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Liquid Membranes for Extraction

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Abstract—Types and peculiarities of liquid membrane extraction are surveyed. The properties of bulk, supported, and emulsion liquid membranes are given. The basic principles of liquid membrane extraction, the types of carriers, and the stability of systems in the course of processes are considered. The use of liquid membranes for the separation of gas mixtures is demonstrated. The advantage of membrane extraction is the possibility of achieving high degrees of extraction and concentration in a single stage. At the same time, the organization of a membrane extraction process is more complicated than that of traditional processes.

Keywords: liquid membranes, membrane extraction, supported liquid membranes, emulsion liquid membranes, gas separation

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1. INTRODUCTION

Liquid membranes, as solid membranes, are semipermeable barriers between two liquid or gas phases [1–3]; they can be used for the separation and concentration of substances. The effectiveness of liquid membranes is demonstrated by nature itself: cellular membranes regulate metabolic processes between the cell and the environment, and intracellular membranes divide a cell into organelles, in which certain intracellular fluid conditions are maintained. The liquid membrane can be considered as a model of biological membranes. The phospholipid bilayer containing proteins, which are responsible for the transport of different substances, can be represented as a liquid membrane with selective carriers [4].

Membrane extraction was among the first areas of application of liquid membranes [2, 5]. The liquid membrane, which contained a carrier substance, separated two aqueous solutions. Under the action of a chemical potential gradient, the selective transfer of an extracted component from the first aqueous solution to the second one was accomplished.

Note that the term *membrane extraction* was also used for another process proposed earlier, when a selective solid membrane, to which an electric potential could be applied, separated the aqueous and organic extraction phases [6, 7].

At present, the systems with liquid membranes are promising for use in analytical chemistry [8, 9] and biotechnology, for the purification of wastewater [10], and for the separation of expensive or toxic metals, organic compounds, etc. A number of surveys and books on the use of liquid membranes have been published [11–15].

Studies related to the use of liquid membranes for the separation of gas mixtures became have received wide acceptance in recent years [16–18].

2. BASIC PRINCIPLES AND VERSIONS OF MEMBRANE EXTRACTION

In membrane extraction, the processes proceed in a system of three liquid phases. In this case, one of the phases—the liquid membrane—separates two immiscible solutions with different composition. From one side, the liquid membrane S contacts with the feed solution F and with the back-extracting or receiving solution R from the other side (Fig. 1).

Membrane extraction has a number of advantages over traditional extraction. The most important merit of membrane extraction is the possibility of simultaneously conducting the processes of extraction and back extraction of substances and, correspondingly, a decrease in the number of processing stages. The combination of extraction and back extraction makes it possible to reach high diffusing substance concentration differences between the feed and receiving phases at one stage. If the diffusing substance dissociates or forms an insoluble compound in the phase R, the almost complete extraction of the target substance from the initial phase F can be reached.

The results to be obtained by a multistage process of usual extraction can be reached in a single step by membrane extraction. This is especially important in the extraction of expensive or highly toxic substances and in the processing of low-concentrated solutions.

Depending on the problem to be solved, both the almost complete extraction of a target component from the feed solution and the maximally possible

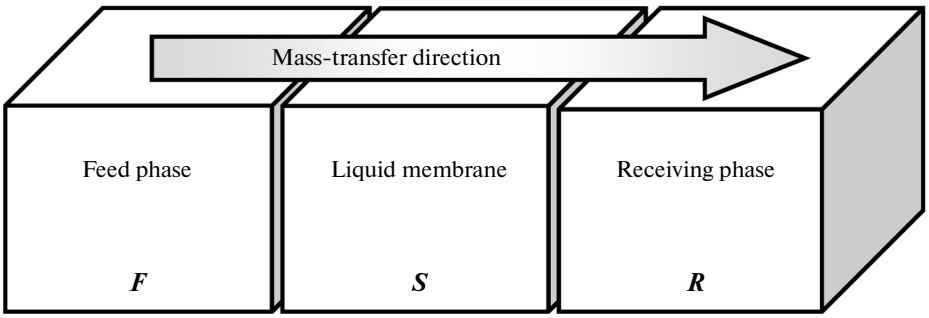

Fig. 1. Diagram of membrane extraction.

concentration in the receiving solution for the given system can be attained.

Extractant losses due to both dissolution and droplet entrainment depend on extractant concentration, all other factors being equal. The extractant concentration in membrane extraction is considerably lower than that in usual extraction.

On the other hand, membrane extraction is more complex than usual extraction in terms of process organization.

Various versions of membrane extraction can be divided into the following three main types: extraction through free (bulk), impregnated, and emulsion membranes (Fig. 2).

2.1. Extraction with Free Liquid Membranes

Free or bulk liquid membranes are bulk organic phases (with a thickness of 0.1–5.0 cm) contacting with two aqueous phases spatially separated from each other. The simplest are U-shaped diffusion cells with three immiscible liquids [19, 20].

In spite of certain advantages of free liquid membranes, only experimental facilities that operate on this principle are currently available. This is due to noticeable liquid membrane entrainment in the course of extraction and the contamination of feed and receiving solutions by the organic components of a liquid membrane. Emulsification or gel formation frequently occurs at the liquid membrane surface; this makes the process difficult to perform under required hydrodynamic conditions and decreases the permeability of porous membranes. These factors restrict the industrial use of this method.

2.2. Extraction with Impregnated (Supported) Liquid Membranes

Impregnated or supported liquid membranes are obtained upon the impregnation of the pores of a solid matrix, in which a liquid is retained under the action of capillary forces.

