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Solvent screening for the separation of ethylbenzene and *p*-xylene by extractive distillation

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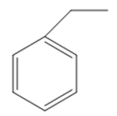
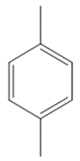
Abstract−Extractive distillation is one of the most effective processes for the separation of ethylbenzene and *p*-xylene. The goal was to find single solvents or combinations of multi-solvents with good properties while minimizing the ratio of solvent to feed. The distillations were performed at equilibrium to determine the relative volatility of ethylbenzene to *p*-xylene with the extractive solvents under isothermal condition. For a single extraction solvent, 1,2,4-trichlorobenzene had the highest relative volatility at 1.123. In some cases, combinations of two or three solvents were used as well as different ratios of solvent to feed to investigate the synergy effect of the mixture solvents. The binary solvent mixture of 1,2,4-trichlorobenzene and maleic anhydride (2 : 1) had the best performance with a relative volatility of 1.228 at the solvent/feed ratio of 1 : 1. Some of the solvents were further studied at different solvent/feed (S/F) ratios. Selected solvents generally tended to have higher relative volatilities at high S/F ratios, but the operation cost will increase. Therefore, it is important to find the proper conditions to optimize the S/F ratio for extractive distillation from the industrial point of view.

Keywords: Ethylbenzene, *p*-Xylene, Extractive Distillation, Solvent Screening, Relative Volatility

INTRODUCTION

Ethylbenzene (EB) and *p*-Xylene (PX) have a great importance in petrochemical industries for their use as a main base for the synthesis of many organic compounds. For example, ethylbenzene is a major precursor for styrene, which is principally used in the manufacture of plastics. *p*-Xylene is used on a large scale to manufacture terephthalic acid, which is a basic feedstock of the polyester industry. Thus, pure ethylbenzene and *p*-xylene are in great demand. In the industrial field, these two feed stocks can come from mixed xylene, which comes as a mixture of *o*-xylene, *m*-xylene, *p*-xylene and ethylbenzene [1-4]. Recuperation and purification of each isomer are essential processes for high value products. The purity of ethylbenzene and *p*-xylene for the subsequent process is required with a high grade. For the dehydrogenation of ethylbenzene to styrene, greater than 99.5% of the ethylbenzene purity is demanded. The presence of impurities affects the catalytic reaction of producing styrene and may promote a side effect which prevents to adjust the desired purity of the product. However, this is technically a difficult process due to the large similarity of their physical properties, which makes the relative volatility low (Table 1) [5,6]. The relative volatility of ethylbenzene to *p*-xylene is 1.06; thus, the separation of ethylbenzene and *p*-xylene by distillation is impractical and uneconomical because of their close boiling points and vapor pressures. This conventional rectification of ethylbenzene and *p*-xylene needs the use of fractional columns containing more than 200 plates and high reflux ratio to assure effective separation thereof [7]. Since ethylbenzene and *p*-xylene are C8 aromatic isomers, the separations by chemical means are not quite attractive for the industrial applications [8,9]. Therefore, the distillation characteristics are of considerable practical importance. The effective separation of these two components by the addition of the solvent to increase the selectivity is a challenge to realize the industrial process.

Table 1. Chemical structures, physical properties, and uses of ethylbenzene and *p*-xylene

	Ethylbenzene	*p*-Xylene
Structure		
Normal boiling point [K]	409	411
Normal melting point [K]	178	221
Use	Styrene	Ester production

Extractive distillation is one of the most effective processes for separating compounds with close boiling points. The Krupp-Kop-

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[‡]This article is dedicated to Prof. Hwayong Kim on the occasion of his retirement from Seoul National Univeristy.

