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WATER-PERMEATION SWELLING OF EMULSION LIQUID MEMBRANE

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ABSTRACT

Water-permeation swelling resulting from osmotic pressure was studied both theoretically and experimentally. Flat-bed and hollow-sphere models considering the change of permeation area with agitation time were proposed. Mean rate coefficients of water-permeation swelling were obtained from the models. The so-obtained rate coefficients predict the solubility of water in the membrane containing surfactants. The model prediction fits the experimental data well. This model can be used to calculate the permeation-swelling ratio for all swelling cases, such as pure water as inner or outer aqueous phase, or two aqueous phases with different electrolyte concentration. It was found that at the late stage of swelling, the hollow-sphere model gives a better prediction. Experimental studies indicate that control of the swelling can be achieved by surfactants that have lower water solubility, such as EM-301. As for effective factors, increasing surfactant concentration resulted in an increased swelling ratio. Different carriers had different effects on the water-permeation swelling ratio, and addition of all kinds of nonphosphatic carriers to the Span-80 membrane caused severe breakage of the membrane.

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INTRODUCTION

The previous work (1-4, 6) based, generally, on the assumption that the swelling of emulsion membrane was caused by water transport by osmosis across the oil phase which separates the inner aqueous phase of the emulsion drops from the outer or bulk aqueous phase. The osmotic pressure is created by the concentration differences of electrolyte concentrations in the inner aqueous phase and the outer aqueous phase. Recently, it is recognized that there is, in addition to water-permeation swelling, also entrainment swelling caused by entrainment during the dispersion process (5, 7). Entrainment swelling ratio can be too big to be neglected for some commercial surfactants (i.e., Span-80). Only total swelling ratio is obtained from experiments. Li (5) made some reasonable assumptions and proposed a method for calculating the two different swelling ratios respectively.

Earlier work (1-4) showed that the difference in concentration of electrolytes or surfactants, volumetric ratio of the inner aqueous phase to the outer aqueous phase, and the agitation speed exerted an influence on the water-permeation swelling ratio. The effect of the carrier was uncertain. While some of them caused increased swelling, some showed no effect. Among the variety of water-permeation swelling mechanisns and mathematical models, Fujinnawa and coworkers (1) have proposed a formula for calculating the swelling ratio that is based on the flat-bed model assuming fixed membrane thickness and permeation area. Colinart and coworkers (6) proposed a mathematical model based on the assumption of water-surfactant associations and carrier-mediated water transport. The purpose of this study is to propose two mathematical models of water-permeation swelling, considering the relationship between agitation time and the permeation area, and to reveal the effect of the main process characteristics.

MATHEMATICAL MODELS

Researchers found that the water-permeation swelling is caused by the osmotic pressure gradient acting across the oil-phase layer that separates the inner aqueous phase from the outer aqueous phase, because of the concentration difference of electrolytes in these two phases. The hydrophilic group of the surfactant molecules that are adsorbed on the oil-water interface have a strong hydration function. In a dynamic equilibrium process, surfactants exchange their position between interface and membrane phases, and water is solvated into the membrane by such movement. When there is no concentration gradient between inner and outer aqueous phases, the dynamic equilibrium kept the membrane phase with a constant for water; otherwise, it kept a constant flux of water solving into the

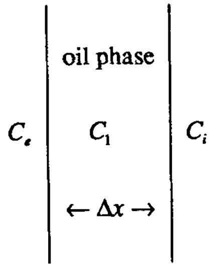


Fig. 1. Flat - bed model

membrane phase from the outer or inner aqueous phase, and the water diffusing into the inner or outer aqueous. Thus, the water-permeation swelling took place. In deriving the mathematical model, the following assumptions were made:

- The sauter mean-diameter d_{32} indicates the diameter of emulsion liquid drops.
- The mass-transfer resistance of water in the outer-aqueous-phase interface can be neglected, as a result of a much higher concentration of water in the outer aqueous and the strong hydrating function of the hydrophilic groups of the surfactant molecules. Mass-transfer resistance on the interface between the oil and the inner aqueous phases can also be neglected, since the interface area of the inner water drops is much larger than that of the outer interface.
- The effective thickness of the liquid membrane is constant with the agitation time.
- The breakage ratio of the emulsion liquid drops is small enough to be neglected.

