

# Free Supported Liquid Membranes

V. V. Belova

*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

*e-mail: belova@igic.ras.ru*

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**Abstract**—A comparative analysis of the processes that occur at continuous and stepwise phase contact has been carried out. The free supported liquid membrane technique has been shown to be a step version of the conventional technique using supported liquid membranes.

**Keywords:** liquid membrane principle, extraction column, cascade of mixer-settlers, continuous and stepwise phase contact

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## INTRODUCTION

Liquid extraction is one of the most popular hydro-metallurgical methods for extracting and separating metals from technological solutions and effluent water [1]. The liquid membrane technique (membrane extraction), i.e., a nonequilibrium single-step process combining extraction, reextraction and regeneration of an extractant, was suggested as an alternative method [2].

The considerable interest in the liquid membrane method has been increasing in the last few years. This is explained by its advantages over liquid extraction, such as the ease of operation, low power consumption, high selectivity, possibility of using expensive extractants, lower consumption of the chemicals, and lower operating costs [3–5].

Liquid membranes can generally be divided into three types, i.e., free liquid membranes, supported liquid (impregnated) membranes, and membrane extraction in a multiple emulsion (emulsion membranes). In each case, extractants in the organic phase are similar to those used in liquid extraction. In general, the stoichiometry of metal extraction is the same as in liquid extraction, but the process is kinetically limited, i.e., it is characterized by a nonequilibrium mass transfer [6, 7].

As a rule, the liquid membrane consists of an organic solvent that separates the two aqueous phases (the feed and stripping phases) [8–10]. Upon contact between the liquid membrane with the two aqueous phases, a substance is transferred from the feed to the stripping phases.

From a practical point of view, supported liquid membranes are of special interest due to their stability and simplicity [11–13]. In the supported liquid membranes, the organic phase is usually located in small

pores of the polymer carrier and held there by capillary forces. Feed phase is pumped to one side of the polymer membrane, while the stripping phase is pumped to another side of the membrane. Metal ions are extracted from the feed to the stripping phase via the membrane. Because the used volume of the organic phase is very small, supported liquid membranes are the best variant of membrane extraction from an environmental point of view. The application of supported liquid membranes for the selective separation, purification, and concentration of toxic waste and precious metals from aqueous solutions is currently being studied [13, 15].

Emulsion liquid membranes [16–18] are water-in-oil or oil-in-water emulsions. In this case, membrane extraction takes place in a multiple emulsion, where a dispersion medium is a feed phase and the stripping phase is dispersed in a liquid membrane using a surfactant to form a stable water-in-oil emulsion. Compared with free and impregnated membranes, a multiple emulsion provides a higher rate of mass transfer. However, several steps are required to arrange a continuous process besides introducing the surfactants needed to stabilize the extracting emulsion. The emulsion liquid membrane must be stable enough to prevent the leakage of the internal stripping phase. However, the liquid emulsion membranes may be needed in cases when the solute concentrations are relatively low and other methods cannot be applied.

In recent years, in the laboratory of chemistry and technology of the Institute of General and Inorganic Chemistry (Russian Academy of Sciences), a new direction in the field of liquid membrane technology has been in development. A number of technical solutions developed in collaboration with the Bayer Company have been patented in Europe, Japan, China, and the United States, e.g., [21–24]. This trend is a

combination of free and supported liquid membranes, which can be referred to as free supported liquid membranes (FSLMs) [25]. The theoretical description of various FSLM processes is given in [26–28].

The FSLM technique was experimentally tested on a standard water–acetone–toluene extraction system [29]. The processes of copper extraction from sulfuric acid solutions (organic phase was LIX-84 solutions in aliphatic solvents) [30] and phenol separation from sulfuric acid solutions (organic phase–butyl acetate) were studied [31]. The purpose of this paper is to analyze the opportunities for the further development of this trend and the prospects of practical application of FSLM.

## RESULTS AND DISCUSSION

Two variants of SPZHM principle can be implemented, i.e., in the system of mixer settlers or in three-phase column extractors. The two ways of connections for mixer settlers based on the FSLM principle, i.e., (a) direct- and (b) counterflow movement of the raffinate and reextract phases, are shown in Fig. 1.

