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Study of Operating Condition Affecting Mass Transfer Rate in Liquid Surfactant Membrane Process

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ABSTRACT

The removal of acetic acid from its dilute solution by liquid surfactant membrane (LSM) has been investigated by batch test. Some important factors affecting the mass transfer rate, such as surfactant and its content, stirring speed, ratio of reagents, treating ratio and volume ratio of membrane phase to internal phase, have been studied. The breakage and the swelling of the emulsion have also been investigated. The transport mechanism of HAc across the membrane in the system is referred to as I-II facilitated transport mechanism.

INTRODUCTION

The LSM method was advanced by N.N. Li in 1968(1). Such membranes are characterized by large contact areas, fast rate of mass transfer and high efficiency of separation. More attention has been paid to LSM method which is applicable for many industrial processes (2-7). However, it is a new technique and there are still many problems with LSM to be studied.

In this paper, aqueous solution of acetic acid (HAc) was used to investigate some important factors which affect the mass transfer rate in LSM.

EXPERIMENT AND HANDLING OF DATA

The experiments were carried out in an experimental stirring vessel of 92 mm diameter. The liquids were stirred by a four-blade propeller stirrer of 41 mm diameter and of 12.5 mm width. During the processes of emulsifying and extraction, the total volumes of the liquids were 260 ml and 480 ml, respectively.

All tests were undertaken under the atmospheric pressure at 20 °C. The other experimental conditions for each test are shown in the figures.

NaOH (CP) aqueous solution was used as an internal phase (I). N205 - kerosene was the membrane phase (II). Where, N205, having an average molecular weight of 790, is a nonionic polyamine derivative (8). The average molecular weight of kerosene is 190. An emulsion of the phase (I) and phase (II) was created at a stirring speed of 1600 rpm for 20 minutes. Then the emulsion was dispersed into the external phase (III) which is an HAc solution. The samples of the external phase were picked at regular intervals for the determination of the concentrations of HAc and sodium ion.

The concentration of HAc was analyzed by titration. The concentration of sodium ion was determined by means of sodium ion electrode.

The experimental data were handled by the following equations:

$$\eta = \frac{C_{III_0} - C_{III}}{C_{III_0}} \times 100\% \quad (1)$$

$$E_b = \frac{[Na^+]_{III} \cdot V_{III}}{[Na^+]_{I_0} \cdot V_I} \times 100\% \quad (2)$$

$$E_s = \frac{V_{e_0} - V_e}{V_{e_0}} \times 100\% \quad (3)$$

$$r_E = \frac{C_{I_0} \cdot V_I}{C_{III_0} \cdot V_{III}} \times 100\% \quad (4)$$

where

η - removal efficiency of HAc, %

E_b - breakage of the emulsion, %

E_s - swelling of the emulsion, %

C_{I_0} - original concentration of NaOH solution in internal phase, M

C_{III_0}, C_{III} - original and instantaneous concentration of HAc in the external phase, respectively, M

$[Na^+]_I$, $[Na^+]_{III}$ - concentration of sodium ion in the internal and external phases, respectively, M

r_E - ratio of equivalents of internal reagent and external solute

V_I , V_{III} - volumes of the internal and the external phases, respectively, m^3

V_{e_0} , V_e - original and instantaneous volumes of the emulsion, respectively, m^3

RESULTS AND DISCUSSIONS

The Removal Efficiency of HAc

The removal efficiency of HAc results mainly from the ratio of reagents (r_E), the stirring speed (N), the treating ratio (V_{III}/V_e) and the volume ratio of membrane phase to internal phase (V_{II}/V_I). The effects of these factors on the removal efficiency of HAc are illustrated in the following figures.

It can be seen from Fig. 1 that the concentration of HAc in external phase decreases intensely with the increasing of stirring speed. The reason of this phenomenon is that the total areas of mass transfer in the system increase at high stirring speed, while the size of emulsion globules decreases. But the stability of the emulsion decreases at high stirring speed since the membrane can not stand the high shearing force. Curve B shows that the concentration of sodium ion in external phase increases with N, i.e. the breakage of the emulsion increases with N. However, when N<350 rpm, the concentration of Na ion keeps in a low value.

