Separation of m-Xylene and Ethylbenzene in Gaseous Carbon Dioxide

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Separation of *m*-Xylene and Ethylbenzene in Gaseous Carbon Dioxide

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Abstract

The separation of an equal amount of ethylbenzene (EB) and *m*-xylene on silicalite using carbon dioxide as the carrier was studied. The experimental results indicated that operations in gaseous carbon dioxide provide a better separation efficiency than those at supercritical conditions. The effects of temperature, pressure, and flow rate on separation were also examined. It was found that the most appropriate conditions for obtaining purities of EB and *m*-xylene over 98% were a temperature around 353 K, a pressure of 40.8 atm, and a flow rate about 15 cm³/ min. Comparison of the response curves for single- and two-component injection systems indicated that the model proposed by Gu et al. might be employed to interpret the data.

INTRODUCTION

Ethylbenzene (EB) is a raw material for the production of styrene. One of its sources is xylene mixtures in naphtha crackers and reformers. Because the boiling points of EB and xylene isomers are relatively close, it is difficult to separate them by distillation. In industrial practice, separation is generally achieved by the adsorption method that uses zeolite as the adsorbent under liquid-phase operation (*2–6*). In a recent publication, however, Santacesaria et al. (*7*) observed that separation could be improved by gas-phase operation. They attributed this improvement to the higher mass transfer rate in the gas phase. But for both operations, a desorbent is required. Isopropylbenzene, *p*-diethylbenzene, and toluene are usually employed as desorbents (*8, 9*).

Because supercritical carbon dioxide possesses several special characteristics and physiochemical properties, such as higher mass transfer rate,

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low viscosity, solubility to organic compounds depending on density, and nonflammability, it appears to be an alternative desorbent. In a study of the separation of m- and p-xylene on silicalite in carbon dioxide, Tan and Tsay (10) observed that the separation effectiveness was promising in gaseous carbon dioxide which acted not only as a desorbent but also as a carrier. The objective of this report is to study the separation of EB and m-xylene on silicalite in carbon dioxide. The effects of temperature, pressure, and flow rate on separation efficiency are examined.

To learn more about this separation process, a comparison of the response curves for single- and two-component injection systems is also made.

EXPERIMENTAL

The apparatus used for the pulse injection experiments is shown in Fig. 1. Silicalite pellets of 0.16 cm diameter and 0.62 cm length were used as the packing material. Before use, these pellets were dried at 393 K for 4 h and activated at 873 K for 24 h. About 39.5 g of sample was packed into a stainless steel 316 column of 2.12 cm i.d. and 25 cm length. In order to

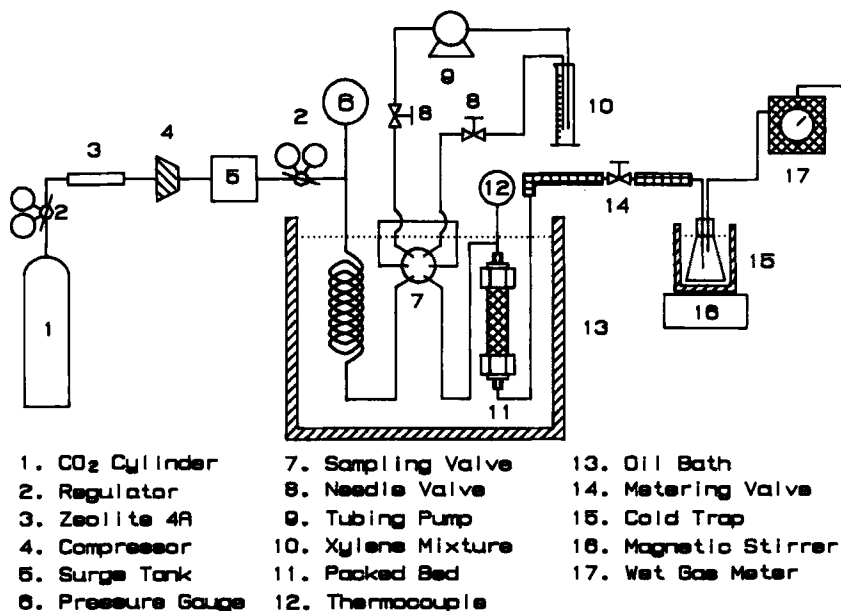|		
1. CO_2 Cylinder	7. Sampling Valve	13. Oil Bath
2. Regulator	8. Needle Valve	14. Metering Valve
3. Zeolite 4A	9. Tubing Pump	15. Cold Trap
4. Compressor	10. Xylene Mixture	16. Magnetic Stirrer
5. Surge Tank	11. Packed Bed	17. Wet Gas Meter
6. Pressure Gauge	12. Thermocouple	

