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PHENOMENOLOGICAL AND MATHEMATICAL DESCRIPTION OF THE OSMOTIC INFLUENCE IN THE LIQUID MEMBRANE TECHNIQUE

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ABSTRACT

Osmosis is a function of many parameters. The liquid membrane equilibrium driving force is given by a difference in ionic strengths. The dynamical behavior is strongly influenced by surface-active substances. A surfactant has to be used to stabilize the W/O-emulsion. Additionally, the transport of heavy metal ions necessitates the use of a carrier, which is also interfacially active. A synergism in respect to the osmosis between these two interfacially active substances dissolved in the membrane phase can be found. Process conditions such as pH, ionic strength, temperature, and viscosity of solvent influence the degree of swelling phenomenon of W/O-emulsion during liquid membrane permeation. It allows prognosis of osmosis and breakup, important factors for industrial optimization of the liquid membrane technique.

INTRODUCTION

The liquid membrane technique represents a useful tool in purification of contaminated wastewater. With liquid membrane permeation, organic solutes (ammonia, phenols) or heavy metal ions (Zn^{2+}, Cu^{2+}, Pb^{2+}, ...) can be concentrated in the receiving phase to such an extent that recycling is possible; however, some problems like osmosis and breakup still arise during the permeation step: osmosis because of the necessity of different ionic strength between feed and internal receiving phase and breakup due to low stability of W/O-emulsions.

More than 20 years ago, N. N. Li (1968) applied for a patent on the industrial use of liquid membranes (1). By this, the foundation for a new, promising purification process was laid (2). Since then, different processes have been developed to take advantage of liquid membranes for industrial applications. Some of them have been utilized in pilot plants (3-12). In addition, an Austrian company has installed a commercial application of W/O-emulsion liquid membranes for treatment of wastewater (13). Figure 1 shows the steps necessary for the liquid membrane process.

During the permeation step, water, in addition to a solute, is transported across the liquid membrane. This leads to swelling of the emulsion so that the solute in the receiving phase is diluted, which renders the recycling difficult. In addition, the receiving phase droplets of about 5-μ diameter, may swell significantly. A partial breakup of the emulsion may result and cannot be neglected. Investigations showed that interfacially active substances have the most significant influence on the transport of water. There also exists a strong interaction between the carrier and the surfactant, leading to a minimal dependence of the osmosis on the carrier concentration (see Fig. 2).

The problem of osmosis and breakup is multidimensional (14) so that prognosis, in which osmosis can be described as a function of some parameters, is very difficult. Numerous experiments were done to verify the validity of the developed mathematical description (15).

EXPERIMENTAL

System

Experiments were done with a reagent-grade feed phase instead of an industrial wastewater. The system investigated is introduced in Table 1. Only the surfactant (ECA 4360, also: Paranox 100; Exxon) and the carrier [bis (2-ethylhexyl) monothio phosphoric acid, also: MTP; Höchst (Hoef 3787)] are of industrial grade.

Apparatus

Experiments carried out in an agitated vessel (16-19) have the great advantage that mass transfer proceeds very rapidly. For this, the agitated vessel has to be

