Effects of Ultrasonic Waves on Vapor-Liquid Equilibrium of Cyclohexane/ Benzene

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Abstract— Separation of azeotropic mixtures is one of the most challenging separation processes in chemical industry. Special separation techniques such as azeotropic and extractive distillation are required to separate these mixtures. In this work, an innovative technique which incorporates ultrasonic waves during separation of Cyclohexane (Chx)/ Benzene (Bz) via distillation process was explored. The effects of ultrasonic wave at different intensities at 50, 100, 200 and 250 W/A.cm^2 and at a fixed frequency of 40 kHz on vapor-liquid equilibrium (VLE) of Chx/ Bz were investigated. Studies were also done to examine the effects of ultrasonic frequencies on the VLE data at 25 and 68 kHz. It was found that ultrasonic waves at 100 W/A.cm^2 intensity and 25 kHz frequency gave the highest relative volatility, α at 2.505 and completely eliminated the azeotropic point. The results revealed that ultrasonic waves had potential to favourably manipulate α, and hence, the VLE of Chx/ Bz.

Keywords— Azeotropic mixtures, cyclohexane/ benzene, vapor-liquid equilibrium, relative volatility, ultrasonic wave

I. INTRODUCTION

Separation of cyclohexane/ benzene is among the most complicated processes in the petrochemical industry due to the small difference in their boiling points, which is only 0.6 ^{0}C. The existing process which is conventional distillation process is very impossible to achieve high product purity [1-3]. Presently, azeotropic distillation and extraction distillation are usually used in industry to separate either close boiling mixtures or azeotropic mixtures. These methods rely on some additional mechanism, such as addition of third component called solvent or entrainer to overcome the azeotropic barrier and modify the vapor-liquid behaviour of the components. However, additional distillation columns are also required to recover the solvent or entrainer [4].

The used of ultrasonic wave in various fields including separation process have gain the global interest [5-7]. For example ultrasonic is used as a homogenizer to enable determination of vapor-liquid-liquid equilibrium (VLLE) data in the system with limited miscibility [8, 9]. Recent studies have reported the influence of ultrasonic waves on vapour-liquid equilibrium of methyl tert-butyl ether (MTBE)-methanol and methanol-water [10, 11]. However, the use of ultrasonic wave to improve separation of Chx/ Bz has never been explored prior to this work. The objective of this study is to investigate the effect of ultrasonic waves at different ultrasonic intensities and ultrasonic frequencies on vapor-liquid equilibrium of Chx/ Bz mixture using a developed VLE apparatus. The results showed that ultrasonic waves could favourably change the VLE data and eliminate the azeotropic point, thereby allowing a satisfactory cyclohexane recovery in just a single distillation column.

II. METHODOLOGY

A. Material

Cyclohexane and benzene used in this study was supplied by R&M Chemicals, UK and MERCK, Germany, respectively. The purity of the chemicals was 99.7% for

benzene and 99.5 % for cyclohexane. The chemicals were used without further purification.

B. Procedure

The VLE measurements were carried out using an apparatus called Ultrasonic-Distillation System, which consist of distillation flask, condenser, water bath, ultrasonic generating equipment, and thermocouples. This apparatus was designed for a charge of 250 cm^3 mixtures and can be operated at low or moderate pressure. The distillation flask was immersed in the water bath equipped with 40 kHz ultrasonic transducer and heater. The ultrasonic transducer, supplied by Crest Ultrasonic (M) Sdn Bhd, was connected to 500 Watts ultrasonic generator. A heater, equipped with temperature controller, was used to provide heat for boiling processes in the distillation flask. Vapor and liquid temperatures was measured using thermocouples, TC-08 with precision of $0.01^{o}C$ and linked using data logger to a computer. Sample from the distillation flask (liquid) and condensed vapor were taken once the vapor temperature remained constant for a period of 10-20 minutes. Their compositions were measured using Gas Chromatography. During the experimental study, mixtures with different composition of cyclohexane in benzene solutions were prepared and fed into the distillation flask. This experiment was firstly done at atmospheric condition to obtain VLE data of cyclohexane-benzene without the presence of ultrasonic wave. Then, it was repeated using ultrasonic power at 50, 100, 200 and 250 Watts respectively at frequency of 40 kHz to obtain the most suitable ultrasonic power. After that, the same procedure was repeated using frequency of 25 kHz and 68 kHz [10, 11]. The analysis using gas chromatography was run under specific conditions as stated in Table 1.

