



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 CBr₄ 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 CBr₄ 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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IN THE PRESENCE OF CARBON TETRABROMIDE

by

Randi Wright Wytcherley

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

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MONTANA STATE UNIVERSITY
Bozeman, Montana

May 1987

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ACKNOWLEDGMENTS

The author would like to thank the faculty and staff of the Chemical Engineering Department at Montana State University for their guidance and assistance. The advice and encouragement given throughout the course of this research by my advisor, Dr. F.P. McCandless, is greatly appreciated. The author also wishes to thank Dr. Bradford P. Mundy and doctorate candidate Mr. Dave Barnekow of the Chemistry Department at Montana State University for their assistance with the infrared spectroscopy.

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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.

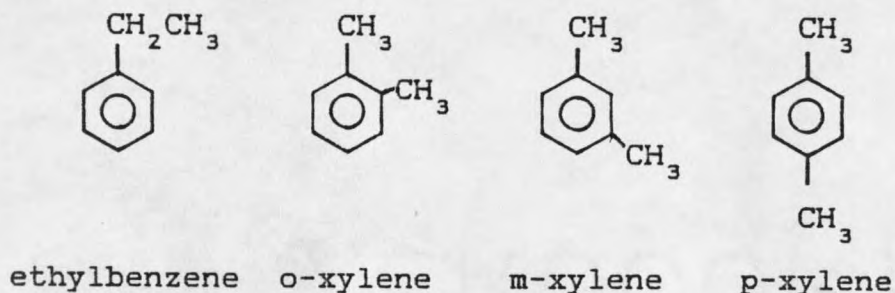
When CBr_4 was added to a mixture of para and meta xylene, a solid complex was formed between the CBr_4 and the p-xylene under certain conditions. An association between the CBr_4 and p-xylene was present in the liquid phase under certain conditions. The complex or association formation was dependent 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:



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 C₈ Aromaticsa. Boiling points and melting points of the C₈ aromatics

ISOMER	B P	M P ^a
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 equimolar complex is formed between CCl_4 and p-xylene which freezes at $-3.9^\circ C$. 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

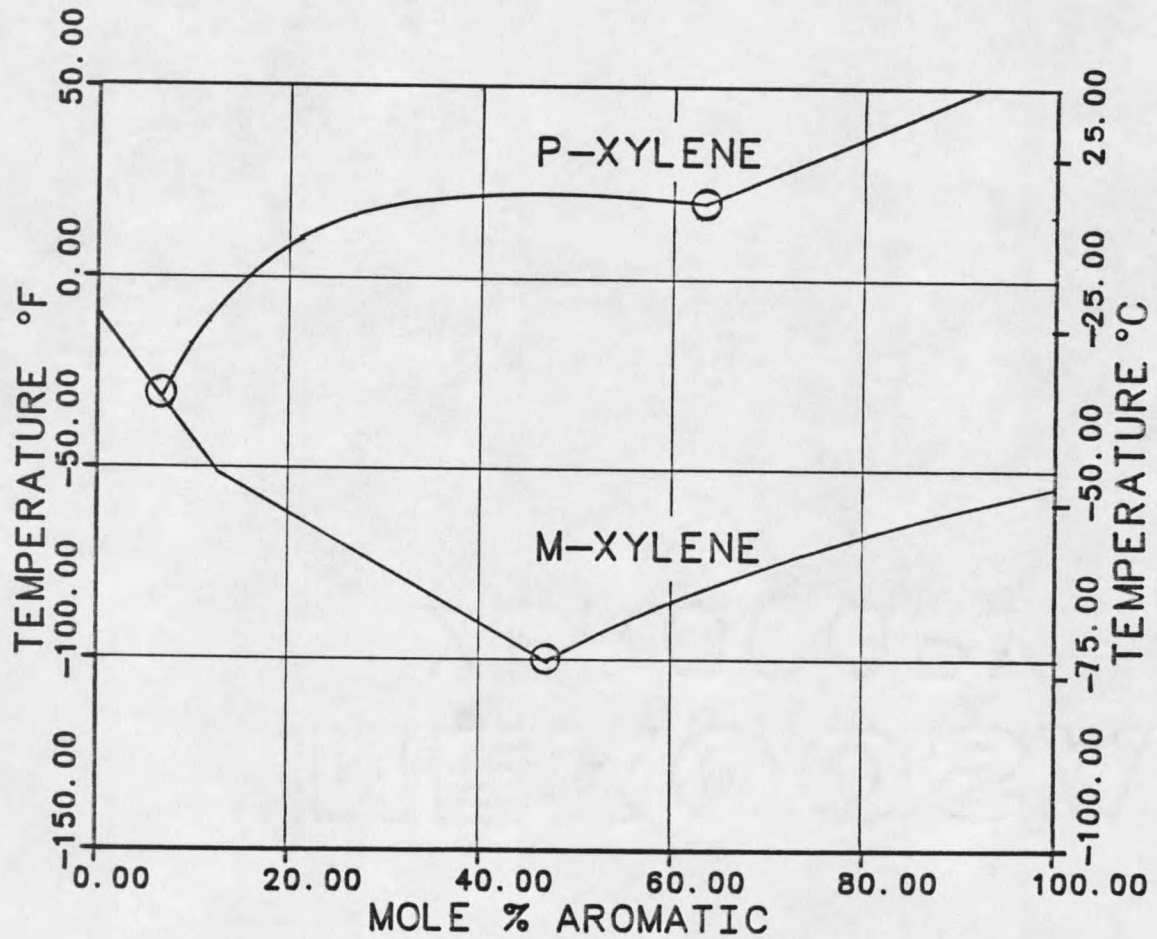


Figure 1. Initial crystallization temperature of binary mixtures of carbon tetrachloride and a xylene. with the eutectic points circled.

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

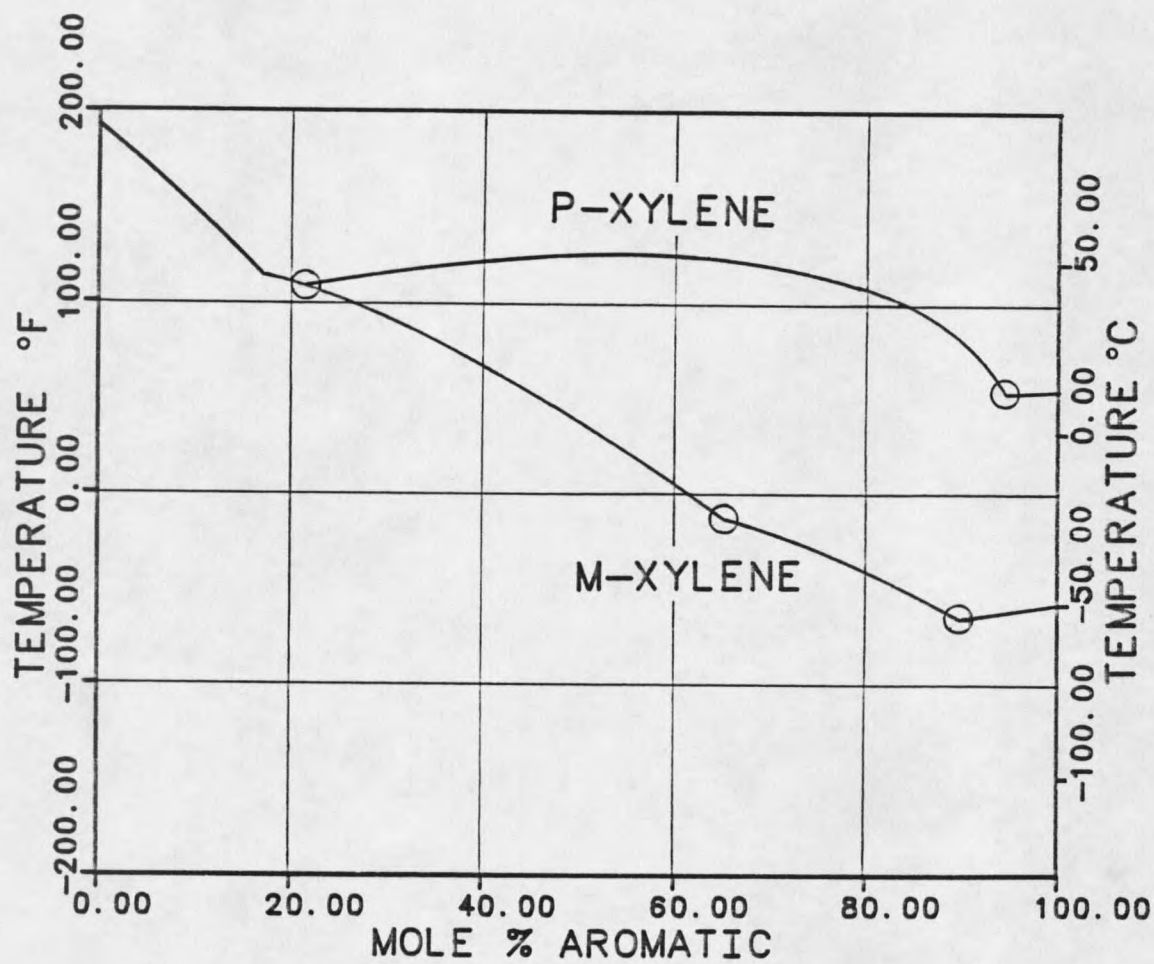


Figure 2. Initial crystallization temperature of binary mixtures of carbon tetrabromide and a xylene with the eutectic points circled.

since it has a higher temperature of complex formation and it is less toxic than CCl_4 .

Due to the limited availability of membrane material, a Dupont polypropylene membrane which was on hand was used. Since the complexing agent tied up the p-xylene while the membrane was selective to the p-xylene, the separability of the para to meta xylene varied greatly, depending on which effect was greater.

Separation Factor

The separation factor (α) is calculated using the following equation:

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

α = separation factor with respect to p-xylene
y = fraction p-xylene in product
x = fraction p-xylene in feed

This equation gives a separation factor in terms of p-xylene. The separation factor is somewhat similar to the relative volatility in distillation. If the separation factor is greater than 1.0, there would be a greater transfer of p-xylene across the membrane than m-xylene or the membrane would be selective to the p-xylene. If the separation factor is between 0.0 and 1.0 the membrane is selective for the m-xylene. In the research, the interest lay in decreasing the amount of p-xylene available in the feed, which could diffuse through the membrane, by

complexing it with the carbon tetrabromide. Since the amount of m-xylene available to permeate through the membrane was unchanged, the m-xylene was concentrated in the product. This would appear as a lower separation factor or an increased selectivity of the process for m-xylene.

RESEARCH OBJECTIVES

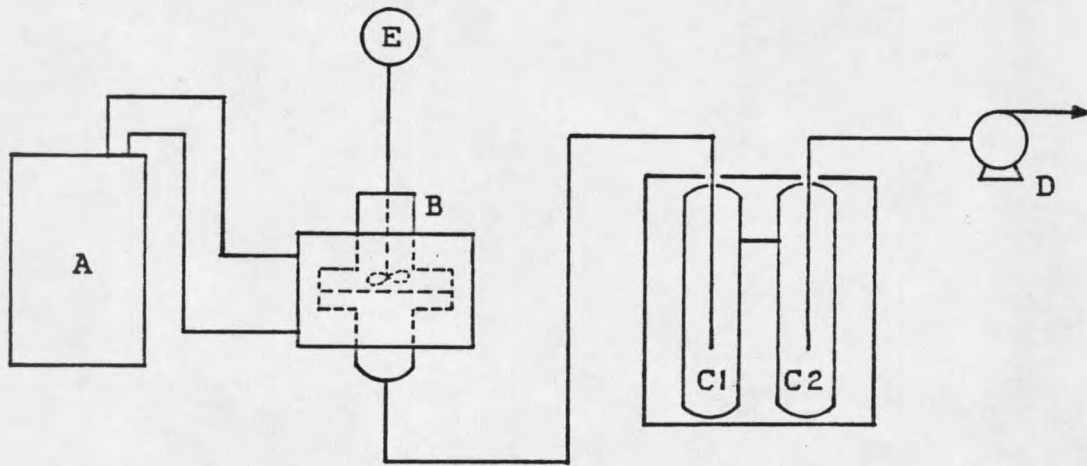
This research was conducted to determine if the addition of carbon tetrabromide as a complexing agent would change the pervaporation separation of a liquid mixture containing para and meta xylene. The effects of adding carbon tetrabromide to the xylene feed mixture were examined to determine if the p-xylene available to permeate through the membrane decreased, thereby increasing the m-xylene in the product. The effect of concentration of the CBr_4 and p-xylene along with the temperature was investigated for both the complexing and the separability.

EXPERIMENTAL APPARATUS AND PROCEDURE

A pervaporation test cell was used to conduct the experiments for separation of the para and meta xylene. Figure 3 illustrates the equipment setup. The known concentration of liquid feed was placed in (B) the pervaporation cell where it was constantly mixed (E). The constant temperature bath and circulation system (A) controlled the temperature of the liquid feed in the cell. The vacuum system (D) pulled the vapor product into the cold traps (C) where it was crystallized using liquid nitrogen as the cooling medium. When a sufficient amount of product had been collected in C1, the vacuum pump was turned off and the product was weighed on a Mettler P1200 balance to ± 0.01 grams and analyzed using a gas chromatograph (GC).

Pervaporation Test Cell

The pervaporation test cell is shown in detail in Figure 4. The test cell was constructed of two 8 cm diameter stainless steel flat face flanges made by modifying a large pipe union. These were held together by a large stainless steel nut. Inside the bottom flange was space for a 3.8 cm diameter perforated disc and filter paper which was used to support the membrane. This flange was



- A. Controlled Temperature Bath and Circulating System
- B. Pervaporation Cell
- C. Cold Traps
- D. Vacuum Pump
- E. Mixer

Figure 3. Pervaporation Equipment Diagram.

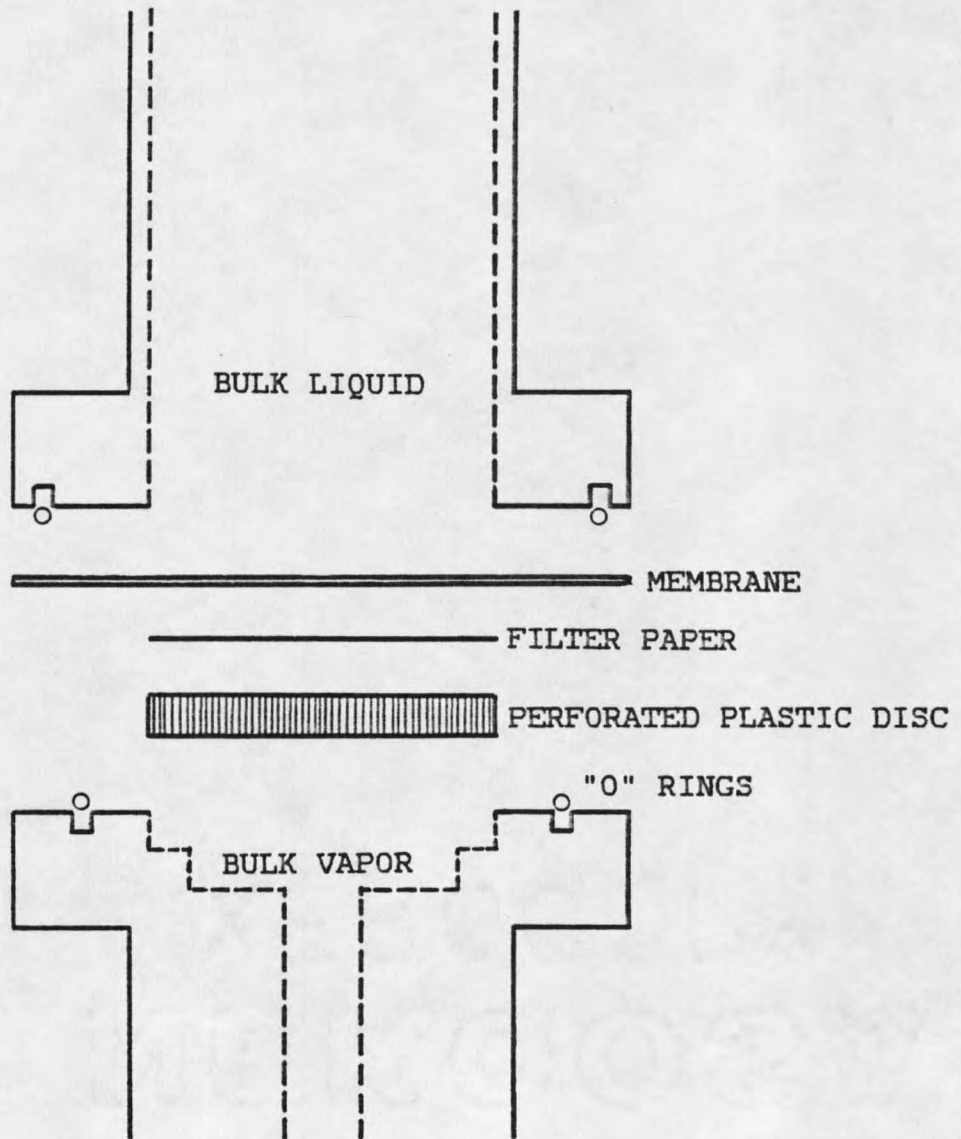


Figure 4. Pervaporation Test Cell.

connected to the vacuum system with swedgelock fittings and 1/2" teflon tubing. The top flange had threads to match the large nut and an open cavity to hold the liquid feed. This feed was constantly mixed to avoid any concentration gradients against the membrane. The Dupont polypropylene, Clysar® 350P-1A3, 20 μ m, membrane was held between the two flanges and the large nut tightened securely to prevent any leakage. Two viton "O" rings were offset on the flanges to provide the protection against leakage.

The liquid feed was placed in the upper flange cavity where the mixer simulated a perfectly mixed system. The mixer consisted of a converted variable speed drill with a variac power control.

Constant Temperature Bath and Circulating System

The constant temperature bath was a 2095 Bath and Circulator made by Masterline Forma Scientific. This had the capability of circulating an ethylene glycol/water mixture held at a specified temperature. The ethylene glycol/water mixture was circulated through insulated tubing into insulated casing which surrounded both upper and lower flanges. The temperature of the liquid feed was monitored by a 2108A digital thermometer (manufactured by Fluke). The feed could be controlled to a temperature usually within $\pm 1^{\circ}\text{C}$. The temperatures ranged from -23°C to 61°C depending on the temperature desired.

Vacuum System and Cold Traps

Two cold finger Pyrex condensers were connected in series to the vacuum line and to the test cell using ground glass fittings and spring clamps. One condenser collected the permeate while the other was used to prevent back diffusion from the vacuum pump and mercury manometer. The condensers were placed in a dewer flask containing liquid nitrogen. A two stage duo-seal vacuum pump running at capacity provided a vacuum of 0.5 μm Hg. The vacuum was monitored by a mercury U-tube monometer and at times a McCloud guage.

Product Analysis

A quantitative analysis of the permeate was found using a Varian Aerograph Series 1400 gas chromatograph and Sargent-Welch recorder, model SRG. The column was packed with Bentone 34 modified with diisodecylphthalate for the para and meta xylene analyses, but for the quantitative determination of CBr_4 , SR-30 packing was required. SR-30 packing is also known as a boiling point packing. The analyses usually required 1 hour to 1 1/2 hours and the peaks quantified using a disc integrater.

Experimental Procedure

At the beginning of a run a fresh membrane was placed between the flanges. The upper flange was greased with

vacuum grease and placed on a sheet of Dupont polypropylene membrane to serve as the cutting pattern. The membrane was cut to size around the flange. The flanges were then carefully placed together to avoid wrinkling the membrane and securely fastened together with the large nut.

Twenty to forty grams of the feed mixture were placed in the feed cavity. The amount of feed required was dependent on the number of runs to be made with a membrane. A fresh membrane was used for each different feed composition. Runs were made varying the following three parameters:

1. concentration of the complexing agent
2. ratio of the para to meta xylene
3. temperature

The combinations studied are presented in Table 2. Each set of runs made using a single membrane consisted of a specific mixture of CBr_4 , p-xylene, and m-xylene, separated

Table 2. Various Mole % CBr_4 Added to Complex with p-Xylene in the Para and Meta Xylene Feed Mixture.

