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DERIVATION OF A SEPARATION CURVE BASED ON THERMODYNAMIC CONSIDERATIONS AND VARIATION OF SPLITTING FORCE

A theoretical separation curve was derived and calculated for a hypothetical system consisting of surfactant, water, and air. The surfactant is preferentially adsorbed at the water/air interface and the surface layer is separated from the bulk solution to create a surfactant concentrate and a tailing. The separation is performed as equilibrium process, which is governed by the thermodynamic Gibbs equation. The splitting force regulates the amount and quality of concentrate. It was shown in the paper that having a well defined system it is possible to create separation curves, which can predict the results of separation.

1. INTRODUCTION

Separations are common in everyday life. They occur in technological, chemical, biological, geological, social, and other real and virtual systems. They provide products, which differ in quantity or quality and quantity. Delineation, analysis, evaluation, and comparison of results of separation can be accomplished by different methods and from different perspectives. When identity of a selected component in products and in the feed is considered along with the quality and quantity of products, the procedure of analysis of the separation data can be called upgrading. When the value of the feature of the selected component is utilized, it can be termed classification. Other approaches are also possible. In this work the component will be a chemical compound and its identity will be used to analyze the results of separation from the upgrading perspective.

Separations can be delineated starting with equations based on physics, mechanics, thermodynamics, probability, and their combinations, etc. (Drzymala, 2001). Those and other elements of separation systems are presented in fig.1.

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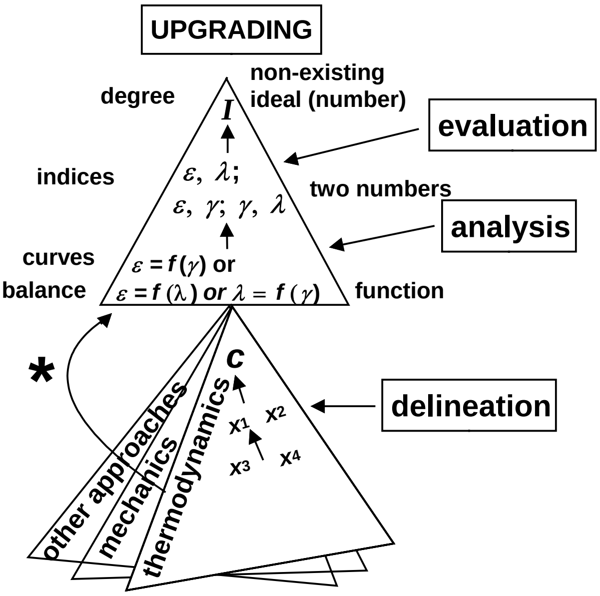

Fig.1. Elements of separation process (Drzymala, 2001). Star (*) indicates the area (derivation of theoretical separation curves based on thermodynamics) of separation considered in this work. Symbols: ε - component recovery in a product, γ - product yield, λ-component content in a product, I – non-existing ideal individual parameter (number) capable of characterizing separation, x_1 , x_2, ... parameters of separation, C feature utilized for separation

Examples of prediction of separation results based on theoretical considerations and the values of operational variables are available (Urvantsev, 2000; Neethling and Cilliers, 2002) but are not common in mineral processing literature. In this work a thermodynamic approach based on energy balance, will be derived and used.

2. OUTLINE OF A SEPARATION PROCESS

Separation of material (substrate, feed, etc.) into products of different quantities and qualities is accomplished by application of separating forces. The term “separation forces” is a broad expression for various ordering, disordering, splitting, and other forces which can operate in the system (fig. 2.). The separating forces or energies can be of different origin (Kelly and Spottiswood, 1982). They can be mechanical, chemical, gravitational, magnetic, electric, interfacial, thermal, etc. in nature. They operate due to specific features of components forming the system. The feature, which is utilized in the separation, is usually called the main feature of the separation system.

The products of the separation in mineral processing are usually called concentrate and tailing but other terms such as upper and lower, leaner and richer, wanted and unwanted products are also used. During separation the feed is split into two or more products. When more than two products are generated, it still can be considered as a two-product process by treating the third product, for instanc, as the concentrate, while the remaining products as the tailing.