The ratio of equivalents of internal phase reagent to external solute (which can be briefly called the ratio of reagents) is a measure of the emulsion capacity. Two groups of experiments (A and B) were arranged to investigate the effect of r_E on η.

It can be found from Fig. 2,

1. the effects of r_E on η can be divided into two sections, when $r_E<5$, the transport of HAc is greatly promoted by increasing r_E, when $r_E>5$, the effect of r_E on η is not appreciable.

2. comparing the curve of 10 minutes with the curve of 5 minutes, it is obvious that the increasing effect of r_E on mass transfer rate in long extraction time is more significant than that in short extraction time.

The effect of the treating ratio (V_{III}/V_e) on η is illustrated in Fig. 3. The removal efficiency of HAc decreases with the increasing of the treating ratio owing to the fact that the higher the treating ratio, the less the volume of emulsion in unit volume of external phase, consequently the less the mass transfer areas.

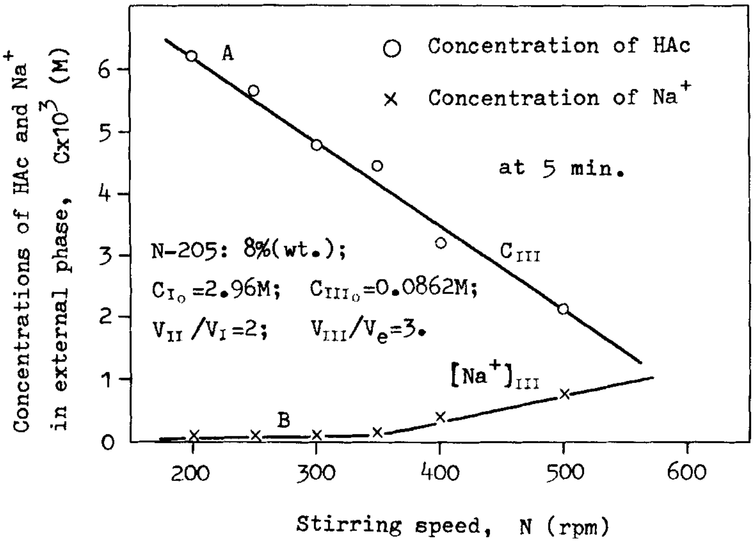
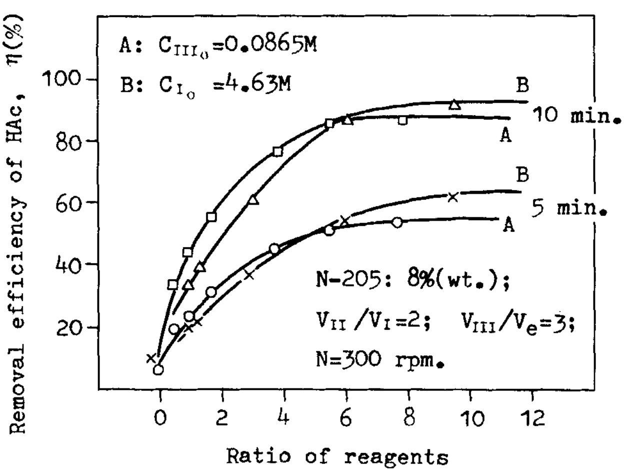


Fig. 1 Relationships of N to concentrations of HAc and Na^+ in external phase



o Test A at 5 min. × Test B at 5 min.
□ Test A at 10 min. Δ Test B at 10 min.

