RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Studies on the stability of supported liquid membrane and its cleaning protocol†

Mriganka Sekhar Manna,* Prabirkumar Saha*‡ and Aloke Kumar Ghoshal*

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

This paper is a logical continuation of the previous work published by Manna *et al.* in *RSC Advances*, 2014, **4**, 26247. The referred paper established a technique for separation and recovery of trace amount of bioactive catechins from tea extract and its subsequent iron complexation through Flat Sheet Supported Liquid Membrane (FS-SLM). However the technique suffers with problems such as instability and fouling of membrane support. In this work, the issues related to the instability and fouling of SLM have been investigated. The components of the process such as solvent, aqueous phases, membrane support, electrolyte, surfactant etc. were extensively studied for detecting the best operating condition that would yield better stability. Critical displacement pressure differentials (ΔP_c) for liquid membrane were determined. Thermodynamic aspects for emulsion formation were investigated with addition of surfactants. At the best condition, the membrane was found to be stable for 120 hours with flux (of catechin) of 23.34×10^{-8} kg.m^{-2}.s^{-1}. The best condition for FS-SLM were re-employed in a similar experimentation using hollow fiber supported liquid membrane (HF-SLM) module. An experimentally evolved membrane cleaning protocol is reported.

1 Introduction

Supported liquid membrane (SLM) is regarded as one of the most promising techniques for recovery of trace amount of value-added bioactive compounds. It also has other applications such as separation of heavy metal ions from aqueous solutions, removal of contaminants from waste water, gas separation etc.[1–5] However, commercial application of this technique is very limited, mostly due to instability of the SLM. The stability of SLM is defined as the ability to immobilize the LM in the pores of the support membrane during the transportation operation. The very general problem of SLMs (both in flat sheet and hollow fiber membrane) is the immobilization of the solvent (*a.k.a* organic phase or liquid membrane) in the pores of polymeric support that can withstand the hydraulic forces acting upon it during the transport operation. Loss of solvent due to mutual dissolution of the organic and aqueous phases is the prime reason for instability of the liquid membrane. The instability of SLM affects in several ways. The flux declines with time that affects the overall transportation of solute.[6,7] At the same time, the complete recovery of the solvent from the aqueous phases is difficult. Moreover, the loss of solvent from the pores of polymeric support may cause direct channelling between the aqueous phases (feed and stripping solutions) and this intermixing of phases defeats the purpose of the LM operation.[8] Because mixing of organic phase with the aqueous phases, especially to the stripping phase, deteriorates the quality of product. Hence, a detailed introspection of the physico-chemical parameters of the LM components is necessary for higher stability of the LM. In addition, various forces acting on LM should be adjusted for increasing its longevity so that it can be employed in commercial level.

Researchers investigated the factors and mechanisms influencing the stability of SLM since it was established as the advanced alternative technique of conventional solvent extraction. Danesi and Rickert[9,10] reported three probable reasons of instability of SLM as: (i) solubility of the organic phase in aqueous solutions, (ii) progressive wettability of the pores of polymeric support which is induced by interfacial tension (γ) away from critical interfacial tension of membrane support, (iii) and most importantly the differential pressure existing between both sides (aqueous phases) of the LM caused by stirring and/or pumping of the flow streams.

Takahashi et al.[11] studied the stabilities of two types of SLMs, viz. flat sheet SLM and hollow fiber SLM, in terms of leakage of water across the membrane. Various reasons for the instability of membrane were reported by them. They argued that SLM system would be more stable when solvent is of higher interfacial tension and of lower surface tension than the critical surface ten-

‡ *Author for corresspondence*
* *Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam 781039, INDIA. Fax: +91.361.2582291; Tel: +91.361.2582257; E-mail: p.saha@iitg.ac.in*

sion of the polymeric solid support. Thus, aliphatic hydrocarbons, which are chemically more inert to polymeric solids and of higher boiling points, are suitable as solvents. The imbibition rate (q) of aqueous phases that is caused by the solubility of aqueous and organic phases, progressive wettability, vaporization of solvent, forces exerted due to hydraulic pressure etc. as a combinatorial effect, can be expressed by the Rideal-Washburn equation:[12]

$$q = \frac{r_i \gamma \cos\theta}{4\mu\delta} \quad (1)$$

Therefore, the stability of the LM in the pores will be higher if radius of pore (r_i) and interfacial tension (γ) are low whereas contact angle (θ), viscosity of solvent (μ) and thickness of membrane (δ) are high. The same problem of progressive wettability also arises (by an aqueous solution) with polymeric support that absorbs an organic solvent.[13] Once the organic liquid is absorbed by the polymer, the adhering water solution would progressively spread throughout the membrane in accordance with buoyancy, capillary action and pressure forces; a rate of leakage-curve is obtained in course of time. This has to be attributed to hydrodynamics and thermodynamic properties of LM and the support material.[14]

On the other hand, a polymeric support can be well wetted with an organic solvent of surface tension (σ) which is smaller than the critical surface tension(σ_c).[15] LM is held in the pores by capillary forces. The critical displacement pressure (P_c), that the LM can withstand, depends upon the structure (size and shape) of pores and the interaction (chemical compatibility) between LM and the material (polymer) of support; as implied by the Young-Dupre equation.[16]

$$P_c = \left(\frac{2\gamma}{r_i}\right)\cos\theta \quad (2)$$

A support-LM combination with high interfacial tension and smaller pore size can withstand higher pressure. The value of $\cos\theta$ depends on the smoothness of the surface of support material as well as the shape of the pores.[17] The interfacial tension and the contact angle have the opposite effects on the stability of LM, as implied by the eqs. (1) and (2). Hence, these two parameters need to be optimized in order to achieve more stable LM. The loss of organic phase i.e. LM is least when shape of pore is cylindrical. Larger it deviates from cylindrical shape, more is the loss of organic phase.[17]

Several hydrodynamic conditions, caused by the stirring and flow of streams, were analyzed and reviewed by other researchers.[18–20] They discussed various types of instability that may occur in SLMs. The instability at the aqueous/organic interface arises when the phases move in different tangential velocities. This instability occurs in flat sheet SLMs because membrane phase is a stationary phase and the aqueous phases are in circulatory motion. This instability is called the Kelvin-Helmholtz instability. Rayleigh-Taylor instability arises when lighter phase is accelerated due to movement of heavier phase. Instability may also arise from turbulence and the difference of densities of the LM and the aqueous phases because of buoyancy forces.

Hence, the optimization of the physico-chemical properties of the concerned phases and the functional forces related to the stability of SLM are important areas to explore further for commercialization of SLM techniques. In this study, we have explored the stability of SLM through characterization of the solvents, carrier and polymeric supports as well as optimization of other operating parameters *viz*., rate of stirring, use of electrolyte and surfactant. The whole stability study has been carried out for separation of catechin, a bioactive compound, using flat sheet SLM.

