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Separation of Anthracene from Crude Anthracene Using Gas Antisolvent Recrystallization

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Abstract

Pure anthracene is mostly used for conversion to anthraquinone, an intermediate for the synthesis of very powerful vat dyestuffs. A coal tar distillate, crude anthracene, which contains 30% anthracene, 25% phenanthrane, 15% carbazole, and other impurities, was used as the model mixture. In this study, 90% by weight purity anthracene was obtained using gas antisolvent (GAS) recrystallization. The GAS process induces the separation of solids by introducing an antisolvent, carbon dioxide (or the supercritical fluid), into acetone which was used as the liquid solvent. The dissolution of the compressed gas into the solute-laden solution selectively lowers the solubilities of solid solutes and salts them out. The results showed that high purity anthracene was obtained at a high feed concentration and high pressure conditions. The separation factor of anthracene versus phenanthrene is close to 30.07.

INTRODUCTION

In recent years a large number of applications of supercritical fluid extraction have become available for industry. This process uses a supercritical fluid as the solvent to extract and separate solid solutes from a solute-laden solution, based on the selectivity of the supercritical fluid. The yield of solid is dependent on the density of the gas and the solid distribution factor between two phases (*1–4*).

Some gases dissolve to a great extent in many organic solvents at elevated pressures. The solubilities of a few gases in liquids were studied by Francis (*5*). Under pressure, a part of the gas could become miscible with the liquid, such as ammonia in water, ethylene in water, carbon dioxide in acetone, etc. (*6*, *7*). Crystallization, which is widely used to separate and

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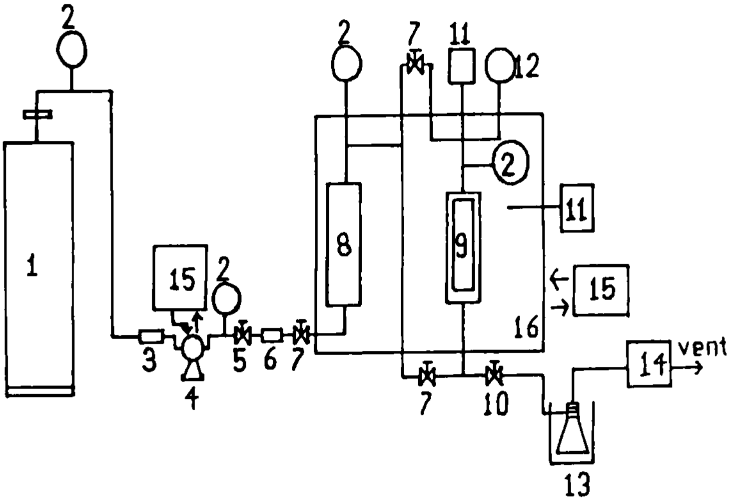
purify a product from a mixture, always yields high purity crystalline materials. Conventional cooling crystallization exploits the concentration change of the solute in a solution by cooling. This action allows the solid to precipitate in the crystalline form (*8*). Gas antisolvent recrystallization (so-called GAS process) is a kind of crystallization that occurs in the liquid phase with the dissolution of an antisolvent gas into the solution. Gallagher et al. used this technology to study the particle morphology of nitroguanidine (*9*). By using GAS recrystallization, a separation study of *trans*-β-carotene and *cis*-β-carotene was investigated by Chang and Randolph (*10*).

There are three keys to applying GAS crystallization. (1) The chosen solid solute must dissolve in a small amount of a selected liquid solvent.



1. CO_2 cylinder
2. pressure gauge
3. stainless steel filter
4. high-pressure pump
5. relief valve
6. check valve
7. valves
8. surge tank
9. Jerguson gauge
10. micrometering valve
11. temperature controller
12. back-pressure regulator
13. separation flask
14. wet gas meter
15. cooler
16. air bath

FIG. 1. Schematic flow diagram of the gas antisolvent recrystallization process.

(2) The solid must be insoluble in the antisolvent gas. (3) The gas must be at least partially miscible with the liquid solvent.

Crude anthracene, which was used as the solute in this study, is a raw material used to make anthraquinone. A few studies have been published about the separation and purification of crude anthracene. Gurevich et al. (*12*) and Litvinenko et al. (*11*) used liquid crystallization and the selectivity of acetone to separate anthracene from crude anthracene. They obtained at least 90% anthracene by the acetone method but with a long cooling period (8 to 18 h).