TEMPERATURE °C	-20	5	22	50	60
RATIO OF p/m					
10/90	0,10,24	0,10,24	0,10,24	0,10,24	10,24
30/70	0,10,24	0,10,24	0,10,24	0,10,24	10,24
50/50	0,10,24	0,10,24	0,10,24	0,10,24	10,24
70/30	0,10,24	0,10,24	0,10,24	0,10,24	10,24
90/10	0,10,24	0,10,24	0,10,24	0,10,24	10,24

at the various temperatures of approximately -20°C , 5°C , 22°C , 50°C , and 60°C . The warmer temperatures did not seem to significantly improve the separation obtained when no CBr_4 was present. Therefore the 60°C runs were only made where there was some CBr_4 present. Under these conditions the CBr_4 was completely soluble in the feed mixtures.

Prior to each run, the cold finger pyrex condenser used to collect the product was cleaned, dried and weighed. The dry weight was recorded to use in determining the amount of product collected. After the system was assembled, the liquid feed was allowed to reach a steady state temperature and the vacuum pump was started. At this point the time was recorded along with the feed temperature, and barometric pressure. The run time varied depending on the amount of product collected. This was determined by visual examination. The maximum run time was during the -20°C runs and was about 48 hours. At 60°C , the run time was usually only about 1 hour.

After a sufficient amount of product was collected in the cold finger Pyrex condenser, the vacuum line was disconnected. The Pyrex condenser with the product was then warmed to room temperature and weighed. The time, temperature, and product weight were recorded.

RESULTS AND DISCUSSION

Figure 5 illustrates the separation factors (α) vs temperature obtained from the pervaporation separation at varying percent p-xylene across a polypropylene membrane with no CBr_4 added. Figure 6 presents the same results but in terms of an x vs y diagram, or the % p-xylene in the product vs the % p-xylene in the feed with no CBr_4 added.

The separation factors obtained when the complexing agent was added can be seen plotted against temperature in Figures 7 through 11. Figures 12 through 16 present the effect of adding CBr_4 in terms of % p-xylene in the product vs % p-xylene in the feed.

Figure 5 illustrates how the selectivity of the process changed depending on temperature and the % p-xylene in the para and meta xylene feed mixture. With 10% and 30% p-xylene in the feed mixture, the separation process was selective for p-xylene at all temperatures. When the separation factors were greater than 1.0, the p-xylene was concentrated in the product and the process was selective for p-xylene. For the 50%, 70%, and 90% p-xylene mixtures, the separation process was selective for p-xylene only at the warmer temperatures. With 50% and 70% p-xylene in the feed mixture, when the temperature was lowered to -20°C , the

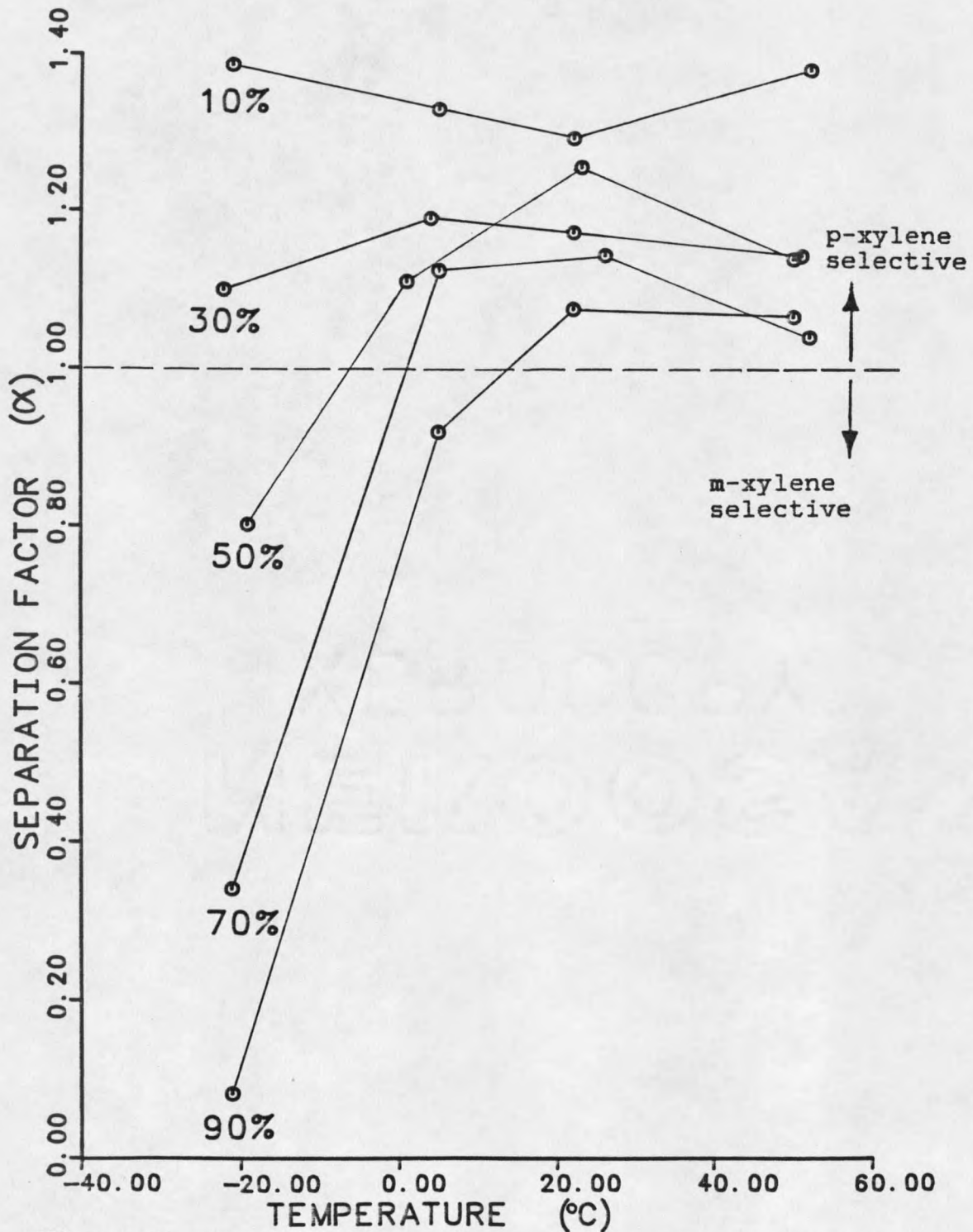


Figure 5. Separation factors vs temperature at varying percent p-xylene in the para and meta xylene mixture across a polypropylene membrane with no CBr_4 added.

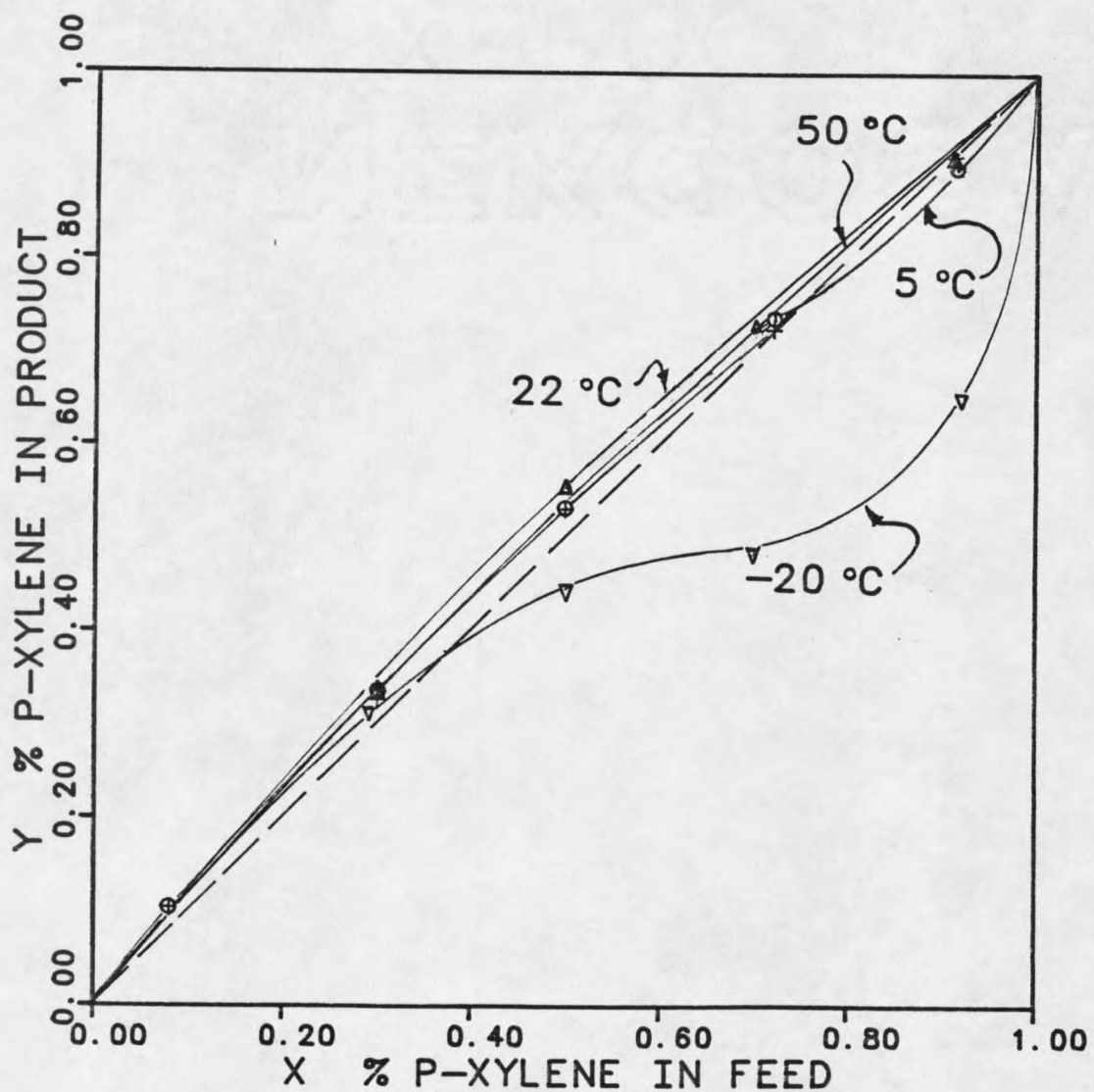


Figure 6. Percent p-xylene in product as a function of % p-xylene in feed at varying temperatures with no CBr_4 added.

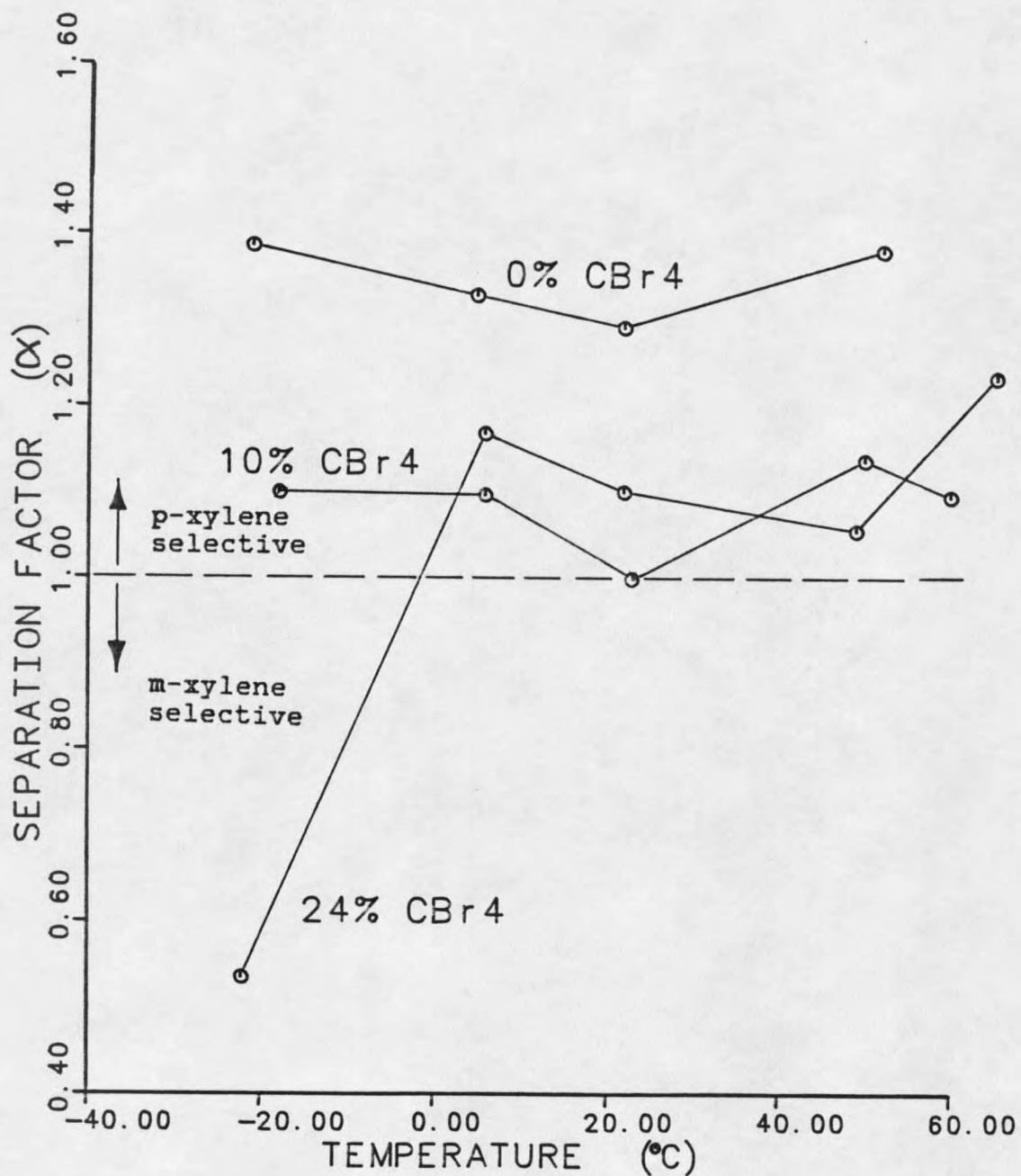


Figure 7. Separation factor vs temperature for 10% p-xylene and varying % CBr₄ additions.

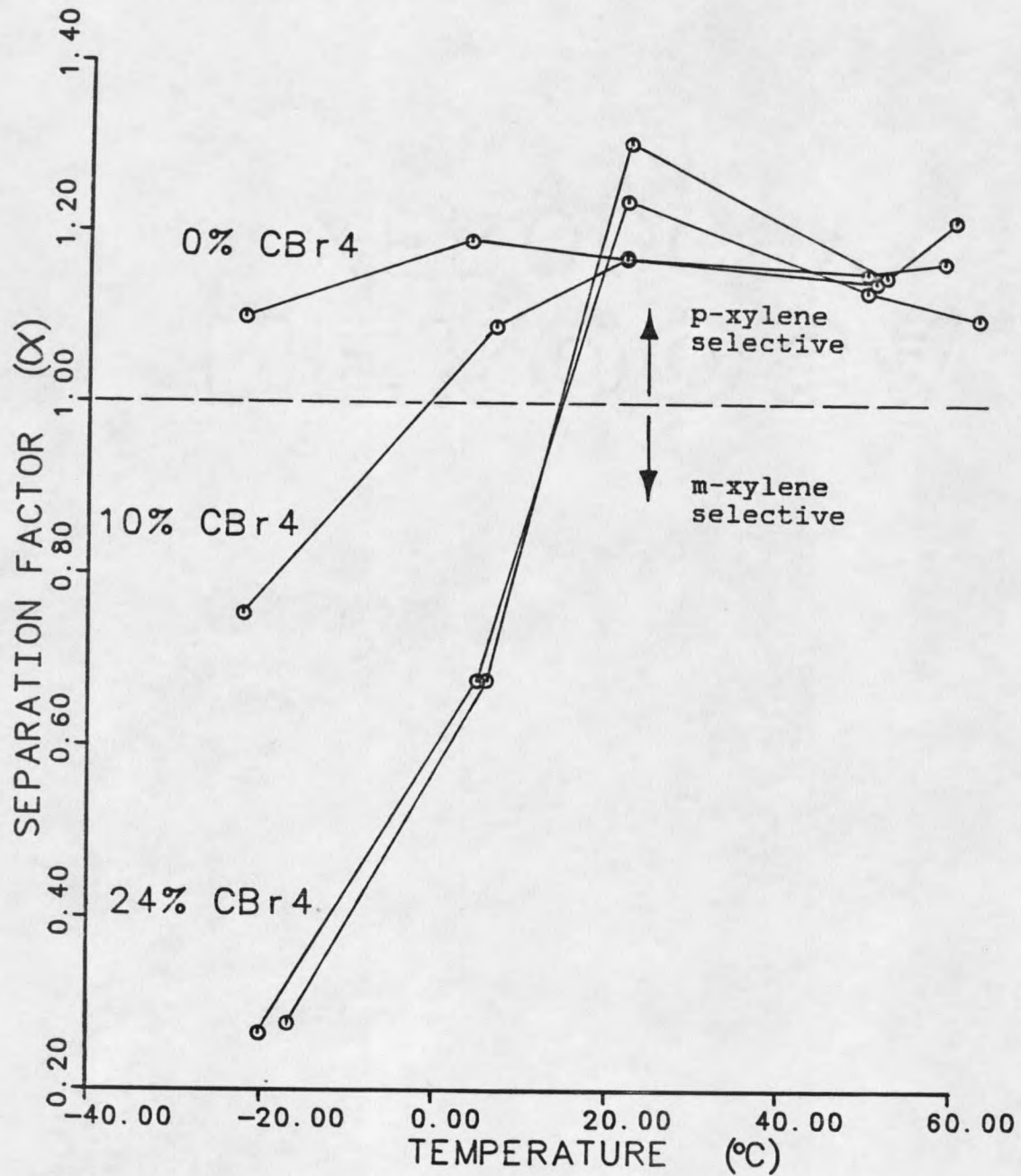


Figure 8. Separation factor vs temperature for 30% p-xylene and varying % CBr₄ additions.

