

Applicability of Liquid Membranes in Environmental Protection

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Abstract

One of the modern techniques of mixture separation is the application of liquid membranes. They reveal the ability of selective transport of mixture components in which a liquid membrane constitutes a separate phase which separates two other liquid or gas phases. This property of membranes makes them useful in the textile and food industries, in hydrometallurgy, medicine, biotechnology, environmental protection, in the separation of hydrocarbons and gases, and in the concentration and separation of amino acids, metal ions and other mixtures and suspensions.

Keywords: applications of liquid membranes, emulsion liquid membranes, supported liquid membranes, bulk liquid membranes, environmental protection

Introduction

Industrial development is accompanied by a growing quantity of waste products harmful to the natural environment. Thus, there is a growing demand for new technologies allowing the re-use of raw materials recovered from waste products.

The first scientists to describe liquid membranes (LM) in 1902 were Nernst and Riesenfeld [1]. They investigated the properties of systems consisting of an oil layer separating electrolyte solutions. More interest was aroused by man-made liquid membranes when Li [2, 3] developed methods for emulsion liquid membrane production.

Liquid Membrane - Structure and Mechanisms

Classification and Composition of Liquid Membranes

Liquid membrane is a separate liquid phase which separates two solutions: feeding from received one.

In practice, LM can be divided into several groups [4-10]:

- bulk liquid membrane - BLM,
- supported liquid membrane - SLM,
- emulsion liquid membranes - ELM.

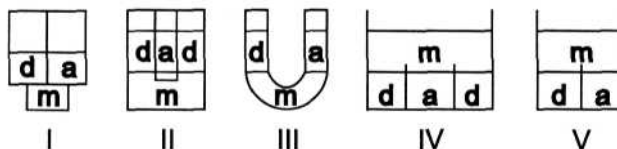


Fig. 1. Bulk liquid membrane systems:

I, II, III - liquid membrane density higher than the density of water,

IV, V - liquid membrane density smaller than the density of water.

a - acceptor phase (water solution), d - donor phase (water solution), m - membrane (organic solution).

A schematic of the simplest liquid membrane is shown in Fig. 1. In the case of BLM the membrane phase is usually mixed intensively so that the diffusion path is limited to the distance of the boundary layer. In the case of transport of substances from aqueous solutions, the membrane is an organic phase of density different than that for water phases.

A decrease of LM (organic phase) volume in relation to solution volume is obtained in the case of SLM. Pores of a polymer medium are saturated with a liquid membrane (Fig. 2). The most popular supports are membranes made of propylene, polysulfone, polyvinylidene fluoride and cellulose acetate. The choice of a polymer

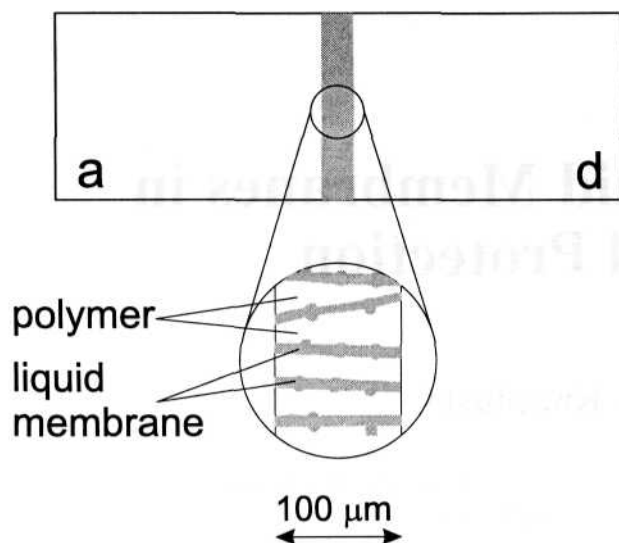


Fig. 2. Schematic of liquid supported membrane.

depends on corrosion resistance in the organic environment and time-independent and sufficiently high porosity. A direct influence on the mass flux is effected by the LM thickness, i.e. the length and bendiness of the diffusion path. SLM contains very small amounts of LM, which enables the application of expensive, selectively operating compounds. The main disadvantage of these membranes is their insufficient stability, i.e. elution of the LM from the support pores and polymer corrosion.