Supercritical fluid extraction was used to extract anthracene from coal tar distillate by Lisicki et al. (*13*) and Sako et al. (*14*). They concluded that the solubility and the distribution factor of anthracene in supercritical carbon dioxide are very low, hence the efficiency of the separation is poor.

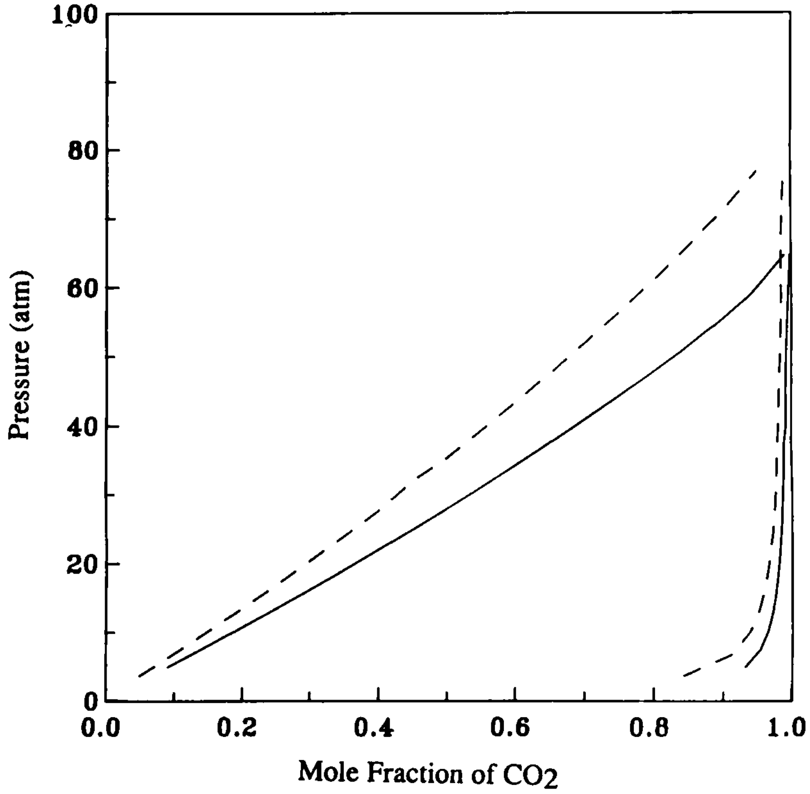


FIG. 2. Phase diagram (*p-x-y*) of CO_2 and acetone at 27 (——) and 40°C (- -) as predicted by the Peng–Robinson equation of state.

TABLE 1
Solubilities of Solids at 30°C in This Study Compared with Literature Data

	Anthracene	Phenanthrene	Carbazole	Crude anthracene
This study	1.12	37	—	6.793
Gurevich et al. (1977)	1.13	42	9.74	—

In this study, crude anthracene was used as a model solid mixture; acetone, a highly selective organic solvent, was chosen as the solvent; and carbon dioxide was used as an antisolvent.

EXPERIMENTAL

The schematic flow diagram of GAS recrystallization is shown in Fig. 1. Liquid carbon dioxide (99.5 + %), compressed by a high pressure pump