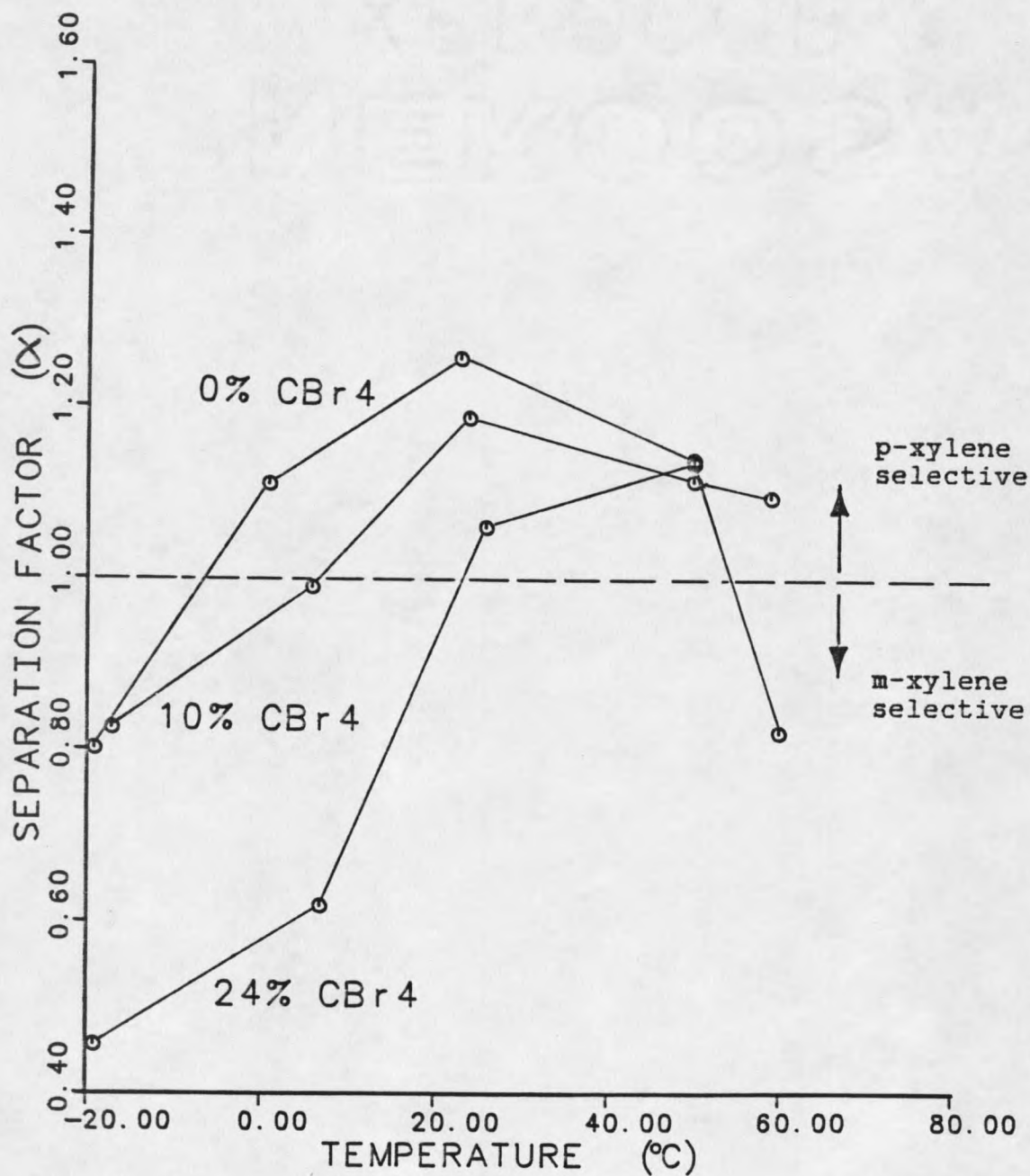


Figure 9. Separation factor vs temperature for 50% p-xylene and varying % CBr₄ additions.

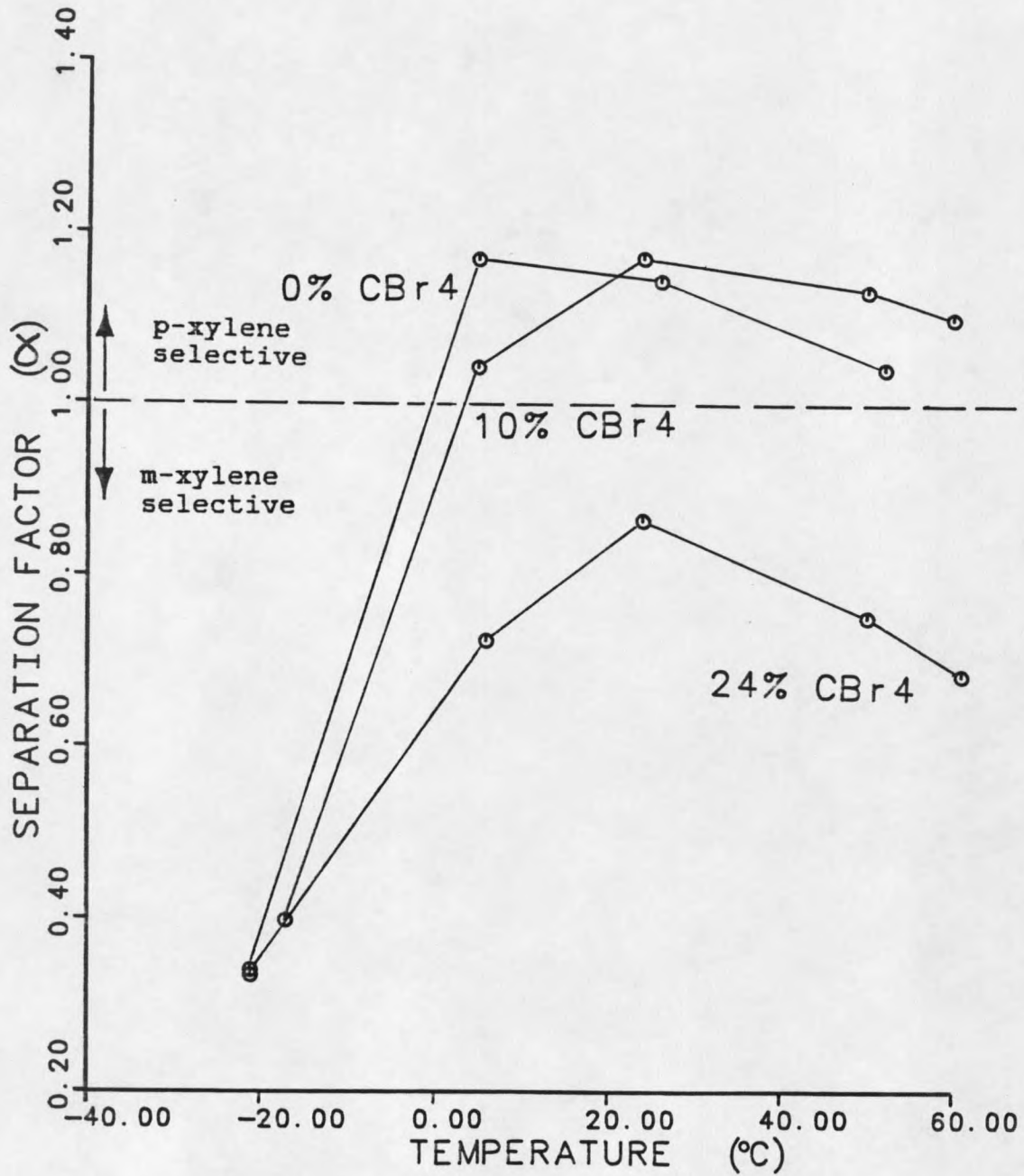


Figure 10. Separation factor vs temperature for 70% p-xylene and varying % CBr₄ additions.

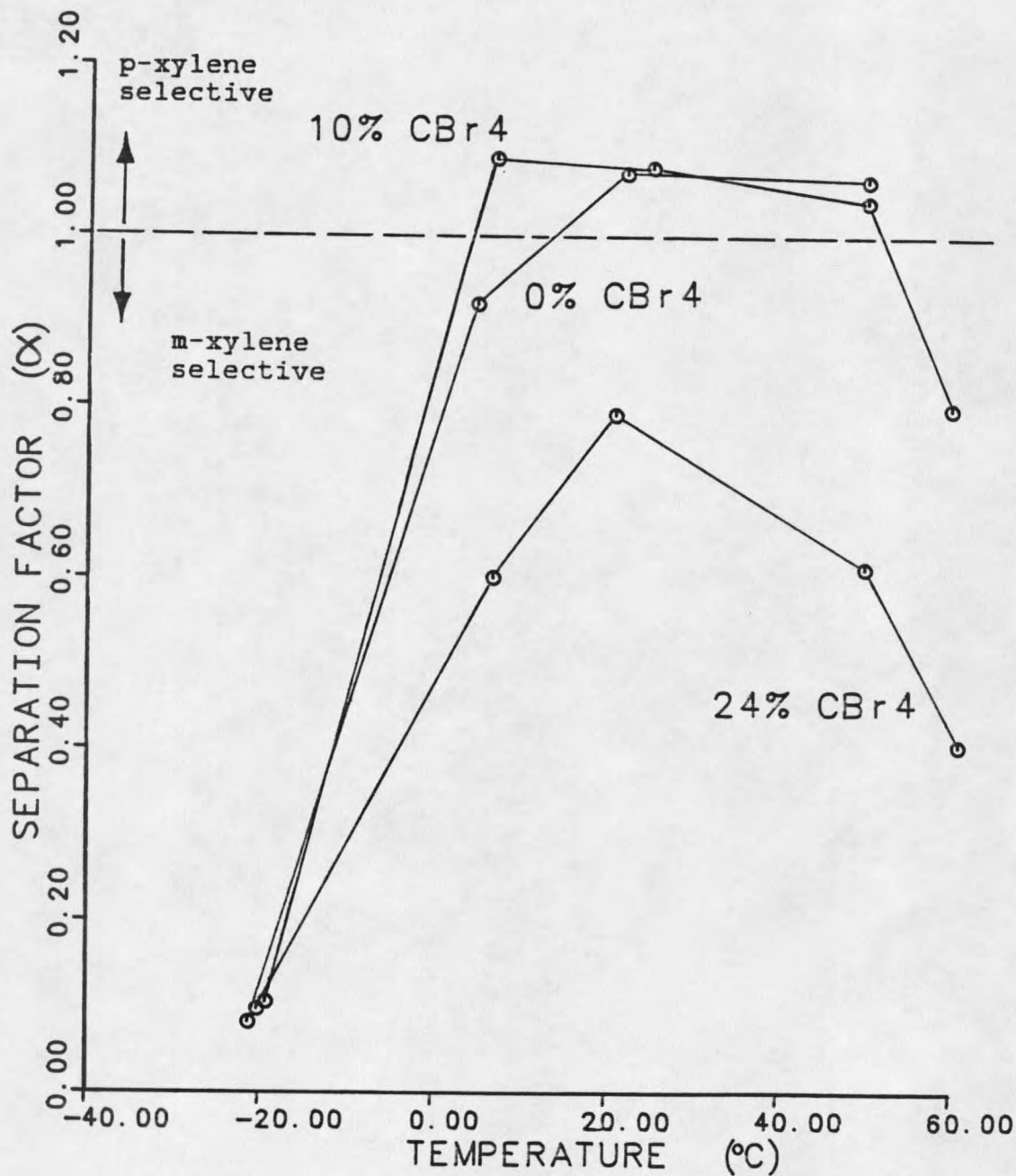


Figure 11. Separation factor vs temperature for 90% p-xylene and varying % CBr₄ additions.

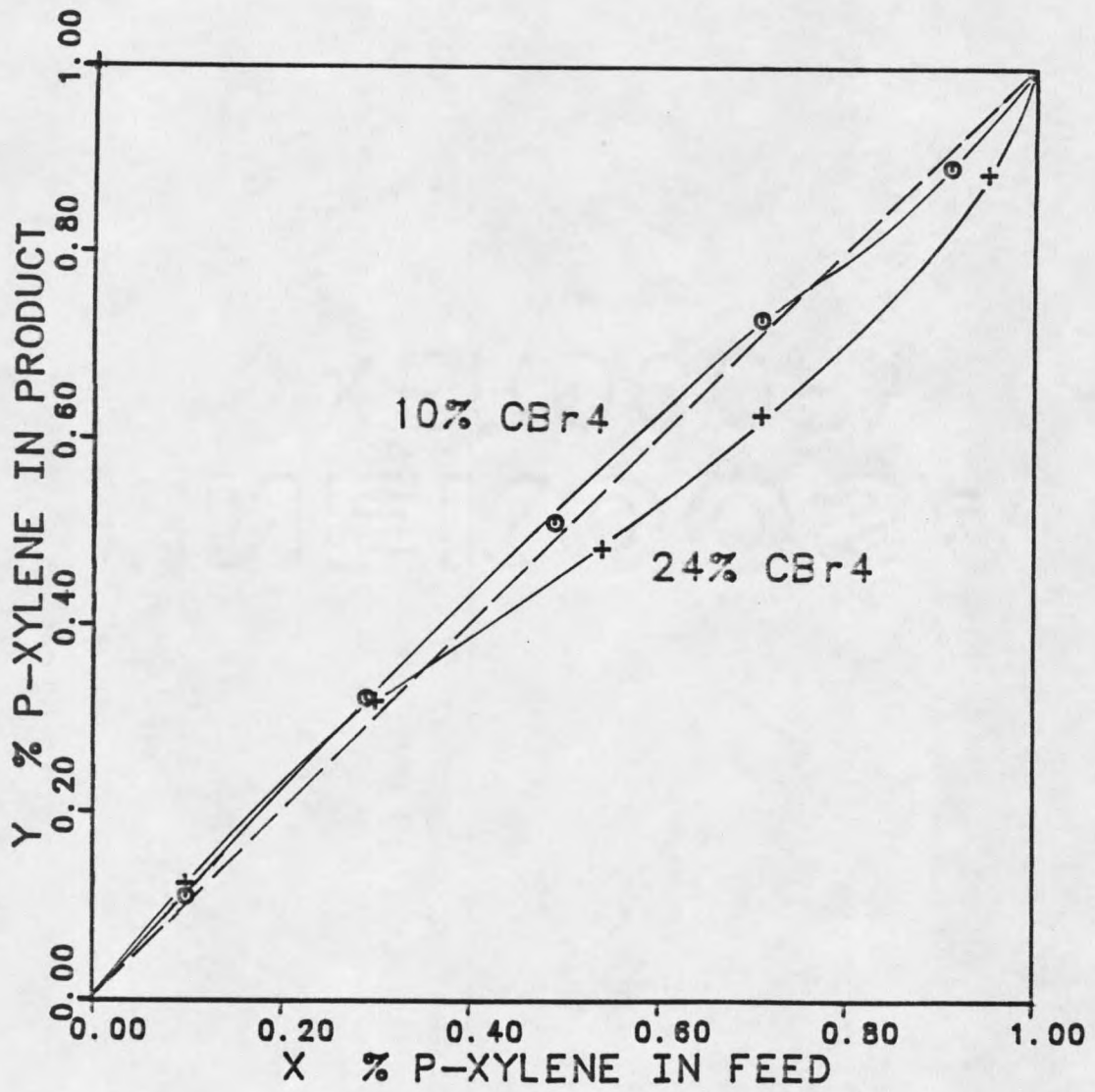


Figure 12. Percent p-xylene in product as a function of % p-xylene in feed with 10 and 24 mole % CBr₄ added at 60°C.

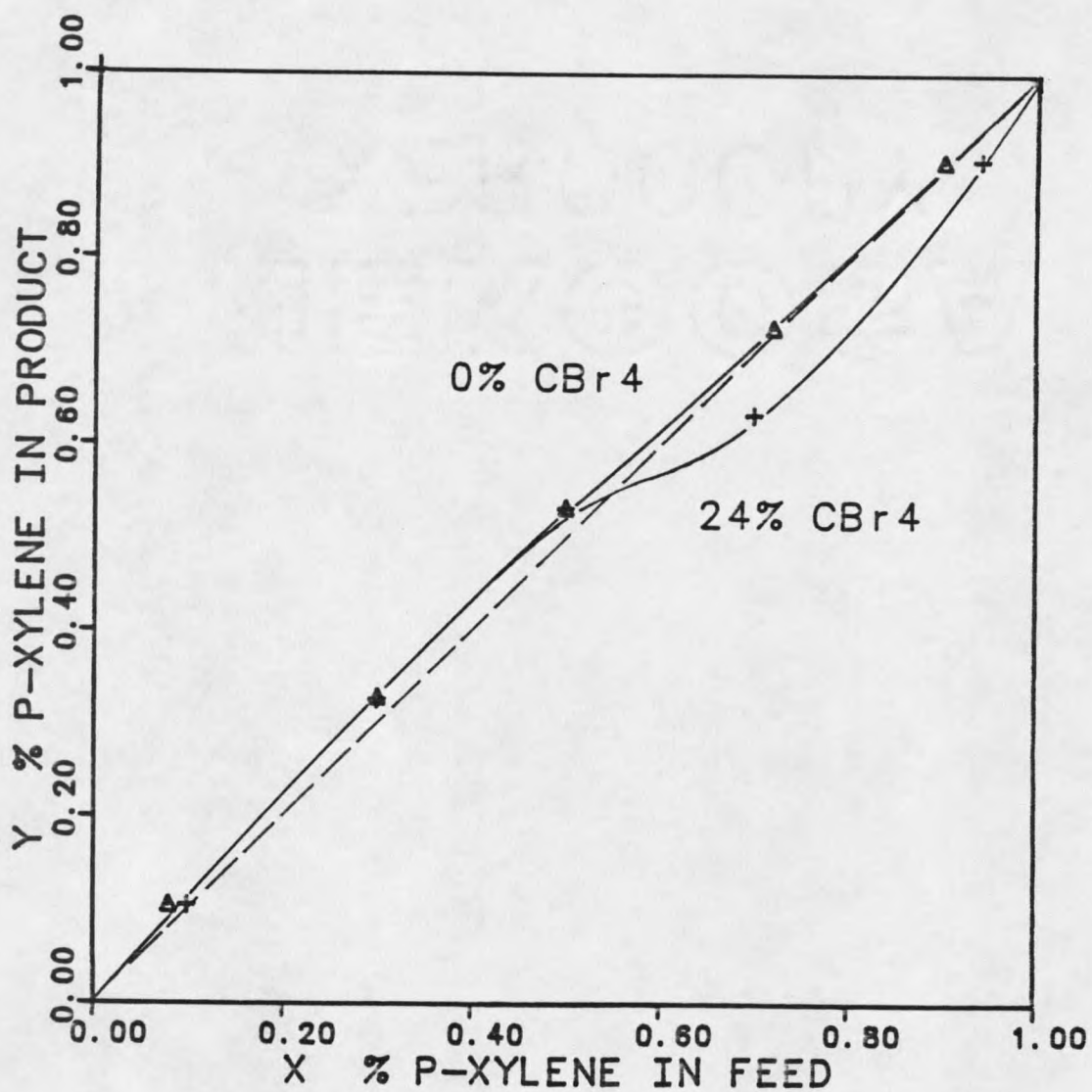


Figure 13. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr₄ added at 50°C.

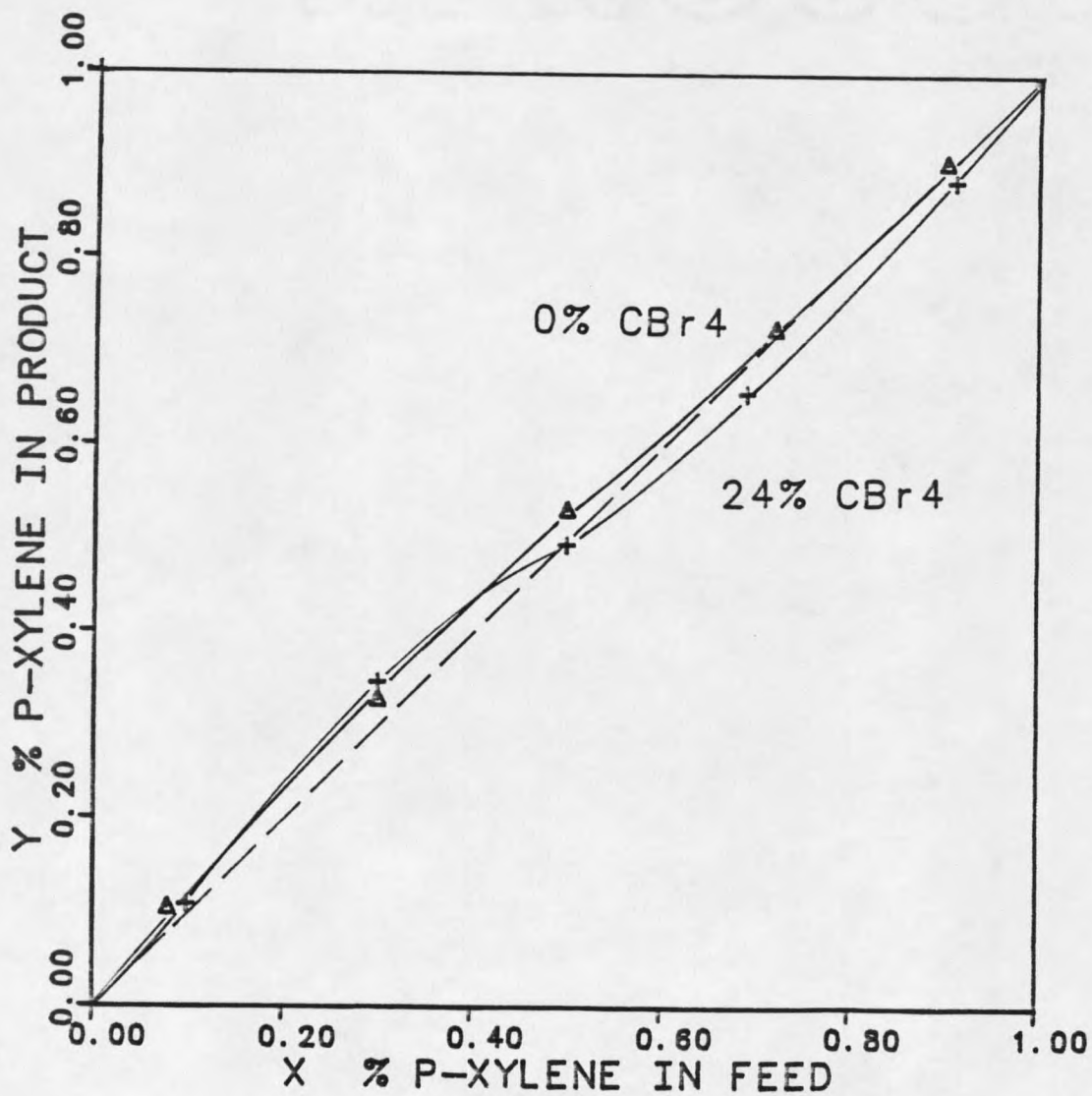


Figure 14. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr_4 added at 22°C .

