EXPERIMENTAL INVESTIGATION OF THE OIL/WATER/OIL LIQUID-MEMBRANE SEPARATION OF TOLUENE AND n-HEPTANE

I. BATCH TEST OF A MIXER-SETTLER

SON-KI IHM*, YEON-HO JEONG and YANG-SOO WON

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul (South Korea)

(Received December 11, 1985; accepted in revised form December 9, 1986)

Summary

The separation of toluene/n-heptane mixtures was investigated through the liquid-membrane permeation method employing a batch mixer-settler. The separation performances, represented by the permeation rate, emulsion stability and separation factor, were analyzed systematically by varying the operation parameters: the contact time, the ratio of the volume of solvent to that of emulsion, the ratio of surfactant solution to that of feed in emulsion, the surfactant concentration and the mixing intensity.

1. Introduction

Among the various membrane processes, the liquid membrane process has many advantages [1-5], e.g. small membrane thickness, large mass-transfer area and semi-permanent membrane life due to the ease of formation and recovery. Since Li made the first attempt at the separation of hydrocarbons by a liquid surfactant membrane in 1968 [1,5], efforts have been made to apply liquid membranes to other separation processes. Among the applications are the separation of chemical species [2,6-10], the control of water pollutants [10,11], and the recovery of metals [10,12,13].

The separation of hydrocarbons by liquid-membrane permeation is based on the selectivity which arises from the difference in the permeation rate of individual species in the feed through the liquid membrane. The feed to be separated is first emulsified by the surfactant solution. The emulsified droplets surrounded by the surfactant solution are contacted with a selected solvent to receive the permeables. The more permeable component is easily transferred

*To whom all correspondence should be addressed.
into the solvent phase while the less permeable component tends to remain in
the emulsion phase. After a sufficient contact time, the components in the
solvent phase are separated by distillation and the surfactant solutions are
recovered by demulsification.

The difference in boiling point between toluene and n-heptane is so small
that they are not easily separated from each other by conventional distillation.
Although azeotropic distillation is often used to separate these close-boiling
mixtures, a new efficient separation process is required. The liquid-membrane
process has proven to be one of the most promising alternatives for the sepa-
ration of these close-boiling mixtures [1,3–6].

Most of the research on the liquid-membrane process has been confined to
a small-scale batch test [1,2,4–7]. The continuous process on pilot-plant scale
[14] will be desirable for evaluating the applicability of the liquid-membrane
process to the actual plant. In the present study, a batch test employing a
mixer–settler was carried out to investigate the system variables and to obtain
useful ideas and design data for developing a continuous process. The effec-
tiveness of the separation of toluene and n-heptane mixtures by the liquid
membrane was experimentally demonstrated and the different variables which
affect the system performance were systematically investigated and analyzed.
The variables studied were the contact time with solvent, the ratio of the vol-
ume of solvent to that of the emulsion, the ratio of the volume of surfactant
solution to that of the feed in emulsion, the surfactant concentration in the
surfactant solution, and the mixing intensity.

2. Mechanism of permeation

The emulsion aggregates contact with the solvent in the mixer as shown in
Fig. 1 [15,16].

The flux of component A permeating through the liquid membrane can be
represented in terms of the concentration difference between the emulsion
phase and the solvent phase as follows [16]:

\[ N_A = K_A (C_{AF} - C_{AS}) \]  \hspace{1cm} (1)

The overall mass transfer coefficient \( K_A \) is given as follows.

\[ \frac{1}{K_A} = \frac{1}{k_{AP}} + \frac{S}{H_AD_A} + \frac{1}{k_{AS}} \]  \hspace{1cm} (2)

where \( 1/k_{AP} \) is the sum of the resistances of the boundary layer between the
feed and the feed-side surfactant layer and that of the feed-side surfactant
layer; \( S/H_AD_A \) is the resistance of the inner water layer; and \( 1/k_{AS} \) is the sum
of the resistances of the solvent-side surfactant layer and that of the boundary
layer between the solvent and the solvent-side surfactant layer.

