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Extraction of ethanol from aqueous solutions by emulsion liquid membrane: optimization of operating conditions and influence of salts in the feed phase

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ABSTRACT

Extraction of ethanol from aqueous solutions with or without salts by emulsion liquid membranes (ELMs) was investigated. The important parameters governing the extraction behavior of ethanol were analyzed. These parameters were surfactant concentration and nature, type of diluents, volume ratio of membrane phase to internal phase, emulsification time, stirring speed and treat ratio. Excellent performances in terms of both extraction efficiency and kinetics were achieved by using a w/o (water-in-oil) emulsion formulated on the basis of Span80 as a surfactant, hexane as a diluent and distilled water as an internal phase. The highest ethanol extraction was obtained by using 8 wt% of Span 80, volume ratios of organic membrane phase to internal phase of 1 and of emulsion to external phase of 0.0667, an emulsification time of 10 min and a stirring speed of 400 rpm for an initial ethanol concentration in the external phase of 0.8 M. The ethanol extraction was close to 95%for a contact time of 8 min. It was observed that the presence of a salt in the external aqueous phase decreases the extraction efficiency of ethanol, and that this phenomenon depends on both salt nature and concentration. It was found that the lowering of the ethanol extraction efficiency follows the following order: $CaCl_2$>NaCl>KCl, which was assigned to both osmosis phenomenon and co-transport of water by salt diffusion.

Keywords: Emulsion liquid membrane; Ethanol; Extraction; Salt effect; Span 80

1. Introduction

Wastewater is a potential source of pollutant causing serious problems to environments. The methods commonly used for the removal of soluble organic pollutants contained in waters are activated carbon adsorption, reverse osmosis or nanofiltration, chemical or biological oxidation and advanced oxidation technologies. However, these techniques have their own limitations [1]. Alternative techniques have then been developed to remove and recover organic (and inorganic) contaminants from wastewater. The emulsion liquid membrane (ELM) separation provides a potentially powerful process for performing such separations. When compared with above-mentioned methods, the ELM technique displays some attractive features, e.g., simple operation, high extraction yield, simultaneous extraction and desextraction, large interfacial transfer area compared to solid membranes, reusability, low energy consumption and possibility of continuous operation [2]. Since the ELM method was proposed by Li [3] for separation of hydrocarbons, this technology has proved to be efficient for a variety of separation operations. Many studies have been conducted for recovery and concentration of metals [4–7] and biochemical molecules [8–12], separation

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of mixtures of saturated and aromatic hydrocarbons [13,14], removal of cyanide from wastewater in gold processing [2], treatment of wastewaters contaminated with metal ions and phenols [15–18] and regeneration of catalysts after chemical reaction [19, 20]. In this article, we will study the application of ELM to the extraction of ethanol from aqueous solutions with and without salts. Ethanol is a solvent used in the formulation of paints and varnishes, inks, plastics, adhesives, explosive, perfumes, cosmetics, etc. It has a certain recognized toxicity and its recovery has become a necessity [21,22]. Many methods such as reverse osmosis [23–25], pervaporation [26,27], adsorption on zeolites [28] or activated carbon [29], etc. have been implemented for the recovery of this product.

In alcoholic beverages area, Hogan et al. used osmotic distillation for removing ethanol from wine [30]. They showed that osmotic distillation of wine at high alcohol content performed between 10 and 20°C and by using water as a stripping agent decreased quickly the alcohol percentage to 6% with a low loss of aromatic components. Diban et al. [31] studied the dealcoholization of wine solutions by hollow fiber membranes at ambient temperature. The results revealed that a partial dealcoholization of about 2% (v/v) led to acceptable aroma losses without damaging the final product quality. However, the loss of aromatic compounds could reach almost 100% when the residence time of the feed stream increased. Etuk and Murray [32] took advantage of the use of ELM for the production of low-alcohol beer. Chanukah and Rastogi [33] also showed the efficiency of ELM for the extraction of ethanol from wine. In optimal conditions with paraffin as the membrane phase, the maximum extraction efficiency was about 26%. The extension of this method was dependent on other parameters such as the type of emulsifier used and its concentration. In another work, the same authors studied the removal of ethanol from aqueous solutions by ELM, which was formulated from hexane and heptane as the diluents, Span 80 as the emulsifier and pure water as the inner phase. Under the best conditions, alcohol extraction was 51.45% and 49.5% with hexane and heptane as membrane phases, respectively. Alcohol was successfully extracted by more than 92% from grape wine with multistage extraction under optimized conditions. It was also found that the swelling rate of ELM increases with mixing time [34].

Experimental observations have also shown that alcohol extraction efficiency from fermentation broth,which contained cells, salts and other compounds was better than that from pure water [35]. As an example, Murphy et al. [36] observed an increase in the distribution coefficient for ethanol by a factor of 1.5 by the addition of KCl to the fermentation broth. This phenomenon was ascribed to the "salting out" effect, which has been extensively investigated [37]. The term "salting-out" is usually used to denote an increase in the activity coefficient of the non-electrolyte with increasing salt concentration. Malinowski and Daugulis [38] performed experimental studies to assess the effect of salt addition on the extraction of ethanol from dilute aqueous solutions using cyclopentanol, n-valeraldehyde, tert-amyl alcohol and Adol 85NF (comprised largely of oleyl alcohol) as extractants. The liquid-liquid partitioning was studied for some strong electrolytes in a wide range of concentrations. Results showed that the distribution coefficient and selectivity in systems with reduced water activity resulting from the addition of salts were strongly increased. These results could be explained on the basis of the hydration theory. It was also found that addition of strong electrolytes to the feed aqueous phase decreased extractant solubility in the aqueous phase, leading to lower solvent losses. Results showed that the increase in the salt concentration beyond a threshold that lowers the water activity to a value of 0.92, did not affect significantly the extraction efficiency.