(1) Flat-Bed Model

The effective thickness of the membrane is generally much smaller than the diameter of the emulsion liquid drops, so the spheric membrane can be treated as a flat-bed membrane (see Fig. 1).

As we know,

$$\Delta\mu_1 = \overline{V}_1(\Delta P - \Delta\pi), \qquad (1)$$

where $\Delta P = 2\sigma / R$. Generally, it can be neglected. The osmotic pressure of a solution can be indicated by the practical osmotic coefficient Φ

$$\pi = \frac{\Phi\gamma RTM_1 m}{1000\overline{V}_1}, \tag{2}$$

where $\gamma = \gamma_+ + \gamma_-$, and $m = \frac{C}{\rho - 0.001CM_B} \approx \frac{C}{\rho}$.

We know

$$\frac{M_1}{1000\overline{V}_1} = \rho_1. \tag{3}$$

So

$$\Delta\pi = \Phi\gamma RT\rho_1\left(\frac{C_i}{\rho_i} - \frac{C_e}{\rho_e}\right) \approx \Phi\gamma RT(C_i - C_e). \tag{4}$$

Now, J_1 can be written as

$$J_1 = -D_1\frac{dC_1}{dx} = \frac{1}{S\overline{V}_1}\frac{dV_i}{dt} = \frac{D_1C_1\overline{V}_1}{RT\Delta x}\cdot\Phi\gamma RT(C_i - C_e) \tag{5}$$

During the water-permeation process, the total volume of water in the inner and the outer aqueous phases is constant:

$$V_T = V_{io} + V_{eo} = V_i + V_e \tag{6}$$

and

$$C_i = \frac{n_i}{V_i},\ C_e = \frac{n_e}{V_T - V_i}, \tag{7}$$

$$S = \frac{3}{R}(V_i + V_m) = 3(V_i + V_m)\cdot\frac{1}{R_o}\cdot\sqrt[3]{\frac{V_{io} + V_m}{V_i + V_m}}$$
$$= 3\frac{\sqrt[3]{V_{io} + V_m}}{R_o}\cdot(V_i + V_m)^{\frac{2}{3}}. \tag{8}$$

Substituting Eqs. 6-8 into Eq. 5 yields

$$\frac{dV_i}{dt} = \frac{3D_1C_1\overline{V}_1^2\Phi\gamma\sqrt[3]{V_{io} + V_m}}{\Delta x R_o}\left(\frac{n_i}{V_i} - \frac{n_e}{V_T - V_i}\right)\sqrt[3]{(V_i + V_m)^2} \tag{9}$$

Using the initial conditions:

$$t = 0,\ V_i = V_{io}. \tag{10}$$

The integration of Eq. 9 yields:

$$\frac{1}{4C}(y^4-y_o^4)+\frac{D-AC}{C^2}(y-y_o)-\frac{k(D^2-ACD+BC^2)}{3C^2D}\cdot$$
$$\left\{\frac{1}{2}\begin{bmatrix}\ln\dfrac{(y+k)^2}{(y^2-ky+k^2)}-\\ \ln\dfrac{(y_o+k)^2}{(y_o^2-ky_o+k^2)}\end{bmatrix}+\sqrt{3}\begin{bmatrix}\tan^{-1}\dfrac{2y-k}{\sqrt{3}k}-\\ \tan^{-1}\dfrac{2y_o-k}{\sqrt{3}k}\end{bmatrix}\right\}$$
$$=\frac{D_1C_1\bar{V}_1^2\Phi\gamma y_o}{\Delta x R_o}\cdot t=y_oKt, \tag{11}$$

where

$A=V_T+2V_m$;

$B=V_mV_T+V_m^2$;

$C=n_i+n_e$;

$D=n_iV_m+n_eV_m+n_iV_T$;

