



A flat-sheet supported liquid membrane based on Aliquat[®] 336 as carrier for the removal of salicylic acid from aqueous solution

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ABSTRACT

This study deals with the extraction of salicylic acid (SA) from aqueous solutions through a flat-sheet supported liquid membrane system. Tricaprylmethylammonium chloride (Aliquat[®] 336) diluted in 2-octanol is used as membrane organic phase. In a previous work, 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$) or ethylammonium nitrate (EAN) is used instead of the above mixture. Transport efficiency around 50% and 9 days stability has been obtained. In this work, the use of 10% (v/v) Aliquat[®] 336 in 2-octanol improves the transport efficiency of the system (around 90%). The important operational variables affecting the facilitated transport of SA are concentration of Aliquat[®] 336, membrane viscosity, feed phase pH, stripping agent concentration, initial SA concentration, polymeric support type, and membrane stability. Regardless of its higher SA transport efficiency, the SLM based on the mixture Aliquat[®] 336/2-octanol exhibits shorter long-term stability (time dependent-negative tendency) as compared to the use of $[C_6mim][PF_6]$ or EAN.

Keywords: Supported liquid membrane; Tricaprylmethylammonium chloride (Aliquat[®] 336) ionic liquid; Salicylic acid; Facilitated transport; Supported liquid membrane stability

1. Introduction

Human and veterinary pharmaceuticals are a group of “emerging” contaminants [1]. Residues of these biologically active compounds can enter the environment via different transport pathways emissions during manufacture, disposal of unused or expired medicines, human and animal excretion in urine and feces, direct discharge of aquaculture products, and manure and slurry spreading [2]. Sewage treatment plants are not able to remove these drugs and their excretion metabolites completely, and they are discharged to different

environmental compartments at concentrations ranging from $ng L^{-1}$ to $\mu g L^{-1}$. In addition to river and sea water, recent studies have shown they may even enter drinking water produced from groundwater [3,4]. Although contamination levels are lower than for other pollutants (approx. tens of $\mu g L^{-1}$) and detailed knowledge about the toxicological effects of these compounds is still lacking, the growing use of pharmaceutical products is becoming a relevant environmental problem. On this basis, the demand for developing efficient systems for removing these substances from water has assumed a great research interest. Membrane technology is one of the most important topics in today's

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research, because it is increasingly employed in many industrial sectors and being an important alternative to classical separation processes such as distillation, crystallization, solvent extraction, precipitation, etc. [5–7]. Among membrane-based separation processes, the use of supported liquid membranes (SLMs) has received growing attention during recent years. SLMs have been studied in the transport of various metal ions [7–9], as well as different molecules of biological interest [6,10,11] and organic compounds [12–14]. In SLM, usually organic liquid is imbedded in small pores of a polymeric support and is kept there by capillary forces [15]. SLMs are promising because they combine the processes of extraction and stripping, and the amount of solvent in the SLM process is also much lower than in the solvent extraction process. Despite many advantages of SLMs, they are not yet used at a large scale in industrial applications because of their low stability [16,17]. Their instability has been attributed to loss of solvent from the supporting membrane, either by evaporation or by dissolution/dispersion into the adjacent phases [18]. Several approaches have been proposed to minimize instability problems, such as the use of mild operating conditions, protection of the SLM with a gel layer [19], adequate design of both the supporting membranes and the contacting phases [20] and recently the use of ionic liquids (ILs) as organic phase.

ILs are organic salts that are liquid close to room temperature and which normally consist of an organic cation and either an organic or an inorganic anion. Their negligible vapor pressure, the possibility of minimizing their solubility in the surrounding phases by adequate selection of the cation and anion [21,22], and the greater capillary force associated with their high viscosity, which could reduce displacement of the liquids from the micron pores and therefore increase membrane stability [23–25].

Acidic pharmaceuticals are considered among the major environmental contaminants. Salicylic acid (SA) and its derivatives are largely used to ease aches and pains, to reduce fevers and also as constituents of some rubefacient pharmaceuticals. This metabolite has been, already, detected in sewage effluents, wastewater, and surface water [26,27]. For this reason, many researchers have been interested in the extraction (removal) of this compound from water. Payan et al. [28] suggested the application of hollow fiber-based liquid-phase microextraction (HF-LPME) using a polypropylene membrane supporting dihexyl ether for the determination of acidic pharmaceuticals (ibuprofen, diclofenac, and salicylic acid) in wastewater. These authors mentioned that the extraction effectiveness for the analyzed substances is unrelated to the type of wastewater, remaining practically constants (about

100% SA, 71% diclofenac, and 52% ibuprofen). We can notice the complete extraction of SA but no data have been provided about the dihexyl ether-SLM system stability. Kumar et al. [29] developed an electrochemical membrane process with three compartments (anolyte, catholyte, and central compartment) based on in-house prepared cation-exchange membrane to achieve *in situ* ion substitution and recovery of salicylic acid from its sodium salt. A SA recovery with current efficiency close to 90% has been attained but the energy consumption was around 10 kWh/kg of the SA produced.

