Journal of Chromatography A, 1217 (2010) 2318–2325

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Critical parameters in a supported liquid membrane extraction technique for ionizable organic compounds with a stagnant acceptor phase

Luke Chimuka[a,*], Titus A.M. Msagati[b], Ewa Cukrowska[a], Hlanganani Tutu[a]

[a] School of Chemistry, University of the Witwatersrand, P/Bag 3, Wits, 2050 Johannesburg, South Africa
[b] School of Chemistry, University of KwaZulu-Natal, P/Bag X54001 Westville Campus, Durban 4001, South Africa

ARTICLE INFO

Article history:
Available online 11 January 2010

Keywords:
Supported liquid membrane extraction technique
Critical parameters
Ionizable organic compounds

ABSTRACT

The reviews cover important critical parameters that are often optimized in a supported liquid membrane extraction technique in both flat sheet and hollow fibre designs for ionizable organic molecules. Understanding of these parameters can enable one to predict the behavior of the compound before hand and thus reduce the number of optimization experiments. Moreover, less number of experiments can be also generated using statistical techniques which are now becoming more commonly used. Supported liquid membrane extraction optimal parameters such as the conditions of the pH of the acceptor and donor phases should easily be fixed from the pKa values of the compounds. Other parameters, including the polarity of the compound can help to predict the partitioning into the membrane and the behavior of the compound. The influence of parameters such as temperature on the mass transfer in supported liquid membrane depends on the design of the module, experimental design and type of mass transfer controlling the extraction process.

Contents

1. Principles of supported liquid membrane extraction technique

Supported liquid membrane extraction technique is now a well known sample preparation tool. This has been reviewed by several authors [1–4]. Most of these reviews have focused on the principles of the SLM extraction technique [1,2,5,6] and/or its applications [3,7,8]. This review focuses mainly on critical parameters that affect the extraction process. This is very important because often SLM extraction is optimized for certain chemical species without proper understanding of these critical parameters. The review also includes attempts to use statistical techniques to help in optimization of the critical parameters [9–12]. Both flat sheet and hollow fibre membranes are discussed.

Some of the critical parameters can be seen from the principles of SLM extraction technique. The extraction process in a SLM technique involve partitioning of the analyte from the sample into the organic liquid impregnated in the membrane, diffusion through the membrane into the acceptor side, ionization and diffusion into the bulk of the acceptor solution. The process of ionization and diffusion into the bulk of the acceptor side is also called back-extraction. Therefore, for these desired extraction sequences to occur, critical parameters such as the pH of the sample (donor solution) and of the acceptor solution must carefully be chosen

* Corresponding author. Tel.: +27 11 7176703; fax: +27 11 7176749.
E-mail address: luke.chimuka@wits.ac.za (L. Chimuka).

0021-9673/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2010.01.004

[5,13]. The pKa of the compound is another critical parameter that must be known [5,9,13]. The polarity and size of the compound is also important because it affects the dissolution and diffusion into the membrane to the bulk acceptor side [14,15]. Other important parameters include extraction temperature [16–18], stirring rate [19,20] or sample flow rate [21,22], thickness of the porous membrane [19,22], extraction time [13,19,21] design of the extraction module [17,18,23], influence of humic substances [19,22] and salting out effect [13,22].

During optimization of the SLM performance, the extraction efficiency (E) and the concentration enrichment (E_e) in the acceptor side are measured [2,13]. The extraction efficiency is defined as a ratio of the amount of analyte extracted to that in the original sample. The concentration enrichment factor is a ratio of the concentration of analyte extracted to that in the original sample. The extraction efficiency and concentration enrichment factor are related by Eq. (1). Extraction efficiency and to some extent concentration enrichment factor (Eq. (1)) is the measure of the rate of mass transfer through the membrane. The extraction efficiency and enrichment factor are constant only at infinite trapping with specified extraction time, flow rate, phase composition, temperature, and ionic strength.

$$E = \frac{n_A}{n_I} = E_e \left(\frac{V_A}{V_I}\right) \quad (1)$$

where n_A and n_I are the total amounts of analyte found in the acceptor and present in the incoming (extracted) sample, respectively; V_A is the volume of the stagnant acceptor phase and V_I is the volume of the extracted sample.

2. Critical parameters affecting mass transfer

2.1. Choice of the pH of the aqueous phases

Detailed mass transfer kinetics including the influence of pH in the two aqueous phases has been reported by Jönsson et al. [5]. In this study, it has been shown that theoretically for nearly complete trapping of the analytes, the pH of the acceptor solution should be at least 3.3 pH units higher than the pKa of the analyte of interest for the extraction of acidic compound. For the extraction of basic compounds, pH of the acceptor phase has to be 3.3 units lower than the pKa of the analyte. In cases where a group of similar compounds need to be extracted with different pKa values, analyte with highest and lowest pKa values determines the pH of the acceptor solution for acidic and basic compounds, respectively. Depending on the sample, it has been shown that matrix components that are co-extracted can decrease the pH of the acceptor solution leading to an incomplete trapping [24]. For this case, it is advisable to use a high buffer capacity of the acceptor solution to compensate for change in pH due to matrix components that are co-extracted.

Chimuka et al. [13] is also reported to have carried out a detailed study on the influence of pH of the acceptor solution on the mass transfer in a supported liquid membrane technique. In this study, the theoretically predicted maximum enrichment factors for a group of basic compounds were compared with experimental values and good agreements were obtained. From the pKa of the compound and pH of the acceptor solution, it is possible to calculate the fraction of the analyte that is not ionized (α_A). This allows predicting the maximum enrichment factor that can be obtained [13]. α_A is given by [5,13]:

$$\alpha_A = \frac{K_a}{[H^+] + K_a} = \frac{1}{1 + 10^{s(pH_A - pKa)}} \quad (2)$$

where K_a is the ionization constant and $[H^+]$ is the concentration of hydrogen ions. $s = 1$ for acids and $s = -1$ for bases. pKa is the ionization constant of the compound and pH_A is the pH of the acceptor solution.