$y=(V_i+V_m)^{1/3}$;

$y_o=(V_{io}+V_m)^{1/3}$;

$k^3=-D/C$;

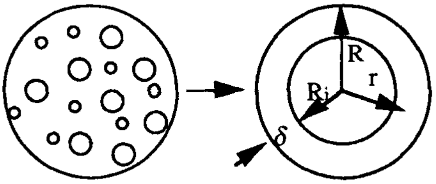
$$K=\frac{D_1C_1\bar{V}_1^2\Phi\gamma}{\Delta x R_o}=const.(cm/s). \tag{12}$$

The water-permeation swelling ratio can be written as

$$F_{so}=\frac{-V_{io}+V_i}{V_{io}+V_m}=\left(\frac{V_i+V_m-V_{io}-V_m}{V_{io}+V_m}\right)=\left(\frac{y}{y_o}\right)^3-1. \tag{13}$$

(2) Hollow-Sphere Model

To describe the process of water-permeation swelling more realistically, the hollow-sphere model can be used. The real emulsion liquid drop is equivalent to a sphere that has a core of an inner aqueous phase and a shell-of-oil phase.



δ = effective membrane thickness
R = mean radius of the emulsion liquid drops
Ri = radius of inner sphere
r = radius from the center to an arbitrary point in the sphere

Fig. 2. Hollow sphere model

Considering an unstable diffusion through the membrane, the following equations can be written for the model:

$$\frac{\partial \mu}{\partial t} = D_1 \frac{\partial}{\partial r}\left(r^2 \frac{\partial \mu}{\partial r}\right) \quad (R_i < r < R,\ t > 0). \tag{14}$$

Using the boundary conditions:

$$\mu(R,t) = \mu_e, \tag{15}$$

$$\mu(R_i,t) = \mu_i, \tag{16}$$

and substituting $u = r\mu$ into Eq. 14, we obtain

$$\frac{\partial u}{\partial t} = D_1 \frac{\partial^2 u}{\partial r^2}. \tag{17}$$

Using the boundary conditions:

$$u(R,t) = R\mu_e, \tag{18}$$

$$u(R_i,t) = R_i\mu_i, \tag{19}$$

the differential Eq. 17 can be solved as

$$\frac{u - u_i}{u_e - u_i} = \frac{erf\left(\frac{r}{2\sqrt{Dt}}\right) - erf\left(\frac{R_i}{2\sqrt{Dt}}\right)}{erf\left(\frac{R}{2\sqrt{Dt}}\right) - erf\left(\frac{R_i}{2\sqrt{Dt}}\right)}, \tag{20}$$

with

$$erf(x) = \frac{2}{\sqrt{\pi}}\left(x - \frac{x^3}{1!\cdot 3} + \frac{x^5}{2!\cdot 5} - \frac{x^7}{3!\cdot 7} + \cdots\right). \tag{21}$$

If we used only the first term, the error is smaller than $\frac{x^3}{1!\cdot 3}$ for the common liquid membrane system, $x = r/(2\sqrt{Dt}) < 0.2$; so the error is smaller than 0.26%. Substituting $erf(x) = (2/\sqrt{\pi})x$ into Eq. 23 yields

$$u = \frac{r - R_i}{R - R_i}(u_e - u_i) + u_i = \frac{r - R_i}{\delta}(u_e - u_i) + u_i. \tag{22}$$

So

$$\mu = \left(\frac{R}{\delta} - \frac{R^2}{r\delta} + \frac{R}{r}\right)(\mu_e - \mu_i) + \mu_i, \tag{23}$$

$$\frac{\partial \mu}{\partial r}\Big|_{r=R} = \left(\frac{1}{\delta} - \frac{1}{R}\right)(\mu_e - \mu_i). \tag{24}$$

