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Hydrodynamic Behavior of Water—Tri-*n*-butylphosphate Emulsions during Ultrafiltration

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Abstract

The behavior of tri-*n*-butylphosphate (TBP)–water emulsion is studied during ultrafiltration through two membranes with pore diameters of 1.2 and 1.5 nm, respectively. The emulsion is stabilized with two surfactants: Montane 80 and Montanox 80, which are lipophilic and hydrophilic, respectively. Their percentages never exceeded 10% of the organic part. The organic/water ratio decreases more (i.e., from 1/3 to 1/7) the higher the permeate flow when the pressure above the membrane is constant. The more the O/W ratio increases, and the more the flow rate of the emulsion above the membrane decreases, a so-called polarization layer appears at the membrane surface and a reverse emulsion (water in TBP) is noticed along with a sudden change in the behavior of the ultrafiltration process. This is due to a change from a capillary transfer model to a diffusional model. The best operating conditions seem to be for a lower O/W ratio and a large retentate flow rate because the formation of the polarization layer is more difficult with a turbulent flow above the membrane surface.

INTRODUCTION

The increase of the percentage of organic phase in an emulsion is a subject of considerable importance in the food industry (*1–3*), in the pharma-

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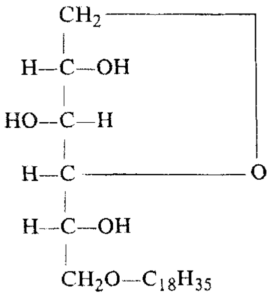
cological industry (*4, 5*), and in recovery from wastewater (*6, 7*). Recent progress in membrane technology permits one to perform ultrafiltration with high flow rate. Some authors have studied these kinds of applications for photographic emulsions (*10, 11*), polymer emulsions (*8, 9*) and cutting oil emulsions (*12, 13*). The aim of the present work is to study the hydrodynamic behavior of water–tri-*n*-butylphosphate (TBP) emulsions when applied to the recovery of dilute metal solutions by selective extraction (*14, 15*). One of the major features occurring at the membrane surface is the formation of a reverse emulsion, i.e., a water-in-oil emulsion in the polarization layer. It is well known that a capillary model applies for a perfect membrane (the permeate flow is a linear function of the pressure across the membrane), but if a polarization layer is present at the membrane surface, the above model fails and a diffusional model has to be used to explain the experimental data (the permeate flow rate is independent of the applied pressure, but the emulsion flow rate on the upper side of the membrane becomes the major parameter).

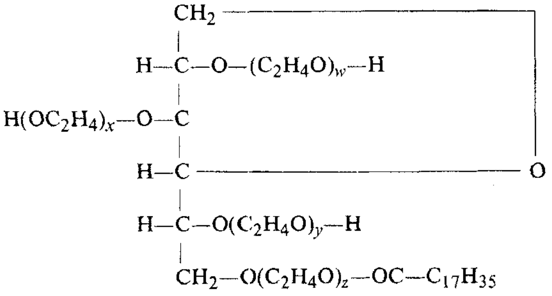
EXPERIMENTAL PART

Reagents

The selected phase was tri-*n*-butylphosphate (TBP) (Prolabo, France) and was used without further purification. The aqueous phase was made of distilled water and 3.5×10^{-2} *M* KSCN (analytical grade, Prolabo, France). This salt is necessary when metals are extracted as neutral complexes (*14, 15*). The emulsion was stabilized with two surfactants, an hydrophilic one (Montanox 80) and a lipophilic one (Montane 80). These two compounds were available from Seppic, France, and have the following formulas:



Montane 80



Montanox 80
($w + x + y + z = 20$)

The total surfactant amount never exceeded 10% with respect to the organic volume.

Apparatus

Emulsions were prepared as follows: TBP, Montanox 80, Montane 80, and water were placed in a beaker in the required proportions. Then this mixture was vigorously stirred with an Ultraturax device (Janke and Kunkle, Germany) for about 10 min. The maximum rotating speed (20,000 rpm) was used.

The ultrafiltration device was a CEC 1 model with a Diaflo membrane (Amicon Corp., U.S.A.). The membrane area was 64 cm^2 and was a thin layer of a noncellulosic polymer (from 0.1 to 0.5 nm).