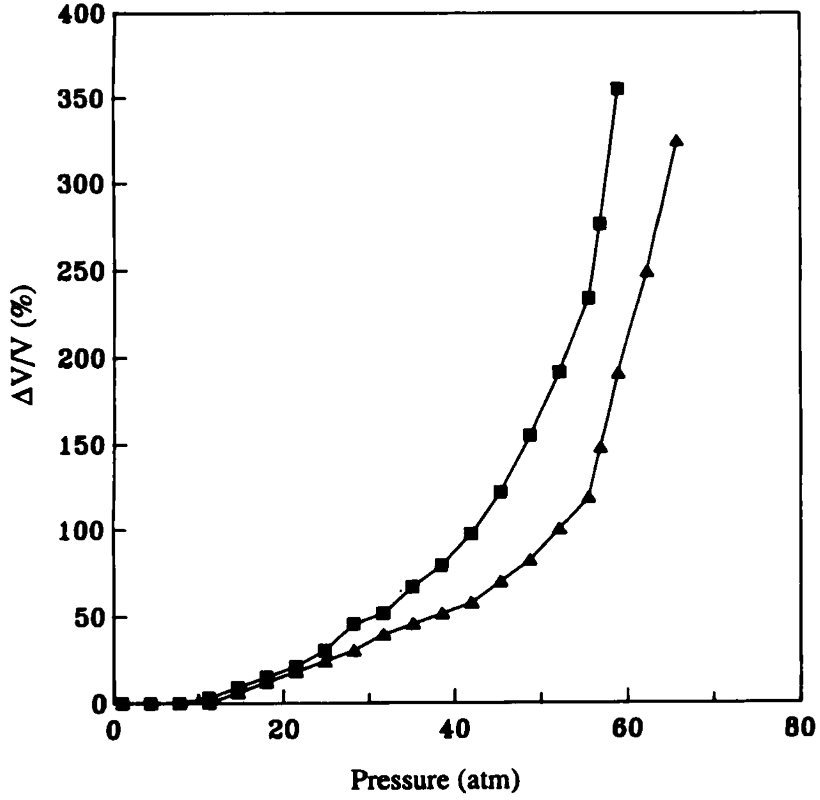


FIG. 3. Solvent expansion behavior of CO_2 in acetone at 27 (■) and 40°C (▲).

(Milton Roy, NSI-33R), flowed into a surge vessel (Whitey, DOT-3A-1800) and attained the desired temperature and pressure. The compressed carbon dioxide was introduced through a bottom valve into a salting-out vessel with a sight glass (Jerguson gauge, 4-T-20). A certain amount of solute-laden solution was held at the bottom of the vessel by a filter paper (Millipore, 0.45 μm) and a stainless steel filter. The pressure was controlled by a backpressure regulator (Haskel, 27741-4) with an accuracy of 0.7 atm. The temperature was controlled at 27°C by a constant temperature air bath. In the separation study, carbon dioxide was dissolved in acetone and expanded to a 50-mL solution at the same time the solids were precipitated from the solution. After crystallization, the injection valve was closed and the top washing and the bottom letdown valves were opened. Fresh liquid carbon dioxide was used to wash and dry the salted-out solids; the purpose of this action was to remove any residual solvent inside the solids. The

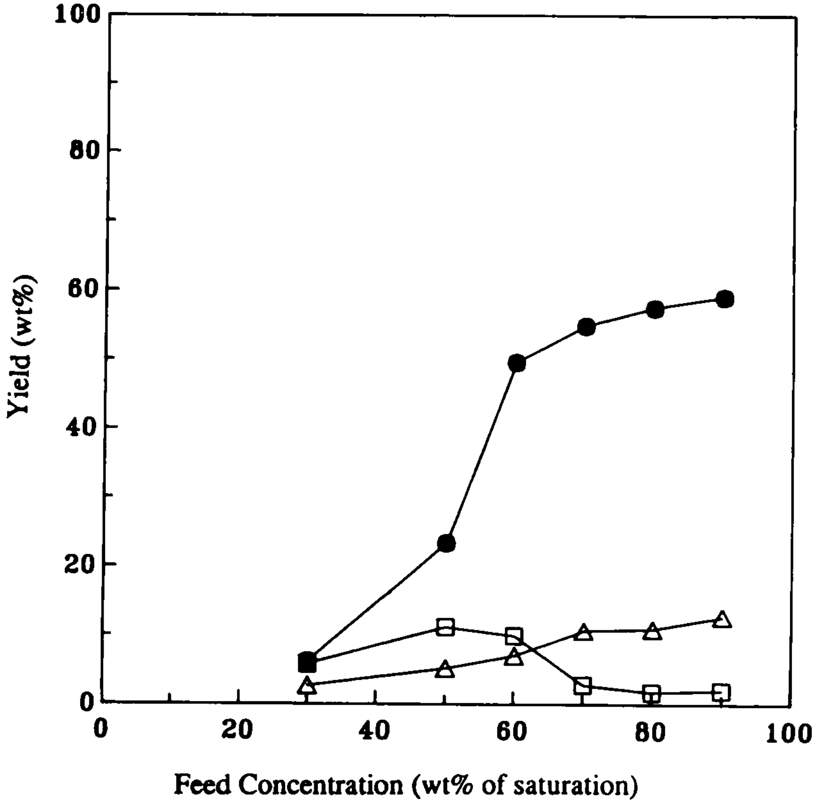


FIG. 4. Yield of anthracene (●), phenanthrene (□), and carbazole (△) in GAS recrystallization at 52 atm and 27°C.