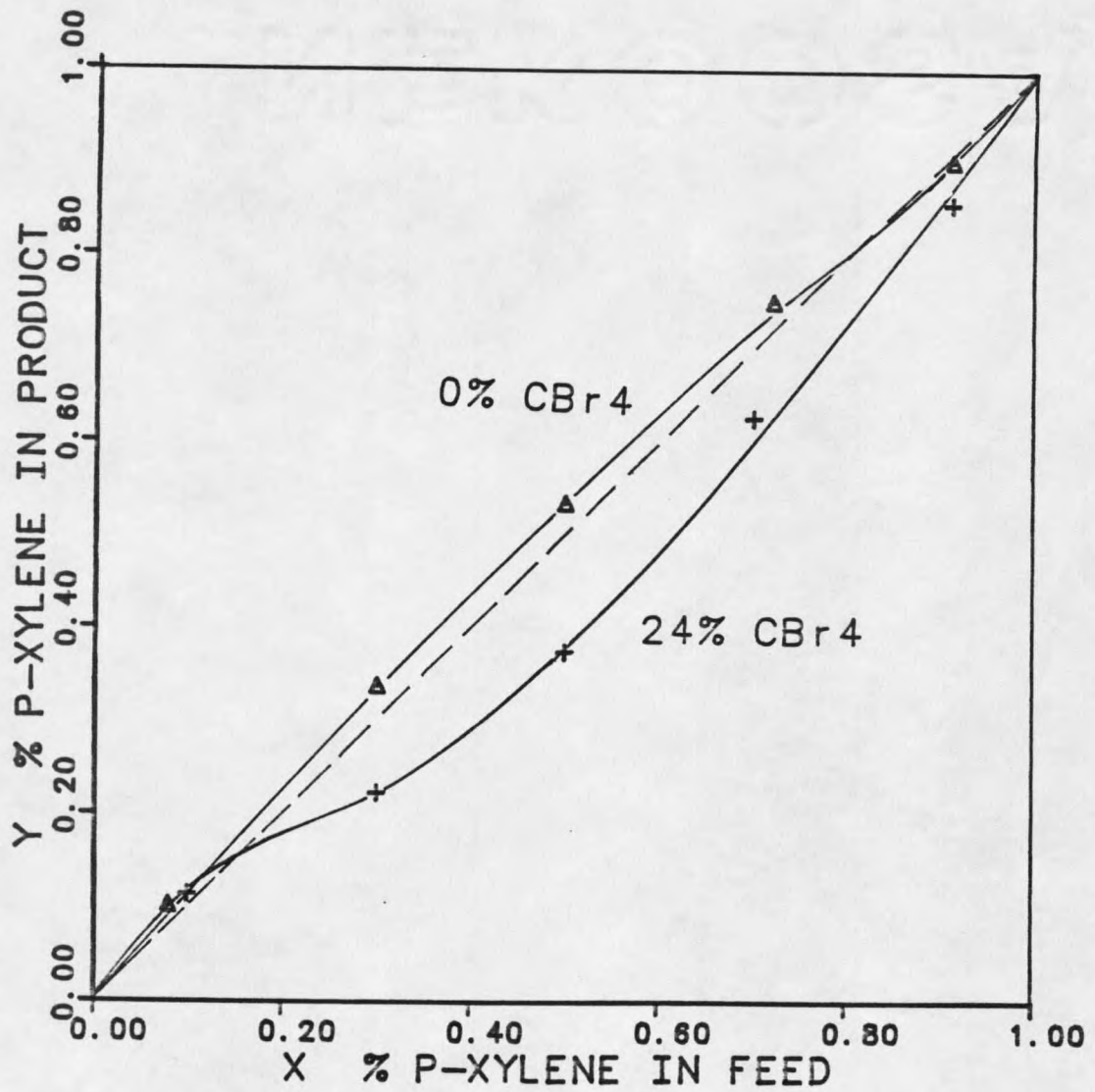


Figure 15. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr₄ added at 5°C.

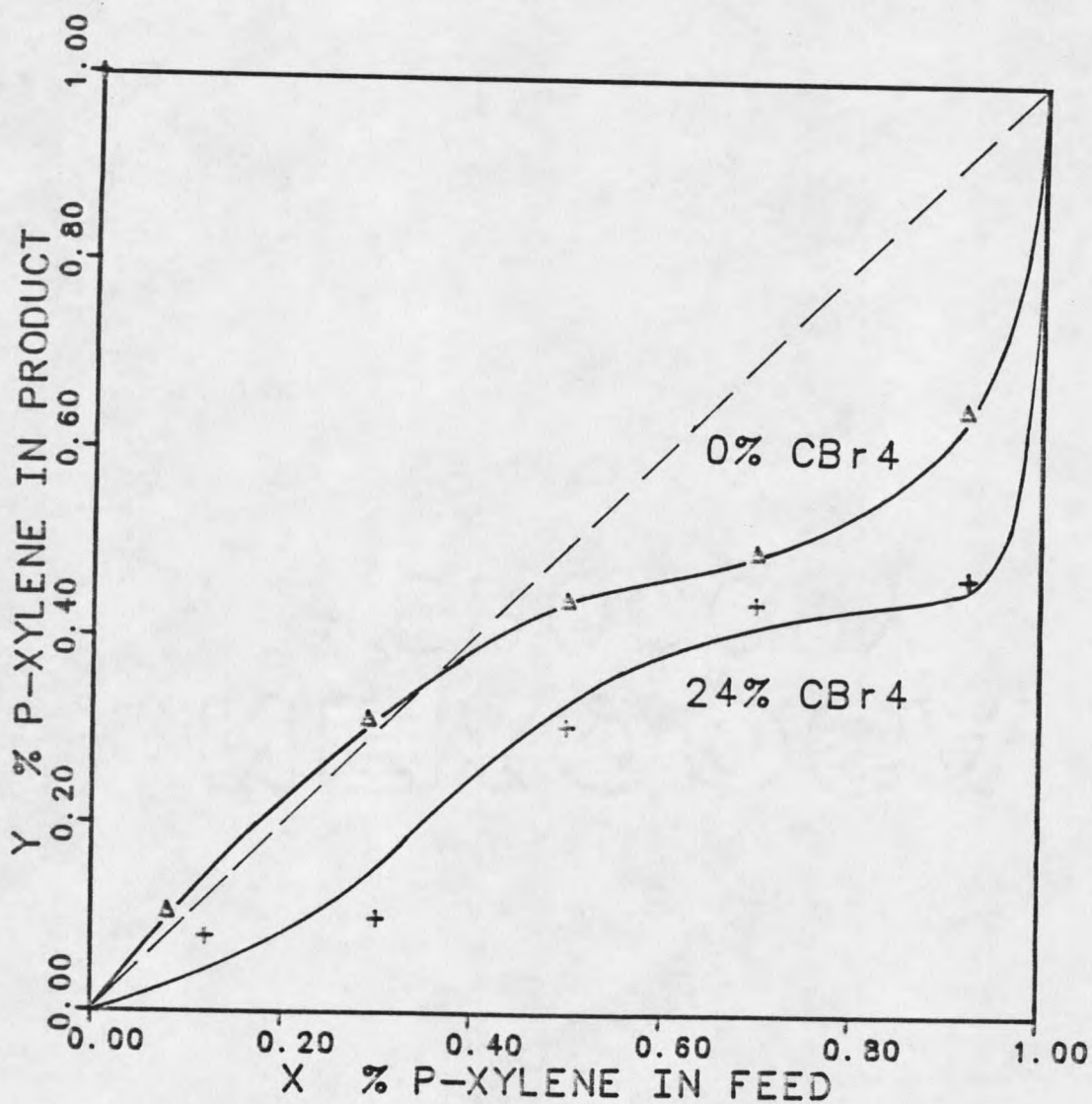


Figure 16. Percent p-xylene in product as a function of % p-xylene in feed with 0 and 24 mole % CBr₄ added at -20°C.

selectivity of the separation process changed so that m-xylene was concentrated in the product. The separation factors are between zero and 1.0 when the process was selective for m-xylene. For a feed mixture with 90% p-xylene, the selectivity of the process was for m-xylene at both 5°C and -20°C.

Figure 6 presents the same results as in Figure 5, but on an x vs y diagram which shows the % p-xylene in the product as a function of the % p-xylene in the feed. This diagram conveniently illustrates the degree of selectivity of the process. Points on the diagonal represent the cases of no separation, where there is the same amount of p-xylene in the feed as in the product. As the degree of separation, or the selectivity of the process, increases, the difference in the concentration of p-xylene in the feed from that in the product becomes greater. This is shown by the points on the x vs y diagram which are farther away from the diagonal. Points above the diagonal indicate selectivity for p-xylene because there is a higher concentration of p-xylene in the product than in the feed. Points located below the diagonal represent process selectivity for m-xylene, or less p-xylene in the product than in the feed. Figure 6 shows that the greatest change in selectivity occurs at a temperature of -20°C and where the feed mixtures have a concentration of

p-xylene of 50% and higher. Under these conditions the process is selective for m-xylene.

The separation factors obtained at various temperatures with varying percent additions of CBr_4 are shown on separate graphs for each different percent p-xylene in the feed mixture. The experimental results when the feed concentration of p-xylene was 10% are shown on Figure 7. Under the conditions with no CBr_4 and 10 mole % CBr_4 additions, the selectivity of the process was for p-xylene at all temperatures. When 24 mole % CBr_4 was added to the feed mixture and the temperature was -20°C , the selectivity of the process was for m-xylene. Experimental runs at the warmer temperatures resulted in the process being selective for p-xylene.

Figure 8 illustrates the results when there was 30% p-xylene in the feed mixture. When no CBr_4 was added, the selectivity of the process was for p-xylene. With the addition of 10 mole % CBr_4 , the selectivity of the process was for p-xylene at temperatures of 5°C and warmer. But at -20°C the selectivity changed so the process was selective for m-xylene.

When 24 mole % CBr_4 was added, the process was selective for p-xylene at 22°C and warmer. The selectivity at both 5°C and -20°C was for m-xylene. In order to evaluate the reproducibility of the data, the experiments which had 30% p-xylene in the feed mixture with 24 mole %

CBr_4 added were duplicated. The results are shown on Figure 8.

Figure 9 presents the experimental results when the xylene feed composition was 50% p-xylene. This time the separation process when no CBr_4 was added was selective for m-xylene at -20°C . At the warmer temperatures the process was still selective for p-xylene when there was no CBr_4 added to the xylene feed mixture. With 10 mole % CBr_4 added to the feed mixture, the process was selective for m-xylene at 5°C and -20°C . For the remaining experimental results at 10 mole % CBr_4 addition, the process was selective for p-xylene. A 24 mole % CBr_4 addition to the feed mixture at temperatures of -20°C , 5°C , and 60°C resulted in the separation process being selective for m-xylene. At 22°C and 50°C the process was selective for p-xylene.

Figure 10 depicts the experimental results found when the feed mixture contained 70% p-xylene. At -20°C the separation process was selective for m-xylene regardless of the amount of CBr_4 added. For the cases with no CBr_4 and 10 mole % CBr_4 added, where the temperatures were 5°C and warmer, the separation process was selective for p-xylene. When 24 mole % CBr_4 was added to the xylene mixture, the selectivity of the process was for m-xylene at all temperatures.

Figure 11 illustrates the experimental results obtained with 90% p-xylene in the feed mixture. The separation

process with this feed mixture at -20°C , regardless of the amount of CBr_4 added, was selective for m-xylene. When no CBr_4 had been added, the process was still selective for m-xylene at 5°C , but at the warmer temperatures, the process was selective for p-xylene. With 10 mole % CBr_4 added to the feed mixture, the process was selective for p-xylene at 5°C , 22°C , and 50°C . But the selectivity changed to m-xylene at 60°C . The separation process was selective for m-xylene at all temperatures when 24 mole % CBr_4 had been added to the feed mixture.

Figure 12 shows the experimental results produced at a temperature of 60°C in terms of an x vs y diagram. The results when 10 mole % and 24 mole % CBr_4 were added to the feed mixture of varying concentrations of p-xylene and m-xylene are compared. The separation process was selective for m-xylene when 24 mole % CBr_4 was added to the feed mixture containing a concentration of 50% or greater p-xylene. In these cases, Figure 12 shows the % p-xylene in the product was less than the % p-xylene in the feed.

Figures 13 through 16 compare the experimental results when 24 mole % CBr_4 was added to the feed, with the runs when no CBr_4 was present. Figure 13 presents the results when the separation process was operated at 50°C . The selectivity was for m-xylene at feed concentrations of 70% or greater p-xylene. The experimental results shown in Figure 14 were collected at a temperature of 22°C . The

selectivity of the process was for m-xylene at 70% and 90% p-xylene in the feed mixture. Figure 15 shows the experimental results obtained from the separation process when operated at a temperature of 5°C. The separation process was selective for m-xylene at all concentrations of p-xylene in the feed except 10%. Figure 16 shows that at a temperature of -20°C, all experimental runs were selective for m-xylene regardless of the concentration of p-xylene in the feed mixture.

Discussion of Results

Background separability data for para and meta xylene across a polypropylene membrane were produced at the desired temperatures. This background data served as a basis from which the effect of complexing the p-xylene with the CBr_4 could be compared. As Figure 5 shows, most of the separation factors are greater than 1.0. This is not surprising since the membrane is selective for p-xylene. But at the higher concentrations of p-xylene and the lower temperatures the pervaporation process is selective for m-xylene. These are the points below the 1.0 separation factor line.

The pervaporation process is selective for m-xylene at high concentrations of p-xylene and low temperatures because of the crystallization that occurs on the feed side of the membrane. Pure p-xylene freezes at 13.3°C, but when m-xylene is added, the freezing point is depressed. Table 3

presents the initial crystallization temperatures for the binary mixtures of p-xylene and m-xylene (21).

Table 3. Initial Crystallization Temperatures for Binary Mixtures of p-Xylene and m-Xylene.

% p-Xylene	Temp °C
100	13.3
90	10
70	- 1
50	-13
30	-29
13	-52.8
10	-52
0	-47.8

For any concentration of para and meta xylene, as the temperature is lowered below the initial crystallization temperature, pure p-xylene crystallizes out until the minimum temperature of -52.8°C is reached. At that point the binary eutectic of the mixture is reached and both p-xylene and m-xylene crystallize out. The concentration of the solid phase at the eutectic is 13% p-xylene and 87% m-xylene.

Crystallization affected the separation of the pervaporation process at feed concentrations of 50% p-xylene and higher when the temperature was below 5°C . At 30% p-xylene, the p-xylene does not begin to crystallize until -29°C . Since the experiments were run at a minimum temperature of -23°C , the 30% and lower p-xylene mixtures were not affected by the crystallization of p-xylene. This

can be seen on Figure 6, as even for runs at the lowest temperature the pervaporation process was selective for p-xylene at 30% and lower p-xylene mixtures. In both the 50% and 70% p-xylene feed mixtures, the p-xylene begins to crystallize at about -13°C and -1°C respectively. So the -20°C runs had crystallization, but not the 5°C run. For a 90% p-xylene mixture, p-xylene will begin to crystallize out at 10°C , therefore both the 5°C and -20°C runs had crystallization.

As can be seen, in every run where crystallization was present, the selectivity of the membrane process was for m-xylene. Since the p-xylene is in crystalline form, it cannot permeate through the membrane, but the m-xylene can. So although the membrane is selective for p-xylene when conditions are such that crystallization is present, the membrane process is selective for m-xylene.

p-Xylene, m-Xylene, and CBr_4 System

The complexing agent, CBr_4 , was added in amounts of 10 mole % and 24 mole % to the various para and meta xylene mixtures. It was expected that an equimolal $\text{CBr}_4 \cdot$ p-xylene complex would form as shown by Egan et al. (22). In the 10 mole % CBr_4 runs, the mixture in which there was enough p-xylene to utilize all the CBr_4 as an equimolal complex was at the 10/90 ratio p-xylene to m-xylene. Therefore, every other run at 10 mole % CBr_4 had a p-xylene concentration in

excess of that required to complex with all the CBr_4 . For the 24 mole % CBr_4 runs, an equimolal ratio of p-xylene to CBr_4 existed where there was a 30/70 para to meta ratio in the feed mixture. There was excess p-xylene present for para to meta ratios greater than this.

The results which indicate the pervaporation process was selective for m-xylene are presented in Figures 7 through 16, and can be interpreted in terms of a p-xylene, m-xylene, and CBr_4 freezing point diagram, and selective complex formation between the CBr_4 and p-xylene.

The behavior of para and meta xylene in the presence of CCl_4 was studied by Egan et al. (23). The data was conveniently represented by the ternary freezing point diagram (shown in Figure 17a). The triangular diagram is divided into four areas to indicate the composition of the solid phase that crystallizes out first when a solution of a given composition is cooled.