The most important advantage of the impregnated liquid membranes is low membrane phase consumption. However, at this small amount of a membrane phase, it is rapidly washed out with the destruction of the impregnated membrane [13].

Different constructions of pertractors (film, film–disk, fiber, spiral, column, etc.) were developed to increase specific interfacial surface areas with the retention of high mass transfer coefficients [21–25]. In these installations, all of the three phases are in motion, and the interface is constantly renewed.

A serious drawback of column pertractors is complexity and a long time taken to put them into operating conditions. These devices are not intended for the treatment of solutions containing solid impurities, which block the pores of flat and fiber membranes. The noteworthy entrainment of phases frequently occurs in film apparatuses.

2.3. Membrane Extraction in Multiple Emulsions

Membrane extraction in a multiple emulsion is the most complex process. It consists of the following four main stages: the preparation of an extracting emulsion, the contact of the extracting emulsion with an feed solution, the separation of a raffinate, and the phase separation the extracting emulsion (Fig. 3).

Although the version of membrane extraction in a multiple emulsion is efficient, additional problems appear here related to the stabilization of the emulsion during extraction and, in the majority of the cases, the need for the subsequent phase separation in the emulsion. Furthermore, in the case of high requirements imposed on the product purity, an additional problem of the removal of a surfactant used for the stabilization of extracting emulsions appears.

Various combined versions of a membrane extraction process have been also proposed in the literature. Thus, for instance, the extracting emulsion can be separated from the feed phase by a microporous solid membrane. This principle is implemented in pertractors of different types and in hollow fiber extractors. Figure 4 shows a fiber apparatus, in which the receiving phase dispersed in an organic liquid membrane is supplied to the internal channels of hollow fibers, and the feed solution flows outside the fibers.

3. EXTRACTION SYSTEMS

The recovery of a substance depends on the compositions of the initial and receiving solutions. Extractant in a membrane phase is only a carrier, which interacts with the extracted substance on its transport from the feed phase into the receiving phase. Therefore, the high capacity of a liquid membrane and high partition coefficients are not as critical in the method of liquid membranes as in traditional liquid extraction.

3.1. Feed and Receiving Phases

The recovery of extracted substances in liquid membrane extraction essentially depends on the compositions of the feed and receiving phases. The extractant is a carrier, and it is mainly responsible for the rate of the extraction process. If the extracted substance undergoes chemical transformations in the receiving phase, a low concentration of the diffusing substance in the receiving phase is maintained to facilitate the more complete extraction of the substance. In the limiting case, the concentration of the diffusing substance in the receiving phase can be almost zero due to the occurrence of irreversible reactions; in this case, the substance is extracted almost completely and irreversibly. In due time, this version of membrane extraction was figuratively referred to as the Charon mechanism [28] by analogy with the ferryman who brought souls of the dead in the Greek mythology; it is well known that he carries in the opposite direction under no circumstances. This mechanism can be useful in the concentration and immobilization of toxic substances in extracting emulsions [29].

In the general case, the compositions of feed and receiving phases have a determining effect on the degrees of extraction of substances. The effects of the concentration of an extracted substance, salt composition, pH, and reagent concentrations in the phases on the efficiency of membrane extraction in particular systems have been described in the literature [30–34].

For example, Wan et al. [30] studied the effect of the pH of the feed solution on the extraction of phenol. They found that membrane extraction effectively occurred at pH < 4 because the undissociated form of phenols, which exists at the given values of pH, is soluble in the liquid membrane.

In the extraction of metals by liquid membranes with a carrier, the equilibrium constant of a reaction between the carrier and the extracted metal ion at the liquid membrane/feed solution interface depends on the pH of the feed solution. Thus, on the extraction of chromium with an Aliquat 336 carrier, the partition coefficient sharply decreased at pH > 6 [31]. This was due to the fact that quaternary ammonium salts possess high extraction capacity for univalent oxy anions, that is, for $HCrO_4^-$. At pH > 6, chromium occurs as the CrO_4^{2-} anion.

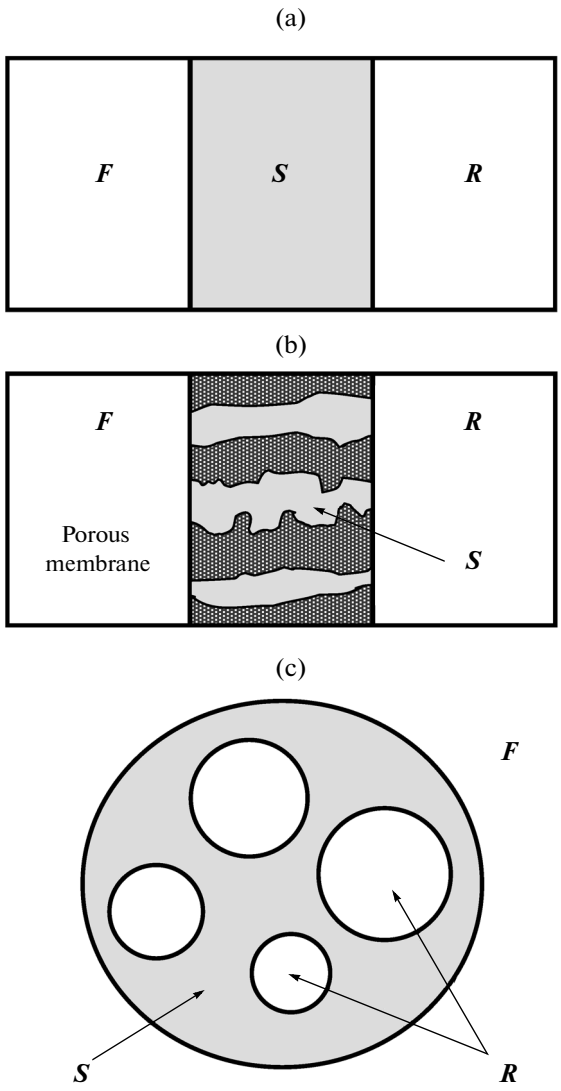

Fig. 2. Main versions of extraction processes with liquid membranes: (a) free, (b) impregnated, and (c) emulsion membranes.