depleted solution and carbon dioxide were separated in a flask. The amount of carbon dioxide was obtained from a wet gas meter (Shinagawa, W-NK-1A). The purified solids, which settled on top of the polymer filter and on the wall, were collected and analyzed. For the study of acetone expansion behavior, 20 mL acetone was poured into a Jerguson gauge, compressed carbon dioxide was introduced, and the acetone expanded. The liquid level of the mixture was measured with an interval of 3.4 atm from 1 to 65 atm. The difference between initial and expanded volumes was calculated.

REAGENTS AND ANALYSIS

Crude anthracene samples were donated by Chinese Steel Corporation. Anthracene (Merck, 96+%), phenanthrene (Ferak Berlin, 98+%), carbazole (Merck, 98+%), and naphthalene (Merck, 99+%) were used as

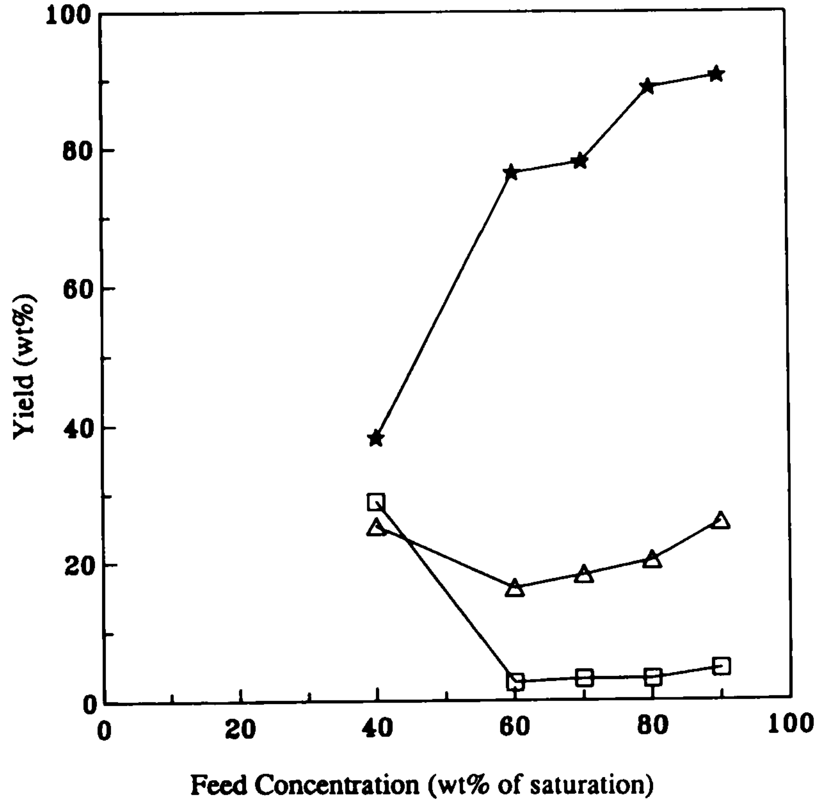


FIG. 5. Yield of anthracene (★), phenanthrene (□), and carbazole (△) in GAS recrystallization at 103 atm and 27°C.

received. These pure materials were used to create the calibration curve. The purity and the yield of solid samples were analyzed by HPLC chromatography (Waters, model 510) equipped with an UV detector. A C-18 column was used with a mobile phase containing 70% (v/v) methanol and 30% (v/v) water at 1 mL/min flow rate. Naphthalene was used as the internal standard. The retention times of anthracene, phenanthrene, carbazole, and naphthalene were 13.78, 12.01, 3.40, and 5.05 min, respectively.