α_A is related to the maximum concentration enrichment factor by Eq. (3) [5,13]:

$$E_{e(max)} = \frac{c_A}{c_{I(max)}} = \left(\frac{\alpha_D K_D}{\alpha_A K_A}\right) = \frac{D_D}{D_A} = D \quad (3)$$

where c_A and c_I are the concentration of analyte found in the acceptor and present in the extracted sample, respectively; α_D is the fraction of uncharged compound in the sample. K_A is the partition coefficient for the analyte between the membrane phase and acceptor phase. K_D is the partition coefficient for analyte between the donor and membrane phases. D is the distribution factor of the analyte between the donor and acceptor phases. D_D and D_A are the distribution constants of analytes between the organic liquid and donor solution and between the organic liquid and acceptor solution, respectively.

If K_A is assumed to be equal to K_D, then [5]

$$E_{e(max)} = \frac{\alpha_D}{\alpha_A} \quad (4)$$

All the analyte in the sample solution (donor) is usually kept uncharged so that it can dissolve in the membrane so α_D is kept at 1. The maximum enrichment factor then is $1/\alpha_A$ provided the volume ratio of the donor and the acceptor allows it. Therefore, in any supported liquid membrane extraction technique, it is possible to predict the theoretical $E_{e(max)}$.

Where K_A and K_D are not equal (for example, due to different ionic strengths in the acceptor and donor phases) these can be calculated from the following equations as in a study by Chimuka et al. [13]:

$$K_A = \frac{D_A}{\alpha_A} \quad (5)$$

$$K_D = \frac{D_D}{\alpha_D} \quad (6)$$

D_A can be calculated from Eq. (7) [13]

$$D_A = \frac{[A]_M}{[A]_A + [AH^+]_A} = \frac{[A]_M}{[A]_A} \quad (7)$$

$[A]_m$ is the equilibrium concentration of the analyte in the organic liquid. $[AH^+]_A$ and $[A]_A$ are the equilibrium concentrations of the analyte in the ionized and nonionized forms in the aqueous acceptor solution, respectively.

$$K_D = \frac{[A]_M}{[A]_D} \quad (8)$$

Both D_A and K_D can be experimentally determined by liquid–liquid extraction if needed.

Table 1 shows the pKa of weak bases and values of α_A at different pH [13]. The table shows strong dependence of α_A on pKa and pH of the acceptor solution. In this study, a comparison of the maximum concentration enrichment factors experimentally obtained from SLM extraction and from theoretical calculations [13] was performed. The obtained good agreement of the two maximum concentration enrichment factors allows predicting beforehand this value once the acceptor pH is decided upon. This also allows reducing the number of experiments needed to optimize the acceptor pH since this can be predicted theoretically.

Fig. 1 shows the concentration enrichment factors obtained for some analytes in Table 1. The maximum concentration enrichment factor was attained easily with simazine and atrazine, which are more weakly basic and therefore not easily trapped in 1 M sulphuric acid used as acceptor solution [13]. These results agree well

Table 1
pKa's of the studied weak bases and α_A values at different pH values with permission from American Chemical Society [13].

Compound	pKa	α_A values at pH calculated by Eq. (2)		
		~1.0	~0.7	~0.0
Atrazine	1.68		9.13×10^{-2}	2.04×10^{-2}
Simazine	1.65		9.52×10^{-2}	2.13×10^{-2}
Terbuthylazine	2.0		4.57×10^{-2}	9.8×10^{-3}
Ametryn	4.1	6.82×10^{-4}		
Desmetryn	4.0	9.22×10^{-4}		
Dimethametryn	4.0	6.82×10^{-4}		
Terbutryn	4.3	4.62×10^{-4}		
Aniline	4.61	2.26×10^{-4}		2.42×10^{-5}
3-Methyl-5-nitroaniline	2.34	4.21×10^{-2}		4.51×10^{-3}
3-Chloro-4-methylaniline	3.97	9.86×10^{-4}		1.06×10^{-4}
3,5-Dichloroaniline	2.48	2.96×10^{-2}		3.27×10^{-3}

with Table 1. The concentration of uncharged analytes in the acceptor phase increases as the extraction continues until a plateau is reached which decreases the flux across the membrane. At the plateau, the flux ceases because the concentration of uncharged analyte in the acceptor solution and membrane equals that in the solution reaching equilibrium. In a recent study on the mass transfer in an incomplete trapping extraction of triazole fungicides using a single hollow fibre supported liquid membrane as module, theoretical maximum concentration enrichment factor (assuming $K_D = K_A$) was much higher than observed [17]. This was due to differences in the two partition coefficients. K_A was found to be much larger than K_D (see Eqs. (3) and (4)). Stripping of the analytes from the membrane into the acceptor solution was the rate limiting step.

In order for the analyte to dissolve into the membrane, it has to be uncharged. It is therefore important that the pH of the sample is adjusted as such. A safe pH of the sample is where α_D is >0.99 which leads to maximum 1% loss of efficiency [5]. Mathematically, this corresponds to pH of the sample greater than 2 units the pKa of the basic compound [5]. For acidic compound, pH of the sample should be at least 2 units less than the pKa value. Once the pKa value of the compound is known, it is possible to predict the appropriate pH of the sample solution. This therefore can reduce the number of optimisation experiments for the best pH of the sample.