In the same manner, a ternary freezing point diagram has been constructed for the p-xylene, m-xylene, and CBr_4 system. This diagram is shown in Figure 17b. Each side of the triangle represents a binary mixture. Information on the initial crystallization temperatures and the eutectics of the binary mixtures were taken from plots located in the article by Egan et al. (also shown in Figures 1 and 2) (24). An equimolal complex of p-xylene and CBr_4 is shown on the

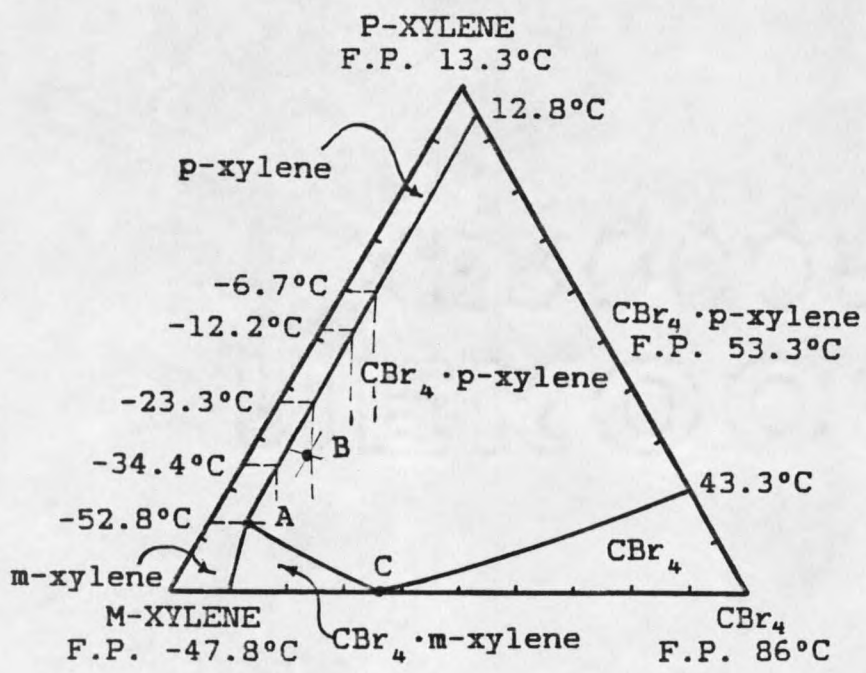
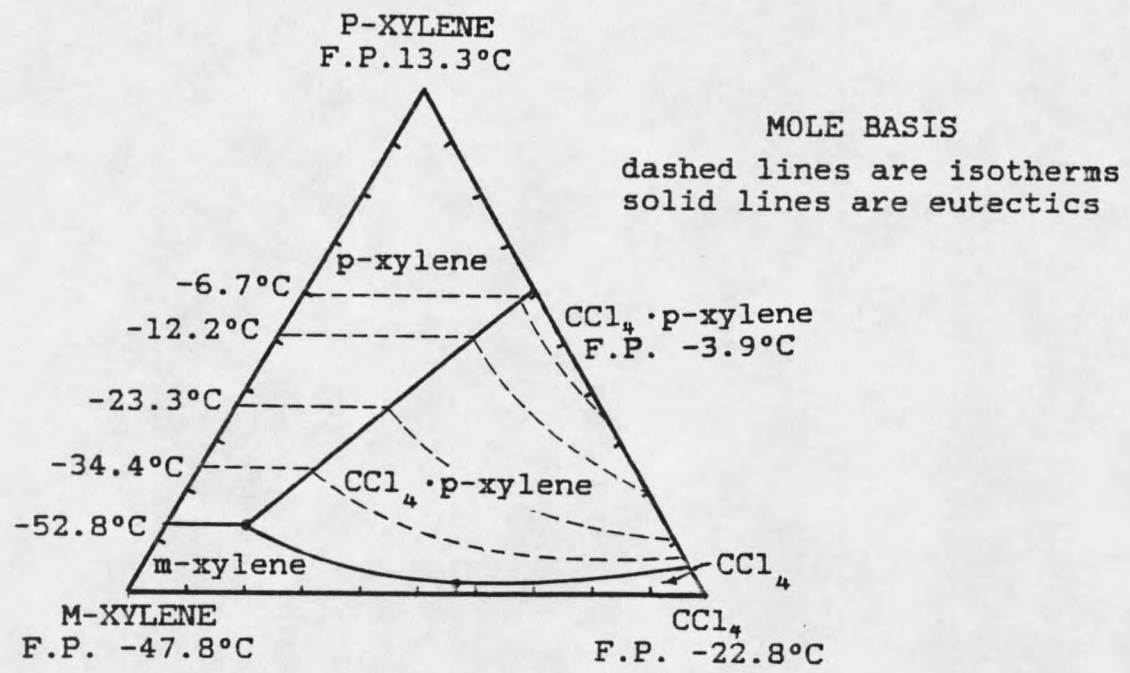


Figure 17. Freezing point diagrams for mixtures of p-xylene, m-xylene, and CCl₄, and p-xylene, m-xylene, and CBr₄.

right side of the triangle and has a freezing point of 53.3°C.

CBr_4 also forms a complex with m-xylene under certain conditions. Therefore the ternary freezing point diagram for p-xylene, m-xylene, and CBr_4 , is divided into five labeled areas. Each area indicates the composition of the solid phase that crystallizes out first when a solution of a given composition is cooled. The five solid lines separating the areas are the binary eutectics. The main assumption in Figure 17b concerns the location of the quaternary (point A) between the CBr_4 , the complexes, and the xylenes.

The eutectic between para and meta xylene is shown as a horizontal dashed line following the -52.8°C isotherm. The quaternary will be located somewhere along this p-xylene and m-xylene eutectic, at the point of intersection of the other eutectics. The separation factor resulting from the experimental run having a feed mixture of 30/70 para to meta xylene with 10 mole % CBr_4 addition (point B) at a temperature of -20°C was below 1.0. This indicated some solid formation occurring which effectively changed the separation factor making the process selective for m-xylene. If the solid forming were p-xylene instead of the CBr_4 ·p-xylene complex, the temperature would have to be about -34.4°C (note the -34.4°C isotherm located slightly below point B). Therefore the solid forming must be the

$\text{CBr}_4 \cdot \text{p-xylene}$ complex since the temperature is only at -20°C . So, the $\text{p-xylene} - \text{CBr}_4 \cdot \text{p-xylene}$ eutectic must be located to the left of point B. Determination of the exact location for the quaternary is beyond the scope of this research. The phase diagram is nevertheless helpful in interpreting the experimental results.

The quaternary formed is located at the intersection of the lines representing $\text{p-xylene} - \text{CBr}_4 \cdot \text{p-xylene}$ eutectic, $\text{CBr}_4 \cdot \text{p-xylene} - \text{CBr}_4 \cdot \text{m-xylene}$ eutectic, $\text{CBr}_4 \cdot \text{m-xylene} - \text{m-xylene}$ eutectic, and the $\text{m-xylene} - \text{p-xylene}$ eutectic (point A). A ternary is also shown at point C, intersecting the $\text{CBr}_4 \cdot \text{p-xylene} - \text{CBr}_4$ eutectic, $\text{CBr}_4 - \text{CBr}_4 \cdot \text{m-xylene}$ eutectic, and $\text{CBr}_4 \cdot \text{m-xylene} - \text{CBr}_4 \cdot \text{p-xylene}$ eutectic.

The isotherms in Figure 17 are represented by dashed lines. The isotherms in Figure 17b are more vertical than in Figure 17a. This is due to the difference in the freezing points of CBr_4 and CCl_4 . The negative temperatures in Figure 17b go from the left to the bottom side of the triangle since there are no negative temperatures on the right side of the triangle. Although the p-xylene , m-xylene , and CBr_4 ternary freezing point diagram is only an approximation, it proves helpful in the discussion of the effects of crystallization on the pervaporation separation of para and meta xylene in the presence of CBr_4 .

The results of the 10/90, 30/70, and 50/50 ratio para to meta xylene mixtures at 22°C and above were all similar.

The change in separation factors, if any, did not result in a separation factor less than 1.0 regardless of the amount of CBr_4 added except at 50% p-xylene with 24 mole % CBr_4 at 60°C . At concentrations of 50% and less p-xylene in the feed, no solid $\text{CBr}_4 \cdot \text{p-xylene}$ complex formed at room temperature of 22°C .

It was desired to know what composition of p-xylene was required in the feed mixture to form a solid $\text{CBr}_4 \cdot \text{p-xylene}$ complex at room temperature of 22°C . GC analyses were conducted to find at what ratio of p-xylene the complex formed. The analyses were conducted with 24 mole % CBr_4 for varying ratios of para to meta xylene. Figure 18 shows the % CBr_4 in liquid as a function of the feed p-xylene concentration at 22°C and illustrates graphically where the decrease in CBr_4 in the liquid occurs. The initial concentration of CBr_4 was 24 mole %. When the CBr_4 in the xylene mixture complexes with the p-xylene, the amount of CBr_4 that is detected by the GC is reduced. Therefore the solid complex formation is indicated by a decrease in the CBr_4 detected in the liquid phase. The $\text{CBr}_4 \cdot \text{p-xylene}$ complex first forms when there is 24 mole % CBr_4 present and when the ratio of para to meta xylene is 60/40. The CBr_4 remains in solution at concentrations of p-xylene less than 50% of the para and meta xylene mixture. The amount of CBr_4 in the liquid decreases as the % p-xylene is increased due to the formation of the $\text{CBr}_4 \cdot \text{p-xylene}$ complex. There is

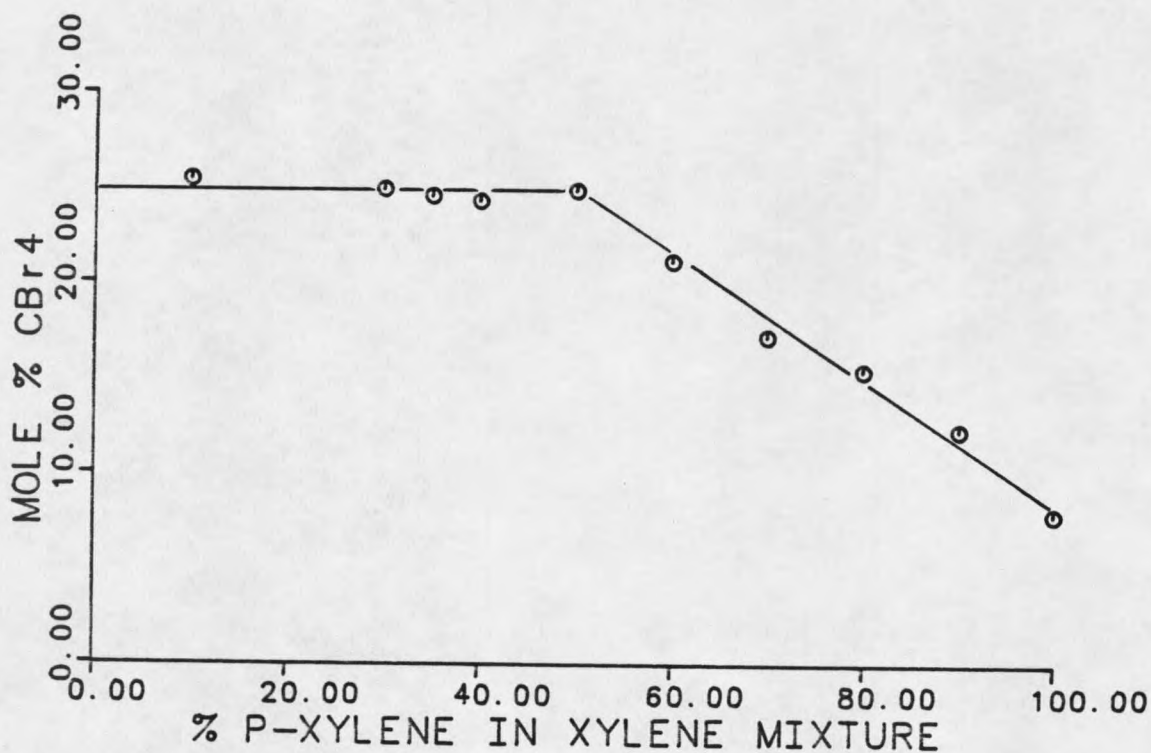


Figure 18. Mole % CBr₄ present in liquid phase as a function of p-xylene concentration in the para and meta xylene mixture at 22°C with an initial concentration of CBr₄ at 24 mole %.

also a corresponding decrease in the p-xylene concentration in the remaining liquid. This explains how even though the membrane is selective for p-xylene, when the $\text{CBr}_4 \cdot \text{p-xylene}$ complex is formed, the pervaporation process is selective for m-xylene. Since some of the p-xylene is tied up in the complex, it cannot permeate through the membrane. But the m-xylene continues to permeate and so the result is a greater concentration of m-xylene in the product. This results in a very good separation of m-xylene from p-xylene by the pervaporation process.

For the 10/90 runs, a temperature of 5°C was not cold enough to cause any xylene crystallization. Since the p-xylene concentration was low, no complex was formed. But at -20°C there was a significant change in the separation factor with the addition of 24 mole % CBr_4 . This change in the separation factor can be explained by referring to the phase diagram in Figure 19. At 10 mole % CBr_4 , if the temperature was low enough, the composition of the solid phase that would crystallize out first would be pure m-xylene. Therefore at 10 mole % CBr_4 there would be no $\text{CBr}_4 \cdot \text{p-xylene}$ complex. At 24 mole % CBr_4 , the solid phase which would form first is the $\text{CBr}_4 \cdot \text{p-xylene}$ complex. So, at -20°C the $\text{CBr}_4 \cdot \text{p-xylene}$ complex forms in the feed and effectively changes the separation factor for the pervaporation process. The pervaporation process is

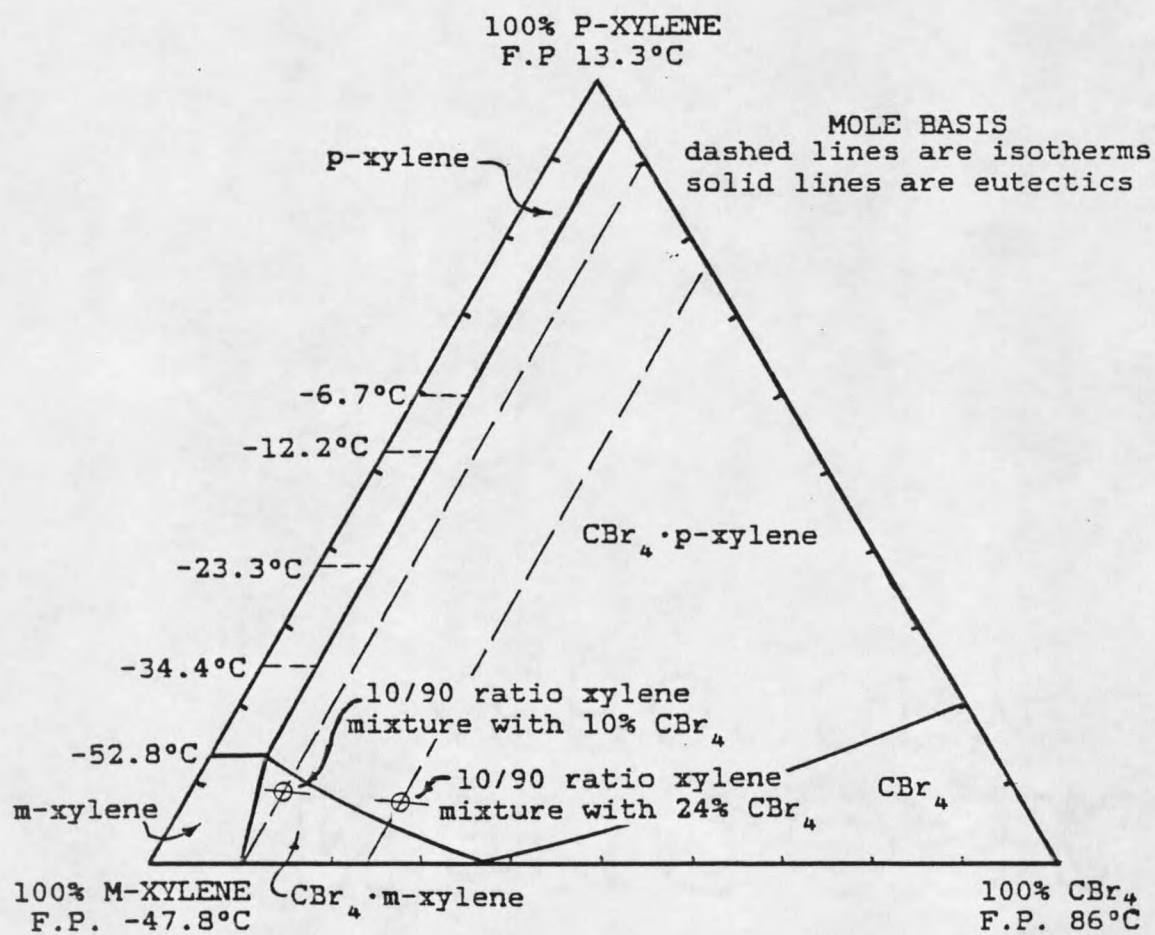


Figure 19. Freezing point diagram for mixtures of p-xylene, m-xylene, and CBr₄.

now selective for m-xylene as the m-xylene is concentrated in the product.

For the experimental runs with a 30/70 ratio para to meta xylene feed mixture, solid complex formation in the feed did occur at -20°C for both the 10 and 24 mole % CBr_4 additions. Only the feed containing 24 mole % CBr_4 had solid complex formation at 5°C . At -20°C , the pervaporation process became more selective for m-xylene with increasing amounts of CBr_4 . Since there was an excess of p-xylene for the 10 mole % CBr_4 case, as more CBr_4 was added, more complex was formed. In the 24 mole % CBr_4 runs, the amount of complex was greater so the amount of p-xylene available to permeate through the membrane was less. With less p-xylene available to permeate through the membrane, and the m-xylene permeation rate unchanged, the m-xylene ends up being concentrated in the product.

For the 50/50 ratio para to meta xylene mixture runs, solid complex formation occurred at 5°C and -20°C for mixtures with both 10 and 24 mole % CBr_4 . The more CBr_4 present, the more complex was formed, and as before, this leads to the m-xylene being concentrated in the product and a greater separation of m-xylene from p-xylene. At -20°C , with no CBr_4 present, the p-xylene would crystallize out in the feed. The p-xylene in crystalline form cannot permeate through the membrane so this changes the selectivity of the process to m-xylene.

For both the 70/30 and 90/10 mixtures, complexing was apparent in the runs with 24 mole % CBr_4 as expected. The addition of 10 mole % CBr_4 to the feed mixture did not change the selectivity from the case where no CBr_4 was added. This indicates the temperature was not low enough to cause any solid complex formation. At -20°C , the separation factors for 0, 10, and 24 mole % CBr_4 were very close. In this case, there is solid complex formation occurring at both 10 and 24 mole% CBr_4 additions, and when no CBr_4 is added, pure p-xylene crystallizes out. The results for the 70/30 ratio para to meta run can be seen by referring to the phase diagram in Figure 20. Beginning at point A, which is 24 mole % CBr_4 , with a 70/30 ratio (para to meta) xylene mixture for the other 76 mole %, cooling the mixture would crystallize out $\text{CBr}_4 \cdot \text{p-xylene}$ complex. The complex would crystallize out until about -12°C (B), at which point the remaining crystallization would occur along the $\text{CBr}_4 \cdot \text{p-xylene} - \text{p-xylene}$ eutectic (down to point C). When the final temperature of approximately -20°C was obtained the remaining xylene mixture would contain about 42% p-xylene. This is roughly the same product concentration of p-xylene which was obtained experimentally.