Some recent works have also shown that filtration of organic compounds through nanofiltration membranes could be affected by the presence of a salt and this phenomenon was dependent on the salt nature [39–42]. Several assumptions have been proposed to explain this phenomenon, which include the decrease in the effective size of the molecules due to their partial dehydration by the surrounding ions (phenomenon known as the "salting-out" effect) [39–42]. The influence of salts in the feed solution on the extraction of ethanol was also explored in the present work. To the best of our knowledge, this is the first time that the salt effect on the extraction of organic compounds by ELM is studied.

The objective of the present work was to develop an ELM system for the extraction of ethanol from aqueous solutions. The system under study consists of three phases: an internal aqueous phase (receiving phase)which is emulsified in an immiscible membrane phase, a membrane phase (oil phase) which forms a water-in-oil (W/O) emulsion with the internal aqueous phase, and an external phase in which the emulsion globules are dispersed. As a result, an emulsion-in-water dispersion is formed and the internal phase never directly contacts the external aqueous phase. Ethanol (target component) in the external aqueous phase diffuses (without assistance of a carrier) through the membrane due to its solubility in it to the internal aqueous phase. Permeation stops when activity equilibrium is reached. In this transport, ethanol does not react chemically with liquid membrane and is in the same form in the external phase, liquid membrane, and internal phase. Ions (non-target species) present in the external aqueous phase also diffuse through the membrane. It is expected that the competition between the ethanol extraction and salt extraction lowers the ethanol extraction because the driving force and the mechanism for extraction of all of them is the same. It should be mentioned that the solubility of ethanol in water is nearly infinite (because of strong hydrogen bonding). On the other hand, the salts that will be added in the feed solution have limited solubility in water. As a result, the solubility of ethanol in the aqueous phases (both internal and external) is not influenced by the presence of these salts. Particular attention was paid to the emulsion stability by investigating the effect of several parameters such as emulsification time, surfactant concentration and type, volume ratio of membrane phase to internal phase, volume ratio of emulsion to external phase, diluent type and stirring speed. The influence of the presence of a salt in the feed solution on the ethanol extraction efficiency was examined by changing the salt nature and concentration.

2. Experimental

2.1. Reagents

Three commercially available surfactants were tested: sorbitan monooleate, known as Span80 and supplied by

Sigma Aldrich (S^{t}-Louis, Missouri, USA), HelmolA5106andLorama A5019, supplied by ENAP ("Algerian National Company of Paints" located in Souk-Ahras, Algeria). The sorbitan monooleate is anester-type nonionic surfactant with a hydrophile/lipophile balance (HLB) of 4.3 as recommended for W/O emulsions. Its density is 1.0 g/cm^3 at 20°C. Helmol A5106 is a nonylphenol ethoxylate and Lorama A5019 a carboxylic acid ester. Their densities are 1.03 and 0.95 g/cm^3 at 20°C, respectively. No information about their HLB values is provided by the manufacturer. Four diluents of analytical grade were used: hexane, cyclohexane, dichloromethane and kerosene. The first three were obtained from Merck (Darmstadt, Hessen, Germany) and the fourth from Sonatrach ("National Company for Research, Production, Transport, Transformation and Marketing of Hydrocarbons" located in Hassi Messaoud, Algeria).

The external aqueous phases were prepared from distilled water and ethanol at a concentration of 0.8 M. The salts used were KCl, $CaCl_2$ and NaCl of analytical grade at concentrations of 0.1 M and 1 M. The pH of the various solutions was 6.0±0.2 without any adjustment.

2.2. Equipment

A Wise Stir MS-MP8 magnetic stirring platform was used to stir the prepared solutions. pH measurements were performed with a potentiometer Consort C831 with combined glass electrode. The weights were measured with an electronic balance (KernABS-type). A Bomannhomogenizer (Bomann Stabmixer SM 384 CB, maximum stirring speed of 18000 rpm) was used for preparing the stable primary emulsion. The UV-visible spectra were recorded using a spectrophotometer Jenway (type 6705). The conductivity of solutions was measured with an Ionolab conductometer (model Cond 730).

2.3. Emulsion preparation

The liquid membrane phases (organic phases) were prepared by dissolving 2–10 wt% of Span80 or 8 wt% of Helmol A5106 or 8 wt% of Lorama A5019 as a surfactant in an appropriate diluent, i.e. hexane, cyclohexane, dichloromethane or kerosene. The primary emulsion W/O (water-in-oil) was obtained by mixing the organic phase with distilled water (internal phase) in a well-defined volume ratio between 0.5 and 2. The stirring speed was varied from 250 to 500 rpm and the emulsification time from 2 to 14 min.

A volume of the prepared emulsion was then added to a certain volume of the aqueous phase to be treated, namely 0.8 M ethanol solution with or without salt. The mixture was stirred for 12 min using a magnetic stirrer, and a double emulsion W/O/W (water-in-oil-in-water) was obtained during this step. The external phase was periodically sampled to measure its ethanol concentration. It was determined by UV–visible spectrophotometry at the wavelength of 206 nm (corresponding to the maximum absorbance) using a calibration curve (Fig. 1a). The extraction efficiency of ethanol was calculated using the following equation:

$$E_{ext} = 100 \times [(C_0 \times V_{0,ext} - C_f \times V_{f,ext})/(C_0 \times V_{0,ext})] \qquad (1)$$

where C_0 and C_f are the initial and final ethanol concentration in the external phase, respectively, while $V_{0,ext}$ and $V_{f,ext}$ are the initial and final volume of the external phase, respectively.