THEORY

The permeation process through an ultrafiltration membrane may be compared to a capillary transfer mechanism, the membrane being represented by a large number of parallel, very small diameter pipes (capillaries). The permeate flow is given by Poiseuille's law (*16*):

$$Q_p = N \frac{\pi r^4 \Delta P}{8 \eta \Delta x} \tag{1}$$

where N = number of capillaries
r = mean radius of capillaries
ΔP = pressure difference across the membrane
η = absolute solution viscosity
Δx = effective length of capillaries

From Eq. (1) it is obvious that the permeate flow is proportional to the pressure difference across the membrane, and for a pure liquid this will be obeyed. During ultrafiltration with a membrane characterized by a given molecular weight cut-off, the macromolecules having a large size stay at the membrane surface and, by accumulation, this leads to a polarization layer. As this layer becomes compact and thicker, the capillary transfer model stops operating and a diffusional transfer model has to be applied. It obeys the following law:

$$Q_p = k_0 \log \frac{c_l}{c_0} \tag{2}$$

where k_0 = mass transfer coefficient
c_0 = concentration of macromolecules in the bulk solution
c_l = concentration of macromolecules in the polarization layer

An analogy between mass transfer and heat transfer as frequently used in chemical engineering, allows k_0 to be determined.

Turbulent Flow

In the case of turbulent flow of the emulsion reaching the membrane surface, we have to introduce three nondimensional numbers:

Sherwood number: $\mathrm{Sh} = k_0 d_h / D = m \mathrm{Re}^a \mathrm{Sc}^b$ (3)
Reynolds number: $\mathrm{Re} = u d_h / \nu$ (4)
Schmidt number: $\mathrm{Sc} = \nu / D$ (5)

where d_h = hydraulic diameter
D = diffusion coefficient
u = circulation rate
ν = kinematic viscosity

From the above nondimensional numbers and after rearrangement, we obtain

$$k_0 = D^{(1-b)} d_h^{(a-1)} m \nu^{(b-a)} u^a \tag{6}$$

Some authors have determined the average experimental values of m, a, and b to be $m = 0.09$, $a = 0.8$, and $b = 0.33$ (*17, 18*).

Laminar Flow

In the case of laminar flow of the emulsion reaching the membrane surface, the k_0 constant is

$$k_0 = 1.62[u D^2 d_h^{(1-a)}]^{0.33} \tag{7}$$

From Eqs. (6) and (7) it is obvious that the k value, and consequently Q_p, varies with the circulation rate in two different ways, and it appears that experimentally it will be possible to determine the nature of the emulsion flow above the membrane surface.

EXPERIMENTAL DATA AND DISCUSSION

Influence of the Water to Organic Ratio

We first verified that with pure water we do not observe any polarization phenomenon, as shown on Figs. 1a, 1b, and 1c, because the permeate flow Q_p versus the differential pressure across the membrane (ΔP plot) is a straight line. Conversely, for emulsions the permeate flow Q_p first linearly increases with the ΔP value and then reaches a maximum and slowly decreases as ΔP is made larger. Comparison between Figs. 1a and 1b for two

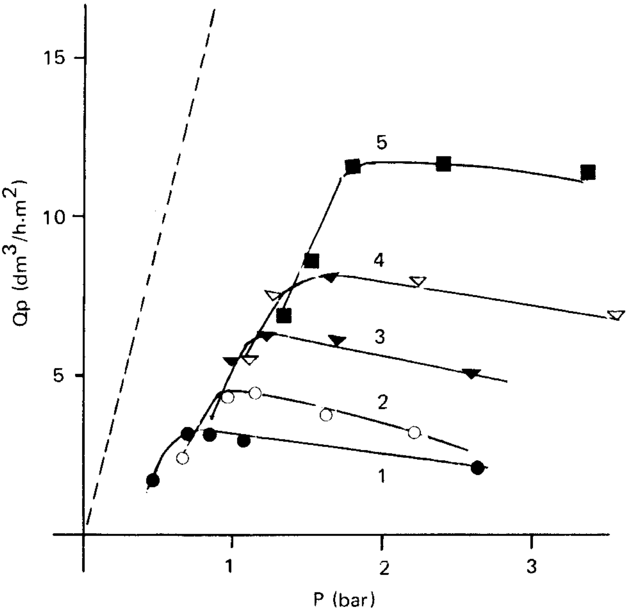


FIG. 1a. Evolution of permeate flow versus applied pressure at constant retentate flow for the emulsion water–tri-n-butylphosphate. W/O = 3/1. UM 10 membrane. d_1 = 1.5 nm. Dashed line: distilled water. Retentate flow values (dm^3/h): (1) 9, (2) 18, (3) 37, (4) 56, (5) 94

