

Lecture 13 «Extraction. Physical bases of extraction process. Diagram of extraction»

Aim: Characterize the extraction. Formulate the physical bases of extraction process. Describe the diagram of extraction.

Lecture summary: Extraction is the process of extracting one or more components from a mixture of substances by treating it with a liquid solvent that has the ability to selectively dissolve only recoverable components.

In the chemical industry, extraction in liquid-liquid systems is most common. Liquid extraction involves two technological operations:

- contacting the initial mixture with the solvent, during which the actual mass-exchange process is carried out, i.e. transition of a component through the interface from one phase to another;

- separation of the resulting solution from the remaining liquid mixture.

Thus, liquid extraction assumes incomplete mutual solubility of the initial mixture and solvent – otherwise the second operation is unworkable. The operation of contacting the phases is usually carried out by distributing (splitting) one phase in the form of drops in the volume of the other.

Separation of liquid mixtures by extraction is carried out at low temperatures, which makes it possible to separate a mixture consisting of thermally unstable components. Extraction can be divided into azeotropic mixtures, as well as mixtures consisting of closely-boiling components.

An extract is called an extractant containing the recovered component and a portion of the starting solvent. The initial mixture, depleted by the extractable component and containing a certain amount of extractant, is called a raffinate.

The extractant must have selectivity, easy regenerability, differ from the initial solution in density and viscosity, providing the process of phase separation. In addition, the extractant should, if possible, be low-volatility, non-toxic, affordable and low-cost.

Separation of the formed phases can occur due to the difference in densities, or under the action of the field of centrifugal forces. Regeneration of the extractant from the raffinate and extract can be carried out by distillation, rectification, evaporation and other methods.

Industrial methods of extraction can be carried out in the apparatus of periodic and continuous action. In the first, the initial mixture and the solvent are charged periodically, and during the extraction process, only one component of the initial mixture can be continuously released. In continuous installations, loading of the initial mixture and the solvent is carried out continuously, and both components of the separated initial mixture are continuously separated.

Currently, liquid extraction is used in chemical technology, hydrometallurgy, analytical chemistry for extraction, separation, concentration and purification of substances. Extraction processes are used in the production of organic products, antibiotics, food products, rare earth elements, a number of rare, non-ferrous and noble metals, in nuclear fuel technology, in wastewater treatment.

Physical basics of the extraction process

The physical essence of extraction consists in the transition of the extracted component from one phase to another – the phase of the extractant – upon mutual contact of the initial mixture and the extractant, as a result of the system's striving for a state of equilibrium.

In a state of equilibrium at a certain temperature, the concentrations of the dissolved substance in the extract and in the raffinate are in a functional relationship

$$y = f(x) \quad (1)$$

This dependence on the diagram in the x - y coordinate system can be represented as a curve whose course is determined experimentally on the basis of simple measurements (Fig. 1). Sometimes equilibrium can be depicted in the x - y diagram as a straight line or by the equation

$$y = k_p x, \quad (2)$$

where k_d – a constant at a given temperature, is called the distribution coefficient.

In this case, the system obeys the law of equilibrium distribution of matter between the extract and the raffinate.

Equation (2) is valid under the condition that the initial solvent and the extractant are mutually completely insoluble, there is no association or dissociation of the molecules of the extracted substance and there is no chemical interaction between the phases.

The extraction processes obey the general laws of mass transfer. The equation of material balance for the extraction process in general form can be written:

$$-Ldx = Gdy \quad (3)$$

Equation (3) is integrated within the limits depending on the extraction conditions.

