Separation by pervaporation of para and meta xylene in the presence of tetrabromide
by Randi Wright Wytcherley

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
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Abstract:
The separation of para and meta xylene was investigated by pervaporation in the presence of CBr across a polypropylene membrane. Data was collected for experimental runs varying percent p-xylene at 10%, 30%, 50%, 70%, and 90% in the para and meta xylene mixture, for temperatures of -20°C, 5°C, 22°C, 50°C, and 60°C, with zero, 10, and 24 mole % CBr4 added to the xylene mixture. Evaluation of the data determined if the degree of separation was affected by any of the variables. The results were compared using a calculated separation factor which is somewhat similar to the relative volatility in distillation. Since p-xylene is the more volatile of the two isomers, and the membrane used is selective for p-xylene, it was chosen as the basis when calculating the separation factor.

When CBr4 was added to a mixture of para and meta xylene, a solid complex was formed between the CBr and the p-xylene under certain conditions. An association between the CBr4 and p-xylene was present in the liquid phase under certain conditions. The complex or association formation was dependent on the concentration of p-xylene in the xylene mixture, the amount of CBr4 added, and the temperature. Both the solid complex and the association tied up the p-xylene in the feed and reduced the amount of p-xylene available to permeate through the membrane. The amount of m-xylene which was available to permeate through the membrane was unchanged. Therefore, more m-xylene permeated through the membrane than p-xylene and so the m-xylene was concentrated in the product. The result was an increased separability of the pervaporation process for m-xylene.

The greatest separation occurred at -20°C with 90% p-xylene in the para and meta xylene mixture, and 24 mole % CBr4 added to the xylene mixture. These conditions yielded a separation factor for p-xylene of 0.05. The inverse of the p-xylene separation factor is the separation factor for m-xylene, so under these conditions, the resulting m-xylene separation factor was 20.

In general, the separation of para and meta xylene by pervaporation can be significantly enhanced when 24 mole % CBr4 was added to the feed side of the membrane with high p-xylene content in the feed at temperatures between 5°C and -20°C.

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by

Randi Wright Wytcherley

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TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
ACKNOWLEDGMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xiv
INTRODUCTION	1
Separating the Xylenes	2
Pervaporation	4
Previous Related Work	6
Selective Complex Formation with Aromatics	7
Separation Factor	11
RESEARCH OBJECTIVES	13
EXPERIMENTAL APPARATUS AND PROCEDURE	14
Pervaporation Test Cell	14
Constant Temperature Bath and Circulating System	17
Vacuum System and Cold Traps	18
Product Analysis	18
Experimental Procedure	18
RESULTS AND DISCUSSION	21
Discussion of Results	38
p-Xylene, m-Xylene and CBr_4 System	40

TABLE OF CONTENTS--Continued

	Page
Formation of CBr_4 · p-xylene Association in Liquid Phase	52
Carbon Tetrabromide in Product	53
Advantage of Using Pervaporation Process	54
Effect of Complexing Agent on Flux	55
CONCLUSIONS	59
SUGGESTIONS FOR FUTURE RESEARCH	61
LITERATURE CITED	62
APPENDIX	65
Cross Plots for Figures 13 through 17	65

LIST OF TABLES

Table		Page
1.	Physical Data for the C_8 Aromatics.....	2
2.	Various Mole % CBr_4 Added to Xylene Feed Mixture to Complex with the p-Xylene.....	19
3.	Initial Crystallization Temperatures for Binary Mixtures of p-Xylene and m-Xylene....	39
4.	Melting Points for the $CBr_4 \cdot$ p-xylene complex at High Concentrations of p-Xylene in the Xylene Feed Mixture.....	53
5.	CBr_4 Present in the Product of the 30/70 Ratio (para to meta) Xylene Run with 10 mole % CBr_4.....	53
6.	Flux for the Runs at 0, 10, and 24 Mole % CBr_4.....	57

LIST OF FIGURES

Figure Page

1. Initial crystallization temperature of binary mixtures of carbon tetrachloride and a xylene with the eutectic points circled..... 8

2. Initial crystallization temperature of binary mixtures of carbon tetrabromide and a xylene with the eutectic points circled..... 10

3. Pervaporation Equimpment Diagram..... 15

4. Pervaporation Test Cell..... 16

5. Separation factors vs temperature at varying percent p-xylene in the para and meta xylene mixture across a polypropylene membrane with no CBr_4 added..... 22

