

## Separation of Hexane-Benzene Mixtures by Emulsion Liquid Membrane.

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### Abstract

The effect of operating parameters on the batch scale separation of hydrocarbon mixture (benzene and hexane) using emulsion liquid membrane technique is reported. Sparkleen detergent was used as surfactant and heavy mineral oil as solvent to receive the permeates.

From the experimental results, the parameters that influenced the permeation are, composition of feed, contact time with solvent, ratio of volume of solvent to volume of hydrocarbon feed, ratio of volume of surfactant solution to volume of hydrocarbon feed, surfactant concentration, mixing intensity and glycerol as polar additive in the surfactant solution to eliminate drop breakup.

The best conditions for the separation in this study were found to be: composition of feed (mole fraction of benzene=0.5245), contact time of 10min. , ratio of volumes of solvent to feed equal 3.5 , ratio of volumes of surfactant solution to feed of 0.4, surfactant concentration of 1wt%, mixing intensity equal 1000rpm and 70% by weight of polar additive. These conditions gave a separation factor of (8.0).

**Keywords:** liquid membrane, hydrocarbon separation, hydrocarbon permeation, emulsion liquid membrane.

### Introduction

Membranes have been developed which made separation process within range of being economically and technically feasible. Liquid membrane extraction was introduced as an alternative separation technique to the liquid-liquid extraction and to the separation by means of solid polymeric membranes. On the other hand, liquid membrane was first suggested in 1968 by Li. Liquid membranes are generally formed by first making an emulsion of two immiscible phases and then dispersing the emulsion in a third phase (continuous phase). Emulsion Liquid Membrane (ELM) is effective in separation hydrocarbon of different kinds, including these similar in their physical and chemical properties. It is a film composed of surfactants and their solvent. The film consists of water and one or more water soluble surfactant. This kind of film serves two purposes in a process of separating hydrocarbon. First, it permits selective permeation by one or more components of the feed. Second, it keeps the hydrocarbon feed from mixing with a solvent used to carry away the permeates.

Furthermore liquid membrane is a film formed at an oil / water interface by a surfactant solution .Such films are formed by dispersing the solution to be separated in the form of droplets in a surfactant solution .The droplets covered with an organic solvent phase received the permeates .During this process one of the components of mixture transfers from the droplets through the liquid membrane and into the organic solvent at a faster rate than the other .The organic solvent becomes rich in the more permeable component, and the droplets become rich in the less permeable component , thus achieving a separation of the component (15). Where, the separation factor is a parameter to evaluate the process efficiency with respect to distillation process:-

$$\text{Separation factor} = \frac{\text{distribution coefficient of benzene}}{\text{distribution coefficient of hexane}} \\ = \frac{\text{mole fraction of benzene in permeated product}}{\text{mole fraction of benzene in mixture contained in emulsion phase}} \div \frac{\text{mole fraction of hexane in permeated product}}{\text{mole fraction of hexane in mixture contained in emulsion phase}}$$

Li (1971a) indicated that separation factor is a function of the solubility of permeate in water as well as the diffusivity of the permeate through the surfactant and water layers. Also found that the separation of hydrocarbons is independent of surfactant concentration in the ranges from (0.001-0.1) wt%.

Li (1971b) studied the effect of glycerol on membrane life, permeation rate and separation factor. His results showed that 70 wt% of glycerol appear to be optimum concentration. Also found that separation factor depends on solubility of permeates and its diffusivity.

Stelmaszek (1977) measured the equilibrium curves for benzene and hexane and studied the dependency of the separation coefficient of the mixture on the feed composition, flow rate, and the effect of the solvent flow rate on the volume fraction of hexane in the raffinate and permeate was determined.

## **Experimental Work**

In the present study benzene and hexane mixture is separated with an aqueous solution of sparkleen detergent as the surfactant solution. It contains all sodium cations with 50 wt% sodium hexametaphosphate, 10 wt % sodium alkyl benzene sulphonate as anionic surfactant and 0.5 wt % as nonionic surfactant. It also contains 39.5 wt % sodium carbonate and sodium bicarbonate as pH buffering agents. The heavy mineral oil as the organic phase to receive the permeates. In this study the effectiveness of the liquid membrane technique to separate the hydrocarbon mixture as compared to fractional distillation was investigated.

