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Selection of Organic Phases for Optimal Stability and Efficiency of Flat-Sheet Supported Liquid Membranes

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Abstract

The efficiency and the stability of flat-sheet supported liquid membranes (SLMs) were studied in the case of the active transport of an amino acid, L-valine. Independent measurements on the organic phase (valine distribution, water concentration and viscosity) combined with the determination of some surface properties (interfacial tension and drop point) permit the description and prediction of the experimental permeability and stability of SLMs. The lifetime of the SLM was explained by taking into account diluent solubility in the aqueous phase, water concentration in the organic phase, interfacial tension between organic and feed phases, and drop point of the SLM. The experimental efficiency could be modeled by a mathematical expression involving the distribution coefficient of the solute and the viscosity of the organic solution.

INTRODUCTION

The liquid membrane process was first developed by using emulsions and applied to hydrometallurgy (*1*, *2*), oil recovery (*3*), wastewater treatment (*4*, *5*), and biomedical engineering (*6*, *7*). New applications concern bioseparations and are achieved with water-in-oil emulsions (*8*) or supported liquid membranes (SLMs); several investigators have examined the use of SLMs for the downstream processing of biochemicals on a laboratory scale (*9–11*).

For the development of the SLM technique as an industrial process, the solute permeability, the selectivity, and the stability of the SLM must be reliable.

Concerning the permeability, modeling of permeation through SLMs is frequently reported in the literature. Several mass transfer resistances are assumed to control the total rate of transmembrane transport: diffusion through aqueous boundary layers, interfacial reactions at both sides of the membrane, and diffusion across the SLM. These stages depend on experimental conditions: hydrodynamics (thickness of the aqueous boundary layers), composition of the organic phase (distribution coefficient, viscosity), and nature of the support (geometry).

Despite its fundamental importance, there has been little study on membrane lifetime, and information on SLM stability is often conflicting. Previous work has shown that the destabilization of SLMs could be due to pressure differences larger than the drop point of the SLM across the membrane (*12*), attrition of the organic film due to the lateral shear forces (*13*), losses of organic solvent (*14*) or carrier (*15*) by dissolution, and incorporation of water in the organic phase. This "hydrophilization" of SLMs can be caused by direct solubilization in the diluent (*16*), hydration of carrier (*17*), and reversed micelles formation (*8*). In addition, when the water content in the organic phase is high, the instability increases with the osmotic gradient across the SLM (*18*), utilization of an organic phase with a low organic–water interfacial tension (*15*), and a low viscosity (*9*).

In this work we develop criteria for the selection of the organic phase that give the best possible permeability and stability to SLMs. It is shown that measurements of the physical properties of feed and organic phase (surface tension, viscosity, distribution of valine, incorporated valine, interfacial tension) and other determinations (bubble and drop points, osmotic pressure gradient) can predict the performance of SLMs. These evaluations were established from pertraction assays of an amino acid (L-valine) through a liquid membrane (organic solution of a quaternary ammonium salt: Aliquat 336) immobilized in a microporous PTFE support.

A schematic representation of the transport of the amino acid and the counter transport of chloride ion by Aliquat 336 is described in Fig. 1. The L-valine present in the neutral feed phase (pH 8.0) is distributed between the aqueous and organic phases at the feed interface. The complex constituted by Aliquat 336 and valine diffuses across the organic layer to the stripping interface, where valine is exchanged for a chloride anion. The reaction involved is given by the following:

$$\mathrm{Val^- + NR_4^+Cl^- \rightleftharpoons NR_4^+Val^- + Cl^-} \qquad (1)$$

MATERIALS

The feed phase contained L-valine (25 g/L) and glucose (30 g/L), used as a tracer to check the selectivity of the transport. The osmotic pressure of this solution was about 9 bar.

The stripping phase was a solution of sodium chloride (1.0 or 4.0 *M*, according to the experiment), and its osmotic pressure was close to 46 and 223 bar, respectively.

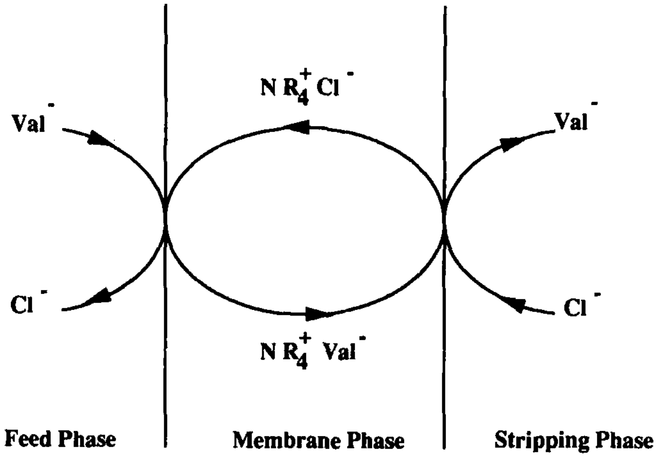

FIG. 1. Chloride countertransport of L-valine through the SLM by Aliquat 336.