The simplest method to increase diffusion rate through the membrane is an increase of the membrane-solution contact area and shortening of the diffusion path. This conclusion was a basis for developing ELM by Li [2, 3] in 1968 and its modification - a surface-active membrane. The method of ELM production is illustrated in Fig. 3. The ELM structure corresponds to the double water/oil/water emulsion which is formed as a result of emulsifying the organic phase in the aqueous solution which is a receiving solution in the membrane system. To obtain an emulsion of satisfactory durability it is necessary to have a properly chosen surfactant.

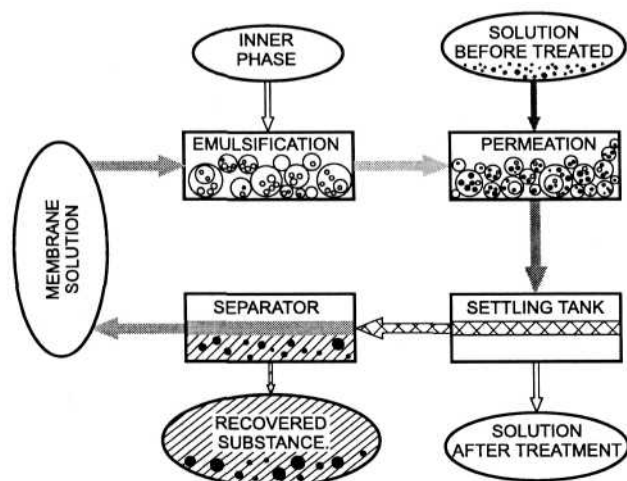


Fig. 3. Diagram representing recovery of a substance by means of ELM.

Practical properties of BLM, SLM and ELM are given in Table 1.

Table 1. Comparison of the characteristics of liquid membranes [4, 11-13].

Membrane type		A_m/V_m m	V_f/V_m -	J_m/V_m mol m ⁻³ h ⁻¹
BLM	-	0.1-1	0.2-10	0.6
SLM	flat module	10-100	100-1000	5
	spiral module	100-1000	-	-
	capillary module	1000-10000	2000-10000	-
ELM	-	1000-3000	-	10-200

A_m/V_m - quotient of the membrane surface and its volume,
 V_f/V_m - quotient of the feeding solution volume to membrane phase volume,

J_m/V_m - mass flux in terms of the membrane phase volume.

When selecting LM in the case when it separates water phases (which is the most frequent case), the following should be kept in mind:

- solubility of LM in water should be as low as possible,
- the LM should be a selective solvent for substances being separated,
- its fugacity, especially when toxic, should be low,
- viscosity of LM should be as small as possible to obtain possibly high diffusion coefficients.

Transport Mechanism

In all types of liquid membranes mentioned above the transport mechanism is the same, and according to the film model of mass transfer it can be divided into the following steps:

- diffusion through the boundary layer in the feed solution,
- sorption on the feed solution/liquid membrane interface,
- diffusion through the boundary layer on the feed side,
- transport in the membrane, e.g. convective transport in the mixing zone,
- diffusion through the boundary layer on the receiving side,
- desorption on the membrane/receiving solution interface,
- diffusion through the boundary layer in the receiving solution.

Five types of mass transfer can be distinguished: simple mass transfer, combined co- and countercurrent mass transfer with a carrier, as well as simple and complex mass transfer with a carrier whose mechanisms are illustrated in Fig. 4.

A chemical compound which plays a role of a carrier in the LM should be characterized by