At 10 mole % CBr_4 following the cooling line from D to E, pure p-xylene would crystallize out. At the final temperature of -20°C about 42 % p-xylene would again remain in the liquid. As for the case with no CBr_4 added, using

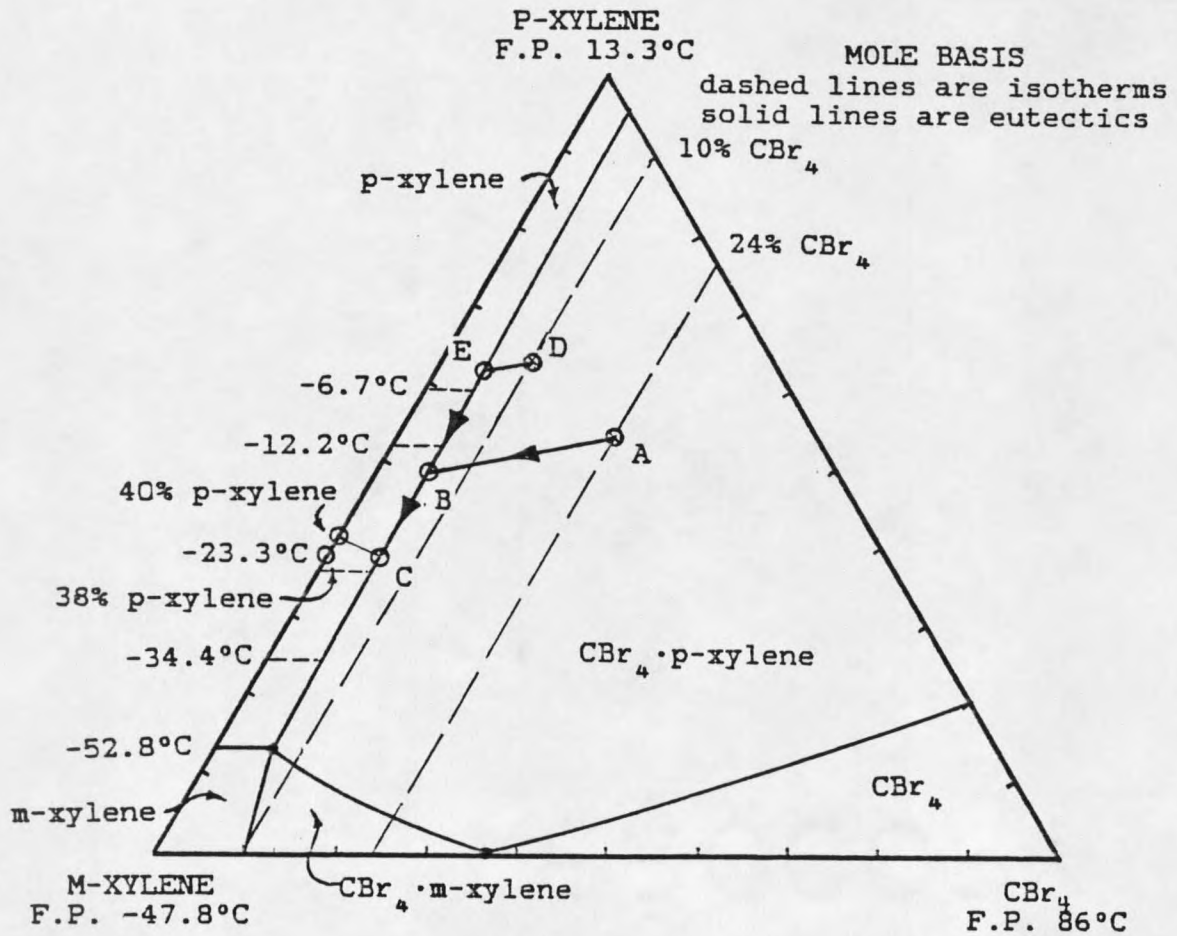


Figure 20. Freezing point diagram for mixtures of p-xylene, m-xylene, and CBr₄.

the phase diagram, a final p-xylene concentration of approximately 36 % would be expected. Since these final p-xylene concentrations are similar to the product concentrations found experimentally, it is evident that the solid complex formation or pure p-xylene crystallization are the predominant separating mechanisms at the high p-xylene concentrations and low temperatures. Both situations decrease the amount of p-xylene in the feed which is free to permeate through the membrane. So, although the membrane itself is selective for p-xylene, under the conditions where the solid complex formation of p-xylene crystallization are present, the pervaporation process is selective for m-xylene. The separation of the xylenes is greatly enhanced over the separation obtained by just pervaporation.

Formation of $\text{CBr}_4 \cdot \text{p-xylene}$ Association in Liquid Phase

For the experimental runs with a feed concentration of 50% and higher p-xylene, the membrane process became more selective to m-xylene at the higher temperatures. This change in selectivity cannot be due to solid complex formation between the CBr_4 and p-xylene since the complex melting points are as follows:

Table 4. Melting Points for the $\text{CBr}_4 \cdot \text{p-Xylene}$ Complex at High Concentrations of p-Xylene in the Xylene Feed Mixture.

% p-Xylene in Feed	mole % CBr_4	Melting Point °C
50	24	<22°C
70	10	<22°C
70	24	37°C
90	10	<22°C
90	24	45°C

At temperatures of 50°C and 60°C, the complex is in the liquid phase for all feed compositions examined. The change in selectivity must be due to an association between the CBr_4 and p-xylene which effectively ties up the p-xylene. The p-xylene in the association is unavailable to permeate through the membrane and therefore the process is selective for m-xylene.

Carbon Tetrabromide in the Product

The products from the 10 mole % CBr_4 and 30/70 ratio para to meta xylene mixture were analyzed for CBr_4 using an infrared spectrometer (IR). The presence of CBr_4 was found in all products tested with IR. The products were then analyzed with a GC and the results are shown in Table 4.

Table 5. CBr_4 Present in the product of the 30/70 Ratio (para to meta) Xylene Run with 10 mole % CBr_4 .

Temperature	-20°C	7°C	22°C	50°C	59°C
mole % CBr_4	0.00	3.02	3.11	3.02	2.93

As can be seen the CBr_4 did not show up on the GC when the product of the -20°C run was analyzed. Although it was indicated by the IR, it was a very weak peak indicating a very low concentration.

Advantage of Using Pervaporation Process

The separations occurring in the feed resulting from solid complex formation and p-xylene crystallization appear to be as good as these separations when combined with pervaporation. If anything, they would be a bit better without pervaporation across the membrane since the solid formation and crystallization both decrease the p-xylene in the liquid phase of the feed, and the pervaporation process would take what p-xylene is available in the liquid phase of the feed and concentrate it in the product. In other words, the m-xylene is being concentrated on the feed side of the membrane, but diluted on the product side. There would be a greater percentage of m-xylene in the liquid phase of the feed than in the product.

One advantage of using the pervaporation process over separation by means of just solid complex formation and p-xylene crystallization exists in the reduction of CBr_4 present in the product. Without pervaporation, the amount of CBr_4 present in the liquid was still about 8 mole % with an excess of p-xylene and no m-xylene (see Figure 18). When m-xylene was introduced into the system, the amount of CBr_4

remaining in the liquid increased. The CBr_4 present in the product of pervaporation separation regardless of the amount of para or meta xylene present was at most 3.11 mole %. The end uses of the separated xylenes would have to be examined as to the effect of CBr_4 as an impurity. There would also be some cost involved from the loss of the CBr_4 .

Effect of Complexing Agent on Flux

The average flux, as a function of temperature for each mole % CBr_4 is shown in Figure 21. It is evident from Figure 21 that the flux decreases with an increase in the amount of the CBr_4 ·p-xylene complex. This is probably due to the fact the membrane is selective for p-xylene, and thus p-xylene permeates faster than m-xylene. When the p-xylene is complexed with the CBr_4 , it reduces the amount of p-xylene present, which results in an overall decrease in the total flux because of the lower permeation rate of m-xylene. Therefore the more CBr_4 added, the more complex and the lower the flux. The flux for the individual runs with 0, 10, and 24 mole % CBr_4 added, along with the average flux for the runs at each temperature are located in Table 6.

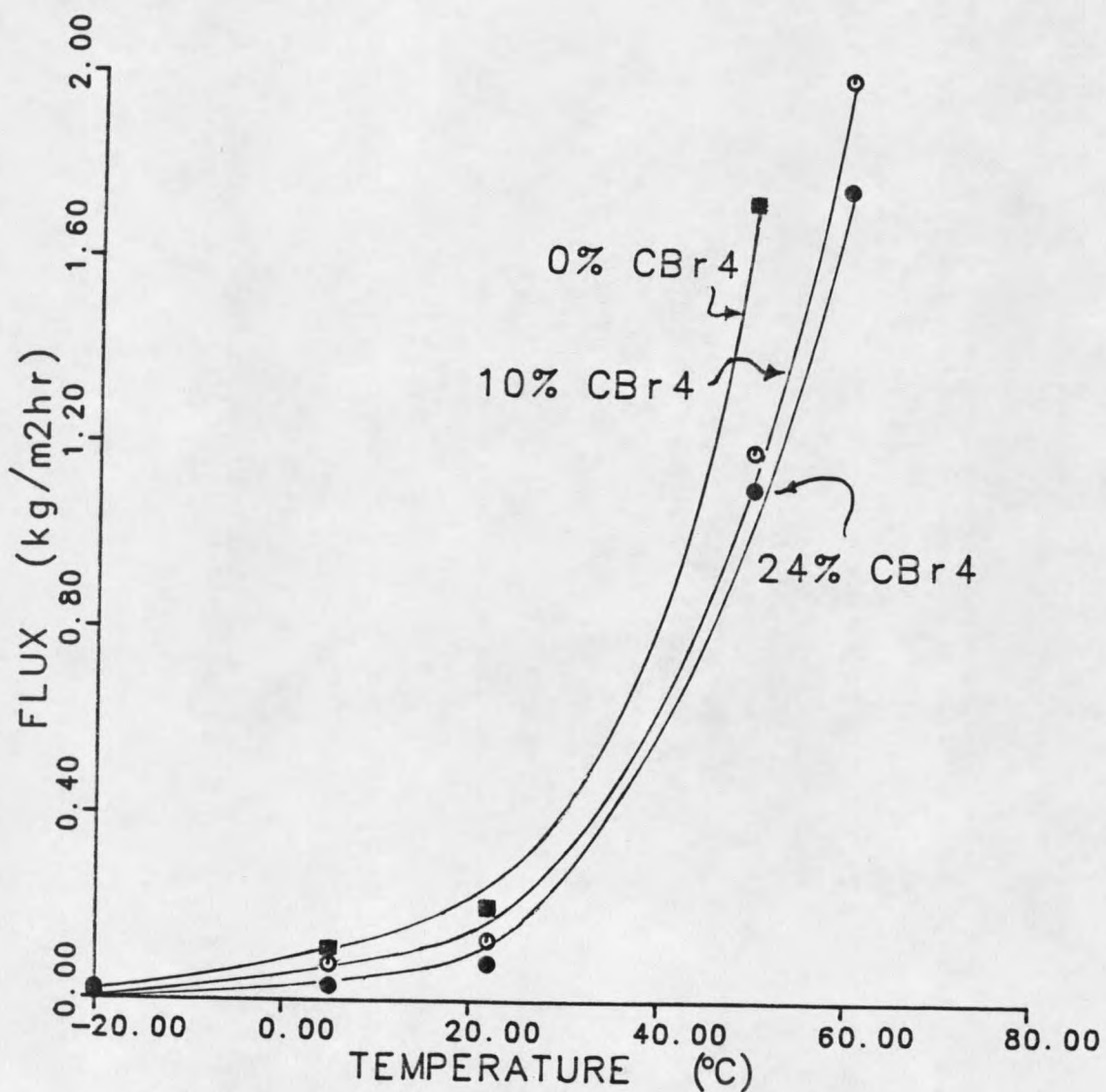


Figure 21. Average flux for pervaporation process with 0, 10, and 24 mole % CBr₄ added.

Table 6. Flux For the Runs at 0, 10, and 24 Mole % CBr_4

a. Flux in $\text{kg/m}^2\text{hr}$ for varying temperatures and concentrations with 0% CBr_4 .

CONC. ratio p/m	10/90	30/70	50/50	70/30	90/10	AVE
TEMP °C						
-20	0.023	0.034	0.021	0.022	0.014	0.023
5	0.111	0.048	0.158	0.078	0.146	0.110
22	0.121	0.310	0.097	0.281	0.169	0.200
50	1.623	1.921	1.302	2.280	1.536	1.730

b. Flux in $\text{kg/m}^2\text{hr}$ for varying temperatures and concentrations with 10 mole % CBr_4 .

CONC. ratio p/m	10/90	30/70	50/50	70/30	90/10	AVE
TEMP °C						
-20	0.010	0.014	0.007	0.032	0.018	0.020
5	0.055	0.080	0.064	0.088	0.100	0.077
22	0.076	0.215	0.103	0.110	0.131	0.130
50	1.106	1.129	1.358	1.256	1.106	1.190
60	1.911	2.019	1.922	2.260	1.896	2.000

c. Flux in $\text{kg/m}^2\text{hr}$ for varying temperatures and concentrations with 24 mole % CBr_4 .

CONC. ratio p/m	10/90	30/70	50/50	70/30	90/10	AVE
TEMP °C						
-20	0.002	0.008	0.015	0.003	0.040	0.014
5	0.040	0.025	0.018	0.019	0.072	0.030
22	0.041	0.025	0.080	0.136	0.108	0.080
50	0.650	1.060	0.743	1.493	1.627	1.110
60	1.313	1.527	1.580	2.384	2.020	1.760

The flux did not appear to be appreciably reduced during separations where crystallization was present. The flux was below $0.2 \text{ kg/m}^2\text{hr}$ for most of the runs when the temperature was below 50°C . At 50°C the flux increased

significantly, ranging from 1.3 kg/m²hr to 2.3 kg/m²hr.

This is about a 10 fold increase over the 20°C flux.

CONCLUSIONS

1. CBr_4 forms a solid molecular complex with the p-xylene and therefore decreases the amount of p-xylene in the pervaporation product at high concentrations of p-xylene and low temperatures.
2. In general, the addition of 24 mole % CBr_4 changed the separability of the pervaporation process so it was selective for m-xylene at low temperatures for all concentrations of p-xylene, but the 10 mole % CBr_4 addition only affected the separability at low temperatures for higher concentrations of p-xylene.
3. The degree of separation varies with temperature, the greatest separation in the presence of CBr_4 occurring at -20°C where solid complex formation was present.
4. At 22°C , 24 mole % CBr_4 complexes with p-xylene when the xylene mixture has at least 60 wt % p-xylene (and 40 wt % m-xylene).

CONCLUSIONS--Continued

5. At temperatures of 50°C and 60°C, where the solid complex has melted and there is above 50% p-xylene in the xylene feed mixture, an apparent association is present between the CBr_4 and the p-xylene which ties up the p-xylene in the feed and changes the process selectivity to m-xylene.

SUGGESTIONS FOR FUTURE RESEARCH

1. Different complexing agents should be experimentally evaluated to find one which complexes with m-xylene. This would be advantageous since the complexing agent would then be working with the membrane's selective nature instead of against it, as with the CBr_4 .
2. Determine the behavior of the molecules in terms of a phase diagram so the conditions where the CBr_4 ·p-xylene complex forms can be more accurately predicted for specific compositions and temperatures.
3. Continue the current experimental research at temperatures above 60°C to see if the trend towards greater m-xylene selectivity continues. Examine the association formed between the CBr_4 and the p-xylene at these higher temperatures.

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APPENDIX

CROSS PLOTS FOR FIGURES 13 THROUGH 17

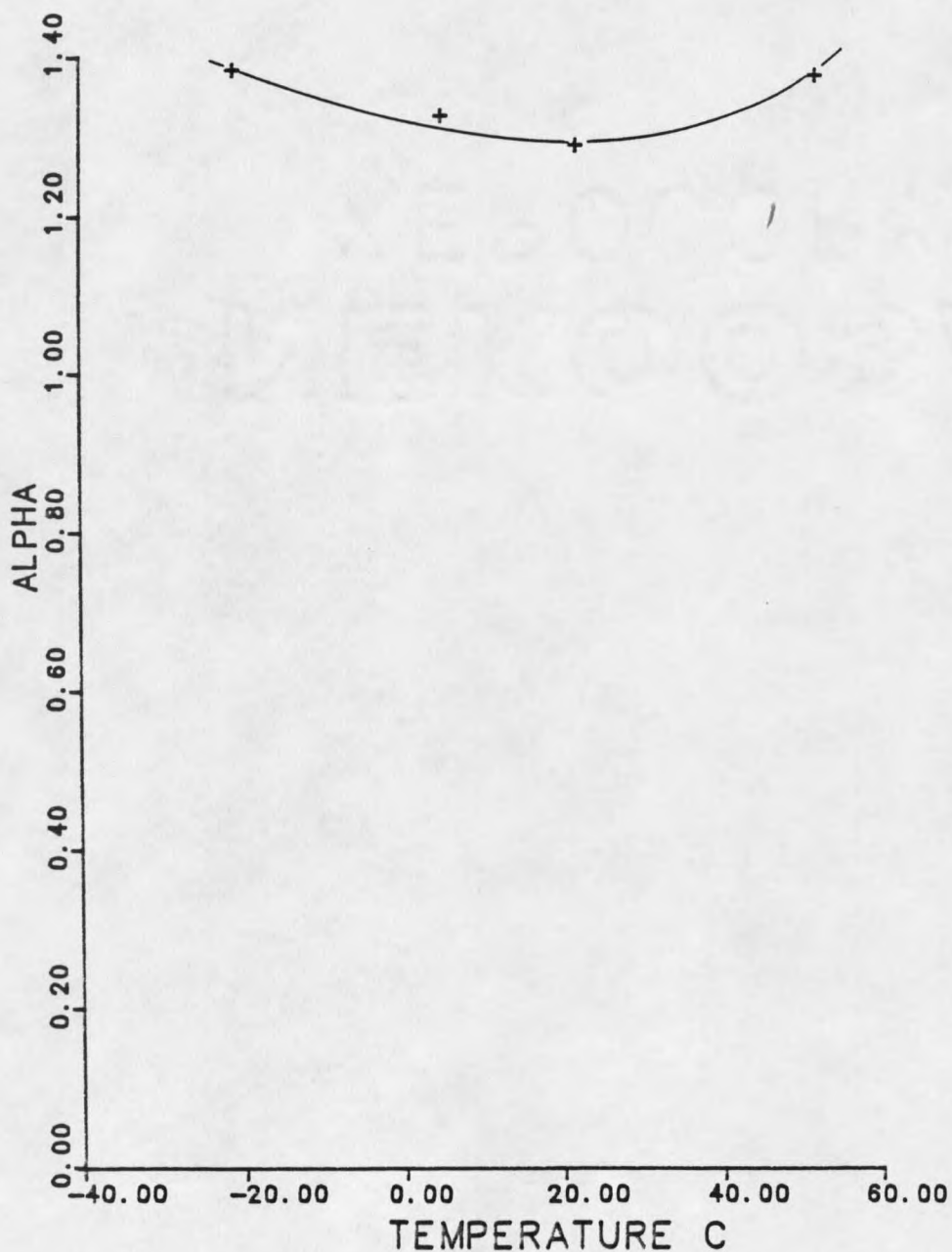


Figure 22. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with no CBr_4 added.

