Separation of Ethylbenzene from p- and m-Xylene by Extractive Distillation Using Mixtures of Oxygenated Organic Compounds

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BACKGROUND

The separation of ethylbenzene from p- and m-xylene by rectification is difficult because of the low relative volatility. Ethylbenzene–p-xylene is 1.06, ethylbenzene–m-xylene is 1.08. Thus, to separate ethylbenzene from p-xylene in 99% purity by conventional rectification requires a minimum of 157 theoretical plates at total reflux, somewhat more at a finite reflux ratio. With an extractive distillation agent such as 1,2,4-trichlorobenzene, the relative volatility goes to 1.11 and only 87 plates are now required. The best extractive distillation agents that were found in this work push the relative volatility up to about 1.25, and they will reduce the plate requirement to 41 plates.

Extractive distillation typically requires the addition of an equal amount to twice as much extractive agent as close boiling compounds on each plate in the rectification column. The extractive distillation agent should be heated to about the same temperature as the plate into which it is introduced. Thus, extractive distillation imposes an additional heat requirement on the column as well as somewhat larger diameter plates for the same production output.

To be economically attractive, the extractive distillation system must save more in the reduction of the number of theoretical plates and the size of the column than it adds in the cost of larger plates and additional heat requirement. This will vary depending on the difficulty of the separation and the cost of heat. In the separation of ethylbenzene from p-xylene and/or m-xylene, the extractive agent should increase the relative volatility to about 1.2 to make the process economically attractive under the equipment and heat costs in effect at the time of this investigation.

Another consideration in the selection of the extractive distillation agent is its recovery from the bottom product. The usual method is by rectification in another column. To keep the cost of this operation to a minimum, a 20°C boiling point difference between the compound being separated and the extractive agent is desirable.

Ethylbenzene is the major precursor to most processes for producing styrene. Styrene is used principally in plastics manufacture. In the preparation of high polymers, extreme purity is absolutely necessary. It is the presence of impurities that stops chain growth and prevents polymerization to the desired molecular weight. To make high purity styrene, it is necessary to use high purity ethylbenzene. Ethylbenzene is frequently found admixed with its isomers, the xylenes. Since ethylbenzene boils 2.3°C from p-xylene and 3.1°C from m-xylene, separation of ethylbenzene from these xylenes by conventional rectification to produce high purity ethylbenzene is almost impossible. One of the major sources of ethylbenzene is the C_8 fraction of hydroformed naphthenic petroleum and here the xylenes will be present with the ethylbenzene.

It was the purpose of this research to develop a system of extractive distillation that will enhance the apparent relative volatility of ethylbenzene and the xylene in their separation in a rectification column, to identify suitable mixtures of oxygenated organic compounds which will increase the apparent relative volatility of ethylbenzene to p-xylene and/or m-xylene to about 1.2 or higher which are stable and can be separated from the xylenes by rectification with relatively few theoretical plates, and finally, can be recycled to the extractive distillation column with little or no decomposition.

A mixture of approximately equal parts of phthalic anhydride and maleic anhydride when used as the agent in extractive distillation to separate ethylbenzene from p-xylene and/or m-xylene, will give a relative volatility of 1.21 when the amount of agent is between one and two parts per part of ethylbenzene–xylene mixture. When phthalic anhydride is used alone, the volatility is 1.17, when maleic anhydride is used alone, it is 1.13. Thus the mixture is considerably more effective than either the phthalic anhydride or the maleic anhydride when they are used alone.

Phthalic anhydride, maleic anhydride and phthalic anhydride–maleic anhydride mixtures melt so high that they freeze in the presence of ethylbenzene relatively close to the boiling point of ethylbenzene which is 136.15°C. While this does not preclude the use of the phthalic anhydride–maleic anhydride mixture, there is an advantage in the ease of operation to adding a third component to the phthalic anhydride–maleic anhydride mixture to lower the freezing point.