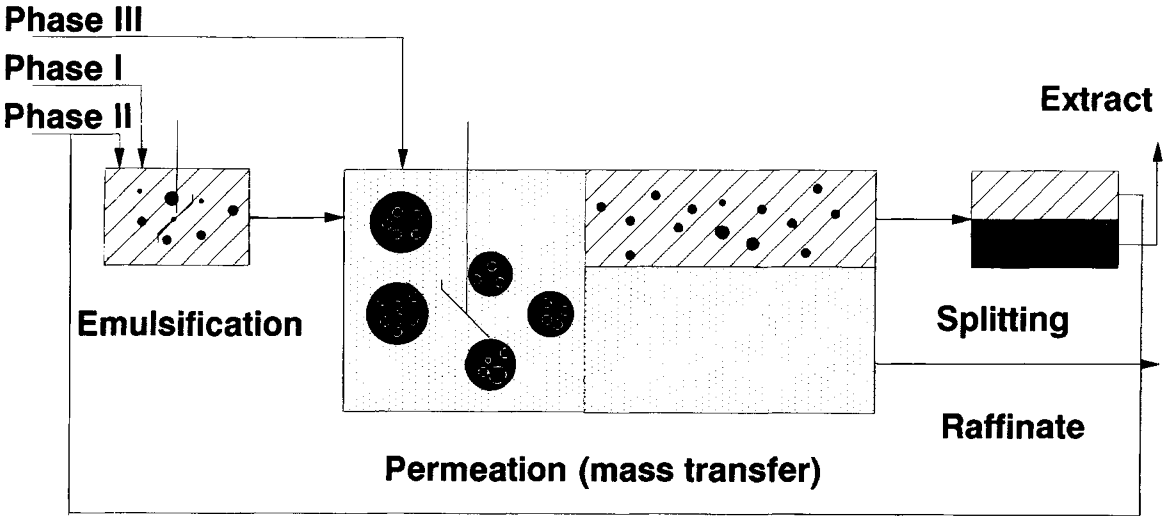

Fig. 1. Schematic presentation of the liquid membrane process basing on W/O-emulsions.

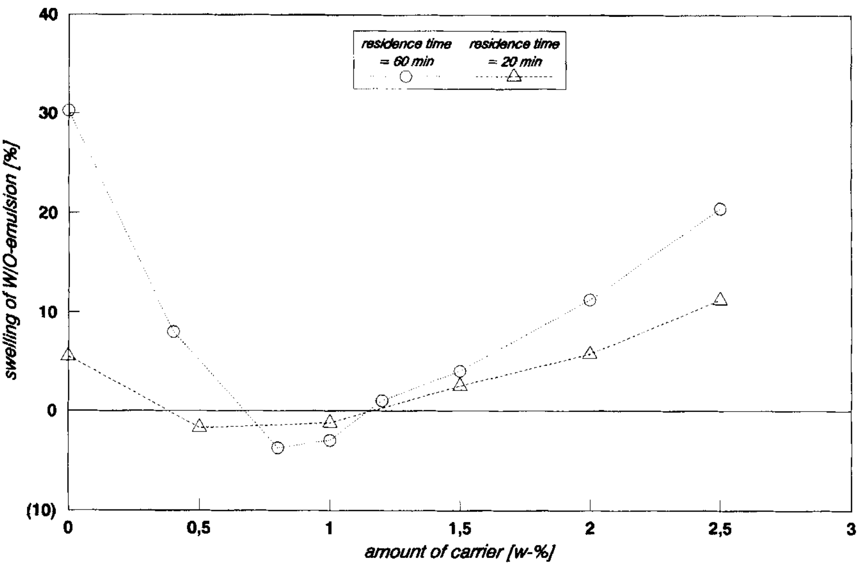

Fig. 2. Influence of carrier concentration on osmosis. (Parameter contact time during mass transfer in a vessel.)

TABLE 1. COMPOSITION OF THE W/O/W EMULSION ($\Phi_R = 0.125$; $\Phi_E = 0.15$)

Phase	Solvent	Dissolved Substances	Concentration
Feed	Distilled water (pH = 5)	$ZnSO_4.7H_2O$	0.5 g Zn/L
Membrane	n-Alkanes (from C_7H_{16} to $C_{12}H_{26}$)	ECA 4360 MTP	2-20 wt % 0-10 wt %
Receiving	Aqueous sulfuric acid		C_{H2SO4} = 1-6 M

modified for polydispersed systems. The fast mass transfer of solutes is detrimental to the investigation of osmosis, which takes a longer time.

Extreme agitation in a vessel increases the breakup of the W/O-emulsion and broadens the size distribution of the emulsion droplets. Thus, it is very difficult to determine exactly the mass-transfer-limiting interface between feed and emulsion phase.

Another possible experimental device is the Nitsch cell, a modified Lewis mass transfer cell (20). It allows exact measurements of mass transfer from the feed phase into the W/O-emulsion, because the mass-transfer-limiting interface between feed and membrane phase is small but well known. The mass transfer of the solute will occur quickly in relation to osmosis. In order to have comparable conditions in regard to ionic strength and solute transport, a semicontinuous operation was chosen (21).

Analytical Procedures

The concentration of zinc was measured photometrically as a zinc-zincon-complex by a Shimadzu Spectralphotometer UV-160A at 617 mm; pH was determined using an Orion 940 automatic titrator.