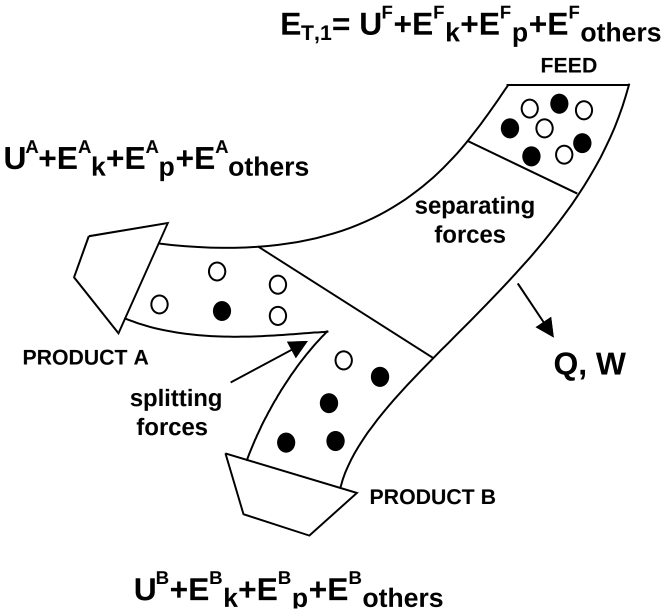

Fig. 2. Graphical representation of a separation system based on thermodynamic approach (Q is heat, W work, U internal energy, E_k kinetic energy, E_p potential energy, E_{other} other energies involved in the system)

The feed and the products of separation consist of two or more components. By analogy to two-product approach, at any point of the process the feed and the products can be treated as materials containing the component under question and the remaining components. Thus, any separation process can be treated as a two-component two-product system. One-component two-product and two-component one-product systems are special cases of the considered here two-component two-product system.

In considered here example of a continuous separation system the multi-component feed is first subjected to the ordering force and next is split into two products due to a splitting force (fig. 2.).

3. THERMODYNAMICS OF THE DISCUSSED SEPARATION PROCESSES

3.1.GENERAL CONSIDERATIONS

During separation, one or more streams or their mixtures are split into two or more streams due to action of internal, external or both sorts of separating forces. The total energy E_T of such an open system before ($E_{T,1}$) and after ($E_{T,2}$) separation is the same that is:

$$E_T = E_{T,1} = E_{T,2} \tag{1}$$

Since the stream of the feed that is subjected to separation may consists of one or more streams a, b, c...., the total energy of the system before separation can be written as:

$$E_{T,1} = E^a + E^b ...... \tag{2}$$

The stream of products of separation may contain one or more streams A, B, C ...... and their total energy is:

$$E_{T,2} = E^A + E^B .... \tag{3}$$

The total energy of the system before separation is a sum of various forms of energy including internal U, kinetic E_k, potential E_p, and others E_{others}:

$$E_{T,1} = (U^a + E_k^a + E_p^a + E_{others}^a) + (U^b + E_k^b + E_p^b + E_{others}^b) ...... \tag{4}$$

or briefly

$$E_{T,1} = (U^F + E_k^F + E_p^F + E_{others}^F) \tag{5}$$

where superscript F denotes feed and stands for a sum of various streams (F=a+b+c .....) within the feed.

For the streams after separation, the total energy consists of a sum of various energies in the products of separation as well as the heat Q and work W exchanged with the system:

$$E_{T,2} = \left(U^A + E_k^A + E_p^A + E_{others}^A\right) + (U^B + E_k^B + E_p^B + E_{others}^B) ... + Q + W \tag{6}$$

The heat (Q) exchanged during the process can be written as:

$$Q = TS^* \tag{7}$$

while the total work W, which can be of different character including mechanic (pV), surface (σA), chemical (μn), electric, magnetic, etc.:

$$W = -pV^* + \sigma A^* + (\Sigma \mu_i n_i)^* + others^* \tag{8}$$

where T is temperature (Kelvin), S entropy, p pressure, V volume, σ surface energy, A surface area, μ chemical potential, n number of moles. Symbol Σ means that the chemical energy is a sum of all individual species. Symbol * denotes exchanged quantity.

Combining the previous equations one gets:

$$
\begin{aligned}
&(U^F + E_k^F + E_p^F + E_{others}^F) = \left(U^A + E_k^A + E_p^A + E_{others}^A\right) \\
&+ (U^B + E_k^B + E_p^B + E_{others}^B) \ldots\ldots + TS* - pV* + \sigma\Phi + \Sigma n_i \mu_i * + other*
\end{aligned}
\tag{9}
$$

General Eq. 9 is a good starting point for various thermodynamic calculations including the relationships between the magnitude of the separating and splitting forces as well as the results of separation.