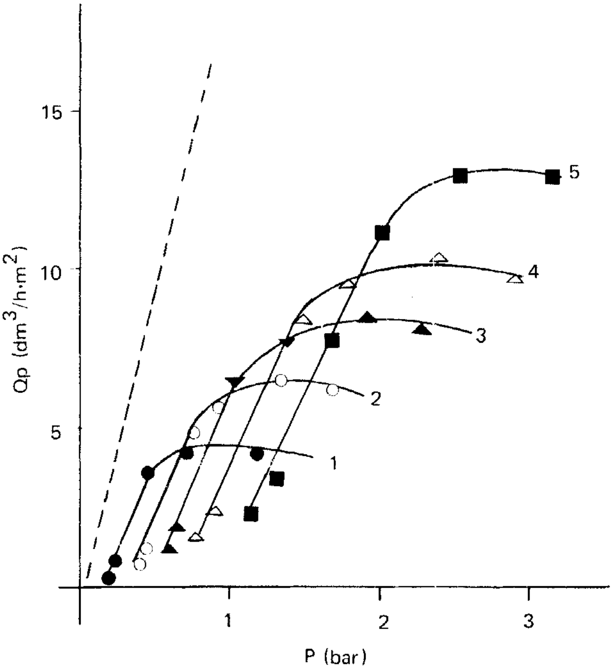


FIG. 1b. The same as Fig. 1a but with the following values. W/O = 7/1. UM 10 membrane. d_1 = 1.5 nm. Dashed line: distilled water. Retentate flow values (m^3/h): (1) 5, (2) 9, (3) 11, (4) 18, 5 (28).

kinds of emulsions shows a similar behavior, and the small differences may be discussed as follows. In Fig. 1a are reported the Q_p values vs ΔP for a 3/1 water–TBP emulsion with a 10,000 molecular weight cut-off membrane. One can see that the linear dependence of Q_p vs ΔP is only observed at low pressure, and that the maximum occurs at higher pressure because the retentate is higher too. In Fig. 1b, similar to Fig. 1a, the emulsion is a 7/1 water–TBP mixture, so the curves are different because, for a given pressure, the permeate flow rate is higher than that observed for the 3/1 emulsion for an identical retentate flow rate. This is consistent with the fact that the more the emulsion is diluted with water, the more its behavior resembles that of water. In addition, we see that at the surface membrane when water is flowing through the pore, the organic globules are in an emulsion with a very high percentage of organic phase compared to water. Then the emulsion changes suddenly to become an inverse emulsion of water in TBP, leading to a polarization layer. The phenomenon is more progressive with the 7/1 water–

TBP emulsion (Figs. 1a and 1b). Tanny et al. have discussed similar behavior for a 100/3 water to organic ratio emulsion (*6, 7*). These observations indicate the transition from the capillary model to the diffusional transfer model. A plot of log Q_p versus log u leads to a straight line with a correlation coefficient of 0.99 and a slope of 0.84, clearly showing that the turbulent flow applies here since in Eq. (8) it is established that k_0 varies according to $u^{0.8}$ (*17, 18*). For a laminar flow, the dependence is on $u^{0.33}$ (Eq. 9).

Another interesting point is a low flow rate. The smaller the retentate flow, the more maximum permeate flow occurs at low pressure (ΔP). To explain such a phenomenon, we assume that the polarization layer is more easily formed when the relative movement of the TBP droplets is low, i.e., at low flow rates Q_p and Q_r. Inversely, the more important the flow rates are, the more turbulence appears, and the contact time between the droplets is shortened. This hypothesis is consistent with Figs. 1a and 1b because the polarization layer is more easily observed with the 3/1 water–TBP emulsion, even for a high retentate flow rate, because of the high ratio of the organic phase. For the 7/1 emulsion the phenomenon is shifted toward higher pressure values because of the lower ratio of TBP.

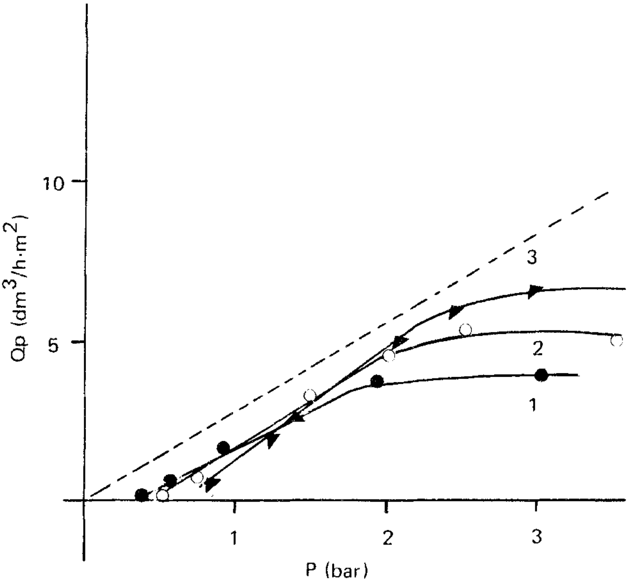


FIG. 1c. The same as Fig. 1a but with the following values. W/O = 7/1. UM 2 membrane. d_2 = 1.2 nm. Dashed line: distilled water. Retentate flow values (n^3/h: (1) 5, (2) 9, (3) 14.