TABLE 1
ANALYSIS SPECIFICATION

Samples Analyzed	GC Conditions
Chx/ Bz	Column - SPB-1, 30m x 0.53 mm ID, 5.0 µm Carrier Gas - Nitrogen, 90 psi Detection - Flame Ionize Detection, 220 ^{o}C Injection Volume - 0.2 µL, split injection at 220 ^{o}C Oven Temperature - 40 ^{o}C (5 min) to 185 ^{o}C at 10 ^{o}C/min

III. RESULTS AND DISCUSSIONS

A. VLE Study Without Sonication

The VLE data for cyclohexane and benzene was measured at atmospheric pressure. The data obtained was compared with the literature in order to verify the reliability of the developed system to obtain VLE data. Figure 1 and Table 2 show that the average deviation of VLE data obtained from this work with literature is 3.2 %. This confirmed the practical feasibility of using the developed apparatus to obtain VLE data and for studying the effect of ultrasonic waves on VLE of Chx/ Bz.
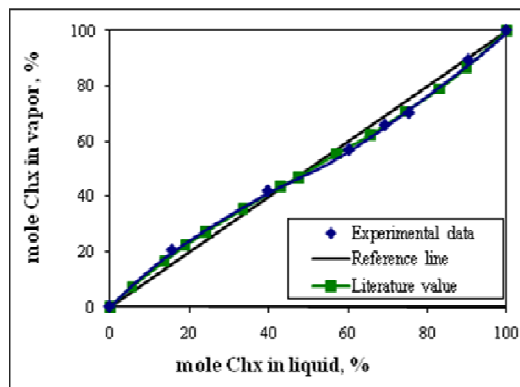

Fig. 1 Equilibrium diagram of Chx - Bz without the presence of ultrasonic wave at atmospheric pressure [●] experimental value [■] literature value [12]

TABLE 2
VAPOR AND LIQUID COMPOSITION OF CHX/ BZ

x_{Chx}, %	y_{Chx}, %		% Deviation
	Experimental Data	Literature Value [12]	
10	14.0	13.0	7.7
20	25.0	23.0	8.7
30	33.5	32.0	4.7
40	42.0	40.5	3.7
50	49.0	49.0	0.0
60	56.0	57.0	1.8
70	67.0	67.0	0.0
80	78.0	77.0	1.3
90	89.0	88.0	1.1
	Average Deviation		3.2

B. VLE Study at Different Ultrasonic Intensity

1) Effects of Ultrasonic Intensity on VLE

The VLE of Chx/ Bz at different ultrasonic intensity is shown in Fig. 2. The equilibrium curve was shifted upwards with the increase of ultrasonic intensity up to 100 W/A.cm^2 and downwards at intensity beyond 100 W/A.cm^2. The changes of equilibrium curve also affect the azeptropic point of the mixture. Fig. 3 shows the plot of azeotropic point against ultrasonic intensity. As can be seen in this figure, the azeotropic point of Chx/ Bz was shifted to 85 mole % of cyclohexane at intensity of 50 W/A.cm^2 and then eliminated at intensity of 100 and 200 W/A.cm^2. However, the azeotropic point was decreased to 68.5 mole % Chx with the application of ultrasonic wave beyond 200 W/A.cm^2. This situation indicates that the separation process is easier at intensity lower than 200 W/A.cm^2.
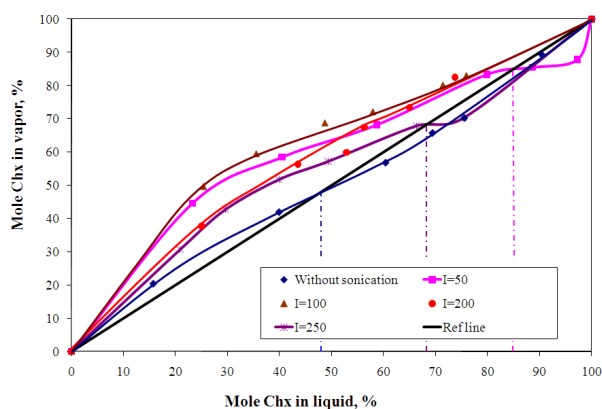
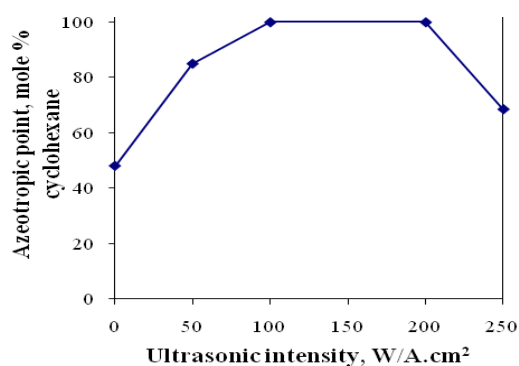Fig.2 xy- diagram of Chx/ Bz system with different ultrasonic intensities