Water transfer is determined by five different methods (Table 2). In our work, we used the volumetric growth rate of W/O-emulsion.

Water transfer has to be calculated dimensionless, when using different methods. As a measure for osmosis, the relative alteration in volume of the emulsion may be used (Eq. 1):

$$\Delta V_{rel} = \frac{V_r - V_o}{V_o}. \tag{1}$$

Breakup of the W/O-emulsion was calculated using a tracer, which must not react with the carrier. Fe^{II} was used as an inert tracer, not affected by the extractant MTP.

THEORY

The transfer of water across liquid membranes is phenomenologically treated in literature (16-20, 22-24). A detailed survey is given by Ramaseder (15).

TABLE 2. DIFFERENT METHODS FOR DETERMINING THE WATER TRANSFER ACROSS A LIQUID MEMBRANE.

Method		Advantages and Disadvantages[*]
Altering of the volume of W/O-emulsion	☺	Simple
	☹	Measurement possible only at the beginning and at the end; breakup influences measurement
Growing of internal receiving-phase droplets	☺	Osmosis independent of residence time; no influence of breakup; little volume of sample necessary
	☹	Complicated
Alteration of density	☹	Measurement possible only at the beginning and at the end; breakup influences measurement
Alteration of viscosity	☹	Measurement possible only at the beginning and at the end; breakup influences measurement
Alteration of volume of Phase I	☹	Measurement possibly only at the beginning and at the end; influence of breakup; after splitting a film remains

[*] Advantage = ☺; disadvantage = ☹.

As mentioned above, interfacially active substances have the most important influence on water transfer. Water molecules are nearly insoluble in the organic nonpolar membrane phase so that they are in need of a carrier species in the organic solvent. Surfactant molecules are assumed to act in this function. On the one hand, their polar groups can bind water by hydrogen bonds; and on the other hand, they can form aggregates (e.g., reversed micelles) and solubilize water molecules.

These effects are influenced by different process parameters. A higher temperature means less viscosity of the membrane phase, which facilitates diffusion.

The difference in ionic strength between the feed and the receiving phase is increased by stronger acidity of the internal droplets.

Colinart et al. proposed a mathematical model (25), which is based on water-surfactant associations and carrier-mediated water transport. It cannot be compared with our model, since this model involves only the influence of the surfactant. Additionally, there are a lot of simplifications and assumptions (e.g., no water transfer by reversed micelles because of their low diffusion coefficients, the emulsion is represented as a dispersion in a continuous organic medium consisting of droplets encapsulated in an exceedingly thin layer of pure organic phase, which separates them from the aqueous feed solution, ...), which do not apply to our system.

RESULTS AND DISCUSSION

Phenomenological Description of Water Transfer Across Liquid Membranes

Parameters influencing the water solubilization in the organic membrane phase are numerous. As mentioned above, interfacially active substances represent the most significant. Besides this, process conditions like ionic strength, temperature, etc., affect the water transfer. When using cosurfactants (e.g., i-tridecanol), osmotic water transfer across the liquid membrane rises enormously.

Figure 3 gives the swelling in regard to surfactant concentration. A good stability of the W/O-emulsion is reached at an amount of surfactant greater than 2 wt %. Therefore, breakup decreases, while water transport rises; for example, ECA 4360 favors water transfer across the organic membrane in various ways. Water molecules hydrate the polar groups of the surfactant molecules or are included by inverse micelles. Additionally, increasing amounts of surfactant lower the Sauter-diameter of both the droplets of the inner receiving phase and the W/O-emulsion, increasing interfacial area for mass transfer.

The next main parameter is represented by the carrier. Figure 2 demonstrates the dependence of osmosis on the amount of carrier present. Measurements with a MGW Lauda film balance show that the interfacial area required per molecule is

