LIQUID MEMBRANE TECHNIQUE FOR SEPARATION OF BENZENE AND HEXANE MIXTURE.

Mussab Kadem Rashed
Institute of technology / Baghdad

ABSTRACT

The effect of operating parameters on the batch scale separation of hydrocarbon mixture (benzene and hexane) with emulsion liquid membrane technique is reported. An emulsion liquid membrane is a film composed of surfactants and their solvent. The sparkleen detergent is used as surfactant and heavy mineral oil as solvent to receive the permeates. The parameters that influenced the permeation are, composition of feed, contact time with solvent, ratio of volume of surfactant solution to volume of hydrocarbon feed, surfactant concentration. 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 surfactant solution to feed of 0.4 and surfactant concentration of 1wt%. These conditions gave a separation factor of (8.0). the process efficiency is evaluated by the separation factor is a parameter to evaluate the process efficiency with respect to distillation process.

$$\textbf{Separation factor} = \frac{distribution\ coefficient\ of\ benzene}{distribution\ coefficient\ of\ hexane}$$

1. Introduction:

Many chemical engineering separation processes are based on a difference in a physical property, like distillation, crystallization, centrifugation, and gas absorption. These processes work well at separating and concentrating different solutes when there is a large variation in the physical property of interest and high selectivities are not required[1].

The 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 [2]. Where is the first hand, liquid membrane was first suggested in 1968 by LI [3].

The 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 a achieving a separation of the component [4].An actual separation scheme is illustrated in figure (1).

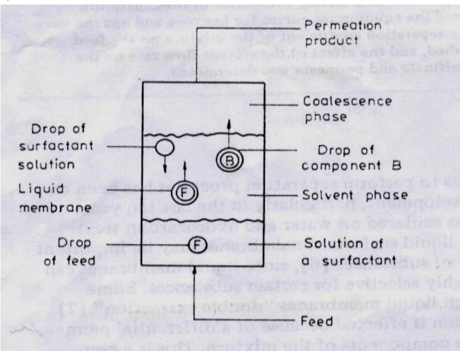

Figure (1) Separation of liquid mixture

Li,et.al (1968) [5] stated a process for separating hydrocarbons like isoparaffins from naphthenes or normal paraffin's from naphthenes, The anionic surfactants that are used with this invention like nonylphenoxy polyethyleneoxy ethanol. Other surfactant includes poly vinyl alcohol, a surface active macromolecule; trimethyl dodecyl ammonium surfactant; sodium dodecyl sulphate and saponin. The solvents that may be utilized for washing the emulsion and separating the more permeable member of the hydrocarbon mixture are kerosene and solvent 100 neutral which is a heavy paraffin oil. They estimate the separation factor as a permeability parameter.

The highest values of separation factor suggest that the technique could be more effective than fractional distillation for separating mixture of benzene and hexane.

Li, et.al (1971) [6] presented a liquid surfactant membranes for hydrocarbon separation. They separated hydrocarbons like benzene, hexane and toluene, heptane. The surfactants like saponin, igepal-850 and sodium dodecyl sulphate (see table 2.1) are used for this process. The solvents that utilitized any hydrocarbon having boiling point higher than the feed components. The permeation mechanism is analyzed in term of the effects of surfactant concentration, surfactant structure and chain length, the nature of permeate and the solubility in water.

Their results 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%. A permeability parameter is defined by separation factor for different systems.

Goswami et.al (1985) [7] stated the effect of parameters on batch scale permeation of hydrocarbons from benzene –heptane mixtures and straight naphtha through liquid membrane. The operating parameters studied include: mixing intensity, surfactant concentration, treat ratios, contact times, temperature and additives. The variations observed in the two key properties of selectivity and aromatic recoveries as well as in product composition with change in operating parameters discussed. Surfactant concentration, contact time during permeation, type and concentration of additive used appear to exert a marked effect on the enrichment obtained.

The careful optimization of operating parameters give selectivities as high as 50 and aromatic recoveries of 75% in one stage at 30^0C. Comparison of data with batch liquid-liquid extraction data from extraction of similar feed mixtures with the most widely used solvent, sulpholane, under typical industrial conditions, has shown that selectivities and aromatic recoveries in liquid membrane permeation are much higher.

The mass transfer coefficient and selectivities correlate very well with work of transfer, the additives also influence the solubility of the diffusing species and under conditions of equal work of transfer, this effect is measured in terms of finite dilution activity coefficient. The results leaded to advocate the use of additives for improving transfer rates in permeation of kerosene- range hydrocarbon mixtures and should aid in selection of the type of additive to be used for such mixtures. Also they modeled the permeation process as a parallel step process consisting of (i) selective transmembrane diffusion transport; and (ii) non-selective transport due to emulsion breakage.