RESULTS AND DISCUSSION

Solubilities of Carbon Dioxide and the Solids in Acetone

The Peng–Robinson equation of state (*16*) was used to predict the phase equilibria of acetone and carbon dioxide at 25 and 40°C. The results agree

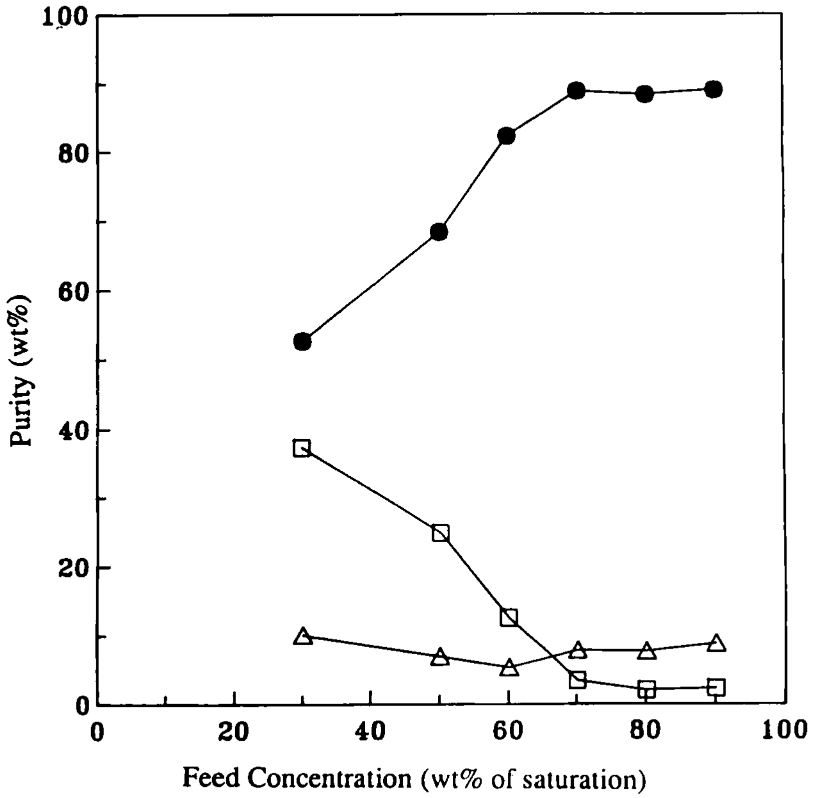


FIG. 6. Purity of anthracene (●), phenanthrene (□), and carbazole (△) in GAS recrystallization at 52 atm and 27°C.

well with Katayama's data (*15*). The predicted *p-x-y* phase diagrams at 27 and 40°C are shown in Fig. 2. They show that the solubility of carbon dioxide in acetone is approximately 80 mol% at 27°C and pressures above 45 atm. The gravimetric method was used to measure the solid solubility in acetone. The experimental and literature solubilities of anthracene, phenanthrene, carbazole, and crude anthracene in acetone are listed in Table 1. Anthracene has the lowest solubility (1.12 g/100 mL acetone).

Acetone Expansion Behavior

When carbon dioxide is dissolved in acetone under pressure, this action expands the solution. The more the pressure is increased, the more carbon dioxide dissolves in acetone, and the more the solution expands. The experimental solvent expansion behaviors at 27 and 40°C, as a function of