Table I lists the relative volatility of a number of the three component systems and the relative volatility of each binary combination as well as the relative volatility of the solvent. Note that the relative volatility of phthalic anhydride is 1.17, of maleic anhydride, 1.13. The relative volatility of the phthalic anhydride–maleic anhydride mixture is 1.22. In every case in Table I the ratios of the solvent to the ethylbenzene-xylene mixture is 1 and 1.5, of the binary combinations 1/2:1/2 and 3/4:3/4 per part of ethylbenzene-xylene and the phthalic anhydride-maleic anhydride-solvent is 0.4:0.4:0.2 and 0.6:0.6:0.3 per part of ethylbenzene-xylene. To evaluate the data shown in Table I, consider the first solvent listed, o-toluic acid. The mixture phthalic anhydride-maleic anhydride–o-toluic acid has a relative volatility of 1.20. Phthalic anhydride–o-toluic acid is 1.10 and 1.12, maleic anhydride–o-toluic acid is 1.11 and 1.12 and o-toluic acid alone is 1.17 and 1.11. Thus the three component mixture is considerably more effective than any of its components used singularly or in binary combinations. Table I shows this comparison for several of the solvents investigated.

The following experiment illustrates the utility of this separation. A column consisting of two 20-plate sections of 25 mm. diameter glass perforated plates equipped with a Corad constant reflux ratio distilling head and a vacuum jacket was employed. Between the Corad head and the top of the column, a feed line from a constant flow pump was introduced. The stillpot was equipped with a sampling tube. The column was calibrated with a test mixture of ethylbenzene and p-xylene, which mixture possesses a relative volatility of 1.06. At a constant reflux ratio of 10 to 1, this column calibrated twelve theoretical plates. A run was then made with a charge of approximately 20% ethylbenzene, 80% p-xylene in the stillpot. The column was operated at total reflux for about an hour, then switched to 10:1 reflux ratio and the pump started at a rate to deliver about one part of extractive agent to one part of ethylbenzene–p-xylene mixture being boiled up. The extractive agent in this example was 40% phthalic anhydride, 40% maleic anhydride and 20% isobornyl acetate. The following data were obtained:

Time, Hours	Overhead Comp., %EtBn	Stillpot Comp., %EtBn	Relative Volatility
1	46.5	13.8	1.152
2	55.9	12.32	1.202
3	57.2	12.05	1.209

It will be noted that after two hours, equilibrium has been achieved

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TABLE I. RELATIVE VOLATILITY OF SINGLE COMPONENT, BINARY AND TERNARY MIXTURES AS EXTRACTIVE DISTILLATION AGENTS