Catechins are major tea polyphenols present mostly in the green tea leaves and in lesser amount in some fruits and vegetables. The chemopreventive, cardioprotective and antioxidant capacity of catechin compounds were confirmed by various ethnopharmacological studies.[21–24] Jovanovic *et al.*[25] reported catechins extracted from green tea as more active antioxidant than vitamin-E. Catechins exist in the plant sources in very trace quantity, that too with impurities, such as tannins, caffeine, theophylline and theobromine, that are hazardous to the health.[1,26–29] Hence, separation of catechins is essential from their respective sources prior to their usage as specific components for medicinal application. Transportation of catechins from synthesized solution as well as from real extract of green tea leaves through FS-SLM[11] and HF-SLM[30] respectively, have already been studied by this research group. We also studied the iron complexation of pharmaceutical catechins through selective separation for the enhancement of antioxidant property of catechins.[31] Tributyl phosphate (TBP) in *n*-decane was found to be an ideal carrier-solvent combination whereas ethanol was found to be the best stripping agent.

In this paper, we have investigated the factors influencing the longevity of SLM. All the stability criteria evolved in experimentations with FS-SLM were incorporated in the recovery of catechin and its derivatives from real extract of green tea leaves through HF-SLM module. Fouling of membrane is another problem for SLM while working with real extract from tea leaves. The problem was more serious in HF-SLM module. Consequently, a membrane cleaning protocol for HF-SLM module has also been investigated in this work.

2 Experimental studies

2.1 Materials and methods

Aqueous solutions were prepared with Milli-Q® de-ionized water (Millipore, USA). Synthetic (+) catechin hydrate ($C_{15}H_{14}O_6.H_2O$) was procured from National Chemicals, India. Other derivatives of catechin were procured from Sigma Aldrich and used as standards. Solvents *n*−decane and *n*−decanol and the carrier tributyl phosphate (TBP) were procured from Merck, Germany. The surfactants with various HLB values and other chemicals were procured from Merck, India. The flat sheet polymeric membranes (support materials) such as polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE), polyethersulphone (PES), nylon,6 and HF-SLM module (made of polyethersulphone) were procured from Pall Life Science Corporation, India.

2.2 Analytical methods

Experimental samples were first centrifuged (Eltek, TC 800 D) in order to obtain a clear solution prior to measurement of concentration of catechin in UV-vis. spectrophotometer (Thermo Scientific, Spectrascan UV-2300). The other instruments include digital pH meter (Eutech Instruments, pH Tutor) and the shaking incubator (Daihan Labtech Co. Ltd, LSI 3016R) for two phase equilibrium studies. Oswald viscometer and tensiometer (Kruss Germany, K9) were used for measurement of viscosity of LM and the interfacial tension of LM with the aqueous phases, respectively. Mutual solubility of LM and aqueous phases and the emulsion droplet size were measured by Karl-Fischer Titrator (787 KF Titrino, Metrohm) and Delsa Nano particle size analyzer (Beckman Coulter Delsa Nano C), respectively. Individual catechin derivatives in the extract of tea leaves and the standards were analyzed using a Shimadzu LC-20AD HPLC (Tokyo, Japan) equipped with a ternary pump delivery system and UV detector. Catechin derivatives were identified and quantified through Reversed phase HPLC analysis with the help of the standards of $(+)$catechin and its derivatives $(-)$EGC, $(-)$EGCG and $(-)$ECG.[11] The real extract of tea leaves was prepared by extraction of 1 g of ground green tea leaves (Assam, India) in 130 mL deionized water at 60°C for 10 h under continuous stirring at 500 rpm. The eluting phases were a binary system of A (water/acetic acid, 100/0.1 vol %) and B (acetonitrile/acetic acid, 100/0.1 vol%). They were applied in the ratio of 70:30 (A:B) at a flow rate of 1.0 mL.min^{-1}.

2.3 Procedures of transportation of catechin

Two aliphatic solvents of straight chain with same length of carbon chain, *viz.* $n-$decane and $n-$decanol were used in the experimentation. On the other hand, carrier tributyl phosphate (TBP) has good extracting capacity of catechin and it was used in our previous work for LM based transportation of catechin in three different configurations *i.e.* bulk liquid membrane (BLM), FS-SLM and HF-SLM.[1,30,32] The amount of carrier (TBP) was varied for each solvent and thereby different compositions of LM were produced. Five runs (each of 24 h) of experiments were carried out with same membrane but with fresh feed and strip solutions in each run. The stability was measured in terms of the maximum flux achieved in 5^{th} run.

Two types of SLMs were used for the studies of catechin transportation *viz.*, FS-SLM and HF-SLM. All the stability criteria were checked and analyzed in the process of permeation of catechin through FS-SLM. Further, HF-SLM was also used to exploit the higher interfacial surface for the mass transfer per unit volume of the HFM module. The preparations of FS-SLM and the HF-SLM have been reported elsewhere.[1,30] PVDF membrane was used in all transportation studies if not mentioned specifically. Catechin was transported from the feed solution of 100 mg.L^{-1} catechin to the stripping solution of 0.4 M ethanol through the LM immobilized into the pores of size 0.2 μm. The permeation cell and the procedures of transportation were described in detail in our previous work.[1] The procedure was repeated five times with the same membrane but with fresh feed and strip solutions to check the extent of stability of the SLM. The parameters, optimized for most stable FS-SLM, were employed in the transportation of various catechin compounds from real extract of tea leaves through HF-SLM. The details of characteristics of HFM module and working flow rates have been given in our previous work.[30] All the experiments were performed thrice and the avearge values have been reported. Results are shown with the help of standard error bars whenever applicable.

3 Results and discussions

3.1 Analysis of stability

3.1.1 Role of liquid membrane

The LM was selected based on solute extracting capacity of carrier and the solvent-carrier compatibility based on their physicochemical properties. The maximum flux in fifth run and the corresponding physical parameters related to stability of SLM were shown in Table 1.