6. Percent p-xylene in the product as a function of the % p-xylene in the feed at varying temperatures with no CBr_4 added..... 23

7. Separation factor vs temperature for 10% p-xylene and varying % CBr_4 additions..... 24

LIST OF FIGURES--Continued

Figure | Page

8. Separation factor vs temperature for 30% p-xylene and varying % CBr_4 additions..... 25

9. Separation factor vs temperature for 50% p-xylene and varying % CBr_4 additions..... 26

10. Separation factor vs temperature for 70% p-xylene and varying % CBr_4 additions..... 27

11. Separation factor vs temperature for 90% p-xylene and varying % CBr_4 additions..... 28

12. Percent p-xylene in product as a function of % p-xylene in feed with 10 and 24 mole % CBr_4 added at 60°C..... 29

13. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr_4 added at 50°C..... 30

14. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr_4 added at 22°C..... 31

15. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr_4 added at 5°C..... 32

LIST OF FIGURES--Continued

Figure Page

16. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr_4 added at -20°C..... 33

17. Freezing point diagrams for mixtures of p-xylene, m-xylene, and CCl_4, and p-xylene, m-xylene, and CBr_4..... 42

18. Mole % CBr_4 present in liquid phase as a function of p-xylene concentration in the para and meta xylene mixture at 22°C with an initial concentration of CBr_4 at 24 mole%..... 46

19. Freezing point diagram for mixtures of p-xylene, m-xylene, and CBr_4..... 48

20. Freezing point diagram for mixtures of p-xylene, m-xylene, and CBr_4..... 51

21. Average flux for pervaporation process with 0, 10, and 24 mole % CBr_4 added..... 56

22. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with no CBr_4 added..... 66

23. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with no CBr_4 added..... 67

LIST OF FIGURES--Continued

Figure Page

24. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 50% p-xylene in the xylene mixture with no CBr_4 added..... 68

25. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 70% p-xylene in the xylene mixture with no CBr_4 added..... 69

26. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 90% p-xylene in the xylene mixture with no CBr_4 added..... 70

27. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with 10 mole % CBr_4 added..... 71

28. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with 10 mole % CBr_4 added..... 72

29. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 50% p-xylene in the xylene mixture with 10 mole % CBr_4 added..... 73

LIST OF FIGURES--Continued

Figure Page

30. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 70% p-xylene in the xylene mixture with 10 mole % CBr_4 added..... 74

31. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 90% p-xylene in the xylene mixture with 10 mole % CBr_4 added..... 75

32. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with 24 mole % CBr_4 added..... 76

33. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with 24 mole % CBr_4 added..... 77

34. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 50% p-xylene in the xylene mixture with 24 mole % CBr_4 added..... 78

35. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 70% p-xylene in the xylene mixture with 24 mole % CBr_4 added..... 79

LIST OF FIGURES--Continued

Figure Page

36. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 90% p-xylene in the xylene mixture with 24 mole % CBr_4 added..... 80

ABSTRACT

The separation of para and meta xylene was investigated by pervaporation in the presence of CBr_4 across a polypropylene membrane. Data was collected for experimental runs varying percent p-xylene at 10%, 30%, 50%, 70%, and 90% in the para and meta xylene mixture, for temperatures of -20°C, 5°C, 22°C, 50°C, and 60°C, with zero, 10, and 24 mole % CBr_4 added to the xylene mixture. Evaluation of the data determined if the degree of separation was affected by any of the variables. The results were compared using a calculated separation factor which is somewhat similar to the relative volatility in distillation. Since p-xylene is the more volatile of the two isomers, and the membrane used is selective for p-xylene, it was chosen as the basis when calculating the separation factor.

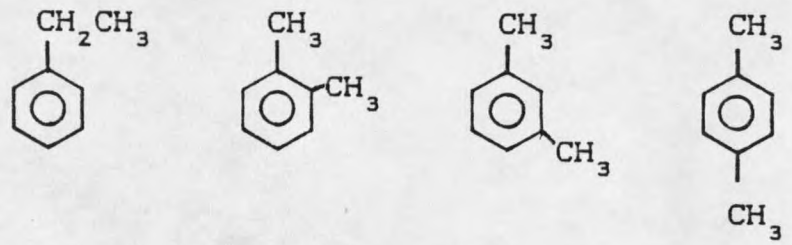
When CBr_4 was added to a mixture of para and meta xylene, a solid complex was formed between the CBr_4 and the p-xylene under certain conditions. An association between the CBr_4 and p-xylene was present in the liquid phase under certain conditions. The complex or association formation was dependent on the concentration of p-xylene in the xylene mixture, the amount of CBr_4 added, and the temperature. Both the solid complex and the association tied up the p-xylene in the feed and reduced the amount of p-xylene available to permeate through the membrane. The amount of m-xylene which was available to permeate through the membrane was unchanged. Therefore, more m-xylene permeated through the membrane than p-xylene and so the m-xylene was concentrated in the product. The result was an increased separability of the pervaporation process for m-xylene.