Depending on the concentration of the extracted compound in the feed solution, the degree of extraction of substances frequently passes through a maximum [32–34].

3.2. Liquid Membrane

Organic liquids, which contact with the aqueous feed and receiving phases, are commonly used as a membrane for performing membrane extraction. At the same time, systems with an aqueous membrane, which separates two organic liquids, can be developed [13]. However, such systems are used considerably more rarely because they are less stable due to the high volatility of water.

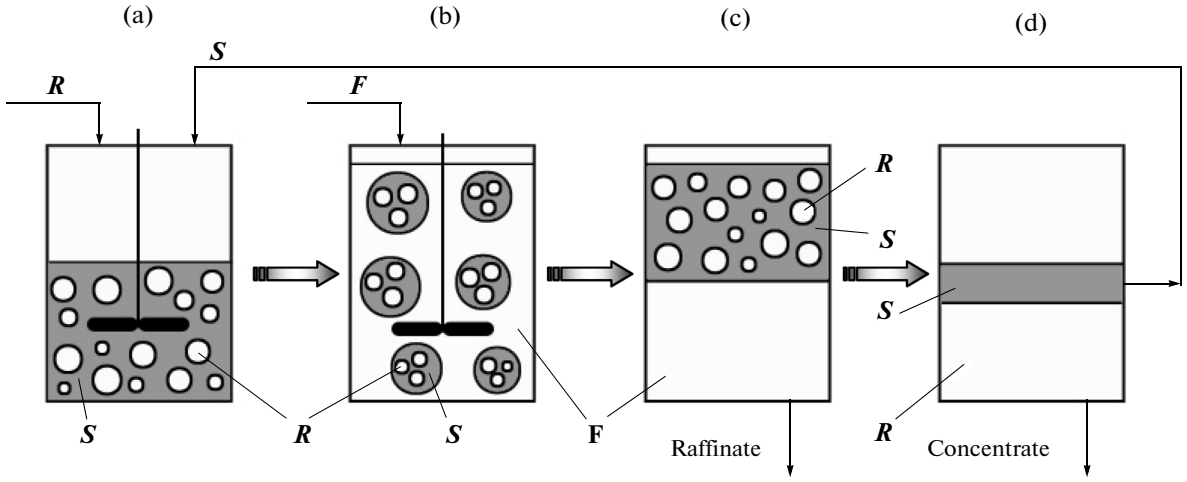

Fig. 3. Diagram of a membrane extraction process in a multiple emulsion: (a) preparation of the extracting emulsion, (b) contact of the extracting emulsion with the feed solution, (c) phase separation in raffinate, and (d) phase separation in the extracting emulsion [26].

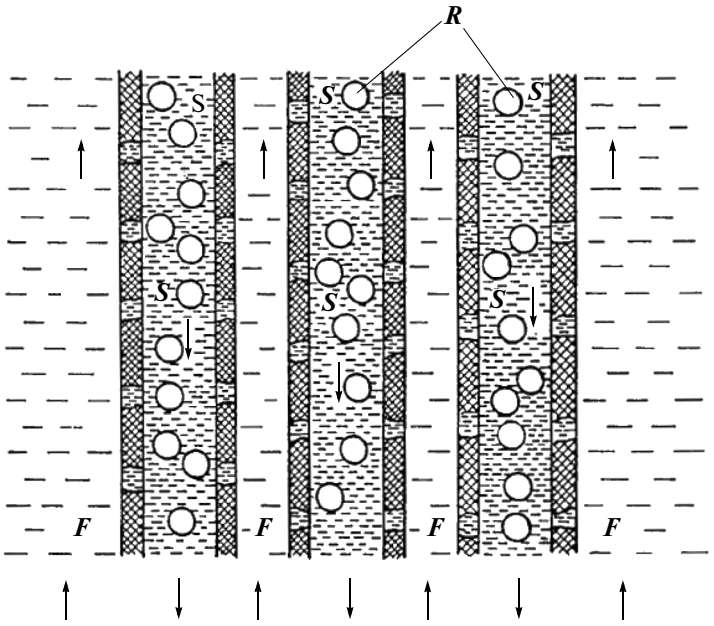

Fig. 4. Schematic diagram of flow directions in a fiber apparatus with the dispersion of the receiving solution [27].

3.2.1. Extractant Carriers

An extractant carrier is mainly responsible for the rate and selectivity of the process. Therefore, the process can be performed at low carrier concentrations in the liquid membrane, and extractants that are ineffective in terms of usual liquid extraction but less toxic and less expensive can be used as carriers.

Broad experience in the use of different types of extractants for the liquid extraction of various compounds has been accumulated. Therefore, as a rule, a search for carriers and back extraction solution compositions is based on experience in traditional extraction and backward extraction processes.

Cation-exchange carriers are used for the transport of cations and cationic metal complexes. The carriers of this class include the derivatives of phosphoric, phosphonic, and phosphinic acids (M2EHPA, D2EHPA, PC-88A, extractants of the Cyanex class, hydroximes, and β-diketones (extractants of the LIX and Acorga classes), carboxylic acids, etc.