3.2. THERMODYNAMIC ANALYSIS OF A HYPOTHETICAL SEPARATION PROCESS

Aqueous solution of a surface-active agent is passing through a pipeline and next is exposed to the air in a tank (fig. 3). The air/water interface attracts surfactant molecules and they accumulate at the interface. The adsorption reduces the concentration of the surfactant in the solution, while its concentration at the interface increases. The process is continuous and the system is at the thermodynamic equilibrium. At the end of the tank the stream of aqueous solution of the surfactant is split into two products: upper (concentrate) and lower (tailing). The position of the splitter is adjustable.

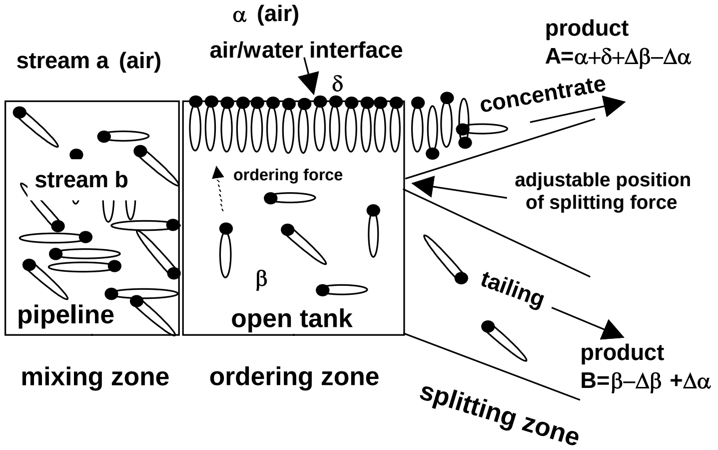

Fig. 3. A sketch of hypothetical separation system considered in this work. Δβ indicates that some β phase is transferred to concentrate A leaving phase β forming tailing B while Δα is for air transfer. Not to scale

The thermodynamics of adsorption of the surfactant at the interface is generally governed by Eq. 9. Since in the considered here separation system the kinetic, potential energies do not change and other energies marked with symbol * are equal to zero (lack of exchange of energy), Eq. 9 reduces to a general equation:

$$
E_T = U^F = U^a + U^b = U^\alpha + U^\beta + U^\delta = U^A + U^B \tag{10}
$$

For our particular separation system Eq. 10 will be modified following the procedure proposed by Gibbs (Hunter 1987; Adamson 1982, Davis and Rideal, 1963). In the considered here case there is a gas phase α, aqueous phase β, and interfacial phase δ. The internal energy of each phase is given by:

$$U^{\alpha} = TS^{\alpha} - pV^{\alpha} + \Sigma\mu^{\alpha}_{i}n^{\alpha}_{i} \tag{11}$$

$$U^{\beta} = TS^{\beta} - pV^{\beta} + \Sigma\mu^{\beta}_{i}n^{\beta}_{i} \tag{12}$$

$$U^{\delta} = TS^{\delta} + \sigma A + \Sigma\mu^{\delta}_{i}n^{\delta}_{i} \tag{13}$$

respectively. The interfacial region δ contains the same components as the bulk phases α and β. It is possible to eliminate the input of the components to the energy of interfacial region δ coming from the same components present in the bulk of phases α and β. To accomplish that one can use the quantity excess internal energy of the interfacial region (denoted as s) calculated by subtracting the energy of phases α and β from the total energy of region δ. The excess internal energy of the interfacial zone s is given by:

$$U^{s} = TS^{s} + \sigma A + \Sigma\mu^{s}_{i}n^{s}_{i} \tag{14}$$

Differentiation of Eq. 13 leads to:

$$dU^{s} = TdS^{s} + S^{s}dT + \sigma dA + Ad\sigma + \Sigma\mu^{s}_{i}dn^{s}_{i} + \Sigma n^{s}\, d\mu \tag{15}$$