Table 1 The physical properties of LMs and their corresponding maximum fluxes in the 5^{th} run

Solvent	TBP conc. (M)	Viscosity (mPa.s)	Interfacial tension (mN.m^{-1})	Density (kg.m^{-3})	Flux $\times10^8$ (kg.m^{-2}.k^{-1})
	0.75	8.08	9.3	858.3	2.12
$n-$decanol	1.2	6.04	9.8	872.6	5.6
	1.5	4.81	10.1	886.9	3.4
	0.75	1.01	12.6	778.5	13.2
$n-$decane	1.2	1.20	11.8	802.8	16.34
	1.5	1.253	10.7	827.0	15.89

The values of fluxes of catechin were better for every concentration of carrier in case of $n-$decane compared to that of $n-$decanol due to lower viscosity of LM comprising $n-$decane. The effective diffusivity of a solute-carrier complex is inversely proportional to its viscosity according to Stokes Einstein equation:[33]

$$D_{eff} = \frac{kT}{6\pi\eta r} \quad (3)$$

and it was supported by the experimental results. The maximum flux (16.34×10^{-8} kg.m^{-2}.s^{-1}) in 5^{th} run was 16% less compared to that in 1^{st} run where the flux was 19.45×10^{-8} kg.m^{-2}.s^{-1}. The interfacial tension values were comparable but marginally greater for $n-$decane. The greater interfacial tension provided the greater stability and also contributed in yielding higher flux. Density of the LM played a role too. If the density of LM is much different from the density of aqueous phases, then a buoyancy force affects the stability of the LM in the pores of the support. The density of the LM with $n-$decanol (872.6 kg.m^{-3}) was closer to the density of aqueous phases (1000 kg.m^{-3}) compared to that with $n-$decane (density 802.8 kg.m^{-3}). So, the stability of LM should be higher for $n-$decanol compared to that for $n-$decane. However, the effect of lower viscosity and higher interfacial tension were dominant and the flux was better for *n*-decane as solvent. Hence, further stability analyses were performed with $n-$decane as the solvent. The change of viscosity with the TBP concentration in the LM and the effect of this on the transportation of the catechin were investigated. Solvent $n-$decane and

carrier TBP have the viscosity of 0.92 mPa.s and 3.8 mPa.s, respectively. So, the viscosity of LM increases with increasing concentration of TBP in LM (Fig.1). Adding carrier in the LM has

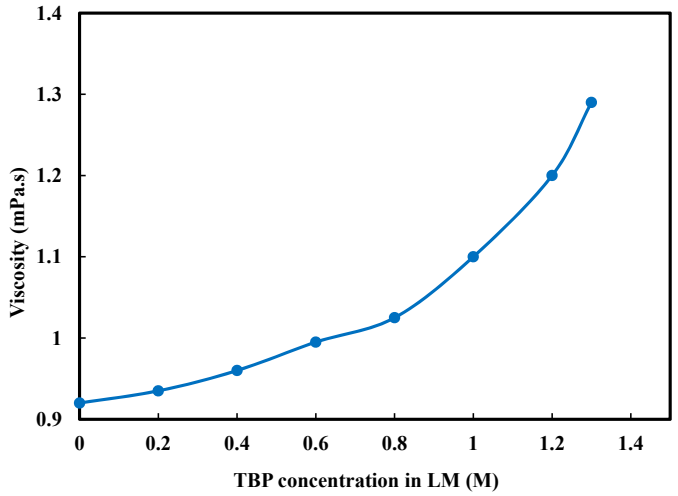


Fig. 1 Change of viscosity of the LM with TBP concentration

two opposite effects. With increasing TBP concentration in LM, percentage of transportation of solute increases up to 1.2 M TBP which is saturation concentration of TBP in membrane phase,[1] but the flux decreases as the viscosity increases. Hence, 1.2 M TBP was used in the subsequent experimentations. As TBP concentration increased in LM, the mutual solubility of organic–aqueous phases might increase. The water content of LM was checked by the Karl Fisher Titration experiments described in subsequent section.

3.1.2 Effect of mutual solubility of phases

The mutual solubility of the membrane phase and aqueous phases affects the stability of LM in the pores of the support.[10] After the equilibrium between aqueous and organic phases was reached in two phase equilibrium study, the two phases were separated by settling. The water contents dissolved in the LM were examined by Karl Fisher Titration method (787 KF Titrino, Metrohm) and the results were reported in Table 2.

Table 2 Mutual solubility of the organic-aqueous phases in various concentration of TBP

TBP concentration in LM (M)	Water solubility in LM (% wt.)	
	The feed phase containing 100 mg.L^{-1} catechin	The stripping phase with 0.4 M ethanol
0.2	0	0
0.5	0	0.0007
0.8	0.0006	0.001
1.2	0.0012	0.002
1.4	0.0016	0.0025

Solubility of water in the membrane phase with 1.2 M TBP were found to be 0.0012% and 0.002% when they were equilibrated with feed (100 mg.L^{-1} catechin) and strip (0.4M ethanol) phases, respectively. The solvent *n*−decane is insoluble in water and solubility of TBP in water is 160 ppm *i.e* 0.016%. With rigorous stirring, both the aqueous phases (260 mL) can dissolute maximum 0.0416 mg TBP. The amount of LM used in the experiment was 55.4 mg and the amount of TBP in this LM was 22.04 mg. Hence, only 0.186% of TBP can be lost into the aqueous phases through dissolution under rigorous stirring condition. However, in practice the extent of dissolution may be much less than this value, because the exposed area of LM inside the pores to the aqueous phases was very small and the stirring in actual SLM studies was not very rigorous. The details have been provided in later section. Nevertheless, this mutual solubility of the two phases was further minimized in the following sections by the use of electrolyte in the aqueous phases and surfactant in LM phase.

3.1.3 Role of electrolyte (NaCL) in aqueous phases

Presence of electrolyte in the aqueous phases increases the interfacial tension between membrane phase and aqueous phases. Increasing interfacial tension (γ) increases the stability of the LM. Various amounts of electrolyte (NaCl) were added both in feed and stripping phases in order to assess its role in increasing the stability of LM. Fig. 2 and Table 3 demonstrate the detail of the

Table 3 Effect of NaCl in aqueous phases on flux of catechin

NaCl in aqueous phases (M)		Interfacial tension (γ) (mN.m^{-1})		Maximum flux in 5^{th} run × 10^8 (kg.m^{-2}.s^{-1})
feed phase	strip phase	with feed phase	with strip phase	
0.0	0.0	10.2	10.4	16.34
0.2	0.2	10.9	11.2	16.81
0.4	0.4	11.3	11.7	17.5
0.5	0.5	11.5	11.9	18.05
0.6	0.6	11.6	12.0	18.64
0.8	0.8	11.7	12.1	18.72
1.0	1.0	11.8	12.2	18.61
0.8	0.4	11.7	11.7	20.05