Thus, the osmotic flux of water can be written as

$$J_1 = -\frac{D_1C_1}{RT}\cdot\frac{\partial\mu}{\partial r}\Big|_{r=R} = -\frac{D_1C_1}{RT}(\frac{1}{\delta}-\frac{1}{R})(\mu_e-\mu_i)$$
$$= -\frac{D_1C_1}{RT}(\frac{1}{\delta}-\frac{1}{R})\cdot\Delta\mu_1$$
$$= \frac{D_1C_1\overline{V}_1}{RT}(\frac{1}{\delta}-\frac{1}{R})\Delta\pi. \tag{25}$$

Substituting Eq. 4 into Eq. 25 gives

$$J_1 = (D_1C_1\overline{V}_1\Phi\gamma)(\frac{1}{\delta}-\frac{1}{R})(C_i-C_e) = \frac{1}{S\overline{V}_1}\cdot\frac{dV_i}{dt}. \tag{26}$$

Substituting Eq. 7 and 8 into Eq. 26 and rearranging the terms yields

$$\frac{dV_i}{dt} = \frac{3\sqrt[3]{V_{io}+V_m}D_1C_1\overline{V}_1^2\Phi\gamma}{R_o}(\frac{1}{\delta}-\frac{1}{R})\cdot$$
$$(\frac{n_i}{V_i}-\frac{n_e}{V_T-V_i})\sqrt[3]{(V_i+V_m)^2}. \tag{27}$$

Using the initial conditions:

$$t = 0, V_i = V_{io} \tag{28}$$

because

$$R = \sqrt[3]{\frac{(V_i+V_m)}{(V_{io}+V_m)}}\cdot R_o. \tag{29}$$

It can be assumed that

$$\delta = R/\lambda,\ \lambda = const.. \tag{30}$$

Substituting Eqs. 28 - 30 into Eq. 27 and by integrating yields

$$\frac{1}{5C}(y^5-y_o^5)+\frac{D-AC}{2C^2}(y^2-y_o^2)+\frac{D^2-ACD+BC^2}{3C^3k}\cdot$$
$$\left\{-\frac{1}{2}\left[\ln\frac{(y+k)^2}{y^2-ky+k^2}-\ln\frac{(y_o+k)^2}{y_o^2-ky_o+k^2}\right]+\sqrt{3}\left[\tan^{-1}\frac{2y-k}{\sqrt{3}k}-\tan^{-1}\frac{2y_o-k}{\sqrt{3}k}\right]\right\}$$
$$= \frac{D_1C_1\overline{V}_1^2\Phi\gamma y_o^2(\lambda-1)}{R_o^2}\cdot t = y_o^2K't, \tag{31}$$

where

$$K' = D_1C_1\overline{V}_1^2\Phi\gamma(\lambda-1) = const.(cm/s). \tag{32}$$

From Eqs. 11, 13, and 31, the water-permeation swelling ratio can be calculated, and the rate coefficient $K(K')$ of the swelling can be obtained from experiments. K and K' increased with the increase of D_1, C_1, and Φ and decreased with the increase of δ and R .

EXPERIMENTAL SECTION

Surfactants:

- Span-80 (sorbitane monoleate): Longyou County Chemical Reagent Co., Zhejiang Province, China.
- E644 (polyamine): Shanghai Oil Refinery Co., Shanghai, China.
- EM-301 (unspecified): Institute of Chemical Engineering, South China University of Science and Technology, Guangzhou, China.

Preparation of the Original W/O/W Emulsions.

According to the phase ratio and components, inner aqueous phase was added to the oil phase, followed by 3-min. homogenization (Supersonic Mixing Device, Shanghai Supersonic Device Co., China).

Multiple emulsions were prepared by dropwise addition of the above emulsion to the outer aqueous phase at a constant stirring speed. The phase was allowed to settle for several minutes, then, the emulsions were added into density bottles and weighted or used to make samples to measure dropsize in the inner aqueous phase.

Analytical Methods.

For measurements of the swelling ratio, the density and particle size methods were used(4-5).