According to thermodynamics, the procedure for a small and reversible change occurring in the surface phase δ very close to equilibrium, the change of internal energy must be given by:

$$dU^{s} = TdS^{s} + \sigma dA + \Sigma\mu^{s}_{i}dn^{s}_{i} \tag{16}$$

Thus, the remaining terms of Eq. 15 must obey the equation:

$$S^{s}\, dT + Ad\sigma + \Sigma(n_i d\mu_i)^{s} = 0 \tag{17}$$

and for a process taking place at a constant temperature T ($dT = 0$) as well as since $\Gamma^{s}_{i} = n^{s}_{i} / A)$ we obtain:

$$(d\sigma)_T = (-\Sigma\Gamma^{s}_{i}d\mu^{s}_{i}) \tag{18}$$

The considered here system consists of a nonionic surfactant dissolved in water. Therefore for a two-component system at a constant temperature:

$$(d\sigma)_T = -\Gamma^{s}_{H_2O}d\mu_{H_2O} - \Gamma^{s}_{surfactant}\,d\mu_{surfactant} \tag{19}$$

Moreover, since $\Gamma^{s}_{H_2O}$ and $\Gamma^{s}_{surfactant}$ are defined relative to an arbitrarily chosen dividing surface, it is possible to place that surface so that $\Gamma^{s}_{H_2O} = 0$. Therefore:

$$(d\sigma)_T = -\Gamma^{s}_{surfc\,\tan t}\, d\mu_{surfac\,\tan t} \tag{20}$$

Equation 17 is known as the Gibbs equation.

Thus the chemical potential of a species in aqueous solution is:

$$d\mu_i = RTd(\ln a_i) \tag{21}$$

where R is the gas constant, T temperature, a_i is the activity of species *i*. Finally for the considered here case we get the equation:

$$(\mathrm{d}\sigma)_T = -RT\ \Gamma^{s}_{surfcant}\,\mathrm{d}(\ln a_{surfactant}) = -RT\ \Gamma^{s}_{surfcant}\ \frac{\mathrm{d}a}{a} \tag{22}$$

where a_i is activity ($a_i = f\,c_i$, where c_i is concentration and f is a dimensionless activity coefficient). Equation 22 predicts that for a given activity of the surfactant in the feed solution the separation (ordering) force (energy) results from the surface tension (σ). The surface force changes the concentration of surfactant in the solution and moves the surfactant molecules to the interface with air in the amount of $\Gamma^{s}_{surfcant}$ or shortly Γ.

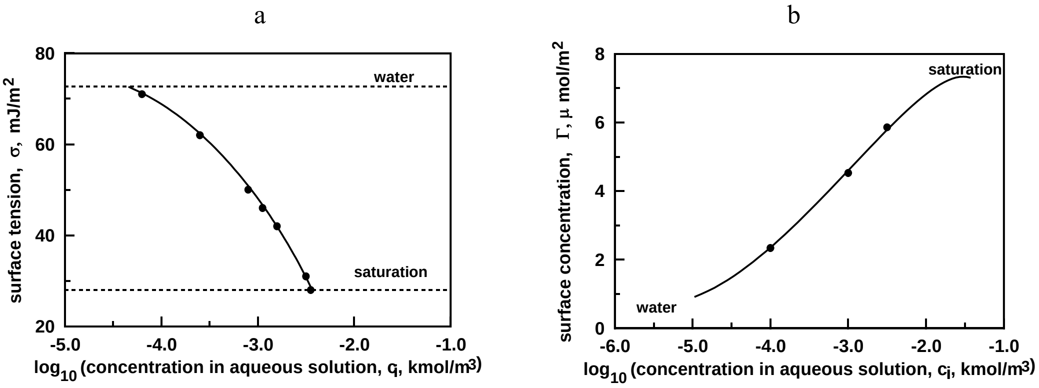

Fig. 4. Experimental data for n-octanol ($C_8H_{17}OH$) after Deafay illustrating the Gibbs equation (Eq. 22): a) relationship between σ and c_i, 1966, and b) between Γ and c_i.

Let's assume that the surfactant is n-octanol. The equilibrium concentration of n-octanol at the air/water interface versus its concentration in the aqueous phase is given, after Deafay, in fig. 4a. According to Eq. 22, the values of Γ can be calculated from the slope of the curve from fig. 4a. The calculated values of Γ were plotted as a function of the equilibrium concentration of the surfactant in fig. 4b. Both figures are useful for determination of Γ and σ of surfactant for a given equilibrium concentration of n-octanol in the solution. It also results from Eq. 22 and figs. 4a-b that for a given concentration of the surfactant there will be only one value of surface tension which is the driving (ordering) force of separation.