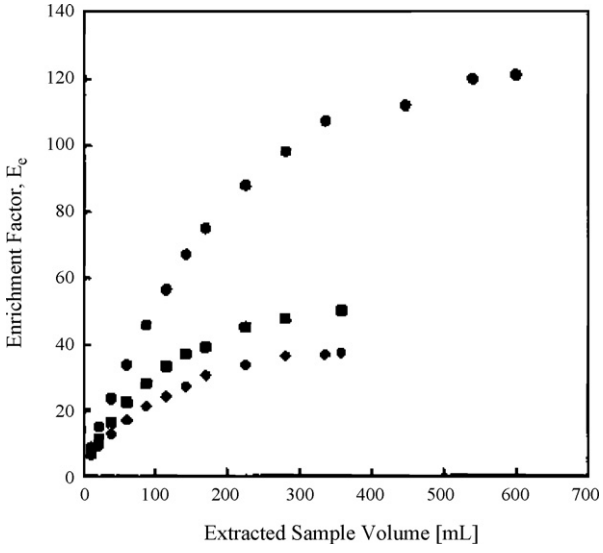

Fig. 1. Variation of concentration enrichment factor (E_e) with extracted sample volume for chloro-*s*-triazines (0.40 ppm each). The acceptor solution contained 1.0 M (pH ~0.0) sulphuric acid: (♦) simazine, (■) atrazine, (●) terbuthylazine with permission from American Chemical Society [13].

2.2. Choice of the impregnated liquid, polarity of the compound, type of membrane support and module

Selection of the membrane solvent for immobilization in the support material is one of the most critical steps in SLM extraction. For optimum extraction efficiency, it is desired that the partition coefficient of the analyte should be as large as possible and it should have very low water solubility [2,12].

Two common organic solvents that have been frequently used are undecane and dihexylether [13,15,16,21]. A detailed study on the role of the polarity of the compound on the mass transfer with dihexylether and undecane as membrane liquids was studied [15]. In this case, K_D in the two solvents was first measured for a group of phenolic and triazine compounds. This was then correlated with log *P* values (Fig. 2). The good correlations obtained indicate that log *P* value of a compound can be used as a measure of its dissolution in a supported liquid membrane technique. Another interesting observation (Fig. 2) is that as the compound becomes more non-polar, the difference in K_D in the two solvents reduces. This means that for non-polar compounds with log *P* values close to 4 and above, K_D contribution to the differences in the extraction efficiency in the two solvents becomes small (Fig. 2).

In this same study [15], a plot of log *P* values against the extraction efficiency resulted into a bell shaped pattern (Fig. 3). The first region between log *P* 0 to ~2 had the lowest extraction efficiency. This is followed by middle region with log *P* ~2.4 to ~3.3 which gives an optimum window with highest extraction efficiency. The

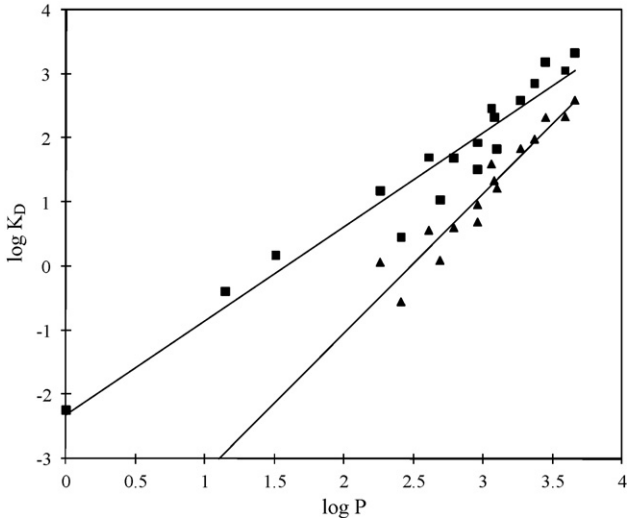

Fig. 2. Collander plots of the *s*-triazines in the two solvents used as membrane liquids: (■) di-n-hexyl ether and (▲) n-undecane, with permission from Elsevier [15].

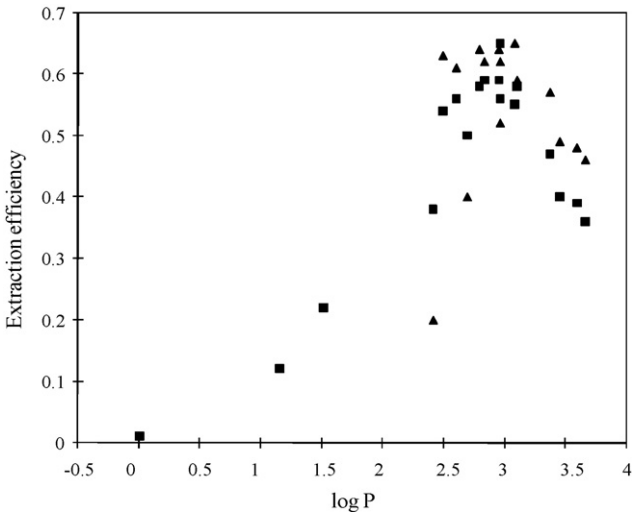

Fig. 3. Extraction efficiency vs log *P* plots for various triazines. Extraction efficiencies were obtained with SLM impregnated with (■) di-n-hexyl ether and (▲) n-undecane, with permission from Elsevier [15].