RESULTS AND DISCUSSION

Table 1 shows that values K and K' are approximately equal. When one of the aqueous phases is pure water, Eq. 11 and 13 can be simplified as

$$\frac{1}{4C}(y^4 - y_o^4) + \frac{D-AC}{C^2}(y - y_o) = Ky_o t \tag{33}$$

$$\frac{1}{5C}(y^5 - y_o^5) + \frac{D-AC}{2C^2}(y^2 - y_o^2) = K'y_o^2 t. \tag{34}$$

TABLE 1. MEAN K, K' VALUES (cm/s)

Surfactant	Inner aq. phase	Outer aq. phase	K	K'
Span-80	6N HCl	H_2O	0.0594	0.0613
	4N HCl	H_2O	0.0516	0.0540
	4N HCl	1N HCl	0.0511	0.0555
E644	6N HCl	H_2O	0.0227	0.0238
	4N HCl	H_2O	0.0220	0.0220
	H_2O	2.2N HCl	0.0296	0.0290
EM-301	6N HCl	H_2O	0.0125	0.0128
	4N HCl	H_2O	0.0114	0.0111

Figures 3 -6 show that both flat-bed and hollow-sphere model predictions are in fair agreement with the experimental data of all types of permeation swelling when outer or inner aqueous phases are pure water or when the two aqueous phases are electrolytes with different concentrations. At the latter stage of swelling, the hollow-sphere model gives better prediction.

The water-permeation swelling increased with agitation time. Increasing the concentration difference of electrolytes in the inner and outer aqueous phases resulted in an increase in the osmotic pressure and the permeation swelling ratio. The chemical-potential gradient acting across the oil-phase layer is the driving force of water-permeation swelling. While that gradient creates only necessity for water to permeate the liquid membrane, it is the solubilization of water in the oil phase containing surfactant that gives the possibility for water permeation. This solubilization because of the addition of surfactant to the oil phase increases the solubility of water in the oil phase more than a hundred times. So it can be said that the key of the permeation swelling is the solubility of water in surfactant solutions. From experimental results, it was also found that $K(K')_{Span-80} > K(K')_{E644} > K(K')_{EM-301}$. Because the water solubilities of E644 and EM - 301 were lower, their permeation-swelling ratio was lower than that of Span-80. EM-301 is a new kind of surfactant. Not only is it heat, acid or alkali resistant, but also its swelling ratio is the lowest. Moreover, in China, this new surfactant draws more and more favor in emulsion-liquid membrane separation.

Figure 7 shows that increasing the agitation speed reduces the mean diameter of emulsion drops and increases the permeation swelling ratio. Figure 8

