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Separation of Toluene–Trichlorotrinitrobenzene Mixture with CO_2 at Elevated Pressures

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Abstract

A flow apparatus was used to study the separation of toluene from a liquid mixture containing mainly toluene and TCTNB (trichlorotrinitrobenzene) with CO_2 at elevated pressures. Experimental results indicated that toluene of 100% purity could be obtained when the operating pressures were below the critical pressure of the CO_2–toluene mixture. The most appropriate operating conditions were found to be at a temperature of 311 K and at a pressure of 61.2 atm. Because the solubility of toluene in CO_2 for the system CO_2–toluene–TCTNB was found to be close to that for the binary system CO_2–toluene, the data for the latter system could be used to model the present extraction operation. The effects of several packings, including glass beads of different sizes and structure packing, on mass transfer rate were also measured in this work. The data indicated that the interphase mass transfer resistances played an important role during the extraction.

INTRODUCTION

In the production of TATB (triaminotrinitrobenzene), a heat-resistant explosive, a waste solution containing mainly toluene (about 95%) and TCTNB (trichlorotrinitrobenzene) (about 3%) is generated. Because of concern with process economics and pollution of the environment, toluene needs to be recovered from the waste. However, due to the presence of a small amount of TATB in the waste, the distillation method is generally not considered to achieve this purpose for safety reasons.

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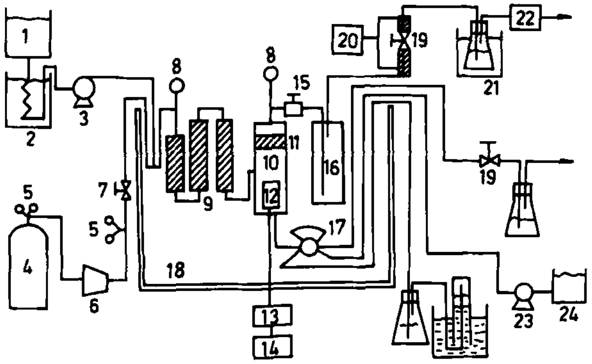
Supercritical carbon dioxide extraction appears to be an alternative method because it can be operated at low temperatures and the carbon dioxide is nonflammable and inexpensive. The applications and principles of supercritical fluid technology have been reviewed extensively in the literature (*1–6*). Equilibrium data are available for the system CO_2–toluene at high pressures (*7*) but not for the system CO_2–TCTNB, as far as we know. Because of different functional groups and molecular weights possessed by toluene and TCTNB, their solubilities in CO_2 are not expected to be the same. If this is the case, separation of toluene and TCTNB with CO_2 may be achieved. The first objective of this study is to investigate this expectation. A flow apparatus was used to obtain the solubility data.

As pointed out by Rathkamp et al. (*8*), a packed column may be a suitable device to carry out extraction at supercritical conditions. However, data for the effects of packings on the extraction rate at elevated pressures are scarce, although they are extensive at or near atmospheric pressure (*9*, *10*). The second objective is to provide these data for high pressure operations. Glass beads with different sizes and structure packing were used in this study.

EXPERIMENTAL

The experimental apparatus used in this work is illustrated in Fig. 1. The entire apparatus was constructed with o.d. 0.63 cm stainless steel 316 tubing, except the packed columns and separator. The waste solution was provided by Chung-Shan Institute of Science and Technology. Its composition, analyzed by GC and HPLC, was found to consist of about 95% toluene, 3% TCTNB, 1% TCDNB (trichlorodinitrobenzene), 0.2% TATB, and some other impurities. Three o.d. 2.54 cm packed columns were connected in series. Their lengths were 10, 15, and 15 cm, respectively. Glass beads of 0.07, 0.1, 0.2, and 0.3 cm diameter and structure packing were employed as the packing materials. The structure packing was fabricated from 80 mesh woven wire cloth. The details of this packing can be found elsewhere (*11*). The separator had an o.d. of 3.3 cm and a height of 20 cm. It contained a demister at the top to prevent possibly entrained liquid drops and a liquid-level sensing capacitor at the bottom to determine the position of the liquid. The capacitor had a diameter of 3.2 cm and a height of 5.5 cm. It was connected to an oscilloscope on which the position of the liquid was displayed. The assembly of the capacitor and oscilloscope was similar to that reported by Chao et al. (*12*).