The residual concentration of the salt in the external phase was assessed by conductimetry using established calibration curves (Fig. 1b to 1d). The extraction efficiency of salts was determined from Eq. (1). The range of parameters

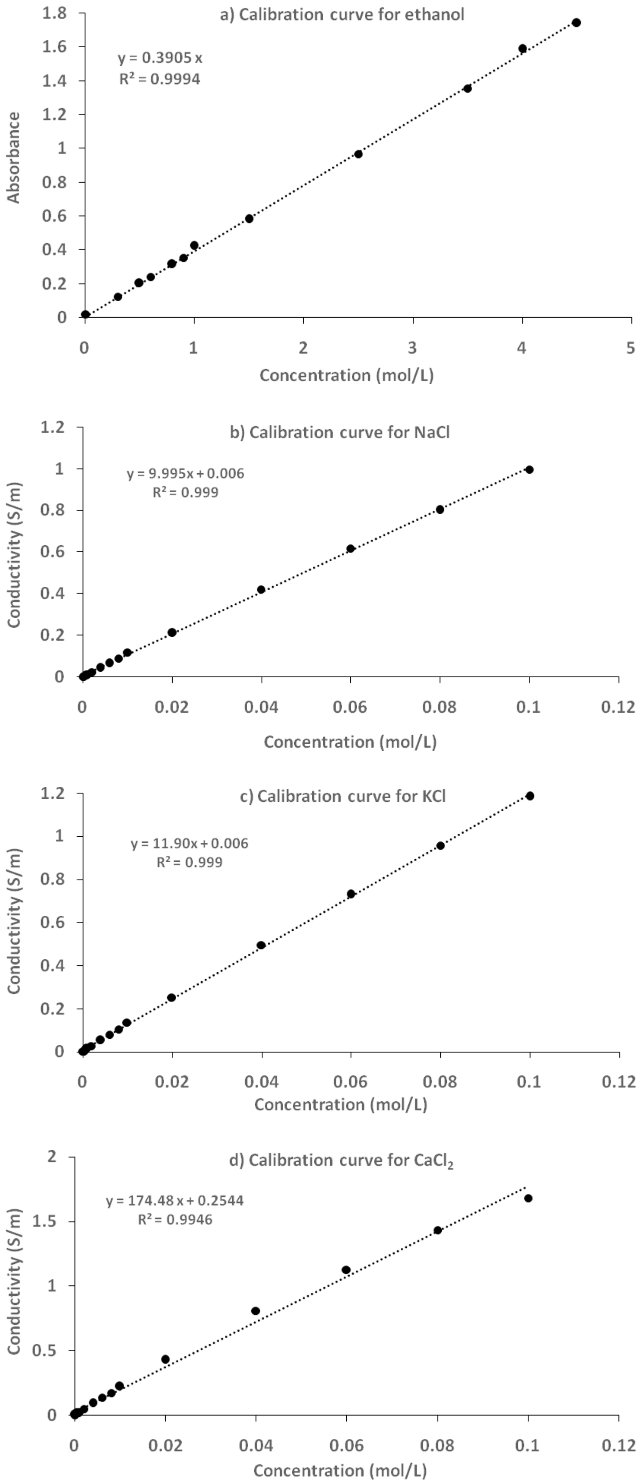

Fig. 1. Calibration curves for (a) ethanol in water (absorbance measured at 206 nm); (b) NaCl; (c) KCl and (d) $CaCl_2$.

used for the present study in the ELM extraction of ethanol is collected in Table 1.

3. Results and discussion

3.1. Search for optimal conditions of ethanol extraction

3.1.1. Effect of surfactant concentration

The surfactant concentration plays an important role in solute extraction by ELM. The effect of the surfactant concentration on the ethanol extraction was investigated with Span 80 using hexane as a diluent, distilled water as an internal phase, emulsification time of 6 min., a stirring speed of 300 rpm, a concentration of ethanol in the external phase of 0.8 M and volume ratios of organic membrane phase to internal phase of 1 and external phase to emulsion of 10. The surfactant concentration was in the range of 2–10 wt%.

As shown in Fig. 2, the ethanol extraction efficiency increases with surfactant concentration. This can be explained by the fact that addition of more surfactant decreases the surface tension and results in smaller droplet size of the W/O emulsion, which gives a larger mass transfer area and thus more efficient solute extraction. The maximum extraction efficiency is close to 74% for a contact time of 10 min and a surfactant concentration of 8 wt%. Beyond this concentration, the ethanol extraction efficiency decreases because the resistance to mass transfer becomes significant and causes an increase in the viscosity of the W/O emulsion,which slows the kinetics of extraction. The same phenomenon was observed during the extraction of bisphenol by ELM [43]. A non-monotonous variation of the extraction rate with contact time can also be observed for all surfactant concentrations. The optimum value is reached after 8 min for surfactant concentrations of 2, 4 and 6 wt%, this time being considered adequate for a good transfer of the solute, while for higher concentrations (8 and 10 wt%), the optimum is reached after 10 min. The difference in the optimum times can be explained by a better stability of the emulsion when the surfactant content is higher. Beyond this optimum time, the emulsion started to destabilize due to the swelling of the membrane (phenomenon that was observed during experiments), which caused a decrease in the extraction.

3.1.2. Effect of emulsification time

The emulsion was prepared under the same conditions as mentioned previously, using the optimum surfactant concentration of 8 wt%. The emulsification time was varied from 2 to 14 min and the extraction kinetic of ethanol was followed over a 12-min period (Fig. 3). For contact times less than 8 min, it appears that the extraction efficiency increases with the emulsification time because the primary emulsion droplets become smaller resulting in a more stable emulsion (the breakage decreases because the droplets have smaller size, which makes the droplets difficult to coalesce) with larger mass transfer. A different behavior is observed for contact times greater than 8 min. The ethanol extraction for an emulsification time of 10 min becomes more efficient than that for 14 min. Unfortunately, we have not been able to find any explanation. Since the highest extraction yield was obtained for contact times greater than 8 min, an emul-