pers (KK) extractive distillation method is used with different nonvolatile components as solvents. With extractive distillation as opposed to azeotropic distillation, the extractive agent boils at a much higher temperature than any of other the mixture components. The solvent should be easily separable from the bottom product, and should not react chemically with the components or the mixture, or cause corrosion in the equipment. This prevents the formation of low-boiling azeotropes, thus rendering pure distillates after a single extractive distillation [10,12]. Although extractive distillation has a wide acceptance in some hydrocarbons--for example, toluene from nonaromatic hydrocarbons, this separation method has not been recently investigated in separating ethylbenzene and *p*-xylene. The advantage of using extractive agents for this separation is the possibility of increasing the relative volatility (EB/PX), which leads to a reduction of the theoretical plates when the ethylbenzene separates from the *p*-xylene with a purity of 99%. From the literature, the relative volatility of 1.11 requires 87 plates and the relative volatility of 1.20 will even reduce the plate requirement to less than 50 plates. Therefore, some researchers tried some extractive agents to increase the relative volatility to more than 1.20 before, but these were either ineffective or unstable. Possible candidates with a large potential are the ionic liquids which have a high chemical and thermal stability, broad liquid range and high capacity for the extractive distillation of ethylbenzene and *p*-xylene. They have been studied for the extractive solvents as single compounds to increase the relative volatility for EB and PX separation, such as aromatics, chlorinated aromatics, carbonyls, straight chains, alcohols, cyclics, sulfoxides and phosphates. For example, 1,2,4-trichlorobenzene increases the relative volatility from 1.06 to 1.11, which shows an enhancement in the performance of EB and PX separation [12-15].

For the mixture of the agents, Berg found that the mixtures with two or three components are more effective than the single compounds. However, the mechanism of separating ethylbenzene and *p*-xylene by extractive distillation was not clearly proved of their complex phenomena when the solvent was applied [12-14]. Generally, the effectiveness of an extraction solvent is related to the ways that it interacts on a molecular level with the feeds to be distilled. The extraction solvent's ability to effect a separation of the two components depends on its molecular size, shape, and charge distribution. In general, non-ideal behavior of solvent with the ethylbenzene and *p*-xylene mixture is hard to estimate by the current knowledge. A good assay requires that many solvents of different structures, electronic configurations, and polarities be tested. From a practical point of view, the solvent must alter the relative volatility by a wide enough margin for a successful result. Toxicity, quantity, cost and availability of the solvent should be considered for practical uses [13-15]. Sometimes, the engineering bottleneck is the ratio of solvent to feed (mixture to separate) because of the solvent cost and the separation energy of the solvent. Therefore, a wide variety of different solvents at different conditions need to be tested to cover the possible process evaluation.

We examined different extractive agents, referred to herein as "solvents," for their abilities to separate ethylbenzene and *p*-xylene. Under consistent experimental conditions, various ionic liquids and several solvents were evaluated for their abilities if they could adjust the relative volatilities of a 1 : 1 mixture of *p*-xylene and ethylbenzene. Specific binary and ternary solvents were tested to investigate the effect of combined mixtures. The ratio of solvent to feed (S/F) was also varied for selected solvents to monitor solvents with high separation ability at low quantity.

EXPERIMENTAL SECTION

1. Materials and Solvent Selection

The feed materials were ethylbenzene (Sigma-Aldrich, anhydrous, 99.8%) and *p*-xylene (Yakuri Pure Chemicals, ≥99%). In general, commercial simulator PRO/II provides a high-level and field-proven degree of detail in simulating processes. It may be reliable for conventional hydrocarbons when the ionic liquids may have some deviations from the experiments. In our case, however, we observed the trend in the separation of EB and PX by different solvents. Therefore, a commercial simulator PRO/II was used to calculate the infinite dilution activity coefficient for the estimation of the ehtylbenzene selectivity for the solvent pre-selection. Estimated solvents included aromatics, chlorinated aromatics, carbonyls, straight chains, alcohols, cyclics, sulfoxides and phosphates. Some solvents and the three other ionic liquids were selected from other research of aromatics extrac-