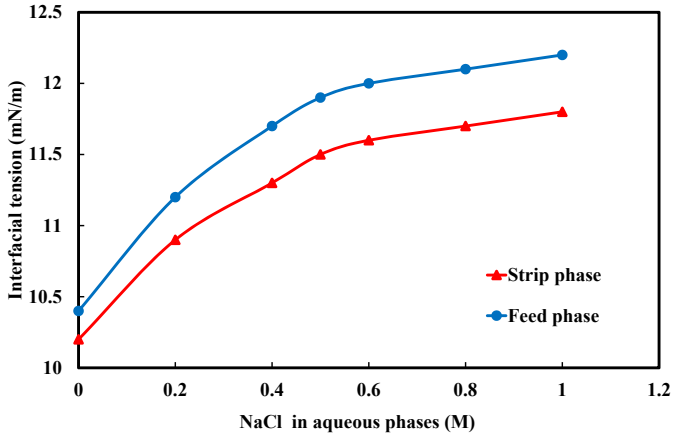


Fig. 2 Interfacial tension between LM and aqueous phase(s) with varying concentration of electrolyte (NaCl)

effect of NaCl in the aqueous phases with values of the interfacial tension between aqueous and organic phases against varying concentrations of NaCl. One of the reasons for instability of SLM is the gradient of surface tension between feed and stripping phases and the SLM is more stable when this gradient is zero.[34] With 0.8 M NaCl in feed phase the interfacial tension of the LM with the feed solution is 11.7 $mN.m^{-1}$. The same value of interfacial tension between LM and the strip phase is obtained when 0.4 M NaCl is added in it. In other words, 0.8 M NaCl in feed phase and 0.4 M NaCl in the strip phase provide the zero gradient of surface tension in the system which ensures the best stability. Hence, the subsequent experiments were carried out with feed and strip phases containing 0.8 M NaCl and 0.4 M NaCl, respectively and the resulting flux of catechin was found to be 20.05 $kg.m^{-2}.s^{-1}$. This result can also be explained as the neutral gradient of osmotic pressure which provided the highest stability of LM in the pores.

3.1.4 Role of surfactant

Various researchers reported the role of surfactants in the stability of SLM which depends on the hydrophilic-lipophilic balance (HLB) of the surfactants. Presence of surfactants with lower HLB values (3-5) in the LM increases its hydrophobicity.[35] The interfacial tension between LM and the aqueous phases increases with addition of suitable surfactant. As a result the stability of membrane phase inside the pores increases. On the other hand, the surfactants with higher HLB values (8-15) are not favourable for this purpose. In this work, 3 surfactants of different HLB values were considered for experimentation. In each run, one of them was mixed with LM for transportation of catechin. The flux was measured as described earlier. The maximum flux, at the end of the 5^{th} run, was measured and reported in Table 4. The flux was

Table 4 Role of surfactants on SLM stability

Surfactant in membrane 0.2% (w/w)	HLB value of surfactant	Viscosity (mPa.s)	Interfacial tension ($mN.m^{-1}$)	Maximum flux at 5^{th} run $\times 10^8$ ($kg.m^{-2}.s^{-1}$)
None	-	1.20	11.8	16.34
Span 65	2.1	1.22	12.6	17.82
Span 60	4.7	1.204	12.3	22.05
Tween 80	15.0	1.23	0.6	Not measured

maximum (22.05×10^{-8} $kg.m.s^{-1}$) when 0.2 % (w/w) span 60 was used. Span 65 with HLB value of 2.1 was too hydrophobic to maintain the organic-aqueous interface for the transportation of catechin and as a result the flux was less. The flux of 22.05 $\times 10^{-8}$ kg.m $.s^{-1}$ is certainly higher as compared to 20.05×10^{-8} $kg.m.s^{-1}$ when the experiment was performed without any surfactant (Table 3). The surfactants with lower HLB value (3-5) provide the highest stability as they form water in oil (W/O) emulsion and minimize the loss of LM. The surfactant with higher HLB value tends to form oil in water (O/W) emulsion and facilitates loss of LM, and the loss was even higher than the case when there was no surfactant in the LM.

3.1.5 Characterization and stability of emulsions

One of the reasons of instability of the SLM is the formation of emulsion between the LM and aqueous phases. The probability of emulsification was studied in three conditions of the phases. The effect of emulsification in SLMs can be studied through the characterization of the emulsion droplets by their size, numbers and determination of stability as a function of process and product variables prevailing in a particular SLM system.[19] Emulsions of LM in aqueous solutions were prepared by the ultrasonic agitation and the size distribution of droplets was measured in Delsa nano particle size analyzer. In order to obtain a precise measurement, the job was done immediately after agitation (emulsification) has been stopped. The solubility of LM was found more in strip phase as compared to that in feed phase, as observed before (Table 2). Hence, the strip phase was selected as the aqueous phase for formation of emulsion. The volume (0.2 mL) of LM in all samples of aqueous phases, the time of emulsification and the power of ultrasonic agitation were kept constant. A comparison of the size distribution of droplets, at different conditions of organic/aqueous phases, provides a quantitative measure of dispersion of emulsions. Hence, the proper selection of aqueous/organic phase can be achieved and the factors applicable for reducing emulsification and increasing stability of membrane can be realized. Liquid membrane initially remains in the support pores (State I). During operation, if it comes to the aqueous phases (State II), the free energy change during formation of emulsion can be predicted as:[35]

$$\Delta G = \left(U_A^{II} + U_O^{II}\right) - \left(U_A^{I} + U_O^{I}\right) + \gamma_{OA}\left(A_O^{II} - A_O^{I}\right) - \gamma_{OS}A_C^{I} - TS_O^{II} \quad (4)$$

where superscripts I and II represent states I and II, the subscripts A and O, represent the aqueous and organic phases respectively, γ is the interfacial tensions between corresponding phases, U is the total bulk internal energy for respective states and phases, A is the interfacial area between the phases, T and S are the absolute temperature and the configurational entropy of the oil droplets formed, respectively. With various assumptions and simplification the Eq.(4) can be resulted as:[35]

$$\Delta G = \gamma_{OS}\left(n\pi d^2\right) - \frac{4\varepsilon\delta A_m}{d_p}\gamma_{OS} + nkT\left\{\ln(\phi_0) + \left(\frac{1-\phi_0}{\phi_0}\right)\ln(1-\phi_0)\right\} \quad (5)$$

where n, d, ε, δ, A_m, k, d_p, ϕ_0 and γ_{OS} are the number of emulsion droplets, diameter of emulsion droplets, porosity of support, thickness of support, interfacial area of membrane, the Boltzmann constant, the diameter of pores, the volume fraction of the LM in the aqueous solution and the interfacial tension between solid support and the membrane phase, respectively. The first term of right hand side of Eq.(5) is normally greater than the last two terms in absolute value unless the interfacial tension γ_{OS} is very small, and therefore ΔG is mostly positive. Hence the emulsification in the aqueous phases is not a spontaneous process. The minimum external energy (equal to ΔG), which is required for the emulsification to take place, must be supplied to the system. Hence, the problem of emulsification can be avoided (or at least minimized) by minimizing the supply of energy from agitation (stirring and/or streams flow). On the other hand, minimum stir-

ring is necessary for reduction of concentration polarization of solute (or solute-carrier complex) and thickness of laminar sublayer at the interfaces. Hence, the stirring speed has been optimized and described later. The size of the droplets in emulsion was found to be largest when 0.2% (w/w) span 60 was added in LM and 0.4M NaCl was added in strip phase (Fig. 3). The