Let us consider the case when the liquids are mutually insoluble. The solvent is used as a pure, not used, and therefore the initial content of the dissolved substance in it is $y_0 = 0$. Let x_0 denote the initial content of the extracted component in the initial mixture, and let x_1 denote the final content of the extracted component in the same mixture, the final content of the extractable component in the extractant as y_1 . Then, with a single contact of liquids (the initial mixture and the extractant), the material balance equation is integrated in the range from x_0 to x_1 and from 0 to y_1 , i.e.

$$-L \int_{x_0}^{x_1} dx = G \int_0^{y_1} dy, \quad (4)$$

whence

$$-L(x_1 - x_0) = Gy_1 \quad (5)$$

From equation (5), the working line on the diagram in the x - y coordinates will be a straight line with a negative tangent of the slope angle (Fig. 2):

$$y_1 = -\frac{L}{G}(x_1 - x_0) \quad (6)$$

In Fig. 2 the straight line of the working line FE crosses the equilibrium curve at the point E , determining the composition of the extract y_1 and raffinate x_1 .

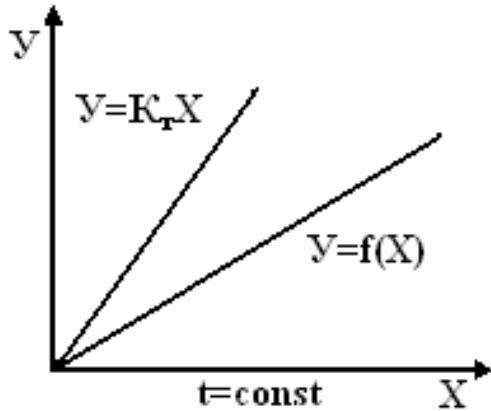


Fig. 1. Extraction equilibrium at complete mutual insolubility of solution and extractant

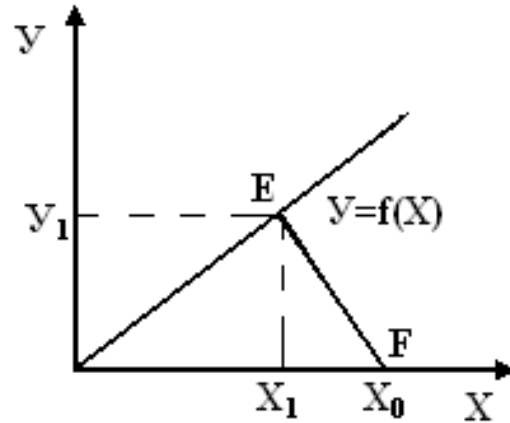


Fig. 2. The position of working line with a single contact

If the distribution law is valid, then the joint solution of the equilibrium equation (2) and equation (5) leads to the relation:

$$-L(x_1 - x_0) = Gkx \tag{7}$$

or

$$Lx_0 = Lx_1 + kGx_1, \tag{8}$$

whence

$$x_1 = \frac{Lx_0}{L+kG} \tag{9}$$

Equation (9) makes it possible to calculate the composition of the liquid after extraction [3].

Triple systems

With the partial mutual solubility of the phases A and C , each of the phases during extraction will be a three-component solution whose composition is not be depicted in the diagram with the coordinates $x - y$. It is convenient to represent the compositions of such three-component phases in a triangular coordinate system – on the so-called triangular diagram (Fig. 3).

The vertices of an equilateral triangle A , B and C are pure components: the solvent of the initial solution – A , the extractant C and the distributable substance B . Each point on the sides AB , BC and CA corresponds to the composition of two-component solutions (Fig. 3).

Each point on the area inside the diagram corresponds to the composition of a three-component solution (or a triple mixture). To measure the content of each component in the

solution, scales are plotted on the sides of the diagram, with the length of each side taken as 100 % (by weight, by volume or by mole) or per unit. The composition of the solution or mixture is determined by the length of the segments drawn parallel to each side of the triangle before crossing with the other two.