The experiment started with compression of carbon dioxide (minimum purity 99.8%) by a diaphragm compressor (Superpressure Inc.) and the waste solution by a minipump (Milton Roy). These two pressurized streams were mixed and sent to the packed columns which were immersed in a



1. Liquid Solution
2. Cold Bath
3. Minipump
4. CO_2 Cylinder
5. Regulator
6. Compressor
7. Check Valve
8. Pressure Gauge
9. Packed Column
10. Separator
11. Demister
12. Capacitor
13. Signal Generator
14. Oscilloscope
15. Back Pressure Regulator
16. Vessel
17. Six-Port Sampling Valve
18. Constant Temperature Bath
19. Metering Valve
20. Thermo-Controller
21. Cold Trap
22. Wet Test Meter
23. Tubing Pump
24. Alcohol Solution

FIG. 1. Schematic diagram of experimental apparatus.

constant temperature bath. The temperature of the bath could be maintained to within 0.2 K. The pressure of the mixed stream was read by a pressure gauge (Heise) with an accuracy of ±0.03 atm. The stream discharged from the last packed column was sent to a separator where gas and liquid were separated. By adjusting the metering valve located downstream of the separator, the position of the liquid level in the separator could be maintained. The capacitor was generally kept half immersed. The gas stream leaving the separator was expanded across a metering valve which was wrapped with a heating tape. The condensed liquid, after expansion, was collected in a cold trap which contained 1 L alcohol. The temperature of the cold trap was about 273 K. Samples of 0.5 cm^3 were frequently sent to a FID gas chromatograph (Varian 3700) and a HPLC (Waters 440) for composition analysis. The amount of CO_2 was measured by a wet test meter. From the measured amounts of CO_2 and condensed solutes, the composition of the gas could then be determined. At least five measurements at different times (approximately every hour) were carried out to see if the composition reached a stable value. The results indicate that the deviation in composition among these measurements was less than 1.5%.

The composition in the liquid phase was determined by analyzing the sample collected in a sampling loop whose volume was 0.5 cm^3. The amount of CO_2 in the loop was determined by measuring the volume displaced in a column which was filled with presaturated water. 100-cm^3 alcohol was used to circulate the loop and the cold trap after expansion by a tubing pump (Cole-Parmer). Samples of 0.5 cm^3 of the alcohol solution were analyzed by GC and HPLC. The composition in the liquid phase could thus be obtained in a way similar to that mentioned above for the gas phase.

RESULTS AND DISCUSSION

In order to assure that the present apparatus was reliable to study the separation effectiveness, vapor–liquid equilibrium data for the binary system CO_2–toluene were first measured at pressures of 40.1, 55.1, and 68.4 atm and at 311 K. Data are available in the literature (7) for these operating conditions. The packing material used for this purpose was 0.1 cm glass beads. When the flow rate of toluene was kept at 0.6 cm^3/min, it was observed that equilibrium could be obtained when the flow rate of CO_2 was less than 1.0 cm^3/min (at the operating conditions). Because a significant amount of CO_2 was absorbed into toluene, the flow rate of CO_2 was referred to the rate measured in the gas stream after the separator. The measured equilibrium data were found to agree well with the reported ones, with a maximum deviation of less than 3.0%. The reproducibility tests were also performed at the above operating conditions. The results indicated that all the experimental data could be reproduced to within 2.0%. The vapor–liquid equilibrium data over the presently studied ranges can be interpreted well by the Peng–Robinson equation of state, as has been pointed out by Ng and Robinson (7).