- quick binding and release of particular substances,

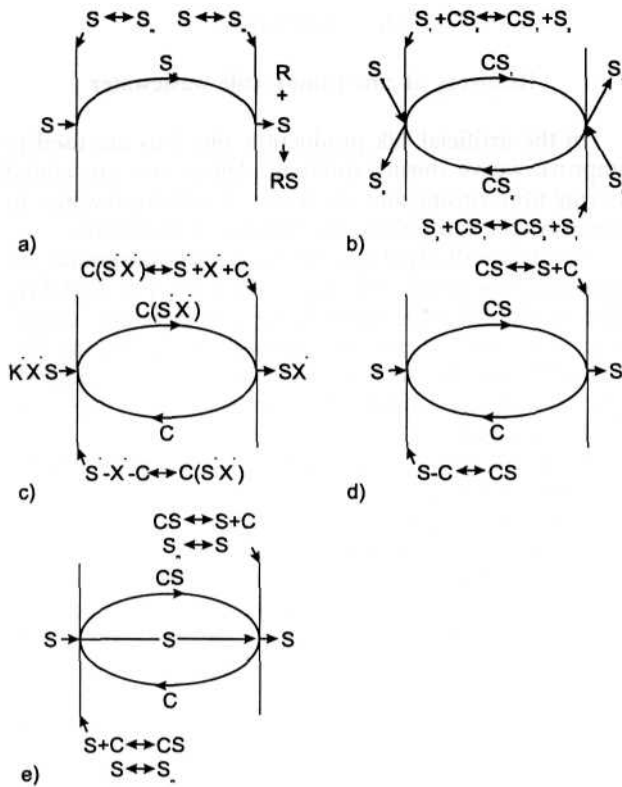


Fig. 4. Mechanisms of transport in LM:

- a) simple mass transfer,
- b) combined cocurrent mass transfer with a carrier,
- c) combined countercurrent mass transfer with a carrier,
- d) simple mass transfer with a carrier,
- e) complex mass transfer with a carrier.

- ability to selective and reversible binding of a component in the solution,
- non-binding with a solvent,
- lack of ability to coalesce,
- intoxicate.

The most frequently used carriers include phospho-organic compounds, crown ethers, hydroximes and amines. Their structure and properties are discussed in the literature [4, 8, 13, 14].

A disadvantage of liquid membranes, which limits their industrial applicability, is instability. This is revealed by elution of the carrier from the membrane to aqueous solutions and formation of emulsions on the membrane/aqueous solution interface.

Applicability of Liquid Membranes

Applications of Bulk Liquid Membranes

BLM's have not found application in industry mainly due to a small contact area of the membrane with other phases, and slow process kinetics. They are used, however, in laboratory measurements for evaluation of various process kinetics constants employed in the description of transport through membranes. This is because of

their easy construction, strictly determined mass transfer area and membrane thickness.

An attempt to increase mass transfer area is undertaken by using pertractors shown in Fig. 5 [15]. Rotating surfaces covered with hydrophilic or hydrophobic material are so located that for some time they are immersed in the membrane and then in the feed (receiving) solution. This causes an increase of mass transfer area because liquid wet the rotating surface and can be taken over by the other phase.

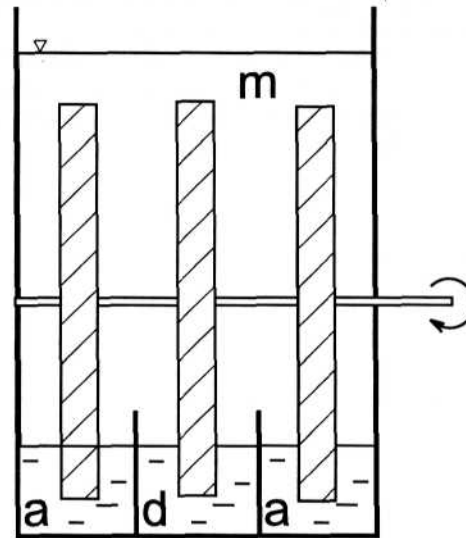
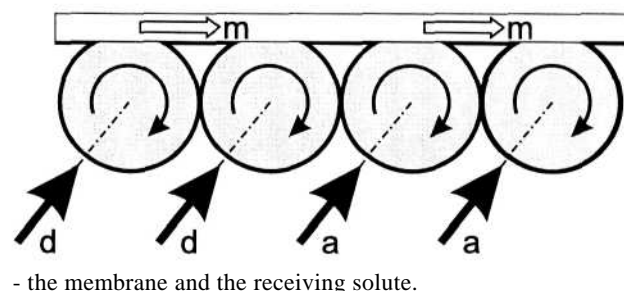


Fig. 5. Rotary pertractor.

Another attempt to increase the mass transfer effectiveness without producing emulsion is crossing the flow of two streams: membrane and the feeding solution, or the membrane and the receiving solution, so that they are put in vortex motion along their own axis by each other. This causes a multiplication of the contact area renewal and considerable intensification of mass transfer. A schematic of the process is shown in Fig. 6 [16].

Fig. 6. Schematic representation of vortex flow of: d/m - the feeding solute and the membrane, m/a



- the membrane and the receiving solute.