Recently, we have studied the extraction of SA through a flat-sheet-supported liquid membrane (FSSLM) using as liquid membrane the ILs 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$) and ethylammonium nitrate (EAN) [30]. In spite of the good expectancy for the lifetime of the elaborated SLM system, lower extraction efficiencies not exceeding 50% were acquired. Among the various air-stable room temperature ILs, tricaprylmethylammonium chloride (Aliquat[®] 336) IL was one of the most studied as an effective extractant for the extraction of some metal ions species and organic compounds [31]. The aim of this work is to examine the use Aliquat[®] 336 to study the extraction of SA from aqueous solution through a FSSLM. Several operational variables influencing the SLM extraction system efficiency were studied such as nature and concentration of the stripping agent in the receiving phase and Aliquat[®] 336 concentration in the membrane organic phase. The stability of the SLM system was also evaluated.

2. Experimental

2.1. Reagents and membranes

Aliquat[®] 336 (tricaprylmethylammonium chloride) is a mixture of C_8 (octyl) and C_{10} (decyl) chains with C_8 predominating. Aliquat[®] 336 procured from Fluka is a quaternary ammonium salt. It is a clear reddish-brown liquid with a molecular mass of $0.404 \text{ kg mol}^{-1}$. 2-octanol was purchased from Fluka. Cyclohexane was obtained from Merck. Toluene was procured from Prolabo and hexane is a Fisher Scientific product. Viscosity and dielectric constant of these organic solvents are given in Table 1.

Two different flat-sheet polymeric supports were evaluated. Their physical characteristics are collected in Table 2.

Feed solutions were prepared by dissolving salicylic acid sodium salt ($MW = 160.11 \text{ g mol}^{-1}$, purity $\geq 99.5\%$, Fluka) in ultrapure water (Milli Q

Table 1
Viscosity and dielectric constant of organic solvents [32]

Solvent	Viscosity (cP, 20°C)	Dielectric constant ϵ_r (20°C)
2-octanol	10.60	10.30
Toluene	0.59	2.40
Hexane	0.31	2.02
Cyclohexane	0.98	2.00

Table 2
Physical characteristics, experimental and normalized initial SA fluxes and recovery percentage of used polymeric supports. Feed solution: 10^{-3} M SA at pH 3; Support: Accurel® PP or Durapore® PVDF; Organic phase: Aliquat® 336 (10%, v/v) in 2-octanol; Stripping solution: 2 M NaOH

Polymeric support	Accurel® PP 2E-HF; Membrana, Germany	Durapore®; Millipore, USA
Material	Polypropylene	
Polyvinylidene difluoride		
Thickness (d_0 ; μm)	160	120
Pore diameter (d ; μm)	0.2	0.2
Porosity (ϵ ; %)	75	65
Tortuosity ($\tau=1 - \ln \epsilon$) [33]	1.29	1.43
$\epsilon/d_0\tau$ ($10^{-3} \mu\text{m}^{-1}$)	3.63	3.79
J_{exp} ($10^{-6} \text{mol m}^{-2} \text{s}^{-1}$)	6.9	9.0
J_N ($10^{-6} \text{mol m}^{-2} \text{s}^{-1}$)	6.9	8.6
R (%; 8 h)	87.7	89.6

Plus Colum, Millipore). The pHs of these solutions were maintained at different values ranging from 1 to 8. Mixtures of solutions of potassium chloride (Fluka) and hydrochloric acid, citric acid (Fluka) and sodium citrate (Fluka), acetic acid and sodium acetate (Fluka), 2-(N-morpholino)-ethane sulfonic acid (MES, Sigma) and sodium hydroxide (Carlo Erba) and N-[Tris(hydroxymethyl)methyl]glycine (Tricine, Fluka) and triethanolamine (Fluka) were prepared to obtain, respectively, the pHs of 1, 3, 4.7, 6, and 8. Reagents of analytical grade or higher were used without further purification.

2.2. Analytical methods

SA concentration measurements in both aqueous source and receiving solutions were carried out using

a UV–visible Perkin-Elmer double-beam spectrophotometer type Lambda 20 at a wavelength of 305.4 nm. A pH meter (C861 Consort) was used for pH measurements.