For example, di-2-ethylhexylphosphoric acid (D2EHPA) is used for the membrane extraction of

Cd(II) [35, 36], Co(II) [37, 38], Cu(II) [36, 37, 39], Fe(III) [36, 40], Ni(II) [36, 37], Zn(II) [37, 41–43], Pb(II) [36], Mn(II) [44], and Ag(I) [45]; the extractants from the Cyanex class extract Bi(III) [46, 47], Cd(II) [48], Cu(II) [37], Co(II) [37, 49], Li(I) [49], Hg(II) [50], Ni(II) [37], Zn [37], and the cyanide complexes of gold [51]; and alkylphosphonic acids, for example, PC-88A, extract Cu(II) [52].

Various commercial reagents are chelating carriers. LIX 54, LIX 84, LIX 860, and LIX 973N are used for the extraction of Cu(II) and Ni(II) [37, 52, 53]; LIX 984N is used for the extraction of Cu(II) and Zn(II) [54]; Acorga M5640 extracts Cu(II) and Ni(II) [55]; the 8-hydroxyquinoline derivatives Kelex 100 extract Cd(II) and Pb(II) [56]; and the oximes 2H5DBA and MOC-55 TD extract Cu(II) [57].

Cation-exchange carriers effectively extract metals from the neutral and slightly acidic solutions ($pH \geq 2.5$). Because metal cations are exchanged for the H^+ ions in membrane extraction, the pH value of the feed phase gradually decreases, and the rate of mass transfer decreases. Therefore, alkaline reagents should be added to the feed solution or buffer mixtures should be used to perform membrane extraction with cation-exchange carriers.

Anion-exchange carriers are used for the extraction of anions and anionic metal complexes. In the majority of cases, the process is organized as codirectional transfer with hydrogen ions as a complex salt of an organic base.

Aliphatic amines and different commercial reagents are used as anion-exchange carriers: trioctylamine for the extraction of Cd(II) [58], Cr(VI) [59], Hg(II) and As(III) [60]; triethanolamine, for Co(II) [61], Cr(III) [62], Ag(I) [63], and Mn(VII) [64]; Alamine 336, for Fe(III), Cu(II), and Ni(II) [65]; tricaprylamine N235, for Cd(II) [66]; Hostarex A 327, Amberlite LA 2 (secondary amines), and Primene JMT (primary amines), for $Au(CN)^{2-}$ [67]; etc. The extractant Aliquat 336 extracts Cd(II) and Zn(II) [68], Cr(VI) [69], Cd(II) [70, 71], Cu(II) [72], uranium [73], Co(II) [74], Rh(III) [75], As(V) [76], Pt(IV) [77], and Au(III) [78].

Neutral carriers, such as high-molecular-weight organic alcohols, ketones, ethers, esters, trialkylphosphine oxides, and sulfoxides can transport metal salts and simple and complex acids.

The neutral carriers include tributyl phosphate, which is used for the membrane extraction of uranyl nitrate [79], Nb(V) [80], Cd(II) [81], and Cr(VI) [82]; trioctylphosphine oxide is used for the extraction of U(VI) [83], Ga(III) [84], Ag(I) [85], Cr(VI) [86], etc.

Macrocyclic carriers—stereospecific ligands—initiate the passive transfer of metals together with salt anions in the form of ion pairs. The metal cation is retained in the macrocycle cavity with high electron density by ion–dipole or dipole–dipole interaction forces.

The carriers of this type include various unsubstituted and substituted crown ethers, for example, dibenzo-18-crown-6 (DB18C6), which is used for the membrane extraction of Cu(II), Ag(I), Zn(II) [87], Cs(I) [88], Cu(II), and Ag(I) [89]; cryptands [90], calixarenes [91], and macrocyclic polyethers, for Cu(II), Ag(I), and Zn(II) [92]; and carbocyclic compounds, for Cr(III) [93].

The selectivity of macrocyclic carriers mainly depends on the correspondence between the cavity size of the macrocycle and the diameter of the hydrated cation, which is inserted into this cavity upon the formation of a transported compound at the interface.

Micelles, microemulsion and nanoemulsion droplets can serve as carriers in the liquid membranes. The formation of micelles occurs in the systems containing surfactants soluble in the liquid membrane. Surfactants are specially introduced into the extracting emulsions for stabilization. A number of publications were dedicated to the use of microemulsions as liquid membranes for the extraction of Na^+ and K^+ picrates [94, 95]. Dodecyl ether of tetraethylene glycol was used as a surfactant for the formation of microemulsions, and aliphatic alcohols were used as additional surfactants (cosurfactants). The participation of nanoemulsion (nanodispersion) drops in the process of cholesterol extraction and water transfer from the feed phase into the receiving phase was reported [26, 29, 96].

3.2.2. Impregnated Membranes

Usually, organic liquid membranes immobilized in a polymer matrix are used. Inorganic matrices—ceramics, including glass and porcelain, and metal matrices—are used more rarely.

The stability of the impregnated liquid membranes largely depends on the matrix microstructure—the porosity and the shape, size, and curvature of pores. Matrices should be mechanically strong but thin in order to shorten the diffusion path of the extracted substance and to ensure the high rate of mass transfer through the membrane. To meet these requirements, asymmetric matrices are frequently used, for example, Fluoropore FG, in which one microporous layer is used for impregnation with a liquid membrane and the second porous layer ensures the mechanical strength. Polymers such as polypropylene, polyethylene, and polytetrafluoroethylene are commonly used as matrices for the impregnated membranes. Tables 1 and 2 summarize the main types of commercially produced polymer matrices for flat and fiber membranes [15].