Solvent			o-Toluic Acid		Isophorone		Isobornyl Acetate	
Solvent			1.17	1.11	1.08	1.06	1.10	1.04
Phthalic Anhydride, Solvent			1.10	1.12	1.11	1.08	1.10	1.11
Maleic Anhydride, Solvent			1.11	1.12	1.16	1.09	1.09	1.15
Ph. Anh., Mal. Anh., Solvent			1.20	1.20	1.14	1.21	1.25	1.22
Solvent	Propionic anhydride		Anisole		p-Tert. Amyl Phenol		Isoborneol	
Solvent	1.02	1.04	1.15	1.09	1.16	1.07	1.08	1.06
Ph. Anh., Solvent	1.12	1.15	1.12	1.12	1.10	1.07	1.10	1.10
Mal. Anh., Solvent	1.18	1.16	1.10	1.13	1.08	1.12	1.11	1.10
Ph. Anh., Mal. Anh., Solv.	1.21	1.21	1.18	1.18	1.23	1.21	1.21	1.23
Solvent	Adiponitrile		Methyl Benzoate		Diethyl Maleate		Butyl benzyl Phthalate	
Solvent	1.05	1.09	1.07	1.08	1.07	1.09	1.10	1.18
Ph. Anh., Solvent	1.15	1.12	1.12	1.15	1.08	1.08	1.06	1.09
Mal. Anh., Solvent	1.07	1.14	1.09	1.07	1.08	1.03	1.17	1.10
Ph. Anh., Mal. Anh., Solv.	1.25	1.19			1.17	1.21	1.21	1.23
Solvent	Diethylene Glycol Diethyl Ether		Benzyl Acetate		Phenyl Acetate		Hexyl Acetate	
Solvent	1.05	1.10	1.03	1.04	1.05	1.06	1.05	1.08
Ph. Anh., Solvent	1.04	1.10	1.12	1.09	1.15	1.09	1.12	1.15
Mal. Anh., Solvent	1.18	1.11	1.06	1.09	1.12	1.06	1.11	1.15
Ph. Anh., Mal. Anh., Solv.	1.22	1.20	1.20	1.21	1.20	1.21	1.23	1.21
Solvent	2,6-Di-t-Butyl p-Cresol		2,5-Di-t-Butyl Hydroquinone		Ethylhexyl Acetate		3,5-Dimethyl Phenol	
Solvent	1.06	1.03	Will not dis.		1.15	1.15	1.13	1.05
Ph. Anh., Solvent	1.18	1.07	1.16	1.17	1.15	1.09	1.17	1.08
Mal. Anh., Solvent	1.12	1.10	1.12	1.07	1.06	1.02	1.09	1.13
Ph. Anh., Mal. Anh., Solv.	1.23	1.20	1.23	1.23	1.22	1.23	1.17	1.21
Solvent	Ethylene Glycol Butyl Ether Acetate		Ethylene Glycol Diacetate		Glycerol Triacetate		Myristic Acid	
Solvent	1.04	1.10	1.12	1.12	1.10	1.04	1.16	1.17
Ph. Anh., Solvent	1.11	1.09	1.17	1.07	1.11	1.12	1.10	1.12
Mal. Anh., Solvent	1.08	1.11	1.13	1.14	1.14	1.07	1.14	1.11
Ph. Anh., Mal. Anh., Solv.	1.21	1.21	1.23	1.20	1.20	1.20	1.22	1.23
Solvent	Acetophenone		Hexylene Glycol Diacetate		Triethylene Glycol Diacetate		Ethylene Glycol Butyl Ether	
Solvent	1.17	1.08	1.05	1.07	1.07	1.06	1.17	1.09
Ph. Anh., Solvent	1.13	1.11	1.09	1.10	1.07	1.12	1.12	1.09
Mal. Anh., Solvent	1.11	1.10	1.11	1.11	1.10	1.09	1.08	1.06
Ph. Anh., Mal. Anh., Solv.	1.16	1.19	1.23	1.22	1.15	1.22	1.18	1.20
Solvent	n-Octanol		Diethyl Oxalate		Methyl p-Hydroxy Benzoate		Butoxy Propanol	
Solvent	1.12	1.06	1.06	1.06	1.12	1.10	1.13	1.05
Ph. Anh., Solvent	1.05	1.12	1.04	1.09	1.14	1.16	1.10	1.07
Mal. Anh., Solvent	1.06	1.03	1.10	1.06	1.11	1.15	1.17	1.18
Ph. Anh., Mal. Anh., Solv.	1.19	1.23	1.21	1.22	1.20	1.22	1.19	1.22
Solvent	Propoxy-Propranol		Catechol		Ethyl Aceto-Acetate		2-Octanone	
Solvent	1.07	1.05	1.07	1.03	1.08	1.04	1.09	1.10
Ph. Anh., Solvent	1.07	1.14	1.09	1.06	1.15	1.15	1.15	1.13
Mal. Anh., Solvent	1.04	1.12	1.14	1.08	1.08	1.09	1.02	1.11
Ph. Anh., Mal. Anh., Solv.	1.19	1.19	1.23	1.21	1.20	1.21	1.20	1.20
Solvent	Benzyl Alcohol		Phenethyl Alcohol		Phenol		Benzophenone	
Solvent	1.13	1.08	1.08	1.04	1.09	1.07	1.04	1.08
Ph. Anh., Solvent	1.11	1.13	1.10	1.13	1.13	1.07	1.07	1.14
Mal. Anh., Solvent	1.11	1.08	1.09	1.14	1.11	1.09	1.13	1.03
Ph. Anh., Mal. Anh., Solv.	1.19	1.19	1.21	1.22	1.20	1.20	1.19	1.20
Solvent	p-Ethyl Phenol		Dibenzo-Furan		m-Nitro Benzoic Acid		o-Sec. Butyl Phenol	
Solvent	1.07	1.10	1.04	1.11	m.p. too high		1.13	1.05
Ph. Anh., Solvent	1.15	1.17	1.18	1.05	1.24	1.22	1.11	1.09
Mal. Anh., Solvent	1.17	1.11	1.18	decomp.	1.10	1.12	1.10	1.15
Ph. Anh., Mal. Anh., Solv.	1.20	1.22	1.21	1.21	1.22	1.20	1.21	1.21
Solvent	2-t-Butyl Phenol		Diethylene Glycol Dimethyl Ether		Hydro-bis Phenol A		Phenyl Acetic Acid	
Solvent	1.15	1.11	1.05	1.10	1.10	1.18	1.03	1.09
Ph. Anh., Solvent	1.08	1.04	1.04	1.10	1.06	1.09	1.13	1.09
Mal. Anh., Solvent	1.15	1.15	1.18	1.11	1.17	1.10	1.17	1.13
Ph. Anh., Mal. Anah., Solv.	1.20	1.21	1.22	1.20	1.21	1.23	1.21	1.22
Solvent	Cuminaldehyde		Butyrolactone		Acetonyl Acetone		4-Nitro Toluene	

