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SEPARATION OF AROMATIC INTERMEDIATES OF BIOLOGICAL INTEREST USING EMULSION LIQUID MEMBRANES

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Abstract

Established applications of emulsion liquid membranes (ELM) refer to refining in hydrocarbons and hydrometallurgical processing, rehabilitation of poisoned patients. In this work we investigated the separation of aromatic compounds of biological interest, more often encountered as intermediates in dyes and drugs industry: aniline, nitrobenzene, ortho and para-toluidine, using emulsion liquid membranes. The experimental results showed that in the case of basic substances separation the main physicochemical characteristics which have to be considered are alkalinity and water solubility. Thus, for the liquid emulsion membranes operation it is preferred to have a basicity as high as possible and a solubility as low as possible.

Key words: aromatic intermediates, biological interest compounds, liquid membranes, separation

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1. Introduction

Nowadays, wastewater is a potential source of pollution causing serious problems to the environments (Gómez et al., 2009; Manea et al., 2013; Modrojan et al., 2014). Thus, the amounts of wastewaters discharged in the environment from a high variety of industrial activities represent an important source of toxic, refractory, carcinogenic and low degradability compounds (Arsene et al., 2013; Santos and Rodrigues, 2014).

Due to the complex composition of the effluents, most of the treatment techniques such as: chemical precipitation, coagulation-flocculation, flotation, ion exchange, electro-oxidation and adsorption have their own limitations (Modrojan and Pincovschi, 2014; Tjoon et al., 2013). In this context, the treatment of wastewater using emulsion or supported liquid membranes represents an intense

process, with a huge application potential (Diaconu et al., 2012).

In particular, emulsion liquid membranes (ELM) are becoming more frequently used in the field of wastewater treatment because they are capable to successfully compete with traditional schemes (Craciun et al., 2009; Kurniawan et al., 2006).

The presence of organic toxic solutes in industrial wastewater is a common environmental problem (Namane et al., 2014; Orbeci et al., 2014). Aniline (amino-benzene) is known to be a harmful and persistent pollutant and its presence in wastewater requires treatment before disposal. Aniline is a carcinogenic chemical common in industry and industrial wastewater (Agrawal et al., 2008). Hence, alternative technique identification is required. Emulsion Liquid Membrane (ELM) is one of the techniques used to remove and recover

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contaminants from wastewaters (Craciun et al., 2011). The field of liquid membrane technology is currently undergoing a rapid expansion in research, as well as its application as an industrial separation process (Zaharia et al., 2013).

Membrane separation, especially ELM enjoys a great success in the field of separation techniques due to its outstanding characteristics such as: simultaneous pollutants removal and materials recovery in a single unit, high efficiency due to large surface area available for mass transfer, high selectivity especially when carrier agents are used in the membrane phase that bind exclusively with target compounds; high fluxes, reusability and low energy consumption compared to other separation processes, low costs (Park et al., 2006; Zaharia et al., 2012).

In this work, the emulsion liquid membrane was employed in removal of biological interest aromatic compounds, more often encountered as intermediates of dyes and drugs industry: aniline, nitrobenzene, ortho and para-toluidine. Also, the research was focused on establishing the influence of operational parameters such as: contact time, pH, HCl concentration in the receiving phase and primary emulsion volume on the extraction yields.

2. Experimental

2.1. Materials and methods

HCl 25% (Merck) and distilled water were analytical grade, while SPAN 20 and SPAN 80 (Sigma-Aldrich) have a technical purity.

2.2. Experimental procedure description

The analysis of aromatic derivatives content in the source, receiving (aqueous) and organic phase was carried out by means of spectrophotometric extractive technique. The aqueous solutions used as source phase in the experiments were prepared in the laboratory.

The characteristics of the chemical substances considered for the extraction and their physical and chemical characteristics are listed in Table 1.

Tehnico-economical considerations require that the primary emulsion volume (toluene or cyclohexanol / acidic aqueous receiving phase) to be as small, in order to avoid the high cost of the surfactant, large emulsion volumes handled and excessive consumption of acids. Through this study, in the case of source phases containing basic and neutral organic compounds the minimum amount of emulsion is determined, or more accurately the volume ratio, R, primary emulsion / source phase, which can be used without seriously affecting the extraction yield.