The organic phase consisted of Aliquat 336—a mixture of trialkylmethylammonium chlorides, principally trioctyl and tridecyl—dissolved in various diluents (10% w/w). Some physical properties of these organic diluents are reported in Table 1.

The hydrophobic support used for immobilizing the liquid membrane was made of polytetrafluoroethylene (PTFE) and purchased from Millipore (type FHLP). It had the following properties: thickness, 60 μm; porosity, 85%; average pore diameter, 0.50 μm; and critical surface tension, 37 dyn/cm.

TABLE 1
Physical Properties at 20°C of Organic Solvents Used as a Diluent of Aliquat 336

Solvent	Specific gravity (kg/m^3)	Dynamic viscosity (cP)	Surface tension (dyn/cm)	Interfacial tension (dyn/cm)	Solubility		Molecular weight
					$\sigma_{w/s}/\sigma_{s/w}$	(wt%)	
Decanol	830	11.3	27.6	8.0	3.77	0.07	158
Isodecanol	838	18.9				0.05	158
Acropol 91	832	16.6				0.01	156
Undecanol	830	12.4	28.4	8.0	3.58	0.003	172
Dodecanol	822					0.003	195
Isotridecanol	844	24.5	29.2		1.0	0.002	193
Triisobutylphosphate	976	3.39	27.9		4.67	0.04	266
Diphenylether	1070	2.14	38.8		0.39	0.39	170

EXPERIMENTAL METHODS

Surface and Interfacial Tensions

Surface and interfacial tensions were measured at 30°C with a Krupp K10 digital tensiometer by using the ring method of Du Nouy.

Bubble and Drop Points

The SLM was placed in a special cell (bulloscope) in which one side was pressurized with air or a liquid (pure water or feed phase) until the pressure overcame the capillary forces retaining the organic phase in the micropores of the support. The pressure at which the first bubble or the first drop appeared defined the bubble point and the drop point, respectively.

Liquid–Liquid Equilibrium

The distribution coefficient of valine was determined after mixing the standard feed phase with each organic phase at 30°C for 16 h.

Viscosity

The determination of the kinematic viscosity of organic phases was performed at 30°C with a capillary tube viscometer. The dynamic viscosity was obtained after determining the specific gravity of the organic phases with a picnometer.

Permeation

Permeation experiments were carried out in the apparatus described in Fig. 2. The feed solution was circulated by a peristaltic pump at a low flow rate (10 cm^3/min) in order to maintain a low hydrostatic pressure gradient across the SLM. The pH was kept at 8.0 by controlled addition of 1.0 *N* NaOH. The permeation cell was set in a rotative shaker (Roucaire) stirred at 250 rpm and thermostated at 30°C. The volumes of the feed and the stripping solutions were 30 and 2 cm^3, respectively; the support area was 7.1 cm^2.

Analysis

The valine concentration was evaluated after stoichiometric reaction with ninhydrine by using spectrophotometry at 575 nm.

Glucose was determined by the Wako test method (multienzymatic reactions and spectrophotometric measurement at 505 nm).

The water incorporated into the organic phase at equilibrium was measured by coulometry by using a Tacussel Aquaprocessor.

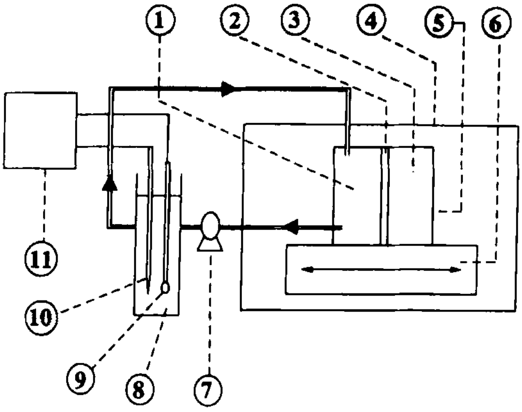

FIG. 2. Schematic diagram of the experimental apparatus: (1) feed phase compartment; (2) SLM; (3) stripping phase compartment; (4) thermostated chamber; (5) permeation cell; (6) rotative shaker; (7) peristaltic pump; (8) feed phase tank; (9) pH probe; (10) controlled addition of NaOH; (11) titrimeter.

EXPERIMENTAL RESULTS

Surface Properties

Surface Tension and Bubble Point

The application of a SLM necessitates the use of a microporous support wetted by the organic phase and nonwetted by the aqueous phases. The ratio $\Gamma/\Gamma c$ permits prediction of the wettability of a solid material of critical surface tension Γc by a liquid of superficial tension Γ: the solid is not wetted when $\Gamma/\Gamma c > 1$ (*19*). The critical tension value of the Teflon microporous support used was provided by the manufacturer (Γc = 37 dyn/cm).

Experiments were performed to determine the surface tension of numerous organic phases. Table 2 indicates the results of measurements on Aliquat 336 solutions (10% w/w) in different diluents, and Table 3 presents the results for various concentrations of Aliquat 336 in isotridecanol.

