Translated from *Uspekhi Khimii* **60** 2422–2447 (1991) U.D.C. 542.61:62-278:541.182.42/43

Extracting emulsions for the extraction of substances from aqueous media

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ABSTRACT. The characteristic features of the extracting emulsions used to extract and concentrate substances from aqueous solutions are examined. The influence on the properties of the extracting emulsions of the conditions in their preparation, of the properties of the disperse phase (the ionic strength and the pH of the aqueous solutions), the properties of the dispersion medium (viscosity, dielectric constants), as well as the presence of polar organic substances in the emulsions is discussed. The influence of the nanodispersion formed on mass transfer through the interface and on the properties of the extracting emulsions is demonstrated. The approaches to the mathematical description of the kinetics of the processes in extracting emulsions are discussed and it is shown that extracting emulsions with various properties designed for a wide variety of applications can be developed on the basis of the study of the physicochemical properties of such disperse systems.

Examples of the use of extracting emulsions in chemical engineering for the extraction of substances from aqueous media by membrane extraction into a multicomponent emulsion, for preliminary concentration in analysis, for therapeutic and prophylactic purposes in medicine, and for the protection of the environment are considered.

The bibliography includes 102 references.

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I. The membrane extraction method and extracting emulsions

Considerable interest in extracting emulsions, i.e. emulsions extracting or concentrating various substances, arose in connection with the first publications on membrane extraction into a multicomponent emulsion.[1,2]

Nowadays, together with the overall increased interest in liquid membranes,[3,4] a method of membrane extraction into a multicomponent emulsion has been developed for applications in various fields: for the isolation and concentration of substances from technological solutions, in analytical practice, in the solution of problems concerned with the protection of the environment, and for the detoxification of biological liquids involving the removal of harmful substances of exogenic and endogenic origin.[5–12]

The extraction and re-extraction stages in the membrane extraction process occur simultaneously in a system comprising three liquid phases. One of the phases (the liquid membrane) separates two solutions of different composition and immiscible with it: the initial solution (to be exhausted) and the re-extracting solution (the recipient) (Fig. 1). The membrane usually consists of an organic liquid, but systems are known with an aqueous membrane, used mainly for the separation of organic compounds.[13–19]

The membrane extraction method has many advantages compared with the usual extraction. One of the main ones is the reduction of the number of stages in the process. The combination of extraction and re-extraction makes it possible to achieve in a single stage the maximum possible, for the given system, differences between the concentrations of the extracted substance between the extracted and receiving phases. If the extracted substance in the phase F1 (Fig. 1) is bound in a weakly dissociating complex or forms an insoluble compound, then this ensures the most complete extraction from the initial phase F1.

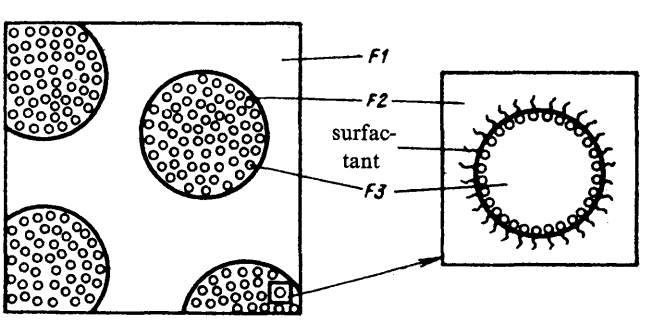


Figure 1. A multiple emulsion: F1 = solution to be extracted; F2 = liquid membrane (dispersion medium of the extracting emulsion); F3 = recipient solution (disperse phase of the extracting emulsion).

The degree of extraction in the membrane extraction process depends mainly only on the compositions of the initial and receiving solutions. The extractant in the phase F2 (Fig. 1) is merely a transferring agent, which interacts with the extracted substance

during its transport from the phase F1 to F3. Therefore the liquid membrane does not as a rule have to meet the requirements of a high capacity and high partition coefficients. The extractant-transferring agent determines mainly the rate and selectivity of the process. Thus in membrane extraction it is possible to use low concentrations of the transferring agents in the liquid membrane or to employ extractants which are relatively ineffective from the standpoint of two-phase extraction as transferring agents. This factor is attractive not only because of its economic aspect but also because of its ecological aspect.

Membrane extraction is a promising procedure for correcting the homeostasis and detoxification of biological liquids[8-11,20,21] and also for the extraction of metabolic products from enzyme solutions.[22,23] In this case, membrane extraction has an additional advantage associated with the possibility of preventing (or reducing to a minimum) the direct contact between the substances contained in the internal phase with the biological medium by virtue of the presence of the liquid membrane, consisting in the given instance of inert substances and, if necessary small amounts of the transferring agent. The amount and type of transferring agent are chosen to ensure, on the one hand, an acceptable rate of transport of the extracted substance through the liquid membrane and, on the other hand, so as not to traumatise the biological medium from which extraction takes place.

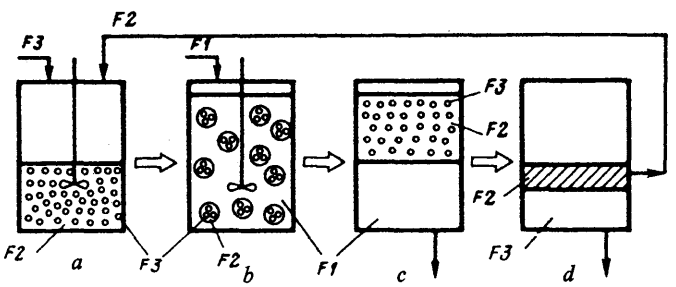


Figure 2. Schematic illustration of the membrane extraction process in a multiple emulsion: *a*, preparation of the extracting emulsion; *b*, bringing of the extracting emulsion into contact with the solution to be extracted; *c*, separation of the refined solution; *d*, separation of the extracting emulsion into layers.

In the case of extraction in a multiple emulsion, the process takes place in a system consisting of the extracting emulsion dispersed in the solution F1 to be extracted. The dispersion medium of the extracting emulsion F2 is the liquid membrane. The extracted solution F3 is dispersed in the liquid membrane F_2 with the aid of a surfactant (Fig. 1). The entire process consists of four stages (Fig. 2). In the first stage, the re-extracting aqueous solution is vigorously dispersed ($\omega = 200-2000\ s^{-1}$) in the organic phase containing the transferring agent and the emulsifier and an emulsion of the "water in oil" type is obtained (Fig. 2*a*). It is then brought into contact with the solution to be extracted under the conditions of "gentle" stirring ($\omega = 10-50\ s^{-1}$). This extracting emulsion is dispersed into individual globules and a multiple emulsion of the "water–oil–water" type is formed (Figs. 1 and 2*b*). At the end of the mass transfer, the extracting emulsion is separated from the refined product by means of gravitational separation into layers (Fig. 2*c*) and in the final stage the aqueous phase enriched in the target component and the organic phase are separated (Fig. 2*d*).

One of the characteristic features of the membrane extraction process in a multiple emulsion is the possibility of the constant renewal of the interface in the extracting emulsions during stirring, which is a positive factor in the extraction of substances in systems where interfacial films are formed. Such interfacial films, which retard the rate of diffusion of substances between phases, can be produced into systems containing both inorganic substances[24,25] and organic (protein) compounds.[26]

In analytical practice, the extracting emulsions can be used for the preliminary concentration of substances. Here not only the stability of the emulsions but also the distribution of water in the system, frequently leading to the "swelling" of emulsions (the transport of water into the extracting emulsion), which lowers the rate of concentration of the extracted substance, is very important. The use of kinetic factors for optimising the extraction time makes it possible, as will be shown below, to reduce to a minimum the negative effect of the swelling of extracting emulsions.

The region of possible applications of extracting emulsions is much wider than merely in the process involving membrane extraction in a multiple emulsion. Extracting emulsions can be used for the detoxification of various surfaces and media in the solution of ecological and medical problems. In particular, the employment of extracting emulsions as protective-prophylactic ointments, protecting (and cleaning) the skin against the action of harmful substances of different origin, in the first place the toxic substances present in industry, is a very promising application.[10,27] Extracting emulsions used for this purpose consist of thin films in which the contribution of the heterocoagulation resulting from the effect of the surface of the skin is enhanced.

II. Properties of extracting emulsions

The extracting emulsions must meet a number of requirements which are essential for their effective utilisation. These are stability throughout the period of application of extracting emulsions and minimal water transfer to the inner phase of the emulsions. It is also essential that the emulsions should be fairly stable throughout the long period of their storage before use. The emulsions must have definite properties depending on the specific process in which they are applied. Thus in technological processes, where the extracted component is concentrated in the inner aqueous phase, and the emulsions must then be separated into layers, the latter must be fairly stable throughout the extraction process, but after extraction they must be capable of separating rapidly into layers with the aid of the available methods. The emulsions used in medicine must be highly stable in order not to release the inner phase of the emulsion into the biological fluid.