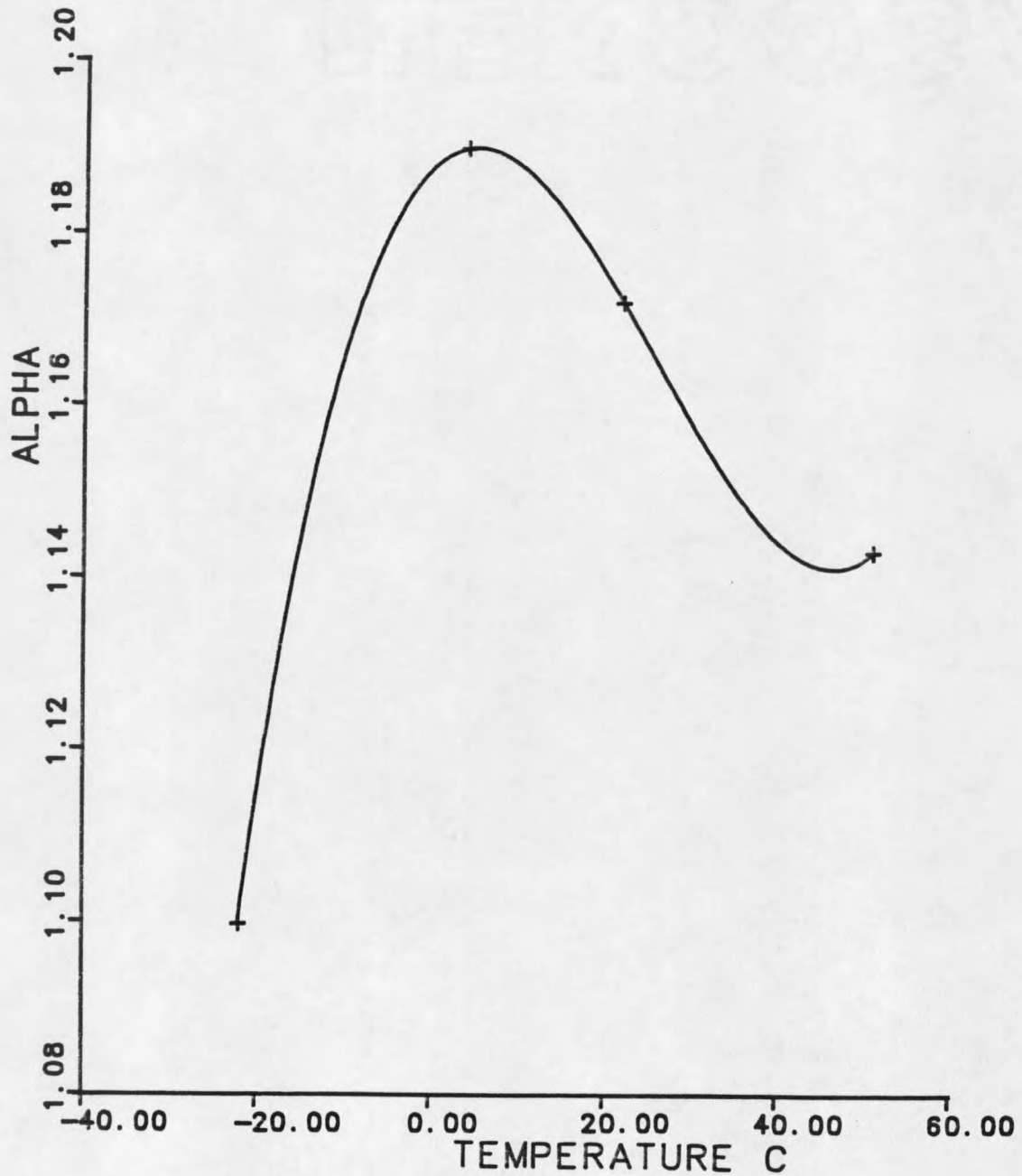
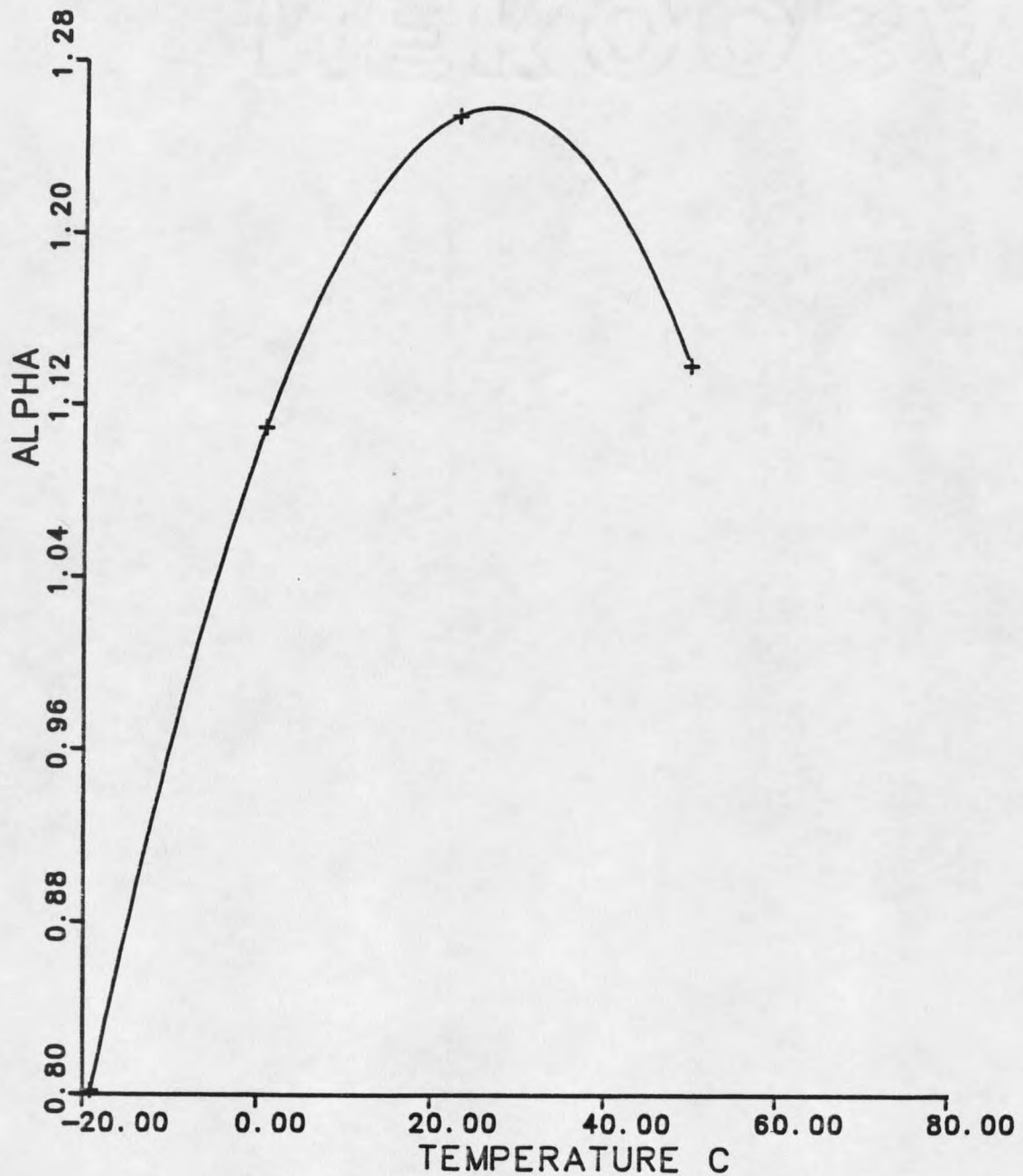


Figure 23. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with no CBr_4 added.



xi
Figure 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.

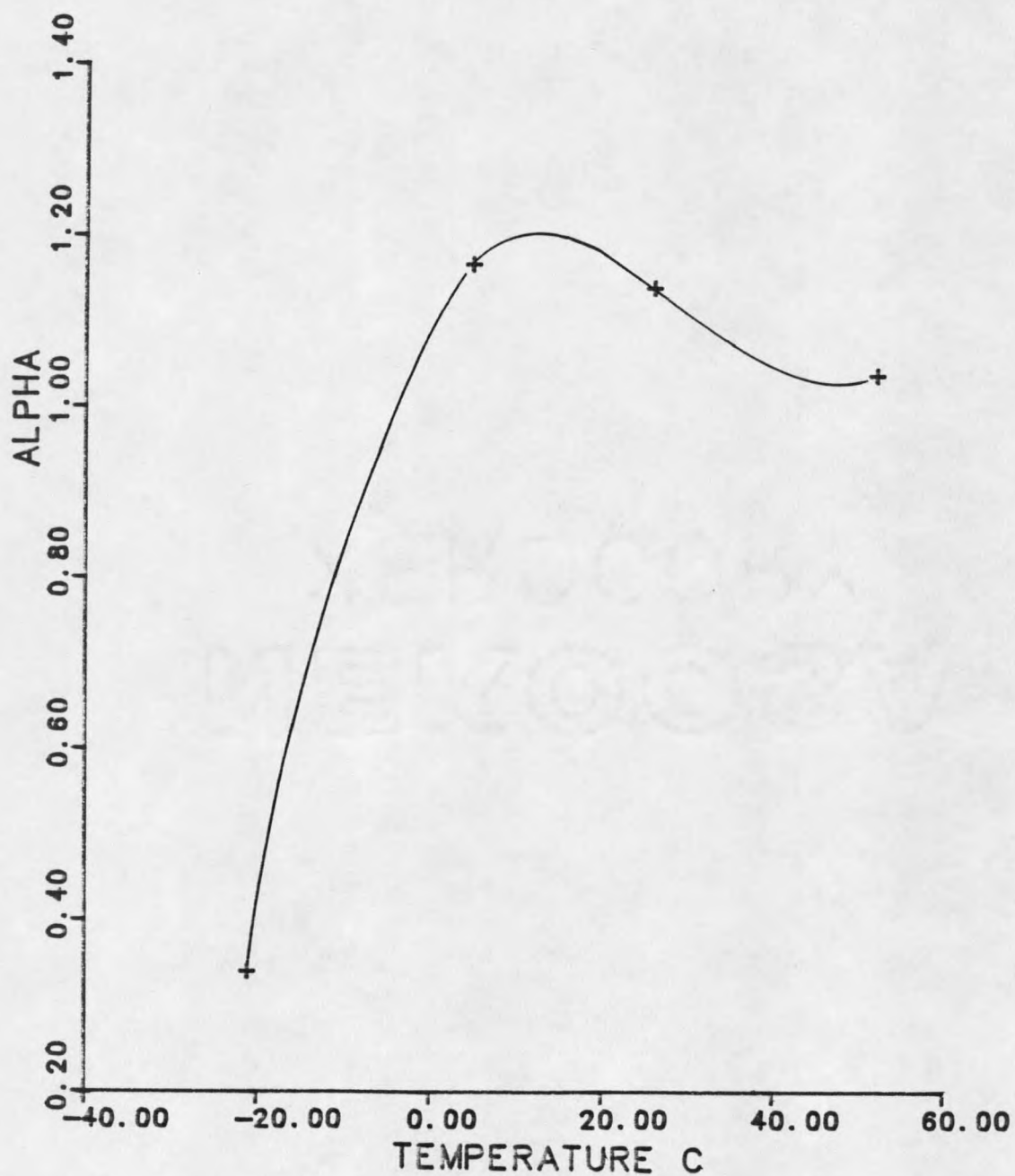


Figure 25. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 70% p-xylene in the xylene mixture with no CBr_4 added.

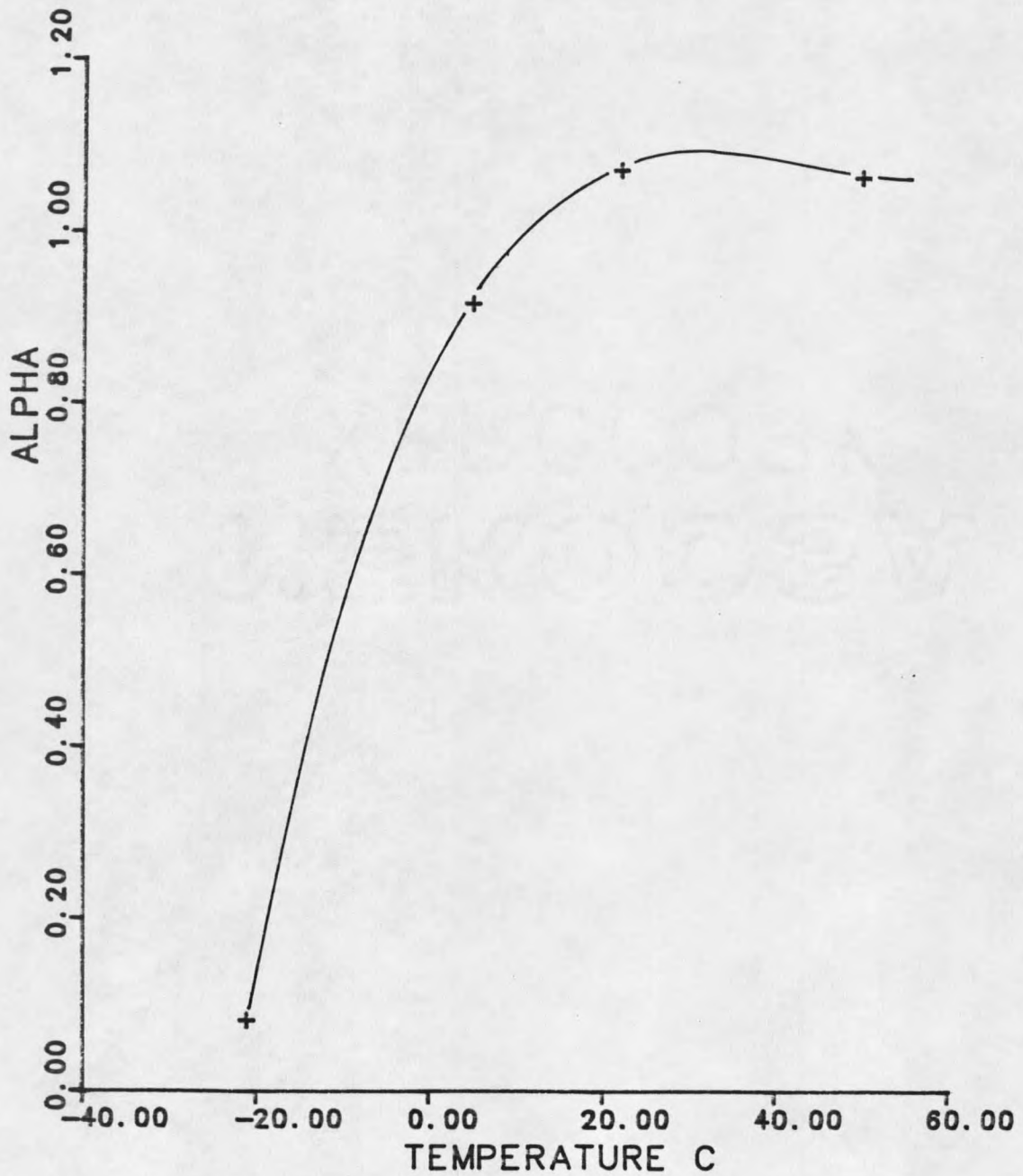


Figure 26. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 90% p-xylene in the xylene mixture with no CBr_4 added.

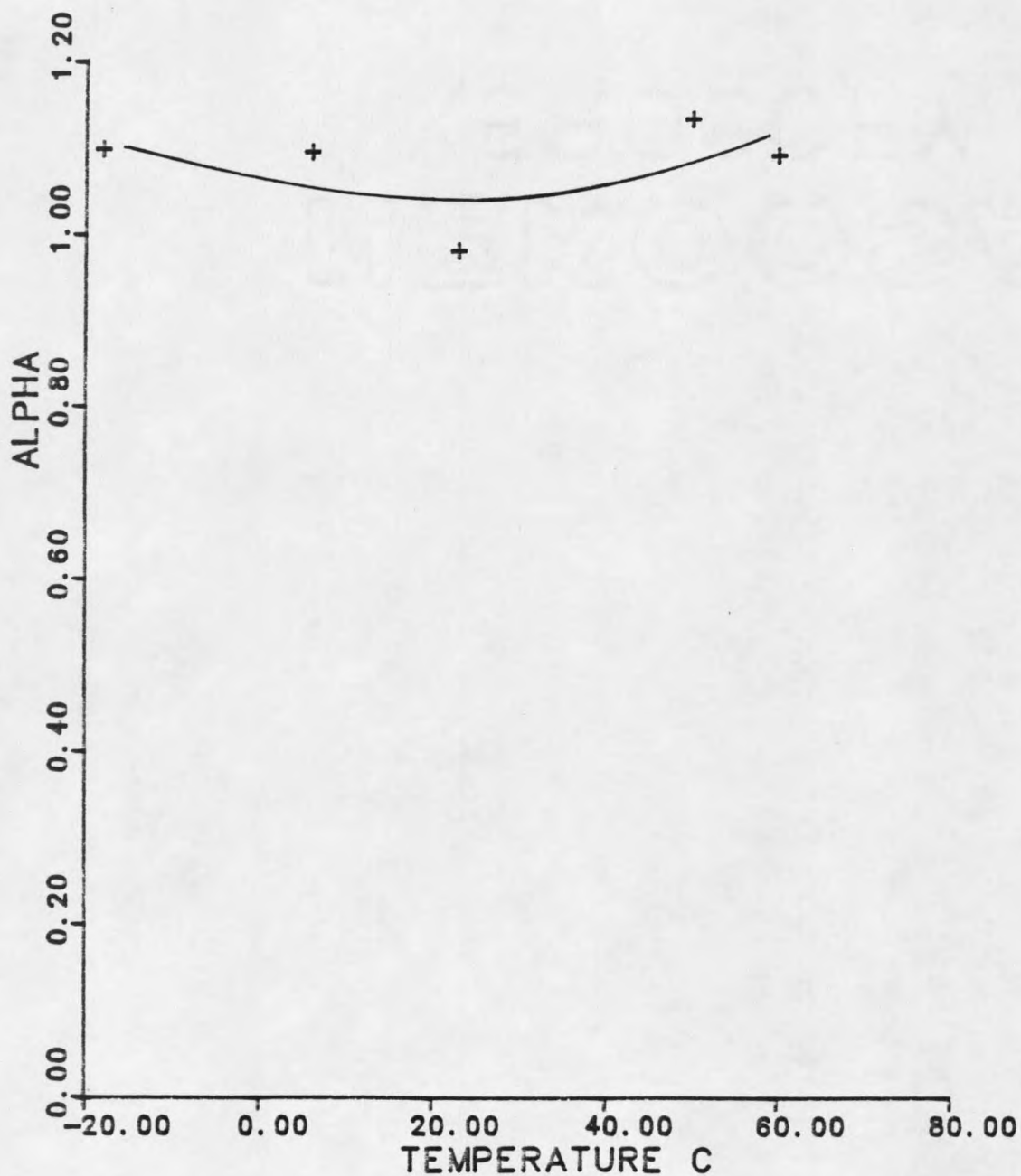


Figure 27. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with 10 mole % CBr_4 added.

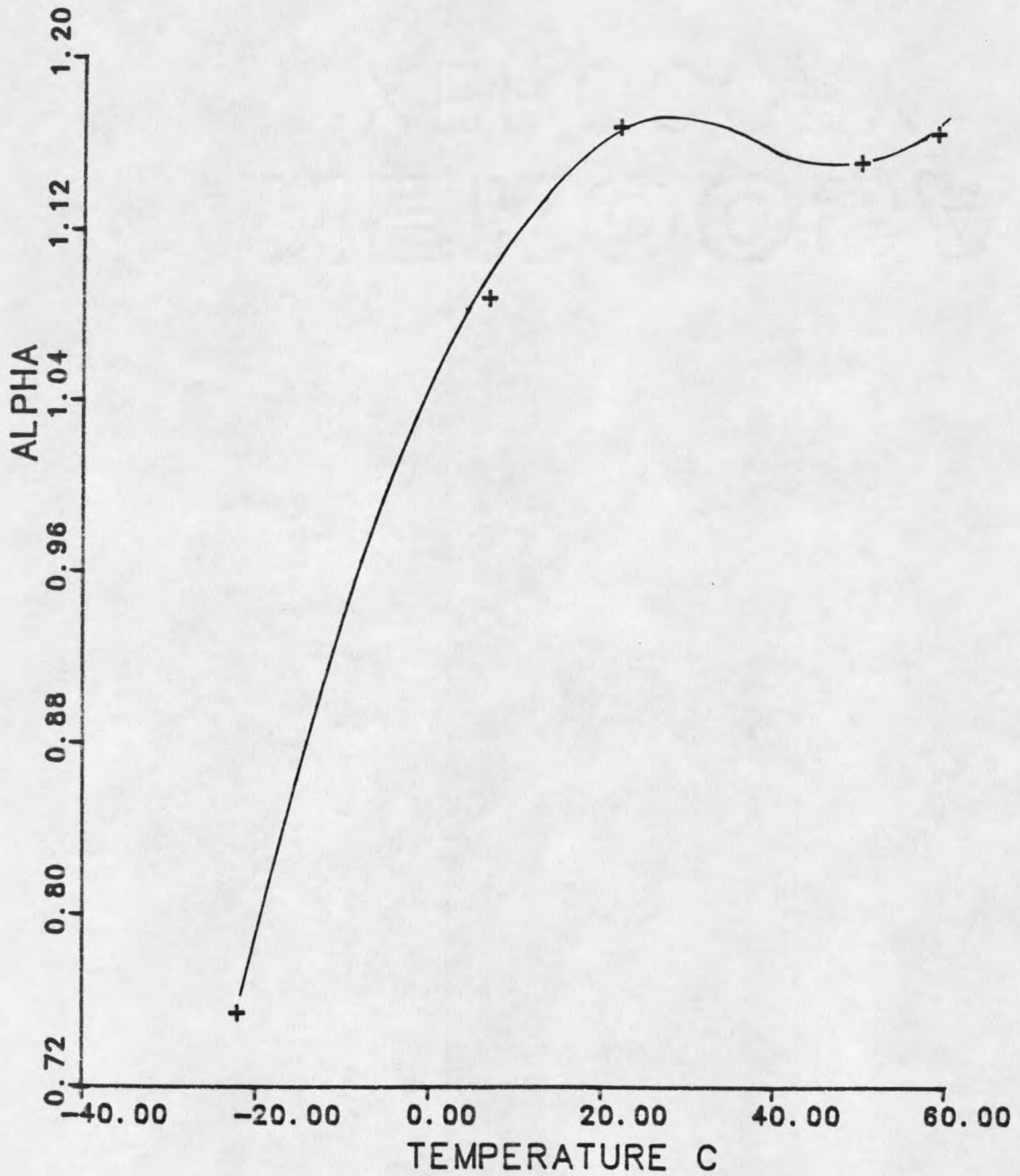


Figure 28. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with 10 mole % CBr_4 added.