The surface tension of most of the organic phases tested is about 28–30 dyn/cm, indicating good wettability of the support. Only diphenylether has a surface tension closer to Γc (Γ = 34.4 dyn/cm). Note that the Aliquat 336 concentration in isotridecanol does not modify the surface tension of the mixture.

The surface tension of the aqueous phases has also been measured, and its shows that the support should not be wetted. However, the surface tension of the feed phase is lower than that of pure water (53.7 and 64.6 dyn/cm, respectively) due to the surface activity of valine.

TABLE 2
Effect of the Diluent of Aliquat 336 on the Physicochemical Properties of the Organic Phase and the Corresponding SLM[a]

Diluent	Surface tension (dyn/cm)	Interfacial tension[b] (dyn/cm)	Drop point[c] (bar)	Water content (g/L)	Dynamic viscosity (cP)	Valine distribution coefficient
Decanol	28.3	5.8[d]	0.37[e]	35.4	12.8	0.071
		5.4	0.33			
Isodecanol	27.6	5.3	0.30	30.9	14.8	0.067
Acropol 91	28.4	5.3	0.30	30.5	12.4	0.062
Undecanol	28.9	5.6	0.35	23.7	14.3	0.045
Dodecanol	29.5	4.3	0.30	29.5	19.1	0.071
Isotridecanol	28.0	6.5	0.35	15.4	32.3	0.059
Triisobutylphosphate	26.7	2.1	0.15	81.8	5.4	0.007
Diphenylether	34.4	2.8	0.25	18.0	4.5	0.038

[a] All determinations were made at 30°C.
[b] Interfacial tension between organic phase and aqueous feed phase.
[c] Drop point with pressurized aqueous feed phase.
[d] Interfacial tension between organic phase and pure water.
[e] Drop point with pressurized pure water.

The immobilization of the organic phase inside the support was estimated by bubble point determination. The values obtained with all the organic phases studied are approximately similar and close to 1.0 ± 0.1 bar.

Interfacial Tension and Drop Point

In actual conditions of separation, the SLM is in contact with the aqueous phases. The relevant parameter is then the interfacial tension Γ' between

TABLE 3
Effect of Aliquat 336 Concentrations in Isotridecanol on the Physicochemical Properties of the Organic Phase and the Corresponding SLM[a]

Aliquat 336 concentration (wt%)	Surface tension (dyn/cm)	Interfacial tension[b] (dyn/cm)	Drop point[c] (bar)	Water content (g/L)	Dynamic viscosity (cP)	Valine distribution coefficient
0	28.0	14.5	0.60	10.0	30.0	<0.001
5			0.40	11.4	30.7	0.035
10	28.0	6.5	0.35	15.4	32.2	0.059
15				17.8	38.8	
20		5.5	0.33	22.0	48.1	0.059
30	27.8	4.5	0.30	32.8	72.3	0.060
50	27.6	2.9	0.20	58.9	188.6	0.059

[a] All determinations were made at 30°C
[b] Interfacial tension between organic phase and aqueous feed phase.
[c] Drop point with pressurized aqueous feed phase.

organic and aqueous phases, which can be related to the surface tension of each single phase (*20*). Interfacial tensions between organic and aqueous phases were measured and are reported in Tables 2 and 3. The values are low for the long chain alcohol solutions (about 5 dyn/cm) and even more for diphenylether and triisobutylphosphate solutions (less than 3 dyn/cm). Note the reduction of 7% in the interfacial tension between the decanol solution and the aqueous phase when pure water is changed for a feed phase containing valine.

The influence of Aliquat 336 concentration on the interfacial tension with isotridecanol as diluent is shown in Fig. 3. The interfacial tension decreases when the Aliquat 336 concentration increases, particularly from 0 to 10% w/w.

From analogy with bubble point determination, we characterize the retention of the organic phase inside the support during contact with the aqueous phase by the drop point *Dp*. The drop point results follow similar trends in interfacial tensions when the diluent, the Aliquat 336 concentration in organic solutions, or the aqueous phase composition is changed (see Tables 2 and 3 and Fig. 3). With long chain alcohols, the drop point is mostly between 0.3 and 0.4 bar. At high Aliquat 336 concentration or with diphenylether and triisobutylphosphate, the drop point is only 0.2

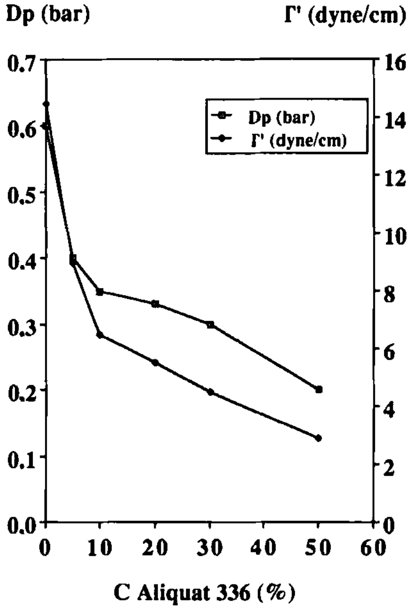

FIG. 3. Effect of Aliquat 336 concentration on the drop point of the SLM and the interfacial tension between organic and aqueous feed phases. Diluent: isotridecanol.

bar. In all cases the drop point is significantly higher than the transmembrane pressure generated by the circulation pump of the feed phase ($\delta P \leq 0.03$ bar).