2.3. SLM transport experiments

The FSSLM was prepared at room temperature by impregnating the porous film with the organic membrane liquid for at least 24 h. Then, it was wiped with a soft paper to eliminate the excess of IL. Obtained SLM was placed in the middle of a two-compartment permeation cell described elsewhere [8,34]. The exposed membrane area was 3.1 cm^2 . The feed and the stripping solutions (50 mL each) were placed in each compartment of the cell. Both aqueous feed and stripping solutions were magnetically stirred at 600 rpm at $25 \pm 1^\circ \text{C}$ to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. About 1 mL sample of each feed and stripping solutions was periodically taken to determine SA concentration. All experiments were carried out in duplicate and standard deviations were less than $\pm 5\%$.

The efficiency of SLM system can be evaluated using the extraction percentage $E(\%)$, the recovery percentage $R(\%)$ and the initial flux J of SA

The extraction percentage, $E(\%)$, was calculated by Eq. (1):

$$E(\%) = \frac{[\text{SA}]_{\text{feed},0} - [\text{SA}]_{\text{feed},t}}{[\text{SA}]_{\text{feed},0}} \times 100 \quad (1)$$

where $[\text{SA}]_{\text{feed},0}$ is the initial SA concentration in the feed solution and $[\text{SA}]_{\text{feed},t}$ is the SA concentration in the feed solution at time t .

The recovery percentage, $R(\%)$, was calculated by Eq. (2):

$$R(\%) = \frac{[\text{SA}]_{\text{strip},t}}{[\text{SA}]_{\text{feed},0}} \times 100 \quad (2)$$

where $[\text{SA}]_{\text{strip},t}$ is the SA concentration in the stripping solution at time t .

The initial flux, J , for the SA can be expressed as follows [8,9,34]:

$$J = \left(\frac{V}{S}\right) \cdot \left(\frac{d[\text{SA}]_{\text{strip}}}{dt}\right) \quad (3)$$

where V is the volume of the aqueous stripping solution (L), S is the effective exposed surface area of

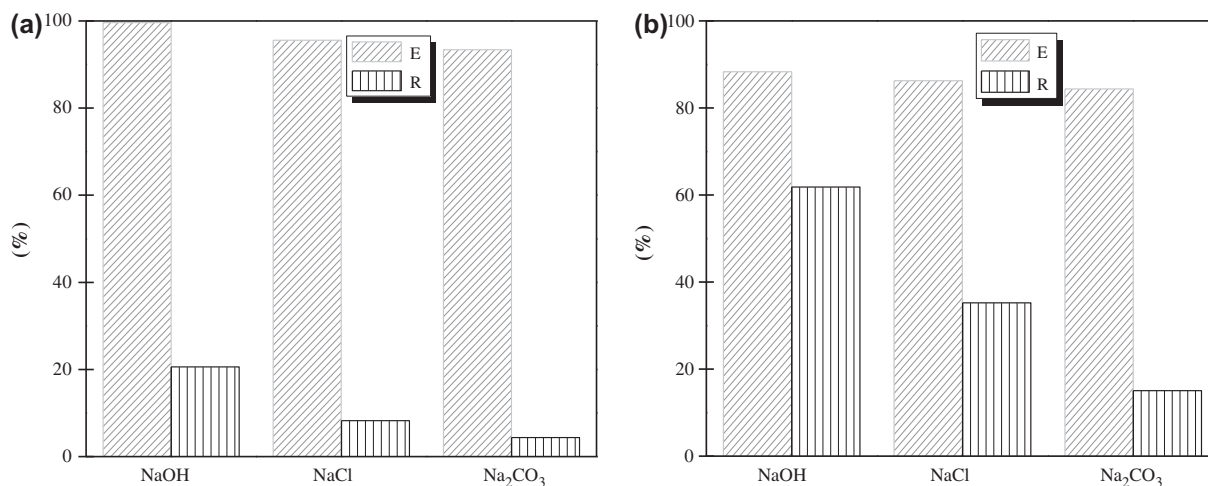


Fig. 1. Effect of the organic membrane phase composition on the SA extraction and recovery percentages. Feed solution: 10^{-3} M SA at pH 1; Support: Accurel[®] PP; Stripping solution: 1 M NaOH, NaCl or Na₂CO₃. (a) Organic phase: Aliquat[®] 336 and (b) Organic phase: Aliquat[®] 336 (20%, v/v) in 2-octanol; Transport time: 8 h.

the membrane (m^2), and $[SA]_{strip}$ is the concentration of SA in the stripping phase (mol L^{-1}) at elapsed time (s).

