_R}{G_0} = 100\frac{G_F}{G_0}$$

$$= 100\left(\frac{c_{L,F}V_{L,F} + \Gamma S}{c_{L,0}V_{L,0}}\right)$$

$$= 100\left(\frac{c_{L,F}}{c_{L,0}} + \frac{\Gamma S}{c_{L,0}V_{L,F}}\right)\frac{V_{L,F}}{V_{L,0}} = 100R^f_{min} \quad (50)$$

It can be seen from Eqn (50) that only two of the three characteristics of the adsorption concentration are independent. For example, at different concentration coefficients, the same degree of extraction can be achieved by the appropriate variation of the water flooding coefficient.

The effectiveness of the removal of impurities from a solution is characterised by the purification coefficient (factor)

$$o = \frac{c_{L,0}}{c_{L,R}} . \quad (51)$$

From the material balance equation, one can obtain an expression for the purification coefficient containing the structural characteristics of foam:[5]

$$o = \frac{c_{L,0}}{c_{L,R}} = 1 + \frac{\Gamma S}{c_{L,R} V_{L,R}} = 1 + \frac{2.7\,\Gamma n}{c_{L,R} a} . \quad (52)$$

Eqns (51) and (52) are of little use for determining the limiting values of the purification coefficient, since in the case of low surfactant concentrations the stability of the foam dramatically decreases, and the foam layer containing the adsorbed product has no time to separate from the solution.

For this reason determination of the minimum residual surfactant concentration necessary to obtain a stable foam provides more precise information on the purification coefficient. The minimum residual concentration is close to that for the formation of black spots ($c_b$) in microscopic foam films ($c_{L,0} = c_{St} = c_b$) in the circumstances where they are formed

$$o_{max} = \frac{c_{L,0}}{c_b} . \quad (53)$$

Some researchers, for example, Skvirskii et al[44] and Sontag and Strenge,[45] maintain that a stable foam is formed only when the concentrations of surfactants correspond to the limiting degrees of their adsorption ($\Gamma_\infty$), while others, for example, Venstrem and Rebinder[46] and Ekserova and Sheludko[47], have noted that a stable foam can also be obtained when the surfactant concentrations are much lower than those necessary to reach $\Gamma_\infty$. In fact, a dramatic increase in the lifetime of a foam is typical of the concentration regions corresponding to the formation of black spots in microscopic foam films.[5,48]

The formation of black spots in thermodynamically non-equilibrium films has a probability character.[49,50] It can be observed experimentally if the lifetime of a black spot is greater than the time resolution of the instrument. The probability of the detection can be calculated from experimental data as the ratio of the number of films in which black spots have been observed to the total number of films examined.

The probability ($W_b$) of observing black spots in an ordinary black film from a solution of sodium dodecyl sulfonate exists over a wide concentration range, $2.5 \times 10^{-6}$ to $3.5 \times 10^{-4}$ mol $l^{-1}$. It rises substantially in the initial section, up to a concentration of $\sim 10^{-5}$ mol $l^{-1}$ when the degree of filling of the adsorption layer, $\Gamma/\Gamma_\infty$, is 0.4. However, even when this probability is equal to unity, the complete saturation of the adsorption layer is not yet reached [$\Gamma/\Gamma_\infty = 1$ at $c = (5.0 \pm 0.2) \times 10^{-4}$ mol $l^{-1}$].

The increase in the probability of the formation of Newton black films for the same surfactants lies within a narrow range of surfactant concentrations (from $8 \times 10^{-5}$ to $2 \times 10^{-4}$ mol $l^{-1}$) that correspond to the saturated adsorption layer ($\Gamma/\Gamma_\infty = 1$ at $c = 1.1 \times 10^{4}$ mol $l^{-1}$). It is important to keep in mind this distinction between the concentration dependence of the probability of detecting black spots and the lifetime of the foam, while determining the minimum residual concentration of the surfactant.

A necessary and sufficient condition for the principal possibility of foam separation is that a substance is concentrated in the foam, i.e. $R^f_{min} > 1$.

Eqn (18) implies that in a polyhedral foam the condition $R^f_{min} > 1$ is satisfied when $\Gamma n/0.37a > c_{L,0}$, since $c_{L,F}/c_{L,0} \simeq 1$. This inequality determines both the lower and the upper limits of foam concentration, outside of which concentration is impossible ($R^f = 1$). However, the reasons why this relationship no longer holds are different. Thus, the upper limit of the applicability of the foam separation method is often attributed to the CCM,[4,51] since at this concentration $\sigma$ = const, and $d\sigma/dc = 0$. However, in the region of concentrations not far exceeding the CCM, where $\sigma(c)$ = const, adsorption of a surfactant has a positive value, which is indicated by direct measurements of adsorption in this region. The calculation according to Eqn (18) shows that for typical micelle-forming surfactants ($\Gamma = 3 \times 10^{-10}$ mol $cm^{-2}$, $a = 10^{-2}$ cm) $R^f_{min} > 1$ already at $n > 40$. This expansion factor can be achieved both by using the method of drying with the aid of porous plates and by drying in a gravitational field at a low gas consumption in the separation column and with a high foam column. Thus, if the lifetime of a foam is sufficient for technological processing ($\tau = 10-15$ min), then its high expansion factor can be achieved and adsorption concentration of a substance can be carried out at $c_{L,0} >$ CCM.[22,52]

## IV. Experimental studies on the concentration of individual surfactants and mixtures

The distribution of a substance being extracted between a liquid and a foam, which is characterised by the concentration coefficient, has been studied in foam separation processes under conditions both of gravity[2,22,23,43] and of accelerated syneresis.[7,10,43,52,53]