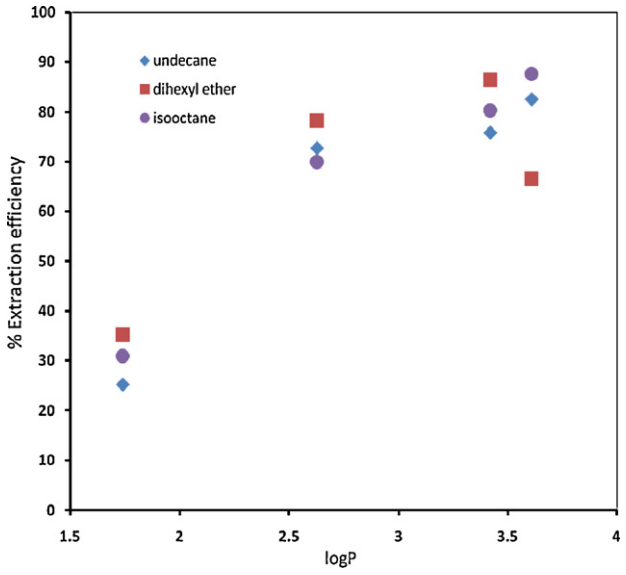

Fig. 4. Extraction efficiency vs log *P* plots for various dinitrophenols in a HF-SLM extraction technique impregnated with various organic solvents. log *P* 1.74 = 2,4-dinitrophenol, log *P* 2.63 = dinitro-ortho-cresol, log *P* 3.42 = 2-tert-butyl-4,6-dinitrophenol, log *P* 3.61 = 2-(1-methylpropyl)-4,6-dinitrophenol, with permission from Elsevier [12]. log *P* values obtained from http://www.chemspider.com [27].

third region beyond log *P* 3.3 showed signs of decreasing extraction efficiency. The first section is due to poor dissolution of the analytes into the membrane liquids because of small log *P* values. The last section is due to too high dissolution into the membrane liquids which results into slow mass transfer of the analytes between the membrane and acceptor solution. In this case, K_A is expected to be too large compared to K_D (see Eq. (3)). This observation can also be explained from Eq. (9) below [15]:

$$E = \frac{n_I - n_W - n_M}{n_I} \approx E_W - \frac{K_D V_m}{2V_I} \quad (9)$$

where n_W is the total amount that remains in the sample after extraction, n_M is the total amounts in the membrane, E_W is the extraction efficiency measured from the donor side of the membrane and can be calculated from Eq. (10). V_M is the volume of the membrane phase.

$$E_W = 1 - \frac{n_W}{n_I} \quad (10)$$

Eq. (9) indicates that if K_D is too high, a considerable amount of analytes will remain in the membrane. Poor trapping in the acceptor phase for compounds with high K_D values will also promote analytes remaining in the membrane. Also if the membrane volume is too high, considerable amount of the analytes will remain the membrane especially for high non-polar analytes. This is why thinner membranes as opposed to thicker ones are recommended in supported liquid membrane extraction technique. For flat sheet module, the porous PTFE membrane (pore size 0.2 μm, total thickness of 175 μm with 115 μm polyethylene supports and porosity of 0.70) from Millipore FG (Millipore, Bedford, MA) has been commonly used. Already, this thickness has been reported to generate slow mass transfer of more hydrophobic compounds from the membrane to the acceptor phase [14,15].

The current common module is the hollow fibre membrane that has replaced the traditional flat sheet module. The hollow fibre module has gained much attention because it is cheap and simple to perform. Various simple extraction designs are easily generated [7]. The Q3/2 Accurel 200/600 Accurel® PP polypropylene hollow fibre tubing (200 μm wall thickness, 600 μm inner diameter and 0.2 μm pore size) supplied by Membrana GmbH (Wuppertal, Germany) is commonly used [7]. High concentration enrichment factors are obtained because of the small nature of the acceptor volumes compared to the sample and the mass transfer into the hollow fibre is much more efficient than in a flat sheet design [23]. Fig. 4 shows a plot of the obtained extraction efficiency against the log *P* values for dinitrophenol compounds in a hollow fibre supported liquid membrane [12]. Results from three organic solvents are included in the figure from others such as toluene, hexylbenzene because they are similar from what has been used in flat sheet module in Fig. 3. The results suggest that in a hollow fibre supported liquid membrane extraction; slow mass transfer of the analytes from the membrane into the acceptor solution is not a major problem even for hydrophobic compounds. This could be attributed to smaller thickness of the membranes. This allows removal of the acceptor solution by passing air into the lumen of the hollow fibre [12,20]. Others studies using hollow fibre supported liquid membrane (HF-SLM) extraction does not indicate any decrease in extraction efficiency for compounds with much higher log *P* values [20]. Applications of the supported liquid membrane extraction in the form of a hollow fibre-liquid phase microextraction (LPME) does not suggest any decrease in extraction efficiency for high log *P* value compounds [25,26]. This is not surprising since in both LPME and HF-SLM extraction, the same type of HF is used and the principles of extraction are the same.

2.3. Donor flow rate/stirring rate, polarity of the compound and extraction time

The extent to which the mass transfer process is influenced by flow/stirring rate is dependent on the configuration of the extraction module, on the polarity of the compound and trapping in the acceptor phase. The influence of donor flow rate in a flat sheet module where the sample is pumped through in the donor phase results into two scenarios (Fig. 5). For the relatively hydrophobic compounds, an increase in donor flow rate is accompanied by an increase in the enrichment factor (Fig. 5). For most polar compounds, however, not much gain in enrichment factor results from an increase in donor flow rate. The variation of the enrichment factor with donor flow rate for compounds with varying polarity where the sample is pumped through has been discussed also by