Fig.3 Azeotropic point of cyclohexane-benzene as a function of ultrasonic intensity at frequency of 40 kHz

2) Effects of Ultrasonic Intensity on Relative Volatility, α

Relative volatility, α, is a measure of the relative ease of separating components by distillation [13]. Separation of two components by distillation is impossible when the relative volatility is equal to 1.0 [14]. The relative volatility of Chx/ Bz was calculated using equation (1):

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \qquad (1)$$

Fig. 4 illustrates the changes of α with respect to ultrasonic intensity. In comparison to the unsonicated data, α of Chx/ Bz has increased with the application of ultrasonic waves. The maximum α value at 2.158 was obtained at ultrasonic intensity of 100 W/A.cm^2 while the lowest α, which is 1.380, was obtained at intensity of 250 W/A.cm^2.

The changes in relative volatility and VLE data of binary mixtures were caused by the cavitational activities that occur during the transmission of ultrasonic wave in liquid medium. When ultrasonic intensity increased, greater ultrasonic energy enters the liquid medium, produces more cavitation

micro bubbles, as well as creates larger vacuum effects inside the liquid medium [15].

According to Wu and Ondruschka [16], the mass transfer of individual component from liquid bulk into cavitation micro bubbles are more affected by its polarity. Component with less polarity (lower polarity indices) will dominate the mass transfer processes. Since benzene and cyclohexane have close difference in their boiling point, polarity effect will play an important role and give major effect to the vaporization process. From the literature, benzene has higher polarity indices compared to cyclohexane. The polarity index of cyclohexane is zero while benzene is 3.0. Concerning the statement given by Wu and Ondruschka [16], cyclohexane has dominated the mass transfer processes from the liquid bulk into cavitation micro bubbles. During the bubble collapse, cyclohexane was released and enriched the vapor phase. Hence, increased the relative volatility of Chx/ Bz.
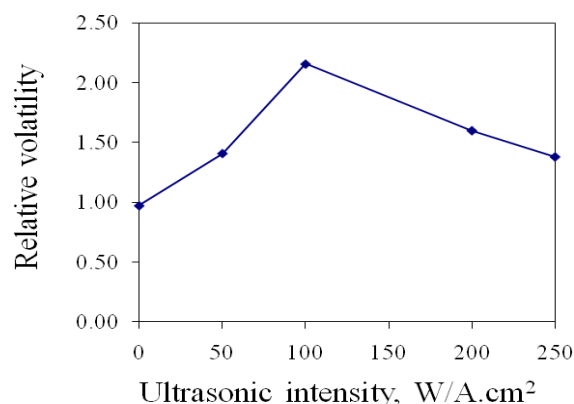

Fig.4 Relative volatility of Chx/ Bz as a function of ultrasonic intensity at frequency of 40 kHz

However, the ultrasonic intensity could not be increased indefinitely [15].This will cause numerous formations of cavitation micro bubbles. In this case, numerous formations of cavition micro bubbles were identified at ultrasonic intensity beyond 100 W/A.cm^2, where the normal cavitation process was perturb and caused an adverse effect. At this stage, the tendency of cavitation bubbles to collide is higher. Therefore, upon collision, bigger micro bubbles are created at intensity higher than 100 W/A.cm^2. Since the time available for the bubbles to collapse is insufficient, these bubbles do not collapse and combine to form a bubble 'cushion' at the radiating face of the ultrasonic transducer which in turns reduce the effects of coupling sound energy to the liquid system [15]. This phenomenon reduces the transmission of ultrasonic energy into the liquid medium and produces less cavitational and vacuum effect. Because of that reason, the increase of ultrasonic intensity beyond 100 W/A.cm^2 decreased the relative volatility and azeotropic point of cyclohexane-benzene as well as shifted the equilibrium curves towards the reference line.