The extraction yields were calculated based on the initial amount of organic compounds and after 15 minutes of contact, in the source phase, in order to be compared with the conventional solvent extraction yield (Diaconu et al., 2011). The systems used in the experimental studies, as source phase were presented in Table 2. For all the systems the following parameters were maintained constant:

- initial source phase volume $V_{fst} = 200 \text{ cm}^3$,
- contact time $t = 15 \text{ minute}$;
- the composition of primary emulsion.

The emulsion was prepared by mixing equal solution volumes of 5% SPAN 20 in toluene or cyclohexanol and receiving aqueous solution at pH = 1 (made with 0.1 M hydrochloric acid).

3. Results and discussion

3.1. Influence of primary emulsion volume on the extraction yield with ELM

The results of the experimental study conducted at volumetric ratios, R, emulsion phase (V_{fe}) / source phase (V_{si}) ranging from 1/10 and 1/1 are shown in Figs. 1-6.

Table 1. The physicochemical characteristics of the used substances

Substance	Chemical structure	Symbol	P_f °C	K_b^* 10^{-10}	d_{20} g/cm ³	Solubility	
						Water g/L	Cyclohexanol or toluene g/L
Nitrobenzene	C ₆ H ₅ -NO ₂	NB	210.9	-	1.210	0.2	Total miscible
Aniline	C ₆ H ₅ -NH ₂	A	184.4	3.82	1.022	3.6	Total miscible
o-Toluidine	<i>o</i> C ₆ H ₅ -NH ₂ (CH ₃)	<i>o</i> -T	192.7	2.50	0.990	1.5	Total miscible
p-Toluidine	<i>p</i> C ₆ H ₅ -NH ₂ (CH ₃)	<i>p</i> -T	200.0	1.48	1.010	2.5	Total miscible

Table 2. Chemical composition of the source phases

Symbol	A (ppm)	NB (ppm)	<i>o</i> -T (ppm)	<i>p</i> -T (ppm)
FS ₁	120	-	-	-
FS ₂	-	120	-	-
FS ₃	-	-	120	-
FS ₄	-	-	-	120
FS ₅	60	60	-	-
FS ₆	60	-	60	-
FS ₇	60	-	-	60

At small R ratios (Figs. 1, 2 and 3) it was found that the source systems containing nitrobenzene or lower alkalinity compounds are harder extractable than those containing aniline and p-toluidine. As shown in Figs. 1-6, the higher the volume ratio R is, the yield increase is most important, regardless of the membrane solvent, and the source phase composition. This leads to the conclusion that the extraction yield strongly depends on the volumes ratio, at the same extraction time and acid concentration in the receiving phase, regardless of the organic substances content in the aqueous solution (Figs. 4, 5 and 6).

However, in all the experiments, the best results were obtained using cyclohexanol as solvent, fact that can be explained by its higher polarity compared to toluene.