In the present study, the separation of mixture of benzene and hexane is studied with surfactant liquid membrane technique. Sparkleen detergent is used as surfactant, and heavy mineral oil as a solvent to receive the permeates, the separation and permeation mechanism are discussed with respect to composition of feed, contact time with solvent, ratio of volume of surfactant solution to volume of solvent, concentration of surfactant. The permeability parameter is defined by the separation factor.

$$\textbf{Separation factor} = \frac{distribution\ coefficient\ of\ benzene}{distribution\ coefficient\ of\ hexane}$$

2. Experemental Procedure:

Figure (2) shows a schematic diagram for experimental apparatus. Mixtures of benzene and hexane were prepared by mixing the required volumes of components by use of 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 was slowly poured into the mixer, then the mixing speed reached 2000rpm. After the emulsion is formed, The emulsion 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 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 transfers to a separator funnel where it allows to separate. The mixture of solvent and emulsion separated into three layers in the separator funnel. The upper layer contains the emulsion is 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 composes of the solvent, heavy mineral oil, containing the permeate mixture of benzene and hexane. Finally the bottom layer consisted of aqueous surfactant solution which has 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. Glyserol ranges from 10 to 70%wt in the emulsion. The recovery of mixture of benzene and hexane from the solvent is done by simple distillation. The boiling point of the solvent is greater than 110^0C where the boiling point of benzene and hexane is less than 81^0C, therefore, if the distillation is carried out at a temperature between 110^0C and 81^0C, 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 [(8)] using the addition of 0.3 M NaCl to the mixture breaking the emulsion into two layers. The upper layer contained the mixture of benzene and hexane. The bottom layer contains of surfactant solution.

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

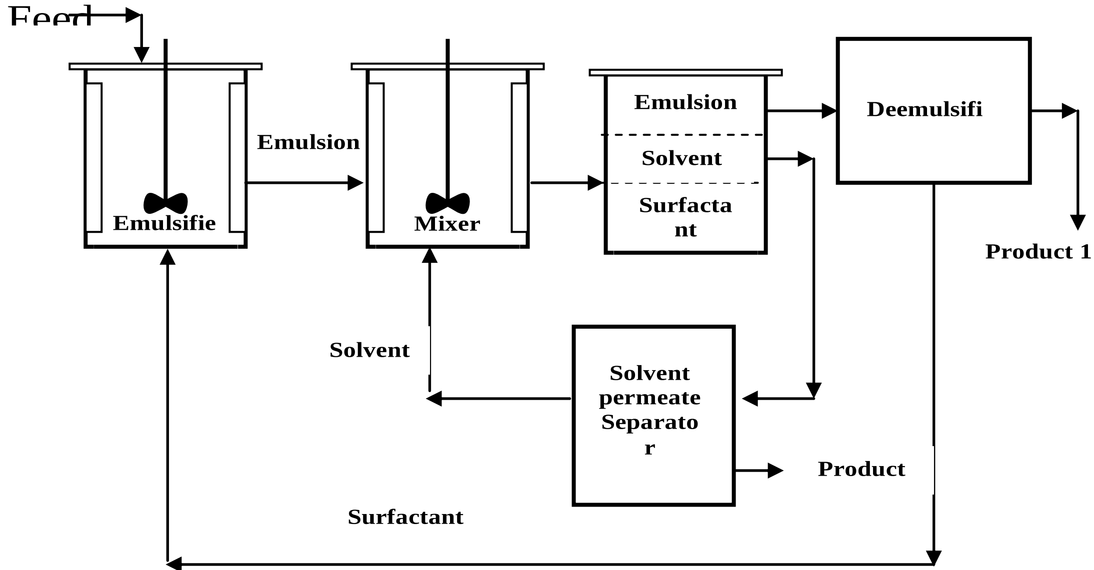

Figure (2) Schematic diagram of operation.

4. Results and Discussion:

Ranges for the variables that used in this study are listed in table (1).

Table (1) Ranges of variables.

Variables	Ranges
Mole fraction of benzene in feed	0.1-0.9
Contact time with solvent (min.)	3-30
Ratio of volume of solvent to volume of hydrocarbon feed	1.5-4.5
Ratio of volume of surfactant solution to volume of hydrocarbon feed	0.1-0.7
Concentration of surfactant	(0.2-2.0)wt%
Mixing intensity of emulsion rpm	200-1200
Glycerol as polar additive	(0-70)wt%

Figure (3) shows the effect of mole fraction of benzene on separation factor at different mole fraction of benzene from (0.1-0.9). Figure (4) shows the relation of the composition of benzene in permeated product and the composition of benzene in 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) [6] 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 solubility factor effect the separation factor, this leads us to that the separation factor is independent of feed composition and this is not reasonable with the results in figures. On the other hand, if we consider only the diffusivity factor to the transfer, the separation factor changes with feed composition to give constant permeate concentration.