The greatest separation occurred at -20°C with 90% p-xylene in the para and meta xylene mixture, and 24 mole % CBr_4 added to the xylene mixture. These conditions yielded a separation factor for p-xylene of 0.05. The inverse of the p-xylene separation factor is the separation factor for m-xylene, so under these conditions, the resulting m-xylene separation factor was 20.

In general, the separation of para and meta xylene by pervaporation can be significantly enhanced when 24 mole % CBr_4 was added to the feed side of the membrane with high p-xylene content in the feed at temperatures between 5°C and -20°C.

INTRODUCTION

Xylenes are important ingredients for the manufacture of plastics and dyes. But in order for the xylenes to be useful they must be high in purity. Xylenes are produced in petroleum refining as a by product from catalytic reforming. They are produced as a mixture of the isomers, ortho (o), meta (m), and para (p), along with ethylbenzene in varying compositions depending on the conditions in the reformer. The structure of these isomers are:



ethylbenzene o-xylene m-xylene p-xylene

The boiling points and melting points for the isomers along with the relative volatilities of the various combinations of the isomers are shown in Table 1 to emphasize the challenging separation problem that this presents.

Table 1. Physical Data for the C_8 Aromatics

a. Boiling points and melting points of the C_8 aromatics

ISOMER	B P	M P
ethylbenzene	136.2 C	-94.4 C
o-xylene	144.4 C	-25.2 C
m-xylene	139.1 C	-47.9 C
p-xylene	138.4 C	13.3 C

b. Relative volatility for binary combinations (1)

BINARY MIXTURE	RELATIVE VOLATILITY
ethylbenzene + o-xylene	1.34
p-xylene + o-xylene	1.28
m-xylene + o-xylene	1.22
ethylbenzene + m-xylene	1.08
ethylbenzene + p-xylene	1.06
p-xylene + m-xylene	1.01

Separating the Xylene Isomers

In order for the isomers to be effectively separated by distillation the relative volatility must be greater than 1.0. If the relative volatility is equal to 1.0, then no separation of the compounds occur. If the relative volatility is greater than 1.0, then the first component listed in Table 1b is concentrated in the product. If the relative volatility is between zero and 1.0 then the second component listed in Table 1b would be the one concentrated in the product. For economical separation by distillation a relative volatility of about 1.25 is necessary (2).

The ethylbenzene and ortho xylene are usually separated from the mixture of isomers by distillation with a large number of plates (3). The challenge comes with the

separation of the para and meta xylenes. The relative volatility of their binary mixture is equal to 1.01, therefore separation by normal distillation is not feasible as it would require an extremely large number of stages at very high reflux ratio.

Several processes have been developed for the separation of para and meta xylene. Some processes are based on crystallization or solvent extraction in the presence of $HF-BF_3$ (4). Currently, the most successful separation method is the Parex process, which was developed by UOP, Inc. (5). This process is based on adsorption by a zeolite in a process that utilizes a complex and expensive rotary valve which allows simulation of a moving bed operation. In principle, this adsorption system operates as a chromatographic column. The xylene mixture is fed to the unit as a pulse followed by a pulse of the desorbent. The unit outlet is collected alternatively as m-xylene and desorbent or p-xylene and desorbent (6).

More recently, another process, based on the same principle, has been developed by Asahi (7). A different type of zeolite with an appropriate desorbent fluid is used in order to improve the displacement chromatography effect of the separation. Both processes are based on the selective adsorption of a liquid mixture of xylene isomers on zeolite. In the above processes the separation of liquid mixtures of the xylenes has been carried out by adsorption

on zeolite particles. Recently Carra et al. proposed the same separation in the gaseous phase (8). Research continues in this area since the commercial methods currently used are very complicated and energy intensive.