The amount of n-octanol present in the concentrate depends not only on σ but also on the position of the splitter, which divides the aqueous stream into concentrate and tailing. Let us consider a separation experiment, in which the n-octanol aqueous solution is passing through a pipeline where the mixing force dominates (fig. 3.). Then, the solution reaches the tank in which the mixing force ceases to operate while the main ordering force is the surface tension. The total amount of n-octanol in the feed (separation tank) is 1004.5 micromoles. The tank has 1m^2 of the water/air interface and is 1mm thick. Thus, the concentration of surfactant, expressed per cross section area of the separation tank is 1004.5μmol/m^2 and consists of 4.5 μmol/m^2 coming from the interfacial concentration and 1000 μmol per 1m^2 of the cross section area of the tank contributed by the bulk solution. The surface concentration equal to Γ = 4.5 μmol/m^2 was taken from fig. 4b at $1.00\cdot10^{-3}$ kmol/m^3 (bulk concentration of the surfactant), that is at the surface tension 50 of mJ/m^2.

During the separation process some of the surfactant is transferred to the interface and the system reaches equilibrium determined by Eq. 22. Next, the stream is split into two streams that is concentrate containing the surface layer of the stream and some of the bulk of solution and tailing containing the rest of the solution. The amount (yield) of the concentrate depends on the position of the splitter. This is shown in fig. 5 as an open circle, assuming that the position of the splitter is 0.001 mm below the surface. Changing the position of the splitter provides different quantities and qualities of the products of separation (table 1).

Table 1

Results of separation for varying position of the splitter Height (h) of tank was 1 mm

Position of splitter, g , mm	Concentrate yield, γ, %	Amount of surfactant in concentrate, z, μmol/m^2	Recovery of surfactant in concentrate, ε, %	ε/γ
0.0010	0.10	5.5	0.547	5.47
0.0030	0.30	7.5	0.747	2.49
0.010	1.0	14.5	1.44	1.44
0.10	10	104.5	10.40	1.04
0.25	25	254.5	25.33	1.013
0.50	50	504.5	50.22	1.0044
1.0	100	1004.5	100.0	

The separation (upgrading) curve of the separation is shown in Fig. 5 as a solid line. The separation line is based on the equation for the total amount of surfactant per cross section area of tank in the concentrate (z):

$$z = \Gamma_{surfcant}^{H_2O} + \frac{c_i V}{P}\frac{g}{h} \tag{23}$$

where:
z - total amount of surfactant per cross section area of tank in concentrate, c_i - concentration of surfactant in bulk solution, V - tank volume, P - tank cross section, h - tank height, Γ - surface concentration of surfactant at water-air interface, g - position of splitter, g/h = r, where r is the fraction of tank height at which splitter is located (assumes values from 0 to 1), ε - recovery (%), γ - yield (%).

For the considered in this work separation system $c_i = 10^{-3}$ mol/dm^3, V = 1dm^3, P = 1m^2, Γ = 4.5 μm/m^2, h=1mm (g is a variable) Eq. 23 reduces to:

$$z = 4.5 + 1.0 \cdot 10^{-3} \cdot r \; (\frac{\mu mol}{m^2}) \tag{24}$$

The recovery is defined as:

$$\varepsilon = \frac{z}{1004.5} 100\% \tag{25}$$

while yield as:

$$\gamma = r \cdot 100\% \tag{26}$$

3.3. UPGRADING CURVE

The simplest separation (upgrading) curve for the considered here separation system should be a relationship between the concentration of the surfactant in the surface layer (or in concentrate) versus its concentration in the tailing. Since the equilibrium concentration of the surfactant in the tailing changes very little such a graph would be of little use. Therefore, another relationship, that is recovery of surfactant in the concentrate divided by yield of the concentrate versus concentrate yield (ε/γ vs γ) was chosen for this purpose. Eqs. 24-26 provide a general formula for the upgrading curve:

$$\frac{\varepsilon}{\gamma} = \frac{(\Gamma^{H_2O}_{surfcant} + \frac{c\,V}{P}\frac{g}{h})}{(\Gamma^{H_2O}_{surfcant} + \frac{c_i V}{P})} (\frac{h}{g}) \quad \text{versus} \quad \gamma = \frac{g}{h} \cdot 100\% \tag{27}$$

where $\Gamma^{H_2O}_{surfcant} = -\frac{1}{RT}\frac{(\mathrm{d}\sigma)_T}{\mathrm{d}(\ln a_{surfactant})} = -\frac{1}{RT}\frac{(\mathrm{d}\sigma)_T}{\mathrm{d}(\ln f \cdot c_{surfactant})}$ and a_i stands for activity (kmol/m^3) and f (dimensionless) for activity coefficient.