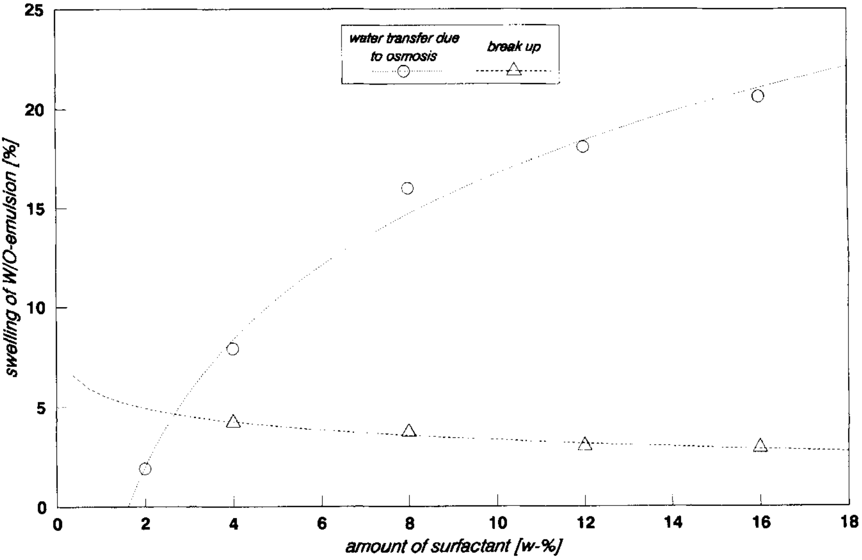

Fig. 3. Dependence of breakup and osmosis from the concentration of surfactant (at 2,5 w-% MTP).

maximal at a definite ratio between surfactant and carrier concentrations. At this ratio, a minimum in the swelling of the W/O-emulsion is observed (see Fig. 4).

The minimum in the carrier-dependence of the emulsion swelling (see Fig. 2) can be explained by the mobility of the smaller carrier molecules, which can settle between the bulky surfactant molecules. By this, the formation of reversed micelles is made more difficult. The greater the amount of carrier molecules at the interface, the smaller the probability of micellation. At a definite ratio between carrier and surfactant dissolved in the membrane phase, their molecules are ideally mixed, and the monolayer behaves like an ideal solution. Hence, micellation is hindered maximally and osmotic water transfer is minimal. At higher amount of carrier, its molecules take over the water transport more and more, so that osmosis increases with higher carrier concentration.

Usually, minimal water transfer can be found at low surfactant concentrations. The higher the amount of surfactant the less intense is the minimum, since breakup is reduced strongly.

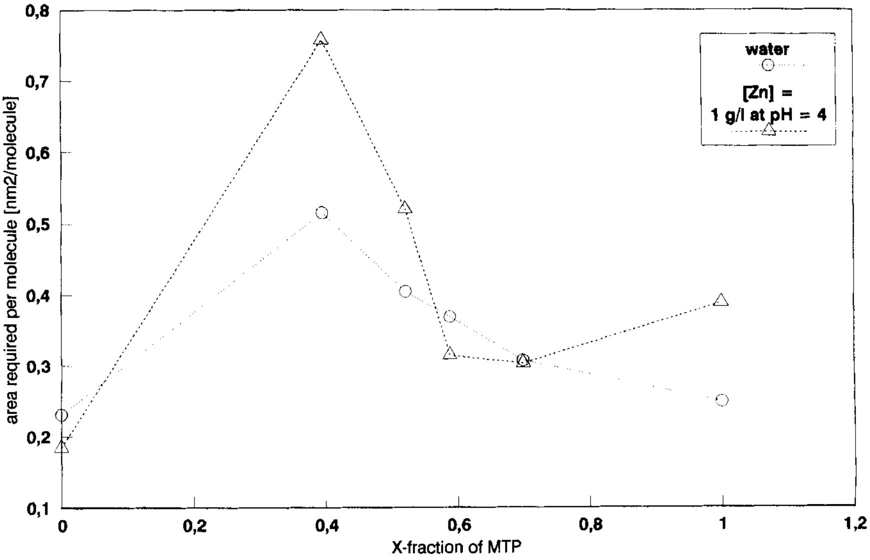

Fig. 4. Interfacial area required per molecule at different ratios carrier/surfactant.

Smaller agitation numbers of the stirrer move the minimum to decreased carrier concentrations (see Fig. 5).

A higher agitation number means a greater interfacial area for mass transfer. Additionally, the thickness of the interfacial film is reduced, so that diffusion of solute is accelerated. Because of this, more solute molecules take part in the complexation reaction with the carrier molecules present at the interface. In this connection, interfacial measurements by a Lauda-film balance point to the influence of the concentration of solute on the need of increasing interfacial area per carrier molecule. The repulsion forces of the surfactants on the interface are strongly influenced by ionic strength, as is well known.