Under the conditions of gravity syneresis, $R^f_{max}$ diminishes with decrease in the height of foam in the separation column (at a constant specific rate of gas delivery to the separation column) or with increase in the rate of bubbling at a constant height of the foam column.[43]

The concentration coefficient $R^f_{min}$ increases with decrease in the size of bubbles only if $n$ = const [Eqn (18)]. If the expansion factor changes simultaneously with dispersity (as is often the case under the conditions of gravity syneresis, since the decrease in the sizes of foam bubbles results in a decrease in the rate of syneresis and in the formation of a foam with a lower expansion factor at the outlet from the foam generator), then a decrease in the size of bubbles often leads to a decrease in $R^f_{min}$, rather than to its increase.[4,43]

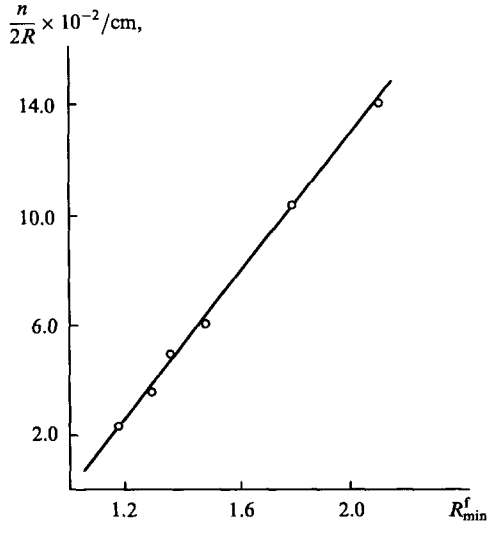



**Figure 2.** The dependence of the ratio $n/2R$ on the coefficient of concentration of sodium butyl diphenylsulfonate in a foam. The initial concentration of the surfactant in the solution was $2.4 \times 10^{-3}$ mol $l^{-1}$.

A study of foam separation of sodium butyl diphenyl sulfonate in an ordinary slightly expanded foam has shown[22] that the concentration coefficient increases linearly with increase in the $n/2R$ value in conformity with relationship (15a) (Fig. 2).

An expansion factor of more than 100 is rarely achieved in standard separation columns, and therefore, under these conditions, the concentration coefficient is of the order of several tens or, occasionally, several hundreds.

Greater magnitudes of the concentration coefficient can be reached in dry foams.[5,7-10,52,53] Kruglyakov and Kuznetsova[7] have studied the influence of the capillary pressure, the expansion factor, and dispersity on $R^f_{min}$. The foam was prepared from solutions of sodium dodecyl benzenesulfonate (DDBSNa) and 20-oxyethylated nonylphenol (NP-20). The concentration coefficient $R^f_{min}$ increased in direct proportion to the expansion factor (at $a = \text{const}$) and in inverse proportion to the parameter $a$ (at $n = \text{const}$) (Fig. 3 *a*, *b*).

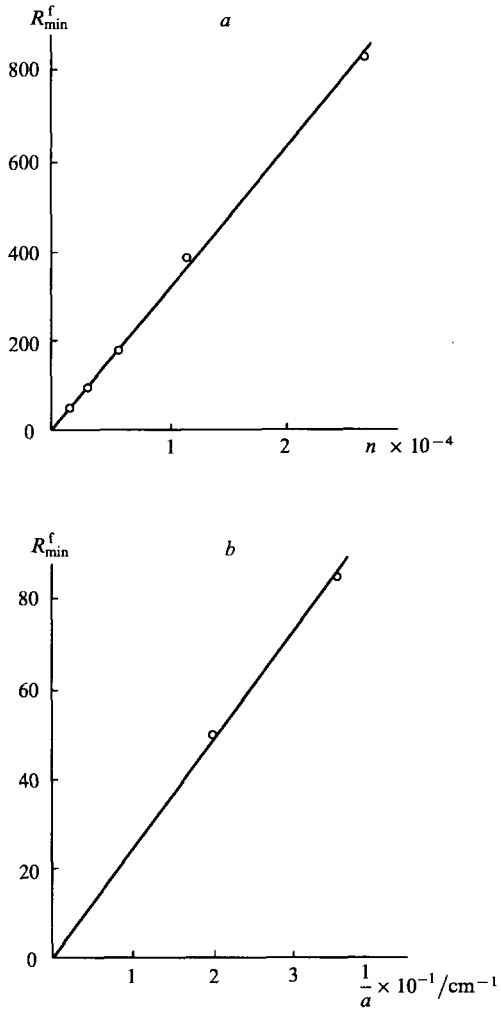



**Figure 3.** The dependence of the coefficient of concentration of a surfactant in a foam on the expansion factor (*a*) and dispersity (*b*) of the foam. (*a*) $a = \text{const}$; (*b*) $n = 1000$.

Interesting results have been obtained in a study of concentration of proteins in a dry foam.[53] Under the conditions of gravity syneresis a foam prepared from proteins has a low expansion factor ($n = 20-30$) and a concentration coefficient of 1.5–3. In the case of accelerated syneresis under the action of high pressure differentials, the foam expansion factor can be as high as 500 and the concentration coefficient is 50–70 (Fig. 4).