From eqn. (2), the instantaneous selectivity \( \beta \) becomes:
Unless the water layer is very thin, the resistance of the water layer controls the selectivity. Since the water solubility ratio of toluene (A) and n-heptane (B) is 515:2.93 [17], the selectivity $\beta$ is greater than unity and toluene transfers to the solvent phase faster than n-heptane.

The relative ease of separation under the specified conditions can be expressed by the separation factor, which is defined as [4,6]:

$$
\beta = \frac{K_A}{K_B} = \frac{N_A(C_{BF} - B_{BS})}{N_B(C_{AF} - C_{AS})} = \frac{1/k_{BF} + S/H_B D_B + 1/k_{BS}}{1/k_{AF} + S/H_A D_A + 1/k_{AS}}
$$

The greater the separation factor, the better is the separation at a given condition.

3. Experimental

Mixtures of toluene and n-heptane, which are not easily separated by conventional distillation due to the very small difference in their boiling points, were chosen as the hydrocarbon feed.

Sodium lauryl sulfate and Tween 60, whose values for the hydrophile–lipophile balance (HLB) are larger than 10, were chosen as surfactant to make the oil-in-water (O/W) type emulsion.
Kerosene was used as a solvent because its density greatly differs from that of the emulsion phase and can easily be separated in a mixer–settler; its boiling point also greatly differs from that of the permeated feed, so it can easily be recovered from the feed by conventional distillation. The light ends of kerosene were distilled off and only the residue oil with a normal boiling point higher than 180°C was used.

The concentration of each component was measured with a gas chromatograph whose column was a copper tube (1/8 inch outer diameter) packed with 2% of squalane coated on chromosorb W of 80/100 mesh.

3.1 Batch tests

A schematic flow diagram of the batch test is shown in Fig. 2 [1,2]. After the feed had been well mixed (50 wt% of each component), the feed and surfactant solution at a specified concentration were stirred slowly in the emulsifier at a specified volume ratio of feed to surfactant solution. Once the emulsions began to form, the emulsifier was agitated with increased speed (2000 rpm) for 30 minutes to form stable emulsions.

The emulsions formed were sent to a mixer and stirred with solvent. The agitating speed of the mixer was controlled by a speed controller and monitored by a tachometer. The oil-in-water-in-oil (O/W/O) emulsion system as shown in Fig. 1 was formed and permeation of feed to solvent took place in the mixer.

After a specified contact time, the emulsions and the solvent were separated from each other by gravity difference in a settler. The separated emulsions were broken by heating and samples for analysis were taken from the solvent and the broken emulsions. The recovered solvent and surfactant solution were reused in the mixer and emulsifier, respectively.

The variables \( R \) and \( K \) are defined as: \( R \) is the ratio of the volume of the surfactant solution to that of the feed in emulsion; \( K \) is the ratio of the volume of the solvent to that of the emulsions in the mixer.

![Fig. 2. Flow diagram of the batch mixer–settler operation.](image-url)
By changing the values of $R$ and $K$, the effect of the relative amount of the surfactant solution in emulsion and that of the solvent can be deduced.

3.2 Emulsion stability tests

Some emulsions are broken when they are exposed to mechanical forces by agitating them in a mixer. Since the breakage of emulsions plays a decisive role in lowering the separation factor, it is very important to find the conditions for the formation of stable emulsions.

The relative stability of the emulsions formed under the various specified conditions was tested by breaking the emulsions in a centrifuge with 3000 rpm. The effects of the time of exposure to the mechanical forces, the surfactant concentration, and the relative amount of surfactant solution on the emulsion breakage ratio were observed.

4. Results and discussion

Among two types of surfactant used, sodium lauryl sulfate always shows the better stability and the larger separation factor than Tween 60.

4.1 Effect of contact time between solvent and emulsion

Figure 3 shows that the separation factor tends to increase to a maximum

![Graph showing the effect of contact time on the separation factor.](image)
with increasing contact time and then decreases again. As shown in the figure, the values of $R$ and $K$ were fixed at 0.3 and 3, respectively.