FIG. 1. Schematic diagram of the experimental apparatus.

achieve a uniform flow distribution in the packed bed, glass beads of 0.1 cm diameter were packed above and below the silicalite packing to heights of about 6.3 and 5.3 cm, respectively. These heights were believed to be enough to satisfy the criterion suggested by Tan and Wu (*11*).

A mixture containing equal amounts of EB and *m*-xylene was prepared by mixing equal weights of research-grade EB and *m*-xylene. This mixture was pumped to a six-port sampling valve (Rheodyne). The volume of the sampling loop was 1.0 cm³. Carbon dioxide with a purity at least 99.7% was used as the carrier. It was first passed through a zeolite bed to remove any water vapor and hydrocarbons, and it was then compressed and sent to a surge tank by a diaphragm compressor (Superpressure Inc.). In each experiment the pressure was maintained to within 5 psi of the desired value. The temperature was controlled in an oil bath whose accuracy was about 0.5 K. A preheating coil was immersed in the bath to allow the fluid to reach the desired temperature.

Before injection of the mixture, the six-port sampling valve was switched to let carbon dioxide bypass the sampling loop. When the flow rate of carbon dioxide reached a stable value, the six-port sampling valve was switched to allow the carbon dioxide carrying the mixture to flow into the packed bed. The effluent fluid from the bed was expanded across a metering valve and flowed through a cold trap whose temperature was about $-20°C$. EB and *m*-xylene were collected in the cold trap which contained 1.0 L alcohol. Samples of 6.0 μL were frequently sent to a GC (Varian 3700) for composition analysis. The flow rate in the packed bed was determined by measuring the volume of the gas with a wet test meter.

For the single-component injection experiments, the same procedures were used except the sampling loop was 0.5 cm³ instead of 1.0 cm³.

RESULTS AND DISCUSSION

The total amounts of EB and *m*-xylene collected in the cold trap were determined by measuring the final concentrations in the cold trap. These amounts were compared with those calculated by integrating the response curves. The agreement was satisfactory. The amounts collected were also found to be close to the injection amounts (deviation less than 5%). This indicates that the injected components were not retained on the adsorbent after the experiment. Reproducibility tests were also performed at several operating conditions. Some typical results in Table 1 show that the data could be reproduced within 8%.

The experimental results at different operating conditions are shown in

TABLE 1

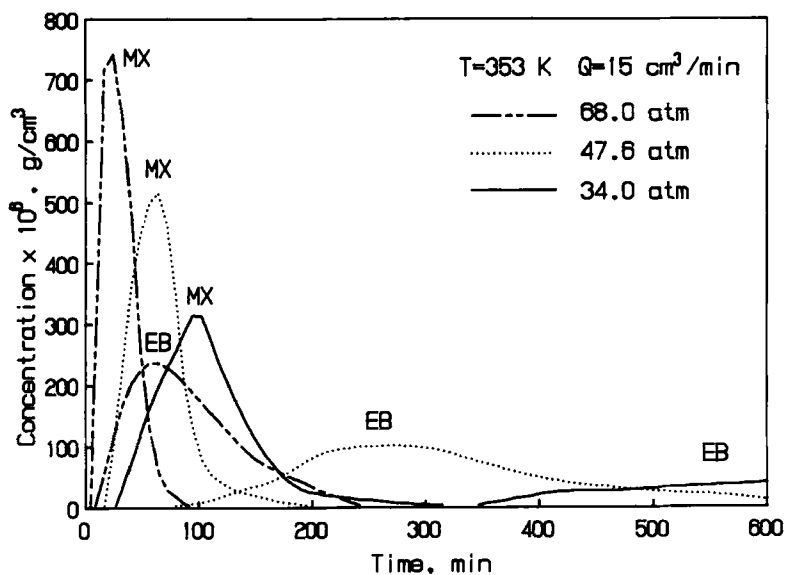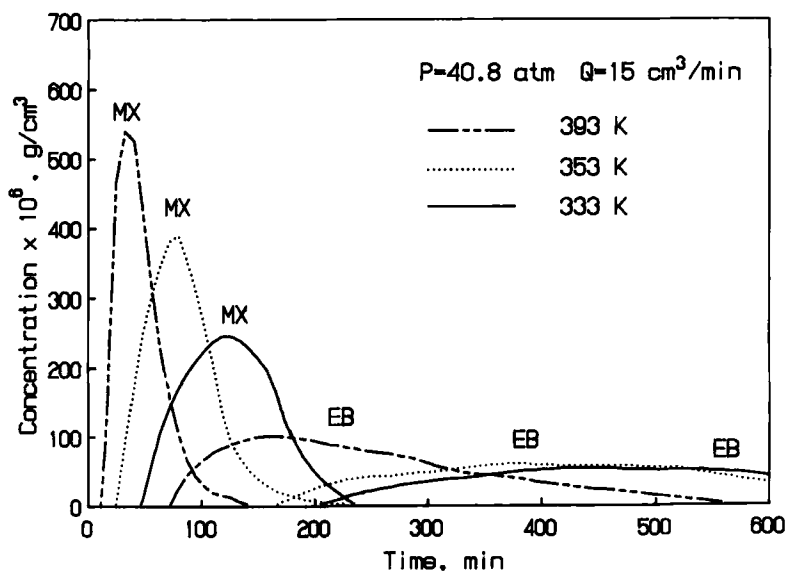Experimental Results of Retention Times and Recoveries at Various Operating Conditions