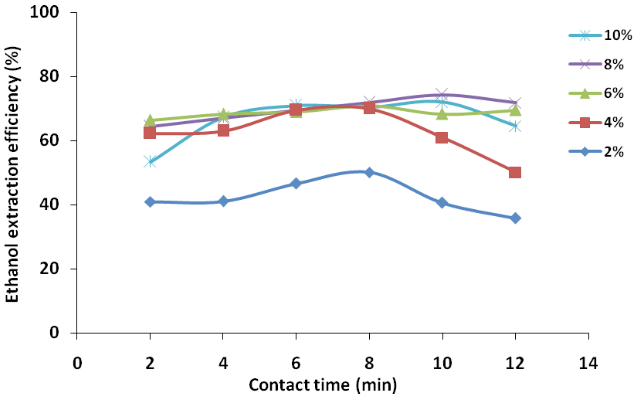

Fig. 2. Effect of Span 80 concentration on the ethanol extraction efficiency. Diluent: hexane; internal phase: distilled water; emulsification time: 6 min; stirring speed: 300 rpm; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.1

Table 1
Experimental conditions used for the preparation of ELMs

External aqueous phases	0.8 mol/L ethanol solution with or without salt (KCl or NaCl or $CaCl_2$)	[salt] = 0.1–1 mol/L
Organic phases (liquid membrane phases)	– Solvents: Hexane or cyclohexane or dichloromethane or kerosene – Surfactant: Span 80 or Helmol A5106 or Lorama A5019	[Span 80] = 2–10 wt% [Helmol A5106] = 8 wt% [Lorama A5019] = 8 wt%
Internal phase	Distilled water	
Emulsification time		2–14 min
Agitation speed for emulsification		18 000 rpm
Stirring speed		250–500 rpm
Membrane phase/internal phase volume ratio (V_{memb}/V_{int})		0.5–2
Treat ratio (V_{em}/V_{ext})		0.05–0.2

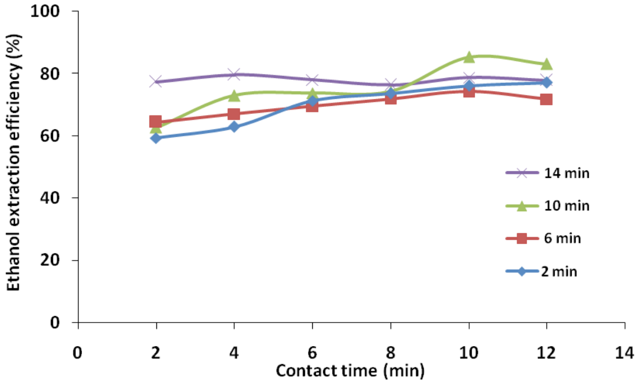

Fig. 3. Effect of emulsification time on the ethanol extraction efficiency. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; stirring speed: 300 rpm; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.1.

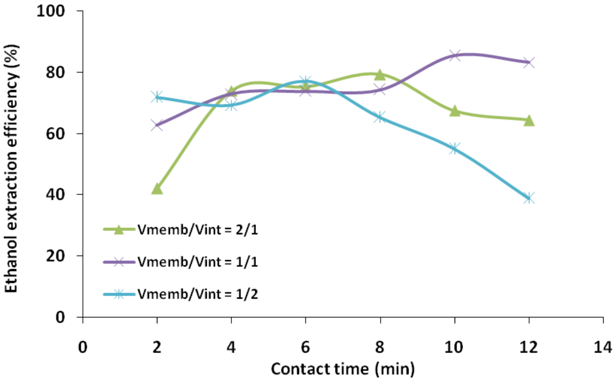

Fig. 4. Effect of V_{memb}/V_{int} on the ethanol extraction efficiency. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; emulsification time: 10 min; stirring speed: 300 rpm; V_{em}/V_{ext}: 0.1.

sification time of 10 min (for which the ethanol recovery efficiency is about 86%) was therefore chosen for further studies.

3.1.3. Effect of the volume ratio of membrane phase to internal phase

The operating parameters were identical to those used previously with an emulsification time of 10 min, an emulsifier concentration of 8 wt% and varying the volume ratio of the membrane phase to internal phase (V_{memb}/V_{int}) from 0.5 to 2. The effect of this volume ratio on the extraction efficiency is shown in Fig. 4. As can be seen, the best ethanol extraction efficiency is obtained for a ratio V_{memb}/V_{int} of 1. The decrease of this ratio below 1 leads to an increase in the stripping solution volume fraction and shifts the internal droplets size distribution toward larger sizes. The increase in the droplets diameter decreases the interfacial contact area between the emulsion and continuous phase, and thereby decreases the extraction efficiency. Additionally, the volume of organic phase is not enough for enclosing all the internal aqueous phase [44]. The increase of this ratio (V_{memb}/V_{int}= 2) decreases both the volume of internal aqueous solution and extraction efficiency. This suggests that the mass transfer resistance in the emulsion globule is important and it may be due to the high fraction of the membrane phase as compared with the internal phase. From Fig. 4, it can also be noted that the extraction efficiency decreases after 6 min for V_{memb}/V_{int} = 1/2 and after 8 min for V_{memb}/V_{int} = 2/1. For the first ratio (V_{memb}/V_{int} = 1/2), it was observed that the membrane film that separates the external and internal phases was less dense after a contact time of 6 min. In other words,the amount of surfactant in this film was probably not sufficient to hold for a longer time, which led to the rupture of the emulsion and to the drop in the ethanol extraction yield. On the other hand, for V_{memb}/V_{int} = 2/1, it was observed that the increase in the volume ratio of the membrane phase to internal phase beyond 1 resulted in less internal phase globules, which were probably concentrated rapidly in ethanol, which led to the reversal of the driving force and to the resulting diffusion of solute from the internal phase to the external phase.