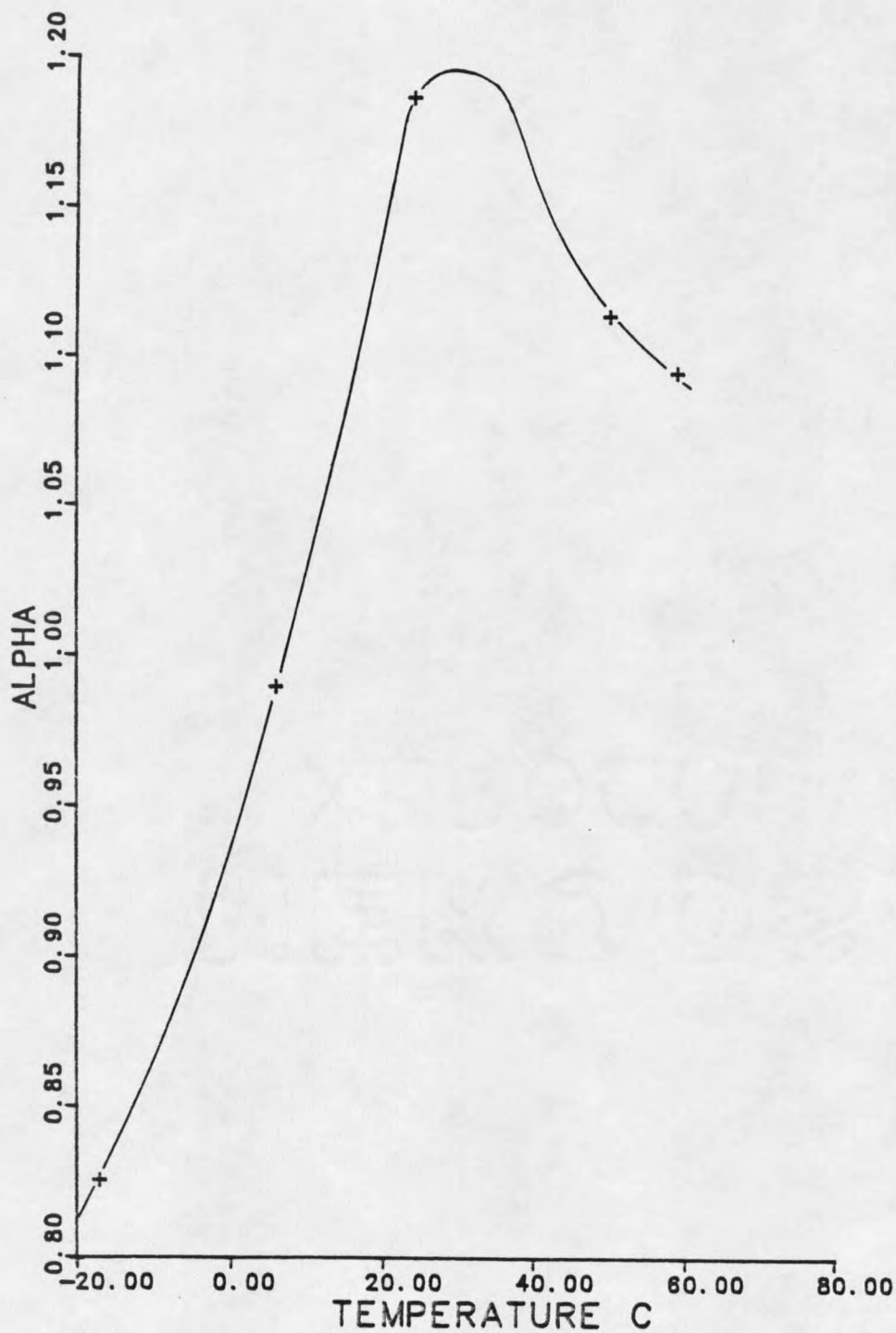


Figure 29. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 50% p-xylene in the xylene mixture with 10 mole % CBr_4 added.

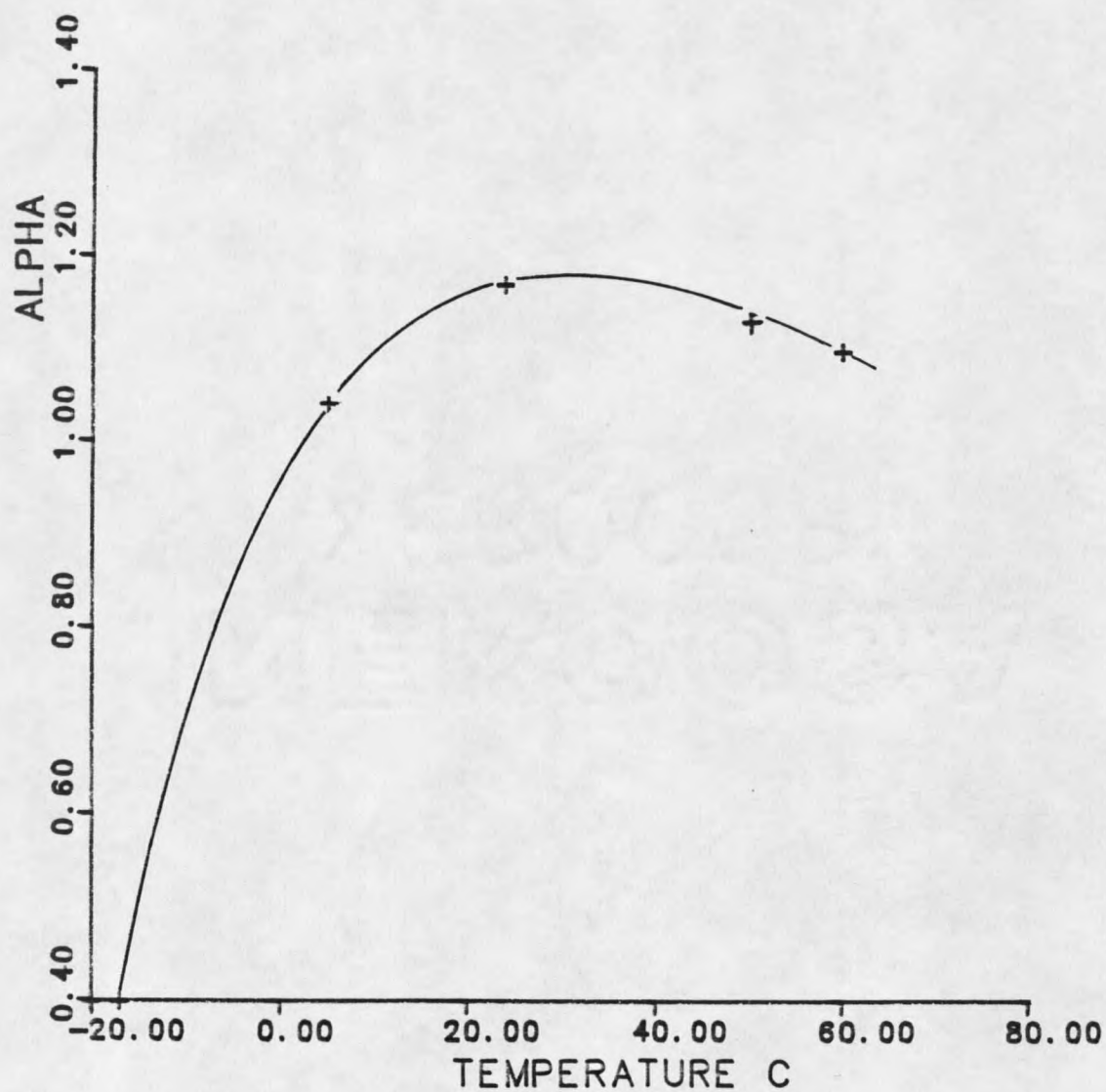


Figure 30. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 70% p-xylene in the xylene mixture with 10 mole % CBr_4 added.

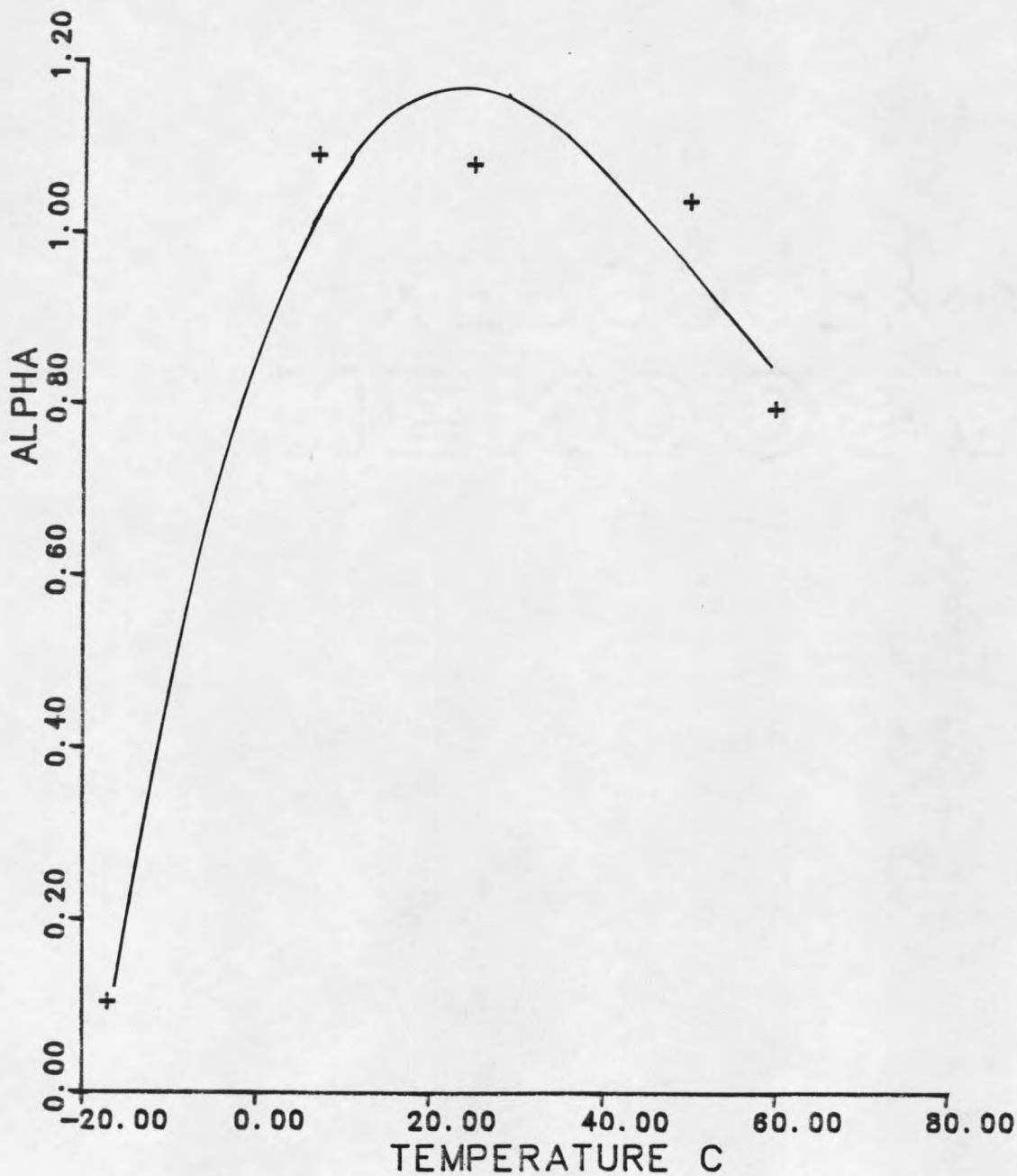


Figure 31. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 90% p-xylene in the xylene mixture with 10 mole % CBr_4 added.

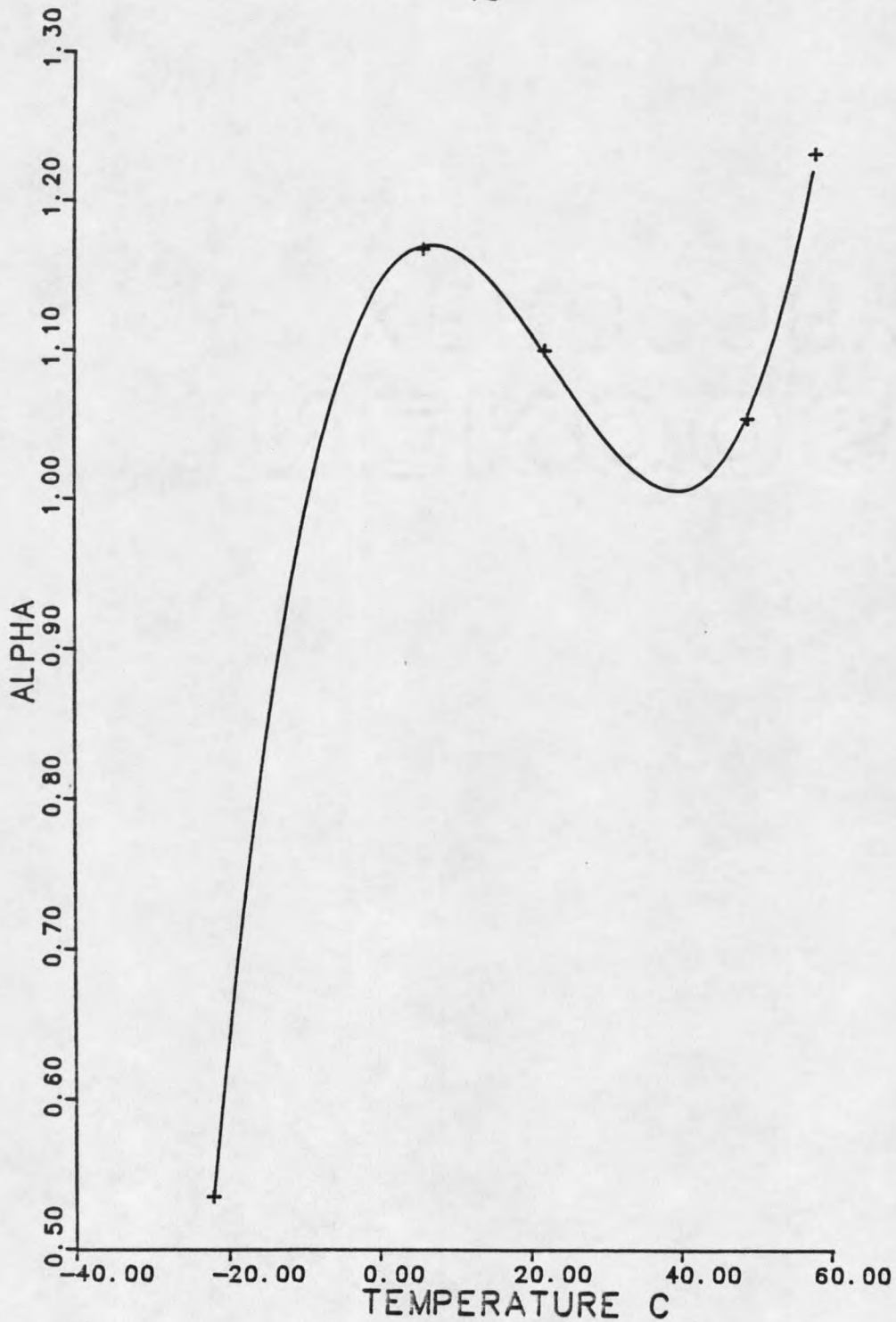


Figure 32. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 10% p-xylene in the xylene mixture with 24 mole % CBr_4 added.

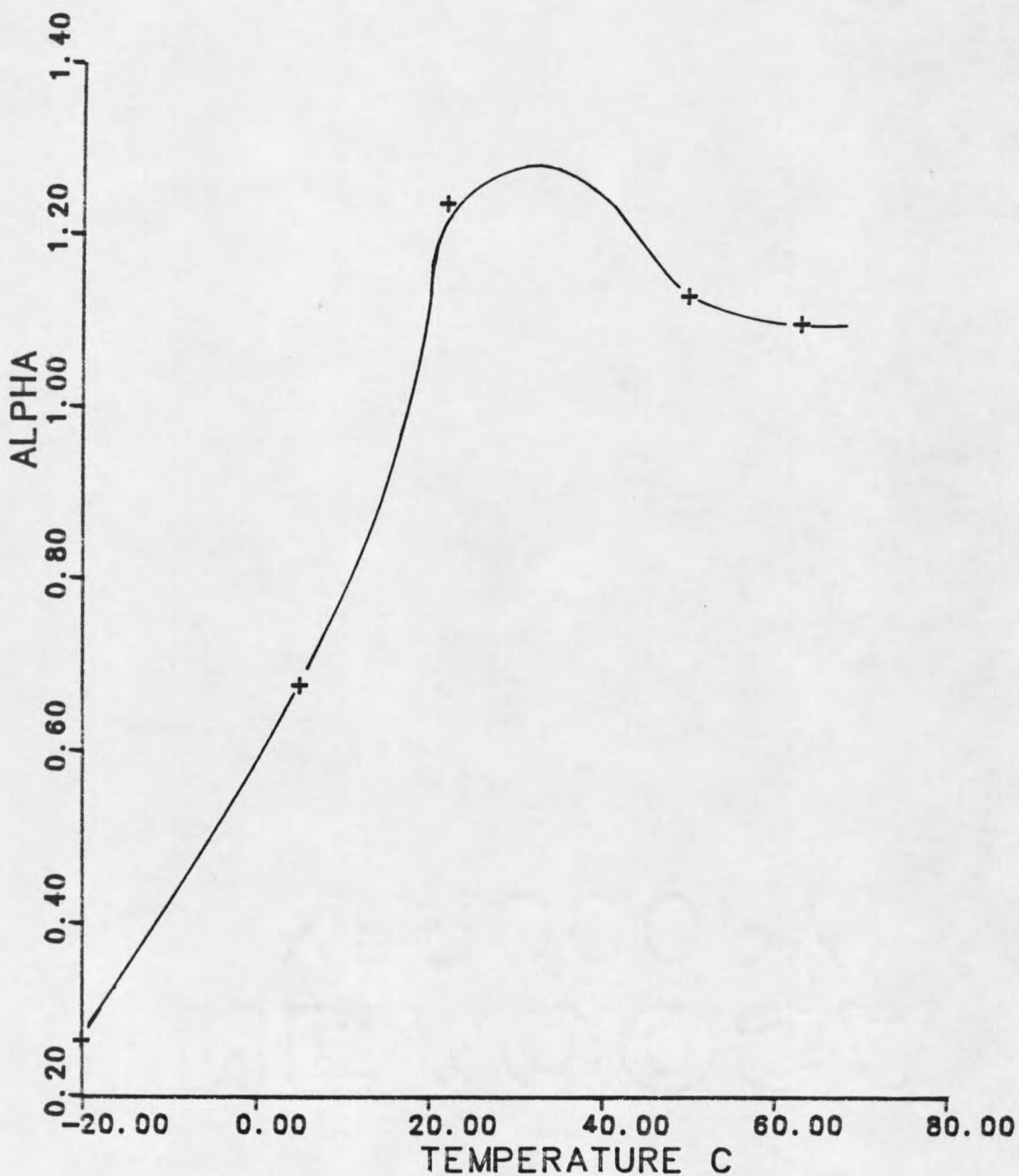


Figure 33. Separation factors (α) produced as a function of temperature from the pervaporation separation of a feed mixture containing 30% p-xylene in the xylene mixture with 24 mole % CBr_4 added.