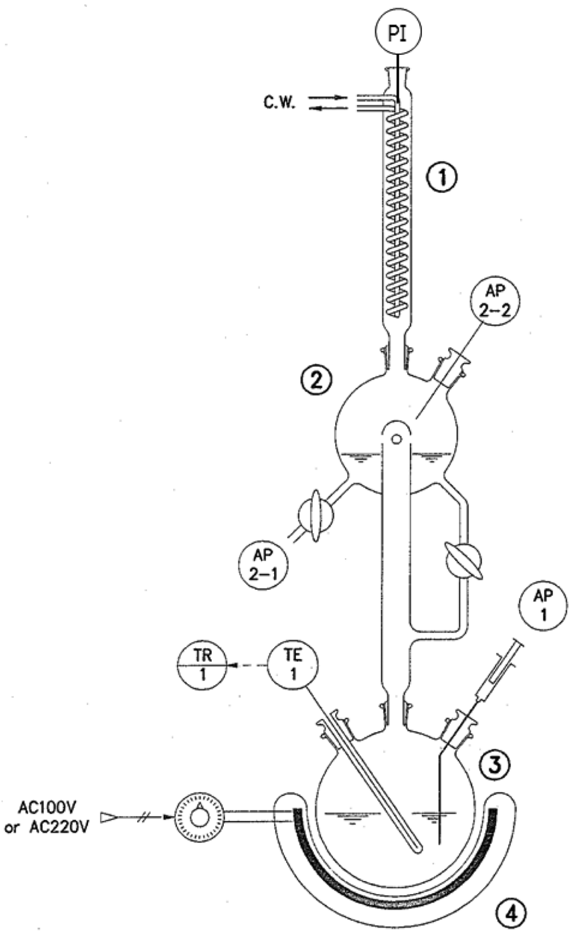

Fig. 1. Experimental setup.
① Condenser
② Reflux drum (250 mL)
③ Boiling pot (500 mL)
④ Heating mantle with magnetic stirrer
TE. Thermocouple type K
TR. Temperature recorder
AP. Sampling point

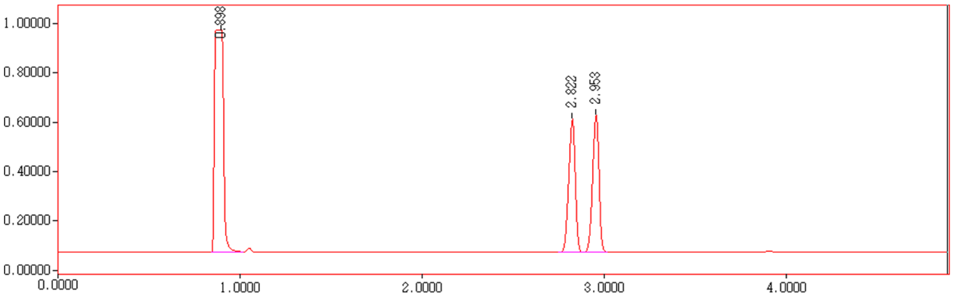

Fig. 2. Gas chromatography profile for the separation of the ethylbenzene and *p*-xylene.

tive distillation [12]. All solvents used for extractive distillation were reagent grade. All chemicals were used as packaged without further purification.

2. Apparatus and Procedure

Distillations were performed in an all-glass dynamic recirculating still, shown in Fig. 1. The still was similar to the Othmer phase equilibrium device, and all experiments were performed as atmospheric distillations. In the still, both the vapor and the liquid phases were continuously recirculated to maintain contact between the phases and quickly establish equilibrium. The still consisted of a 500 mL glass boiling pot, 250 mL reflux drum, condenser, and heating mantle. A magnetic stirring bar and borosilicate glass beads were used in the boiling pot to ensure homogeneity of the mixture during distillation. The vapor condensed at the top in the water-cooled condenser and collected in the reflux drum. The temperature of the boiling pot was controlled with a heating mantle with a thermocouple (type K), which also recorded the temperature. The liquid phase was sampled from AP-1 and the vapor phase from AP-2.

The experiment had to be carefully controlled to ensure consistency and avoid errors. First, the magnetic stirring bar and the glass beads were placed in the flask (boiling pot). Next, 25 mL of ethylbenzene, 25 mL *p*-xylene, and a specific amount of the solvent were added to the pot in that order at room temperature. Extractive distillation typically requires solvent/feed ratios of 1 : 1 to 2 : 1 to be effective for the process; therefore, most experiments used a 1 : 1 solvent-to-feed ratio. Following setup, the boiling pot was heated from room temperature to 423 K under reflux conditions with stirring. The system was assumed to have reached equilibrium after 2 h, when it reached a steady-state, and the boiling pot stayed at a constant temperature of 423 K for at least 30 min. All the experiments carried out under isothermic condition after the system reached the equilibrium condition to select the effective extractive solvent based on the experimental data [12]. The temperature was continuously monitored. The pot and head were sampled two to three times per hour from AP-1 and AP2-2, respectively. To minimize experimental error, no more than 1 mL was removed for each sampling. Finally, the relative volatilities ($\alpha_{EB/PX}$) were calculated based on the GC data and Eq. (1).