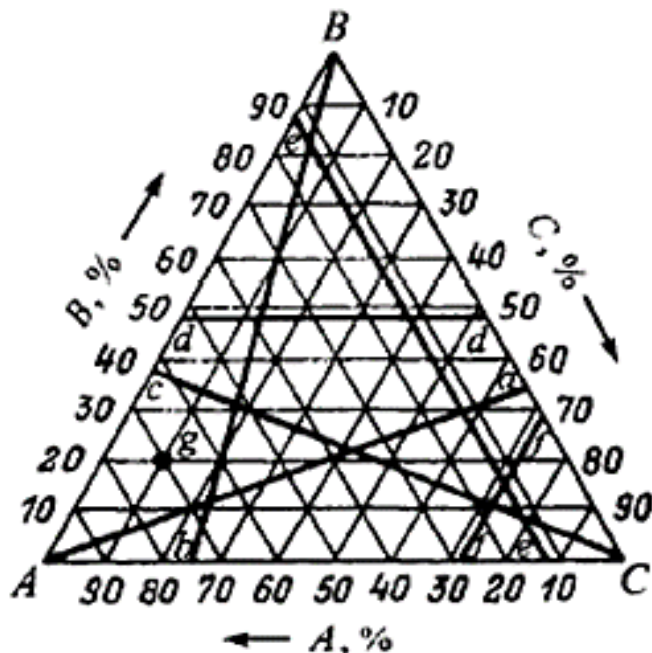


Fig. 3. Triangular equilibrium diagram of a three-component mixture

For example, point *g* characterizes a triple mixture consisting of 70 % of solvent *A*, 10 % of solvent *C* and 20 % of the distributable substance *B* to be distributed. The lengths of the perpendiculars dropped from point *g* to the sides of an equilateral triangle are proportional to the content of the corresponding components in the mixture.

The rays *Aa*, *Bb*, *Cc* drawn from the vertices of the triangle (see Fig. 3) are the geometric locus of the figurative points of the mixtures with a constant ratio of the content of the other two components x_B/x_C , x_A/x_C , x_A/x_B , respectively.

The lines *dd*, *ee*, *ff*, parallel to the sides of the triangle *AC*, *BC*, *AB*, are the geometrical place of the figurative points of mixtures with a constant content of components *B*, *A*, *C*, respectively.

Mixing processes on a triangular diagram. The rule of the lever

When mixing two solutions whose compositions are characterized in the diagram by any points *a* and *b*, the total composition of the mixture is expressed by the point *c* lying on the line *ab*, connecting these points (Fig. 4).

The position of point *c* on the straight line is determined by the rule of the lever if the quantities of solutions taken are known.

The segments *ac* and *bc* are inversely proportional to the masses of the solutions taken (Fig. 4):

$$G_a + G_b = G_c \quad (10)$$

Then

$$G_a ac = G_b bc; G_a/bc = G_b/ac \quad (11)$$

$$\begin{aligned} G_c ac &= G_b ab; \\ G_c bc &= G_a ab; G_c/ab = G_b/ac = G_a/bc, \end{aligned} \quad (12)$$

where G_a, G_b, G_c – the mass of the components of mixture a, b and c , kg; x_a, x_b, x_c – the mass fractions of any component (A, B and C) in mixture a, b and c , %.

In Fig. 5: the line $abcdKd'c'b'a'$ – the boundary (binodal) curve. The field inside of this curve – the region of mixtures that are stratified into two coexisting phases whose composition is expressed by points on the curve. The field outside the boundary curve – the region of non-dissipating (homogeneous) solutions. The point K – a critical point.