Application of Supported Liquid Membranes

Up to now no mention has been made in the literature on a full industrial application of SLM. However, there are many laboratory-scale and pilot-scale installations where these membranes are used. SLM's are a subject of numerous studies.

Gas Separation

A new application of SLM is their use in gas separation processes, e.g. O_2/CO_2 , N_2/CO_2 , $SO_2/CO_2/N_2$, etc. in the production of biogas CH_4/CO_2 [17-19].

Effects of the separation of oxygen and carbon dioxide using SLM in the cellulose acetate membranes are illustrated by the permeation coefficients and CO_2 and O_2 separation coefficient given in Table 2.

Table 2. Comparison of permeability and separation coefficients for CO_2 and O_2 in SLM [6].

Membrane	Permeability coefficient $P \cdot 10^9$ [mol · m/(m ² · s · Pa)]		Separation coefficient a_{CO_2/O_2}
	CO_2	O_2	
Water	703	32	22
Polymer with water	134	6.7	20
Polymer with saturated $CeHCO_3$ solution	251	0.17	1500
Polymer with saturated $CeHCO_3$ solution + 0.5 sodium arsenate	717	0.175	4100

Applications in Analytical Methods

SLM's are also used to prepare samples for analysis and for sampling in the natural environment. The present applications include:

- preconcentration of aliphatic and aromatic amines for chromatographic analysis [20, 21],
- preconcentration of carboxylic acids from air [22, 23],
- preconcentration of herbicides present in natural water [24],
- preconcentration of metals for atomic absorption spectroscopic analysis [25].

Emulsion Liquid Membranes

ELM separates two liquid phases from which one is surrounded by this membrane. Transfer of a given component from the continuous phase to the membrane corresponds to the process of selective extraction. On the inner surface of the membrane, the process of re-extraction to the inner phase takes place.

Metal Separation Recovery of zinc from textile wastewater

In the artificial silk production zinc ions are used to improve weave during spinning. These ions are eluted during fibre rinsing and are removed with wastewater. In this way zinc can pollute the natural environment.

Several methods of zinc recovery from wastewater are applied in the textile industry: precipitation of $Zn(OH)_2$, ZnS or $ZnCO_3$ from waste water, ion exchange, extraction with a solvent, reverse osmosis, distillation and biological treatment. A disadvantage of all these methods are high financial outlays not compensated by the value of zinc recovered.

In the world, there are three zinc recovery installations by the ELM method:

- Glanzstoff, Austria, 0.7 m³/h,
- CFK Schwarz, Germany, 0.2 m³/h,
- AKZO/Ede, the Netherlands, 0.2 m³/h.

Figure 7 shows a schematic diagram of a one-stage zinc recovery installation by the EMC method. A LM, carrier, surfactant and solvent of the inner phase are emulsified in a homogenizer. The obtained emulsions are dispersed countercurrently in the column with a separated solution. At the final stage, the emulsion is broken by electric current of several thousand volts at 1000 Hz [5].

Nickel recovery from spent galvanic solutions

The most popular method of nickel recovery is to precipitate the metal in the form of hydroxides or sulfides. After completing the process, dried sludge is disposed on a dumping site. Reverse osmosis and electrodialysis are used more frequently now. The disadvantages of the above methods are high costs of pretreatment and insufficient removal of metal ions from the permeate. Nickel can be separated using traditional extraction, but the method is relatively expensive if the extraction is expected to be efficient.

At the moment, the best solution seems to be a combination of the ELM process with the traditional extraction. Initially, the process takes place in a permeation column to which spent galvanic solutions are introduced. When Ni is extracted in 90%, the emulsion is transferred to a de-emulsifying apparatus from where Ni is received to be recycled to the galvanic process. Wastewater containing 10% of Ni is transported to the apparatus in which conventional extraction takes place. Organics present in the stream are recycled to the process.

The system described above is implemented in the bicycle factory in Austria. Its throughput reaches 150 dm³/h. The initial solution is concentrated from 3 mg/dm³ to 80 mg/dm³ [26].

Recovery of uranium and copper

Results obtained in the uranium recovery system are presented in studies [27]. In this system 90% of uranium is recovered and concentrated to 6 g/dm³.