Among the inorganic materials used for the preparation of impregnated membranes, ceramics, metals, metal oxides, and zeolites are of interest. The mechanical strength, thermal resistance, chemical stability,

Table 1. Characteristics of the industrially produced polymer matrices for flat impregnated liquid membranes [15]

Trade name	Material	Manufacturer	Thickness, μm	Porosity, %	Pore size, μm
Celgard 2400	Polypropylene	Celanese	25	38	0.02
Celgard 2500	Polypropylene	Celanese	25	45	0.04
Accurel	Polypropylene	Enka	100	64	0.10
Accurel	Polypropylene	Enka	150	70	0.20 or 0.40
Accurel	Polypropylene	Enka	160	75	0.20
Accurel 1E-PP	Polypropylene	Enka	75	73	0.10–0.30
Accurel BS7C	Polypropylene	Armak	50	48	–
Duragard 2500	Polypropylene	Polyplastics	25	45	0.04
FP-DCH	Polytetrafluoroethylene	Flow Lab.	150	80	0.45
FHLP	Polytetrafluoroethylene	Millipore	60	85	0.50
FP-045	Polytetrafluoroethylene	Sumimoto	80	73	0.45
Millipore	Polytetrafluoroethylene	Millipore	125	68	10
Goretex	Polytetrafluoroethylene	Gore	60	78	0.20
Fluoropore FG	Polytetrafluoroethylene/polyethylene	Millipore	60/115	70	0.20
Fluoropore FP-200	Polytetrafluoroethylene	Millipore	100	83	2.0
Fluoropore FP-045	Polytetrafluoroethylene	Millipore	80	75	0.45
Fluoropore FP-010	Polytetrafluoroethylene	Millipore	60	55	0.10
Nucelopore	Polycarbonate	Nucelopore Corp.	10	12	0.40

Table 2. Types and the characteristic of polymeric hollow fibers used as impregnated liquid membranes [15]

Name	Material	Manufacturer	Inner diameter, mm	Thickness, μm	Porosity, %	Pore size, μm
Goretex TA001	Polytetrafluoroethylene	Gore	1.00	400	50	2
Experimental batch	Polyethylene	Ashai Kasei	280	0.05	–	–
KPF-190M	Polypropylene	Mitzubishi Rayon	0.20	22	45	0.16
EHF-207T	Polypropylene	Mitzubishi Rayon	0.27	55	70	0.27

sterilizability, and biocompatibility are important advantages of inorganic membranes.

Inorganic and composite polymer–inorganic membranes are used for the selective extraction of metals [77, 97] and for the separation of propylene and propane [98]. However, in spite of the advantages, the number of publications on the use of inorganic matrices for impregnated membranes is considerably smaller than that on polymeric materials.

In order to prevent emulsification and liquid membrane washing out from pores, structured liquid membranes are used or a special protective layer is created on the membrane surface (Fig. 5). For this purpose, impregnated membranes with gel network are used, which consist of a gel impregnated into the matrix pores or a gel layer on the pore surface [99].

Composite membranes in which a liquid membrane is screened from aqueous solutions by a nonselective polymer film permeable to the target component were developed. Wijers et al. [100] used membranes consisting of an impregnated matrix closed with a film of sulfonated polyether(ether)ketone on both sides for the membrane extraction of copper.

The impregnated composite membranes are obtained by interfacial polymerization [14] and plasma polymerization [101]. In this case, a thin poly-

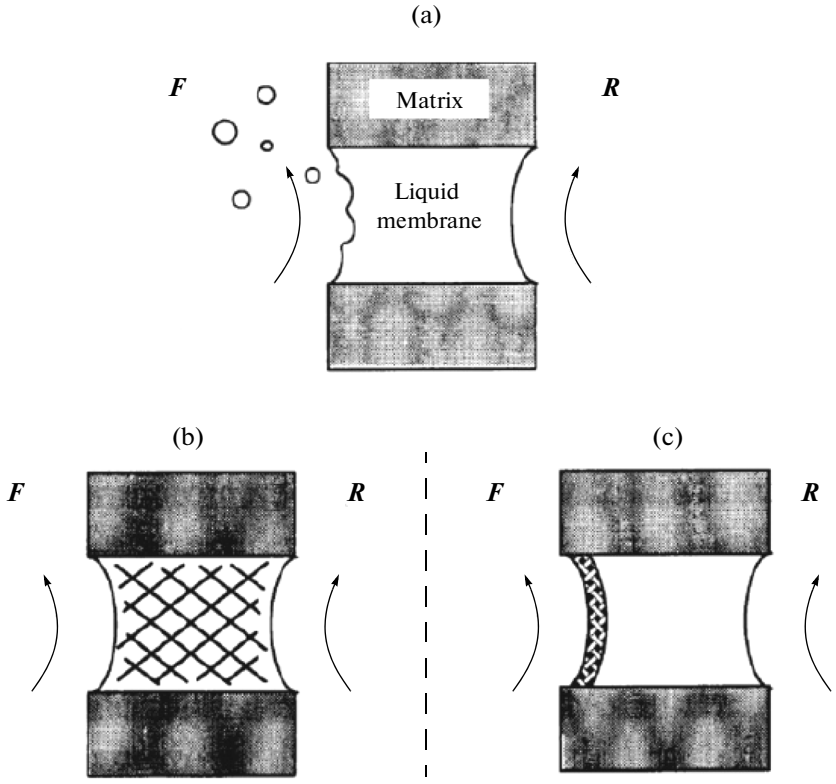

Fig. 5. Impregnated membranes (a) without stabilization and with (b) homogeneous gel network in the bulk of the impregnated membrane and (c) thin dense gel layer at the interface with the feed solution [99].

mer film, which closes the matrix pores, is formed. If this film is permeable to the target component, the rate of membrane extraction is almost not reduced [101, 102].