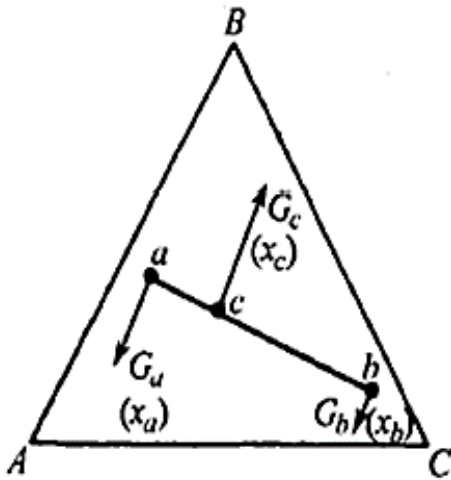


Fig. 4. Rules of the lever in the relations of material balance during extraction

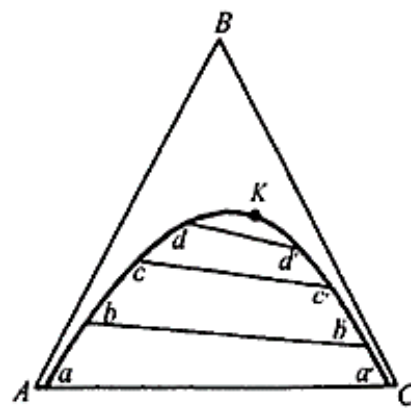


Fig. 5. Isothermal diagram equilibrium of liquid-liquid systems

Material balance of extraction

The material balance of extraction is expressed by the equation (3) common to mass-exchange processes. In the case of partial mutual solubility of the phases A and C, their values will no longer be constant in the height of the apparatus, and consequently, the ratio A/C will be variable. At partial mutual phase solubility, the working extraction line in the $x - y$ coordinate system will not be a straight line.

The equation of material balance by general flows in this case will have the form

$$F + S = R + E, \quad (13)$$

where F and R – respectively the quantities of the initial solution and the resulting raffinate, kg/s; S and E – respectively the amount of extragent and extract obtained, kg/s.

If equation (13) is rewritten in the form $F + S = M = R + E$, the equation of material balance can be represented graphically on a triangular diagram (Fig. 6) as a process of mixing the initial flows $F + S$ (with the formation of a triple mixture represented by a point M , and the subsequent separation of this triple mixture M into final flows $R + E$).

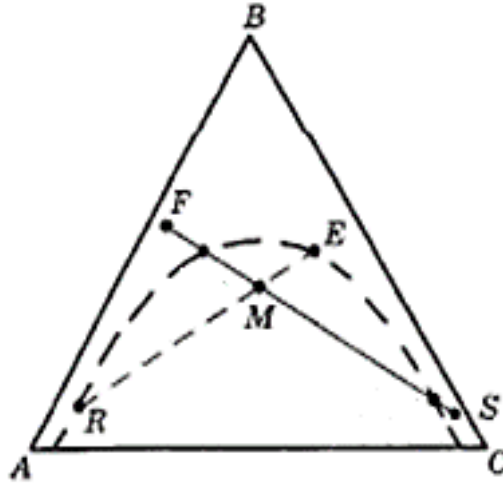


Fig. 6. To drawing up a material balance of the extraction process

From the diagram according to the rule of the lever

$$\frac{S}{F} = \frac{FM}{SM} \quad (14)$$

you can find the amount of extragent required for the process

$$S = F \frac{FM}{SM} \quad (15)$$

or the ratio between the amounts of the raffinate and extract streams obtained

$$\frac{R}{E} = \frac{EM}{RM} \quad (16)$$

as well as the composition of any of the flows, if the compositions and quantities of the other three streams are given.

Questions to control:

1. Give the meaning of the process of liquid extraction. Show the scheme of the process, the scope of application.
2. How is the equilibrium composition and phase state of the three-component liquid mixture determined by the triangular phase diagram?
3. List the main requirements for the extragent.
4. What is the physical meaning of the rule of the lever for the processes of periodic extraction?
5. Formulate the distribution law and explain the extraction isotherms.
6. Explain the triangular diagrams and the construction of equilibrium (binodal) curves.
7. What are the stages of the extraction process?
8. Explain the physical content of the material balance equations for the mixing-slopping stage of continuous extraction.
9. What processes are used to regenerate the extragent?
10. What devices are used in chemical technology for extraction?

Literature

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