3. Sample Analysis

The vapor (cooled to a liquid) and liquid samples were analyzed by gas chromatography (Acme 6000 GC, Younglin) with a capillary column (HP-FFAP, 25 m×0.32 mm×0.5 μm) and flame ionization detector (FID). High-purity helium (0.9999) was the carrier gas.

Very specific conditions were required to resolve the peaks for ethylbenzene and *p*-xylene. First, samples were diluted by with acetone (Sigma-Aldrich, ≥99.0%) amount of 3 : 1 (acetone : sample) and 1 μL of the diluted sample was taken for the GC analysis. For quantitative analysis, benzene (Duksan pure chemical Co., ≥99.0%) was used as an internal standard to get accurate data. The oven temperature of the GC was programmed to start at 70 °C for 5 min, then ramp to 220 °C at a rate of 20 °C/min, and finally maintain 220 °C for 2.5 min. Both the injector and detector were fixed at 200 C, and the carrier gas-inlet pressure was 12 psig with a split ratio of 1/300. Under these conditions, we were able to achieve acceptable resolution to analyze the mixture compositions as shown in Fig. 2. Each sample was analyzed at least twice and the average peak area was calculated to ensure accuracy; thus, the combined standard uncertainty of the mole fraction of each component in the liquid and vapor phases was 0.001.

The property of relative volatility (α) gives a snapshot of the extractive efficiency of a distillation. Eq. (1) was used to calculate the relative volatility of ethylbenzene to *p*-xylene ($\alpha_{EB/PX}$):

$$\alpha_{EB/PX}=(y_i/x_i)/(y_j/x_j) \tag{1}$$

where the subscripts i and j refer to ethylbenzene and *p*-xylene, respectively, and x and y are the mole fractions of the liquid-phase and vapor-phase, respectively. Determining the $\alpha_{EB/PX}$ values allows us to directly compare the effectiveness of different solvents used in the extractive distillation. Our experiment was calibrated with a test mixture of ethylbenzene and *p*-xylene without solvent. We meas-

Table 2. Relative volatilities of ethylbenzene/*p*-xylene distillation with different ionic liquids at a constant temperature of 423 K

No.	Solvent[a]	α^b	Supplier	Purity
1	1-Ethyl-3-methylimidazolium-ethylsulfate ([EMIM][EtSO4])	1.081	Sigma-Aldrich	≥99.0%
2	1-(2-Hydroxyethyl)-3-methyl-imidazolium tetrafluoroborate ([HEMIM][BF4])	1.026	Io-li-tec	≥99.0%
3	1-(2-Hydroxyethyl)-3-methyl-imidazolium hexafluorophosphate ([HEMIM][PF6])	1.081	Sigma-Aldrich	≥99.0%

[a] Experiments were performed at a certain weight ratio of the feeds and solvent (EB : PX : solvent=1 : 1 : 2)
[b] Relative volatility ($\alpha_{EB/PX}$) of ethylbenzene to *p*-xylene

ured a relative volatility of 1.067 for this mixture. This value is comparable to the literature estimate of 1.06 [13].

RESULTS AND DISCUSSION

1. Ionic Liquids

Three different ionic liquids were tested at a 1 : 1 feed/solvent ratio, with the relative volatility data presented in Table 2 (see table for full compound names). A homogeneous liquid phase appeared after these three ionic liquids were stirred with the ethylbenzene/*p*-xylene feed mixture. Imidazolium ionic liquids have been applied in many separations because of their good selectivity [12,16]. In this study, [EMIM][EtSO4] and [HEMIM][PF6] did slightly enhance the relative volatilities to 1.081 compared to the solvent-free distillation (1.067). However, [HEMIM][BF4] actually depressed $\alpha_{EB/PX}$ to 1.026. Moreover, the pot actually solidified during the experiment. We can suggest that the solidification could be due to the super acidity of the ionic liquid which may proceed side effects such as a oxidative dehydration of ehtylbenzene [17]. With the same molecular structure of 1-(2-Hydroxyethyl)-3-methyl-imidazolium ([HEMIM]), the