C. VLE Study at Different Ultrasonic Frequency

1) Effects of Ultrasonic Frequency on VLE

Frequency is another important parameter that defines sound waves and influences the cavitation effects [16]. Concerning the above matter and the theory on cavitation, the selection of suitable operating ultrasonic frequency is very important in order to obtain large cavitational effects and huge vacuum condition in liquid medium. In this section, the influence of different ultrasonic frequencies to VLE data of Chx/ Bz is discussed. Fig. 5 illustrates the VLE results for binary mixtures of CHx/ Bz with ultrasonic frequency of 25, 40 and 68 kHz at 100 W/A.cm^2 intensity. As can be seen in this figure, the presence of ultrasonic waves has altered the equilibrium curve of binary mixtures. The equilibrium curves were shifted downward and closer to the reference line with the increased of ultrasonic frequency. At frequency of 25 and 40 kHz, the equilibrium curves do not show intercept at the reference line. This situation means that no azeotrope exist when Chx/ Bz mixtures sonicated at frequency of 25 and 40 kHz and intensity of 100 W/A.cm^2. the azeotropic point of Chx/ Bz at different ultrasonic frequencies are tabulated in Table 3.
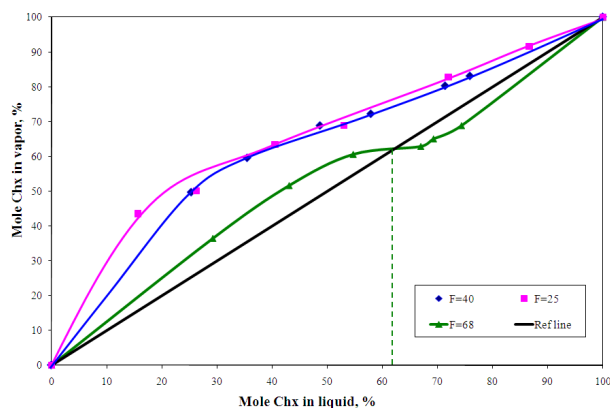

Fig. 5 *xy*- diagram of Chx/ Bz with different ultrasonic frequencies at 00 W/A.cm2 intensity

TABLE 3
AZEOTROPIC POINT OF CHX/ BZ AT DIFFERENT ULTRASONIC FREQUENCIES
AND 100 W/A.CM^2 INTENSITY

Ultrasonic Frequency, kHz	Azeotropic Point,
25	None
40	None
68	62 mole % Chx

2) Effects of Ultrasonic Frequency on Relative Volatility, α

Fig. 6 shows that α of Chx/ Bz decreases with the increase of ultrasonic frequency. Frequency of 25 kHz gives the highest α value at 2.505. As discussed before, the presence of ultrasonic waves changes the VLE data and the relative volatility through the cavitation phenomenon which involves the formation of micro bubbles and generation of vacuum environment in liquid medium during rarefaction cycle of ultrasonic waves. At higher frequencies, the rarefaction cycle is shortened, leading to the formation smaller cavitation micro bubbles and generation of smaller vacuum effects within the liquid medium, and ultimately reduced vaporization of the more volatile component in the liquid mixture [15]. This phenomenon explains the decrease in relative volatility, α at higher ultrasonic frequencies.
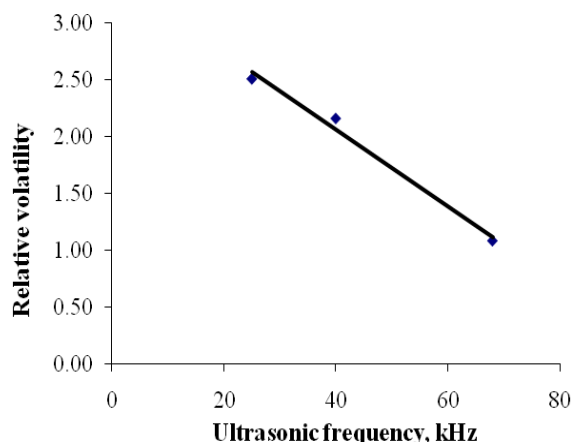

Fig. 6 Relative volatility of Chx/ Bz as a function of ultrasonic frequency at 00 W/A.cm2 intensity

IV. CONCLUSIONS

This work has successfully shows that the ultrasonic waves at different intensity and frequency has potential to manipulate the VLE data and change the relative volatility of Chx/ Bz mixtures. 100 W/cm^2 was identified as the best intensity at 40 kHz frequency. Further increase of ultrasonic intensity beyond 100 W/A.cm^2 decreased the relative volatility and azeotropic point of Chx/ Bz. As the ultrasonic frequency increased from 25 to 68 kHz, the separation process become harder. This is because, the relative volatility of Chx/ Bz decreases with the increase of ultrasonic frequency. The highest value of relative volatility at 2.505 was obtained at frequency 25 kHz and intensity of 100 W/A.cm^2, where the azeotropic point was totally eliminated.

NOMENCLATURE

x_i liquid phase mole fraction
y_i vapor phase mole fraction

Greek letters
α   relative volatility

Subscripts
1, 2   component identification

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