3.1.4. Effect of the volume ratio of emulsion to external phase

The volume treatment ratio (treat ratio) is defined as the volume ratio of emulsion to external phase (V_{em}/V_{ext}). Experiments were conducted to investigate the influence of this ratio on the ethanol extraction efficiency. The treatment ratio was varied from 0.05 to 0.2. According to findings from Fig. 5, it is clear that the extraction efficiency is affected by this parameter. The smaller the volume of external phase to be treated, the less emulsion is required to extract the solute, which is desirable from a processing point of view to ensure maximum enrichment with respect to the feed phase [7]. Therefore, a treatment ratio of 0.0667 was chosen as the best one, giving a maximum extraction efficiency of about 92% after a contact time of 8 min. The maximum in the extraction efficiency observed for the treat ratio of 0.0667 can be explained by the swelling of the emulsion, which was observed during the experiment. The swelling phenomenon may be due to the osmotic effect which causes the transfer of water from the external phase to the internal one, leading to embrittlement of the emulsion and its breakage. This phenomenon results in a decrease of the ethanol extraction yield. It is also notable that the extraction efficiency starts to increase sharply after 6 min for a treat ratio of 0.05. However, no explanation was found to explain this behaviour.

3.1.5. Effect of the diluent nature

Four diluents, namely hexane, cyclohexane, dichloromethane and kerosene were selected to investigate the influence of the diluent type on ethanol extraction, while adopting the same protocol for the formation of emulsion and the extraction procedure. It was found that the best efficiency of ethanol removal from the feed solution is obtained in the presence of hexane as diluents for a contact time of 8 min (Fig. 6). As can be seen, the extraction efficiency strongly depends on the diluent nature. This is due to the fact that diluents affect the physicochemical properties of the emulsion, including its viscosity, which directly impacts extraction performances. From Fig. 6, it appears that hexane and dichloromethane provide better extraction than cyclo-

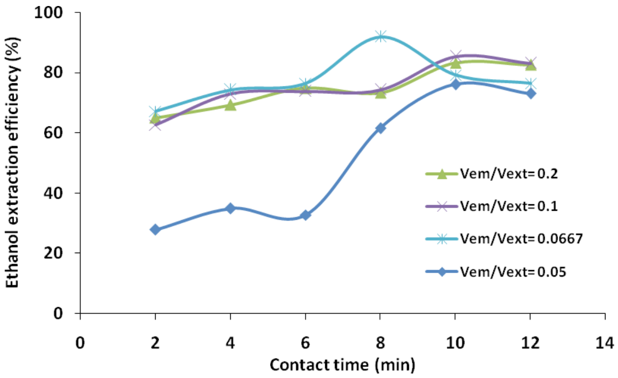

Fig. 5. Effect of V_{em}/V_{ext} on the ethanol extraction efficiency. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; emulsification time: 10 min; stirring speed: 300 rpm; V_{memb}/V_{int}: 1/1.

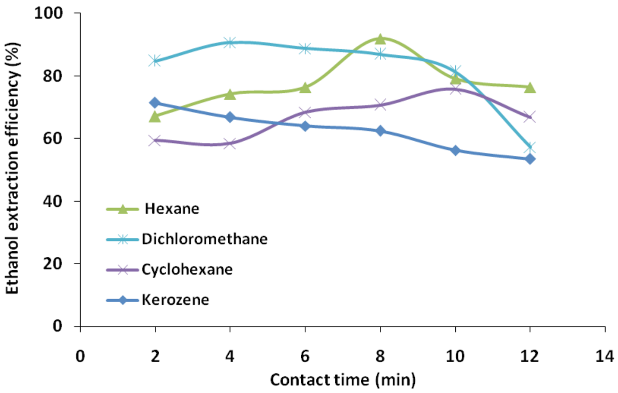

Fig. 6. Effect of the diluent nature on the ethanol extraction efficiency. Concentration of Span 80: 8%; internal phase: distilled water; emulsification time: 10 min; stirring speed: 300 rpm; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL).

hexane and kerosene in the extraction time range considered, except for times beyond 10 min. This behavior may be partly due to the viscosities of hexane (0.33 mPa s) and dichloromethane (0.43 mPa s), which are much lower than those of cyclohexane (0.98 mPa s) and kerosene (1.92 mPas), which led to higher transfer rate of ethanol.

3.1.6. Effect of surfactant type

A comparative study was performed with two other commercial emulsifiers used in the industrial sector for the manufacture of water-based emulsions. The experiments were conducted under optimal conditions (which were previously determined) for a contact time of 8 min (Fig. 7). The ethanol recovery percentage was –68% with Helmol A5106 and –77% with Lorama A5019, compared to –95% with Span 80, for a surfactant content of 8 wt%. Although no information is available about these two new emulsifiers, especially their HLB (Hydrophilic-Lipophilic Balance) value [20], the results obtained with these surfactants look promising and show that they could be exploited in the extraction process by ELM.

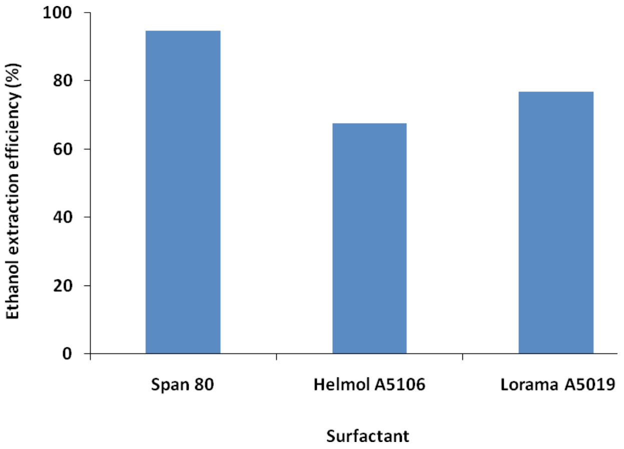

Fig. 7. Effect of the surfactant nature on the ethanol extraction efficiency. Diluent: hexane; concentration of surfactant: 8%; internal phase: distilled water; emulsification time: 10 min; stirring speed: 400 rpm; V_{memb}/V_{int}: 1/1 V_{em} /V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL).

It should be noted that the amount of active material of the emulsifier plays an important role in the emulsion stability [45]. Since the nature and quantity of emulsifier affect significantly several parameters in the ELM process, namely the thickness and viscosity of the membrane phase, a characterization study of these surfactants in terms of viscosity, HLB, critical micellar concentration, etc. is therefore essential to better understand extraction performances.