At the start of contact, the separation factor is low because non-emulsified feed transfers to the solvent phase directly and the surface area for mass transfer is relatively small due to the unequal distribution of large emulsion aggregates in the mixer. However these phenomena tend to disappear as the contact time increases, and the emulsion aggregates become better distributed in the mixer so that the mass transfer rate increases. These phenomena allow the separation factor to show a maximum. After the maximum has been attained, the separation factor decreases with further contact because the amount of the less permeables (n-heptane) in the emulsion phase becomes larger than that of the more permeables (toluene) so that the driving force for the less permeables to transfer to the solvent phase increases. Besides, some parts of the membranes become unstable and break with further contact and this emulsion breakage makes the less permeables of the inner feed mix directly into the solvent phase without passing through the selective membranes. As a result the separation factor tends to decrease.

Figure 4 shows the effect of the contact time on the emulsion stability. The
The separation factor will decrease with further contact due to the instability of liquid membranes.

Figure 5 shows that the ratio of the amount of permeated feed to that of the initial feed increases with contact time. The amount of the permeated feed includes the feed transferred to the solvent phase not only by permeation through the selective membrane but also by direct mixing due to emulsion breakage. The permeated mass of the feed increases with contact time but its permeation rate (the slope of the curve) decreases with contact time due to the decrease in the concentration driving force.

4.2 Effect of the relative amount of solvent (K)

Figure 6 shows the effect of the $K$ values on the separation factor. The separation factor increases to a maximum and then decreases with increasing $K$.

For low values of $K$, the emulsion aggregates tend to coalesce and the mass transfer area is small. Besides, the concentration driving force for low values of $K$ will be small because the concentration of the permeated feed in the solvent phase is relatively higher than for high values of $K$, even when the amount of feed permeated into the solvent phase is the same. Consequently, the separation factor is small.
Fig. 6. Effect of volume ratio of solvent and emulsion on the separation factor.

With gradual increase in $K$, the separation factor tends to increase because the possibility of emulsion coalescence decreases and because the concentration driving force begins to increase.

When the value of $K$ increases further, the overall concentration driving force of the more permeables becomes smaller and that of the less permeables becomes relatively larger than for small values of $K$ because the concentration of the more permeables in the emulsion phase decreases quickly due to their high permeation rate.

The effect of the relative amount of solvent on the separation factor is such that the ratio of the permeated mass to the feed increases with the value of $K$ as shown in Fig. 7.

4.3 Effect of the volume ratio of surfactant solution ($R$)

The horizontal axis of Fig. 8 represents the ratio of the volume of the surfactant solution to that of the feed in the emulsion ($R$ value) and the vertical axis represents the percentage of emulsion breakage in the emulsion stability test. This figure shows the effect of the relative amount of the surfactant solution on the emulsion stability. The percentage of emulsion breakage decreases as the value of $R$ increases to 0.4 but remains constant at values of $R$ above 0.4.
The relative amount of the surfactant solution in an emulsion determines the thickness of the liquid membrane and its stability. When the value of $R$ is small, not all the feed can be enclosed by a liquid membrane and the membranes are so thin that they can easily be broken by mechanical forces. As the value of $R$ increases the membrane becomes thick and the stability of the emulsion increases. However, a further increase of the surfactant solution in the emulsion cannot improve the stability of the emulsion further when the value of $R$ exceeds a certain minimum value ($R=0.4$ in case of Fig. 8). Figure 8 clearly shows that there exists a minimum amount of surfactant solution for the given amount of feed to make a stable emulsion; this minimum value corresponds to the critical micelle concentration.

Figure 9 represents the effect of $R$ on the amount of feed permeated by direct mixing due to emulsion breakage as well as by pure permeation through the selective membrane. This figure shows that the amount of feed permeated decreases to a minimum and then increases to reach a constant value as the value of $R$ increases.

Figure 10 represents the effect of the relative amount of surfactant solution in the emulsion on the separation factor. The figure shows that the separation factor increases as the value of $R$ increases to approximately 0.4 and then
Fig. 8. Effect of volume ratio of surfactant solution and feed on emulsion breakage.

Fig. 9. Effect of volume ratio of surfactant solution and feed on the relative mass of permeated feed.
Fig. 10. Effect of volume ratio of surfactant solution and feed on the separation factor.