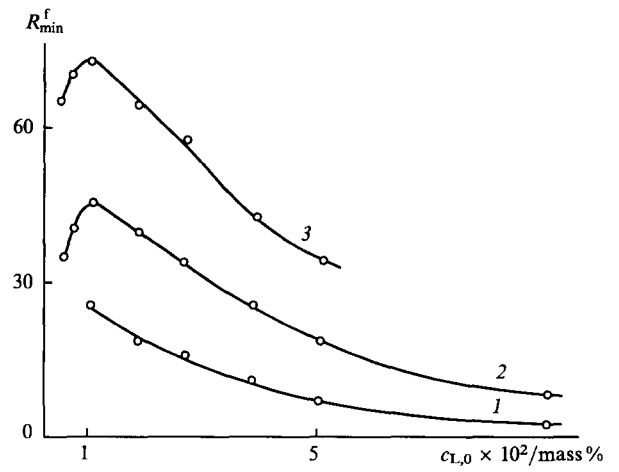



**Figure 4.** The dependence of the concentration coefficient for serum albumin on its initial concentration in a foam-forming system at various degrees of expansion of the foam. *n*: (*1*) 150; (*2*) 300; (*3*) 500.

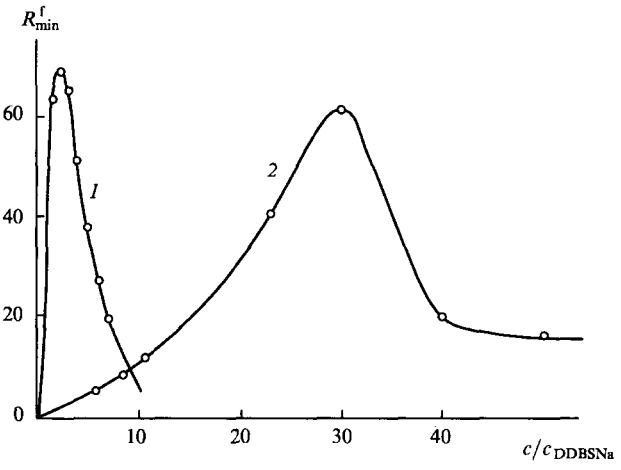



**Figure 5.** The dependence of the coefficient of concentration of saponin (*1*) and valeric acid (*2*) on component concentration ratios in mixtures with DDBSNa. The concentrations of the components in the mixtures are given in percent (*1*) and in mol $l^{-1}$ (*2*).

If a surfactant is not a good foam-forming agent it cannot be concentrated in a dry foam; therefore a good foam-forming agent is introduced in the solution of such compound, and concentration of the resulting mixture is carried out. Valeric acid, saponin, and α-chymotrypsin were concentrated in such a manner (DDBSNa and DDSNa were used as foam-forming agents).[9] When concentration is carried out from a mixture, the dependence of $R^f_{min}$ on the ratio between the components has an extreme character (Fig. 5).

The low-molecular-mass protein antibiotic nisin was successfully concentrated from a culture liquid in a highly expanded foam stabilised by the foam-forming agent Tween-80. In the absence of a special foam-forming agent no stable foam is produced from the culture liquid. By adding Tween-80 one can extract nisin; however, the concentration coefficient in a foam under the conditions of gravity syneresis does not exceed 4–5 (see Ref. 54). To increase the degree of concentration, a multistep process involving destruction of foam and subsequent foaming is required. When nisin is concentrated in a dry foam (dried with the aid of filtering partitions) the degree of concentration can be increased to $R^f_{min} = 350$.

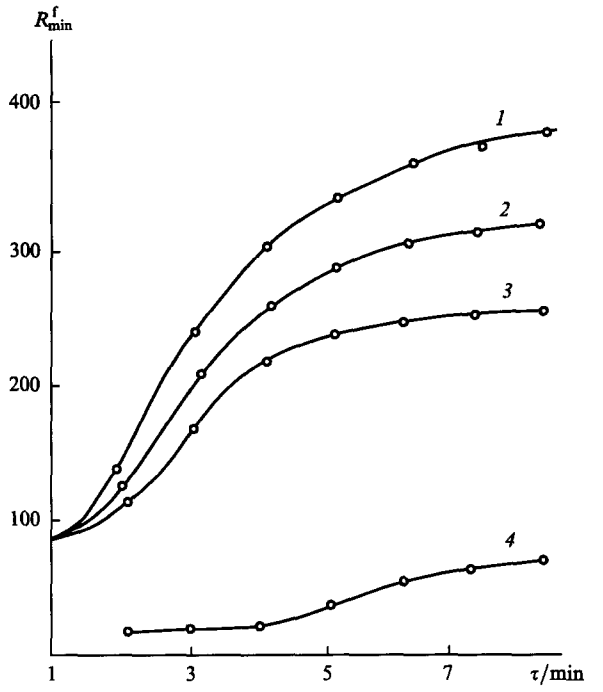



**Figure 6.** The time dependence of the concentration coefficient and its constituents for a foam prepared from a DDBSNa solution.
(*1*) $R_1^f = \Gamma n_\tau / 0.37\, c_{L,0}\, a_0$; (*2*) $R_2^f = R_3^f + R_4^f$;
(*3*) $R_3^f = \Gamma n_\tau / 0.37\, c_{L,0}\, a_\tau$; (*4*) $R_4^f = \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n\, d\varepsilon \Big/ c_{L,0}$.