Table 3. Relative volatilities of ethylbenzene/*p*-xylene distillation with different individual solvents at a constant temperature of 423 K

No.	Solvent[a]	Supplier	α^b	Purity
1	1,2,4-Trichlorobenzene	Sigma-Aldrich	1.123	≥99.0%
2	Maleic anhydride (MA)	Sigma-Aldrich	1.117	≥99.0%
3	Phthalic anhydride (PA)	Sigma-Aldrich	1.112	≥99.5%
4	*o*-Toluic acid	Sigma-Aldrich	1.107	≥99.0%
5	*m*-Tolunitrile	Sigma-Aldrich	1.105	≥98.0%
6	5-Methyl-2-hexanone	Sigma-Aldrich	1.102	≥99.0%
7	Benzaldehyde	Sigma-Aldrich	1.098	≥99.0%
8	1,2-Dichlorobenzene	Fluka	1.097	≥99.0%
9	1,3,5-Trimethylbenzene	Supelco	1.094	≥99.0%
10	Benzonitrile	Sigma-Aldrich	1.089	≥99.0%
11	Methylcyclohexane	Sigma-Aldrich	1.089	≥99.0%
12	Acetophenone	Sigma-Aldrich	1.088	≥99.0%
13	1,2,4-Trimethylbenzene	Sigma-Aldrich	1.088	≥98.0%
14	Benzyl alcohol	Sigma-Aldrich	1.082	≥99.0%
15	Benzyl chloride	Sigma-Aldrich	1.082	≥99.0%
16	Hexylene glycol	Sigma-Aldrich	1.079	≥99.0%
17	4-tert butyl phenol	Sigma-Aldrich	1.077	≥99.0%
18	Phenyl ether	Sigma-Aldrich	1.075	≥99.0%
19	Tricaprylylmethylammonium chloride	Sigma-Aldrich	1.072	≥99.0%
20	Butylbenzene	Sigma-Aldrich	1.07	≥99.0%
21	Tetrahydroxy-ethylenediamine	Sigma-Aldrich	1.07	≥99.0%
22	Propylene carbonate	Sigma-Aldrich	1.068	≥99.7%
23	*m*-Xylylenediamine	Sigma-Aldrich	1.064	≥99.0%
24	Triethyleneglycol	Sigma-Aldrich	1.061	≥99.0%
25	1-Methyl-2-pyrrolidone	Sigma-Aldrich	1.056	≥99.0%
26	*N,N*-Dimethylacetamide	Sigma-Aldrich	1.055	≥99.8%
27	Triethyl phosphate	Sigma-Aldrich	1.053	≥99.8%
28	Triethylene glycol dimethyl ether	Sigma-Aldrich	1.052	≥99.0%
29	Benzyl ether	Aldrich	1.051	≥98.0%
30	ε-Caprolactone	Sigma-Aldrich	1.051	≥99.0%
31	1,4-Dimethoxybenzene	Aldrich	1.046	≥99.0%
32	Dimethylsulfoxide	Sigma-Aldrich	1.042	≥99.9%
33	Tetraethylenepentamine	Aldrich	1.042	≥99.0%
34	ε-Caprolactam	Sigma-Aldrich	1.041	≥99.0%
35	Dimethylformamide	Sigma-Aldrich	1.041	≥99.8%
36	γ-Butyrolactone	Sigma-Aldrich	1.033	≥99.0%
37	Methyl sulfoxide	Aldrich	1.032	≥99.0%
38	Sulfolane	Aldrich	1.031	≥99.0%
39	Diethylene glycol	Sigma-Aldrich	1.026	≥99.0%

[a] Experiments were performed at a certain weight ratio of the feeds and solvent (EB : PX : solvent=1 : 1 : 2)

[b] Relative Volatility ($\alpha_{EB/PX}$) of ethylbenzene to *p*-xylene

anion of hexafluorophosphate shows more positive effects on the selectivity of ethylbenzene and the experiment operation. According to this results, none of the ionic liquids provided sufficient separation of ethylbenzene and *p*-xylene.