Fig. 2 Effect of r_E on η

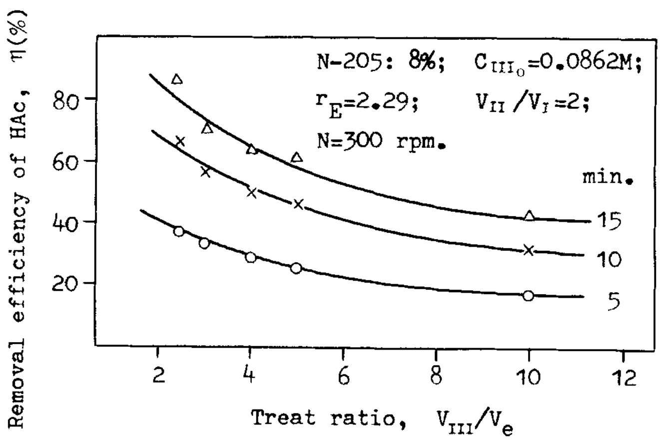


Fig. 3 Effect of treat ratio on η

Fig. 4 shows that the effect of the volume ratio of membrane phase to internal phase (V_{II}/V_I) on the removal efficiency of HAc is not as appreciable as the other factors aforementioned. In the range of V_{II}/V_I=0.8 to 2, the removal efficiency of HAc remains nearly the same. When V_{II}/V_I>2, the removal efficiency reduces with the increasing of V_{II}/V_I slightly.

The Breakage and Swelling of the Emulsion

The separation efficiency in LSM process will be much reduced because of the breakage of the emulsion. It can be seen that the rate of the emulsion breakage is related to the concentration of NaOH solution in internal phase. The higher the concentration, the more the breakage of the emulsion. The emulsion breakage increases with the stirring time. But the breakage of the emulsion is less than 2% within 60 minutes dispite the concentration of NaOH solution is as high as 6M (see Fig. 5). These results confirm that this type of emulsion is stable enough for a lot of industrial application.

The breakage of the emulsion can be reduced by increasing the surfactant content in the membrane phase. In this paper, N 205 was used as a surfactant. The effect of the concentration of N205 on E_b is shown in Fig. 6. The emulsion breakage decreases with the increasing of N205 concentration and levels off when the N205 concentration is above 6% (by weight).

The swelling of the emulsion can also reduce the concentration efficiency of the LSM process. On the other hand, swelling

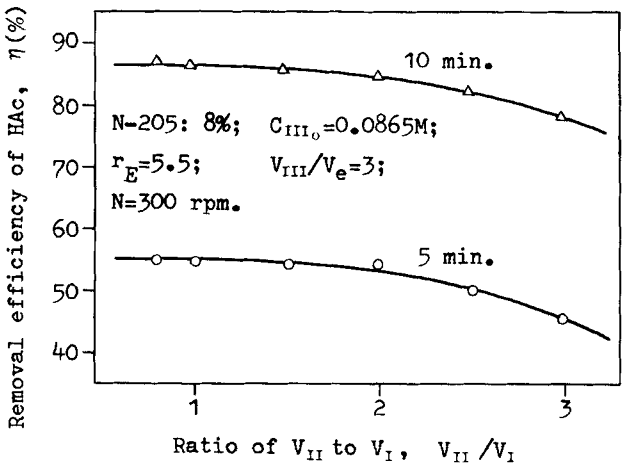
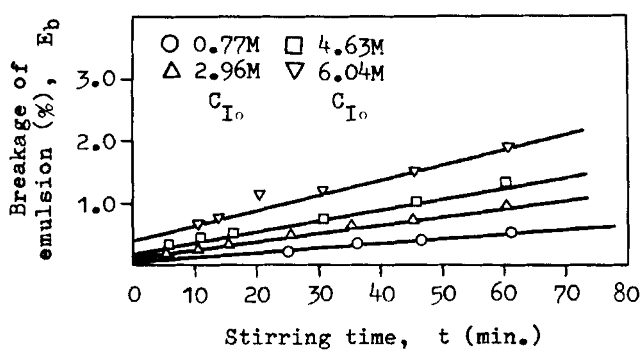


Fig. 4 Effect of V_{II}/V_I on η



N205 - 8%(wt.)