Two types of three-phase column extractors that operate according to the FSLM principle and comprise chambers located in one housing are schematically shown in Fig. 2. In the extractor shown in Fig. 2a, the chambers are separated by a vertical partition, while in the extractor shown in Fig. 2b, the partition is a concentric tube located in the center, with one of the chambers being located in the outer annular space and the other in the central tube. Chambers 1 and 2 with a dispersing device 3 are connected via overflow channels 4 and chambers of different stages intercommunicate through perforated plates 15 working as a dispersing device between the adjacent chambers. The chambers of the three-phase column extractor are equipped with separation zones 6, 7 made at the connecting channel inlet openings 4. There are the nozzles 8, 9 for feeding and 10, 11 for removing the first and second dispersed phases in the extractor. The operating principle of the three-phase column extractor is as follows. The first and second chambers are filled with a continuous organic phase (extractant or membrane phase). Feed and strip aqueous phases are directed to the chamber and then dispersed. Depending on the density of the contacting liquids the drops of the dispersed aqueous phase move up or down in the chambers 1 and 2 and coalesce at the interface. The aqueous phase is dispersed in the chambers of the second and subsequent stages by perforated plates 15. When moving the droplets through the chambers, emulsions of different densities are formed. Thus, upward and downward flows arise in a continuous organic phase, which results in the circulation of the organic phase between the chambers. The three-phase extractor can be used as a device for the FSLM technique. In this case, the initial solution (raffinate phase) is fed into the chamber 1 as a dispersed phase.

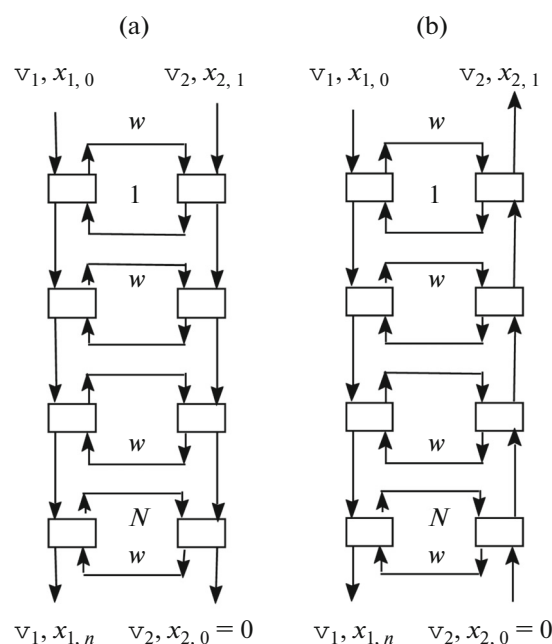


Fig. 1. Schemes of the mixer-settler cascade connection based on the FSLM principle for (a) direct and (b) counterflows of raffinate and strip phase [21].

The substance is extracted into the continuous organic (membrane) phase and transferred into the chamber 2, where its reextraction by the second dispersed phase (reextract phase) takes place. The described multiphase extractor enables efficient separation for a large raffinate and extract phase ratio. The advantages of the three-phase extraction columns include simplicity and cost-effectiveness (low capital and operating costs).

In industry, the extraction process is generally carried out in an extraction column with continuous phase contact or in a cascade of mixer settlers with discrete step phase contact. The devices for coupled extraction and reextraction in (a) columns and (b) a cascade of mixer settlers are illustrated in Fig. 3.

An FSLM (Fig. 3d) can be considered to be a step version of the conventional supported liquid membrane (Fig. 3c) [26, 33–35]. To confirm this, let us compare the processes with continuous and step phase contact.

### Processes with Continuous Phase Contact

For these processes (Figs. 3a, 3c) the initial concentration in the raffinate phase ( $X$ ) is calculated using the equations given below.

For conventional liquid extraction processes (Fig. 3a),

$$X = \frac{x_{1,L}}{x_{1,0}} = \frac{1 - F_1 F_2}{\frac{1 - \phi}{1 - \phi / (F_1 F_2)} - F_1 F_2}. \quad (1)$$