In order to increase the capacity of the extracting emulsions, use is usually made of concentrated disperse systems, close to highly concentrated systems, with a volume fraction of the inner phase $\varphi = 0.6-0.7$. The view has been expressed in the literature that extracting emulsions with $\varphi > 0.5$ have a comparatively low stability,[28] but under certain conditions not only systems with $\varphi > 0.5$ but also highly concentrated emulsions with $\varphi > 0.74$ proved to be stable.[29]

An increase in the fraction of the inner phase above the theoretically possible value (φ_{theor}) for spherical particles of the same size (φ_{theor} is 0.741 for hexagonal packing, 0.686 for cubic centred packing, 0.524 for cubic packing, 0.340 for tetrahedral packing, and 0.64 for random packing[30,31]) involves the deformation of the drops of the disperse phase. Furthermore, real emulsions are polydisperse, which makes it possible to obtain stable emulsions with a high fraction of the disperse phase. The size distribution of the drops is an important characteristic of the extracting emulsion, which influences the stability of the system, its rheological properties, and other technological characteristics. The difference between the size distributions of the drops in emulsions having the same composition is one of the main causes of the discrepancies sometimes observed between the results of studies on membrane extraction in a multiple emulsion.

The properties of the extracting emulsions and in particular their stability are in many respects determined by the degree of dispersion of the inner phase.[28,32–34] The smaller the drop size, the higher the stability of the emulsion obtained. The influence of factors such as the type of stirring device,[28,38] the intensity of stirring, surfactant concentration,[33,34] etc. on the degree of dispersion has been noted.

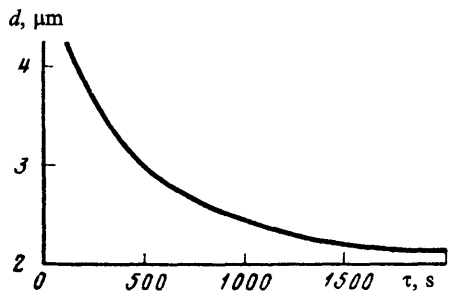


Figure 3. The effect of the emulsification time on the size of the drops of the inner phase of the emulsion of water in xylene (volume fraction of the inner phase φ = 0.5).[34]

Stirring for a period longer than the optimum time gives rise to little improvement in the quality of the emulsions.[33,34] The average drop size diminishes rapidly in the course of the first seconds of the emulsification process (Fig. 3).[34] With decrease in the size of the drops, their rigidity also increases and their size becomes comparable to the size of the eddies in the apparatus and there is no further dispersion. The viscosity of the emulsion diminishes during dispersion (Fig. 4).

The influence of the rate of stirring and of the surfactant concentration on the inner phase drop size is similar to the influence of the emulsification time (Fig. 3).[34]

As the temperature in the mixer is altered, there is a change in the surface tension, viscosity, and adsorption of the emulsifier. The decrease in viscosity and surface tension with increase in temperature improves the emulsification but under these conditions there is a sharp diminution in the degree of adsorption of the surfactant, which lowers the stability of the emulsions.

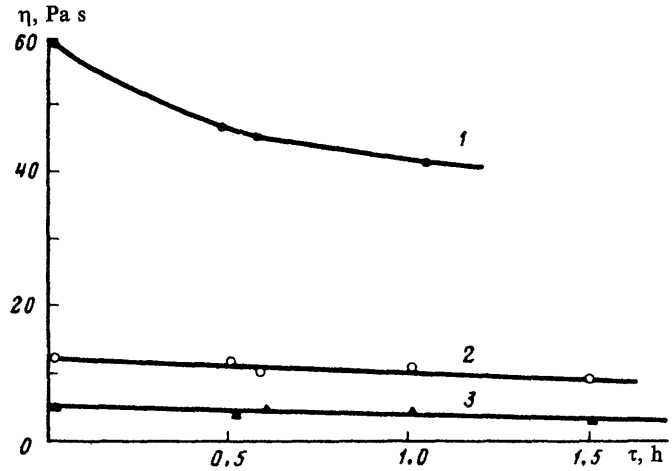


Figure 4. Dependence of the viscosity of the emulsion (η) on the dispersion time after the addition of the inner phase has ended;[34] temperature 25 °C; volume fraction of the inner phase: *1*, 0.65; *2*, 0.50; *3*, 0.40. Rate of displacement 3 s^{-1}.

With increase in the surfactant concentration, the stability of the adsorption layer is known to increase and hence there is an increase in the resistance of the emulsions to coalescence.[33] The dependence of the stability of the emulsions on the surfactant concentration show a maximum at 0.02 M (C_1) for hostacerin DGO and 0.45 M (C_2) for sorbitan oleate (Fig. 5).

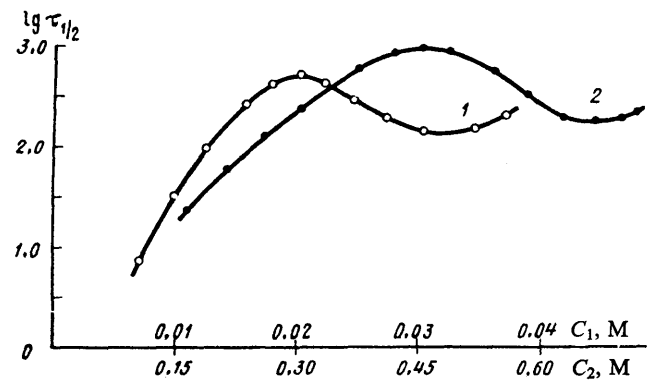


Figure 5. Dependence of the half-separation period ($\tau_{1/2}$) of the aqueous phase of the emulsion at 25 °C on the concentrations of hostacerin DGO (C_1, curve *1*) and sorbitan oleate (C_2, curve *2*). Fraction of inner phase 0.65. Isotonic buffer solution at pH 7.4 in liquid paraffin.

As mentioned above, the radius of the inner phase drops in emulsions initially diminishes with increase in the surfactant concentration and then remains constant,[34] which is associated with

the fact that the disperse system tends to the minimum interfacial energy possible for the given amount of the surfactant, so that, despite the high degree of dispersion of the inner phase, the drops coalesce until the attainment of an emulsifier content at the interface close to the limiting degree of sorption. When the surfactant is present in an amount sufficient for the stabilisation of all the drops of the interface formed as a result of the dispersion, the maximum stability of the emulsion is attained (under the given dispersion conditions).[35]

The increase in the viscosity of the emulsion is also associated with the decrease in the inner phase drop size (for φ = const.) (Fig. 6). After the attainment of the limiting degree of adsorption, the excess surfactant dissolves in the liquid membrane, the viscosity of the emulsions remaining virtually constant under these conditions.

At surfactant concentrations in the dispersion medium exceeding the critical concentration for the formation of non-spherical micelles (CCM-2), structure formation takes place in the organic phase and the viscosity of the emulsions increases with increase in the emulsifier concentration (Fig. 6).

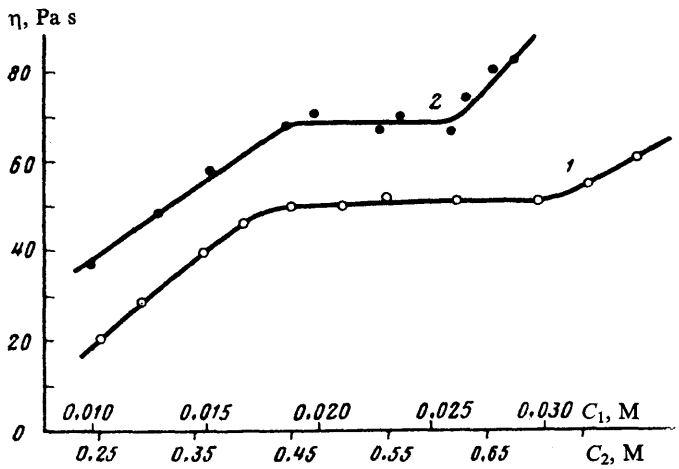


Figure 6. The influence of the concentrations of hostacerin DGO (curve *1*) and sorbitan oleate (curve *2*) on the viscosity of the emulsions at a rate of displacemnt of 3 s^{-1}. Fraction of inner phase 0.65; temperature 25 °C.

The study of the ξ-potential of the inner phase drops showed that, with increase in surfactant concentration above the value necessary for the complete saturation of the adsorption layer at the interface in the emulsion, the ξ-potential of the inner phase drops is seen to decrease. This lowers the repulsion energy between the disperse phase drops, which increases the rate of their coalescence and hence leads to a decrease in the stability of the emulsions.

Some increase in the stability of the emulsions at surfactant concentrations exceeding the CCM-2 in the liquid membrane is apparently associated with the formation of a heteroadsorption layer owing to the adsorption of the surfactant micelles at the interface.[36] When the repulsion energy of the adsorbed micelles exceeds their attraction energy, there is some increase in the stability of the emulsions.