Influence of the Membrane Pore Diameter

We have studied the behavior of a 7/1 emulsion with two kinds of membranes. The first is a UM 2 membrane with a pore diameter of 1.2 nm and the second one a UM 10 membrane with a pore diameter of 1.5 nm. The molecular weight cut-off of these two membranes is 1,000 and 10,000, respectively. By using distilled water we can compare the slopes of the permeate flow, Q_p, versus pressure (Figs. 1b and 1c). We see that the slope is lower for the UM 2 membrane and the slope ratio is 0.35. According to Poiseuille's law (Eq. 1), the slope ratio is theoretically related to the fourth power of the pore radius. For the UM 2 and UM 10 membranes we have $(0.60/0.75)^4 = 0.41$. The difference between experimental and theoretical values may be due to a slight change in membrane compactness with applied pressure. In addition, the polarization effect appears at higher pressure for the UM 2 membrane, and that is consistent with the smaller pore diameter. At constant retentate flow rate we observe that the permeate flow has the same magnitude in both cases. Therefore, the pore diameter is a less important parameter for these two membranes in comparison to the polarization layer effect.

Influence of the Concentration Rate on the Permeate Flow

Another major factor is the concentration ratio

$$X = \frac{Q_r}{Q_p} = \frac{\text{retentate flow}}{\text{permeate flow}}$$

In the present case Q_p is the flow rate of water through the membrane and Q_r is the flow rate of the emulsion which has a higher organic to water ratio when leaving the ultrafiltration cell.

In Fig. 2 we have plotted Q_p versus pressure at a constant X value. The shapes of the curves indicate clearly that the permeate flow rate reaches a maximum when the pressure increases and then decreases severely for the highest X values. It is concluded that the optimal working conditions are on the rising part of the curves of Fig. 2, corresponding to the capillary model.

CONCLUSION

From the above data one may conclude that the formation of a polarization layer at the membrane surface, due to an inversion of the emulsion related to

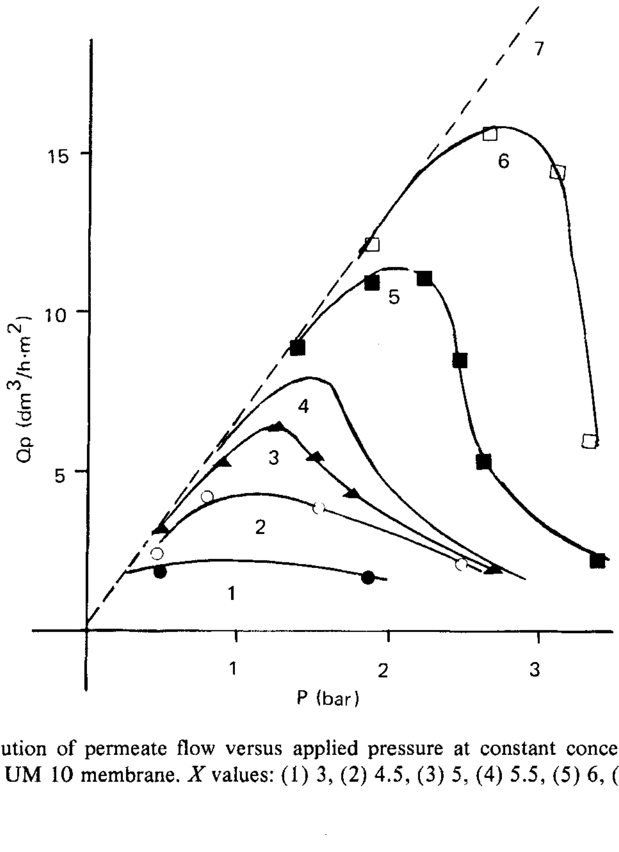


FIG. 2. Evolution of permeate flow versus applied pressure at constant concentration rate. W/O = 3/1. UM 10 membrane. X values: (1) 3, (2) 4.5, (3) 5, (4) 5.5, (5) 6, (6) 7, (7) 11.

enrichment in the organic phase, impairs the correct use of the membrane. The permeate and the retentate flow rates are influenced by the flow rate of the emulsion flowing through the ultrafiltration cell and the optimum conditions. Therefore, the pore diameter appears to be of less importance in the present case than the flow rate.

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