Pervaporation

Pervaporation is a membrane separation process used to fractionate liquid mixtures. Like other separation processes, membrane processes take a feed stream and separate it into two product streams. In one the target species is concentrated and in the other the target species is depleted. In pervaporation a liquid feed is placed in contact with one side of a nonporous membrane. The components of the feed mixture pass through the membrane and leave the downstream side as a vapor. The driving force for separation is the difference in chemical potential between the liquid and the vapor phases. The driving force for the permeation may be attributed to the pressure and concentration differences across the membrane.

There are a few theories as to the behavior of the permeating molecules during pervaporation. One possible theory was proposed by Binning et al. (9) which involves a three step process: 1. Solution of liquid into the film surface in contact with the liquid charge mixture; 2. migration through the body of the film; 3. vaporization of the permeating material at the downstream interface where

the permeate is immediately swept away. With this theory, the permeation rate and separation of the mixture cannot be predicted by the permeation rates of the individual components in the feed since the membrane structure may change due to swelling (10).

Another proposal as to the behavior of the permeating molecules is that in which Michaels et al. (11) postulated that the membrane acted as a simple molecular sieve or screen. In this case the permeation rate of a mixture could be predicted from the permeation rates of the individual components.

The pervaporation process uses nonporous membranes. The permselectivity of these membranes comes from properties inherent to the membrane material. Permselectivity is defined as the rates of flux of the two isomers under equal partial pressure driving forces (12). The permselectivity generally depends on the diffusivity and the solubility of the species being separated in the membrane material. The permselectivity is best when there is a large difference in either the diffusivity or the solubility of the permeating species and the rejected species.

Diffusivity is dependent on molecular size and shape as well as the mechanical properties of the polymer. However, the chemistry of the polymer is also very important. The chemical interactions affect the solubility of the species

in the membrane. In principle, the more soluble a species, the higher the permeability (13).

Pervaporation can sometimes prove helpful in the separation of certain mixtures which are otherwise hard to separate. Liquid mixtures which form azeotropes or which have very close vapor pressures are virtually impossible to separate by conventional distillation. Since pervaporation separation depends on the mechanical properties and the chemical interactions between the molecules and the membrane, a successful separation of close boiling components is sometimes possible.

Previous Related Work

Selective complex formation occurs when an agent is used which forms a complex between the agent and a specific component. The formation of this complex can increase or at least change the selectivity of membrane processes.

Work has been done at Montana State University in the past where the membrane itself was modified using Werner complexes (14). The result was an increased selectivity for the target species.

Recently, work has been done in coupled transport or facilitated transport which somewhat overcomes the membranes inability to make clean separations (15). Selectivity comes from the incorporation of a specific carrier within the membrane. This carrier forms a complex with the target

species on the feed side of the membrane; the complex then diffuses through the membrane and the target species is released on the product side of the membrane.

Another approach is based on the idea of changing the nature of the target species in the feed solution so the membrane will be either more or less permeable to it. This has been done with reverse osmosis (RO) where a complex was formed resulting in a higher molecular weight species (16). The RO membrane is less permeable to the higher molecular weight complex than to the target species. The same idea has been applied to ultrafiltration for removal of toxic heavy metal ions (17). Complexing agents were used to tie up the heavy metal ions, the solution was then ultrafiltered, the metal complex broken and the complexing agent recovered for re-use.

Selective Complex Formation with Aromatics

Previous work discussed by Egan et al. (18) has indicated the formation of solid molecular addition complexes between C_6, C_8, C_9, and C_{10} aromatics with tetrahalogenated methanes. An equimolal complex is formed between CCl_4 and p-xylene which freezes at -3.9°C. Figure 1 shows the temperature of initial crystallization for the binary mixtures of CCl_4 and the xylene isomers (19). A single eutectic observed in the case of meta xylene indicates no complex was formed. Other tetrahalogenated