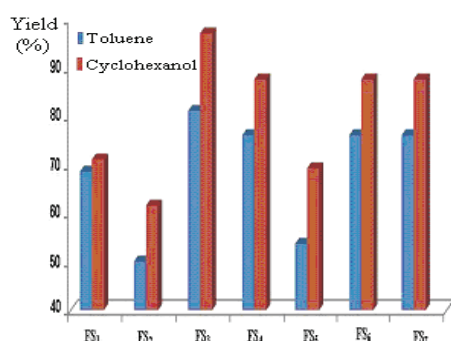


Fig. 1. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/10, F_{SI} system

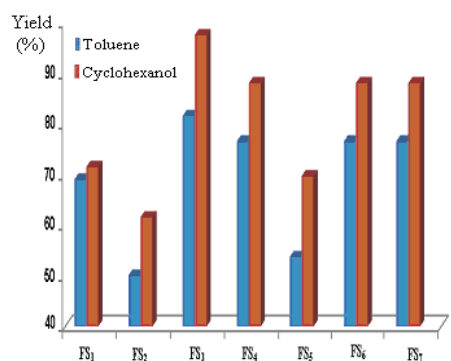


Fig. 2. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/8, F_{SI} system

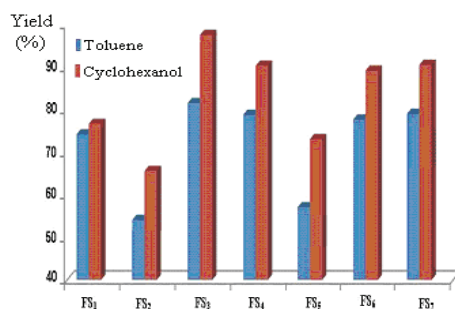


Fig. 3. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/6, F_{SI} system

From the practical point of view, the recommended working conditions for the extraction of basic aromatic derivatives are: polar organic solvent, volume ratio R, emulsion phase (V_{fe}) / source phase (V_{si}) closer to 1, but acceptable, in technologically and economically terms (Fortună et al., 2012).

3.2. The influence of HCl concentration in the receiving phase

For substances having a weakly basic character, respectively aniline, o- and p-toluidine, theoretical, the extraction yield using emulsion liquid membranes is affected by acid concentration in the receiving phase, respectively by its pH.

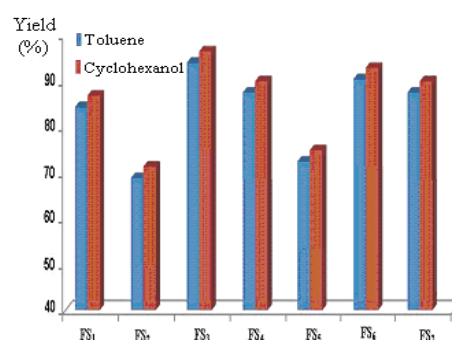


Fig. 4. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/4, F_{SI} system

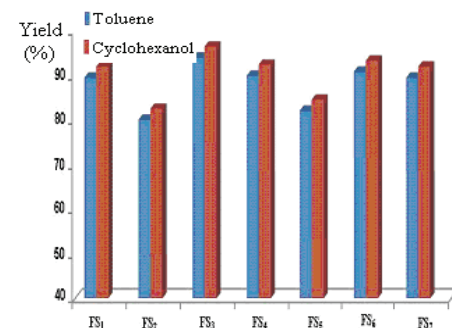


Fig. 5. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/2, F_{SI} system

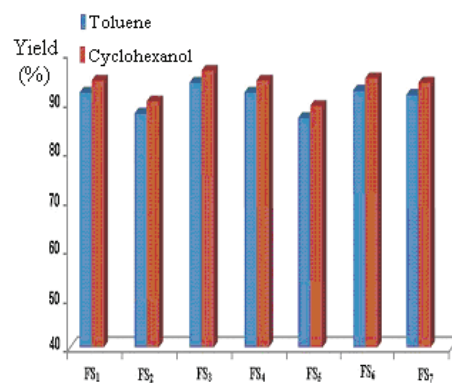


Fig. 6. The extraction yield variation at a volume ratio, R, emulsion phase (V_{fe}) / source phase (V_{si}) = 1/1, F_{SI} system

In laboratory, the extraction studies have been performed with ELM for FS_1 , FS_6 and FS_7 systems with receiving solutions having pH between 1 and 6, adjusted using hydrochloric acid corresponding solutions. Liquid emulsion membranes used in the process were based on SPAN 20 and SPAN 80 in toluene and cyclohexanol (Table 3).

Table 3. Emulsion membranes used in the study

Symbol	Solvent	Surfactant
MTS80	toluene	SPAN 80
MTS20	toluene	SPAN 20
MCHS80	cyclohexanol	SPAN 80
MCHS20	cyclohexanol	SPAN 20

The solvent used for the non-ionic surfactant is toluene or cyclohexanol. The source phase and membrane volumes entered into the system, respectively 200 cm^3 and 50 cm^3 , the contact time, $t = 15\text{ minutes}$ and the chemical composition of the source phase (Table 2) were kept constant. The results are shown in Figs. 7-9. It is noted that in general for all source phases studied, the extraction yields with ELM increase with pH decreasing, the maximum yields being recorded for $\text{pH} = 1$.