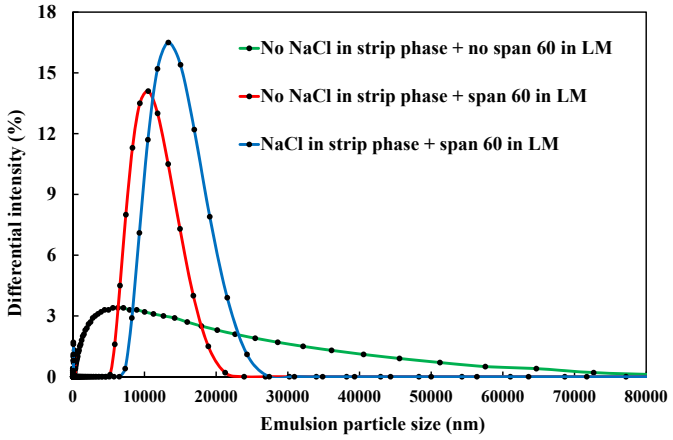


Fig. 3 Effect of emulsification in varied conditions of organic-aqueous phases

largest droplets of emulsion have the lowest stability. The SLM will have the highest stability if the emulsions formed are least stable. Hence, highest stability of SLM can be achieved when 0.4 M NaCl and 0.2% (w/w) span 60 were added in strip phase and LM, respectively (Fig. 3). The advantage of addition of surfactant can be best realized by the reduction in loss of LM. The losses of LM after 5^{th} runs were calculated with conditions for highest stability of SLM, as described above. The details have been reported in subsequent sections.

3.1.6 Significance of polymeric material as support for LM

The pore size of the support has a significant role in increasing the stability of SLM. The LM can withstand only up to a maximum pressure, as given in the Eq.(2). The critical displacement pressure, P_c is inversely proportional to the diameter of the pores and it is assumed that the pores are perfectly cylindrical in shape. We considered four different polymeric materials as support for the LM and studied the influence of their diameters and shapes. All the four polymeric materials, *viz*. PVDF, PTFE, PES and Nylon 6, had same average pore diameter of 0.2 μm. The performances of the individual polymeric supports for the transportation of catechin have been reported elsewhere.[1] The maximum transportation of catechin was obtained with PVDF as the support, followed by PTFE, PES and Nylon 6. The thickness of the PTFE support was 77.2 μm and that of PVDF was 88.5 μm. When all other parameters remain constant, the flux through the membrane is inversely proportional to the thickness of its support. Hence, PTFE support should have yielded more flux compared to PVDF. However, the structure of the pores also contribute in the stability of the LM and consequently on flux of catechin. Fig. 4(a-d) demonstrates SEM analysis of various polymeric supports with identical scale and magnification (4.0 kX). It was observed that the pore structures deviate from the regular cylindrical shape and the extent of irregularity was in the order of PTFE>Nylon,6>PES>PVDF. Hence, in the context of pore structure, PVDF support was better for stability of LM which was consistent with the experimental results.

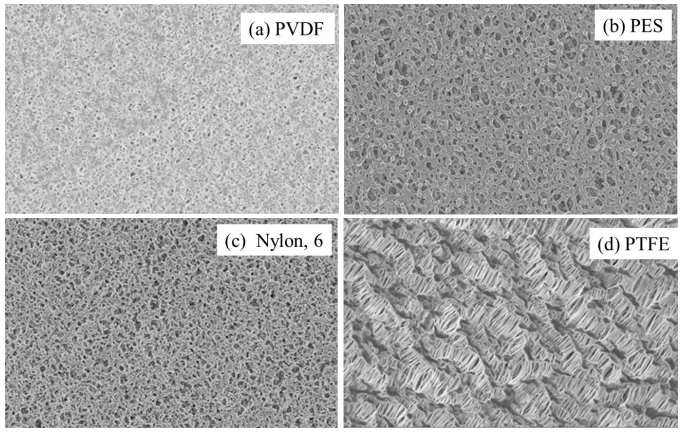


Fig. 4 Images of membrane supports in Scanning Electron Microscopic at magnification of 4.0 Kx each

3.1.7 Critical displacement pressure differential

Critical displacement pressure differentials (ΔP_c) that a LM can withstand were determined through experimentation. The experimental set up was shown in Fig. 5. The procedure of measure-

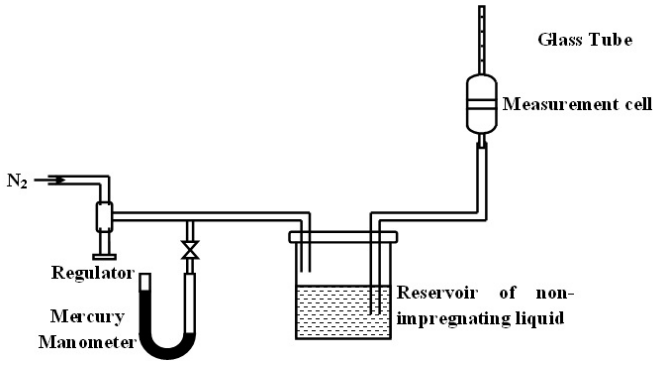


Fig. 5 Schematic of the experimental set up used for the measurement of critical displacement pressure on membrane supports

ment was similar to that followed by Zha *et al.*[17] The effective diameter of the measurement cell was 20 mm. Polymeric support materials, *viz*. PVDF, PES, PTFE each of 0.2 μm thickness and two Nylon,6 supports with thickness 0.2 μm and 0.45 μm, were impregnated with LM consisting of 1.2M TBP in $n-$decane and 0.2% (w/w) span 60 (HLB value = 4.7). Impregnated supports were placed in measurement cell. Same LM was kept on the top of the experimental SLM and also in the glass tube of small diameter. The pressure at the aqueous side of the polymeric support was increased gradually by adjusting the regulator of gas (N_2) cylinder. Pressure was measured with mercury manometer attached to the measurement cell. The lowest pressure, at which the LM in the glass tube started rising up, was taken as the critical displacement pressure differential. Experiments with each support were

Table 5 Critical displacement pressure differentials (ΔP_c) for LM in the pores and loss of LM from the pores for various membrane supports