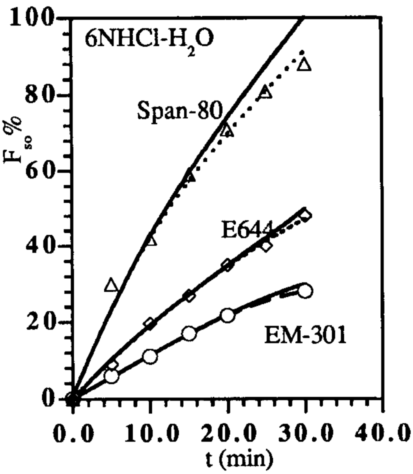


Fig. 3. $F_{so}\%$ .vs. time.* ^

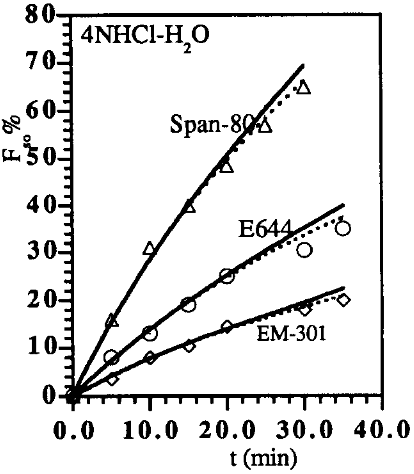


Fig. 4. $F_{so}\%$ .vs. time.* ^

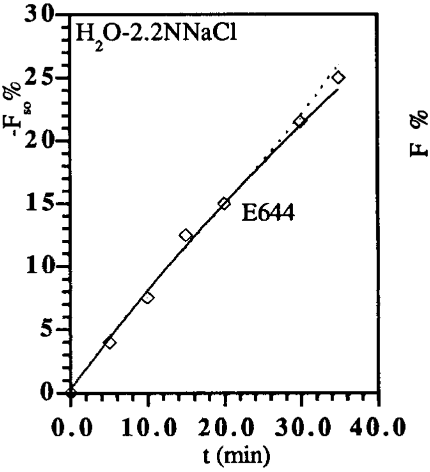


Fig. 5. $F_{so}\%$ .vs. time.* ^

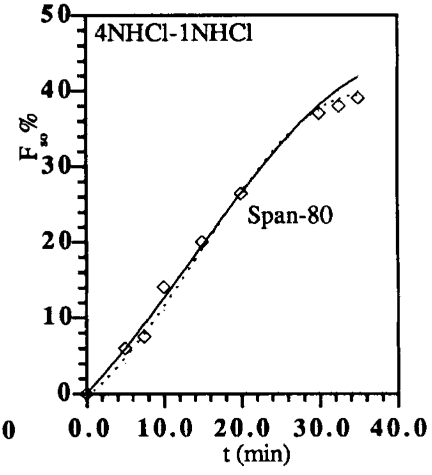
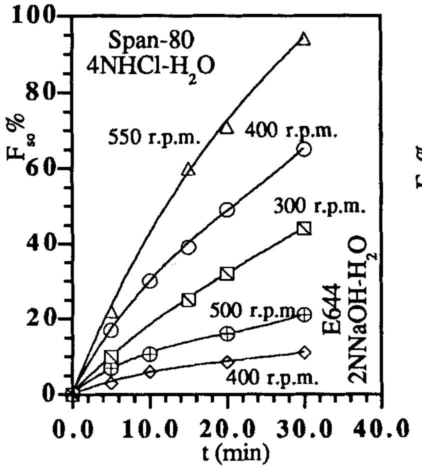


Fig. 6. $F_{so}\%$ .vs. time.* ^

* Figures 3-6, solid lines: values of flat-bed model; dotted lines: values of hollow-sphere model.



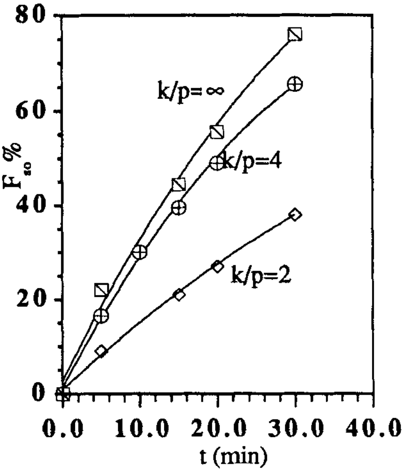


Fig. 7. Effect of agitation speed.^ Fig. 8. Effect of emulsion viscosity.^

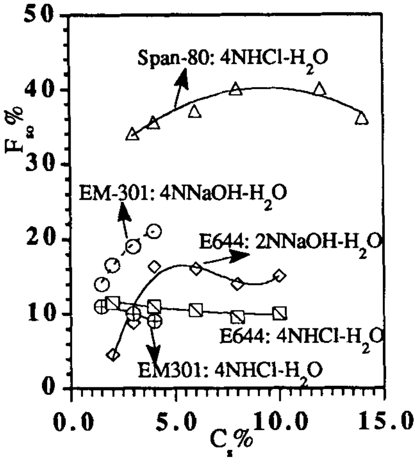


Fig. 9. Effect of surfactant concentration.^

^ Figures 3-9 common experimental conditions:

5% Span-80-k/p=4 (N=400 r.p.m.) or 4% E644-k/p=4 or 3% EM-301 (N=500 r.p.m.) 20°C, R_{ew}=1:3, R_{oi}=2.