In this case, the organic compounds solubilized in the organic phase, reach to the organic phase / receiving phase interface, where due to the hydrochloric acid presence pass into the aqueous phase, shifting the distribution equilibrium between the three stages to a new organic substance transfer from the source phase to the receiving aqueous phase (Barjoveanu and Teodosiu, 2009).

The negative synergistic effects are, however, unexpected, particularly evident for the membrane systems containing o-toluidine, difficult to explain by means of the distribution coefficients or alkalinity constants. Of course, aromatic amines extraction from source phase into receiving depends on the existing substituents in their aromatic ring. It is noted the higher extraction yield of p-toluidine compared to aniline on the full range of pH. This is not justified because $\text{p}K_{\text{b, aniline}} > \text{p}K_{\text{b, p-toluidine}}$.

The explanation lies in the lower toluidine solubility in water and therefore an easier passage in toluene or cyclohexanol (membrane). In order to explain the effect of the $\text{p}K_{\text{b}}$ value on the aromatic amines separation, beside o-toluidine, p-toluidine experiments were carried out.

The low pH value has a positive influence on all the amine's extraction because favours the amine immobilization in the aqueous receiving phase. However, if the amine is more soluble in water (ex. aniline, toluidine compared with o-toluidine) its extraction is going to be more difficult at less acidic pH. Practically, at low pH ($\text{pH} < 3$) the extraction is influenced by $\text{p}K_{\text{b}}$ and at $\text{pH} > 3$ the extraction is influenced by the solubility in water.

The most effective p-toluidine separation is achieved at $\text{pH} = 1$, being the strongest base, while o-

toluidine is extracted better in the range $2 < \text{pH} < 4$ being the less soluble in water.