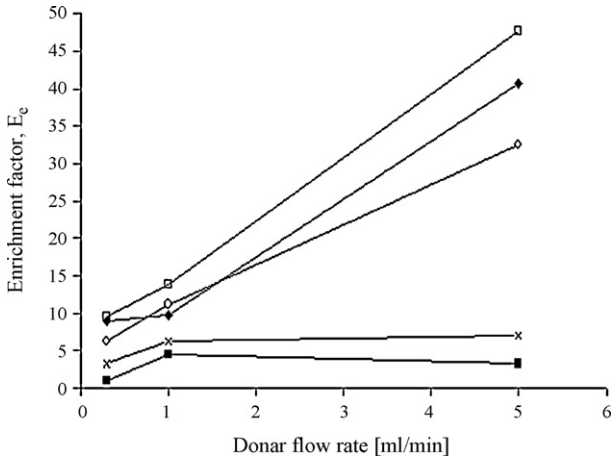

Fig. 5. Concentration enrichment factor dependence on the donor flow rate and octanol–water partition coefficients (log *P*) of the compounds: (■) deisopropylatrazine (log *P* = 1.2), (×) hydroxyatrazine (log *P* = 1.4), (◊) atrazine (log *P* = 2.7), (□) prometryn (log *P* = 3.34), (♦) terbutryn (log *P* = 3.74) with permission from Wiley-VCH GmbH [22].

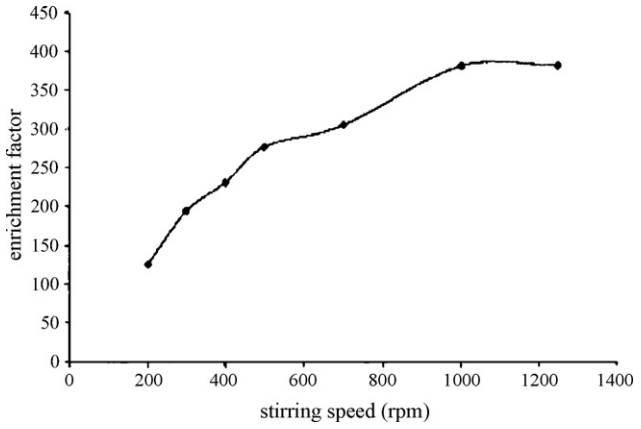

Fig. 6. The influence of magnetic stirring speed using 3,4-dinitrophenol (log *P* = 2.17 [26]) as an example in a hollow fibre-liquid phase microextraction technique. Conditions: 1-octanol as the impregnation solvent, 0.1 M HCl in the donor phase and 0.1 M NaOH in the acceptor phase, extraction time of 50 min, with permission from Elsevier [25].

Jönsson et al. [5] in the theoretical treatment of SLM technique. For extraction which is limited by the diffusion of the analyte from the bulk of the donor solution to the membrane surface (donor-controlled extraction), much better concentration enrichment factors are obtained at higher donor flow rates. This is the case for the more hydrophobic compounds with log *P* greater than 2, i.e. moderately polar to non-polar compounds. On the other hand, for the polar compounds with log *P* less than 2, low dissolution into the membrane limits the mass transfer (membrane controlled extraction). In that case a high donor flow rate does not result in much gain in enrichment factor since the extraction efficiency falls drastically (see Eq. (11))[5].

$$E_e = \frac{EV_I}{V_A} = \frac{E F_D t}{V_A} \quad (11)$$

where F_D is the sample flow rate and t is the extraction time.

From Eq. (11), it is seen that where a sample is pumped through, an increase in donor flow rate increases E_e but E reduces. For hydrophobic compounds, E does not reduce as much as for more polar compounds whose mass transfer is controlled by dissolution into the membrane (Fig. 5).

The results in Fig. 5 further mean that donor flow rate can be used to fine tune selectivity too in a SLM extraction where the sample is pumped through. If moderately polar to non-polar compounds are extracted from surface water which typically has very polar to polar matrix compounds, it is best to use high donor flow rate. This way the enrichment factor favours the moderately polar analytes, therefore enhancing the selectivity.

In a situation where the sample is stirred as in most applications of HF-SLM extraction technique, amount extracted increases with stirring speed both for compounds with low and high log *P* values. This is because in both cases, the contact time between the sample analytes and the membrane increases. However, at too high a stirring speed, the mass transfer is expected to be limited by the dissolution into the membrane. Increase in the amount extracted therefore deviates from linearity and curve moves towards a plateau as in a case where sample is pumped through (Fig. 5). This is supposed to be more pronounced for compounds with low log *P* values. Liu et al. [19] compared the effect of agitation in a HF-SLM extraction of phenoxy acid herbicides. Static extraction was compared with 100 rpm shaking rate. 90% extraction efficiency was reached in 8 h under static while this was reduced to 4 h at 100 rpm shaking rate [19]. The phenoxy acid herbicides studied have log *P* values ranging between 2.5 and 2.95 [15]. Zhu et al. [25] is reported to have varied the stirring speed in the extraction of nitrophenols in a HF-LPME technique. For 3,4-dinitrophenol as a typical example, the extraction efficiency increased with stirring speed until after 1200 rpm where a plateau was reached (Fig. 6) [25]. The log *P* value of 3,4-dinitrophenol is about 2.17 which is a moderately polar compound.

Therefore, in both where the sample is pumped through and where it is stirred, linear regions (Figs. 5 and 6) denotes where the mass transfer is limited by diffusion of the analytes from the solution to the membrane surface especially where complete trapping of analytes occurs. In this region increase in either sample flow rate or stirring rate is accompanied by increase in extraction efficiency and enrichment factor. The non-linear region leading towards a plateau is a region where the mass transfer is limited by dissolution into the membrane or the mass transfer approaches zero reaching equilibrium. This plateau region can also be obtained where all the analytes are almost transferred into the acceptor phase, but in a stirred sample. These two regions are supposed to be more easily attained for compounds with low log *P* values and where the sample is pumped through (Fig. 5).