3. Results and discussion

3.1. Transport studies

To avoid SA accumulation in the membrane phase, strip solution should be exploited to release SA from the membrane phase. In order to obtain the suitable strip solution, three commonly used stripping agents were selected, including sodium hydroxide, sodium chloride, and sodium carbonate. The concentration of the strip solution was 1 M. Initially, the polymeric support was impregnated exclusively with Aliquat[®] 336. It can be seen from Fig. 1(a) that Aliquat[®] 336 is an efficient extractant for SA, since it was almost totally extracted from the source phase, but it is difficult to strip it from the organic phase. In fact, a recovery percentage not exceeding 21% of SA in the receiving phase was obtained using the three different strip solutions. This difficulty to strip was also reported by Matsumoto et al. [5] when they have examined the stripping of penicillin G from the tri-n-octylmethylammonium chloride (TOMAC) phase. The lower stripping efficiency could be related to the high Aliquat[®] 336 viscosity value (1500 cP at 25°C [31]) which made the diffusion of formed Aliquat[®] 336-SA complex to the membrane-receiving phase interface difficult and this complex will load membrane pores.

Taking into consideration that the transport efficiency is related to the viscosity and dielectric constant of the organic membrane phase [35], 2-octanol was added as diluent in the membrane phase to

adjust these physical parameters. As shown in Fig. 1 (b), the addition of 2-octanol improves the recovery percentage of SA using NaOH, NaCl, or Na₂CO₃ as stripping agents due mainly to the decrease in the organic membrane phase viscosity [31]. The results in this figure also reveal that the extraction and recovery are the highest when NaOH is used as stripping agent instead of NaCl or Na₂CO₃. Actually, using a 1 M NaOH solution as receiving phase, a SA recovery percentage of 62% was reached after 8 h of transport process. Therefore, sodium hydroxide was selected

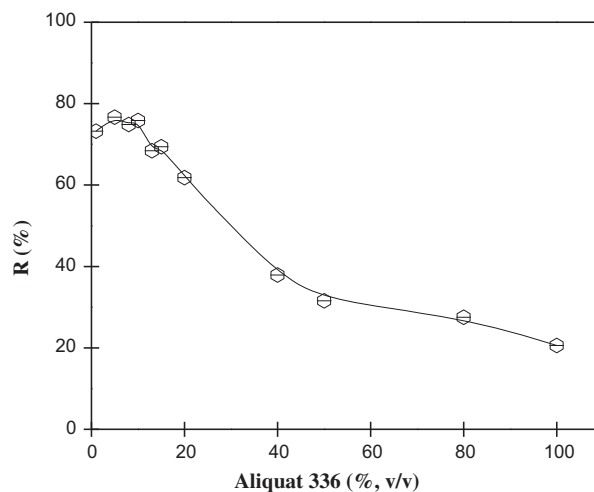


Fig. 2. Effect of the carrier concentration on the SA recovery percentage. Feed solution: 10^{-3} M SA at pH 1; Support: Accurel[®] PP; Organic phase: different Aliquat[®] 336 concentrations in 2-octanol; Stripping solution: 1 M NaOH. Transport time: 8 h.

throughout the study as the stripping agent. Li et al. [36] add diluent kerosene to the organic membrane phase to make the recovery of fumaric acid by hollow-fiber supported liquid membrane with strip dispersion using trialkylamine as carrier simple and easy to do.

3.2. Effect of Aliquat[®] 336 concentration in the membrane phase

The incidence of Aliquat[®] 336 concentration was studied from 1 to 100% (v/v). As it can be seen that from 1 to 10% recovery percentage increases slightly from 73.2 to 75.9% (Fig. 2). Afterwards, the recovery efficiency decreases from 68.4 to 20.6 with increasing Aliquat[®] 336 concentration from 13 to 100%, respectively. The slight increase in the SA recovery efficiency until an optimal value may be explained keeping in view the lower viscosity of the organic membrane solution due to diluent addition and the increasing availability and formation of extractable SA-Aliquat[®] 336 complex, and hence, its diffusion into the membrane organic phase. On the other hand, the recovery percentage decrease after an optimal carrier concentration value is probably due to the increase in the viscosity of the organic solution at higher Aliquat[®] 336 concentrations that leads to an increase in the liquid membrane resistance to the diffusion of SA-Aliquat[®] 336 complex [8,37]. This complex will load membrane pores and the phenomenon of membrane fouling can be observed especially at very higher Aliquat[®] 336

concentrations. In fact, the effective diffusivity of the complex decreases significantly while the reaction rate of its formation increases rather slowly as the Aliquat[®] 336 concentration increases above 10%. In this case, the increase in the carrier concentration at this point does not compensate for the increase in the solution viscosity. A concentration of 10% Aliquat[®] 336 was selected throughout the study.