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 agree with those 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.

Figure (6) shows results the experimental work for the relation between separation factor and surfactant concentration. The results clear that separation factor is low for low concentration of surfactant, and then increases as the surfactant concentration increases. 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 for separation factor.

The decrease in separation factor at higher surface 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 partially on the solubility of the material in the water, the transfer which these are decreased. This leads to decreasing the separation factor at higher surfactant concentration. Also the resistant of surfactant molecules in the membrane increased 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.

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.

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

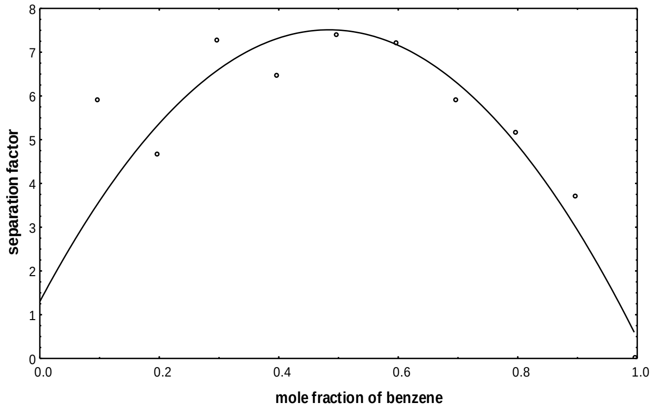

Fig (3) Effect of mole fraction of benzene

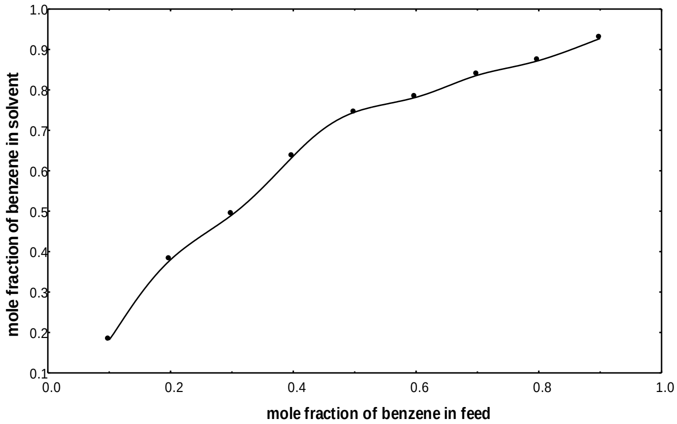

Fig (4) Relationship between mole fraction in feed an in solvent.

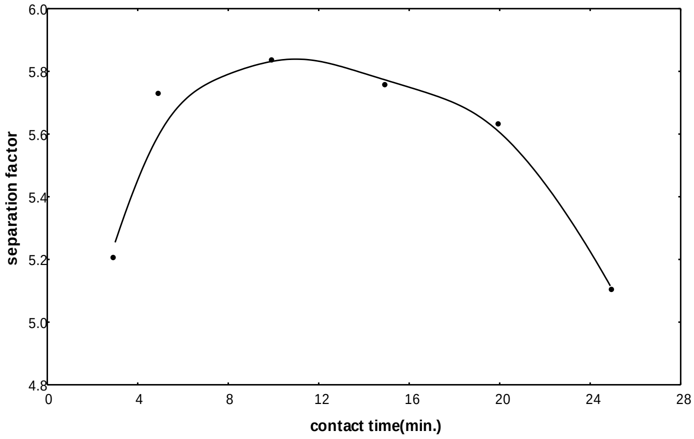

Fig (5) Effect of contact time.

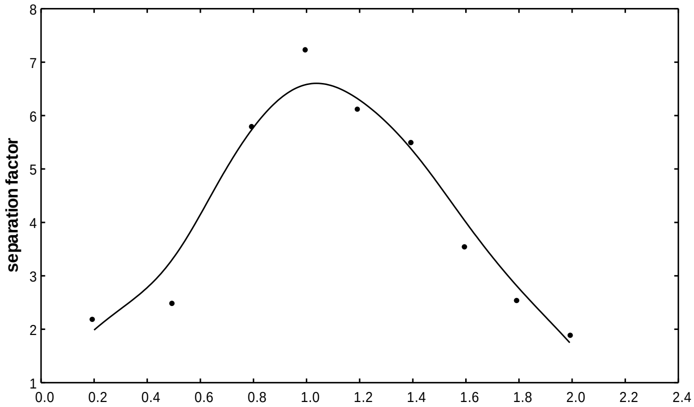

Fig (6) Effect of surfactant concentration.