The influence of the internal disruption on the parameters of foam concentration has been experimentally studied by Khaskova and Kruglyakov.[27,43] They carried out quantitative evaluation of the effect of the internal disruption on the variation of the concentration and extraction coefficients for foams prepared from solutions of DDBSNa and sodium oleate (NaOL) having distinct destruction kinetics.[27,43] Fig. 6 shows the kinetic dependence of the concentration coefficient and its constituents for a foam prepared from a solution of DDBSNa [see Eqn (20)]. Curve *1* corresponds to the variation of $R^f$ occurring as the foam is dried provided that there is no destruction in it. Curve *2* shows the variation of $R^f$ with allowance for foam destruction. Curve *3* reflects the accumulation of the substance in adsorption layers provided $a = \text{const}$, and curve *4* shows the accumulation of the substance in the liquid phase of the foam owing to its internal disruption. The second term of Eqn (20) was calculated by graphical integration on the basis of the $n = f(\varepsilon)$ dependence. One can see that foam destruction results in a decrease in the concentration coefficient.

Similar results were obtained for a foam prepared from a solution of NaOL. In this case, the influence of foam destruction on the concentration coefficient was still more pronounced. The proportion of the quantity

$$\frac{1}{c_{L,0}} \int_{\varepsilon_\tau}^{\varepsilon_0} \Gamma n d\varepsilon$$

in foams prepared from NaOL solutions was $\sim 50\%$ of the theoretical $R^f$ value (in the concentration without destruction). The coefficient of extraction effectiveness is affected by the foam destruction to an even greater degree: for a foam formed from a solution of DDBSNa it varies from $5.4 \times 10^{-8}$ (at the beginning of the process) to $4.7 \times 10^{-8}$ mol cm$^{-3}$ (at the end), and for a foam obtained from a solution of NaOL, it varies from $10.8 \times 10^{-8}$ to $3.89 \times 10^{-8}$ mol cm$^{-3}$ (see Refs 27, 43).

In the course of drying, some liquid is removed from the foam and, if the specific surface area of the foam considerably decreases, the liquid is substantially enriched in the substance being extracted. To determine the loss of a substance with the filtrate one can use the following characteristics

$$\alpha_{D,\tau} = \frac{G_D}{G_{F,\tau}}, \tag{54}$$

$$\alpha_{D,0} = \frac{G_D}{G_{F,0}}, \tag{55}$$

where $G_D$ is the amount of the substance removed from the system with the filtrate, $G_{F,0}$ the initial amount of the substance in the foam, and $G_{F,\tau}$ the amount of the substance in the foam at time $\tau$. The characteristics $\alpha_{D,\tau}$ and $\alpha_{D,0}$, similarly to $R_V$, $R^f$, and $\gamma$, can be expressed in terms of the foam structural parameters, adsorption, and concentration of the surfactant in the solution.[43] If $\alpha_{D,0} \ll 1$ and $\alpha_{D,\tau} \ll 1$, the losses during drying are small.

The losses with the filtrate have been determined under steady-state conditions: a foam with a known volume was prepared from a definite volume of liquid in a separate cell, this foam was then dried in the same cell by increasing the pressure to $\Delta P = 1.6$ kPa. Variations of the expansion coefficient, the pressure in the Plateau–Gibbs channels, and dispersity in the foam were monitored. In the filtrate produced by the drying process the concentration of the surfactant was determined and the losses of the substance to be extracted, which occurred during drying and destruction of the foam, were found from Eqn (54).

The $\alpha_{D,0}$ values for stable foams obtained from solutions of DDBSNa with 0.01 or 0.1 mol l$^{-1}$ of NaCl added are 0.2 and 0.3, respectively. Foams produced from solutions of sodium oleate are destroyed under conditions of forced syneresis much more intensely, and in this case the losses with the filtrate reach $\alpha_{D,0} \simeq 0.6$. When $\alpha_{D,0} > 0.4-0.5$, the filtrate should be returned to the separation column in order to diminish losses of the substance extracted by foam separation.

A negative influence of foam destruction on the concentration and extraction coefficients has also been found[27,43] in the separation of foams with various stabilities carried out under the conditions of gravity syneresis: as a result of the internal disruption of a foam these coefficients decrease over a wide range of concentrations of the surfactant being extracted.

A positive influence of the internal disruption on the concentration coefficient (i.e. its increase) is observed only in the cases where a very small $c_{L,0}$ value lies in the range $c_b < c_{L,0} < c_{\Gamma,\infty}$ ($c_{\Gamma,\infty}$ corresponds to the saturated adsorption layer). This is caused by the fact that desorption from film surfaces during the foam destruction increases the surfactant concentration in the liquid phase of the foam, and, as a consequence, the degree of adsorption increases to the values that ensure formation of a small volume of a stable foam. It therefore becomes possible to separate the foam from the original solution with $R^f > 1$.

A positive influence of the internal destruction on the concentration coefficient due to the internal return of the solution (dephlegmation) has been found experimentally in foam separation processes carried out for solutions of DDBSNa and lysozyme at $c_b < c_{L,0} < c_{\Gamma,\infty}$.[43,55]

Studies on the identification of the upper and lower concentration limits of the applicability of the foam separation method have been reported.[43,52,55]

It was found experimentally that concentration from solutions of surfactants with a concentration $c_{L,0} = (2-3)$CCM is possible with $R^f_{min} = 6-9$ (for foams obtained from solutions of NaOL) or $R^f_{min} = 27-30$ (for foams obtained from solutions of DDBSNa).[43,52]