Table 1 shows the experimental data for the extraction of toluene from the waste solution by CO_2. It can be seen that the presence of TCTNB and other compounds lowered the solubility of toluene in CO_2 about 1 to 3% to that for the binary system CO_2–toluene. From the experimental data it was also found that except for toluene, TCTNB and other compounds were not present in CO_2. But when the operating pressures were higher than the critical pressure of the CO_2–toluene system (for example, at 83 atm), toluene and TCTNB were both detected in CO_2. To assure that the presence of TCTNB in CO_2 was not caused by entrainment, both the liquid and CO_2 flow rates were reduced. Nevertheless, the same results were observed. Since high purity of toluene is required for reuse, it appears

TABLE 1
Equilibrium Solubilities of Toluene in CO_2 at 311 K

	y_t	
Pressure (atm)	CO_2–toluene system	CO_2–waste solution system
40.1	0.0040	0.0039
55.1	0.0057	0.0055
61.2	0.0071	0.0070
68.4	0.0078	0.0077

that appropriate operation conditions should be below the critical pressures of the CO_2–toluene binary system.

Because the solubility of toluene from the waste solution in CO_2 is slightly lower than that for the CO_2–toluene binary system, and the Peng–Robinson equation of state can correlate the vapor–liquid equilibrium data well for the CO_2–toluene system, the most appropriate operating conditions for providing the highest solubility can be chosen by the Peng–Robinson equation of state. Due to the presence of some heat-resistant explosives in the waste solution, the operating temperature should not be too high for safety reasons. With this in mind, operating conditions of 311 K and 61.2 atm and of 328 K and 74.8 atm were first considered. To make the best choice, the work required to make the CO_2 in the cylinder, generally at 298 K and 47.6 atm, reach the desired conditions were calculated. This was done by using path isothermal compression followed by isobaric heating. The calculation indicated that the energy required to obtain 1 mol toluene at 311 K and 61.2 atm was about one-third that at 328 K and 74.8 atm. It is obvious that the most appropriate operating conditions needed to recover toluene from the waste solution are at 311 K and 61.2 atm.

Since only toluene can be extracted by CO_2, the concentration of TCTNB in the waste solution increases after extraction. In order to know the effect of the concentration of TCTNB on the extraction power of CO_2, the solubilities of toluene in CO_2 at various concentrations of TCTNB were also measured at 311 K and 61.2 atm, as shown in Fig. 2. From this figure it can be seen that the solubility of toluene decreased linearly with increasing TCTNB concentration, which may be expressed by

$$y_t = y_t^0 - (4.3 \times 10^{-3})x \tag{1}$$

where $y_t^0 = 0.0071$. When the concentration of TCTNB is larger than 30% in the liquid, coprecipitation of toluene and TCTNB is observed. Therefore, the data at these conditions are not reported in Fig. 2.

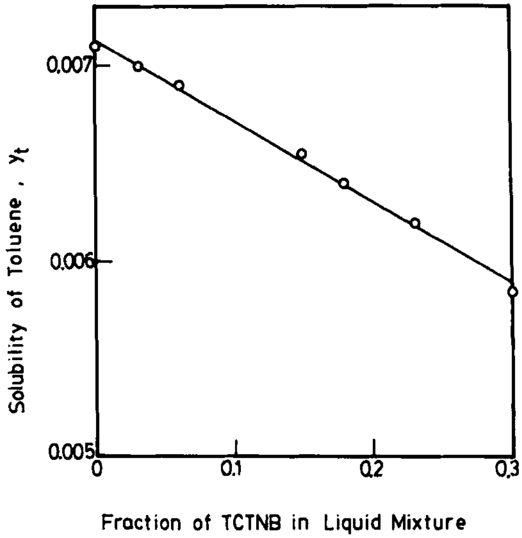


FIG. 2. Equilibrium solubilities of toluene in CO_2 at various TCTNB concentrations at 311 K and 61.2 atm.

Although the presence of TCTNB lowers the solubility of toluene in CO_2, the degree is not significant. To examine the effect of TCTNB on overall performance, the times required to collect a certain amount of toluene from the waste solution in a batch operation were calculated by using Eq. (1) and the equilibrium data for the CO_2–toluene binary system, i.e., $y_t = y_t^0$. The mass balance equation for this operation may be expressed by

$$dM_t/dt = -Qy_t \tag{2}$$

with

$$t = 0, \qquad M_t = M_{t,0} \tag{3}$$

Calculation indicated that the difference between these two periods was only 0.03% for a concentration of toluene in the waste solution of from 95 to 70%. In fact, when the concentration of toluene reached 70%, more than 80% of the toluene in the original waste solution had already been extracted. From this comparison, it is concluded that in order to model the present extraction process at conditions where equilibrium exists, the solubility data for the CO_2–toluene binary system can be used without introducing significant errors. Because of this conclusion, the CO_2–toluene system was used to observe the effects of flow rates and packings on extraction rate.