TABLE 2. EFFECT OF CARRIERS

Inner, outer aq. phase	C_{P507} (wt%)	0	2	5	8	10	15
4N HCl, H_2O	F_{so}%	35.5	43.1	42.1	43.9	43.6	41.1

N=550 r.p.m.; R_{ew}=1:3; R_{0i}=2; 17°C; 4%E644-k/p=4; 5%Span-80-k/p=4

Inner, outer aq. phase	Carrier	0	P_{507}	TBP	N_{1923}	TOA	N_{263}	N_{503}
2N HCl, H_2O	F_{so}%	8.1	11.1	11.7	5.9	-6.5	4.3	2.1
2N NaOH, H_2O		13.5	-	22.0	13.6	10.7	-	21.1

N=500 r.p.m.; R_{ew}=1:3; R_{0i}=2; 15°C; 4%E644-k/p=4; C_c=5%(wt%)

shows that the higher the viscosity of emulsion liquid is, the lower the diffusion coefficient of water (D_1), $K(K')$ values and permeation swelling ratio are. Figure 9 shows that increasing the concentration of surfactant resulted in increased or decreased swelling ratio. This is because increasing C_s results in increased μ and decreased F_{so}, on the other hand, increasing C_s leads to both increased C_1 and F_{so}. Experimental results are the combined results.

From experiments, we also found that addition of any kind of nonphosphatic carrier to Span-80 membrane caused severe breakage of the emulsion membrane. Table 2 showed that different carriers had different effects on the water-permeation swelling ratio.

CONCLUSIONS

1. The water-permeation swelling can be considered as solubilization of water in the membrane phase caused by the surfactant and its diffusion through the membrane because of chemical-potential gradient. Both flat-bed and hollow-sphere models are good for estimating the water-permeation swelling ratio.

2. Experimental results confirm that the use of new surfactant EM-301 can decrease the water-permeation swelling ratio.

3. The concentration changes of carrier and surfactant affect the water-permeation swelling ratio.

NOMENCLATURE

C	concentration of solute	mol/ml
C_1	solubility of water in membrane phase	mol/ml
C_s	concentration of surfactant in oil phase	wt%
C_c	concentration of carrier in oil phase	wt%
D1	diffusion coefficient of water in membrane phase	cm^2/s
d_{32}	sauter mean diameter of W/O emulsion drops	cm
F_{so}	water-permeation swelling ratio	-
J_1	mass-transfer flux of water	$mol/cm^2.s$
k/p	volumetric ratio of kerosene to paraffin	-
M_1	molecular weight of water	g
M_B	molecular weight of solute	g
n	mole number of solute	-
N	agitation speed in dispersion of emulsion	r.p.m.
R	mean radius of emulsion drops	cm
R_{ew}	volumetric ratio of emulsion phase to outer aqueous phase	-
R_{oi}	volumetric ratio of emulsion phase to inner aqueous phase	-
S	total permeation area	cm^2
T	temperature	K
V	volume	ml
V_T	total volume of water in two aqueous phases	ml
$\overline{V}_1$	mole volume of water	ml/mol
K,K'	swelling-rate coefficient	cm/s
t	agitation time	min
λ	R/δ	-
Φ	osmotic coefficient	mol/cm^2
μ	chemical potential	
γ	total mole number of ions of dissociated electrolytes	-
π	osmotic pressure	dyn/cm^2
$\delta, \Delta x$	effective thickness of membrane	cm

Subscript:

i	inner aqueous phase
e	outer aqueous phase
o	initial

REFERENCES

1. K. Fujinawa et al., Kagaku Kogaku Ronbushu 10, 226 (1984).
2. N. Yan and Y. Shi, Huagong Xuebao 3, 378 (1990).
3. M. Matsumoto et al., Nippon Kagaku Kaishi 5, 731 (1983).
4. K. Tsuboi et al., Kagaku Kogaku Ronbushu 13, 110 (1987).
5. W. Li and Y. Shi, Proc. ISEC'90 (Japan).
6. P. Colinart, G. Trouve et al., J. Membr. Sci. 20, 167 (1984).
7. W. Li and Y. Shi, Proc. China-Japan Chem. Eng. Conf., Tanjing, 214 (1991).