T (K)	P (atm)	Q (cm³/min)	$\bar{t}_{MX}$ (min)	$\bar{t}_{EB}$ (min)[a]	Recovery	
					MX (%)	EB (%)
Pressure Effect						
353	34.0	15.1	116	481 (27%)[b]	99.6	100.0
353	37.4	15.3	99	446 (50%)	99.4	100.0
353	40.8	14.8	86	391 (73%)	98.1	98.4
353	44.2	15.1	74	368 (81%)	95.5	94.8
353	47.6	15.2	59	264 (98%)	93.7	89.1
353	68.0	15.3	28	89 (100%)	15.8	59.3
353	81.7	15.4	16	40 (100%)	8.4	34.3
Temperature Effect						
333	40.8	15.2	122	424 (58%)	96.8	96.6
343	40.8	15.1	112	432 (63%)	99.4	100.0
353	40.8	14.8	86	391 (73%)	98.1	98.4
363	40.8	15.3	80	396 (67%)	97.2	95.7
393	40.8	15.3	45	294 (99%)	93.1	85.2
Flow Rate Effect						
353	40.8	10.0	117	441 (44%)	98.7	99.5
353	40.8	14.8	86	391 (73%)	98.1	98.4
353	40.8	20.4	68	333 (92%)	97.7	97.3
353	40.8	25.6	56	297 (97%)	97.5	96.6
353	40.8	30.1	47	250 (98%)	96.2	96.5
Reproducibility Test						
353	40.8	14.8	86	391 (73%)	98.1	98.4
353	40.8	15.2	86	374 (77%)	98.0	97.9
353	44.2	15.1	82	370 (65%)	95.1	93.2
353	44.2	15.1	74	368 (81%)	95.5	94.8

[a]$\bar{t}_{EB}$ was calculated with $t_0 = 600$ min.
[b]The fraction of the injected amount was collected within 600 min.

Table 1, and some response curves are illustrated in Figs. 2 to 4. The mean retention time in Table 1 is defined as

$$\bar{t} = \frac{\displaystyle\int_0^{t_0} ct \, dt}{\displaystyle\int_0^{t_0} c \, dt} \tag{1}$$

FIG. 2. EB and m-xylene response curves at various pressures.