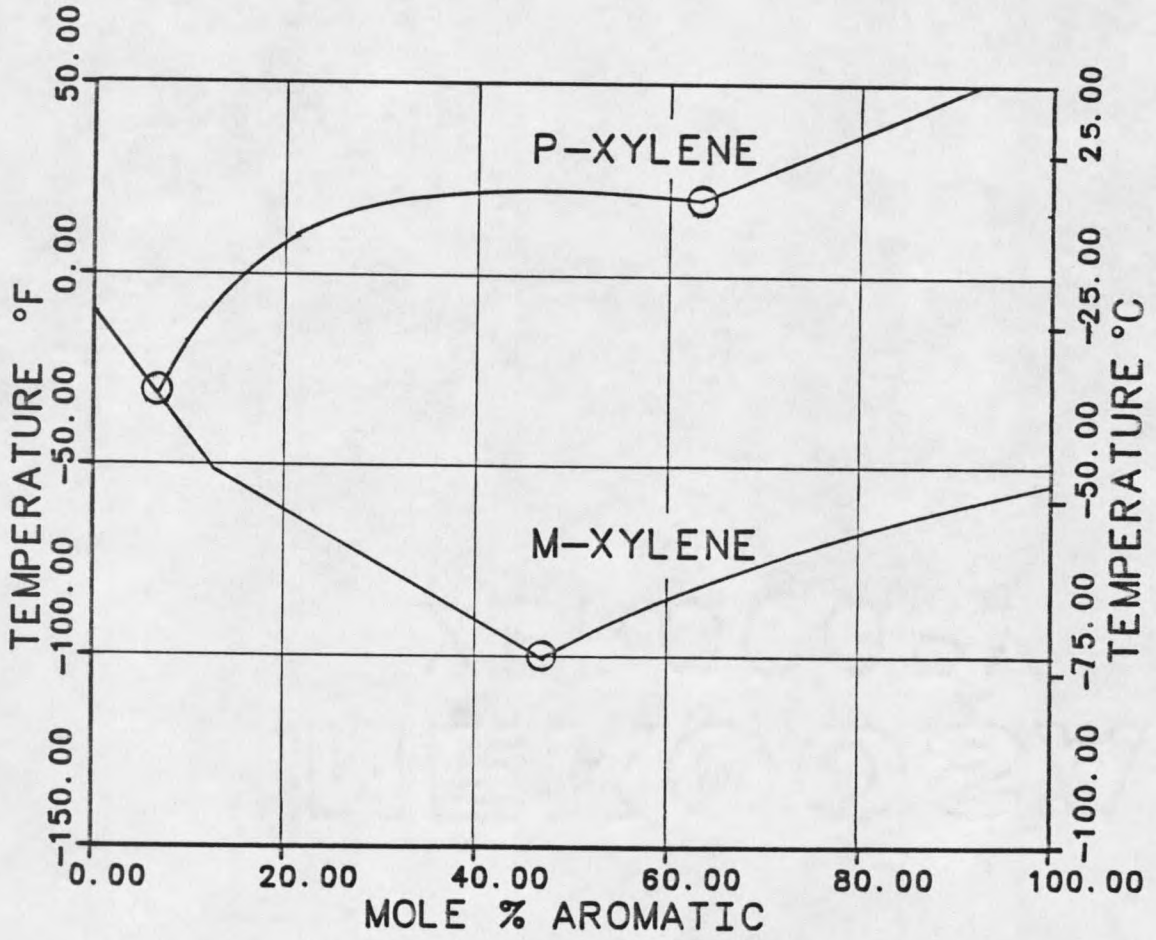


Figure 1. Initial crystallization temperature of binary mixtures of carbon tetrachloride and a xylene. with the eutectic points circled.

methanes were also found to form solid addition compounds with p-xylene. One of these was CBr_4, which was found to form an equimolal complex that freezes at 53.3°C. Figure 2 shows the temperatures where initial crystallization occurred for the binary mixtures of CBr_4 and the xylene isomers (20). Carbon tetrabromide had complex formation with both of the xylene isomers and so was not as selective in forming complexes as CCl_4 which formed a complex with only p-xylene. Complex formation is indicated for both para and meta xylene with CBr_4 since two eutectics are present for each binary mixture. The eutectic points are circled in Figures 1 and 2.

This research project involves the separation of the para and meta xylene isomers in the presence of CBr_4. Under certain conditions a molecular complex is formed between the CBr_4 and the p-xylene. The presence of the molecular complex of CBr_4 and p-xylene in the feed solution reduces the amount of p-xylene which is available to permeate through the polypropylene membrane. This decrease in the amount of p-xylene available to permeate results in less p-xylene present in the product. The amount of m-xylene available to permeate through the membrane is not affected. The result is an increase of separability of the process for m-xylene, with more m-xylene appearing in the product than in the feed. CBr_4 was chosen as the complexing agent