Fig. 11. Effect of surfactant concentration on emulsion breakage.
remains constant at values of $R$ above 0.4. This trend should be expected from the aforementioned explanations for Figs. 8 and 9.

### 4.4 Effect of surfactant concentration

Figure 11 shows the effect of surfactant concentration on the emulsion stability. The emulsion breakage is very high at concentrations around 0.1%, decreases abruptly when the concentration increases to 1% and decreases slowly at concentrations above 1%.

Figure 12 shows the effect of surfactant concentration on the amount of feed permeated. The amount of feed permeated in a given time decreases as the concentration of surfactant increases. The direct mixing of feed with solvent decreases with the concentration of surfactant because the stability of the emulsion increases, as shown in Fig. 11, and also because the pure permeation rate through the selective membrane decreases due to the increase in permeation resistance through the liquid membrane.

Figure 13 shows the effect of surfactant concentration on the separation factor. The separation factor tends to increase to a maximum as the concentration of surfactant increases and then begins to decrease at surfactant con-

![Fig. 12. Effect on surfactant concentration on the relative mass of permeated feed.](image)
centrations above 1%. At very low surfactant concentrations, the percentage of emulsion breakage is very high, as shown in Fig. 11, and direct mixing with solvent dominates (although the total permeation rate is high, as shown in Fig. 12), so the separation factor has a very low value. When the concentration of surfactant increases to 1%, the separation factor increases because the emulsion stability increases. However, the separation factor starts to decrease after the maximum, because the permeation rate decreases due to an increase in permeation resistance.

4.5 Effect of mixing intensity

Figure 14 shows the effect of mixing intensity in the mixer on the amount of feed permeated. The permeation rate increases with mixing intensity. The mixing intensity affects the size of the emulsion aggregates, the geometric dispersion of the emulsion aggregates with solvent in the mixer, and the emulsion stability. As the agitation speed in the mixer increases, the permeation rate increases because emulsion aggregates become smaller and the emulsion aggregates are well dispersed with solvent in the mixer. On the other hand, as the mixing intensity increases further, the emulsion cannot withstand the high mechanical forces and begins to break.

Figure 15 shows the effect of mixing intensity on the separation factor. The separation factor tends to increase to a maximum and then decreases with mixing intensity. This is due to the adverse effect of mixing intensity on the emulsion stability.
Fig. 14. Effect of mixing intensity on the relative mass of permeated feed.

Fig. 15. Effect of mixing intensity on the separation factor.
5. Conclusion

The separation of toluene and n-heptane mixtures, which is not easily achieved by conventional distillation, can be done by employing an O/W/O-type liquid-membrane emulsion in a batch system with a mixer-settler. Both sodium lauryl sulfate and Tween 60 can be used as effective surfactants but sodium lauryl sulfate is found more effective for the present system.

The various factors which affect the permeation rate and the separation factor were investigated systematically and the cause-and-effect relationships among these factors were established. Through the batch test, it was found that the separation factor and the permeation rate depend on the contact time with solvent, the ratio of the volume of the solvent to that of the emulsion in the mixer, the ratio of the volume of the surfactant solution to that of the feed in the emulsion, the surfactant concentration, and the mixing intensity. All the variables, except $R$, have an optimum value which can give a maximum separation factor.

Acknowledgement

This work has been supported by a grant from the Korea Science and Engineering Foundation.

Notation

$C_i$ Concentration of component $i$, g/cm$^3$
$D_i$ Diffusivity of component $i$, cm$^2$/sec
$F$ The ratio of mass of permeated feed to that of the feed
$H_i$ Solubility in water of component $i$, g/g
$K_i$ Overall mass transfer coefficient, cm/sec
$k_i$ Mass transfer coefficient, cm/sec
$K$ The ratio of the volume of the solvent to that of the emulsion in the mixer
$N_i$ Mass flux of component $i$, g/sec-cm$^2$
$R$ The ratio of the volume of the surfactant solution to that of the feed in emulsion
$S$ Thickness of aqueous phase in emulsion, cm
$SLS$ Sodium lauryl sulfate
$t$ Contact time in the mixer, min

Subscript

$F$ Feed side
$s$ Solvent side
References