TABLE I *Continued*

Solvent	1.07	1.10	1.04	1.08	1.18	1.13	1.07	1.09
Ph. Anh., Solvent	1.14	1.13	1.12	1.09	1.18	1.21	1.11	1.12
Mal. Anh., Solvent	1.09	1.06	1.17	1.14	1.16	1.10	1.09	1.13
Ph. Anh., Mal. Anh., Solv.	1.20	1.20	1.18	1.22	1.20	1.20	1.22	1.21
Solvent	Isopropyl Myristate		m-Nitrobenz-Aldehyde		Isobornyl Methyl Ether		m-Nitro Acetophenone	
Solvent	1.06	1.09	1.02	1.06	1.14	1.14	1.17	1.10
Ph. Anh., Solvent	1.11	1.04	1.15	1.18	1.13	1.16	1.10	1.05
Mal. Anh., Solvent	1.17	1.05	1.14	1.11	1.10	1.08	1.20	1.24
Ph. Anh., Mal. Anh., Solv.	1.22	1.23	1.22	1.22	1.22	1.23	1.25	1.20
Solvent	4-Nitro Phenol		2-Phenyl Phenol		2-Undecanone		Benzaldehyde	
Solvent	1.16	1.12	1.05	1.05	1.04	1.06	1.13	1.10
Ph. Anh., Solvent	1.17	1.08	1.09	1.18	1.11	1.15	1.17	1.13
Mal. Anh., Solvent	1.15	1.13	1.11	1.11	1.07	1.12	1.16	1.13
Ph. Anh., Mal. Anh., Solv.	1.23	1.23	1.21	1.21	1.21	1.20	1.20	1.21
Solvent	Diethylphenyl Malonate		p-Ethyl Benzaldehyde		Dimethyl Succinate		9-Fluorenone	
Solvent	1.09	1.08	1.03	1.10	1.07	1.10	1.09	1.17
Ph. Anh., Solvent	1.15	1.05	1.16	1.06	1.16	1.16	1.09	1.05
Mal. Anh., Solvent	1.08	1.14	1.17	1.05	1.16	1.12	1.13	1.17
Ph. Anh., Mal. Anh., Solv.	1.21	1.22	1.20	1.19	1.22	1.20	1.21	1.22

and the relative volatility remains essentially constant at about 1.21. Without extractive distillation agents, it would have been 1.06. A great many compounds and combinations were investigated and failed to enhance the relative volatility. They are listed in Berg, U.S. Patent 4,292,142 (1981).

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Effects of Gas-Adsorbate Momentum Transfer on the Movement of a Mobile Adsorbed Phase over a Uniform Surface

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INTRODUCTION

This paper examined to what degree gas-adsorbate collisions affect the behavior of surface diffusion in a mobile adsorbed phase. In earlier papers from this laboratory (Bell and Brown, 1973; 1974), it was shown that momentum exchange during the collisions between gas molecules and mobile adsorbed molecules can influence noticeably the gaseous transport within porous materials. Ignoring the effects of such collisions usually results in significant errors in the calculation of gas and surface-phase fluxes within the material (Bell and Brown, 1974; Thakur et al., 1980). The inverse-square-root-of-molecular-weight relationship, which has been employed frequently in separating the gas and adsorbate components of the total flux in the presence of surface diffusion (e.g., Jackson, 1977; Okazaki et al., 1981), is apparently not obeyed except in unusual circumstances (Thakur et al., 1980).

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