To evaluate the minimum residual concentration, a rather simple method can be used involving determination of the surfactant concentration above which a stable foam is formed under the conditions of steady-state operation of a separation

column (when the height of the foam column remains constant during the delivery of a gas).[55] The foam-forming ability is estimated based on the ratio $V_F/V_g$ (where $V_F$ is the greatest volume of foam obtained in a separation column over period $\tau$ in the steady-stade regime and $V_g$ is the volume of the gas bubbled into the column over the same period), the parameter $a$ and the rate of gas bubbling being constant during the course of the experiment. The experimental dependences $V_F/V_g = f(c)$, $\tau = f(c)$, and $\Delta N/N = f(c)$ ($\tau$ is the lifetime of the foam and foam films, $\Delta N/N$ the probability of the detection of black films) have similar characters for all surfactant types studied (DDSNa, DDBSNa, lysozyme). The minimum residual concentration is, as a rule, equal to the concentration at which black films arise with a probability of more than 50%. Moreover, if the $V_F/V_g = f(c)$, $\tau = f(c)$, and $\Delta N/N = f(c)$ curves vary by jumps, then the dependences of the concentration coefficient also vary by jumps. The variations described are characteristic of systems in which black spots (ordinary or Newton black films) arise in microscopic films at a definite concentration. If ordinary thin foam films are formed in a system (DDSNa and DDBSNa without an electrolyte, or lysozyme not at the isoelectric point), the lower threshold concentration cannot be distinguished unambiguously. In these systems, the minimum concentration is found from the particular conditions under which the process is conducted (the rate of gas bubbling, dispersity, the foam height in the column, etc) and has no clear-cut limit.

## V. Separation of components of a mixture of surfactants in a foam

In the previous sections we have mostly considered the results of concentration of surfactants in a foam or purification of a solution from surfactants in binary systems. Our goal has been to increase the concentration coefficient or the degree of extraction of one of the components with the aid of the other, rather than to separate the components of the system from one another.

A partial or complete separation of two dissolved components can be carried out by the foam separation process. The separation occurs most easily when one of the components is surface inactive or has very low surface activity. For example, soaps and various synthetic surfactants can be readily separated (purified) from electrolytes; proteins can be separated from amino acids; and so on.

The separation of ions is most frequently carried out by ion flotation methods (without formation of a stable foam) involving ion exchange reactions, formation of nondissociated compounds, precipitation, coprecipitation, and other expedients.[2-4,6] The possibility of separating components without resort to ion flotation methods has been shown for the first time for mixtures of soap and dyes. Ostwald and coworkers[56-58] demonstrated the possibility of separating blue (triphenylmethane) and crimson-red (novococacine azo dye) dyes. With identical concentrations of these dyes in the initial solution (0.01 %), the concentration of the blue dye in the foam reached 0.22%, that for the red dye was 0.02 %. Their concentrations in the residual solution were 0.003 % and 0.01 %, respectively. A similar separation of bromothymol blue into a yellow dye (in the foam) and a blue dye (the residue), and also the separation of congorubin into a wine-red dye and a violet dye, respectively, were achieved in the experiments of Thiele.[59] Separation of other dyes has been considered by Skomorski.[60]

Other papers deal with the processes of partial separation of soap mixtures (sodium oleate and laurate), mixtures of salts of cholic and fatty acids, and a mixture of saponin, sodium oleate, and gelatin.[61-63]

A large number of examples of partial separations, including those of proteins, polymers, and other compounds, are presented in a book by Cassidy[64] and in other papers.[65,66] Analysis of these works shows that purification of sodium dodecylsulfonate from a dodecyl alcohol admixture is perhaps the only example of complete separation of one of the components of the mixture from the other (apart from inactive electrolytes) and that this separation in an ordinary foam is possible only when the concentration of the alcohol is low compared with that of sodium dodecylsulonfate.[64] The thermodynamic theory of the surface separation processes, based on the difference between the compositions of the surface layer and the bulk phases, has been outlined in a monograph.[4]

The fundamental relationship connecting the mole fraction of the $i$-th component of the system ($N_i$) to the change in the total number of moles ($m$) during the surface separation can be presented in the following way

$$\Delta N_i = (N_i^S - N_i)\frac{\Delta m}{m} . \qquad (56)$$

Here $N_i^S$ is the mole fraction of the $i$th component in the surface layer.

If the dependence of $N_i^S$ on the composition of the system is known, one can integrate Eqn (56) and follow the variation of the composition of a solution during foam separation in the concentration space (i.e. follow the course of the lines of surface separation). Experimental studies on the thermodynamic theory of surface separation (in particular on the course of lines of surface separation which show the manner in which the solution composition varies during foam separation) for ternary systems, the components of which do not interact chemically with one another, have been carried out in a number of studies.[4,67]

Surface separation theory implies that the effectiveness of the separation is determined mostly by the selectivity coefficients of the components.

The results of separation in a foam are strongly affected, apart from the adsorption ability, by the stability of the foam, which depends on the nature and concentrations of the components, since it takes a rather long time ($\sim 10-15$ min) for the adsorption equilibrium to be reached and for the excess liquid to separate without destruction of the foam column. The selectivity of foam separation for two or three surfactants from aqueous solutions has been considered in many papers (see, for example, Refs 3, 26, 68, 69). Shinoda and Mashio[68] studied the selectivity for several pairs of anionic surfactants differing in the length of the hydrocarbon radical and the nature of the polar group. It was shown, for example, that the selectivity coefficient for the DDBSNa/DDSNa pair in molecular solutions is 35–50, and for the DDBSNa/potassium undecylsulfonate pair is 180–200. In the case of micellar solutions, the coefficient of selectivity is substantially lower, for example, it amounted to 5–8 for the DDBSNa/TDSNa (TDSNa is sodium tetradecylsulfonate) and $C_{15}H_{31}COOK/C_{13}H_{27}COOK$ pairs; however, the difference in the carbon chain length in these pairs was also much smaller.