Properties of Organic Phase and Distribution of Valine

Water

The amount of water extracted by the organic phase depends strongly on the nature of the diluent, as reported in Table 1 for pure solvents and in Table 2 for Aliquat 336 solutions (10% w/w). It also depends on the Aliquat 336 concentration, as shown in Fig. 4, for isotridecanol solutions; the linear plot indicates that 3 mol water are associated per mole of Aliquat 336 in this diluent.

Valine Distribution

The maximum value of the distribution coefficient of valine between the aqueous feed phase and Aliquat–diluent mixtures is close to 0.07 and was obtained with decyl or dodecyl alcohol solutions of Aliquat 336 (10% w/w).

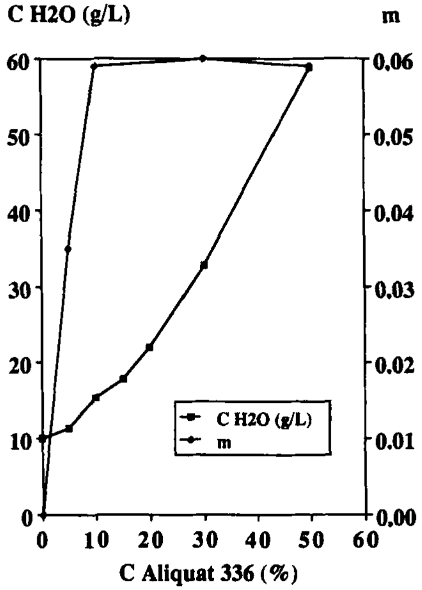

FIG. 4. Effect of Aliquat 336 concentration on the water concentration and the valine distribution coefficient. Diluent: isotridecanol.

In isotridecanol, the distribution coefficient increases with the Aliquat 336 concentration between 0 and 10% w/w, as shown in Table 3 and Fig. 4. Above this concentration the distribution coefficient remains constant: the extraction of L-valine can no longer be described by the simplest expression of the mass action law, deduced from the equilibrium Eq. (*1*), and using the molar concentration of species.

Viscosity

The lowest viscosities of Aliquat 336 mixtures are close to 5 cP, and they are obtained with triisobutylphosphate and diphenylether. For alcohols the viscosity increases with the number of carbons in the chain from 13 cP (decanol) to 32 cP (isotridecanol).

The influence of the Aliquat 336 concentration on the viscosity of the organic phase is shown in Fig. 5 for isotridecanol solutions: the viscosity increases dramatically above 10% w/w of Aliquat 336 until it reaches a

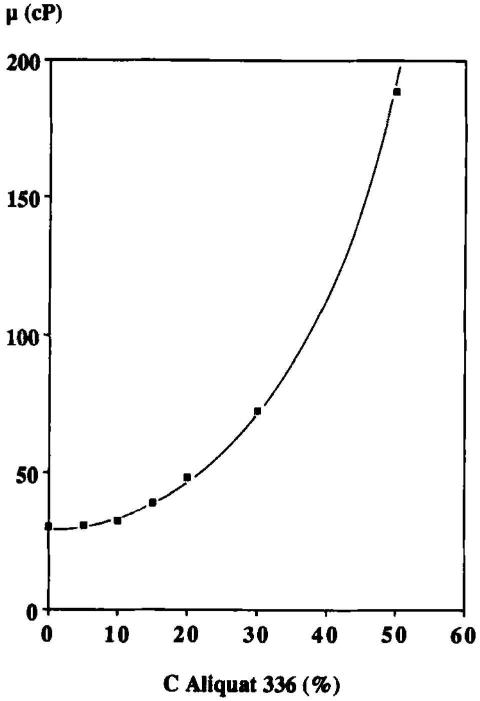

FIG. 5. Effect of Aliquat 336 concentration on the viscosity of the organic phase. Diluent: isotridecanol.

value of 190 cP for 50%, although the viscosity of pure Aliquat 336 is 135 cP at the same temperature (30°C) according to the manufacturer's data.

Influence of Hydrophobicity, Valine Distribution, and Viscosity on Valine Permeability

The transport of L-valine through the SLM was characterized by the permeability. The permeability P of a solute across a SLM is expressed by the equations (*11*)

$$J\Omega = PC\Omega = -V\frac{dC}{dt} \tag{2}$$

$$\ln (C/C^0) = -\Omega/VPt \tag{3}$$

where J is the flux of the solute; C^0 and C are the solute concentrations in the feed phase at initial time and at time t, respectively; Ω is the support area; and V is the volume of the feed phase. The permeability P was calculated from the slope of the linear plot of ln (C/C^0) versus time.