Recovery of toluene from the waste solution by vacuum distillation was also carried out in this study. The results at several operating conditions indicated that at 311 K and 1.5 torr the collected condensed liquid consisted of toluene only. Due to limitations of the apparatus, experiments at temperatures below 311 K and at pressures below 1.5 torr could not be performed. Thus, the above-mentioned temperature and pressure might be the upper limit of the required operating conditions for obtaining pure toluene but they might not be the optimal ones. Nevertheless, the period and the energy to collect a certain amount of toluene from the waste solution by vacuum distillation were compared with those by extraction with CO_2. The calculation was based on a batch operation, and the energy required for vacuum distillation included the energies for distillation and pumping work. More details of the calculation can be found elsewhere (*13*). From the calculated results, it was found that extraction with CO_2 was superior to vacuum distillation because the former method could save about 80% of time and 90% of energy to recover 80% of toluene from the initial waste solution. It should be mentioned that the above comparison did not consider capital costs, which presumably would be higher for extraction by the CO_2 method since the apparatus needs to withstand higher pressures.

For conventional separation technologies, such as liquid extraction and absorption, effective mass transfer area and liquid and/or gas flow rates are the important factors affecting mass transfer rates. To observe their effects on the present extraction rate, the solubilities of toluene in CO_2 at different gas and liquid flow rates and with several packing materials were measured. The packing materials used in this work included 0.07, 0.1, 0.2, and 0.3 cm glass beads and structure packing. Some commonly used packings, such as Rasching rings and Berl saddles, were not employed because of their dimensions. As pointed out by Tan and Wu (*14*), the ratio of the diameter of the column to the diameter of the packing should be at least 10 to achieve uniform flow distribution. For the present apparatus, this criterion would not be satisfied if Rasching rings and Berl saddles were used.

When the liquid flow rate was kept at 0.6 cm^3/min, the solubilities of toluene in CO_2 at 311 K and 61.2 atm for various packings are shown in Fig. 3. It can be seen that for 0.3 cm glass beads, the saturated solubility was hard to obtain at any CO_2 flow rates. One of the probable reasons is due to the nonuniform distribution of the fluids in the packed columns since the ratio of the diameter of the column to the diameter of the glass

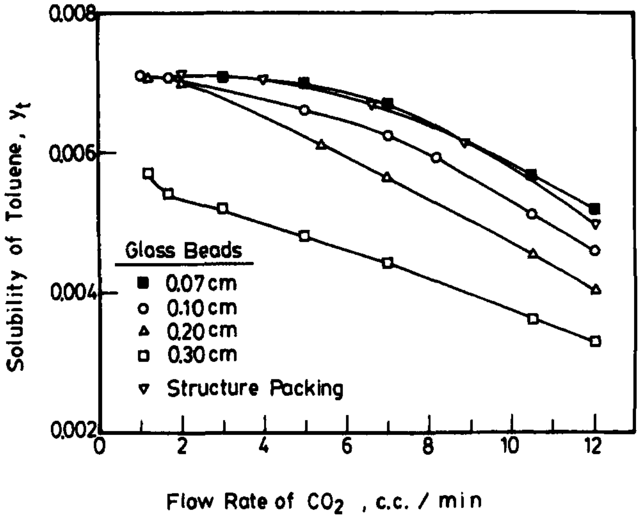


FIG. 3. Effect of CO_2 flow rate on y_t for various packings.