At low concentrations of surfactants the selectivity coefficient increased by a factor of 2.75 when one methylene group was added. The introduction of a benzene ring in the hydrocarbon chain was equivalent to the introduction of 3.5–4 methylene groups.

The selectivity of the isolation of inorganic ions in a foam[69] during their simultaneous adsorption with the cetylpyridinium chloride ion (0.75–1.0 mol $l^{-1}$) increased in the sequence $Cl^- < Br^- < I^- < SCN^-$. The adsorption increased in this sequence from $1.39 \times 10^{-10}$ to $2.8 \times 10^{-10}$ mol $cm^{-2}$. The use of recycling (dephlegmation), which changes the ratio between the components, allows the effectiveness of the separation to be increased, especially for pairs of substances whose surface activities are slightly different.[3]

Hargis and Rogers,[70] who studied foam separation of DDSNa/DDBSNa and DDSNa/BSNa mixtures (BSNa is sodium benzenesulfonate), have noted that the concentration coefficients of these surfactants remain constant over a wide concentration range regardless of the presence of the other component.

The partial separation of components occurring during movement of gas bubbles through a layer of a surfactant solution is regarded by some researchers as a modification of chromatography (see, for example, Refs 4, 64, and 66). One cannot achieve the complete separation of substances by this method because it involves only single-stage adsorption of the components of a mixture, and because of the low concentration coefficients in a foam in which syneresis occurs only under the action of gravity.

The effectiveness of the separation of components dramatically increases when dry foams, prepared under the action of the pressure differential in Plateau–Gibbs channels with the aid of porous plates, are used.[5,7,10,52,53] In this way a complete separation of proteins from deoxyribonucleic acid has been carried out.[10]

The possibility of chromatographic separation of surfactants in a foam has been reported.[71] To perform this process a foam with controlled size of Plateau–Gibbs channels was used. A solution of the mixture of surfactants to be separated (thymol blue dye, $5 \times 10^{-4}$ mol $l^{-1}$, and DDBSNa, $1.5 \times 10^{-3}$ mol $l^{-1}$) was passed through a layer of a foam prepared from a DDSNa solution with 0.4 mol $l^{-1}$ of NaCl added. The foam was con-fined on both sides by porous partitions. The pressures on the outside of these partitions were dissimilar and lower than those on the inside by an amount not exceeding the capillary pressure in the partition pores. The solution of the mixture was delivered through that partition where the outside pressure was higher. Separation of the mixture was achieved owing to the multistage selective adsorption of the components at the surface of foam bubbles with the rate of the solution flow under the action of pressure differential ($\Delta P = 1.3$ kPa) being controlled.

In the mixture under study, DDBSNa and DDSNa are less active than the dye. As a consequence, DDBSNa appeared in the samples from the effluent, together with DDSNa, within 15 min, and within 30 min the effluent contained only DDBSNa. It was not until 40 min after the beginning of the process that traces of the dye appeared, i.e. one of the components (DDBSNa) was isolated by frontal analysis. It should be noted that foam chromatography, which has much in common with conventional liquid chromatography with a solid adsorbent, also has significant differences from it. The first of these is that it is impossible to obtain surfactant-free layers (sections) in foam chromatography. Other peculiarities are associated with the continuous decrease in the surface of the adsorbent (foam). The possibilities of foam chromatography have so far been poorly investigated.

Foam separation can also be used for shifting chemical equilibria or changing the rates of chemical reactions in a foam. If a reversible reaction, for example, the hydrolysis of a soap $NaR + H_2O = NaOH + HR$, can occur between dissolved compounds, the equilibrium in this reaction can be shifted in either direction depending on which component (NaR or HR) is more active. The change in the equilibrium constant in the surface layer compared with its magnitude in the bulk of the solution has been attributed to the concentration of the reactants in the surface layer (and the corresponding change in the activity) and change in the surface energy.[26]

The first quantitative experiments on moving an equilibrium in a foam have been carried out for soap solutions.[26] It was found that the foam, which underwent destruction, was acidic, whereas the remaining solution was alkaline, and the surface tension of this solution was twice as high as that of the liquid obtained from the foam. The hydrolysis is especially pronounced in dilute solutions. When the concentration of sodium oleate was 0.0002%, the ratio between the proportions of the acid and a base in the foam was 2.7, and it was only slightly dependent on the nature of the base. Similar results have been obtained for the foam prepared from a sodium laurate solution.[26]

Catalytic action of cationic surfactants (quaternary pyridinium chlorides) in the hydrolysis of 2,4-dinitrochlorobenzene and in the reaction with aniline in a foam has been observed.[74,75] For example, in the presence of quaternary pyridinium bases, the rate constant of the hydrolysis in a foam increased from $1.42 \times 10^{-7}$ (without the surfactant) to $2.7 \times 10^{-2}$ $m^3$ $mol^{-1}$ $s^{-1}$ (with surfactant), which is greater than in the case of catalysis in micelles ($8.3 \times 10^{-6}$ $m^3$ $mol^{-1}$ $s^{-1}$). A similar acceleration of acid hydrolysis occurs also in the presence of anionic surfactants.[76,77]

In a series of papers[74–77] this catalytic action has been explained in the context of the mechanism of micellar catalysis and has been attributed to the concentration of reactants in adsorption layers of a foam, to a local change in the pH, and to the influence of orientation of reactant molecules in the adsorption layers and of the surface charge on the formation of the transition state (intermediate complex). The higher effectiveness of the film catalysis in a foam as compared with micellar catalysis has been accounted for by the structural features of the surface layers in a foam (the type of adsorption film) that facilitate attainment of transition states of reactions. However, the authors[74–77] undertook no special studies that would have unambiguously confirmed these assumptions.