The influence of the Aliquat 336 concentration on the permeability of valine is described in Fig. 6 for isotridecanol solutions. The permeability increases linearly with the carrier concentration up to 10% w/w, reaches a maximum at 15%, and then decreases. The positive slope of the curve can be explained by the increase of the distribution coefficient, the viscosity of the organic phase remaining approximately constant, and the negative slope corresponding to an increasing viscosity with a constant distribution coefficient.

Table 4 shows the influence of the nature of the diluent and the chloride ion concentration in the stripping phase (characterized by the osmotic pressure) on valine permeability. For alcohols it decreases as the carbon chain increases due to increasing hydrophobicity and viscosity. In this series note the unexplained deviation of the behavior of undecanol, also shown in Table 2 for valine distribution. On the other hand, the increase of chloride ion concentration from 1 to 4 M causes only a slight improvement of valine permeability. For triisobutylphosphate and diphenylether it was not possible to measure the permeability due to the low stability of the SLM.

Selectivity and Stability

The selectivity of the SLM for valine was determined toward glucose, $S(v,g)$, expressed by the ratio of their permeabilities (*11*):

$$S(v,g) = P_v/P_g = \ln (C_v/C_v^0)/\ln (C_g/C_g^0) \tag{4}$$

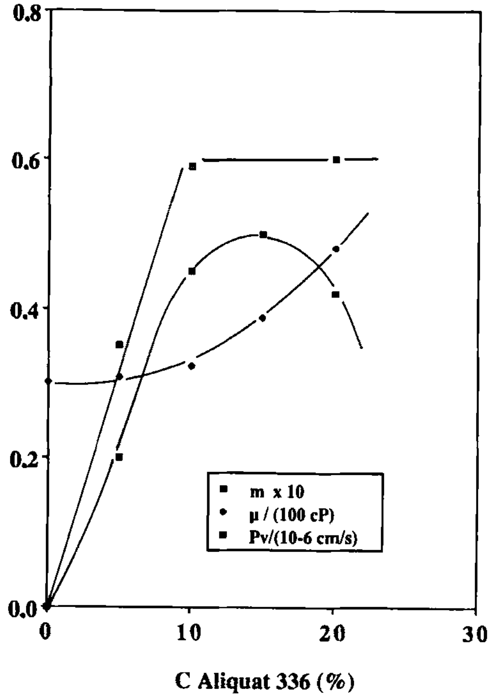

FIG. 6. Influence of the valine distribution and the viscosity of the organic phase on the valine permeability. Organic phase: Aliquat 336–isotridecanol.

The evolution of the selectivity $S(v,g)$ during operation permitted us to define the stability of SLMs: a stable membrane maintains its initial selectivity constant. Different behaviors can occur depending on the organic phase considered: it can remain immobilized in the microporous support, maintaining separation of the two aqueous phases, or it cannot. In the first case, initial selectivities higher than 1 are generally observed and are maintained for a significant time: we call this time the lifetime of the SLM. In the other case, the lifetime is considered to be 0.

The selectivity of SLMs containing increasing concentrations of Aliquat 336 in isotridecanol and exposed to a high osmotic pressure gradient ($\delta\Pi$ = 214 bar) is plotted versus time in Fig. 7. For 10, 15, and 20% of carrier, the initial selectivity is between 60 and 100; beyond 20% it decreases drastically with Aliquat 336 concentration, leading to an unselective SLM for 50% w/w. In terms of stability, these high Aliquat 336 concentrations correspond to unstable SLMs, the lifetime being close to 0 for 50% w/w and lower than 2 h for 30%. The more stable SLMs are obtained for low carrier concentrations, up to 10% w/w (lifetime higher than 50 h).

TABLE 4
Effect of the Diluent of Aliquat 336 on SLM Performances

Diluent	Valine permeability $P_v/(10^{-6}$ cm/s)		Initial selectivity $S(v,g)$		Lifetime t^* (h)	
	$\delta\Pi$ = 37 bar	$\delta\Pi$ = 214 bar	$\delta\Pi$ = 37 bar	$\delta\Pi$ = 214 bar	$\delta\Pi$ = 37 bar	$\delta\Pi$ = 214 bar
Decanol	3.68	4.51	250	100	4	2
Isodecanol		3.10		12		4
Acropol 91		2.99		24		4
Undecanol		0.28		9		20
Dodecanol	1.13	1.46	32	68	>50	8
Isotridecanol	0.41	0.45	140	40	>50	>50
Triisobutylphosphate			≈1		≈0	
Diphenylether			≈1		≈0	