Rak et al. [38] and Yamini et al. [39] have observed similar phenomena when they have respectively studied the transport of aromatic aminophosphonates and salbutamol and terbutaline through SLM using the same carrier.

3.3. Effect of feed solution pH

To assess the role of feed solution pH, pH variation studies in the range 1.0–8.0 were carried out. The receiving solution consisted of 1 M NaOH, whereas Aliquat[®] 336 (10%, v/v) in 2-octanol was used as organic membrane solution. Results given in Fig. 3 show that the extraction percentage increases with increasing feed pH from 1.0 to 3.0. Beyond pH 3.0, the extraction percentage reaches a more or less constant value around 90%. At a feed pH higher than pK_a (2.97), SA is preferentially found in its anionic form, and the extraction takes place by an ion-exchange reaction with Aliquat[®] 336, in which the anionic form of the SA is exchanged with the counter-ion Cl⁻ at the interface [5,39]. In fact, at the feed solution/membrane interface, salicylate forms a neutral ion-pair complex with Aliquat[®] 336 (tricaprylmethylammonium chloride). Due to its concentration gradient, the ion-pair complex diffuses across the membrane porosity. At the stripping solution/membrane interface, salicylate is released in the presence of an aqueous NaOH solution. The driving force to achieve uphill transport of SA is the difference in hydroxide concentration between both aqueous solutions. Taking into account these observations, the feed solution was adjusted at pH 3.0 throughout the study. The same extraction mechanism was suggested in our previous work when EAN was used as carrier to extract SA from aqueous solution through a FSSLM [30].

3.4. Effect of the chemical diluent nature

The effect of the chemical diluent nature on the SA transport efficiency depends on its viscosity, but also on its dielectric constant which affect the balance between the efficiency of the association and dissociation steps for the uptake of the solute by the carrier and its release from the complex at the receiving

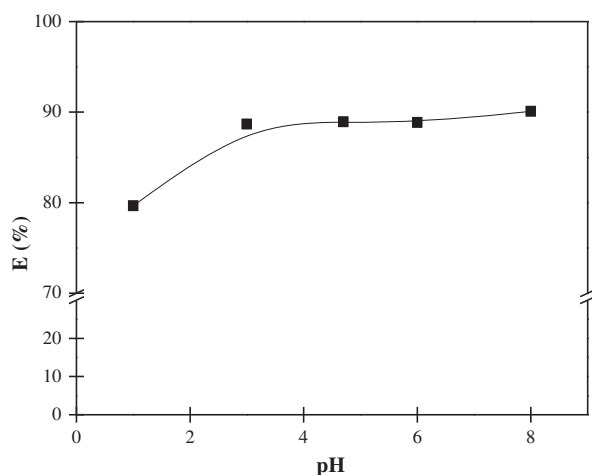


Fig. 3. Effect of the feed solution pH on the SA extraction percentage. Feed solution: 10^{-3} M SA at different pHs; Support: Accurel[®] PP; Organic phase: Aliquat[®] 336 (10%, v/v) in 2-octanol; Stripping solution: 1 M NaOH. Transport time: 8 h.