To the best of our knowledge the influence of the foam structure and especially of the type of thin films (the ordinary and Newton black ones) on the rate of reactions has not been investigated.

## VI. Conclusion

The drying of a foam by developing a pressure differential in the liquid phase with the aid of porous plates allows one to obtain high concentration coefficients for individual surfactants and their mixtures in the case where at least one of the compounds is a good foam-forming agent, and ensures chromatographic separation of substances in a foam.

The identification of the analytical relationships of characteristics of foam separation with the structural parameters of a foam and the properties of a surfactant makes it possible to optimise the process and to take into account the influence of foam destruction on various characteristics of surface concentration.

The internal disruption of a foam and the destruction of a foam column degrade the characteristics of the concentration. A positive influence of foam destruction (internal recycling) and, hence, of the external recycling and multistage separation on the concentration of individual surfactants, is manifested at low surfactant concentrations close to that for the formation of black spots in microscopic foam films.

Investigation of some reactions in a foam demonstrated a more pronounced catalytic action of surfactants in adsorption layers of a foam compared with their catalytic action in micelles.

## References

1. V A Malinovskii *Tsvet. Met.* **8** 83 (1970)
2. A M Gol'man, L M Abolyan, in *Obogashchenie Poleznykh Iskopaemykh (Ser. Itogi Nauki i Tekhniki)* [Enriching of Mineral Resources (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1980) Vol. 14, p. 120
3. *Adsorptive Bubble Separation Technique* (Ed. R Lemlich) (New York: Academic Press, 1972)
4. A I Rusanov, S V Levichev, V T Zharov *Poverkhnostnoe Razdelenie Veshchestv* (Surface Separation of Substances) (Leningrad: Khimiya, 1981)
5. P M Kruglyakov, D R Ekserova *Pena i Pennye Plenki* (Foam and Froth Films) (Moscow: Khimiya, 1990)
6. F Sebba *Ionnaya Flotatsiya* (Ionic Flotation) (Moscow: Metallurgiya, 1965)
7. P M Kruglyakov, L L Kuznetsova *Kolloidn. Zh.* **40** 682 (1978)
8. P M Kruglyakov, L L Kuznetsova *Colloid Polym. Sci.* **258** 451 (1980)
9. P M Kruglyakov, N V Kochubei *Kolloidn. Zh.* **43** 766 (1981)
10. Zdr Lalchev, L Dimitrova, P Tzvetkova, D Ekserova *Biotechnol. Bioeng.* **24** 2253 (1982)