3.1.7. Effect of stirring speed

The stirring speed plays a major role in the extraction kinetics because the turbulence in the external phase acts on solute transfer across the ELM. The process conditions are identical to those used previously with hexane as diluent. The stirring speed was varied from 250 to 500 rpm (Fig. 8). It is observed that increasing the stirring speed from 250 to 400 rpm increases the rate of extraction but further increase in the stirring speed to 500 rpm results in reduction in the degree of extraction. This is probably due to the fact that the sizes of the emulsion droplets become smaller (providing more mass transfer area) with increase in stirring speed during extraction of ethanol. Kargari et al. found that by increasing agitation speed, the shear forces which acts on the emulsion globules increased and this made the globules smaller, resulting in more gold extraction rate [46,47]. In another study performed by the same authors and regarding the removal of phenol from aqueous solutions by a double emulsion (W/O/W), it was found that the stability of the emulsion was extremely sensitive to the speed of agitation. At speeds higher than the critical value, the breakage of emulsion globules became more probable [48]. However, as the stirring speed is increased, the emulsion droplets probably become more unstable and more is the leakage of the internal phase that adversely affects the ethanol extraction rate at larger extraction times. In other words, there would be two competing phenomena involved in the ethanol transport, that is, the diffusion of the ethanol through the membranes into the internal phase and the leakage of the

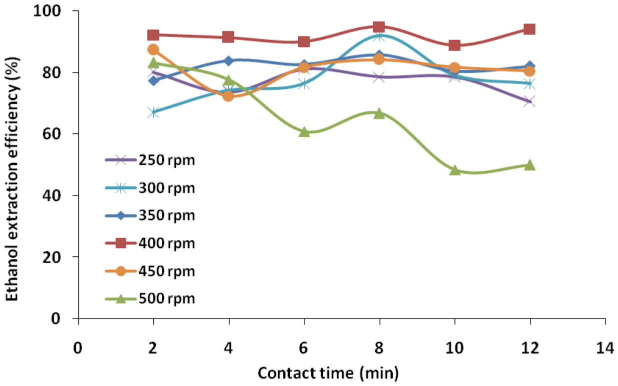

Fig. 8. Effect of stirring speed on the ethanol extraction efficiency. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; emulsification time: 10 min; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL).

internal solution due to breaking of some emulsion globules. In the present work, the optimal stirring rate is found to be 400 rpm with an extraction efficiency of 95% for a contact time of 8 min.

3.2. Effect of the presence of a salt on ethanol extraction

In order to study the influence of salts in the feed solution on ethanol extraction, experiments were carried out in the presence of KCl, NaCl and $CaCl_2$ at concentrations of 0.1 M and 1 M. These salts were selected because they have sufficiently different diffusivities (1.99, 1.61 and 1.33 × 10^{-9} m^2 s^{-1} for KCl, NaCl and $CaCl_2$, respectively) to make it possible to investigate the effect of this parameter. The results of these experiments are shown in Fig. 9. It clearly appears that the presence of a salt in the feed phase leads to a less ethanol extraction, this phenomenon being more important as the salt concentration increases irrespective of the salt. To our knowledge, this is the first time that the effect of salts on the extraction of solutes by ELM is reported. It can be observed that:

- the ethanol extraction efficiency varies between 92 and 94% without salts
- in the presence of a salt at 0.1 M, the ethanol extraction efficiency lies between 63 and 66% with NaCl, 75 and 82% with KCl, and 50 and 55% with $CaCl_2$
- in presence of a salt at 1 M, the ethanol extraction efficiency ranges from 24to 43% with NaCl, 71 to 73% with KCl and 23 to 38% with $CaCl_2$.

In order to better quantify the influence of the salt nature and its concentration on the ethanol extraction efficiency, the relative variation of the latter due to the presence of a salt is plotted in Fig. 10. As can be seen, the decrease in the ethanol extraction efficiency follows the sequence: $CaCl_2$>NaCl>KCl at both concentrations. The largest relative decrease is obtained for 1 M $CaCl_2$ (75% after a contact time of 12 min) and the lowest one for 0.1 M KCl (after 12 min).