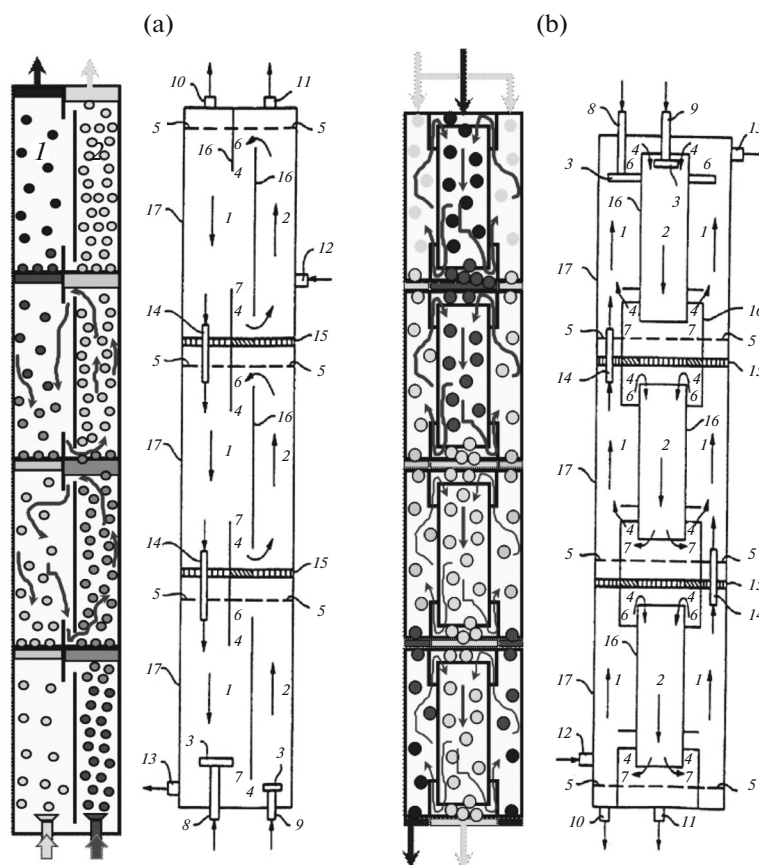


Fig. 2. Scheme and operation of three-phase column extractors [22, 32].

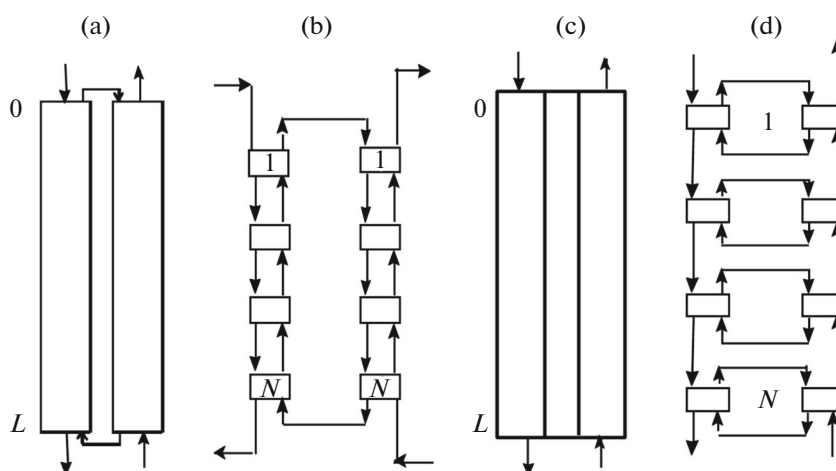


Fig. 3. (a, c) Continuous and (b, d) step embodiments of (a, b) conventional liquid and (c, d) membrane extraction.

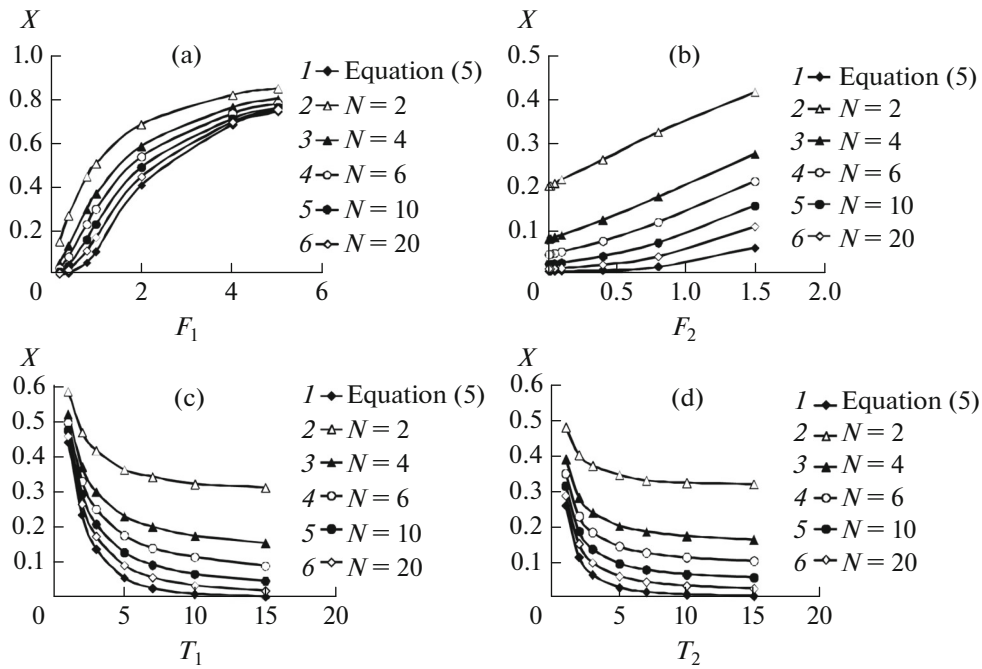
The value of the parameter  $\varphi$  is determined by the equations