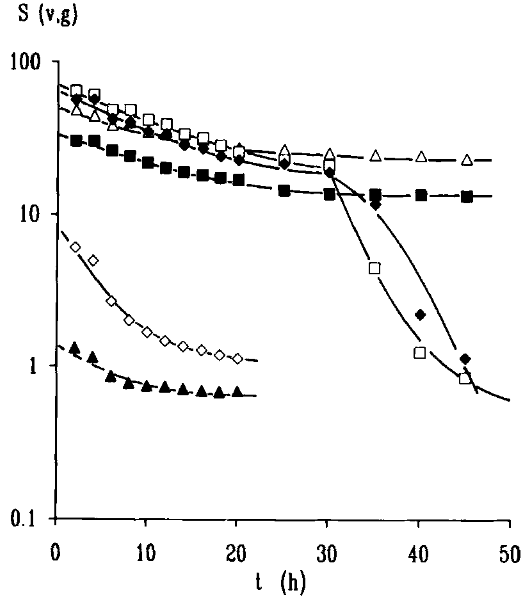

FIG. 7. Effect of Aliquat 336 concentration on the selectivity and the stability of the SLM. C Cl^- = 4.0 *M*; diluent: isotridecanol. C Aliquat 336: (■) 5%, (△) 10%, (□) 15%, (◆) 20%, (◇) 30%, (▲) 50%.

For intermediate concentrations (15 or 20%), the SLM fails after 30 h operation, exhibiting an intermediate lifetime.

Table 4 illustrates the influence of the diluent on the selectivity and the stability of SLMs exposed to different osmotic pressure gradients (37 and 214 bar). The stability of the SLM increases with diluent hydrophobicity; the most soluble solvents (diphenylether, triisobutylphosphate, decanol, or isodecanol) exhibit the lowest lifetimes, even when the osmotic pressure gradient is low. In the series of alcohols, isotridecanol leads to fairly stable SLMs, independent of the osmotic pressure gradient (lifetime higher than 50 h). For dodecanol SLM (stable for $\delta\Pi$ = 37 bar) and decanol SLM, the lifetime decreases when the osmotic pressure gradient increases.

Note that the initial selectivity values are relatively dispersed, between 100 for decanol and 9 for undecanol, at $\delta\Pi$ = 214 bar, largely due to the unreliability of permeability measurements for unstable SLMs.

DISCUSSION

Valine Permeability

The experimental permeability *P* can be fitted by models involving organic phase parameters (distribution coefficient *m* and viscosity μ) and geometrical features of the support (porosity ϵ, tortuosity τ, and thickness e). In the hypothesis of an overall transport rate dependence on diffusion across the liquid membrane and total reextraction in the stripping phase, P is given by (*11*)

$$P = mD\epsilon/\tau e \tag{5}$$

The diffusivity D is estimated by Wilke and Chang's correlation (*21*):

$$D = 7.4 \times 10^{-8} (XM)^{0.5}T/V^{0.6}\mu \tag{6}$$

X is an association parameter characterizing the organic phase, M is the molecular weight of the diluent, T is the absolute temperature (K), and V is the molar volume of the diffusing species (cm^3/mol).

The permeability can thus be written

$$P = \alpha[m(M^{0.5})/\mu] \tag{7}$$

with

$$\alpha = 7.4 \times 10^{-8} X^{0.5}T\epsilon/V^{0.6}\tau e \tag{8}$$

Since $X = 1$ for the different organic phases tested, all the parameters vary when changes in the organic phase are contained in the term $m(M^{0.5})/\mu$.

All the experimental data obtained from permeation experiments and independent measurements of the distribution coefficient and the viscosity of the organic phase led to a linear regression coefficient $\alpha = 5.9 \times 10^{-5}$ mol/s^2.

On the other hand, the value obtained from Eq. (8) is $\alpha = 5.3 \times 10^{-5}$ mol/s^2, with $\epsilon = 0.85$, $\tau = 1.28$, and $e = 60 \times 10^{-4}$ cm given by the support manufacturer and $V = 700$, estimated by contribution group methods (*22*).

The difference between these determinations is close to 10%. When considering the simplicity of the model, based on the assumption of transport limited by diffusion through the SLM, this result appears as fairly satisfactory and justifies the usefulness of applying Wilke and Chang's correlation.

Stability

It appears from the experimental results that the stability of the SLM depends on interfacial properties and organic phase characteristics. Figure

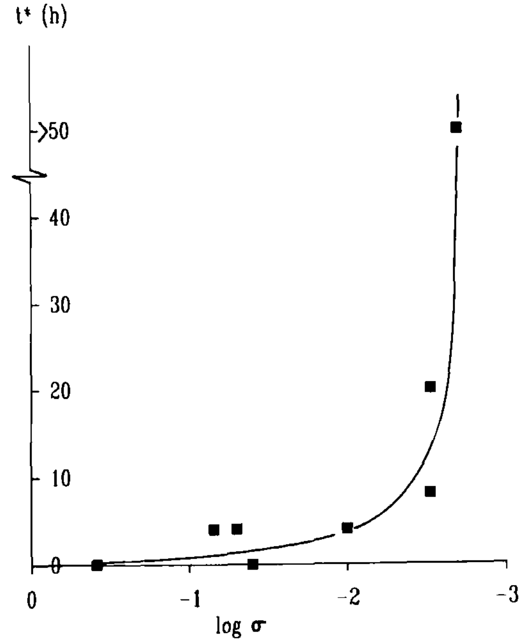

FIG. 8. Correlation between the lifetime of the SLM and the solubility of the diluent in water.