2. Single Solvents

At a 1 : 1 solvent/feed ratio, 39 different individual solvents were screened; the data are arranged in descending order of relative volatility in Table 3. 1,2,4-Trichlorobenzene gave the best enhancement of relative volatility ($\alpha_{EB/PX}$=1.123) in our experiments, much higher than the solvent-free calibrated value of around 1.067. From the industrial point of view, this relative volatility ($\alpha_{EB/PX}$=1.123) can reduce the theoretical plates from 200 to below 80 plates [13-15].

Furthermore, fortunately, 1,2,4-trichlorobenzene has a low melting point of 290 K, avoiding solidification of the mixture, while its boiling point of 487 K is well above the ethylbenzene/*p*-xylene feed mixture. In designing an extractive distillation process, it is important to provide for the recovery of the solvent. The most common method to recover the extractive agent is rectification with another column. To keep the cost of this operation to a minimum, the feed and solvent must have an appreciable difference in their boiling points [11]. Usually, this means the boiling points must vary by 20 K [14, 15]. Yet, solvents with high boiling points may also have high melting points, which would make them less convenient to dispense and transfer. We found that 1,2,4-trichlorobenzene was the most suitable solvent for the separation of EB and PX, even though there is a small difficulty with the toxicity of 1,2,4-trichlorobenzene to handle. Therefore, reducing the use of 1,2,4-trichlorobenzene is an interesting issue to apply it in the industry when binary or ternary solvent system could be the solution.

The oxygenated organic compounds maleic and phthalic anhydride also performed comparably ($\alpha_{EB/PX}$=1.117, 1.112, respectively) to 1,2,4-trichlorobenzene. The melting point of phthalic anhydride is 404 K, which is quite close to the boiling point of ethyl benzene (409 K). Having phase transitions at similar temperatures can increase the risk associated with the extraction. However, maleic anhydride has a melting point of 326 K, making it far more suitable for extraction even though its melting point is still above room temperature. In this view, maleic anhydride was nearly as good as 1,2,4-trichlorobenzene as a single extraction solvent. As a result, the chlorine functional group in 1,2,4-trichlorobenzene and oxygen atom in maleic and phthalic anhydride seem to be effective to separate ethylbenzene and *p*-xylene. Both compounds have high electronegativity on their molecular structure of the functional groups which may be a crucial property for the extraction solvents.

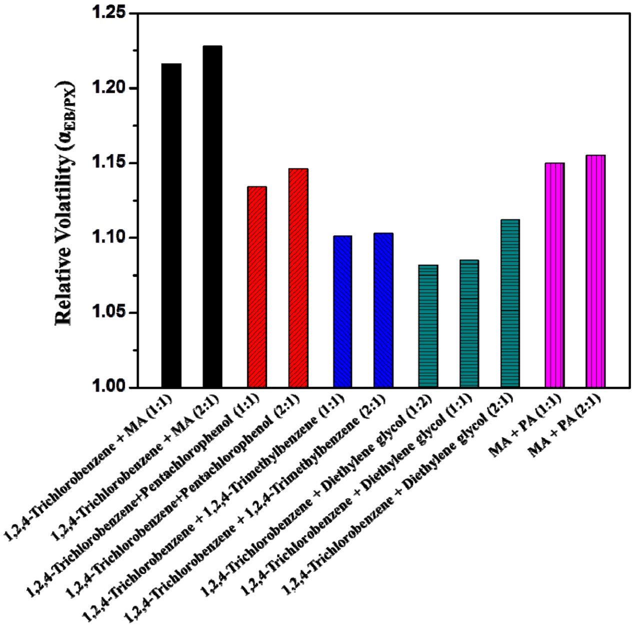

Fig. 3. Relative volatilities of ethylbenzene/*p*-xylene distillation with binary mixtures at a constant temperature of 423 K. Experiments were performed at a certain weight ratio of the feeds and solvent (EB : PX : solvent=1 : 1 : 2). MA=maleic anhydride and PA=phthalic anhydride.