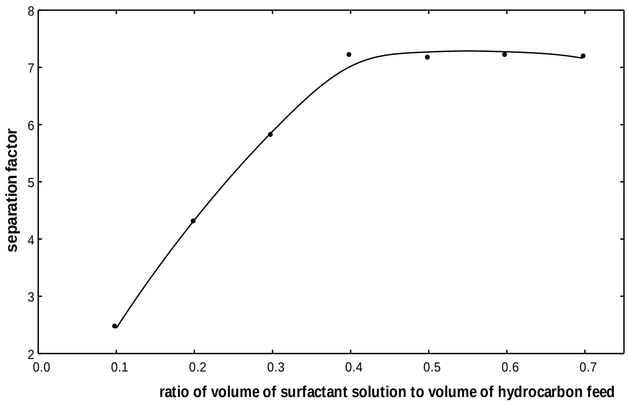

Fig (7) Effect of volume of surfactant solution to volume of hydrocarbon feed .

5- Conclusion:-

Based on experimental results it can be concluded that the increase in mole fraction of benzene in feed cause an increase in the separation factor up to mole fraction of benzene of 0.5245, The separation factor decreases with the increase of mole fraction. The separation factor increases as contact time increased up to contact time of about 10 min. and then decreased with increasing time of contact. As the surfactant concentration increased the separation factor increased up to concentration of (1.0wt %), the separation factor decreases with the increase in surfactant concentration, also The separation factor increase as the ratio of volume of surfactant solution to volume of feed increased up to 0.4, then the separation factor is essentially constant.

References:

1- Noble,R.D and Koval, C.A, .,(march 1989), **" Facilitated transport membrane system**", Chem.Eng.Prog P.P.(58).

2- KralJ, D. and Brecevic, L., (1998), "**Precipitation of some slightly soluble salts using emulsion liquid membrane** ", Croatia chemical ACT, vol. 71, p.p. (1049).

3- Li, N.N and Long, R.B, (Oct.3, 1972) "**Liquid membrane separation process**" U.S.Pat. , 3 696 028.

4- Stelmaszek, J., (1977), "**Separation of liquid mixtures by liquid membranes in a column apparatus**", J.Memb.Sci, vol.2, P.P. (197).

5- Li, N.N, Somerset and N.j, (Nov., 12, 1968) "**Separation hydrocarbon with liquid membrane**", U.S.Pat, 3 410 794.

6- Li, N.N, (1971) "**Permeation through liquid surfactant membranes**", AICHE, vol. 17, p.p. (459).

7- Goswami, A.N and Rawat, B.S, (1985) "**Studies on the permeation of aromatic hydrocarbon through liquid surfactant membranes**", J.Memb.Sci, vol. 24, P.P. (145).

8- Davies j. T and Riddeal E.K, 1963, "**Interfacial phenomena**", second edition.

تقنية الغشاء النفاذي السائل لفصل خليط البنزين والهكسان

اعداد

مصعب كاظم رشيد/ المعهد التقني – بغداد

يتضمن هذا البحث دراسة العوامل المؤثرة على فصل البنزين والهكسان باستخدام تقنية الغشاء النفاذي السائل بشكل دفعات(batch). الغشاء النفاذي السائل عبارة عن طبقة رقيقة تتكون من المواد الخافضة للشد السطحي والمذيبات. استخدم المنظف(sparkleen) كمادة خافضة للشد السطحي وزيت السيارات كمذيب لاستقبال المادة النافذة . العوامل التي تؤثر على عملية التنافذ هي : تركيب المادة الداخلة، وقت التماس مع المذيب نسبة حجم محلول المادة الخافضة للشد السطحي.

افضل الظروف لعملية الفصل في هذه الدراسة وجدت كالتالي : تركيب المادة الداخلة للبنزين هي (0.5245 mole fraction)، وقت التماس هو 10 min. ، نسبة حجم محلول المادة الخافضة للشد السطحي إلى حجم المادة الداخلة هو 0.4، تركيز المادة الخافضة للشد السطحي هو 1% كنسبة وزنية. هذه الظروف أعطت عامل الفصل قيمته (8).

$$\text{عامل الفصل} = \frac{\text{معامل التوزيع للبنزين}}{\text{معامل التوزيع للهكسان}}$$