Membranes in which a carrier is chemically or physically bound to a solid matrix were developed [14]. Because these membranes do not contain a bulk liquid phase, the washing out in the process of membrane extraction is much smaller than that from traditional impregnated membranes.

3.2.3. Emulsion Liquid Membranes

On the dispersion of an emulsion containing the receiving solution in an internal phase, a multiple emulsion is formed in the feed phase. These systems are used for the membrane extraction of substances from an external feed solution into the internal phase of the emulsion.

In membrane extraction performed in a multiple emulsion, it is necessary to consider the stability of the extracting emulsions and the stability of the multiple emulsion in the course of extraction.

Usually, concentrated emulsions close to highly concentrated ones are used for membrane extraction in order to maximally increase their capacity for the target component. The mean diameter of the drops of the receiving solution dispersed in the liquid membrane varies in a range from 0.2 to 5 μm.

At the first stage, the organic phase containing a carrier and a surfactant is intensely stirred with the receiving aqueous solution. For this purpose, mixer apparatuses with propeller and turbine mixers are used. Usually, the mixture is cooled in the process of emulsification.

The continuous process of emulsification can be carried out in a colloid mill, where dispersion occurs upon the entering of immiscible liquids into a narrow gap between a rotor revolving at a high speed and a static stator [103].

Ultrasonic dispersion can also be used to prepare emulsions; it results in emulsions with a narrower size distribution of internal phase drops. However, with the use of this method, effective emulsification occurs only in immediate proximity to the emitting waveguide; the mechanical agitation of the system is necessary for the emulsification of large volumes. Therefore, it is most reasonable to use ultrasonic dispersion for obtaining small batches of extracting emulsions [104].

At present, high-pressure homogenizers, in which dispersion is accomplished by passing liquids through small gaps or microchannels at a high speed under the action of high pressures, are intensively

developed [105]. This method makes it possible to obtain the almost monodisperse drops of the internal phase from 100 nm to several micrometers in size.

The next stage, extraction in a multiple emulsion, is mainly performed in either apparatuses of the mixer–settler type or extraction columns. After the completion of mass transfer, the extracting emulsion is separated from the raffinate by gravitational segregation.

At the final stage, the emulsion is separated into an organic phase and an aqueous phase enriched in the target component. Thermal breakdown or electrical demulsification under the action of electric current on the extracting emulsion is most frequently used for decomposing the extracting emulsions [106]. Centrifugation is effective for unstable emulsions at a significant difference between the densities of the phases. The separation of the extracting emulsion into the phases can be performed on filtration through a porous material [107].

4. AREAS OF APPLICATION OF LIQUID MEMBRANES

Early in the development of liquid membrane technology, the use of this method was mainly oriented to the areas of application of traditional liquid extraction. The more so because, as a rule, already known extractants were carriers in a liquid membrane. Many works on studying the applicability of membrane extraction to hydrometallurgy have been published; however, the subsequent interest in the use of this method primarily remained in the field of wastewater purification. Different practical applications of the membrane extraction method to the extraction of many metals (Cu, Ni, Co, Zn, Cr, U, and Hg) and organic compounds were described in the literature. A detailed survey of these previous works can be found elsewhere [11, 108, 109].

From the very beginning of the development of this method, it was clear that the advantage of membrane extraction consists in the extraction of either toxic or expensive substances, which makes the extraction of substances to very low residual concentrations to be in demand. The corresponding areas of application include wastewater purification and environmental protection from toxic inorganic and organic substances, analytical chemistry, medicine, and the extraction of valuable products in biotechnology [12–15]. In the last cases, an additional advantage of membrane extraction manifests itself: this is the separation of the receiving phase, which contains different chemical reagents, from biological fluids and fermentation media by a relatively nontoxic liquid membrane.

4.1. Analytical Chemistry

Constructions with impregnated liquid membranes are tested for analytical purposes in order to perform sample preparation and preconcentration. Here, the requirement of the miniaturization of such devices is imposed so that the test sample volume should lie in a range of 10–1000 μL. Microfluidic methods have been intensively developed in recent years due to a promising possibility for designing a lab-on-a-chip device [110, 111]. In such devices, microvolume liquid drops and gas bubbles are produced under control in microchannels. This makes it possible to miniaturize chemical and biotechnological processes by transporting liquid microquantities as drops and bubbles through the network of microchannels to a specific section and then to carry out the rapid analysis of the contents of drops.

Wang et al. [112] developed a microfluidic device with a flat impregnated membrane for the separation and preconcentration of haloacetic acids in aqueous media. Pämarsdöttir et al. [113] developed a module with miniaturized impregnated membranes for the selective preconcentration and the subsequent analysis of drug preparations in plasma.

4.2. Wastewater Purification

The membrane extraction method with free liquid membranes began to be actively developed for the removal of radionuclides from aqueous solutions [114]. This method was tested for the extraction and separation of metals, carboxylic acids, amino acids, antibiotics, and enantiomers; for the extraction of ethylene, benzene, propanol, olefin, and aromatic amines from the mixtures of organic compounds; and for the extraction of phenol from wastewater [15]. The use of facilities with free liquid membranes for degassing in bioreactors is promising [115].

However, membrane extraction in a multiple emulsion is most widely used in this area. This method is used for the removal of zinc from wastewater in the production of viscose fibers, for the removal of phenols and cyanides, for the separation of nickel from galvanic solutions, for the extraction of copper from leaching solutions, in biochemical processes, for biomedical encapsulation, etc. [12].