Variation of the fraction of the inner phase in the emulsion leads to the variation of the specific interface. A definite position of the maximum in the dependence of the stability of the emulsion on the fraction of the disperse phase corresponds to each surfactant concentration (Fig. 7). The maximum stability corresponds to the complete saturation of the adsorption layer. For higher fractions of the inner phase at a specified surfactant concentration, the adsorption layer proves to be unsaturated and the stability of the emulsion is therefore diminished; for small fractions of the inner phase, when the interface in the emulsion is saturated to the maximum extent with surfactant molecules, the stability diminishes owing to the presence of an excess surfactant in the dispersion medium, i.e. an effect analogous to the dependence of the stability of emulsions on the surfactant concentration is observed (Fig. 5).

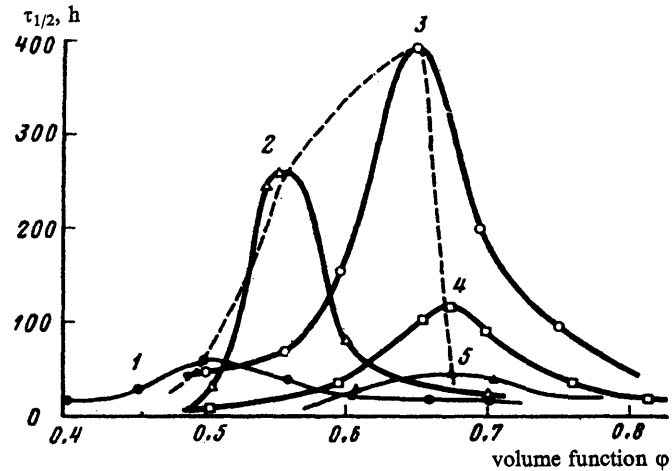


Figure 7. Dependence of the half-separation period of the inner phase of the emulsions at 60 °C on the initial fraction of the inner phase at different molar concentrations of sorbitan oleate: *1*, 0.24; *2*, 0.35; *3*, 0.45; *4*, 0.50; *5*, 0.55.

With increase in the surfactant concentration, the maximum in the stability of the emulsion shifts towards higher fractions of the inner phase.[37] At a surfactant concentration exceeding 0.02 M for hostacerin DGO and 0.45 M for sorbitan oleate, the stability maximum shifts towards higher fractions of the inner phase, but the absolute stability diminishes, the amount of surfactant necessary for the limiting degree of adsorption increasing sharply. For higher fractions of the inner phase, the shape of the drops deviates from the spherical and the drops are distorted, which reduces the stability of the extracting emulsions.

Thus in order to determine the quantitative composition of the most stable emulsion with the given qualitative composition, it is essential to take into account the interrelated influence of the fraction of the inner phase and the surfactant concentration.

The properties of the extracting emulsions can be varied by altering the composition of the dispersion medium, its viscosity, and its polarity. An increase in the viscosity of the outer phase of the emulsions can evidently ensure a certain kinetic stability of the

emulsion as a result of the decrease in the rate at which the thickness of the liquid film between the two surfaces diminishes as the drops of the inner phase approach one another. This fact can play a significant role in reverse emulsions. Fig. 8 presents the dependence of the half-separation time of the aqueous phase of the emulsion on the viscosity of the dispersion medium μ in the range of viscosities of hydrocarbon oils. Fig. 8 shows that the variation of the viscosity of the dispersion medium in the given range exerts an insignificant influence on the stability of the emulsions, but does influence appreciably their viscosity.[38] By altering the ratio of different oils in the organic phase of reverse emulsions, it is possible to alter the viscosity and other properties of the compositions without impairing the stability of the extracting emulsions.

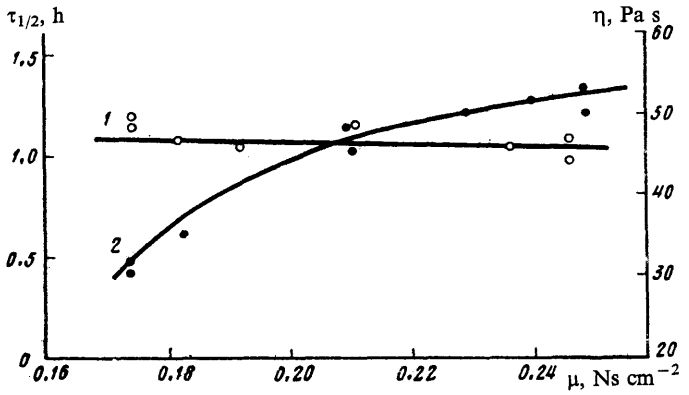


Figure 8. Dependence of the half-separation period of the aqueous phase (curve *1*) and of the viscosity of the emulsion (curve *2*) on the viscosity of the dispersion medium (μ).[38]

However, when the range of viscosities of the dispersion medium is widened, for example, by adding a hydrocarbon with a lower viscosity (decane), the stability of the emulsion is seen to decrease. Although in concentrated emulsions, close to highly concentrated ones, the thickness of the layers of organic phase is small (~20 nm), the hydrodynamic factor plays a fairly considerable role in the stability of the emulsions. Therefore, from the standpoint of the stability of the emulsions, it is useful to employ dispersion media with a fairly high viscosity and account must be taken of the fact that under these conditions the rate of diffusion of the target component falls in membrane extraction in a multiple emulsion.

The extractant-transferring agent forming part of the composition of the dispersion medium exerts a significant influence on the stability of the extracting emulsions. The extractants-transferring agents possess as a rule surface-active properties[24,39] and they therefore reduce the stability of the emulsions as a result of competitive adsorption at the interface. However, as shown previously, in the case of membrane extraction there is no need for high concentrations of the extractants-transferring agents in the liquid membrane and therefore in each specific case it is possible, as a rule, to select the necessary concentrations of the transferring agents both from the standpoint of the rate of extraction of the target component and from the standpoint of the stability of the extracting emulsion.

Apart from the above factors, the stability of the extracting emulsions is influenced significantly by the composition of the disperse phase. Among the factors playing the greatest role in their stability, mention may be made of the pH of the disperse phase, the ionic strength, and the presence of organic substances, which influence the polarity of the inner phase and the properties of the interface.

Fig. 9 presents the dependences of the half-separation period of the aqueous phase and of the viscosity of the emulsions on the NaCl concentration in the inner phase. With increase in the ionic strength of the solution constituting the disperse phase of the emulsions, both the stability and the viscosity of the emulsions increase. This is a positive factor in membrane extraction, since it makes it possible to increase the capacity of the emulsions with respect to the target component by increasing the content of the binding reagent in the inner phase.

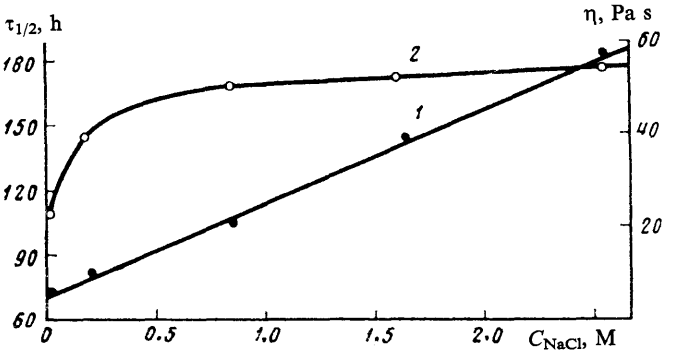


Figure 9. Dependence of the half-separation period of the aqueous phase at 60 °C (curve *1*) and of the viscosity of the emulsions at 25 °C (curve *2*) on the NaCl concentration in the inner phase of the emulsions.

Emulsions containing in the inner phase compounds creating alkaline or neutral media are frequently employed in membrane extraction. Fig. 10 presents the dependences of the stabilities and viscosities of the emulsions on the pH of the inner aqueous phase. In the region of neutral media, the half-separation time of the aqueous phase and the viscosity of the emulsions are virtually constant. The emulsions with alkaline and acid inner phases are characterised by a lower stability and viscosity. This has been attributed to the protonation of the emulsifier in the acid solutions and its hydrolysis in highly alkaline and acid media, which increases the hydrophilic–lipophilic balance (HLB) of the emulsifier and hence lowers the stability of the extracting emulsions.

Apart from other factors, the properties of the extracting emulsions may be appreciably influenced by the presence of organic substances which affect the polarity of the disperse phase. Figs. 11*a* and 11*b* illustrate the influence of the overall concentration of ethanol and diethyl ether ($C_{\text{alcohol+ether}}$), present in molar proportions of 4:1, on the stability and viscosity of emulsions.[35]

The increase in the overall concentration to ~3.0 M diminishes slightly the half-separation period of the emulsions. At concentrations of 3.5 M, there is a sharp fall in stability. This is associated with the fact that an increase in the content of ethanol and diethyl ether in the emulsion entails a decrease in the amount of the surfactant in the adsorption pair at the interface owing to the increase in the solubility of the surfactant in the phases. As a result, the stability of the emulsions falls sharply. Furthermore, an increase in the concentrations of ethanol and diethyl ether in the organic membrane diminishes the difference between the polarities of the phases so much that it becomes difficult to stabilise the system. Therefore at high concentrations of ethanol and diethyl ether in emulsions, an increase in the amount of the surfactant does not lead to an appreciable increase in the stability of the emulsions.