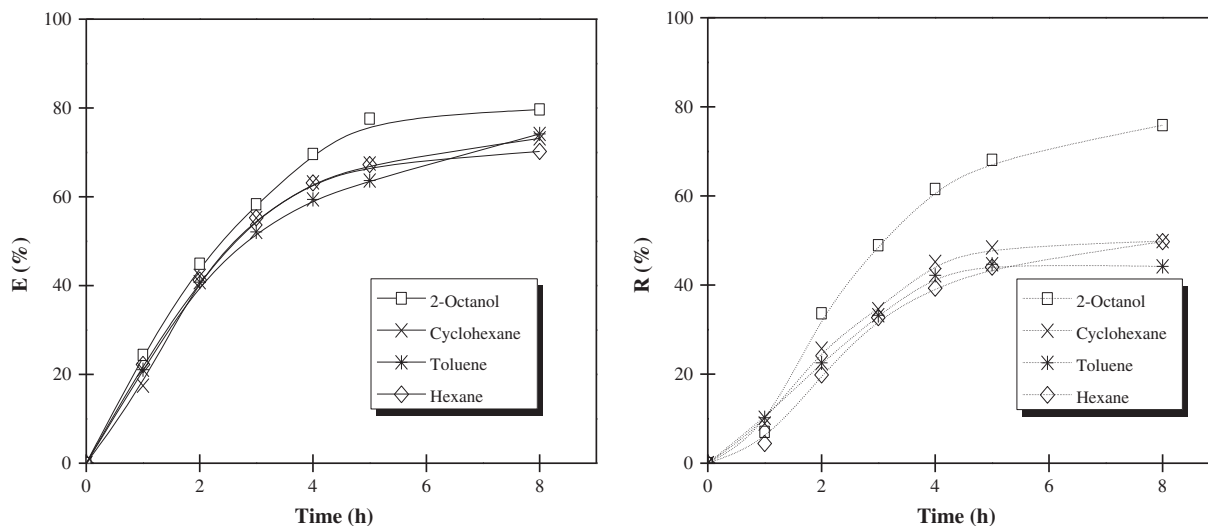


Fig. 4. Effect of the diluent nature on the SA extraction and recovery percentages. Feed solution: 10^{-3} M SA at pH 3; Support: Accurel[®] PP; Organic phase: Aliquat[®] 336 (10%, v/v) in diluent; Stripping solution: 1 M NaOH.

interface [40]. Nevertheless, it is difficult to ascribe the transport of the solute to any particular physical property of the organic diluent. To determine its effect on the present system, experiments were carried out with solutions of 10% (v/v) Aliquat[®] 336 in different diluents as organic membrane phase, solution of 10^{-3} M SA adjusted at pH 3.0 as aqueous feed phase and NaOH 1 M as aqueous stripping phase. The performance of 10% (v/v) Aliquat[®] 336 in various diluents viz. 2-octanol, cyclohexane, toluene, and hexane was examined by determining extraction and recovery efficiencies of SA in these mixtures. Fig. 4 shows that 2-octanol presents higher extraction and recovery efficiencies than cyclohexane, toluene, and hexane. These former provide comparable extraction and recovery efficiencies in relation with their comparable viscosity and dielectric constant values (Table 1). The fact that 2-octanol gives the highest extraction and recovery efficiencies can be explained taking into consideration that this diluent is more polar and can promote extraction by providing a good solvating media for the neutral ion-pair complex. Consequently, we studied the effect of the stripping agent (NaOH) concentration on the SA transport efficiency using 2-octanol as efficient diluent of the organic membrane phase.

3.5. Effect of NaOH concentration in the stripping phase

The pH values of the feed and receiving solutions are important parameters for optimizing the membrane system. To study the effect of the stripping pH value, the concentration of NaOH in the receiving solution was varied over a wide range. The variation of SA recovery percentage as a function of time at

various sodium hydroxide concentrations in the stripping phase is given in Fig. 5. By increasing NaOH concentration, receiving pH increases and rise in recovery percentage of SA was obtained, reaching a maximum at 2 M. While afterwards, the recovery did not increase anymore and remained constant with slighter fluctuations. This concentration of 2 M was selected as the optimum receiving NaOH concentration and was used throughout the study. To obtain complete stripping as stated by Luque et al. [41], the pH of the receiving solution must be at least 3.3 pH units larger than the analyte pK_a value, otherwise total collection in the stripping solution is not achieved and

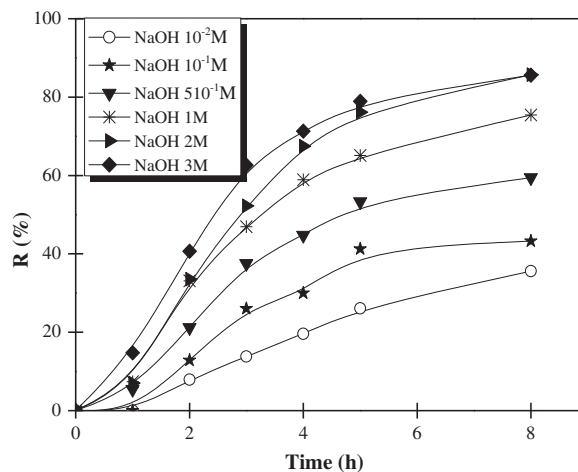


Fig. 5. Effect of the stripping agent concentration on the SA recovery percentage. Feed solution: 10^{-3} M SA at pH 3; Support: Accurel[®] PP; Organic phase: Aliquat[®] 336 (10%, v/v) in 2-octanol; Stripping solution: NaOH at different concentrations.