The first commercial plant for the extraction of zinc from wastewater in the production of viscose fibers was put into operation in 1986 at Lenzing AG in Austria [116]. The process is performed in an Oldshue–Rushton extraction column of 1.5 m in diameter with a working chamber height of 10 m. Zinc is selectively separated from calcium with the use of liquid membranes with a di(2-ethylhexyl)dithiophosphoric acid carrier extractant from wastewater containing 400–600 ppm of zinc to residual concentrations of ~3 ppm. The productivity of the plant is 75 m^3/h. In the receiving phase, which contains 2.5 M H_2SO_4, zinc is concentrated to 60 g/L. The emulsion is separated under the action of an electric field. After the subsequent concentration by evaporation, zinc is returned to the process.

Three additional commercial plants based on an analogous process flow diagram were put into operation at Glanzstoff AG in Austria with a productivity of 700 m^3/h, at CFK Schwarza in Germany, and at AKZO Iede in the Netherlands with a productivity of 200 m^3/h [116]. There is information on the industrial use of this method in China [117].

The removal of phenol from wastewater with the aid of membrane extraction in a multiple emulsion was implemented in 1986 at Nanchung Plastic Factory in Guangzhou (China) [118]. The liquid membrane—the organic phase of the extracting emulsion used in this process—consists of 6.7 wt % liquid paraffin in kerosene, and the internal phase is a 5 wt % aqueous solution of NaOH. The plant makes it possible to purify wastewater with a decrease in the phenol concentration from 1000 to 0.5 ppm.

The main problem of emulsions containing an alkaline solution in the internal phase is low stability to coalescence, which leads to the passage of the back extracting solution into the feed solution in the course of extraction. At the plant in Guangzhou, the LMS-2 surfactant, which was specially developed for this project in order to provide the high stability of emulsions, is used for the stabilization of the extracting emulsions. As a result of the membrane extraction, the phenol content of wastewater decreased from 1000 to 0.5 mg/L.

A commercial plant for the removal of cyanides from wastewater in the production of gold was put into operation at Huang-Hua Mountain Gold Plant near Tientsin (China) [119]. The concentration of cyanides was decreased from 130 to 0.5 mg/L. The organization of this purification process did not require essential expenditures; this made it possible to increase the production volume with the retention of wastewater purification control.

A pilot plant for the removal of metals from wastewater was tested [116]. The liquid membrane contained 5 wt % methylthiopropylamine as a carrier and 3 wt % ECA 11522 polyamine as a surfactant. The tests showed that the efficiency of heavy metal extraction was as high as 99%. The concentrations of Zn^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} were decreased to 0.2, 0.02, 0.007, and 0.01 mg/L, respectively.

Wright et al. [120] reported on the nine-day tests of the extraction of copper from mining wastewater, as a result of which ~25 m^3 of wastewater was purified.

The use of extracting emulsions for the purification and separation of components from the liquid wastes of atomic power plants was tested. The recovery of plutonium from model solutions containing Cs^{137}, Ce^{144}, Ru^{103}, and Ru^{106} was as high as 98%. However, the process efficiency decreased to 84%, if uranium was present in the initial aqueous solution [121]. Yang et al. [122] described a two-stage process for the purification of low-concentrated aqueous wastes, which contained less than 1.1 mM of uranium.

The selective extraction of uranium from solutions containing americium and plutonium [123] and the separation of uranium from thorium [124] were carried out. The selective extraction of plutonium [125], americium [126], cesium [127], etc., was investigated.

4.3. Medicine

Emulsion liquid membranes can find use for the detoxication of biological fluids and for the extraction of poisons of exogenous and endogenous origins [26, 128–131]. With the use of inert liquids as a liquid membrane, direct extraction from blood can be performed.

For the extraction of lipids, including cholesterol and its ethers, emulsions containing ethanol and diethyl ether were developed [130, 131]. In these emulsions, nanometer-sized drops are formed on the mass transfer of ethanol and diethyl ether through the interface. As a result, the specific interfacial area essentially increases; correspondingly, the degree of cholesterol extraction also increases considerably due to adsorption on the surface of the drops of a dispersed phase in the extracting emulsion [132].

The method of membrane extraction in a multiple emulsion can form the basis of the development of preventive creams for skin protection from different toxic substances [26, 133, 134]. A fundamental difference of such creams from currently available ones is that sensitizer substances are extracted from the skin surface and immobilized inside the emulsion in the drops of the internal phase due to the occurrence of irreversible reactions. A wide range of reagents can be used in the internal phase of a shielding cream because they are isolated from the skin by an inert liquid membrane. Creams with this operating principle prevent the penetration of not only sensitizer substances but also other harmful substances, which cause intoxication; this is of considerable current interest because of worsening in the ecological situation. A similar approach formed the basis of the development of a number of particular compositions of preventive creams against different harmful organic and inorganic substances: heavy metals, chromium, antibiotics, aldehydes, ketones, etc. [133, 134].

Emulsion liquid membranes are tested as drug delivery systems for controlled release. Thus, a multiple emulsion was used for the intravenous injection of preparations [135, 136] and for the removal of toxic compounds from the body (oral artificial kidney) [137].