In studying the influence of stirring rate in HF-LPME, some studies [28,29] have observed that too high a stirring rate causes air bubbles to attach to the fibre surface resulting in lower extraction efficiency and high relative standard deviations. Too high a stirring rate can also lead to loss of organic liquid impregnated in the membrane. This is also true where the sample is pumped.

The influence of extraction time on the mass transfer whether in flat sheet or hollow fibre design is commonly understood. Where the extraction efficiency is constant as in many applications, the amount extracted increases with time. If the trapping is nearly complete in the acceptor phase and where the sample is stirred, all the analytes will eventually be extracted. However, in most cases, because of incomplete trapping in the acceptor phase, longer extraction time results in an equilibrium reaching a plateau [13,28,29]. Too long extraction time could results into loss of organic liquid impregnated in the membrane too especially for volatile and not very non-polar solvent.

2.4. Extraction temperature

Very few publications have been reported on the study of the influence of temperature on mass transfer in a SLM extraction

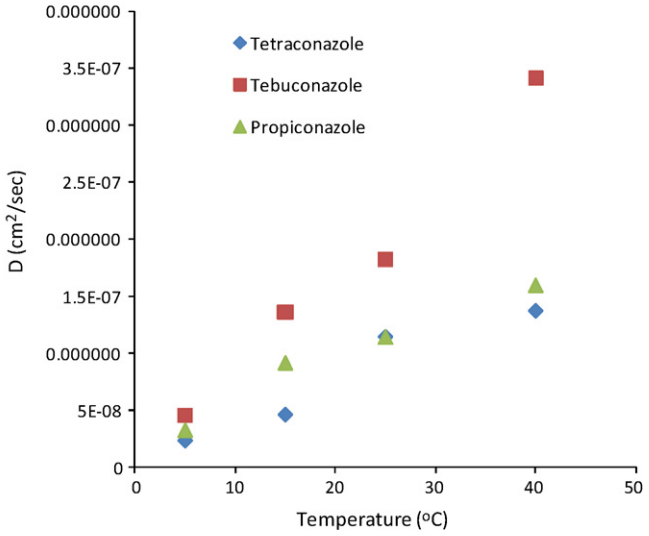

Fig. 7. Plot of the calculated diffusion coefficients against extraction temperature in a hollow fibre SLM technique with permission from Elsevier [17].

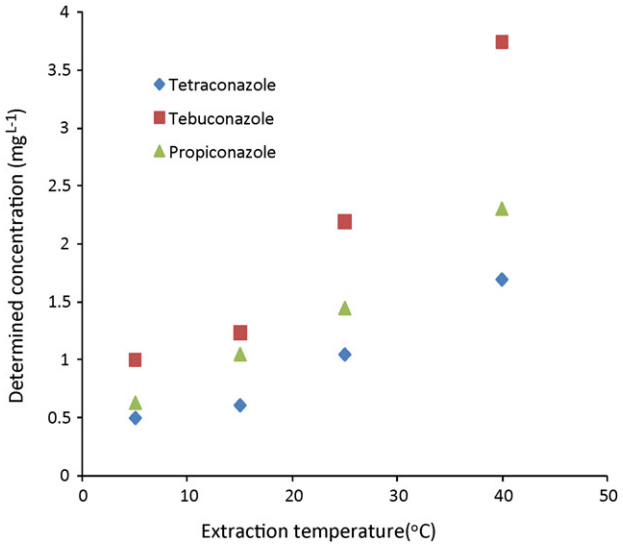

Fig. 8. Plot of the determined concentration in the acceptor solution against extraction temperature in a hollow fibre SLM technique with permission from Elsevier [17].

process [16–18]. Theoretically, the influence temperature can be summarized by Eq. (12).

$$D = \frac{K_\beta T}{6\pi a \eta} \tag{12}$$

where D is the diffusion coefficient of the analyte, η is the viscosity of solvent, K_β is the Boltzmann distribution coefficient, T is the temperature in Kelvins, a is the radius of the molecule.

Since diffusion coefficient (D) is directly proportional to temperature, the latter influence on mass transfer is supposed to be obvious. However, in really application of the supported liquid membrane extraction, the influence of temperature on the mass transfer is not as straight forward as Eq. (12) suggests. Other factors such as the configuration of the module [17,18], type of mass transfer controlling the extraction process [18], whether the sample is stirred or not have been observed to play a role too [17]. In a study of the influence of temperature on mass transfer in a flat sheet module with triazole fungicides as model compounds [18], it was observed that the diffusion coefficient was increasing with increasing temperature but with both donor and acceptor phases flowing. However, when the experiments were performed under same different temperatures and with a stagnant acceptor phase, no noticeable increase was measured in the extraction efficiency. This is important because in really applications of the SLM extraction, it is the extraction efficiency that is measured and under stagnant acceptor phase. In this case increase in diffusion coefficient was not high enough to give noticeable change in extraction efficiency. The extraction process was also controlled by stripping of the analytes from the membrane into the bulk of the acceptor solution [18]. The design of the flat sheet module used could also have limited the temperature effect since the PTFE blocks housing the membrane may have generated a temperature gradient. The same study was then performed but using a hollow fibre module [17]. The results obtained in this case indicated that diffusion coefficient increased with temperature (Fig. 7) and that the amount accumulated in the acceptor phase did also increase with temperature (Fig. 8). These two studies clearly explain the influence of the module and experimental design on how temperature affects the mass transfer in a SLM extraction process.

2.5. Influence of humic substances and salting out effect

The influence of humic substances in a supported liquid membrane extraction technique depends on the amount present in the extracted sample and the extraction conditions especially the donor and acceptor pHs. Humic substances consists of polar functional groups mostly hydroxyl and carboxylic acid groups. Depending on the pHs of the sample and acceptor solutions, these can be co-extracted and enriched along with the target analytes.