Membrane support	Average pore size (μm)	Thickness (μm)	Porosity (ε)	Tortuosity (τ)	Pressure differential (ΔP_c) (kPa)	Weight $\times 10^3$ (kg)			Loss of LM	
						support	support + LM	LM	net loss $\times 10^3$ (kg)	% wt
PVDF	0.2	88.5	0.45	3.44	15.2	0.1082	0.1632	0.055	0.0056	7.62
PTFE	0.2	77.2	0.51	2.92	8.7	0.0783	0.1333	0.055	0.0086	15.7
PES	0.2	107	0.50	3.0	11.3	0.0768	0.1513	0.075	0.018	13.2
Nylon, 6	0.2	102	0.4	4.0	10.2	0.0675	0.1240	0.057	0.007	12.3
Nylon, 6	0.45	102	0.49	2.92	4.7	0.0551	0.1247	0.070	0.021	30.2

repeated for three times and the average value of critical displacement pressure was given in Table 5. Critical displacement pressure for PVDF support was maximum followed by PES, Nylon,6 (of thickness 0.2 μm) and PTFE. The shape of PVDF membrane was most regular (close to cylindrical shape) and that of PTFE was least regular, as observed through SEM analysis (Fig. 4(a-d)). PTFE has "stripe type" structure which was not favourable towards stability issue. Zha *et al.*[17] proposed a theoretical expression for critical displacement pressure that was a function of complicated and varied pore structure of support. They reported similar results whatever we observed through experimentation. Again according to Young-Dupre equation (Eq.2), the critical displacement pressure is inversely proportional to the radius of pore if other parameters remain constant. For a particular support material (Nylon, 6) ΔP_c will be greater as radius of pore is reduced. We used two different supports of Nylon,6 having pore diameters of 0.2 μm and 0.45 μm, and ΔP_c were found as 10.2 kPa and 4.7 kPa for supports with pore diameters of 0.2 μm and 0.45 μm, respectively.

3.1.8 Effect of stirring rate

The effect of stirring of the aqueous phases was studied at three different speeds of 150, 200 and 250 rpm. Stirring of the aqueous phases had two opposite effects. Vigorous stirring adversely affected the stability of membrane by emulsion formation between the LM and the aqueous phases, but yielded the maximum flux of the solute in the transportation process. On the other hand, stability of SLM was higher when speed of stirring was lower because the pressure experienced by the LM was less enough than the critical displacement pressure (P_c) in such situation. Moreover, lower stirring minimizes the chance of emulsion formation. However, flux of the solute got reduced at lower stirring speed. Fluxes of catechin in different stirring conditions were measured during the first run of transportation studies in order to optimize the speed of stirring. The stability of LM did not affect much in the subsequent runs if the optimized speed of stirring was maintained thereon. One run of 24 h was sufficient to check the effect of stirring. The maximum fluxes were found to be 23.4×10^{-8}, 22.8×10^{-8} and 18.7×10^{-8} kg.m^{-2}.s^{-1} for stirring speed of 250, 200 and 150 rpm, respectively (Fig. 6). There was not much improvement in flux when speed of stirring was increased from 200 rpm to 250 rpm, whereas flux got substantially reduced when the speed was lowered to 150 rpm. Hence, 200 rpm was selected as the optimum speed of stirring. It was argued that the stirring speed greater than the optimum value might always be very critical which might affect the stability of SLM adversely.

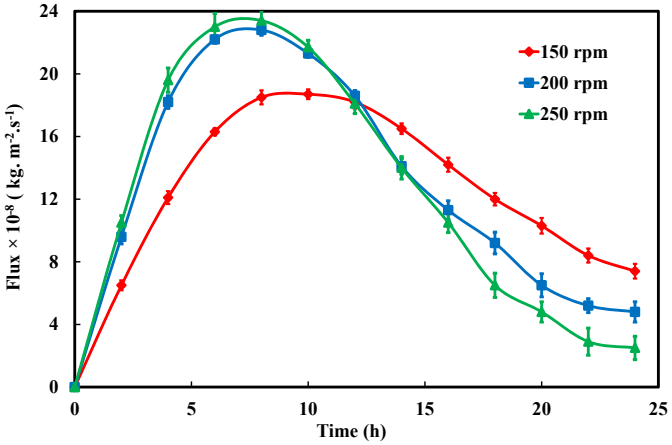


Fig. 6 Effect of stirring speed on the flux of catechins across SLM

3.1.9 Loss of membrane liquid

Loss of membrane liquid from the pores of support, after incorporation of all the stability criteria, was measured after 120 h and the results are shown in Table 5. The loss was measured by the weighing method. The initial weight of the impregnated SLM support before the experiment and the final weight of removed support after the 5^{th} run were measured in a weighing balance and the difference was calculated as the loss of LM. The calculation was done on water free basis. For supports with 0.2 μm pore size, the maximum loss was observed with PTFE (15.7%) and minimum loss was recorded for PVDF (7.62%). With bigger pore size the loss increased and that was confirmed with the result of Nylon,6 support of two different pore sizes. Losses of LM were found to be 12.3% and 30.2% for pore size of 0.2 and 0.45 μm, respectively.

3.2 Case study in HFM module (cleaning and reusability)

One of the limitations of the SLM is the fouling of the micropores of the support in addition to the instability. The problem of fouling is maximum when various catechins are transported from real extract in HFM module. The real extract contains several impurities such as tannins, caffeine, theophylline, theobromine etc. They are not candidates for "selective separation" but clog the surface of pore mouth. The fouling leads to reduction in flux.

Table 6 Efficiency of cleaning: hydraulic head (ΔH)=30 cm of water, permeate volume (V) in 70 min. = 0.1143 $m^3.m^{-2}$, surface area = 0.06 m^2, J = 27.22 $kg.m^{-2}.s^{-1}$

Membrane	$\frac{J_0}{J} \times 100(\%)$	$\frac{J_1}{J} \times 100(\%)$	$\frac{J_2}{J} \times 100(\%)$	V $(m^3.m^{-2})$	UMFI $(m^2.m^{-3})$	UMCI $(m^2.m^{-3})$	% Recovery
Fresh membrane (1^{st} run)	70	75	95	0.1143	12.12	3.124	51.3
After 1^{st} cleaning (2^{nd} run)	65	85	90	0.096	8.09	4.006	46.3
After 2^{nd} cleaning (3^{rd} run)	63	83	87	0.085	7.90	4.48	44.3