In addition, the investigation also included studying the effects on separation factor of several process variables, such as composition of feed, contact time with solvent, ratio of volume of solvent to volume of hydrocarbon feed, ratio of volume of surfactant solution to volume of hydrocarbon feed, concentration of surfactant, mixing intensity between solvent and emulsion and glycerol as polar additive to eliminate drop breakup. When the effect of one of variable was studied all the other variables were kept constant.

### **Procedure**

Mixtures of benzene and hexane were prepared by mixing the required volumes of components by using a pipette to measure volumes. Then the mixture was emulsified in an aqueous phase composed of sparkleen detergent and water. The mixer for emulsification of this mixture is a cylindrical vessel equipped with four baffles. A variable steady speed impeller with four blades is used for mixing.

The mixture of benzene and hexane was stirred at low speed while the required quantity of surfactant solution is

slowly poured into the mixer. After the emulsion is formed, the emulsion was mixed with the solvent, (heavy mineral oil), for the desired length of time. The mixer for contacting the emulsion with solvent is a jar test with two blade steel impeller with 50rpm to ensure uniform contact between the solvent and the emulsion, as shown in figure(1).

As the system is agitated, permeation proceeds out of the droplets, through the aqueous film into the bulk solvent (heavy mineral oil). Since benzene permeates more rapidly through the aqueous liquid membrane than hexane, the residual mixture in the emulsion will be gradually depleted in hexane, while the heavy mineral oil becomes enriched in this constituent.

After contacting the emulsion with solvent, the solution was transferred to a separator funnel where it was allowed to separate. The mixture of solvent and emulsion separated into three layers in the separator funnel. The upper layer containing the emulsion composed of the surfactant solution and that portion of the mixture of benzene and hexane that did not permeate in the solvent. The middle layer composed of the solvent, heavy mineral oil, containing the permeate mixture of benzene and hexane. Finally the bottom layer consisted of aqueous surfactant solution which had not entered the emulsion phase or surfactant solution resulting from droplet breakup.

In this study the effect of polar additive was studied by using glycerol to eliminate drop breakup in the solvent. The range for glycerol content was from (10-70) wt% in the emulsion.

The recovery of mixture of benzene and hexane from the solvent was carried out by simple distillation. The boiling point of the solvent was greater than 110°C where the boiling point of benzene and hexane was less than 81°C; therefore, if the distillation is carried out at temperature between 110°C and 81°C, essentially all benzene and hexane will evaporate leaving the solvent.

The recovery of mixture of benzene and hexane from the emulsion phase was carried out by physical method; i.e. by the addition of 0.3 M NaCl to the mixture will break the emulsion into two layers. The upper layer contains the mixture of benzene and hexane. The bottom layer contains the surfactant solution.

The composition of the mixture of benzene and hexane is determined by measuring the refractive index of the mixture with the Abbe A60 refractometer. A calibration curve relating the refractive index and percent composition was prepared and used to determine the composition of unknown mixtures.

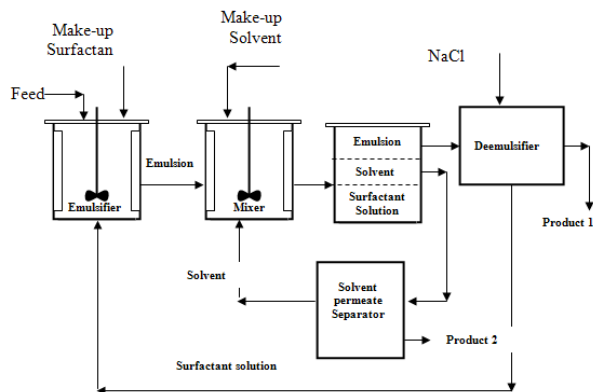


Fig.1 Schematic diagram of operation.