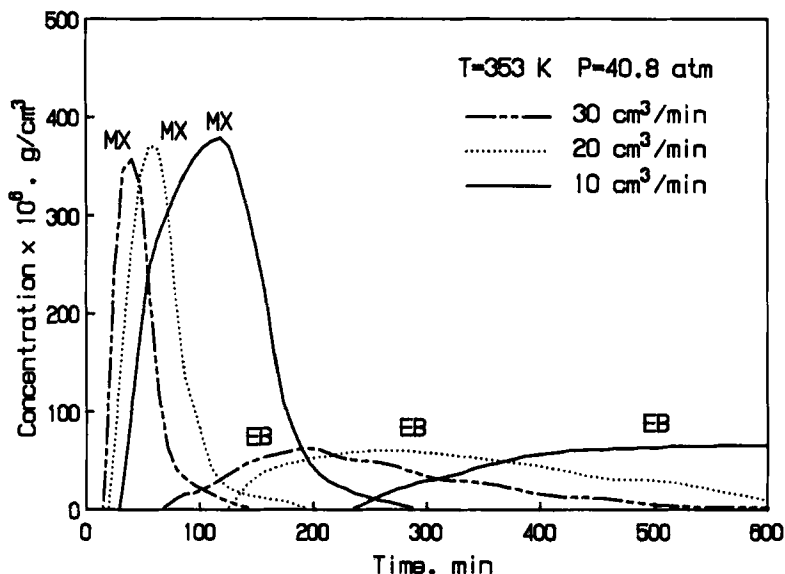FIG. 3. EB and m-xylene response curves at various temperatures.

FIG. 4. EB and *m*-xylene response curves at various flow rates.

where t_0 is equal to 600 min and is less than the time required to complete the experiment. The recovery amount is defined as the amount collected with a purity higher than 98% over the total experimental period divided by the injected amount. A desirable separation process should possess less retention time and higher recovery.

Effect of Pressure

With the temperature and the flow rate fixed at 353 K and 15.0 cm³/min, respectively, Table 1 and Fig. 2 indicate that at relatively lower pressures, for example, at 34.0 and 37.4 atm, the recoveries for both EB and *m*-xylene were high. This means that complete separation was possible. However, operations at these pressures are not recommended because a relatively long operation time was required (see $\bar{t}$ in Table 1). When the pressure was increased to 40.8 atm, the recoveries were reduced about 1.5% but the time required to complete separation decreased about 25%. When the pressure was further increased, the recoveries became less and the desired separation effectiveness could not be obtained. This especially happened near and in the supercritical region of carbon dioxide; for example, at pressures of 68.0 and 81.6 atm. The reduction in recovery with pressure may be due to the fact that at higher pressures (or higher densities) the interacting forces between CO_2 and the solutes are higher than those

between adsorbent and the solutes. For another system, CO_2–toluene, Tan and Liou (12) observed that the adsorption isotherm decreased with increasing pressure. In this situation the screening effect of the adsorbent is reduced and a desired separation is impossible.

It is obvious from Table 1 that a compromise between recovery and retention time exists. If the desired recovery is at least 98%, then the most appropriate pressure is about 40.8 atm. At this pressure, shorter retention times for m-xylene and EB as compared with those at 34.0 and 37.4 atm are required and more EB was collected within 600 min (which was about 73% of the injected amount as compared with 50% at 37.4 atm and 27% at 34.0 atm).

Effect of Temperature

With the pressure fixed at 40.8 atm, Table 1 and Fig. 3 also show that a compromise between recovery and retention time is needed. The smaller recovery at higher temperatures indicates that this separation process might be described by an equilibrium model. This is because the adsorptive capacity decreases with increasing temperature. Based on the desired recovery and the amount of EB collected within 600 min, it is concluded that the most appropriate temperature is about 353 K.

Effect of Flow Rate

From Table 1 and Fig. 4 it is seen that the retention time is influenced more by the flow rate than is the recovery. Since the flow rate has an effect, the interphase mass transfer resistances may play a role during separation. In order to be consistent with the desired recovery and the amount of collected values mentioned above, the suggested flow rate for the present injection amount is about 15 cm^3/min.