The separation curve is given in fig. 5. When more parameters change in the system during separation or when the separating (ordering, mixing, and splitting) forces and the quality of the feed fluctuate, the results of separation can be scattered as it is shown in Fig.5. In such a case both the delineation of separation and evaluation of separation results requires statistical evaluation. This issue is out of the scope of this paper.

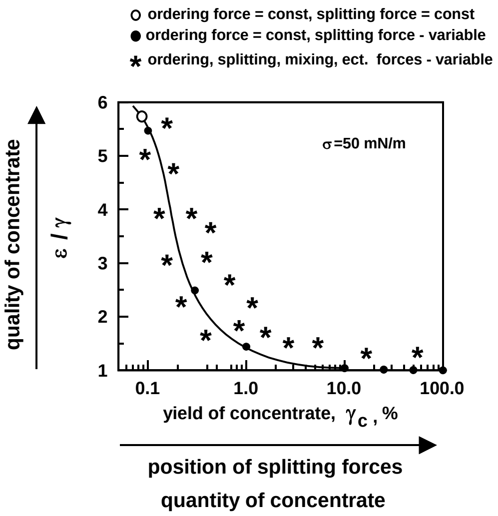

Fig. 5. Results of separation in a graphical form. Changing position of splitter generates the separation curve

3.4. THE MAIN FEATURE OF CONSIDERED SEPARATION SYSTEM

Having equations, which delineate considered in this work separation system it is easy to create a structure of dependence of operational variables with the main feature of the separated component on the top. The main parameter of the system is here the adsorption of the surfactant at the air-water interface ($\Gamma^{s}_{surfcant}$ or shortly Γ) (fig.6).

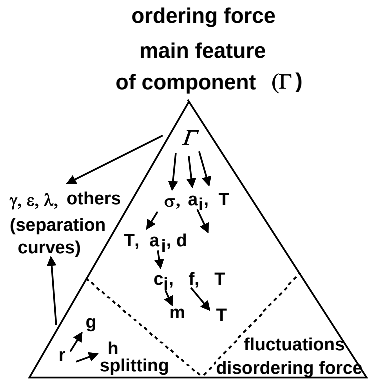

Fig. 6. Temporary structure of dependence of the main feature of the separated component and operational variables. Meaning of the symbols is explained in the text, except m, which denotes mass of a component, and λ which stands for concentration of a component in the feed or products of separation

4. CONCLUSIONS

On the bases of phenomenon, which governs the separation process, as well as the operational variables of the separation system and their relations, it is possible to create and calculate theoretical separation curves. Performed in the paper calculations of separation results were based on thermodynamic considerations determining the magnitude of the ordering and operation conditions determining the splitting forces. The ordering force influences the concentration of components in different regions of the system while the splitting force regulates the concentration of the components in the final products. The separation curve was plotted as an upgrading curve (Drzymala, 2001) taking into account the quality and quantity related parameters of separation.

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separacja, wzbogacanie, klasyfikacja, termodynamika, przeróbka kopalin, rozdział

WYZNACZANIE KRZYWEJ SEPARACJI W OPARCIU O ROZWAŻANIA TERMODYNAMICZNE I ZMIENNOŚĆ SIŁY SEPARUJĄCEJ

Wyznaczono teoretyczna krzywą separacji dla hipotetycznego układu składającego się z powietrza, wody i rozpuszczonego w niej surfaktanta. Surfaktant adsorbuje się na granicy faz woda/powietrze, a utworzona warstwa powierzchniowa oddzielona jest od pozostałego roztworu. Powstaje koncentrat surfaktanta i odpad w postaci pozostałego roztworu. Separacja zachodzi dla układu w stanie równowagi opisywanej równaniem Gibbsa. Siły separujące regulują ilość koncentratu. Wykazano, że w dobrze zdefiniowanym układzie możliwe jest wyprowadzenie krzywych, które pozwalają na opisywanie i przewidywanie wyników separacji.