4.4. Biochemical Processes

Membrane extraction in a multiple emulsion has been studied long ago for the isolation and separation of amino acids and antibiotics from fermentation media [26, 138, 139]. As an example of recent studies, the following publications can be cited:

Table 3. Chemical reactions in a liquid membrane responsible for the selective transport of gaseous products [15, 158]

Transported gaseous product	Reaction
O_2	O_2 + compound Co ⟷ compound Co(O_2)
CO_2	$CO_2 + H_2O + Na_2CO_3 \longleftrightarrow 2NaHCO_3$
C_2H_4 or C_3H_6	$C_2H_4 + AgNO_3 \longleftrightarrow AgNO_3(C_2H_4)$
H_2S	$H_2S + Na_2CO_3 \longleftrightarrow NaHS + NaHCO_3$
CO	$CO + CuCl_2 \longleftrightarrow CuCl_2(CO)$
SO_2	$SO_2 + H_2O + Na_2SO_3 \longleftrightarrow 2NaHSO_3$

Hong and Yang [140] described a system for the continuous separation of L-phenylalanine from fermentation liquors. At pH 2.5, L-phenylalanine was concentrated from an initial concentration of 36 g/L to a concentration of 170 g/L.

Emulsion liquid membranes were used for the selective extraction of acrylic acid from a mixture with propionic and acetic acids in fermentation liquors. The carrier extractant Alamine 336 was used for the extraction of lactic acid [141, 142]. The efficiency of extraction from model solutions was twice as high as that from actual fermentation liquors. The results of studies on the membrane extraction of citric acid from fermentation liquors with the use of the Alamine 336 extractant were reported [143, 144].

Juang and Wang [139] examined the separation of L-phenylalanine from asparitic acid with the use of D2EHPA as a carrier. Pickering and Chaudhuri [145] described the separation of D-phenylalanine from a solution of a racemic mixture of D,L-phenylalanine.

Hano et al. [146] compared the use of different extractants—TOPO, tri-*n*-butyl phosphate (TBP), TOA, and dioctylamine—for the extraction of lactic acid from fermentation liquors.

Schaefer and Hossain [147] studied the extraction of citric and maleic acids from kiwi fruit juice. Impregnated liquid membranes were used for obtaining high-purity aconitic acid from cane molasses solutions, which contained oxalic, maleic, and citric acids [148].

Scheper et al. [149] described the extraction of penicillin *G* with the use of liquid emulsion membranes. Penicillin *G* was extracted through a liquid membrane containing the surfactant Span 80 and the carrier extractant Amberlite LA-2 in kerosene into the internal phase containing the penicillin acylase enzyme, which converted penicillin *G* into the products: phenylacetic acid and 6-aminopenicillic acid. Hano et al. [150] described the extraction of penicillin *G* with di-*n*-octylamine as a carrier and ECA 4360J (Exxon) as a surfactant in a mixture of kerosene and *n*-butyl acetate. The penicillin *G* recovery of 95% was achieved with the use of the Amberlite LA-2 extractant [151]. Lee [152] studied the efficiency of penicillin *G* extraction with a liquid membrane containing a dilute polymer solution for increasing the stability of liquid membranes. Juang et al. [153] studied the mechanism and rate of penicillin *G* transport through impregnated membranes with the Amberlite LA-2 extractant.

Several review papers on the extraction of biological substances and biochemical synthesis products with the use of liquid membranes have been published [154–156].

4.5. Gas Separation

The use of impregnated membranes for the separation of gas mixtures has been intensively studied in recent years. An elevated pressure is produced from one side of an impregnated membrane, and gas molecules form a complex with carrier molecules, which is transferred through the liquid membrane. The gas molecules are desorbed on the reverse side of the liquid membrane, where a reduced pressure is created [157]. The selective transfer of gaseous products is provided by choosing an appropriate carrier. However, nonspecific transport can occur to a certain extent due to gas dissolution in the liquid membrane.

Table 3 summarizes the main reactions responsible for the selective extraction of gases [15, 158].

With the use of this method, it is necessary to ensure the stability of impregnated membranes, which can be destroyed upon the evaporation of a solvent and a carrier. Difficulties emerge in the retention of the integrity of a matrix because a number of chemical reactions occur at elevated temperatures. If thicker matrices are used, their permeability decreases. In the separation of oxygen, a problem with the irreversible oxidation of a carrier appears. All of these factors limit the widespread introduction of this method.

Membranes impregnated with ionic liquids are of special interest. Ionic liquids are characterized by lower volatility; correspondingly, the membranes remain stable for a longer service life. These systems are promising for the selective extraction of gases and for the extraction of compounds from aqueous and organic solutions.

The molecules of ionic liquids consist of an organic positively charged moiety and an organic or inorganic moiety with a negative charge. The cationic moiety usually consists of imidazolium, *N*-alkylpyridinium, tetraalkylammonium, and tetraalkylphosphonium ions. The anionic moieties of the molecules of ionic liquids are halides, nitrates, acetates, hexafluorophosphate ($[PF_6]$), tetrafluoroborate ($[BF_4]$), trifluoromethyl sulfonate, and bis(trifluoromethylsulfonyl)imide.

Ionic liquids are capable of dissolving different organic and inorganic compounds. Depending on a combination of cations and anions and the length of a hydrocarbon chain, the solubility of ionic liquids in aqueous and organic media changes; this makes it possible to use them as impregnated liquid membranes

[159]. There are examples of the use of ionic liquids for the separation of ions [160], gases [17, 18, 161], aromatic and aliphatic hydrocarbons [162], amines, alcohols, and ketones [163].

Thus, liquid membranes along with solid ones can be used for the separation and concentration of substances in liquid media and the separation of gas mixtures and in blood oxygenators; they can serve as sensing elements in ion-selective electrodes.

The development of new methods and the improvement of currently available membrane extraction methods make it possible not only to modernize process technologies but also to better understand processes occurring in living nature.

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