As mentioned above, the degree of osmosis depends also on the process conditions. Osmosis increases exponentially with acidity of the internal droplets. This cannot be explained only by increasing ionic strength, but by higher reaction rate for complexation and micellation at the W/O interface. The transfer of water across the

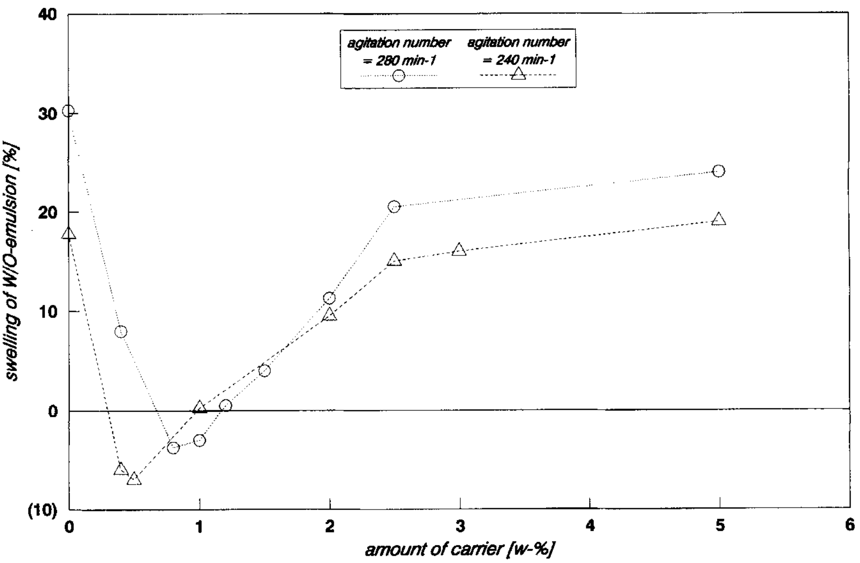

Fig. 5. Influence of hydrodynamic conditions on the dependence of emulsion swelling on the amount of carrier (at 4 w-% ECA 4360).

membrane depends on temperature, which affects formation of reversed micelles, viscosity of the organic membrane, and emulsion viscosity. By using solvents of lower viscosity, the diffusion of reversed micelles is facilitated.

Mathematical Description of the Water Transfer

The mathematical approach to this complex problem is given by Bart and Ramaseder (14). Occlusion of water during settling of the emulsion after mass transfer experiments in a vessel can be neglected in our system. The overall swelling of emulsion consists of transmembrane water transfer due to osmotic swelling ($\Delta V_{\alpha,rel}$) and of breakup of the W/O-emulsion due to a lack of stability ($\Delta V_{\beta,rel}$). Hence, the general valid formula to describe the swelling phenomenon is given by Eq. 2:

$$\Delta V_{r,rel} = \Delta V_{\alpha,rel} - \Delta V_{\beta,rel} \, . \qquad (2)$$

Hydrodynamics in an agitated vessel cause a shrinkage of the emulsion globules, especially in the first minutes (Eq. 3):

$$d_\tau = d_{stab}\,(1 - e^{-\frac{\tau_e}{\tau}}) + d_{stab} + \xi\,\phi_R\tau_e\,. \tag{3}$$

The second and third terms in Eq. 3 describe the time-dependent growth of emulsion globules due to osmosis. The interfacial area for mass transfer is given by Eq. 4:

$$A_\tau = \frac{4}{3}\left(\frac{d_\tau}{2}\right)^3 \pi \frac{V_{Em}}{d_\tau^2\,\pi} = \frac{1}{6}\,\frac{V_{Em}}{d_\tau}\,. \tag{4}$$

During permeation, the difference in ionic strength of feed and receiving phase (Δc_τ) is lowered because of osmotic water transfer (Eq. 5).

$$\Delta c_\tau = \Delta c_o - \xi\,\tau_e\,. \tag{5}$$

The swelling due to osmotic water transfer can be calculated by Eq. 6:

$$\Delta V_{\alpha,rel} = k_{H_2O}\,A_\tau\,\Delta c_\tau\,\tau_e\,. \tag{6}$$

Introducing Eqs. 2-5 gives Eq. 7:

$$\Delta V_{\alpha,rel} = k_{H_2O}\,\frac{V_o}{d_{stab}\,(1 - e^{-\frac{\tau_e}{\tau}}) + d_{stab} + \xi\,\phi_R\,\tau_e}\,(\Delta C_o - \xi\,\tau_e)\,\tau_e \tag{7}$$