## Results and Discussion

### Effect of Mole Fraction of Benzene in Feed on Separation Factor.

Figure (2) shows the effect of mole fraction of benzene (0.1-0.9) on separation factor. Also figure (3) relates the composition of benzene in permeated product and in the feed. It can be seen that both the separation factor and permeate composition vary with feed composition. This is owing to the dependency of membrane structure and thickness on the nature of feed. Li (1971) refers to the fact that the permeation of the molecule through the membrane depends upon the solubility of the molecule in the membrane and the diffusivity of this molecule through the membrane. From this fact, if we say that the only the solubility factor effect the separation, this leads us to that the separation factor is independent of feed composition and this is not reasonable with the results in the figures. On the other hand, if we consider only the diffusivity factor to effect the transfer and hence the separation, then the separation factor changes with feed composition to give constant permeate concentration.

As a result from these facts and the data in figures (2) and (3) it can be said that both the solubility and diffusivity are important in this case.

Benzene is more permeable than hexane in water about (187.5) times, therefore, it is more permeable than hexane through the liquid membrane due to the solubility. This results is analogous to the results that obtained by Stelmazak.

Figure (4) shows the vapor liquid equilibrium for benzene and hexane. From figures (3) and (4), it can be seen that the emulsion liquid membrane separation is the best for benzene-hexane mixture separation.

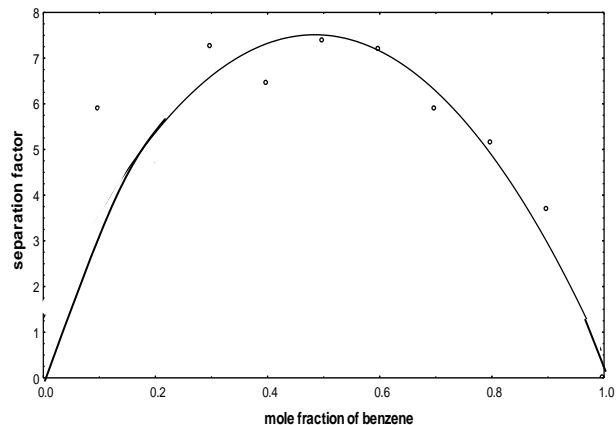


Fig. 2 Effect of mole fraction of benzene on separation factor.

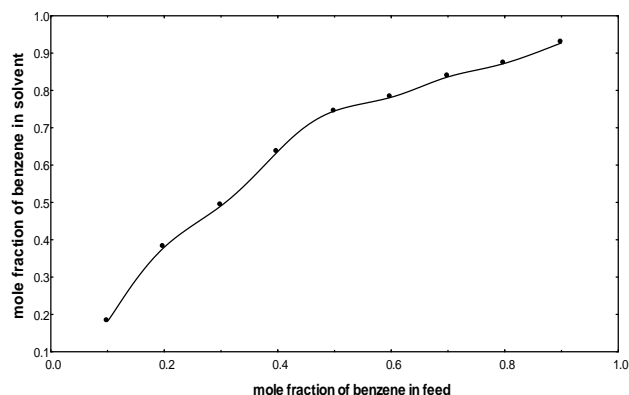


Fig. 3 Relationship between mole fraction of benzene in feed and solvent.

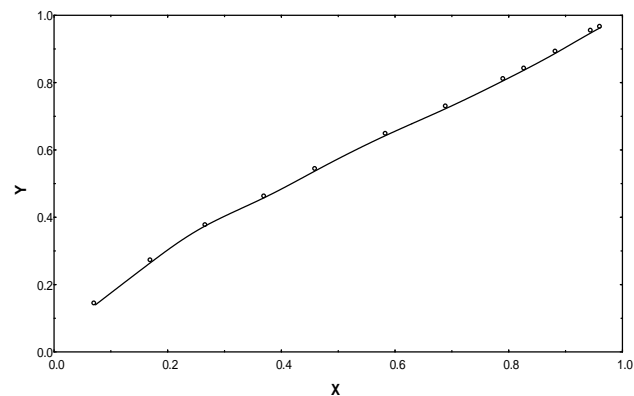


Fig. 4 Vapor- liquid equilibrium curve (benzene/hexane)

Y: Vapor phase mole fraction of benzene in hexane  
X: Liquid phase mole fraction of benzene in hexane

**Effect of Contact Times of Emulsion with Solvent on Separation Factor.**

Figure (5) shows the effect of contact times on separation factor. From the figure we see that for short contact times the separation factor attains high values but decreases with increasing contact times until there is no separation. The maximum value obtained for separation factor occurs at contact time of about 10 minutes. This result is analogous to that of Li (1971).