beads is only about 7, which cannot satisfy the criterion suggested above. Under this situation, channeling and wall flow reduced the contact between gas and liquid. The other possible reason is due to the less effective mass transfer area provided by 0.3 cm glass beads. If the shape of the glass beads is assumed to be spherical, the mass transfer area provided by 0.3 cm glass beads is about two-thirds that of 0.2 cm glass beads and about one-third that of 0.1 cm glass beads. The smaller mass transfer area thus provided means that a smaller amount of toluene can be extracted. This conclusion is also true for glass beads other than those of 0.3 cm, as can be seen in Fig. 3. Figure 3 also illustrates that the maximum CO_2 flow rate obtained at saturated solubility decreases with increasing the dimension of the glass beads and at the same CO_2 flow rate, and when saturation was not achieved, the solubility decreased with increasing glass beads dimension. These observations suggest that interphase mass transfer resistances play a role during extraction. Since a significant amount of CO_2 was also dissolved in the liquid, both gas-side and liquid-side mass transfer resistances might exist if the two-film theory was applied. Although several correlations for gas–liquid mass transfer are available in the literature, they were generally derived at or near atmospheric pressure. Whether these correlations can be applied to the present extraction at elevated pressures remains questionable. In spite of this limitation, a qualitative comparison of the solubility with the product of the mass transfer coefficient (k_m) and mass transfer area (a) was made at the CO_2 flow rates where saturation was not achieved. The correlation provided by Turek and Lange (*15*) was employed for this purpose because it can be applied to relatively higher pressures (up to 4 atm) as compared with other existing correlations. By using this correlation, the ratios of $k_m a$ for 0.1, 0.2, and 0.3 cm glass beads to that for 0.07 cm glass beads are 0.84, 0.64, and 0.54, respectively. From Fig. 3, the ratios of the solubility of toluene in CO_2 for 0.1, 0.2, and 0.3 cm glass beads to that for 0.07 cm glass beads are found to be 0.90, 0.80, and 0.64, respectively, at a CO_2 flow rate of 7 cm^3/min, and 0.88, 0.78, and 0.60, respectively, at a CO_2 flow rate of 12 cm^3/min. The relative closeness of these two kinds of ratios suggests that the interphase mass transfer resistances indeed play an important role during extraction. However, it should be pointed out that a gas–liquid mass transfer correlation suitable for high pressure operations is required in order to quantitatively model the extraction process.

Although the interphase mass transfer resistances decrease with increasing CO_2 flow rate, the higher CO_2 flow rates may result in less contact time between gas and liquid. Hence, a proper range of CO_2 flow rate exists to compromise these two opposite effects. Figure 4 shows that the maximum ratios of CO_2 to liquid flow rates needed to obtain saturated solubility of toluene in CO_2 for 0.07 cm glass beads and the structure packing were larger than those for other sizes of glass beads when the liquid flow rate was kept at 0.6 cm^3/min. The higher ratio means that more CO_2 can be

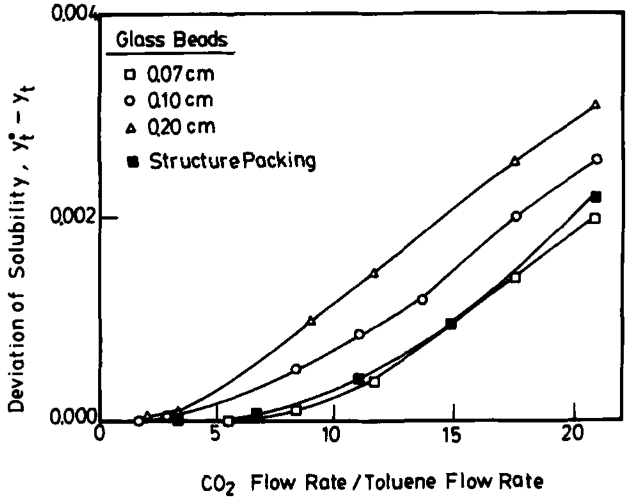


FIG. 4. Deviation of solubility of toluene in CO_2 at various ratios of CO_2 to toluene flow rates at 311 K and 61.2 atm.

used in this situation and more toluene can be collected in a certain period of operation. This is additional evidence that 0.07 cm glass beads and structure packing are the proper packing materials. When the liquid flow rate was raised to 1.2 cm^3/min, the maximum ratios necessary to obtain saturation reduced significantly for all packings. This is not a surprising result, since the higher liquid flow rate reduces the contact time between gas and liquid.

From Fig. 3 it can be observed that the extraction ability of structure packing was similar to that of 0.07 cm glass beads. In the present work the total length of the packed columns was 40 cm, and the pressure drop for 0.07 cm glass beads was therefore not significant. However, this may not be the case for a large-scale operation, but structure packing is recommended in this situation because it provides a smaller pressure drop.