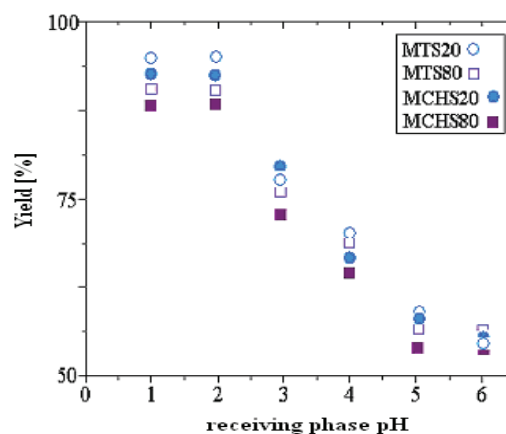


Fig. 7. The pH influence on extraction yield in the FS_1 system

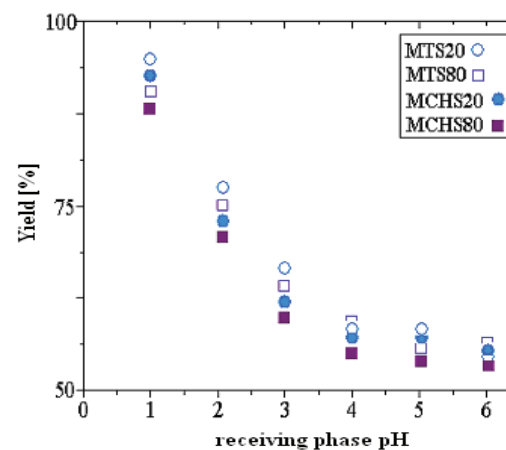


Fig. 8. The pH influence on extraction yield in the FS_6 system

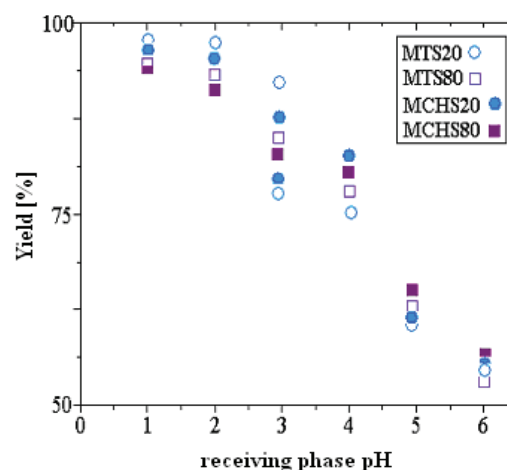


Fig. 9. The pH influence on extraction yield in the FS_7 system

The aniline and o-toluidine extraction yields from the mixture are lower than those obtained for the pure compounds, but the alkalinity influence is the same, o-toluidine extraction efficiency being

higher in this case. The total extraction yield for p-toluidine-aniline mixture is favoured by a positive synergistic effect, but is close to pure components yields. At the same amine content to be extracted, the yield is influenced by the surfactant included in the emulsion membrane, in this case being superior for SPAN 20 compared to SPAN 80 (Fig. 7-9). Favourable influence manifested by SPAN 20 on the extraction is canceled by the osmotic effect leading to swelling of this type of emulsion membrane by water diffusion from the source phase to membrane phase.

Illustrating this effect for FS₆ and FS₇ phases (Figs. 10 and 11), it results that, although the osmotic effect is also observed for the use of SPAN 80 as surfactant, in this case this is much smaller.

The emulsion swelling is an issue that leads to at least three drawbacks:

- ✓ lowering the concentration factor through water transportation into the receiving phase, so is diluted;
- ✓ primary emulsion breakage due to receiving solution particle size increase from the organic solvent, leading to phase mixing;
- ✓ the occurrence of unexplained results in graphs showing the extraction efficiency on pH, making difficult to optimize the working parameters.

3.3. Influence of pH on the concentration factor

For the emulsion membranes extraction, important is the *concentration of the components from the source phase to the receiving phase*, which can be followed, as technological solution, by the application of classical separation and concentration techniques, leading to *classic hybrid membrane technology* (Musteret and Teodosiu, 2007). In the case of primary source phase, solvent extraction would involve the use of high capacity containers, and significant amounts of solvent, which would involve, ultimately, unacceptable operating costs from technical and economical point of view.

Another problem appears when the solvent is contacted with the source phase, thus system performances depend on stirring and container shape. Using emulsion liquid membranes, the contact surface problem is solved, because an enormous surface mass transfer is achieved (Negoescu et al., 2013). In this case, when the concentration is achieved in the internal receiving phase, the problems related to the subsequent extraction with solvents or other separation process, it is solved the operated volumes being a few times lower. In this study was monitored how often the receiving phase was concentrated in aniline, o-toluidine, p-toluidine, and their mixture, depending on the internal phase pH and the surfactant nature used in the primary emulsion preparation, in the case of cyclohexanol as membrane solvent. The results are presented in Table 4. Although the extraction yields are high with MCH S20, however, due to strong swelling of the receiving phase, concentration factors are smaller.