A similar pilot-plant installation described in [28] was used for copper recovery. A carrier was a compound

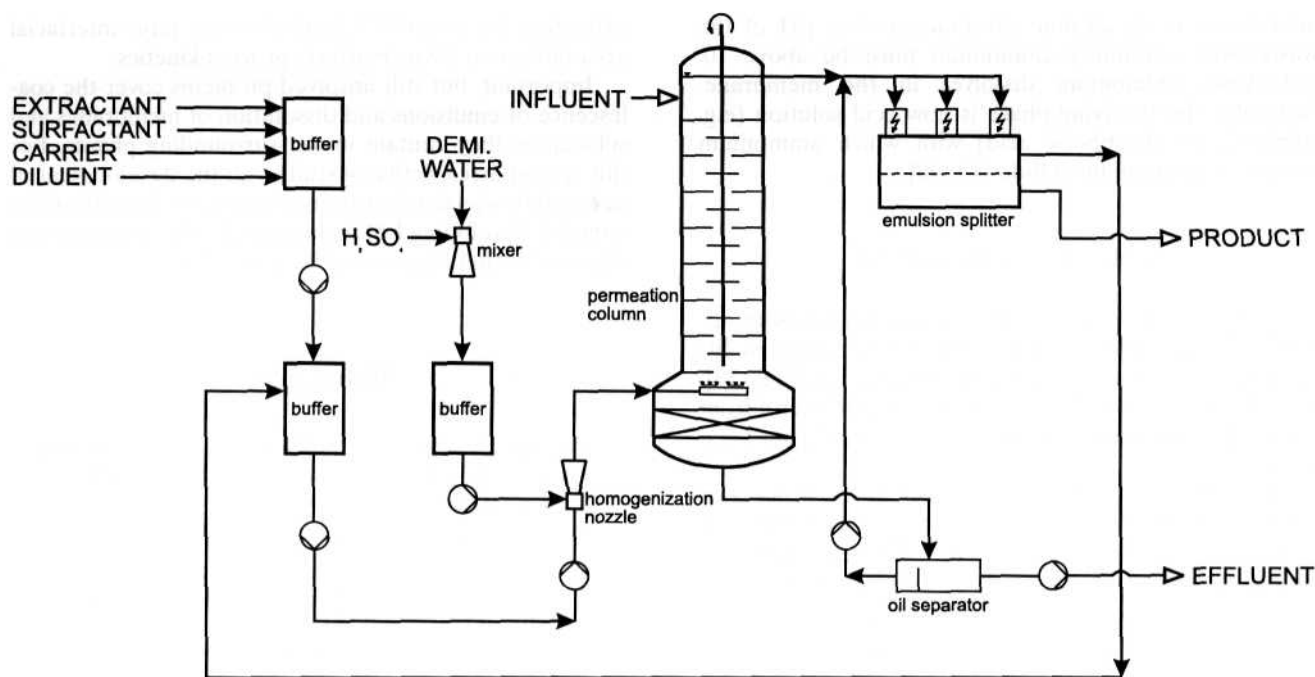


Fig. 7. Schematic of a one-stage ELM plant for zinc removal.

from hydrooximes group of concentration equal to 2.5%, and a receiving solution was 20% sulphuric acid. The installation throughput was $2.7 \cdot 10^4$ tons Cu/year.

Disposal of heavy metals in metallurgical plants and incineration plants

Wastewater from metallurgical plants usually contains a large amount of ions of various metals. Results obtained in the pilot-plant installation for metal recovery, of throughput 0.2 m³/h are given in Table 3 [5]. In connection with a selective action of carriers in specified conditions, such metals as Zn, Cd, Cu and Pb were extracted from the feed solution much better than the others.

Table 3. Results obtained in the pilot-plant installation for metal recovery [5].