CONCLUSIONS

A flow apparatus was used to study the separation of toluene from a liquid mixture containing 95% toluene, 3% TCTNB, and some other heat-resistant explosives with CO_2 at elevated pressures. The experimental results indicate that when the operating pressure is below the critical pressure of the CO_2–toluene binary system, 100% purity of toluene could be obtained after expansion of CO_2. The solubilities of toluene from the liquid mixture in CO_2 at these conditions were observed to be close to those for the CO_2–toluene binary system, therefore the data for the latter system could be used to select the most appropriate conditions. From energy and safety concerns, a temperature of 311 K and a pressure of 61.2 atm were found to be the best operating conditions. The effects of the presence of TCTNB on extraction was also measured in this work; however, its effect was found to be small. To model extraction at equilibrium, solubility data for the CO_2–toluene system could be used without introducing significant errors.

Separation by vacuum distillation was also carried out in this study. At 311 K and 1.5 torr, toluene of 100% could be recovered after condensation. Compared with extraction with the CO_2 method, this method is not recommended because it consumes more energy and it takes a longer time to recover a certain amount of toluene.

Several packings, including 0.07, 0.1, 0.2, and 0.3 cm glass beads and structure packing, were used to examine their effects on the mass transfer rate. The experimental results indicated that interphase mass transfer resistances play an important role during extraction. In order to reduce those resistances and to obtain a higher extraction rate, 0.07 cm glass beads and structure packing were found to be the best packing materials. For future large-scale operations, structure packing is recommended because it provides a smaller pressure drop.

NOTATION

M_t	amount of toluene present in liquid for a batch operation (g)
Q	CO_2 flow rate (mol/min)
t	time (min)
x	weight fraction of TCTNB in liquid mixture
y_t	solubility of toluene in CO_2 (mol/mol)
y_t^0	saturated solubility of toluene in CO_2 for the CO_2–toluene binary system (mol/mol)

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REFERENCES

1. W. Gangoli and G. Thodos, *Ind. Eng. Chem., Prod. Res. Dev., 16,* 208 (1977).
2. M. E. Paulaitis, J. M. L. Penninger, R. D. Gray, and P. Davidson, *Chemical Engineering at Supercritical Fluid Conditions,* Ann Arbor Science, Ann Arbor, Michigan, 1983.
3. M. E. Paulaitis, V. J. Krukonis, R. T. Kurnik, and R. C. Reid, *Rev. Chem. Eng., 1,* 179 (1983).
4. J. M. L. Penninger, M. Radosz, M. A. McHugh, and V. J. Krukonis, *Supercritical Fluid Technology,* Elsevier, New York, 1985.
5. M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction, Principles and Practice,* Butterworths, Stoneham, 1986.
6. S. S. H. Rizvi, A. L. Benado, J. A. Tollweg, and J. A. Daniels, *Food Technol.,* p. 55 (June 1986).
7. H. J. Ng and D. B. Robinson, *J. Chem. Eng. Data, 23,* 325 (1978).
8. P. J. Rathkamp, J. L. Bravo, and J. R. Fair, *Solvent Extraction and Ion Exchange, 5,* 367 (1987).
9. J. M. Coulson and J. F. Richardson, *Chemical Engineering,* Pergamon Press, Oxford, 1964.
10. R. T. Treybal, *Mass-Transfer Operations,* McGraw-Hill, New York, 1980.
11. J. L. Bravo, J. A. Rocha, and J. R. Fair, *Hydrocarbon Process.,* p. 91 (January 1985).
12. K. C. Chao, H. M. Lin, and G. D. Nageshwar, *Phase Equilibrium in Coal Liquefaction Processes,* Report to Electric Power Research Institute, 1980.
13. B. S. Chen, MS Thesis, National Tsing Hua University, Taiwan, 1990.
14. C. S. Tan and Y. C. Wu, *Chem. Eng. Commun., 68,* 119 (1988).
15. F. Turek and R. Lange, *Chem. Eng. Sci., 36,* 569 (1981).

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