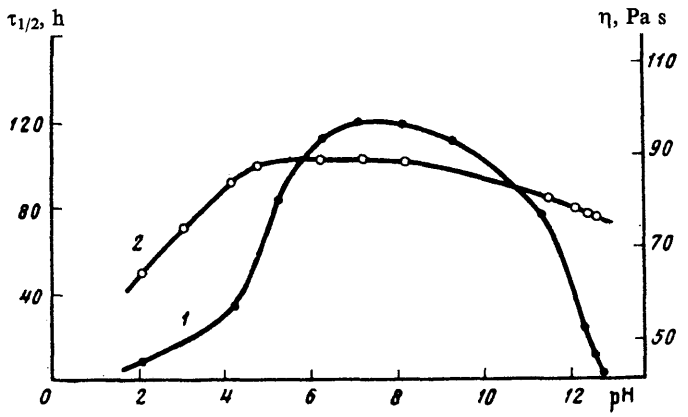


Figure 10. Dependence of the half-separation period of the aqueous phase at 100 °C (curve *1*) and of the viscosity of the emulsions at 25 °C (curve *2*) on the pH of the disperse phase.

It is noteworthy that, with increase in the contents of ethanol and diethyl ether (in the given concentration range), the viscosity of the emulsions decreases linearly (Fig. 11*b*).

Thus, depending on the type and concentration of the surfactants used to stabilise the system and also on the composition of the dispersion medium and the disperse phase, it is possible to obtain emulsions with different properties for each specific application.

III. The nanodispersion in the extracting emulsion

One of the most important phenomena which may occur at the interface in the extracting emulsion is the formation of a secondary emulsion made up of small particles of the order of 10–100 nm. The formation of such an emulsion is promoted by the presence of a surfactant and a cosurfactant in the system[40–42] and by the disequilibrium between the phases of the extracting emulsion, i.e. by the mass transfer of the components of the phases and the solvents through the interface. The formation of such dispersions in the presence of mass transfer has been investigated[25] in two-phase non-emulsion systems.

The spontaneous formation of an emulsion at the interface is possible when chemical reactions occur, including the formation of new surfactants, and also in the presence of aliphatic alcohols.[43–46] However, in the given instance, the authors observed the formation of larger drops—more than 200 nm in diameter.

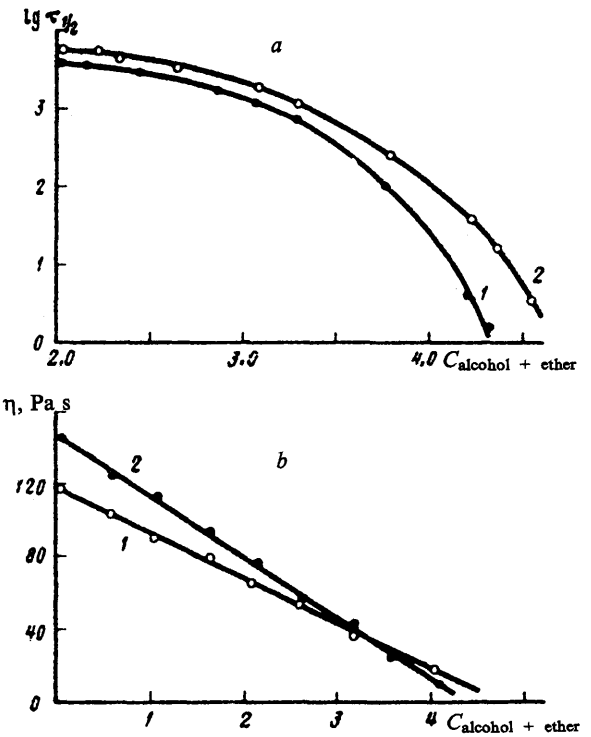


Figure 11. The effect of the overall concentration of ethanol and diethyl ether on the half-separation period of the aqueous phase (*a*) and of the viscosities (*b*) of emulsions stabilised by hostacerin DGO (line *1*) and sorbitan oleate (line *2*) at 25 °C.[35]

The formation of a secondary emulsion has been frequently referred to as microemulsification and the resulting emulsion was called a microemulsion. However, the term microemulsion has come to imply only thermodynamically stable disperse systems comprising particles 10–100 nm in diameter.[47,48] Furthermore, the diffusion coefficients of the microemulsion are much lower than those of the monomers—individual surfactant molecules. As the equilibrium shifts towards a decrease in the concentration of the surfactant monomer, there is no decomposition of the microemulsion drops.[49]

Thus, to solve the problem of classifying a particular emulsion, formed in the presence of diffusion of the substances in the heterogeneous system, as a microemulsion, one requires information about the particle size, the diffusion coefficients, and the thermodynamic stability of the system.

In the case of membrane extraction, the hypothesis of the formation of a microemulsion has been put forward mainly in connection with the transport of water.[50–52] However, the lack of

direct evidence enabled the authors to conclude that the hypothesis of the solubilisation of water by micelles or microemulsions in the course of its transport is invalid and they explain this phenomenon by the transport of water by individual surfactant molecules.[53,54]

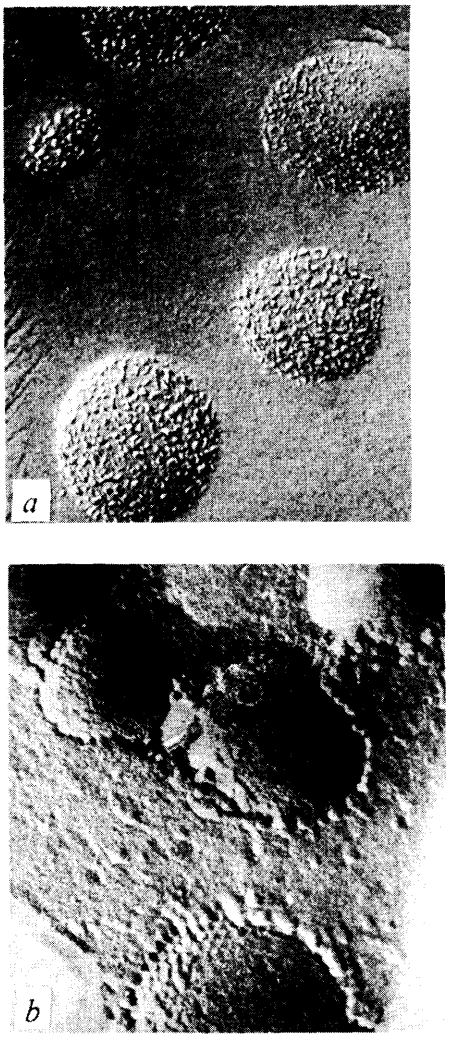


Figure 12. Photomicrographs of an emulsion containing an aqueous solution of ethanol and diethyl ether suspended in liquid paraffin and stabilised with sorbitan oleate: *a*, before extraction (× 100 000); *b*, after extraction (× 130 000).[57]

Data concerning the size distribution of drops in the emulsion before and after the membrane extraction of cholesterol have been published.[55,56] Photomicrographs of the Pt/C replicas of the cleavage plane of the emulsion, obtained by the freezing-cleavage method,[57] are presented in Fig. 12. The data obtained indicate the absence of a microemulsion from the initial emulsion before extraction and the subsequent formation of drops 17–25 nm in size in the course of the extraction process. The calculated effective diffusion coefficients of the substances forming part of the composition of such drops exceed by 2–3 orders of magnitude the molecular diffusion coefficients. Thus the small drops formed in the course of mass transfer in the extracting emulsion have two features of a microemulsion. The study of the thermodynamic stability of such systems is difficult since extracting emulsions are non-equilibrium systems.

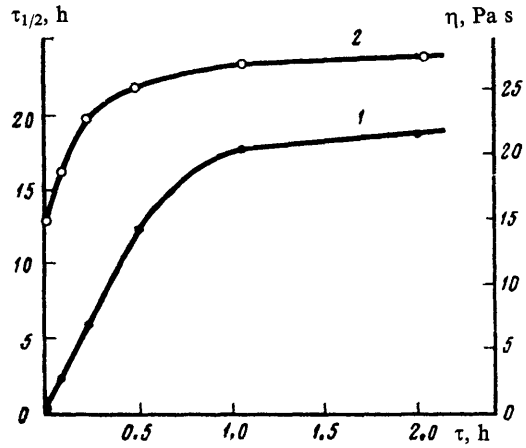


Figure 13. Dependence of the half-separation period at 70 °C (curve *1*) and of the viscosity of the emulsions at 20 °C (curve *2*) on the duration of the extraction of cholesterol.