The low values of separation factor for short contact times are due to that the emulsion of the mixture of benzene and hexane with sparkleen surfactant under the conditions of the experiment such that some of the mixture of benzene and hexane is not emulsified. Thus when the emulsion is contacted with the solvent, the mixture that not emulsified pass immediately into the solvent without separation and leads to a low value of separation factor.

As the contact time increases, the solvent phase becomes rich in benzene, therefore, the separation factor increases. The decrease in values of separation factor is due to the following reasons: the stability of the emulsion is limited then the emulsion will break allowing all of the benzene and hexane to go into the solvent, and the drops become rich in hexane and lean in benzene which result in an increase in the transfer rate for hexane because of the concentration gradient , which will reduce the separation factor.

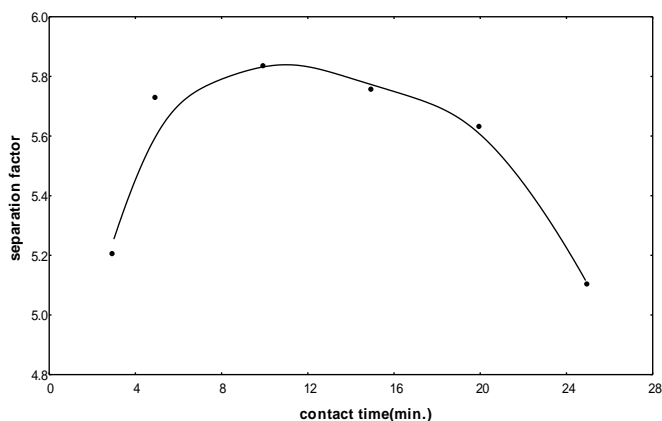


Fig. 5 Effect of contact times on separation factor.

**Effect of Ratio of Solvent to Volume of Hydrocarbon Feed**

Figure (6) shows the effect of ratio of solvent to feed on separation factor. It can be seen that the separation factor is low for relatively small volumes of solvent. As the relative volume of solvent increases, the separation factor increases and reaches a maximum at a ratio of (3.5).

The low values of separation factor is because the droplets are close together in the solvent, therefore, the drops are more likely to coalesce. This process reduces the total surface area for mass transfer. For large volumes of solvent the separation factor decreases. This decrease is due to the fact that for both components the overall driving force (i.e. the difference of the concentration of the components between the drops and the solvent) increases where the droplets are more dispersed, resulting in nearly equal transfer rates for both benzene and hexane.

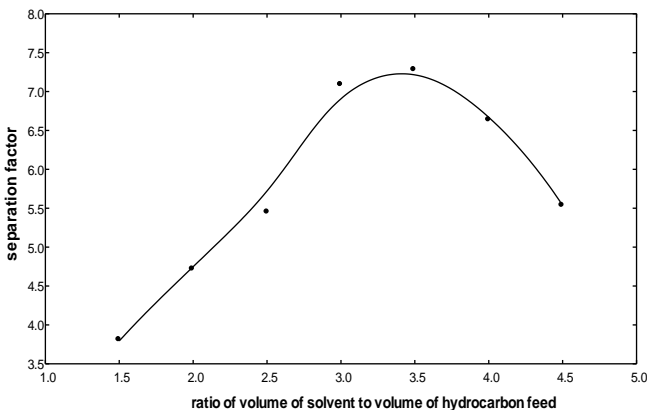


Fig. 6 Effect of ratio of volume of solvent to volume of hydrocarbon feed on separation factor.