In this work, physical and chemical methods for cleaning have been demonstrated separately. Cleaning agents and their specifications were suggested as outcome of the experiments. The cleaning procedure was investigated with moderate positive findings. The transportation experiments were conducted according to the procedure given in earlier section. The characteristics of HFM module and the flow velocities in lumen side and shell side have been provided in our previous work.[30] A filtration protocol against the fouling of membrane was evaluated comparing with the flux (J) of clean water. Extent of fouling after the use of membrane as well as the cleaning efficiency after each run was determined. The lumen side outlet was locked and the de-ionized water was allowed to pass through from lumen side to shell side at a particular hydraulic pressure (30 cm of H_2O) through the pores. Any changes in flux will determine the extent of fouling or cleaning efficiency. Flux (J_0) through the fouled membrane after a 70 minutes run was found to be reduced to 70% of the initial flux (through fresh membrane). Two steps cleaning were executed. Water backwashing was performed for 30 minutes to reach a clean water flux of (J_1), followed by chemical washing by 10 $mg.L^{-1}$ sodium hypochlorite (NaOCl) solution for 60 minutes to reach a clean water flux of (J_2). Sodium hypochlorite dissociated in water solution to hypochlorite ion ($-OCl$) and proton (H^+) and the extent of dissociation depended on the pH of the solution. The reactivity and the oxidizing power of sodium hypochlorite depended on the available chlorine in the solution but, as a solution it was much easier to handle sodium hypochlorite for cleaning than handling chlorine. The hydroxyl groups of the macro-molecule tannins etc. were oxidized by strong ($-OCl$) to form various salts and water. The salts were highly soluble in aqueous solution and thereby pores got cleaned. The same procedure for cleaning was performed after each run of transportation through the same HFM module. The flux values were used to generate a fouling profile pursuant to this filtration protocol and quantified using Unified Membrane Fouling Indices (UMFIs). The principles of UMFIs were reported in details elsewhere.[36] UMFIs were the measures of rates of membrane fouling observed within a certain timeframe of interest and calculated using the following equation:

$$\frac{J_{if}}{J_{ff}} = 1 + V\,(UMFI) \qquad (6)$$

where J_{if} and J_{ff} were the values of fluxes before and after fouling (transportation experiment) and V was the volume of circulated feed for washing. Based on the principle of UMFIs, Unified Membrane Cleaning Indices (UMCI) was also defined and calculated from following equation:

$$\frac{J_{ic}}{J_{fc}} = 1 - V\,(UMCI) \qquad (7)$$

where J_{ic} and J_{fc} were the values of fluxes before and after cleaning The cleaning efficiency was calculated in terms of flux of water after the cleaning (Table 6) and that was re-checked in terms of recovery efficiency for individual run. The maximum recovery of catechins in subsequent runs decreased despite cleaning of the membrane after each run. The fluxes in these three runs of transportation were studied with progression of time and the results were plotted in Fig.7. The maximum fluxes in all three cases were fixed by the concentration gradient across the LM. So, they were found same at $16.67 \times \times 10^{-8}$ $kg.m^{-2}.s^{-1}$ in all runs. But, the resistance to catechins permeation through LM increased even with cleaning after each subsequent run, resulting in the reduction of fluxes at the beginning of the permeation study in later runs.

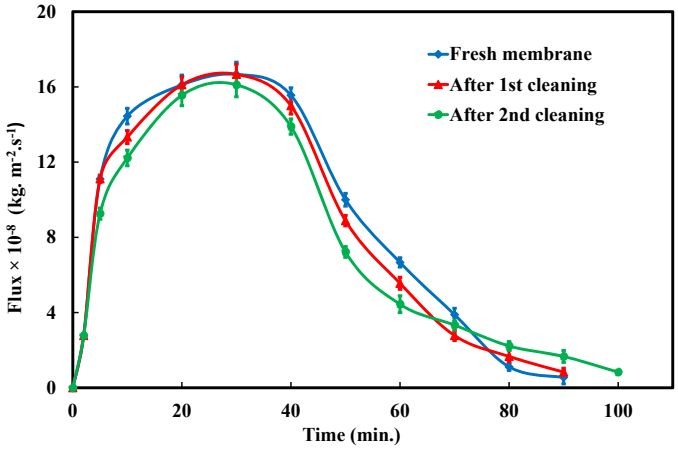


Fig. 7 Comparison of catechins flux with time in successive cleaning of hollow fiber membrane: initial catechin concentration=0.001 M, strip concentration=0.4 M, strip flow rate = 40 $cm^3.min^{-1}$, feed flow rate = 32 $cm^3.min^{-1}$

4 Conclusions

Two severe limitations of supported liquid membrane were addressed in this study, *viz.* the instability of membrane liquid in the pores of membrane support and the fouling of membrane pores. Various components of the system such as solvent, carrier and support materials etc. were optimized in order to achieve an efficient transportation as well as substantial stability of SLM. Direct stability measurement is difficult. Hence, stability was measured

in terms of average flux of catechin for a long duration (120 h) at different conditions of operability. The improved flux upon application of an added condition was measured. In comparison to Zidi et al.[4], who used TBP as carrier in kerosene (instead of *n*−decane, used in this work) for transportation of phenol (instead of catechins, used in this work) from aqueous feed and obtained stable SLM only upto 72 h, that too with low recovery, we achieved the stability of 120 h with a flux of 23.34×10^{-8} $kg.m^{-2}.s^{-1}$. The reduction in the loss of LM from the pores of support to the aqueous phases is also an indication of increased stability of an SLM. The loss of LM from the pores of SLM was only 7.62%, even after 120 h. The rate of the stirring of aqueous phases was optimized by the measurement of fluxes at various stirring speed. The conditions, which lead to reduction in emulsion formations, were optimized too. The optimized parameters for highest stability in FS-SLM were employed in transportation studies through HF-SLM. Various grades of catechins were transported and recovered from the real extract of tea leaves using an HF-SLM. The fouling of the pores of support membrane was measured in terms of reduction in flux of catechins in aggregate. We obtained better results than Yang et al.[37] who obtained 100 h stability with higher reduction in flux while transporting copper from aqueous feed through SLM that comprised of LIX 984 in kerosene. Thereby, a membrane cleaning protocol was obtained. Sequential cleaning in physical mode and then chemical mode proved to be excellent. The strongly reactive hypochlorite group (-OCl) oxidized the hydroxyl groups of the macro-molecule tannins, theobromine etc. to colorless and water soluble salts, and thereby cleaned the fouled membrane. The reduction of % recovery in the 3rd run was found to be 13.6% only.