C_{III_0} = 0.0865M V_{II}/V_I = 2

V_{III}/V_e = 3 N = 300 rpm

Fig. 5 Relation of E_b to stirring time

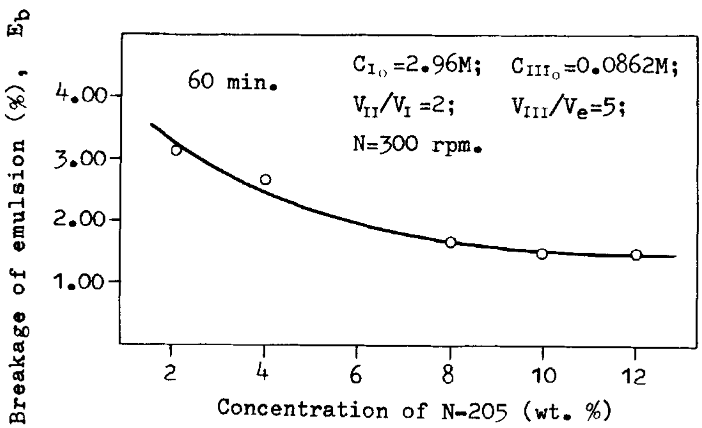


Fig. 6 Effect of N205 content on E_b

makes the membrane thinner thereby the emulsion less stable. the value of the swelling of emulsion is defined as the ratio of the volume increment to the original volume of the emulsion (see Eq. 3).

Two reasons for swelling have been proposed by Terry et al (7),

1. swelling owing to osmotic pressure,
2. swelling caused by the "entrainment" of addition water during the dispersion process.

The results of present experiment indicate that during the contacting process of emulsion and external phase, the swelling of the emulsion is caused by the osmotic pressure on two sides of the membrane if there is no redispersion of the emulsion. But if the emulsion phase is redispersed after coalescence, the swelling will increase intensely. The experimental results are listed in the following tables. The conditions of these tests are as follows:

V_{e_0} = 50 ml $\qquad V_{III}/V_e$ = 3

V_{II}/V_I = 2 $\qquad$ N = 300 rpm

N205 - 8% (wt.)

stirring time = 30 min.

Table 1 shows that if there is no osmotic pressure and coalescence of emulsion, the effect of "entrainment" of water on swelling is negligible (these values are within the bounds of experimental error).

TABLE 1
Effect of "Entrainment" of Water during Mixing Process

No.	Internal phase	External phase	E_s (%)
1	2M NaOH	2M NaOH	0.4
2	2M NaCl	2M NaCl	0
3	0.1M NaCl	0.1M NaCl	-0.6
4	H_2O	H_2O	0.2

The data in Table 2 were obtained by stopping the stirring of the emulsion which was redispersed while the emulsion globules have coalesced. The result shows that the more times the emulsion is dispersed, the larger the swelling of the emulsion. For this reason, the application of multiple mixing-settlers is not appreciated.

Table 3 shows that the swelling of emulsion is proportional to the osmotic pressure between the internal phase and the external phase.

However, the emulsion swelling can be reduced by increasing the volume ratio of membrane phase to internal phase, since such increasing has not much effect on the removal efficiency of HAc. Fig. 7 illustrates that the emulsion swelling decreases with the increasing of V_{II}/V_I despite the high osmotic pressure on both sides of the membrane attributed to the high concentration of NaOH solution in this test.

The Transport Mechanism of HAc Across the Membrane

It has been known that HAc as a weak acid has a low but significant solubility in kerosene, so it can permeate through the membrane made by kerosene alone. In addition, N205 was added to kerosene for these experiments and it can react with HAc due to its three $-\overset{|}{N}-$ functional groups. Therefore, N205 acts as both an emulsifier and a carrier in the system. The transport mechanism of HAc across the membrane may be illustrated schematically in Fig. 8, where acetic acid is transported across the membrane in two ways:

1. The molecular of acetic acid permeates through the membrane as a solute of kerosene based on the potential difference of its concentration across the membrane.