Breakup is described by a simple linear relation (Eq. 8).

$$\Delta V_{\beta,rel} = \xi_\beta\,\tau_e\,. \tag{8}$$

The terms necessary for determining the swelling are listed in Table 3 (15). Here the process conditions, which most influence the osmotic behavior, are taken into account. With the presented formulas, it is very easy to calculate osmosis dependence on the most important parameters. It is not possible to alter more than one parameter, because interactions of the parameters, as described above, have to be taken into account. Additionally, the cited equations in Table 3 are only valid for agitation vessels, in which the experiments were carried out. For other types of apparatus, it is necessary to determine these equations.

TABLE 3a. TERMS NECESSARY FOR DETERMINING THE SWELLING OF W/O-EMULSION

Concentration of Surfactant	Formula
Size of emulsion globule at stability	$d_{stab} = 0.679 - 3.715 \times 10^{-2} \ln c_{surf}$
Water transfer coefficient	$k_{H_2O} = 7.3 \times 10^{-2} + 1.87 \times 10^{-2} \ln c_{surf}$
Slope in time-dependence of ionic strength	$\xi = 0.151 + 2.25 \times 10^{-2} \ln c_{surf}$
Slope in time-dependence of breakup	$\xi_\beta = 1.983 \times 10^{-4} - 1.658 \times 10^{-4} \ln c_{surf}$
<u>Concentration of Carrier</u>	
Size of emulsion globule at stability	$d_{stab} = 0.722\, c_{car}^{-2.54 \times 10^{-2}}$
Water transfer coefficient	$k_{H_2O} = 8.83 \times 10^{-2} + 1.84 \times 10^{-2} \ln c_{car}$
Slope in time-dependence of ionic strength	$\xi = 6.2 \times 10^{-2} + \ln (1 + c_{car})^{0.751}$
Slope in time-dependence of breakup	$\xi_\beta = 1.557 \times 10^{-4}\, c_{car}^{-0.437}$

Based on the above presented formalism, a computer simulation program was provided. The mathematical description of the swelling phenomenon occurring during liquid membrane permeation is compared to data in Fig. 6. The marked points represent experimental data, the dotted line the simulated results.

The model allows prognosis of the emulsion swelling not only in its dependence on various parameters (e.g., concentration of interfacially active substances, pH, viscosity of solvent, and temperature) but also in its time-dependent growth,

TABLE 3b. TERMS NECESSARY FOR DETERMINING THE SWELLING OF W/O-EMULSION

Viscosity of Solvent	Formula
Size of emulsion globule at stability	$d_{stab} = 0.596 + 6.75 \times 10^{-2}\,\eta_{org} + 4.55 \times 10^{-2}\,\eta^2_{org}$
Water transfer coefficient	$k_{H_2O} = 1.655 \times 10^{-2} + 3.054 \times 10^{-3}\,\eta_{org}$
Slope in time-dependence of ionic strength	$\xi = 8.1 \times 10^{-2}\,\eta_{org}^{-0.135}$
Slope in time-dependence of breakup	$\xi_\beta = 9.267 \times 10^{-4}\,\eta_{org}^{-0.643}$
Temperature	
Size of emulsion globule at stability	$d_{stab} = 0.5737 + 8.9 \times 10^{-2}\,T$
Water transfer coefficient	$k_{H_2O} = 1.632 \times 10^{-2} - 1.7 \times 10^{-4}\,T$
Slope in time-dependence of ionic strength	$\xi = 9.29 \times 10^{-2} - 6.37 \times 10^{-4}\,T$
Slope in time-dependence of breakup	$\xi_\beta = 3.983 \times 10^{-4}\,e^{2.32 \times 10^{-3}\,T}$

additionally considering the shrinkage of emulsion droplets due to stirring in a batch vessel.

CONCLUSIONS

The liquid membrane technique is a promising tool in purification of contaminated wastewater. In process some nonidealities occur: swelling of emulsion due to osmotic water transfer and breakup due to lack of stability.