**Effect of Ratio of Volume of Surfactant Solution to Volume of Hydrocarbon Feed**

Because the volume of surfactant solution is related directly to the droplet size and membrane thickness, the separation factor for separating benzene and hexane depends on the relative volumes of surfactant solution and feed. For a particular volume of feed, there is likely some minimum quantity of surfactant solution necessary to form a stable emulsion. If the amount of surfactant solution is less than the minimum, the separation factor is low because not all of the droplets of the mixture of benzene and hexane is covered with liquid membrane. It is expected that for large volumes of surfactant solution, the separation factor does not change (Li, 1968).

Figure (7) shows experimental results for this ratio. It can be seen that separation factor is constant when the volume ratio approximately 0.4.

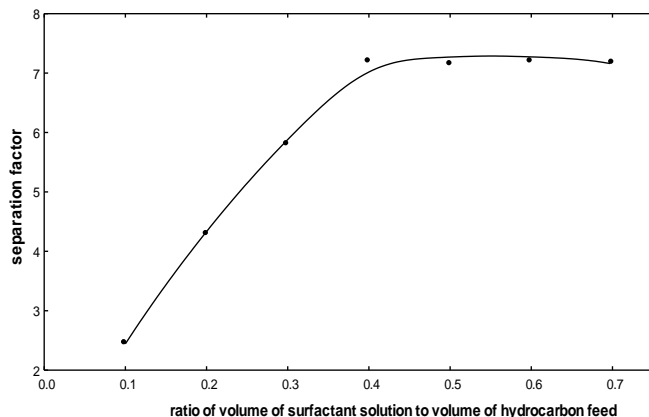


Fig. 7 Effect of ratio of volume of surfactant solution to volume of hydrocarbon feed

### Effect of Surfactant Concentration

Li (1971) found that the separation factor is independent of surfactant concentration from (0.001-0.1) wt%. Figure (8) shows the experimental work for the relation between separation factor and surfactant concentration. The results show that separation factor is low for low concentration of surfactant, and then increases as surfactant concentration is increased. At about 1 wt% surfactant concentration, the separation factor is maximum, then for higher concentration of surfactant, the separation factor decreases. At low surfactant concentration, there are related fewer molecules of surfactant in the membrane surrounding the droplets, therefore, in the absence of enough surfactant molecules in the membrane, there is greater chance for breaking of the membrane that result in low values of the separation factor.

The decrease in separation factor at higher surfactant concentration because that at higher surfactant concentration there are enough molecules in the membrane around the droplets to make the membrane more stable, but when the surfactant concentration is high, there is less water in the membrane. Because the transfer of permeate through the membrane depends in part on the solubility of the material in the water, the transfer of these are decreased. And this leads to decreasing the separation factor at higher surfactant concentration. Also the resistant of surfactant molecules in the membrane increases with increased surfactant concentration at higher values this leads to a decrease in the transfer rates of material through the membrane thus decreasing the separation factor.

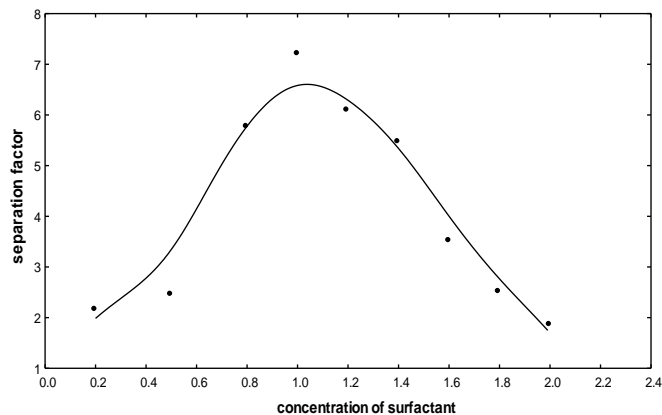


Fig. 8 Effect of surfactant concentration on separation factor.

### Effect of Mixing Intensity

Figure (9) shows the effect of mixing intensity of emulsion on separation factor. It can be noticed that the separation factor increases with increasing mixing intensity up to 1000 rpm where the separation factor becomes constant.