However, in applications of the supported liquid membrane extraction technique, very little influence of humic substances on the extraction efficiency has been encountered [19,22]. Megersa et al. [22] developed an automated liquid membrane extraction and trace enrichment of triazine herbicides and their metabolites in environmental samples and the influence of humic substances was tested by spiking 25 mg L^{-1} of humic acids in the deionized water sample. The results showed that there was no influence of humic acids on the corresponding enrichment factor. In this case, 1 M HCl was used as acceptor solution with sample solution buffered at pH 7.0. In another study by Liu et al. [19], the effects of humic acids in passive extraction and clean-up of phenoxy acid herbicides using hollow fibre supported liquid membrane was studied. The effects of humic acids in the range 0–25 mg L^{-1} (DOC) were studied in the sample solution. The extraction efficiency obtained were not influenced by humic acids and ranged from 98 to 112%. In the application of SLM extraction to chlorophenols in natural waters, a decrease in pH of the acceptor solution was noticed because of possible matrix components that were co-extracted [24]. This reduces the mass transfer across the membrane to the acceptor solution because the target analytes are incompletely trapped. The problem was solved by using a high buffer capacity of the acceptor solution.

Chimuka et al. [13] carried a detailed study on the salting out effect in SLM extraction of triazine herbicides. In this study, the ionic strength of the sample solution was varied from 0.1 to 3.1 for simazine, atrazine and terbuthylazine. The effects of ionic strength on the partition coefficient and maximum enrichment factor were both measured. The partition coefficients of the compounds into the organic liquid increased with increasing ionic strength as in the practice of liquid–liquid extraction. The corresponding maximum enrichment factors also increased for all the analytes. This is in agreement with Eq. (3) where the enrichment factor is directly

proportional to the partition coefficient of the analyte from the donor solution to the membrane liquid. Interesting in this study is the observation that in the initial extraction periods, insignificant differences in enrichment factors for all analytes at various ionic strength was observed [13]. However, as uncharged analytes build up in the acceptor, the differences become more evident [13]. Therefore, the effect of increasing ionic strength on the enrichment factor is more beneficial for longer extractions where the concentration of uncharged analytes in the acceptor solution becomes predominant. The increase in mass transfer with increasing ionic strength for polar to moderately non-polar compounds has been observed by other researchers, e.g. Megersa et al. [22] in the SLM extraction of triazine herbicides and their metabolites in environmental samples.

3. Use of statistical techniques in the optimisation of critical parameters

Supported liquid membrane technique can be used for multiple extractions of compounds especially those in the same family and therefore the application of experimental design using statistical approaches, as well as the utilization of the desirability functions may be used to select the best extraction conditions, with a minimum number of experiments. The classical approach in the optimization of SLM extraction technique has been to optimize one factor at a time. This approach cannot solve the dependence of multivariables which are critical parameters. Therefore, a factorial design is attractive as levels of a given factor are combined with all levels of every other factor in the experiment. This gives a combination of variables near the maximum in searching for maximum extraction efficiency. The chances of missing maximum are also reduced. Multivariable approach overcomes the limitations of classical approach and increases the probability of finding the maximum. Further as the number of variables increases so does the number of experiments. Factorial design can be used to reduce the number of these experiments.

A number of researchers have tried to use statistical techniques to study the extraction process in membrane based extractions. Romero et al. [10] used multivariate optimization of supported liquid membrane extraction of biogenic amines from wine samples prior to liquid chromatography in the determination of dansyl derivatives. Simultaneous optimisation of the membrane composition for all amines was achieved by a desirability function using doehlert's and full factorial designs. Good agreement was obtained between predicted and experimental results using selected carrier compositions. Transfer prediction by linear discriminate analysis and soft independent modelling of class analogy was used in the extraction of pesticides by Carabias-Martinez et al. [9]. Physical properties of the analytes such as molecular weight, boiling point, vapours pressure, octanol–water partition coefficients log *P*, acid dissociation constant pKa, solubility and density of the compounds were investigated on how they influence the extraction process. The modelling and discriminant power of each variable obtained are shown in Table 2. The log *P* values and water solubility of the analyte were seen as variables with greatest discriminant power [9]. The properties of the compounds with greatest modelling power were found to be log *P*, water solubility, molecular weights, and p*Ka* [9]. This way, it was possible to predict the ability of the compounds to cross the membrane. Others such as density and vapour pressure were found not to be critical.

Table 2
Modelling and discriminant power from classification with Soft Independent Modelling of Class Analogy (SIMCA) with permission from Wiley-VCH GmbH [9].

Variable	Modelling power		Discriminant
	Category 1	Category 2	
log *P*	0.9684	0.7356	353.7
Water solubility	0.7448	0.7571	245.2
Molecular weight	0.8428	0.8826	213.2
pKa	0.6298	0.9902	10.5

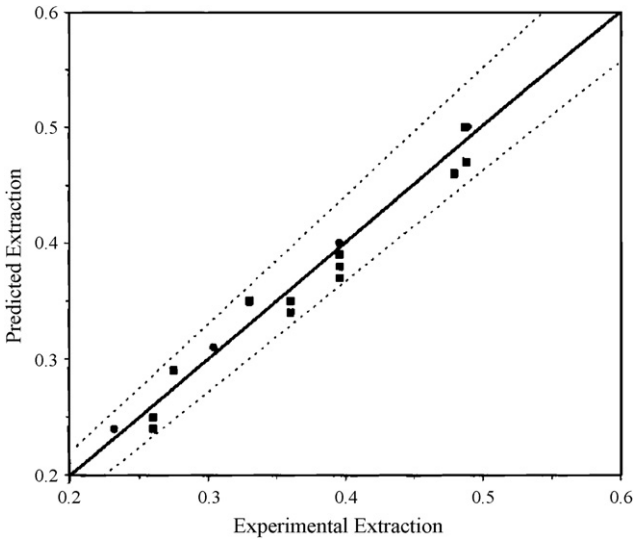

Fig. 9. Comparison of the experimental and predicted extraction from an ANN model with permission from Elsevier [11].