In our view, for particles with diameters ranging from tens to hundreds of nanometers, one can use the term "nanodispersion", which implies both thermodynamically stable disperse systems (microemulsions) and thermodynamically unstable systems (solubilised micelles). The application of the concept of the "nanodispersion" makes it possible to designate clearly the fraction of small drops formed as a result of emulsification at the interface caused by the mass transfer.

The formation of the nanodispersion drops can influence significantly the kinetics and the quasi-equilibrium in processes occurring in extracting emulsions. The nanodispersion drops are distributed in the bulk of the liquid membrane and are concentrated at the interface, forming a structural-mechanical barrier (Fig. 12). This results in an increase in the stability of the extracting emulsions during extraction (Fig. 13) accompanied by an increase in their viscosity, apparently owing to structure formation in the emulsions and an increase in the cooperative interaction of the drops of the disperse phase. Fig. 14 presents kinetic curves for the separation of such emulsions into layers. The plots are characterised by the presence of two sections: rapid separation of a definite fraction of the inert phase slightly stabilised by the nanodispersion and slow separation of the remainder.

The formation of the nanodispersion is a positive factor when it is necessary to have emulsions which remain stable for a long time, for example, in medicine, in analytical methods, and in the preparation

of protecting creams, since the stability of the emulsions increases appreciably under these conditions. On the other hand, in the organisation of a technological process, where rapid separation of the extracting emulsion into layers is necessary in order to regenerate the extracted substance, the formation of nanodispersion is undesirable, since it entails an additional expenditure on the decomposition of the disperse system. An increase in the viscosity of the extracting emulsions increases the probability of paste formation (the coalescence of the globules), which prevents the normal operation of the technological equipment.

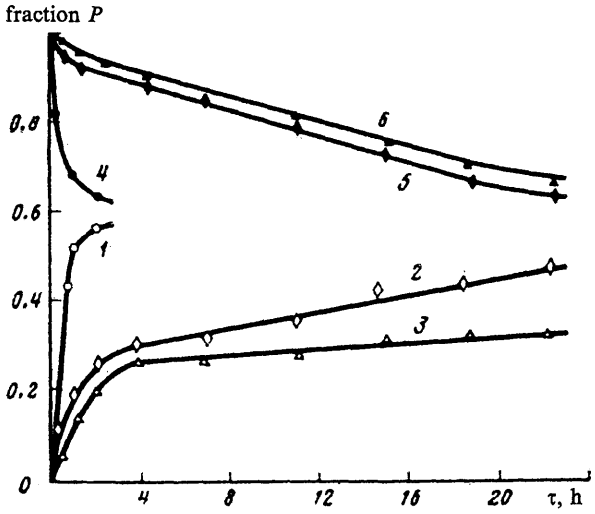


Figure 14. Kinetic curves for the separation of the extracting emulsions into layers (*1*–*3* aqueous phase; *4*–*6* organic phase) at 70 °C as a function of the duration of extraction of cholesterol. Extraction time (h): *1* and *4*, 0 (initial emulsion); *2* and *5*, 0.25; *3* and *6*, 1.

The formation of a nanodispersion is a positive factor also in the extraction of substances with surface-active properties, since the capacity of the extracting emulsions increases as a consequence of the increase in the degree of adsorption of the target component at the interface in the emulsion. The presence of a cosurfactant in the emulsions, for example, of ethanol and diethyl ether in the emulsions for the extraction of cholesterol (see Section V.3), promotes the formation of a nanodispersion as a result of the additional decrease in interfacial tension. By varying the type of cosurfactants and their concentration, the composition of the emulsions for the extraction of cholesterol was selected. For this emulsion composition, the specific interface increases by 55–65% and more,[56] which helps to increase the degree of extraction. The contribution of the adsorption of the target component at the interface to the overall capacity of such emulsions exceeds 50%.

The drops of the nanodispersion and the surfactant micelles can act as transferring agents in the liquid membrane of the extracting emulsions. A number of studies[58–60] have been devoted to the use of nanodispersions in the liquid membrane for the extraction of sodium and potassium picrates and proteins. The dodecyl ether of tetraethylene glycol is used as the surfactant and aliphatic alcohols are used as cosurfactants.

When extracting emulsions containing concentrated aqueous solutions in the inner phase are used, the drops of the nanodispersion can play the role of transferring agents for the solvent, leading to the transmembrane transfer of water to the inner phase (i.e. the swelling of the emulsions), which is an undesirable process. Some of the main factors which determine the rate of transfer of water are the type and concentration of the surfactants in the liquid membrane.[50,54,61] From the standpoint of the intensity of the formation of the nanodispersion, the use of sorbital ethers is undesirable,[54] since a high rate of transfer of water in emulsions stabilised by sorbitan oleate has been noted.[61]

The direction of the transmembrane transfer of water in a multiple emulsion is determined by the sign of the water activity gradients; when the sign is reversed, there is a corresponding change also in the direction of the transport of water.[38] It is noteworthy that the transmembrane transport of water to the inner phase of the extracting emulsions can be effected not only by the drops of the nanodispersion; the transport of water by the molecules of the surfactant and the transferring agent can also make a definite contribution.

In practice, when the extracted component is concentrated in the inner phase, use is made of extracting emulsions whose disperse phase contains concentrated aqueous solutions. For this reason, the swelling of the emulsions is the preferred process.

The emulsion swelling process does not as a rule reach equilibrium, since, as a result of the large difference between the osmotic pressures in the outer and inner aqueous solutions, the swelling of the extracting emulsions may be considerable. This leads to the breakdown of the emulsions in the extractor owing to the rapid coalescence due to the decrease in the degree of adsorption of the surfactant at the interface.

Thus the optimisation of the residence time of the extracting emulsion in the apparatus in order to concentrate the target component in the inner phase to the maximum extent is important.

IV. Mathematical description of the kinetics of the processes in extracting emulsions

An extensive literature has been devoted to the mathematical description of the mass transfer processes in heterophase liquid systems in both diffusional and kinetic regimes (see, for example, Refs. 3 and 62–64).

The description of the mass transfer in a multiple emulsion involves a number of characteristic features associated with the instability of the geometrical shape of the globules of the extracting emulsion and hence of the liquid membrane, the hydrodynamic set up in the latter, and the structure of the emulsion globules. The large specific interfaces in the extracting emulsions are responsible for the appreciable influence of adsorption not only on the extraction equilibrium but also on the rates of the processes in both diffusional and kinetic regimes.

The diffusion in a multiple emulsion is described using approaches based on the consideration of the non-stationary or quasi-stationary transport of the substances.

When quasi-stationary models are used, it is assumed that convective streams of the drops of the disperse phase arise in the liquid membrane owing to the sharp changes in the rate and

direction of the motion of the globules of the extracting emulsion caused by its dispersion in the solution being extracted. It has been noted that the mobility of the drops depends on their number and size and is fairly clearly correlated with the apparent viscosity of the emulsions.[65] Thus it has been suggested that the concentrations of the extracting component in each drop of the inner phase are equal at each instant.

In the given case, the globule of the extracting emulsion can be represented approximately by a hollow sphere (Fig. 15*a*), whose nucleus consists of the re-extracting solution, its composition being averaged over all the drops of the inner phase. Since concentrated emulsions, close to highly concentrated emulsions, are as a rule used for membrane extraction, the curvature of the liquid membrane is frequently neglected and the latter is treated as flat. The curvature factor can be taken into account with the aid of the relation

$$f_{int}/j=2\delta/d\ln[1/(1-2\delta d^{-1})],$$
$$j_{ext}/j=1-2\delta/d,$$

where j, j_{int}, and j_{ext} are the calculated fluxes through the flat membrane and through the inner and outer surfaces of the spherical membrane respectively, d is the diameter of the globule of the extracting emulsion, and δ is the thickness of the liquid membrane.

The coefficients of the mass transfer from the extracted solution, where it is effected by convective diffusion, into the globule of the extracting emulsion can be determined experimentally or estimated with the aid of the correlation equations published by Ivakhno et al.[66]

Molecular diffusion predominates in the drops of the disperse phase. Although this is a slower process, the mass transfer in the re-extracting solution is rarely the rate-limiting stage of the process, since the interface of the inner phase drops is large (10^6-10^8 ml^{-1}) and the re-extraction constants are usually small.