Depending on the surfactant used, some of the drops might breakup in the solvent phase due to rupture of weak membrane; therefore, the separation factor will decrease for low mixing intensity. But for increasing gradually the mixing intensity the emulsion becomes more stable than for low mixing intensity because drop diameters of emulsion decrease, that also improved the permeation rate due to the increasing of surface area for mass transfer. It can be seen that above 1000rpm the separation factor becomes almost constant. This is due to the fact that the droplets reach diameters that do not change at higher mixing intensity. The higher mixing intensity does stabilize the emulsion but does not eliminate drop breakup.

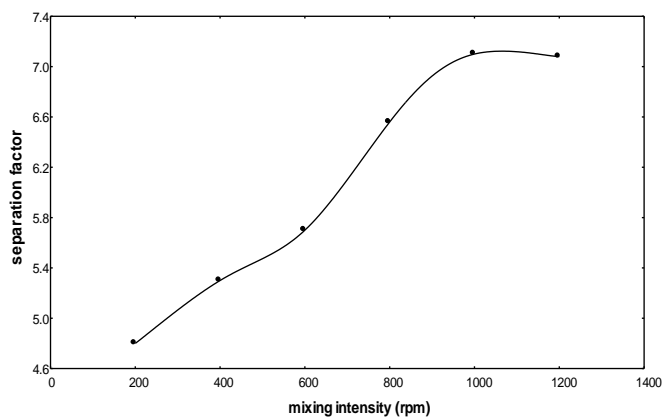


Fig. 9 Effect of mixing intensity on separation factor.

### Effect of Glycerol as Polar Additive on Separation Factor

Figure (10) shows the effect of glycerol as polar additive to strengthen the surfactant membrane resulting in substantial elimination of drop breakup in the solvent phase and marked increase in separation factor. Adding glycerol to a membrane increase the water layer viscosity.

Increasing gradually the percentage of glycerol will increase the values of separation factors. The reasons for this, is that for low values of glycerol added the rate of drop breakup is more than for high values of glycerol added up to 70% percent. After this percentage the surfactant layer becomes too viscous. The decrease for permeation rates of components can be controlled by increasing time to permeate. These results are analogous to that found by Li (1971) and for Li (1971) for that the optimum percentage for polar additives is 70wt%.

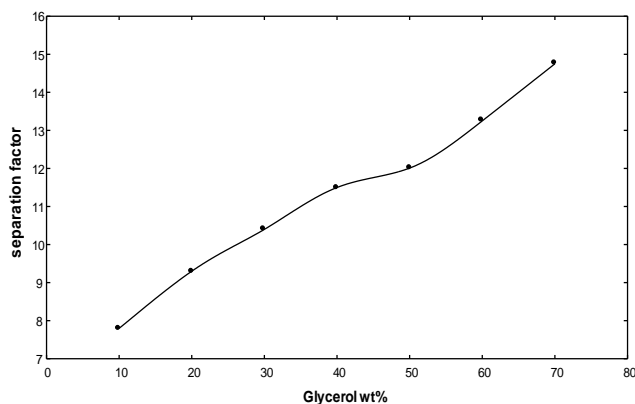


Fig. 10 Effect of glycerol as polar additive on separation factor.

### Conclusions

1. The increase in mole fraction of benzene in feed caused an increase in the separation factor up to mole fraction of benzene of 0.5245, and then the separation factor decreases with the increase of mole fraction.
2. The separation factor increases with increasing contact time up to contact time of about 10 min. and then decreased with increasing time of contact.
3. The increase in ratio of volume of solvent to volume of feed caused an increase in separation factor up to ratio of 3.5, then the separation factor decreases with the increase of the ratio.

4. The separation factor increases as the ratio of volume of surfactant solution to volume of feed increased up to 0.4, then the separation factor is essentially constant.
5. As the surfactant concentration is increased the separation factor increases up to concentration of (1.0wt %), then the separation factor decreases with further increase in surfactant concentration.
6. The increase in mixing intensity caused an increase in separation factor up to 1000 rpm then the separation factor is approximately constant.
7. Glycerol is used as polar additive to eliminate drop breakup in solvent. The separation factor increased with the increase in weight percent of glycerol in surfactant solution up to 70%wt. Further increase in weight percent of glycerol make the liquid membrane is so viscous that no separation can be achieved.

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