While artificial neural network have been applied in a number of sample preparation techniques such as matrix solid phase dispersion [30] and liquid–liquid extraction column [22], very little study has been performed on SLM extraction technique. Chakraborty et al. [11] is reported to have studied the applicability of artificial neural network (ANN) in emulsion liquid membranes. The developed model gave good agreement between the predicted extraction efficiency and the experimentally obtained (Fig. 9). The ability to predict the extraction efficiency in a SLM extraction technique is generally a very attractive idea as it can reduce the optimisation experiments.

4. Conclusion and future perspective

Understanding the factors influencing the extraction process in a SLM extraction in method development has the potential to reduce the number of optimisation experiments. This is because a number of critical parameters can be known beforehand. Future optimisation experiments will therefore merely verify the predicted parameters. The use of statistical techniques is likely to increase as this minimises the number of optimisation experiments. Artificial neural network in particular is likely to be more often used to predict the extraction efficiency.

Acknowledgement

The authors would like to acknowledge the fruitful discussion with Prof Jan Åke Jönsson on some aspects of mass transfer kinetics.

References

[1] L. Chimuka, E. Cukrowska, J.Å. Jönsson, Pure Appl. Chem. 76 (2004) 707.
[2] J.Å. Jönsson, L. Mathiasson, TrAC 18 (1999) 318.
[3] J.Å. Jönsson, L. Mathiasson, TrAC 18 (1999) 325.
[4] T. Msagati, L. Chimuka, E. Cukrowska, Water SA 34 (2008) 421.
[5] J.Å. Jönsson, P. Lövkvist, G. Audunsson, G. Nilvé, Anal. Chim. Acta 227 (1993) 9.
[6] L. Chimuka, E. Cukrowska, J.Å. Jönsson, Modern Extraction Techniques: Food and Agricultural Samples, in: Book Series, ACS Symposium Series 926, 2006, p. 149.

[7] T. Barri, J.Á. Jönsson, J. Chromatogr. A 1186 (2008) 16.
[8] T.A.M. Msagati, L. Chimuka, E. Cukrowska, H. Tutu, R. Majors, LC–GC North America 27 (2009) 100.
[9] R. Carabias-Martinez, E. Rodriquez-Gonzalo, J.L. Perez-Pavon, P. Paniagua-Marcos, J. Hernandez-Mendez, J. Sep. Sci. 24 (2001) 577.
[10] R. Romero, J.Á. Jönsson, D. Gazquez, M.G. Bagur, M.S. Vinas, J. Sep. Sci. 25 (2002) 584.
[11] M. Chakraborty, C. Bhattacharya, S. Dutta, J. Membr. Sci. 220 (2003) 155.
[12] J. Lezamiz, J.Á. Jönsson, J. Chromatogr. A 1152 (2007) 226.
[13] L. Chimuka, N. Megersa, J. Norberg, L. Mathiasson, J.Á. Jönsson, Anal. Chem. 70 (1998) 3906.
[14] T. Miliotis, M. Knutsson, J.Á. Jönsson, L. Mathiasson, Intern. J. Environ. Anal. Chem. 64 (1996) 35.
[15] L. Chimuka, L. Mathiasson, J.Á. Jönsson, Anal. Chim. Acta 416 (2000) 77.
[16] L. Chimuka, M.M. Nindi, M.E.M. ElNour, H. Frank, C. Velasco, J. High Resolut. Chromatogr. 22 (1999) p417.
[17] M. Michel, L. Chimuka, E. Cukrowska, P. Wieczorek, B. Buszewski, Anal. Chim. Acta 632 (2009) 86.
[18] L. Chimuka, M. Michel, E. Cukrowska, B. Buszewski, J. Sep. Sci. 32 (2009) 1043.
[19] J.F. Liu, L. Torang, P. Mayer, J.Á. Jönsson, J. Chromatogr. A 1160 (2007) 56.
[20] F.U. Shah, T. Barri, J.Å. Jönsson, K. Skog, J. Chromatogr. B 870 (2008) 203.
[21] L. Chimuka, M.M. Nindi, J.Á. Jönsson, Intern. J. Environ. Anal. Chem. 68 (1997) 429.
[22] N. Megersa, L. Chimuka, T. Solomon, J.Å. Jönsson, J. Sep. Sci. 24 (2001) 567.
[23] M.D. Luccio, B.D. Smith, T. Kida, T.L.R. Alves, C.P. Borges, Desalination 148 (2002) 213.
[24] M. Knutsson, L. Mathiasson, J.Å. Jönsson, Chromatographia 42 (1996) 165.
[25] L. Zhu, L. Zhu, H.K. Lee, J. Chromatogr. A 924 (2001) 407.
[26] J.B. Quintana, R. Rodil, T. Reemtsma, J. Chromatogr. A 1061 (2004) 19.
[27] http://www.chemspider.com, accessed on 20th September 2009.
[28] J.F. Peng, J.F. Liu, X.L. Hu, H.C. Li, T. Wang, G.B. Jiang, J. Chromatogr. A 1139 (2007) 165.
[29] Y. Tao, J.F. Liu, X.L. Hu, H.C. Li, T. Wang, G.B. Jiang, J. Chromatogr. A 1216 (2009) 6259.
[30] V.I. Bot, V.A. Sakkas, T.A. Albanis, J. Chromatogr. A 1216 (2009) 1296.