2. It transfers as an extraction complex with N205.

TABLE 2
Effect of Coalescence and Redispersion of Emulsion

No.	Internal phase	External phase	Redispersion times (number)	E_s(%)
1	2M NaCl	H_2O	0	12
2	2M NaCl	H_2O	2	18.6
3	2M NaCl	H_2O	5	35.0

TABLE 3
Effect of Osmotic Pressure

No.	Internal phase	External phase	E_s (%)
1	2M NaCl	2M NaCl	0
2	2M NaCl	0.1M NaCl	10
3	2M NaCl	H_2O	12
4	H_2O	H_2O	0.2
5	H_2O	0.1M NaCl	-2
6	H_2O	2M NaCl	-10

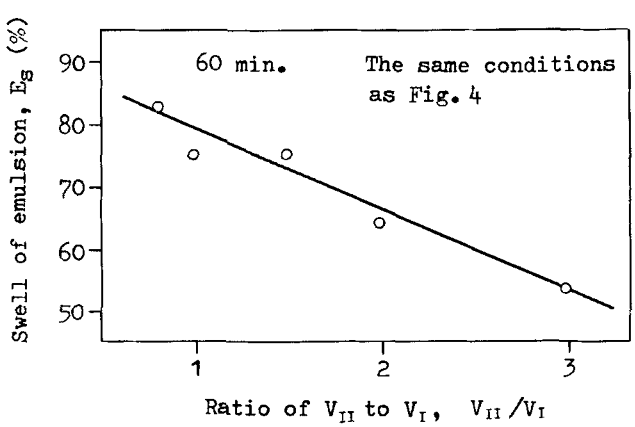


Fig. 7 Effect of V_{II}/V_I on E_s

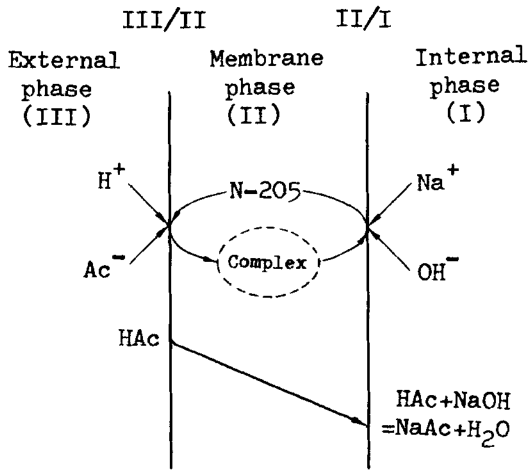


Fig. 8 Schematic diagram of mechanism of HAc transporting across the membrane

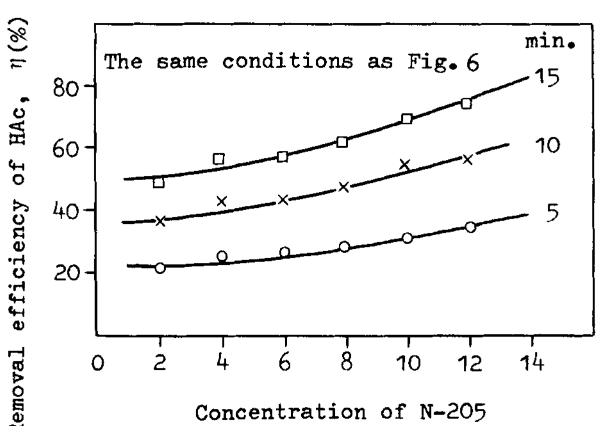


Fig. 9 Effect of N205 content on η

These two forms of mass transport were defined as type I and type II facilitated transport mechanism respectively by Matulevicius et al(2). In this paper, the mechanism of HAc through the membrane is referred to as I-II facilitated transport mechanism.

The facilitating effect of N205 on the transport of acetic acid is shown in Fig. 9. The removal efficiency of HAc increases with the concentration of N205.

CONCLUSION

The stirring speed, the ratio of reagents and the treating ratio have evident effects on the rate of mass transfer in the LSM separation. The swelling of emulsion is mainly caused by both the coalescence and redispersion of emulsion and the osmotic pressure of the system.

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