The models of the quasi-stationary transport do not always describe adequately the mass transfer in a multiple emulsion, especially during the final period of such mass transfer, although they may serve as a convenient mathematical approximation, adequate only along individual sections of the kinetic curves.[67]

Another version of the modelling of the extracting emulsion is based on the hypothesis that all the particles of the disperse phase have negligibly small dimensions, are uniformly distributed, and are fixed within a spherical globule with a radius R at specific reaction points (Fig. 15*b*). The target component or its complex with the transferring agent diffuses from the outer boundary of the extracting emulsion globule to its centre and, as soon as the diffusion front reaches the negligibly small drops of the inner phase, they are instantaneously saturated by the target component owing to extraction. Thus, at a distance r_f from the centre of the spherical globule of the extracting emulsion, there is a boundary between zones containing the inner phase saturated and unsaturated with the target component. The mathematical description includes the solution of the equation for the non-stationary diffusion in terms of spherical coordinates:

$$\frac{\partial C}{\partial \tau}=\frac{D}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right); \quad r_f(\tau)\leqslant r\leqslant R.$$

The moving front (of reaction points) model was first proposed and a solution was obtained for one-dimensional diffusion by Marr and co-workers.[68] Later Ho and Li[69] solved numerically the equation with the aid of the perturbation method. The moving front model has been used to describe the transport of substances in multiple emulsions.[19,70–79]

A number of workers have noted the necessity to take into account the resistance to mass transfer in the boundary layer of the outer phase, particularly at the beginning of the process and in the case of a high concentration of the reactants in the inner phase.[80,81] This is apparently valid only in the case of liquid membranes with a low viscosity. For extracting emulsions based on viscous hydrocarbon oils in the absence of slow reactions, the rate-limiting stage of the process is as a rule diffusion in the liquid membrane. Thus in the extraction of lysine in a multiple emulsion (see Section V.1), the resistance to mass transfer in the bulk of the globule exceeds by a factor greater than 500 the resistance in the outer boundary layer.[38]

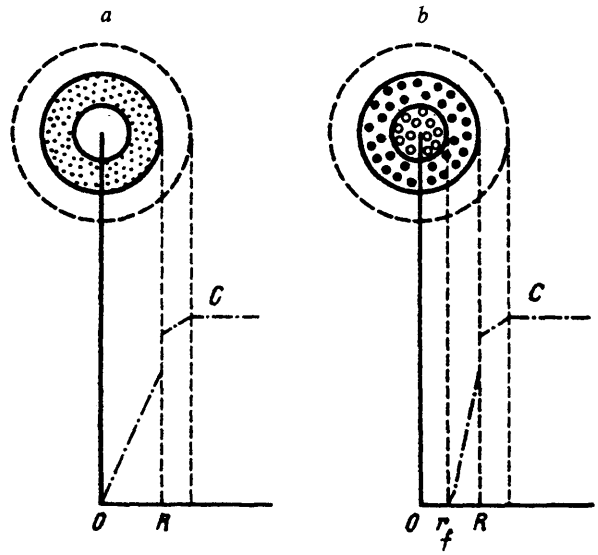


Figure 15. Models of the globules of extracting emulsions: *a*, hollow sphere; *b*, moving front. The dot-dash line represents the profile of the variation of the concentration (C) of the diffusing substance; R = radius of the extracting emulsion globule; r_f = radius of the reaction front in the globule.

The moving front model describes adequately the kinetics of membrane extraction in the case of highly viscous emulsions where the intraglobular convection is suppressed. In practice mainly concentrated emulsions, close to highly concentrated ones, are used, i.e. disperse systems with a high viscosity (see Section II) and therefore in such cases the moving front model is preferred.

The concentrations of the target component $C(t)$ in the solution being extracted have been calculated[38,82] for the membrane extraction of lysine using a model of a moving front with quasi-stationary diffusion (Fig. 16). It was shown that the non-stationary model describes adequately the experimental kinetic curve throughout the process, whereas the quasi-stationary model describes it only in the initial instants.

The mathematical adequacy of the linear functions arises because the complex functions can be fitted by a linear relation along the initial sections of the kinetic curves regardless of the real nature of the mass transfer. The main difference between the non-stationary and stationary models is observed far from the points used for the identification of the model parameters. In the mathematical description of the kinetics of membrane extraction in a multiple emulsion, it is therefore necessary to consider the kinetic curve from the initial instant up to the attainment of quasi-equilibrium in the system.

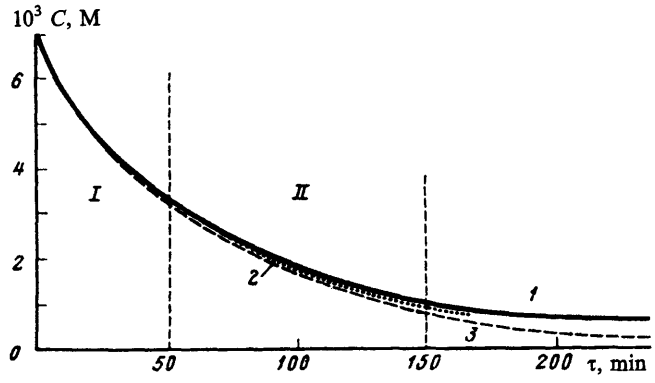


Figure 16. Comparison of the experimental kinetic curve (*1*) with relations calculated on the basis of the moving front (curve *2*) and stationary diffusion-controlled transport (curve *3*) models; *I*, tabulated value of the Fisher statistic f_t = 9.55; calculated Fisher statistics—f_2 = 0.23, f_3 = 0.23; *II*, f_t = 9.12; f_2 = 0.32; f_3 = 1.13; *III*, f_t = 9.12; f_2 = 0.23; f_3 = 13.83.

Information about the nature of the diffusion processes in the liquid membrane can be provided by the "physicochemical probing" method proposed by Frank-Kamenetskii and consisting in the determination of the degree of the power relation between the mass transfer coefficient β and the diffusion coefficient D.[82,83]

The moving front model describes mainly the membrane extraction process in the diffusion regions of the reaction. Special difficulties arise in the transitional region of the reaction, where it is necessary to take into account the influence of the rates of not only diffusion but also of chemical reactions. The analytical solution of the equations for the mathematical description of the kinetics narrows the range of their applicability, since the adoption of certain assumptions is frequently required.

In the given instance, it is best to use a universal, numerical method, which, in contrast to the analytical solutions, makes it possible to obtain an adequate description of the process with constants having a definite physical significance.[84]

In the development of the given model, the following assumptions were made: the diffusion of the components in the liquid membrane is non-stationary; the chemical reactions in the extracting emulsion globule take place at a finite rate and may be both reversible and irreversible; the globule of the extracting emulsion is spherical and is regarded as a pseudohomogeneous medium. For each system component, the following equation is valid:

$$\varepsilon \frac{\partial C_i}{\partial \tau} = D_i\left[\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r}\right] + R_i(\mathrm{C}),$$

where i = 1, ..., N, N is the number of system components, and r = 0, ..., R.

The solution of the above system of equations yields the distribution of the concentrations at any instant and at any point in the system. The system may be solved by employing the method of matrices in combination with the run-through [machine pass] and linearisation methods. In the dimensionless form, we have

$$\hat{\varepsilon}\frac{\partial \bar{C}_i}{\partial T} = \frac{\partial^2 \bar{C}_i}{\partial X^2} + \frac{2}{X}\frac{\partial \bar{C}_i}{\partial X} + R_i(\mathrm{C}),$$

where $X = r/R$, $\bar{C}_i = C_i/C_0$, and $T = (D/R^2)\tau$ for the following initial and boundary conditions:

$$X=1,\ \bar{C}_i=1 \text{ when } T=0,$$
$$d\bar{C}/dX=k\Delta\bar{C} \text{ when } X=1,$$
$$d\bar{C}/dX=0 \text{ when } X=0.$$

The given differential equation is converted into a system of algebraic equations:

$$AC_{i+1}^{k+1}+BC_i^{k+1}+EC_{i-1}^{k+1}=F,$$

where A, B, E, and F are the coefficients of the system of equations which are solved by the run-through method requiring a minimal amount of calculations.

It is noteworthy that, when the specific interface is large and the thickness of the liquid membrane is small, the presence of a surfactant can alter the diffusion coefficient of the target component in the liquid membrane, the partition coefficient between the phases, the reaction rate constant, etc. compared with the corresponding values obtained for a two-phase system of similar composition. The nanodispersion, formed on mass transfer through the interfaces in the multiple emulsion, can also exert a significant influence on the given quantities. This must be taken into account in the determination of the parameters of the mathematical models in independent experiments.

The mathematical description of the kinetics of membrane extraction in a multiple emulsion can include the optimisation of the process either from the standpoint of the attainment of a high degree of concentration (since the molecular diffusion of the target component or of its complex with the transferring agent is appreciably faster than the transmembrane transfer of water leading to the swelling of the emulsion) (see Section III) or from the standpoint of a more effective separation of the substances.[85] Harrington's method, using the so called desirability function as the optimisation parameter, may be used for these purposes.[86]

In the extraction of lysine in a multiple emulsion,[38,82] it has been shown that the maximum efficiency of the lysine concentration process is obtained at time τ_{opt}, which is not the same as the time of attainment of quasi-equilibrium in the system (Fig. 17), since, at times exceeding τ_{opt} in the membrane extraction process, the

concentration of the target component in the inner phase begins to fall because the swelling of the emulsion predominates.

The optimisation of the mass transfer process in extracting emulsions makes it possible to achieve best results in the concentration or extraction of the target component.