11. Bulg. P. 19 398; *Izobreteniya, T'rgovski Marki, Prom. Obraztsy* (1) 7 (1975)
12. Bulg. P. 19 339; *Izobreteniya, T'rgovski Marki, Prom. Obraztsy* (2) 337 (1973)
13. V V Krotov *Kolloidn. Zh.* **46** 15 (1984)
14. R Lemlich *J. Colloid Interface Sci.* **64** 107 (1978)
15. R Lemlich *Ind. Eng. Chem. Process Des. Dev.* **24** 686 (1985)
16. V K Tikhomirov *Peny. Teoriya i Praktika ikh Polucheniya i Razrusheniya* (Foams. Theory and Practice of Preparation and Destruction) (Moscow: Khimiya 1983)
17. C G J Bisperink, A D Ronteltap, A Prins *Adv. Colloid Interface Sci.* **38** 13 (1992)
18. P M Kruglyakov, L L Kuznetsova *Kolloidn. Zh.* **41** 673 (1979)
19. T N Khaskova, P M Kruglyakov, N E Pul'ver, N A Proshina, B V Levinskii, V F Safonov *Peny v Tekhnologii Gornykh Rabot* (Foams in the Technology of Mining) (Irkutsk: Izd. Irkutsk. Univ., 1990)
20. A J de Vries *Rubber Chem. Technol.* **31** 1142 (1958)
21. V V Pushkarev, D I Trofimov *Fiziko-Khimicheskie Osobennosti Ochistki Stochnykh Vod ot PAV* (Physicochemical Features of the Purification of Waste Water from Surfactants) (Moscow: Khimiya, 1975)
22. E Rubin, E L Gaden *New Chemical Engineering Separation Techniques* Part 5 (Ed. H M Schoen) (New York: Interscience, 1962)
23. P M Kruglyakov, V F Safonov, B V Levinskii *Kolloidn. Zh.* **44** 348 (1982)
24. R L Cardozo, P Dejonghe *Nature (London)* **199** 687 (1963)
25. K Shinoda, K Kinoshita *J. Colloid Sci.* **18** 271 (1963)
26. J J Bikerman *Foams* (New York: Springer, 1973)
27. T N Khaskova, P M Kruglyakov *Kolloidn. Zh.* **54** 152 (1992)
28. L D Skrylev, V V Sviridov *Zh. Prikl. Khim.* **47** 102 (1974)
29. T N Khaskova, P M Kruglyakov *Kolloidn. Zh.*. **51** 325 (1989)
30. T N Khaskova, P M Kruglyakov, in *Kolloidno-Khimicheskie Aspekty Ochistki Promyshlennykh Stochnykh Vod (Tez. Dokl. Seminara-Soveshchaniya) Ufa, 1988* (Abstracts of Reports of the Seminar-Meeting on Colloid and Chemical Aspects of the Purification of Industrial Waste Water (Ufa: Ufa Oil Inst., 1988) p. 39
31. L Lauwers, R Ruyssen, in *Proceedings of the Third International Congress on Surface Activity, Cologne, 1962* Vol. 3, p. 146
32. R A Haas, H F Johnson *Ind. Eng. Chem., Fundam.* **6** 225 (1967)
33. R A Leonard, R Lemlich *AIChE J.* **11** 18 (1965)
34. K B Kann *Kolloidn. Zh.* **40** 1100 (1978)
35. V V Krotov *Kolloidn. Zh.* **42** 1089 (1980)
36. V V Krotov *Kolloidn. Zh.* **46** 15 (1984)
37. D Desai, R Kumar *Chem. Eng. Sci.* **38** 1525 (1983)
38. D Desai, R Kumar *Chem. Eng. Sci.* **39** 1559 (1984)
39. G Narsimhan, E Ruckenstein *Langmuir* **2** 230 (1986)
40. G Narsimhan, E Ruckenstein *Langmuir* **2** 498 (1986)
41. A V Pertsov, V N Chernin, B E Chistyakov, E D Shchukin *Dokl. Akad. Nauk SSSR* **238** 1395 (1978)
42. P M Kruglyakov, P R Taube *Zh. Prikl. Khim* **38** 1514 (1965)
43. T N Khaskova, Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1992
44. A A Skvirskii, A A Abramzon, V K Chernyat'eva, A Maiofis *Kolloidn. Zh.* **35** 786 (1973)
45. G Zontag, K Shtrenge *Koagulyatsiya i Ustoichivost' Dispersnykh Sistem* (Coagulation and Stability of Dispersed Systems) (Leningrad: Khimiya, 1973)
46. E K Venstrem, P A Rebinder *Zh. Fiz. Khim* **2** 754 (1931)
47. D Ekserova, A Sheludko *Izv. Inst. Fizikokhim. Bolg. Akad. Nauk* **4** 175 (1964)
48. D Ekserova, D Schumkov *Tenvide* **3** 211 (1966)
49. D Ekserova, A Nikolov, M Zacharieva *J. Colloid Interface Sci.* **81** 419 (1981)
50. Khr Khristov, A Nikolov, M Zacharieva *Colloids Surf.* **11** 39 (1984)
51. S S Lukashova, A I Kiprianov, Yu D Yudkevich *Gidroliz. Lesokhim. Promst.* (8) 7 (1987)
52. P M Kruglyakov, N G Vilkova, T N Khaskova *Gidroliz. Lesokhim. Promst.* (3) 16 (1989)
53. Zdr Lalchev, D Ekserova *Biotechnol. Bioeng.* **23** 669 (1981)
54. M N Sileva, G I Bulenkov, A M Gol'man, G D Strakhova, in *Flotatsionnye Metody Izvlecheniya Tsennykh Komponentov iz Rastvorov i Ochistki Stochnykh Vod* (Flotation Methods of Extraction of Valuable Components from Solutions and the Purification of Waste Water) (Moscow: Nedra, 1973) p. 75
55. T N Khaskova, P M Kruglyakov, in *Proceedings of the 10th International Symposium on Surfactants in Solution, Petroleum Centre, Caracas (Venezuela), 1994* p. 227
56. W Ostwald, A Siehr *Kolloid-Z.* **76** 33 (1936)
57. W Ostwald, A Siehr *Kolloid-Z.* **79** 11 (1937)
58. W Ostwald, W Mischke *Kolloid-Z.* **90** 17 (1940)
59. H Thiele *Kolloid-Z.* **118** 172 (1950)
60. R M Skomorski *J. Chem. Educ.* **4** 470 (1963)
61. R Dubrisay *Kolloid-Z.* **86** 321 (1939)
62. M Abribat *C.R. Hebd. Seances Acad. Sci.* **209** 244 (1939); *Chim. Anal.* **39** 216 (1957)
63. F Schütz *Trans. Faraday Soc.* **42** 437 (1946)
64. H G Cassidy, in *Fundamentals of Chromatography* (New York: Interscience, 1957) p. 327
65. D Peters *Kolloid-Z.* **125** 157 (1952)
66. J Talmon, E Rubin, in *Surfactants in Solution* Vol. 6. (Eds K L Mittal, P Bothorel) (New York: Plenum Press, 1986)
67. V F Litvinov, S A Levichev, A I Rusanov *Kolloidn. Zh.* **36** 1078 (1974)
68. K Shinoda, K Mashio *J. Phys. Chem.* **64** 54 (1960)
69. V V Sviridov, T D Balakina, E I Kazantsev, L D Skrylev *Zh. Fiz. Khim.* **54** 2113 (1980)
70. L G Hargis, L B Rogers *Sep. Sci.* **4** 119 (1969)
71. USSR P. 882 548; *Byull. Izobret.* (43) (1981)
72. A Adamson *Physical Chemistry of Surfaces* (Translated into Russian; Mocow: Mir, 1979)
73. K Martinek, A K Yatsimirskii, A V Levashov, I V Berezin, in *Micellization, Solubilization and Microemulsions* (Translated into Russian; Moscow: Mir, 1980) p. 224
74. V V Sviridov,V I Azarova *Zh. Prikl. Khim.* **41** 1097 (1983)
75. V I Azarova, M A Panyukova, V V Sviridov *Zh. Org. Khim.* **22** 1697 (1986)
76. V V Sviridov, V I Azarova, M A Panyukova *Zh. Prikl. Khim.* **43** 360 (1985)
77. V F Shner, N N Artamonova, T I Petrunina, V F Seregina, B V Salov *Zh. Org. Khim.* **25** 879 (1989)