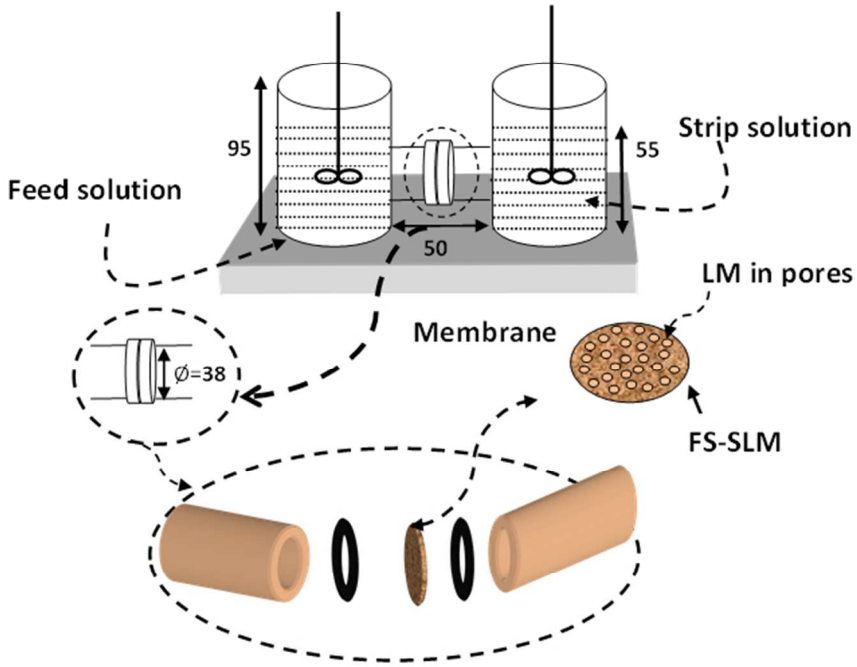
Acknowledgement

We thankfully acknowledge the financial support provided by the Department of Science and Technology (India) through sanction order no. DST/TM/WTI/2K13/125(G) for carrying out this research work. We also thank Central Instruments Facility of Indian Institute of Technology Guwahati for providing SEM analyses of the various membrane supports.

References

1 M. S. Manna, K. K. Bhatluri, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2013, **447**, 325–334.
2 K. Chakrabarty, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2009, **340**, 84–91.
3 K. Chakrabarty, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2010, **350**, 395–401.
4 C. Zidi, R. Tayeb, M. B. S. Ali and M. Dhahbi, *Journal of Membrane Science*, 2010, **360**, 334–340.
5 C. Zidi, R. Tayeb and M. Dhahbi, *Journal of Hazardous Materials*, 2011, **194**, 62–68.
6 A. M. Urtiaga, M. Inmaculada Ortiz, E. Salazar and J. Angel Irabien, *Industrial & Engineering Chemistry Research*, 1992, **31**, 877–886.
7 A. Neplenbroek, D. Bargeman and C. Smolders, *Desalination*, 1990, **79**, 303 – 312.
8 A. Neplenbroek, D. Bargeman and C. Smolders, *Journal of Membrane Science*, 1992, **67**, 121–132.
9 P. R. Danesi, *Journal of Membrane Science*, 1984, **20**, 231–248.
10 P. Danesi, L. Reichley-Yinger and P. Rickert, *Journal of Membrane Science*, 1987, **31**, 117–145.
11 H. Takeuchi, K. Takahashi and W. Goto, *Journal of Membrane Science*, 1987, **34**, 19–31.
12 J. Davies and E. Rideal, *Interfacial Phenomena. 1961*, New York: Academic Press.
13 E. Ruckenstein and S. V. Gourisankar, *Journal of Colloid and Interface Science*, 1986, **109**, 557–566.
14 N. Rathore, J. Sonawane, A. Kumar, A. Venugopalan, R. Singh, D. Bajpai and J. Shukla, *Journal of Membrane Science*, 2001, **189**, 119–128.
15 K. G. Kabza, J. E. Gestwicki and J. L. McGrath, *Journal of Chemical Education*, 2000, **77**, 63–65.
16 Y. Shukla, *Asian Pacific Journal of Cancer Prevention*, 2007, **8**, 155–166.
17 F. Zha, A. Fane, C. Fell and R. Schofield, *Journal of Membrane Science*, 1992, **75**, 69–80.
18 S. Chandrasekhar, *Hydromagnetic and Hydrodynamic Stability*, Clarendon, Oxford, 1961.
19 P. Walstra, *Emulsion stability, In Becher, P. (Ed.)*, Mercel Dekker, New York, 1983, pp. 57–128.
20 E. Gopal, *Emulsion science*, Academic, New York, 1968.
21 H.-H. S. Chow and I. A. Hakim, *Pharmacological Research*, 2011, **64**, 105–112.
22 C. S. Yang, X. Wang, G. Lu and S. C. Picinich, *Nature Reviews Cancer*, 2009, **9**, 429–439.
23 H. Mukhtar and N. Ahmad, *Toxicological Sciences*, 1999, **52**, 111–117.
24 S. V. Jovanovic, S. Steenken, M. Tosic, B. Marjanovic and M. G. Simic, *Journal of the American Chemical Society*, 1994, **116**, 4846–4851.
25 S. V. Jovanovic, Y. Hara, S. Steenken and M. G. Simic, *Journal of the American Chemical Society*, 1995, **117**, 9881–9888.
26 B. Hu, L. Wang, B. Zhou, X. Zhang, Y. Sun, H. Ye, L. Zhao, Q. Hu, G. Wang and X. Zeng, *Journal of Chromatography A*, 2009, **1216**, 3223–3231.
27 Y. Jin, C. H. Jin and K. Ho Row, *Biotechnology Journal*, 2006, **1**, 209–213.
28 Z.-Y. Chen, Q. Y. Zhu, D. Tsang and Y. Huang, *Journal of Agricultural and Food Chemistry*, 2001, **49**, 477–482.
29 Y. Yoshida, M. Kiso and T. Goto, *Food Chemistry*, 1999, **67**, 429–433.
30 M. S. Manna, P. Saha and A. K. Ghoshal, *Journal of Membrane Science*, 2014, **471**, 219–226.
31 M. S. Manna, P. Saha and A. K. Ghoshal, *RSC Advances*, 2014, **4**, 26247–26250.
32 M. S. Manna, K. K. Bhatluri, P. Saha and A. K. Ghoshal, *Industrial & Engineering Chemistry Research*, 2012, **51**, 15207–15216.
33 M. Mulder, *Basic principles of membrane technology*, Kluwer

Academic, Dordrecht, 1991.
34 F. Zha, A. Fane and C. Fell, *Journal of Membrane Science*, 1995, **107**, 75–86.
35 F. Zha, A. Fane and C. Fell, *Journal of Membrane Science*, 1995, **107**, 59–74.
36 H. Huang, T. A. Young and J. G. Jacangelo, *Environmental Science & Technology*, 2008, **42**, 714–720.
37 X. J. Yang and A. G. Fane, *Journal of Membrane Science*, 1999, **156**, 251–263.



The stability of the LM in the micro-pores of solid polymeric membrane support is improved by the optimization of influential parameters

157x128mm (120 x 120 DPI)