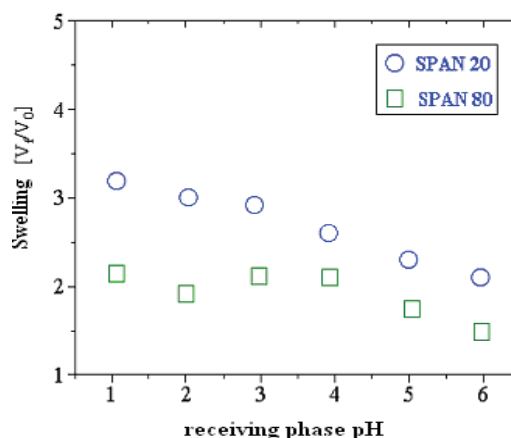


Fig. 10. The pH influence on emulsion membrane swelling for FS₆ system

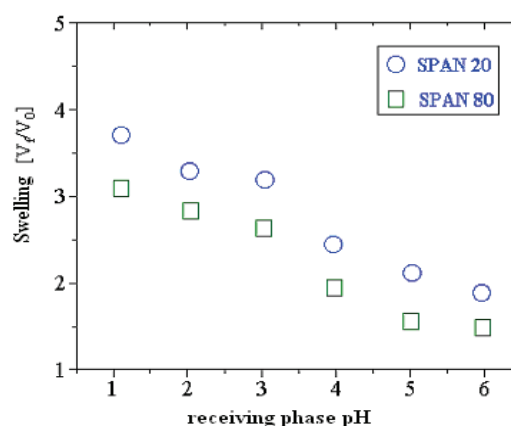


Fig. 11. pH influence on emulsion membrane swelling for FS₇ system

Table 4. The receiving phase pH influence on concentration factor

	$f = \frac{Cf_s}{Cf_R}$					
	pH					
	1	2	3	4	6	Obs
FS ₆	6.2	4.3	0.9	0.8	0.6	SPAN 20
	9.5	7.3	2.4	1.6	0.9	SPAN 80
FS ₇	7.1	3.2	1.8	1.3	0.7	SPAN 20
	8.2	6.7	2.3	1.4	1.0	SPAN 80

It is possible that SPAN 20 to facilitate the aniline and toluidine transport together with an appreciable amount of water. The study done in order to highlight the pH effect reconfirms the previous experiments, namely that at low pH concentration factors are high. The observed differences (especially for SPAN 20) can be justified by breaking the emulsion caused by undesired, retro-osmotic transfer, of water.

3.4. The contact time influence on ELM swelling

It is also interesting the influence of the contact time on the membrane swelling, depending

on the nature of membrane solvent (T - toluene or CH - cyclohexanol). The influence of the receiving phase pH on the swelling, at a determined contact time between the phases was studied.

Maintaining constant the receiving phase pH, SPAN 80 and volume ratio R, was determined the emulsion volume for each source phase type and same type of emulsion. Swelling results are shown in Table 5. It is observed that at a low contact time, swelling varies relatively little according to the source phase composition, but largely depends on the nature of membrane solvent.

Correlating the results and concomitantly following the maximum extraction yield and minimum swelling, the conclusion is that, the optimum working conditions are: contact time, $t \leq 25$ minutes for emulsions with SPAN 80, for all systems FS₁, FS₆, FS₇, and using cyclohexanol as membrane solvent. However at a contact time $t \leq 10$ minutes, for toluene emulsions the results are satisfactory.

Table 5. Contact time influence on emulsion liquid membranes swelling

System		Emulsion swelling at time (min)							
		10	20	30	40	50	60	70	80
FS ₁	M T	1.3	1.4	1.6	1.9	2.0	2.1	2.4	3.2
	M CH	2.0	2.4	2.5	2.6	2.6	2.7	2.8	2.8
FS ₆	M T	1.0	1.5	1.6	1.7	1.9	2.4	3.1	3.3
	M CH	1.9	2.0	2.0	2.1	2.1	2.1	2.2	2.3
FS ₇	M T	2.0	2.1	2.5	2.6	2.8	2.3	2.5	2.9
	M CH	2.0	2.0	2.1	2.1	2.1	2.1	2.2	2.3

4. Conclusions

In this work we aimed to evaluate the influence of operational parameters such as: contact time, pH, HCl concentration in the receiving phase and primary emulsion volume on the biological interest aromatic compounds separation effectiveness, most often found as intermediates in the dyes and drugs industry.

Based on the experimental results it was established that at separation of basic species using emulsion liquid membrane is necessary to provide the following operational conditions:

- surfactant: SPAN 80;
- membrane solvent: cyclohexanol;
- receiving phase/membrane solvent ratio $f_{FR}/S_M = 1$;
- receiving phase pH, close to 1;
- contact time lower than 30 minutes;

The effects of operational parameters above mentioned ensuring consist of:

- concentration factors higher than 2;
- extraction efficiencies higher than 60%.

The primordial physico - chemical characteristics of the basic substances exposed to separation that have to be considered are: alkalinity and water solubility.

Thus, for the operation of liquid emulsion membranes is preferred that: the basicity to be as high as possible and the solubility as low as possible.

Acknowledgements

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