Metal	Flux [mg/dm ³]	Raffinate 1 [mg/dm ³]	Raffinate 2 [mg/dm ³]	Receiving phase [mg/dm ³]
Zinc	230	5	0.2	22000
Cadmium	2.7	0.1	0.02	270
Copper	1.1	0.1	0.007	90
Lead	0.5	0.02	0.01	6
Iron (II)	90	90	90	20
Iron (III)	20	15	12	700
Cobalt	0.4	0.4	0.38	0.1
Nickel	0.3	0.3	0.3	0.1
Manganese	25	24	23	20
Magnesium	37	37	37	4
Calcium	220	220	220	44
Sodium	60	60	60	6

Acidified water used in municipal incineration plants to precipitate heavy metal ions from gases can be treated in a similar way. After initial removal of mercury ions on ion exchangers, wastewater is introduced to the ELM system. Metals are separated at two stages. The MTPA carrier is used which easily releases zinc ions under the influence of diluted sulphuric acid, while the release of other metals ions is much more difficult. Zinc in the concentrated hydrochloric acid can be used immediately in the metallurgical industry. At the second stage, re-extraction with concentrated hydrochloric acid is carried out. Metals concentrated in the acid are then precipitated in the form of salts.

Phenol removal

An industrial installation for the removal of phenol from wastewater was built in China in the late 80's. It treats 0.5 tons of a solution containing 1000 mg of phenol/dm³ per hour. The solution after treatment contains 0.5 mg of phenol/dm³ [29].

The pH value of wastewater must be below 9 so that phenol could be in a not dissociated form. In this state it is soluble in the membrane which consists of an organic phase (e.g. hydraulic oil or kerosene) and a surfactant. In the receiving phase there is a reaction involving a sodium base present there, and as a result sodium phenolate is formed. The dissociated form of phenol, phenolate, is insoluble in the membrane and is concentrated in the receiving phase (in emulsion droplets).

Ammonium removal

The mechanism of ammonium removal by ELM is the same as in the case of phenol, except for the fact that

ammonium is an alkaline substance and so pH of the wastewater containing ammonium must be above 10. Otherwise, ammonium dissolves in the membrane. Naturally, the receiving phase is now acid solution (e.g. sulphuric or phosphoric acid) with which ammonium forms e.g. ammonium sulfide [15, 30].

Applications in biochemistry

Until present there no ELM installation has been applied in biochemistry. Applicability of this method in citric acid extraction [31], recovery of lactic acid [32, 33], penicillin separation [34, 35], removal of cholesterol from blood [5] and separation of amino acids [36, 37] has been studied.

An interesting ELM application is in the process of fermentation in which main problem is the separation of products during fermentation. Usually, this is a multi-stage operation involving precipitation, filtration and crystallization. Instead of the above techniques ELM counter current to the fermentation process can be applied.

ELM's can find applications in protein production [36]. Figure 8 shows transport of proteins through the membrane and their concentration. In the membrane proteins form micelles without which they could be denatured.

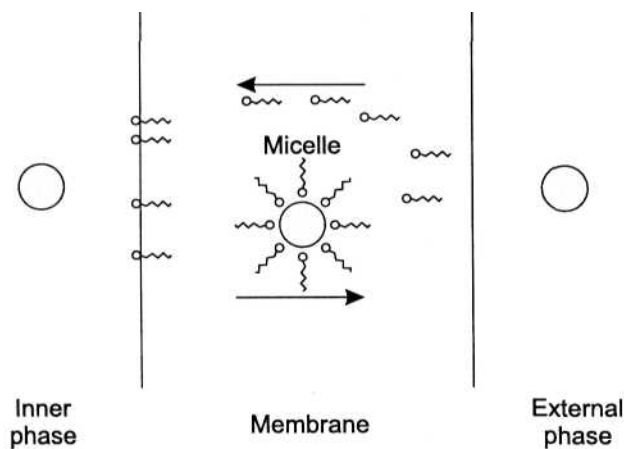


Fig. 8. Extraction of proteins using the membrane process.

Concluding Remarks

Importance of LM in separation processes is a result of the following factors:

- very high separation selectivity,
- mass transfer can take place on carriers,
- solutions of products can be concentrated,
- no expensive pretreatment is necessary,
- the process can be carried out in a continuous way,
- process costs are relatively low.

Membranes enable also a combination of permeation and chemical reactions inside or outside the membrane.

The main advantages of ELM's include much lower solvent consumption than in the case of conventional

extraction (by about 90%) and also very large interfacial area ($10^6 \text{ m}^2/\text{m}^3$) which affects process kinetics.

Important, but still unsolved problems cover the coalescence of emulsions and dissolution of membranes and substances they contain in the surrounding phases. For this reason, irrespective of studies on the development of new highly-selective fast-transport systems, investigations aimed at developing LM techniques for the application in chemical technology should be carried out.

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