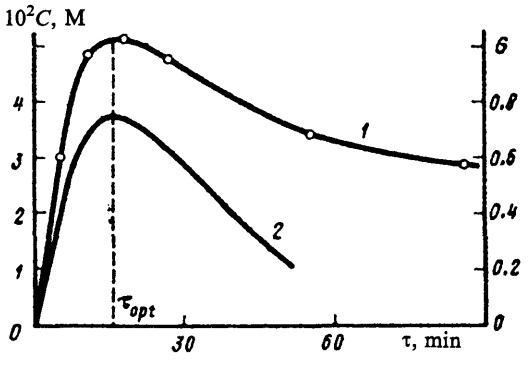


Figure 17. Dependence of the concentration of lysine in the inner phase of the emulsion (curve *1*) and of the generalised desirability function (curve *2*) on the duration of extraction with optimisation of the process.

V. Examples of the practical use of extracting emulsions

1. Application of extracting emulsions in technological processes

Various practical applications of the membrane extraction method in the extraction of numerous metals have been described in the literature: Cu, Ni, Co, Zn, Cr, U, and Hg as well as organic compounds. Detailed reviews of these studies in recent years may be found in the literature.[3,87–89]

Fig. 18 presents as an example a schematic illustration of the experimental-industrial apparatus for the extraction of copper.[5] This process makes it possible to extract more than 99% of the metal. The residual concentration does not exceed 2–7 g m^{-3}, i.e. is 20–30 times lower than in the single-step liquid extraction under comparable conditions. The concentration factor varies from 10[66,90] to 500 and above.[91–94] The emulsifier is usually sorbitan oleate and, more rarely, sorbitan stearate, polyamines, etc. Various hydroxyoximes, β-ketones, and carboxylic or alkylphosphoric acids are used as transferring agents.[66] The inner phase of the emulsions contains 0.5–2.5 M sulphuric acid solution, while the concentration of the sulphuric acid in the extracted solution is not more than 10^{-2} M.

As an example of the extraction of organic substances, one may quote the membrane extraction of aminoacids from enzyme solutions in the microbiological industry.[38,95,96] The extraction of aminoacids proceeds most effectively from weakly concentrated aqueous solutions, especially from dilute liquid waste and wash solutions. Thus the above process can assist in a more complete extraction of aminoacids, in the reduction of their losses, and in the creation of almost waste-free technologies. In one contact step, it is possible to achieve residual concentrations of the order of hundredths of a gram per litre.

The process is of special interest for the extraction of aminoacids sparingly soluble in water, for example tryptophan, since in practice one deals with relatively low concentrations of such aminoacids in aqueous solutions.

A technological scheme has been developed for the recovery of aminoacids (lysine, tryptophan) from their aqueous solutions with the aid of membrane extraction in a multiple emulsion (Fig. 19). The scheme includes the following stages: the preparation of the extracting emulsion, membrane extraction in the multiple emulsion, decomposition of the extracting emulsion after extraction, the evaporation of the solution of the inner phase of the emulsion, and the crystallisation of the aminoacid from the concentrate followed by its washing and drying and the preparation of the commercial product. The ethanol used to wash the aminoacid is periodically redistilled. When the process is carried out in accordance with the above scheme, the aminoacid is freed from other substances present in biological waste: pigments, inorganic salts, etc.[38]

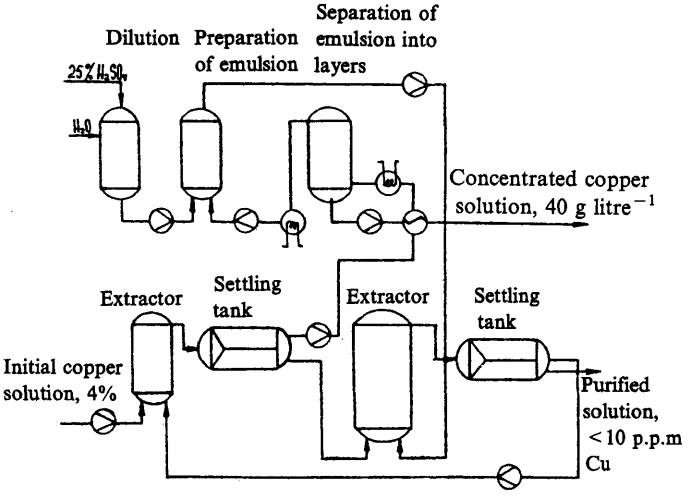


Figure 18. Schematic illustration of the apparatus for the extraction of copper in multiple emulsions.[5]

2. The use of extracting emulsions in analysis

Extracting emulsions can be used for the preliminary concentration of substances for the purpose of their subsequent analysis.[12] These processes may be of special interest in the analysis of the state of the environment, where the test substances are present at very low concentrations unsuitable for traditional analytical methods. Concentration is achieved by allowing a large volume of the test liquid to flow through the cell with the extracting emulsion. Problems of stability are then solved as a rule by selecting the appropriate composition of the extracting emulsion. The situation is more complex as regards the diffusion of water into the extracting emulsion. The swelling of the extracting emulsion impairs the efficiency of the concentration, particularly in extraction from media with low concentrations of the solutes.

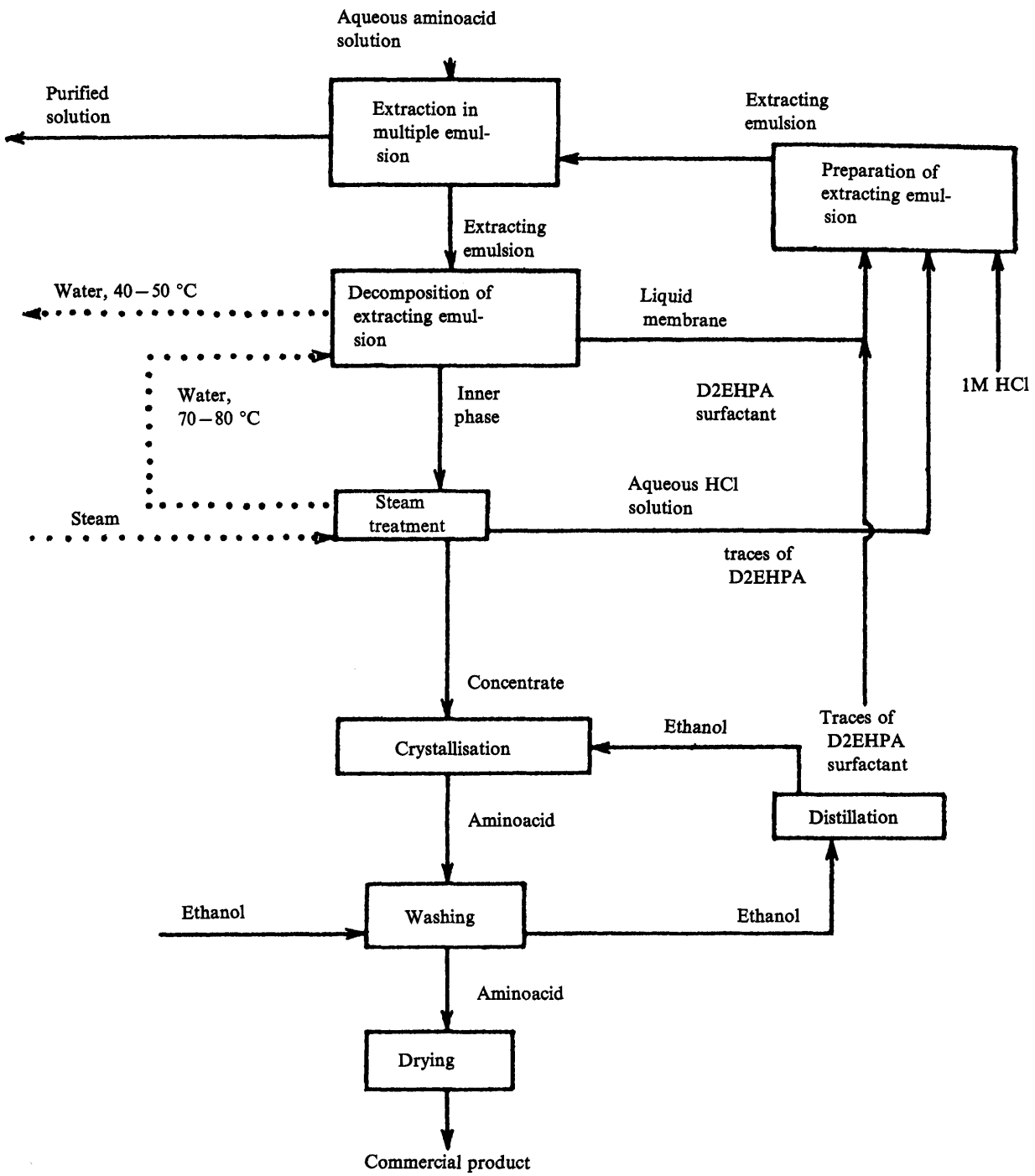


Figure 19. Technological scheme for the isolation of aminoacids (lysine and tryptophan) from their aqueous solutions.