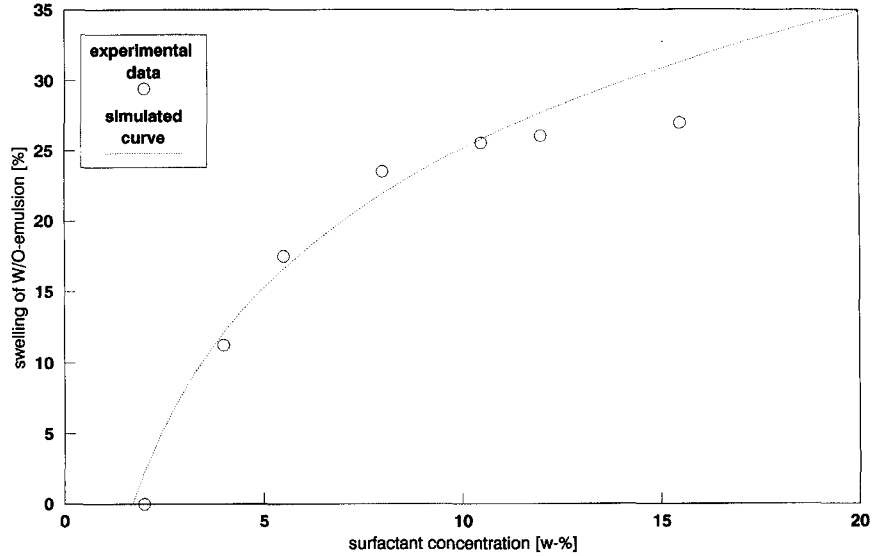

Fig. 6. Comparison of experimental data with simulated curve.

Osmosis is a function of many parameters. As can be seen from experimental data, the influence of interfacial active substances is the most important. A surfactant has to be used to stabilize the W/O-emulsion. Additionally, the transport of heavy metal ions necessitates the use of a carrier, which is also interfacially active. An osmotic synergism can be found between these two interfacially active substances dissolved in the membrane phase. Process conditions such as pH, ionic strength, temperature, and viscosity of solvent influence the degree of swelling considerably.

Altering the pH has an influence on the amount of the physical driving force for mass transfer. Additionally, reaction rate for complexation at the interface depends on the pH. Temperature affects formation of reversed micelles, viscosity of the organic membrane, and emulsion viscosity. The diffusion of reversed micelles is strongly dependent on the viscosity of solvent.

The mathematical description of the swelling phenomenon of W/O-emulsions during liquid membrane permeation allows prognosis of osmosis and breakup, which is important for industrial application of the liquid membrane technique. By means of computer simulation, it can be seen that the presented mathematical description fits experimental data quite well. The modeling of the swelling phenomenon allows not only the simulation of the influence of various parameters (e.g., concentration of interfacially active substances, pH, temperature, and viscosity of solvent) on osmotic swelling and breakup, but also of their time-dependence.

As mentioned above, it is necessary to determine the equations cited in Table 3 for each apparatus, because for describing the osmotic swelling phenomenon by a more fundamental model it is necessary to find out the basic mechanism of water transfer across liquid membranes. This has to be investigated in more detail, which will be done in future work.

SYMBOLS

A_{dis}	surface of a dispersed W/O-emulsion droplet (m^2).
A_r	interfacial area between feed and W/O-emulsion (m^2)
d_{stab}	diameter of emulsion droplets at stability (mm)
k_{H_2O}	water transfer coefficient (mL kg min^{-1} mol^{-1})
n_{dis}	number of dispersed W/O-emulsion droplets (-)
V_0	emulsion volume at the beginning of permeation (mL)
V_r	emulsion volume at residence time, τ_e (mL)
ΔV_{rel}	relative change in emulsion volume (-)
$\Delta V_{\beta,rel}$	relative change in emulsion volume due to breakup (-)
ξ	slope in the time-dependence of the difference of ionic strength between feed and receiving phase (mol kg^{-1} min^{-1})
ξ_β	slope of the time-dependence of breakup (mL min^{-1})
τ	mean residence time (min)
τ_e	residence time (min)
Φ_E	phase ratio between W/O-emulsion and feed phase (-)
Φ_R	phase ratio between receiving and membrane phase (-).

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