3. Binary and Ternary Solvent Mixtures

Fig. 3 presents the $\alpha_{EB/PX}$ data of binary solvent mixtures based on the 1,2,4-trichlorobenzene and maleic anhydride. Mixtures of solvents were tested to see if they could promote more effective separations. We have found that mixtures of solvents can achieve higher relative volatilities than any one solvent alone and can also reduce the use of the 1,2,4-trichlorobenzene. Specifically, the combinations of 1,2,4-trichlorobenzene and maleic anhydride and maleic anhydride and phthalic anhydride gave high relative volatilities, which have the chlorine functional group and oxygen in their molecular structure. We assumed that this behavior was due to an additive combination of electronegativity effects on their molecular structure, same as the single solvents. It was considerably more effective than any other at the 1 : 1 ratio. The amount of 1,2,4-trichlorobenzene was also changed to 2 : 1 (1,2,4-trichlorobenzene : other solvent). Fig. 3 illustrates that the relative volatilities of the binary mixtures slightly increase from 1.216 to 1.228 as the content of the 1,2,4-trichlorobenzene increases. It proves that the 1,2,4-trichlorobenzene shows a dominant property in separation ethylbenzene and *p*-xylene. Overall, the binary mixture of 1,2,4-trichlorobenzene and

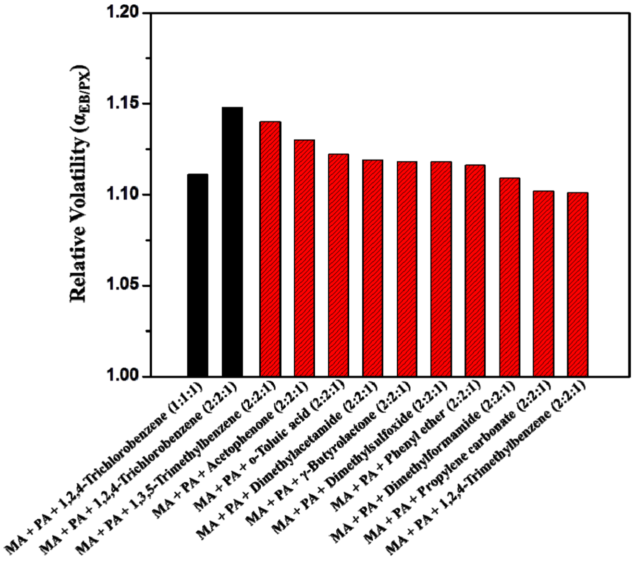

Fig. 4. Relative volatilities of ethylbenzene/*p*-xylene distillation with ternary mixtures at a constant temperature of 423 K. Experiments were performed at a certain weight ratio of the feeds and solvent (EB : PX : solvent=1 : 1 : 2). MA=maleic anhydride and PA=phthalic anhydride.

maleic anhydride (2 : 1) had higher relative volatility of any solvent system tested in this work and it is also comparable with other previous works ($\alpha_{EB/PX}$=1.228) [12]. Moreover, this solvent system provides the advantage of reducing the use of 1,2,4-trichlorobenzene to apply it to the industry. The same tendency was evaluated in the combination of maleic anhydride and phthalic anhydride. From this result, it is verified that more complex mixtures could enhance separation performance. Sometimes, however, adding a solvent with poor performance will drag down a good extraction solvent. For example, the mixture of diethylene glycol and 1,2,4-trichlorobenzene (1 : 1) had a relative volatility of 1.085, which was lower than the single solvent of 1,2,4-trichlorobenzene ($\alpha_{EB/PX}$=1.123). Based on this, it can be estimated that diethylene glycol had a negative effect on the relative volatility of the ethylbenzene with *p*-xylene.

Maleic anhydride- and phthalic anhydride-based ternary solvent mixtures are compared in Fig. 4. The ternary solvent mixtures also had some effects on $\alpha_{EB/PX}$. Basically, the ratio of 2 : 2 : 1 shows a higher performance than 1 : 1 : 1, for example, at the mixture of maleic anhydride : phthalic anhydride : 1,2,4-trichlorobenzene. The same result compared to the binary mixture revealed that the increasing amount of the dominant solvents performs better separation in our system. One of the advantages of ternary systems is that the third component can lower the freezing point to facilitate the process. The mixture of maleic anhydride and phthalic anhydride is a promising solvent, but its melting point is so high that it freezes relatively close to the boiling point of ethylbenzene [10,13,14]. Although, many mixtures in Fig. 4 demonstrated slightly decreased relative volatilities, these mixtures helped avoid problems of the maleic anhydride and phthalic anhydride mixture related to high melting points. Therefore, the properties of these mixtures could help us find optimal conditions for various situations where ethylbenzene and *p*-xylene must be distilled.