$$\varphi = \frac{F_1 F_2 S_1 S_2}{S_2 + F_1 S_1 (1 - S_2)}; \quad (2)$$

$$S_1 = \frac{1 - \exp[T_1(F_1 - 1)]}{1 - F_1 \exp[T_1(F_1 - 1)]}; \quad (3)$$

$$S_2 = \frac{1 - \exp[T_2(F_2 - 1)]}{1 - F_2 \exp[T_2(F_2 - 1)]}, \quad (4)$$

where  $F_1 = v_1/(wD_{\text{ex}})$  and  $F_2 = v_2/(wD_{\text{reex}})$  are the mass-transfer factors in extraction and reextraction, respectively ( $w$  is the organic phase flow;  $v_1$  is the rate of raffinate flow;  $v_2$  is the rate of reextract flow);  $T_1 =$



**Fig. 4.** Relative concentration of the substance ( $X$ ) as a function of (a, b) the mass transfer factor and (c, d) the number of transfer units at (a, c) the extraction and (b, d) stripping in the supported membrane systems (curve 1) and FSLM systems calculated at various stages of extraction (curves 2–6).

$a_1k_1L/v_1$ ,  $T_2 = a_2k_2L/w$  is the number of transfer units at the steps of extraction and reextraction, respectively; and  $L$  is the column height.

For supported liquid membranes (Fig. 3c), the values of  $X$  are calculated from the equation [36]

$$X = \frac{x_{1,L}}{x_{1,0}} = 1 - \frac{1 - \exp\left[\frac{T_2(F_2 - 1/F_1)}{1 + T_2/(T_1F_1)}\right]}{1 - F_1F_2 \exp\left[\frac{T_2(F_2 - 1/F_1)}{1 + T_2/(T_1F_1)}\right]} \quad (5)$$

When  $T_1 = T_2 = T$  and  $F_1 = F_2 = F$ , expressions (1) and (5) become identical and are transformed into the equation

$$X = \frac{x_{1,L}}{x_{1,0}} = 1 - \frac{1 - \exp[T(F - 1)]}{1 - F^2 \exp[T(F - 1)]} \quad (6)$$

*Processes with Stepwise Phase Contact*

For conventional liquid extraction carried out in mixer settlers (Fig. 3b), the output concentration in the raffinate phase is given by [28]

$$X = \frac{x_{1,N}}{x_{1,0}} = 1 - \frac{1}{\frac{1 - F_1^{N+1}}{1 - F_1^N} + \frac{F_1 - F_1F_2}{1/F_2^N - 1}} \quad (7)$$

where  $N$  is the number of steps.

When using an FSLM (Fig. 3d), the initial concentration  $X$  in the raffinate phase is defined by the equation [33]

$$X = \frac{x_{1,N}}{x_{1,0}} = \frac{1 - F_1F_2}{\left[\frac{1 + F_1}{(1 + F_2)F_1}\right]^N - F_1F_2} \quad (8)$$

where  $N$  is the number of circuits in a cascade.

In the case of equal mass-transfer factors at extraction and reextraction ( $F_1 = F_2 = F$ ), Eqs. (7) and (8) become identical and are transformed into the equation

$$X = \frac{x_{1,N}}{x_{1,0}} = \frac{F^N(1 - F^2)}{1 - F^{N+2}} \quad (9)$$

Thus, if the efficiencies of the extraction and reextraction processes are equal, the use of the conventional (Fig. 3b) and FSLM (Fig. 3d) techniques leads to the same results.

It should be noted that formulas (7) and (8) are valid when the interfacial equilibrium is achieved in each mixer settler. For the nonequilibrium case, these relationships are as follows [33]:

$$X = \frac{x_{1,N}}{x_{1,0}} = \frac{1 - F_1F_2}{\left[\frac{1 + AF_1}{(A + F_2)F_1}\right]^N - F_1F_2} \quad (10)$$

where  $A = 1 + 1/t_2 + 1/(F_1 t_1)$ ;  $t_1 = a_1 k_1 V_1 / v_1$ ,  $t_2 = a_2 k_2 V_2 / w$  are the number of transfer units at the extraction and reextraction stages, respectively;  $V_1$  and  $V_2$  are the volumes of the mixers; and  $v_1$ ,  $v_2$ ,  $w$  are the volumetric flows of the phases.

The theoretical relationships between (a, b) the relative concentration of the substance and mass exchange factors and (c, d) the number of transfer units for extraction and stripping in (curve 1) supported membrane systems and (curves 2–6) FSLM systems are demonstrated in Fig. 4. The dependences for the systems with supported liquid membranes and with free supported liquid membranes were calculated using Eqs. (5) and (10), respectively. It follows from the data obtained (Fig. 4) that, if  $N > 10$ , Eqs. (10) and (5) yield similar results, which confirms the similarity of the supported membrane systems and the FSLM.

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