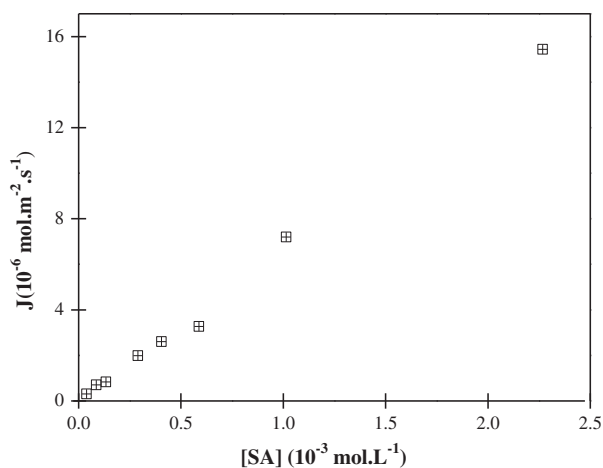


Fig. 6. Effect of the initial SA concentration on the initial flux. Feed solution: different SA concentrations at pH 3; Support: Accurel[®] PP; Organic phase: Aliquat[®] 336 (10%, v/v) in 2-octanol; Stripping solution: 2 M NaOH.

the analyte may be transported back across the membrane. The driving force to achieve uphill transport of SA is the difference in hydroxide concentration (pH) between both aqueous solutions. Therefore, increasing NaOH concentration strengthens the driving force and in turn higher recovery is achieved. On the other hand, at higher NaOH concentration the driving force of the liquid membrane process to reach equilibrium and further increase in the NaOH concentration does not lead to a rise in the SA transport efficiency [38].

3.6. Effect of initial salicylic acid concentration in the feed phase

Salicylic acid initial flux against the concentration of SA in the feed phase ranging from 10^{-5} to 2.25×10^{-3} M is presented in Fig. 6. It can be observed that under mentioned experimental conditions, the initial flux increased with the increase in the initial SA concentration in the feed phase and the membrane saturation phenomenon was not perceived. Taking into account the flux increase in the concentration studied range, the elaborated SLM system can be promisingly applied to extract SA from diluted or concentrated aqueous samples. An increase in flux at low feed concentrations is expected, followed by an approach to a plateau value at high feed concentration when the carrier is fully loaded [42]. As the flux increases almost linearly throughout the studied concentration range in this particular investigation, the liquid membranes have probably not reached saturation.

3.7. Effect of the polymeric support

In this study, two supports with different chemical composition and physical properties were tested under the same experimental conditions.

The concentration time profile of the SA transport was studied over a period of 8 h. For both supports, the time courses of the concentration changes of SA in feed and stripping phases are shown in Fig. 7. It can be noted that for both used supports the concentration of SA in the feed phase decreases sharply for the first 4 h of transport process to reach a plateau afterwards, whereas the concentration of SA in the stripping phase increases linearly in the same manner. Almost 90 and 88% of SA initially present in the feed phase was removed to the stripping phase after 8 h of transport through the SLM system using Durapore[®] and Accurel[®], respectively. Besides the increase in the effective exposed surface area of the membrane could increase the transport efficiency of the system. As seen in the figure, uphill facilitated transport from the feed solution toward the receiving solution was observed for both supports. The driving force of SA transport is a hydroxide concentration gradient between feed and stripping aqueous solutions.

Thickness, porosity, and tortuosity of the support are fundamental parameters that act on the mass fluxes of the solute. Table 2 collects both experimental (J_{exp}) and normalized SA fluxes (J_N) obtained with Durapore[®] related to the thickness d_0 , A , porosity ε_A and tortuosity τ_A of Accurel[®] PP support, as described in the following equation [43,44]:

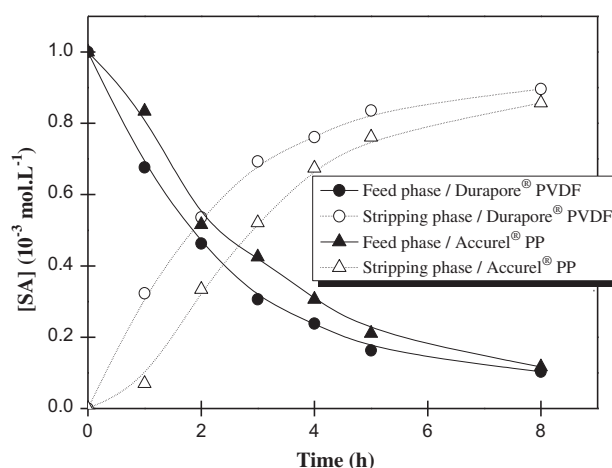


Fig. 7. Time courses of SA concentration in both feed and stripping solutions. Feed solution: 10^{-3} M SA at pH 3; Support: Accurel[®] PP or Durapore[®] PVDF; Organic phase: Aliquat[®] 336 (10%, v/v) in 2-octanol; Stripping solution: 2 M NaOH.