Comparison of Single- and Two-Component Injection Systems

Figures 5 and 6 show that for the two-component (EB + m-xylene) injection system, the peak height of the m-xylene response was decreased and the band was spread more, and the front of the EB response curve was diffused and the tailing was reduced as compared with the corresponding single-component injection systems. This behavior of the m-xylene response is opposite to and that of the EB response is identical to those reported by Gu et al. (1) who developed a model including axial dispersion, interphase mass transfer resistances, intraparticle diffusion, and Langmuir isotherms to simulate a multicomponent chromatography. But if carbon dioxide is the desorbent, and with a proper adjustment of the parameters in the Langmuir isotherms for EB and m-xylene, the behaviors of the m-
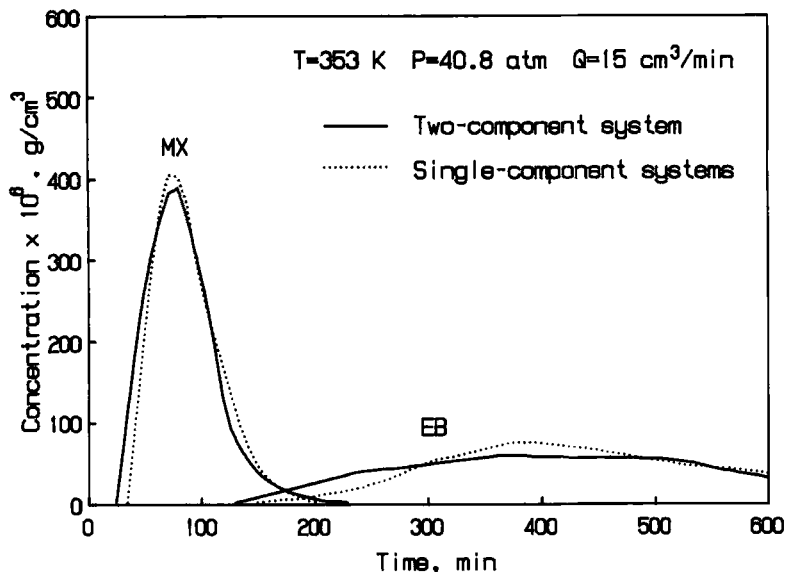
FIG. 5. Comparison of response curves for single- and two-component systems at 353 K and 40.8 atm.
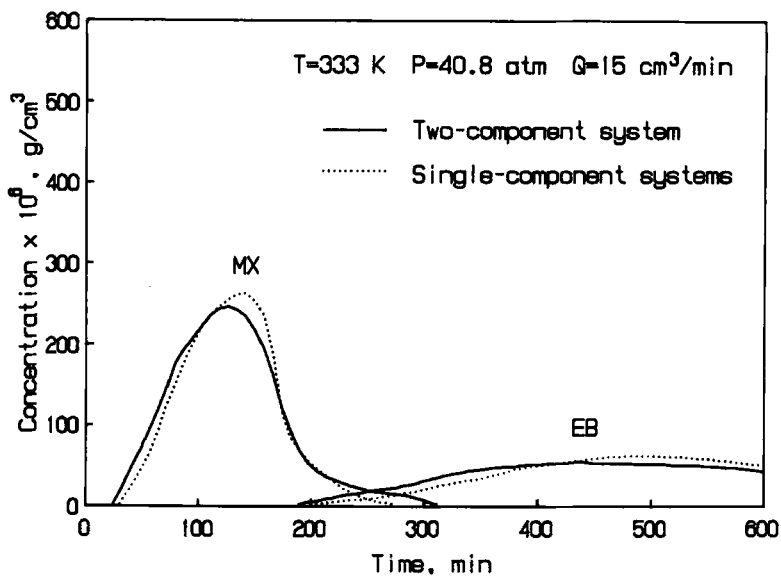

FIG. 6. Comparison of response curves for single- and two-component systems at 333 K and 40.8 atm.

xylene and EB responses might follow those predicted by Gu et al. This suggests that their model may be employed to describe the present separation process. However, due to a lack of information on transport properties and isotherms at supercritical conditions, a quantitative description of the response curves was not made.

CONCLUSION

The separation of EB and m-xylene on silicalite in supercritical and gaseous carbon dioxide was studied. The experimental results indicate that operations in gaseous carbon dioxide offered better separation. The proper separation conditions should be selected by a compromise of the recovery and the retention time. When a recovery of over 98% and more EB collected within a certain period are desired, the appropriate operating conditions appear at a temperature of 353 K, a pressure of 40.8 atm, and a flow rate of 15.0 cm^3/min for a pulse of 1.0 cm^3 of an equal amount of EB and m-xylene. The existence of these proper operating conditions suggests that the adsorption isotherms and the interphase mass transfer resistances should be provided prior to quantitatively describing this separation process.

A comparison of the response curves for single- and two-component injection systems was also made. It indicates that the elution model proposed by Gu et al. (*1*) may be used to interpret the data when carbon dioxide is regarded as a desorbent.

NOTATION

c	effluent concentration (g/cm^3)
t	time (min)
t_0	the scale in Figs. 2 to 4 which was less than the total experimental period (min)
$\bar{t}$	mean retention time (min)

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