4. Different Solvent/Feed Ratios

Some of the solvents were further studied at different solvent/feed (S/F) ratios (Fig. 5). We selected a wide range of solvents with different effects. According to the experimental data, the selected solvents generally tended to have higher relative volatilities at high S/F ratios. Essentially, excess solvent improves performance, but the operating cost will rise. 1,2,4-trichlorobenzene, especially, worked much better at higher S/F ratios ($\alpha_{EB/PX}$=1.197 at S/F ratio of 6), which makes it a promising candidate to optimize the S/F ratio for extractive distillation under the proper conditions. The same tendency was shown with the binary and ternary mixtures. For the solvent with high relative volatility, for example 1,2,4-trichlorobenzene and maleic anhydride (2 : 1), there was no notable increase but still high enough compared to the others. In the S/F range from 1 to 2, however, there is not only an increase but also a decrease of the relative volatilities, which seems to have no effects on increasing the amount of solvent. Especially, the solvents with the relative volatility lower than the solvent-free performance ($\alpha_{EB/PX}$=1.067), for example ε-Caprolactam ($\alpha_{EB/PX}$=1.041), got worse with increasing S/F ratio, signifying that the high ratio itself cannot make up for a solvent with the wrong properties. In this case, large amounts of solvent actually depressed the separation because of the low individual relative volatility and larger affinity for ethylbenzene, so an S/F ratio of 1 : 1 was best for the two tested mixtures. As a result, it is important to find the minimized ratio of S/F from the industrial point of view.

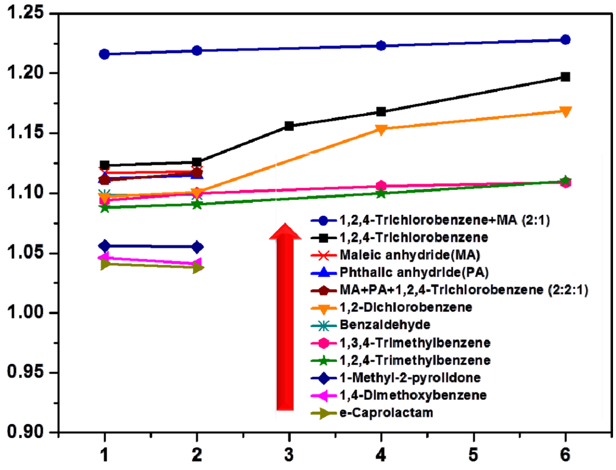

Fig. 5. Relative volatilities of selected solvents at different solvent-to-feed ratio (S/F) at an atmospheric pressure and constant temperature of 423 K.

CONCLUSIONS

An extractive distillation system was set up and various solvents and mixtures of solvents were tested to screen their ability to enhance the separation of ethylbenzene and *p*-xylene. A wide range of solvents was tested including ionic liquids, aromatics, chlorinated aromatics, carbonyls, cyclics, sulfoxides, alcohols, and more. 1,2,4-Trichlorobenzene showed the highest relative volatility for a single solvent ($\alpha_{EB/PX}$=1.123), and the oxygenated organic compounds maleic and pthalic anhydride performed nearly as well. In particular, the chlorinated aromatics and oxygenated organic compounds proved to be highly effective on the ethylbenzene and *p*-xylene separation. Selected solvents were also mixed into binary and ternary systems to enhance the separation efficiency. Mixing some solvents such as 1,2,4-trichlorobenzene and maleic acid (2 : 1), showed a high separation coefficient of 1.228. For some systems, the solvent-to-feed ratio was also varied to observe its effect. In these experiments, the solvent-to-feed ratio was an important factor, and a proper ratio was needed to optimize the effects of different solvent candidates. Although, the separation mechanism of extractive distillation is not clearly understood, this study may make it practically applicable for the separation of ethylbenzene and *p*-xylene.

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