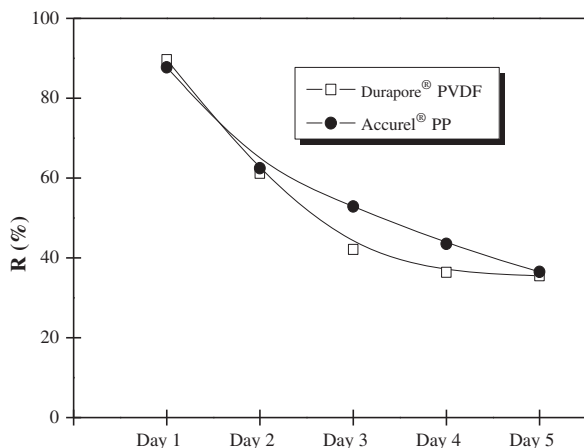


Fig. 8. Stability behavior of the SLM system: SA recovery percentage as a function of time. Feed solution: 10^{-3} M SA at pH 3; Support: Accurel® PP or Durapore® PVDF; Organic phase: Aliquat® 336 (10%, v/v) in 2-octanol; Stripping solution: 2 M NaOH.

$$J_N = J_{\text{exp}} \frac{d_0 \tau}{\varepsilon} \frac{\varepsilon_A}{d_{0,A} \tau_A} \quad (4)$$

Durapore® provides higher fluxes than Accurel® due to its higher ratio $\varepsilon/d_0\tau$ as well as the best SA transport (recovery) efficiency [11,43]. Accurel® in contrast presents the highest flux ($6.9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$) and transport efficiency (87.7% after 8 h) when Aliquat® 336 (10%, v/v) in 2-octanol is used as organic membrane phase instead of $[\text{C}_6\text{mim}][\text{PF}_6]$ ($2.1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$, 47.2% after 24 h) or EAN ($3.2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$, 48.5% after 24 h) [30].

3.8. SLM stability

The stability of both used membrane supports was examined following the SA transport (recovery) efficiency for a period of 5 days under the optimum conditions without re-impregnation of the membrane. The percentage of transported SA was measured throughout 8 h, and after this period of time, the transport process was stopped and the liquid membrane was kept in contact of pure water until 24 h. The same procedure was repeated for 5 days with each time fresh feed and receiving solutions. A plot of the percentage of transported SA vs. time is given in Fig. 8. From the observations made in this figure, it can be observed that both polymeric supports (Accurel® and Durapore®) showed a transport efficiency decrease with increasing operation time and then exhibit a time dependent negative tendency. Actually, the recovery percentage decreases from 89.6 to 35.5% and from 87.7 to 36.5% using Durapore® or Accurel® as polymeric support, respectively.

Nonetheless, Accurel® support can be considered as rather more stable than Durapore® support. On the other hand, a SLM system with $[\text{C}_6\text{mim}][\text{PF}_6]$ or EAN as membrane organic phase seems to be more stable than the use of the mixture Aliquat® 336/2-octanol. The observed transport efficiency decrease is may be due to a loss of the organic liquid membrane solution from the support pores [16,18]. In our case, the addition of 2-octanol as diluent of the membrane organic phase surely increases the transport efficiency of the system but in the same time would drastically decrease the viscosity of the membrane organic phase [31]. This viscosity decrease could enhance displacement of the organic liquid membrane solution from the micron pores and therefore decrease membrane stability.

4. Conclusion

This work has demonstrated that it is possible to extract salicylic acid (SA) successfully from acidic aqueous solutions across a FSSLM using the mixture Aliquat® 336/2-octanol as membrane organic phase. Still, the results indicated that the SA transport efficiency was affected by several operational variables. A transport efficiency value around 90% was obtained using two different polymeric supports impregnated with Aliquat® 336 (10%, v/v) in 2-octanol as membrane organic phase, aqueous SA solution at pH 3.0 as feed phase and a 2 M aqueous NaOH solution as stripping phase. Despite this higher transport efficiency, the elaborated SLM system has presented a short long-term stability compared with the use of 1-hexyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_6\text{mim}][\text{PF}_6]$) or EAN as membrane organic phase. It is clear from this study that the performance of a SLM system is related mainly to its transport efficiency and its long-term stability.

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