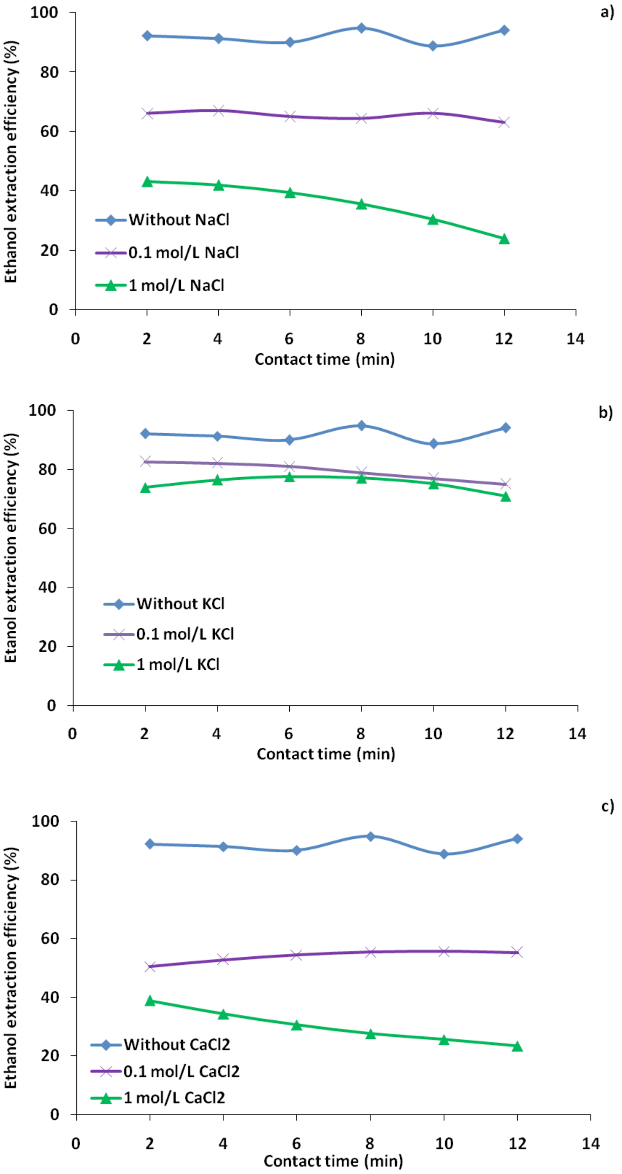

Fig. 9. Ethanol extraction efficiency vs. contact time for single-solute and mixed-solute solutions. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; emulsification time: 10 min; stirring speed: 400 rpm; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL). Mixed-solute solutions: ethanol + NaCl (a), ethanol + KCl (b), ethanol + $CaCl_2$ (c); Symbols: diamond: ethanol; cruz: ethanol + salt at 0.1mol/L; triangle: ethanol + salt at 1 mol/L.

The decrease in the ethanol extraction efficiency can be attributed to both transfer of water from the internal phase to the outer phase (osmosis phenomenon) and co-transport of water by the salts diffusing from the external phase to the internal one. It should be stressed that a significant compression of the emulsion was observed during experiments, which assumes that the first phenomenon is dominant. It results an overall water flux to the internal phase, which opposes the transfer of ethanol from the outer phase to the internal one and thus, causes a drop in the ethanol extraction efficiency (Fig. 11). It is assumed that the co-transport of water molecules by ions occurs otherwise the same extraction efficiency of ethanol would be obtained with

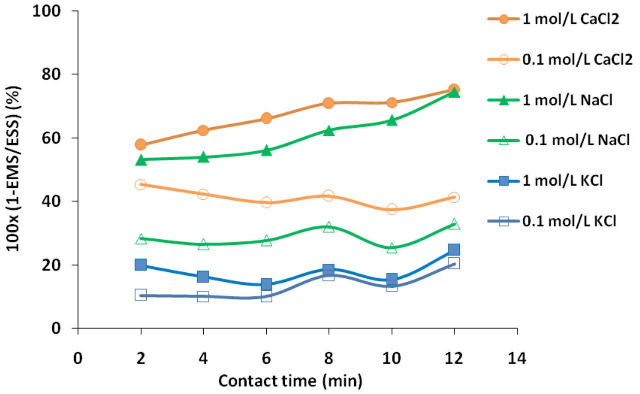

Fig. 10. Variation of the extraction efficiency of ethanol (expressed in %) in the presence of various salts at concentrations of 0.1 and 1 M by comparison with extraction efficiency of ethanol in single-solute solution. R_{SS} and R_{MS} stand for the extraction efficiency of ethanol in single- and mixed-solute solutions, respectively. Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; concentration of ethanol in the external phase: 0.8 mol/L; emulsification time: 10 min; stirring speed: 400 rpm; V_{memb}/V_{int}: 1/1; V_{em} /V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL).

NaCl and KCl salts. Indeed, the initial osmotic pressure is identical with these two salts ($\Delta\Pi$ =2RT Δc) whereas it is higher with $CaCl_2$ ($\Delta\Pi$ = 3 RT Δc). As a result, the water flow should be identical for NaCl and KCl, and larger for $CaCl_2$ if only the osmosis phenomenon occurred. However, a difference of in the ethanol extraction efficiency is observed with KCl and NaCl. This discrepancy could be due to their different diffusion coefficient. Indeed, KCl salt, which diffuses faster than NaCl, could co-transport more water than NaCl during its diffusion to the internal phase. The volume of co-transported water would then follow the salt diffusion coefficient order, i.e., KCl>NaCl>$CaCl_2$. As a result of both osmotic effect and salt diffusion, the overall water flow passing moving from the internal phase to the external phase would follow the following order: $(J_{water})_{CaCl2}$> $(J_{eau})_{NaCl}$> $(J_{eau})_{KCl}$. The ethanol flow, which is in the opposite direction to the overall water flow, would then follow the opposite sequence: $(J_{ethanol})_{CaCl2}$<$(J_{ethanol})_{NaCl}$<$(J_{ethanol})_{KCl}$.

Thanks to conductivity measurements, the salt extraction efficiency could also be assessed. The comparison of Fig. 12a and b shows that the salt extraction efficiency is more important when the initial salt concentration in the feed solution increases due to the increase in the concentration gradient between external and internal phases. It is also noticeable that the salt extraction efficiency depends on the salt nature and the extraction order: $E_{(KCl)}$>$E_{(NaCl)}$>$E_{(CaCl2)}$, follows the order of salt diffusivities: $D_{(KCl)}$> $D_{(NaCl)}$> $D_{(CaCl2)}$. This finding supports the hypothesis that the higher the salt diffusivity and its concentration are, the more important water volume co-transported by the salt is.

4. Conclusion

The extraction by ELM depends on the composition of both emulsion and feed phase containing the species to be extracted. In this work, the target species was ethanol in aqueous phase at 0.8 M. It was found that the best extraction of this solute (which was close to 95%) is obtained after a contact time of 8 min under the following optimum conditions: Span 80 as surfactant at a concentration of 8 wt%, emulsification time of 10 min, volume ratio of membrane phase to internal phase equal to 1, a treatment ratio of 0.0667, hexane as a diluent and pure water as an internal phase and stirring speed of 400 rpm.