8 shows the relation between the stability of the SLM and the solubility of the diluent in water. The lifetime of the SLM decreases with an increase in diluent solubility; the SLMs were unstable (lifetime lower than 10 h) for solubilities higher than 30 ppm.

The influence of the water content of the organic phase on the lifetime of the SLM is shown in Fig. 9. Three domains can be distinguished: in the first (I), when the water concentration in the organic phase is less than 15 g/L, the SLM stability is quite good (lifetime larger than 50 h). When the water concentration increases from 15 to 40 g/L, the lifetime decreases dramatically (domain II), and for higher concentrations the lifetimes are 0 (domain III).

The stability of the SLM is also a function of the interfacial tension between the aqueous feed phase and the organic phase, as shown in Fig. 10. The lifetime of SLMs is about 0 for interfacial tensions lower than 4 dyn/cm, increases between 4 and 6 dyn/cm, and is larger than 50 h for $\Gamma' \geq 6$ dyn/cm.

The relation between the lifetime and the drop point, shown in Fig. 11, follows similar trends. When the drop point is lower than 0.3 bar, the SLM

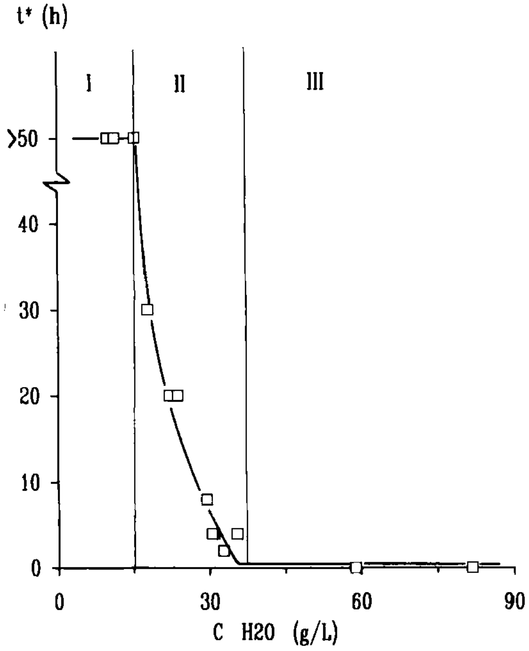

FIG. 9. Correlation between the lifetime of the SLM and the water content in the organic phase.

is unstable; from 0.3 to 0.35 bar the lifetime increases, and the SLM becomes stable for higher drop points. It must be underlined that the unstability observed for drop point lower than 0.3 bar cannot be explained by the mechanical washing out of the organic phase from the support, since the transmembrane pressure difference was maintained below 0.03 bar.

The lifetime of the SLM is thus qualitatively correlated to the diluent solubility, the water content in the organic phase, the interfacial tension, and the drop point before operation. When the water concentration in the organic phase is sufficiently low (less than 15 g/L) and the interfacial tension high enough (more than 6 dyn/cm), the lifetime is independent of the osmotic pressure gradient across the SLM; this was the case for the Aliquat 336–isotridecanol liquid membrane reported in Table 4. When one or several of these conditions is not fulfilled, the organic phase can be progressively removed from the micropores of the support by a flux of water transported from the lower to the higher ionic strength solutions; in this case the lifetime of the SLM decreases with an increase of the osmotic pressure gradient (see Table 4 for SLMs with decyl or dodecyl alcohols).

From the previous results it appears that different methods can be used

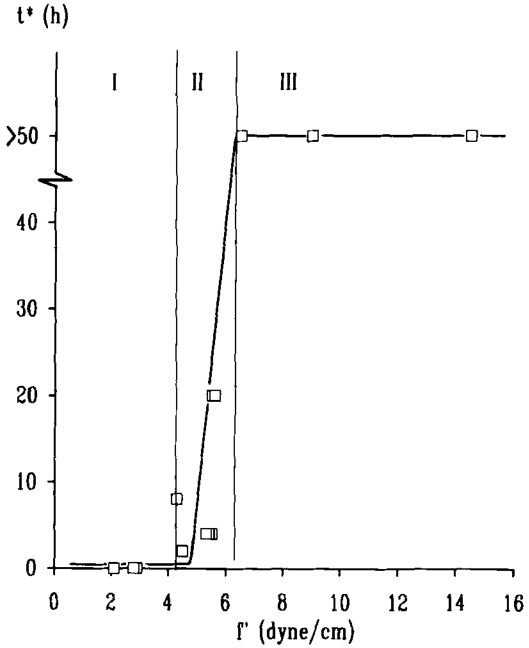

FIG. 10. Correlation between the lifetime of the SLM and the interfacial tension between organic phases and aqueous feed phase.

to predict SLM stability. The first point, by evidence, is to select nonwater-soluble and nonvolatile diluents. The determination of the water content of organic phases can be coupled with preliminary liquid–liquid experiments; it is a practical and sensitive method, leading to reliable results. The interfacial tension between organic and aqueous phases is the parameter more classically assayed (*12*, *15*), but its measurement is relatively difficult to perform and poorly reproducible. The drop point determination necessitates practically the realization of the complete system, including the impregnation of the support and the assembly of the permeation cell with the aqueous feed phase set inside. However, it provides a secure and relevant characterization of the system, applicable to any support geometry, including hollow fibers. In addition, it can be carried out in place on industrial installations.