The effect of swelling can be reduced by optimising the contact time on the basis of kinetic relations, as stated above, and also by employing polymeric surfactants. Examples of the use of extracting emulsions in analysis can be found in the literature[12,97] and the use of the extraction of mercury,[98] lead, and cadmium[12] for analytical purposes has been described.

3. The use of extracting emulsions for the detoxification of biological media

Extracting emulsions can find applications in the detoxification of biological media—for the extraction of poisons of exogenic and endogenic origin.[8–10,21,99,100] When inert liquids are used as the

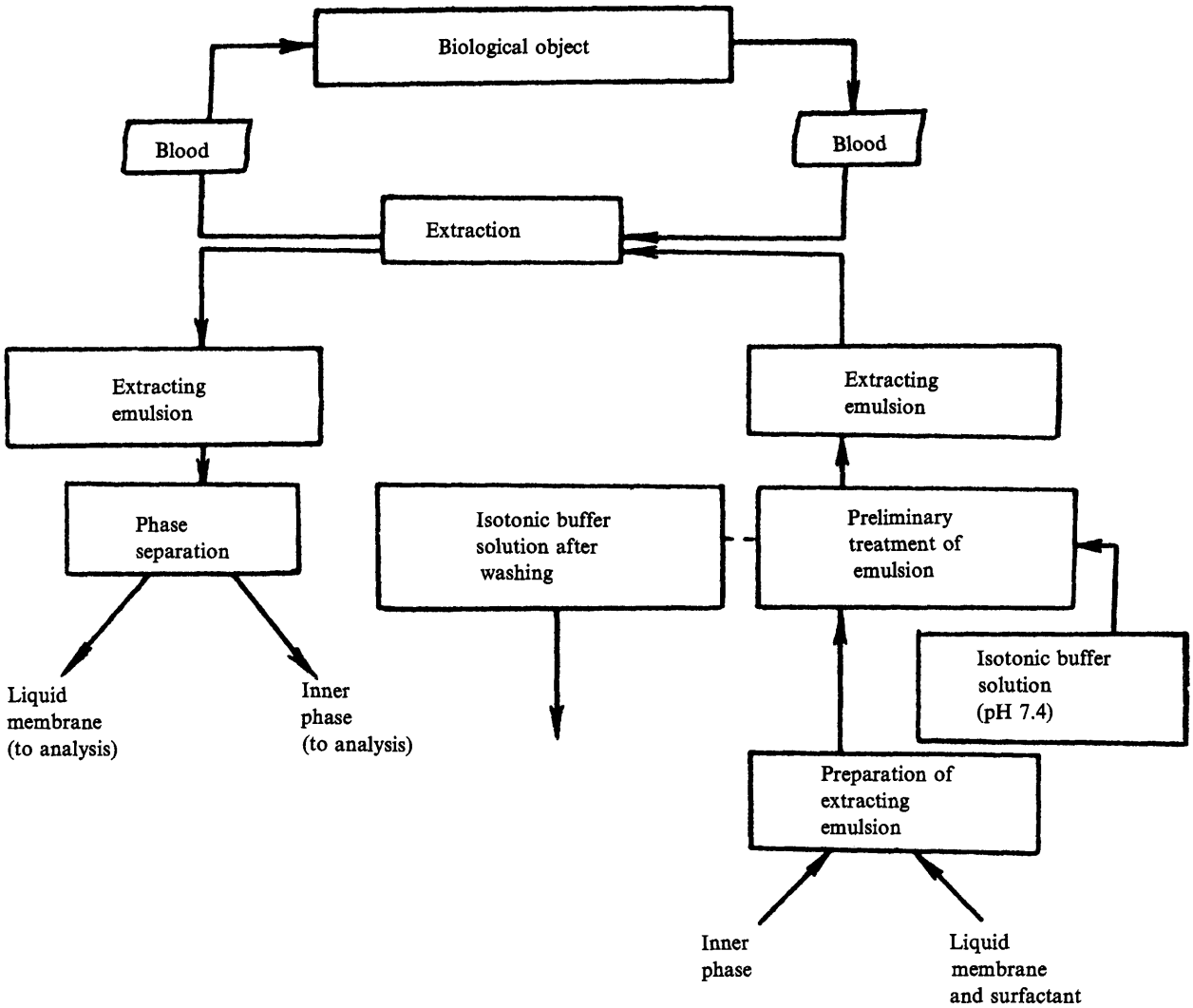


Figure 20. Schematic illustration of membrane extraction from blood using extracting emulsions.

dispersion medium (liquid membrane), it is possible to carry out extraction directly from the blood.

It is noteworthy that many components of biological liquids possess surface-active properties and the contribution of the adsorption component to the capacity of the emulsion can therefore be fairly large; for example it exceeds 50% in the extraction of cholesterol. From this standpoint, membrane extraction in a multiple emulsion has an additional advantage, since extracting emulsions are characterised by a large specific interface (10^6-10^8 m^{-1}). There exist various procedures for increasing the interface, for example as a result of the formation of a nanodispersion, which increases the capacity of the extracting emulsions in the extraction of substances with surface-active properties.

Emulsions containing ethanol and diethyl ether have been developed for the extraction of lipids, including cholesterol and its ethers.[21,35,99] Such emulsions extract cholesterol and lipids into the liquid membrane and sorb them at the interface. In emulsions of this kind, the mass transfer of ethanol and diethyl ether across the interface entails the formation of a nanodispersion. The conditions under which the formation of a nanodispersion is a maximum were selected by varying the concentrations of ethanol and diethyl ether as well as their ratio. The specific interface then increased by 55–65% which resulted in an increase of the degree of extraction of cholesterol owing to adsorption on the interface in the extracting emulsion.[56]

Emulsions containing saponins have been developed for the extraction of non-etherified cholesterol from biological liquids in order to reduce its content in the organism under the conditions of atherosclerosis.[9,21] A water-insoluble equimolecular complex of cholesterol and the saponin is formed in the inner phase of such emulsions. It is almost totally insoluble in water and precipitates. Owing to the haemolytic activity of saponins, preliminary washing of the extracting emulsions with an isotonic buffer solution before extraction from the blood is necessary. After such treatment, the emulsions have no toxic activity since the liquid membrane reliably isolates the saponins present in the disperse phase.

Fig. 2 illustrates schematically the membrane extraction from the blood using extracting emulsions. Blood circulates between the organism and the apparatus in a manner similar to the haemodialysis or haemosorption processes.[10,101] After extraction, the emulsion can be separated into phases in order to determine the concentrations of the substances extracted from blood.

4. Application of extracting emulsions as protection-prophylactic creams

The method of membrane extraction in a multiple emulsion can serve as a basis for the creation of prophylactic creams to protect the surface of the skin against various toxic substances.[11,27,102] Such creams are in many cases more effective than the traditional ones. The difference between them and the existing ointments consists in the fact that the creams extract the sensitisers from the surface of the skin and fix them within their bulk. Traces of the sensitiser on the surface of the skin can also be absorbed by the cream which prevents their accidental incidence on the unprotected sections of the skin.

A process analogous to membrane extraction in a multiple emulsion then takes place. Here the solution of the sensitiser or the upper layer of the skin constitutes the external phase being extracted. Irreversible or reversible reactions involving the binding of the toxic substance may occur in the inner phase. In the latter case, it is necessary to endeavour to make sure that the equilibrium constant of the reversible reaction is as large as possible in order to maintain a minimal concentration of the extractant-transferring agent in the liquid membrane. A fairly wide range of reagents can be used in the inner phase of the emulsion cream, since they are separated from the skin by an inert liquid membrane and do not therefore come into direct contact with the skin.

It is noteworthy that the cream can be not only protecting but also therapeutic and prophylactic, since it can be deposited on the skin already containing a sensitiser, which is extracted from the skin into the emulsion cream.

An important condition for the efficacy of the cream is the maximum extraction of the toxic substance from the organic membrane in contact with the skin into the inner aqueous phase or its fixation in the bulk of the liquid membrane. This is achieved by the strong binding of the sensitiser in a weakly dissociating complex in the inner phase and also by employing low concentrations of the extractant-transferring agent in the organic membrane. Creams whose action is based on this principle prevent the penetration into the skin of not only sensitisers (i.e. substances including dermatitis) but also of other harmful substances (i.e. substances leading to damage of the organism on penetration into the latter through the skin), which is of increasing interest owing to the impairment of the ecological situation.

An important characteristic of the protecting cream is its stability. In this case the emulsions obtained must be even more stable than those employed in technological processes and even in extraction from blood, since in the application of the cream the emulsion is present as a thin layer on the surface of the skin and under such conditions the role of heterocoagulation processes becomes more marked.

A similar approach to the creation of extracting protecting creams served as a basis for the development of a number of specific compositions of prophylactic creams designed against harmful organic and inorganic substances, in the first place sensitisers: heavy metals, chromium, antibiotics, aldehydes, ketones, etc.[11,27,102]

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