The extraction by ELM was therefore proved to be an efficient method, in terms of both extraction efficiency and extraction kinetic, to remove ethanol from aqueous phases. However, it was shown that the presence of salts in the feed solution is not beneficial for ethanol recovery

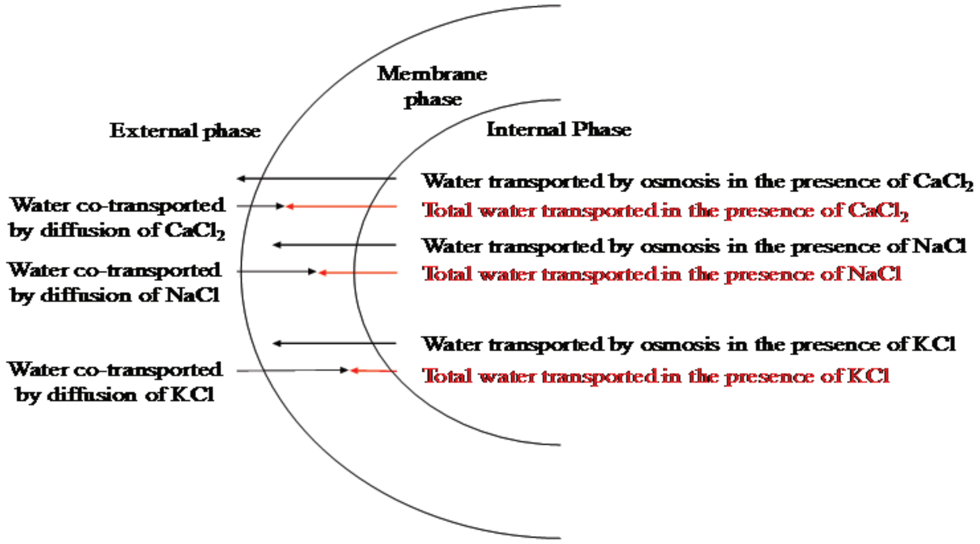

Fig. 11. Transport of water via emulsion liquid membrane in presence of salts. Schematic representation of water transport through the membrane phase.

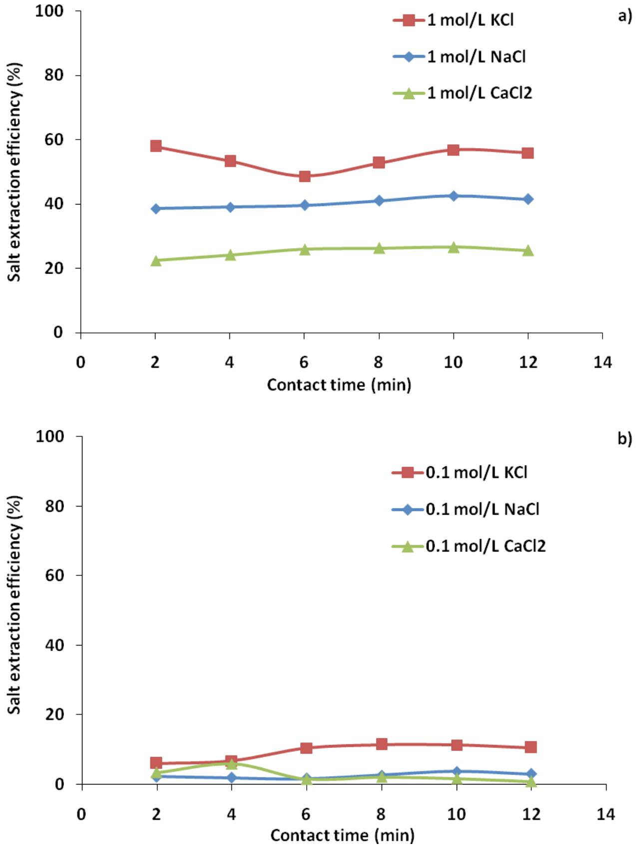

Fig. 12. Salt extraction efficiency vs. contact time for various salts. Salt concentration: 0.1 mol/L (a) and 1 mol/L (b). Diluent: hexane; concentration of Span 80: 8%; internal phase: distilled water; concentration of ethanol in the external phase: 0.8 mol/L; emulsification time: 10 min; agitation speed for emulsification: 18,000 rpm; stirring speed: 400 rpm; V_{memb}/V_{int}: 1/1; V_{em}/V_{ext}: 0.0667 (V_{em} = 12 mL, V_{ext} = 180 mL).

since they significantly reduce the extraction efficiency of ethanol, this reduction being more pronounced with increasing salt concentration. It was also found that the salt effect depends on the salt nature and the decrease in the extraction efficiency follows the sequence: $CaCl_2$>NaCl>KCl. This ranking was ascribed to two phenomena: the osmosis phenomenon, which leads to the transfer of water from the internal phase to the external phase (phenomenon more important with$CaCl_2$ as compared with NaCl or KCl) and the salt diffusion from the external phase to the internal phase with water co-transport (the amount of co-transported water increasing with the salt diffusivity). It was found that the decrease in the extraction efficiency of ethanol can be as high as 75% (the ethanol extraction efficiency falls from 95% to 23%) in the case of a $CaCl_2$ molar solution. The salt effects should be carefully considered in extraction processes using ELM since these solutes may affect dramatically the extraction of a target species, particularly when their concentration is high.

In the context of process intensification, LM separation processes are increasingly evolving towards the application of fluids of greater complexity, containing both organic and mineral compounds. This study has demonstrated that the performance of extracting of an organic solute from a fluid decreases in the presence of a salt and this decrease depends on the salt nature and concentration. The diversity of fluids to be treated therefore requires to optimize the choice of materials and operating conditions for each application.

Symbols

E_{ext} — Extraction efficiency
C_0 — Initial ethanol concentration in the external phase, mol m^{-3}
$V_{0,ext}$ — Initial volume of the external phase, m^3
C_f — Final ethanol concentration in the external phase, mol m^{-3}
$V_{f,ext}$ — Final volume of the external phase, m^3
V_{memb} — Volume of the membrane phase, m^3
V_{int} — Volume of internal phase, m^3
V_{em} — Volume of the emulsion, m^3
V_{ext} — Volume of external phase, m^3
D — Salt diffusivity, m^2 s^{-1}

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