Since the two parameters Γ' and Dp are related by an extension of the Young-Laplace equation (*15*):

$$Dp = 4\Gamma' \cos \theta' \, Sf/d \qquad (9)$$

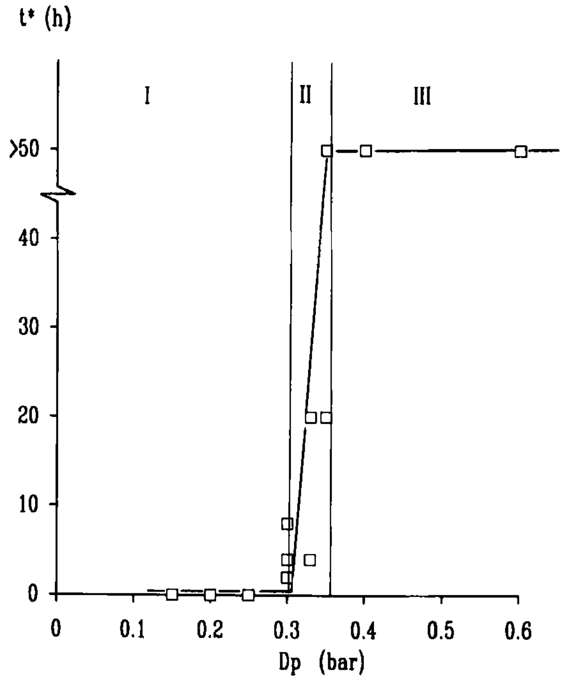

FIG. 11. Correlation between the lifetime and the drop point of the SLM.

where θ′ is the organic–aqueous–solid contact angle, d is the mean pore diameter, and Sf is the shape factor, Eq. (9) is sufficient to measure only one of them.

CONCLUSION

A separation by a SLM involves a complex system constituted by the assembly of four different phases (solid support, organic phase, and aqueous phases). The optimization of permeabilities and stability determines the value of the process.

This work shows that classical and easy independent measurements on organic phases combined with some surface properties determinations permit the description and prediction of the experimental permeability and stability of SLMs. Among the parameters assessed, some of them influence only the permeability (thickness and porosity of the support). In contrast, the pore diameter, the mutual solubilities of water and diluent, and the interfacial parameters ($\Gamma/\Gamma c$, Γ', Dp) mainly concern the stability.

However, the development of a performing SLM system requires the optimization of parameters influencing permeability and stability in opposite ways. It is the case of the distribution coefficient m, as shown previously: the permeability increases with m, while the stability decreases when increasing the carrier concentration or decreasing the chain length of the diluent (series of alcohols); this is directly due to the hydrophilic nature of the transported solute (valine), which is better extracted in a rather hydrophilic organic phase.

On the other hand, a low viscosity of the organic phase and a low tortuosity of the support improve the permeability. Although it has not been quantitatively evaluated in this work, such tendencies are likely to decrease the stability.

The elements of methodology presented in this work should permit rapid prediction of the expected feasibility of a SLM process without it being necessary to carry out long and numerous permeation experiments. In addition, while stability is sometimes assumed to be a major drawback of SLMs, the present approach, and experimental works reported elsewhere (*23*, *24*), confirm that this problem can be predicted or overcome. Continuous permeation operations of more than 40 days were achieved on fermentation broths and plasma protein ultrafiltrates without any problem of stability loss.

NOMENCLATURE

Bp	bubble point (bar)
C	concentration
d	pore diameter (cm)
D	diffusion coefficient (cm^2/s)
Dp	drop point (bar)
e	support thickness (cm)
J	initial flux (mol/h · cm^2)
m	distribution coefficient between organic phase and feed phase
M	molecular weight of the diluent
NR_4^+	Aliquat 336
P	permeability (analogous to a mass transfer coefficient) (cm/s)
$S(v,g)$	selectivity for valine toward glucose
Sf	shape factor
t	time (h)
t^*	lifetime (h)
V	feed phase volume (cm^3)
ϵ	porosity
Γ	surface tension (dyn/cm)
Γ'	interfacial tension (dyn/cm)
σ	solubility (wt%)

Ω	membrane area (cm^2)
Π	osmotic pressure (bar)
θ	solid–liquid contact angle
θ'	solid–organic–aqueous contact angle
μ	viscosity (cP)
τ	tortuosity

Subscripts

g	glucose
v	valine

Superscript

0	initial time

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