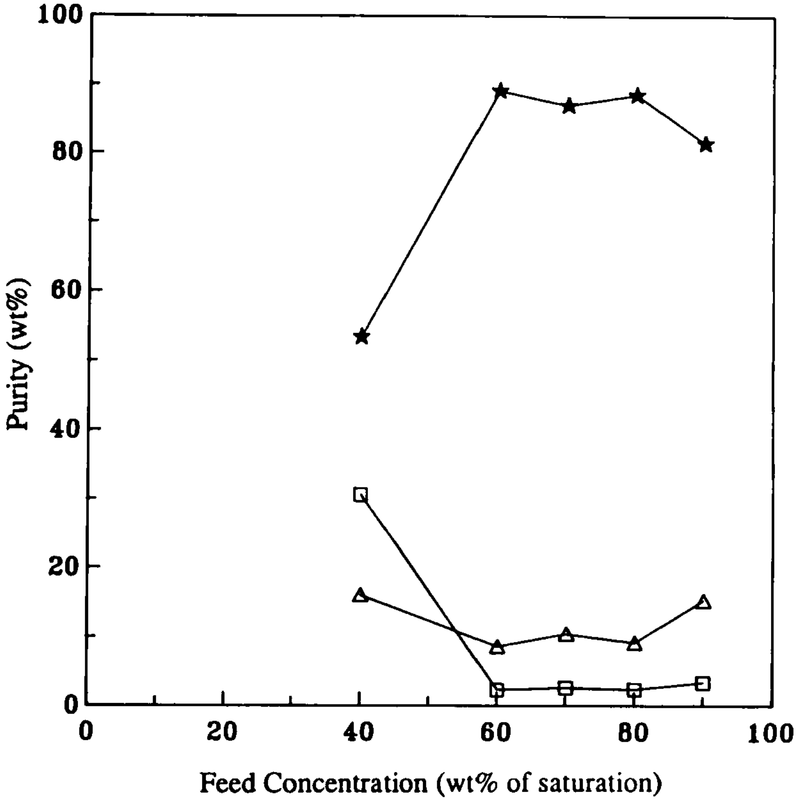


FIG. 7. Purity of anthracene (★), phenanthrene (□), and carbazole (△) in GAS recrystallization at 103 atm and 27°C.

pressure, are shown in Fig. 3. It is evident that at high temperatures the gas has less absorption in the liquid and the liquid has a smaller expansion coefficient than at low temperture.

Purification Tests

After purifications using 52 and 103 atm GAS recrystallization, the samples were analyzed by using HPLC chromatography with an internal standard. The yield of three major compounds in crude anthracene can be determined by the following formula:

$$\text{Yield} = \frac{\text{weight of each component in the precipitate}}{\text{weight of each component in the feed}}$$

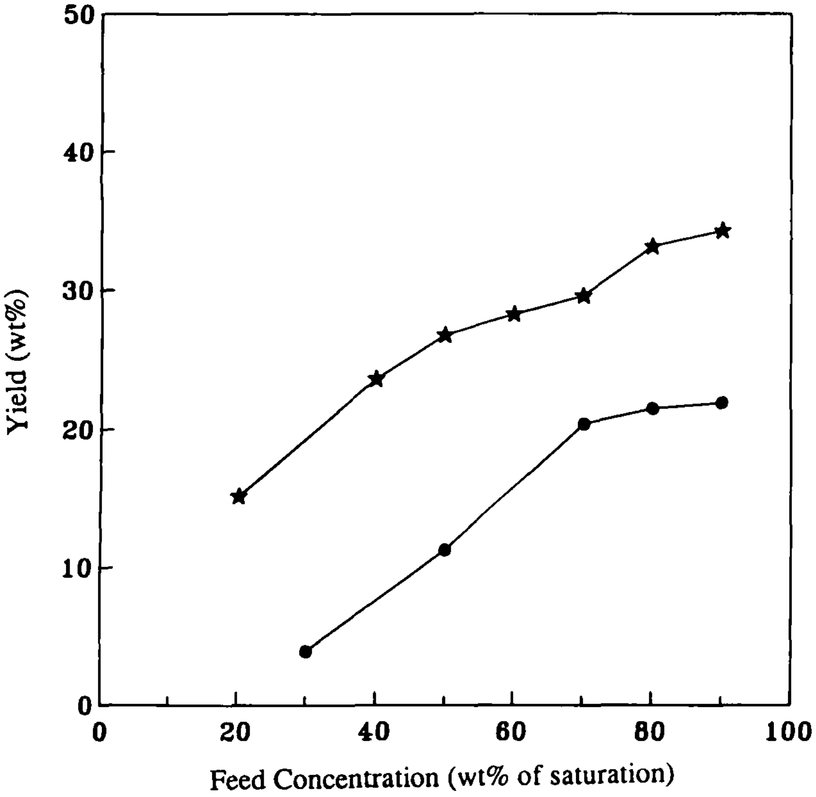


FIG. 8. Total yield of the purified solids in GAS recrystallization at 27°C: (★) 103 atm; (●) 52 atm.

The results are shown in Figs. 4 and 5. The yield increases with an increase in feed concentration. At 103 atm recrystallization the yield of anthracene is highest. If the feed concentration is high (>70% saturation), the purified product shows 90, 2, and 8% for anthracene, phenanthrene, and carbazole, respectively. Figures 6 and 7 show the results.

Summary

In this paper we report on crude anthracene separation at various feed concentrations operated at two pressures. In GAS crystallization, carbon dioxide dissolved in acetone caused solids to precipitate. The solubility of anthracene in acetone was the lowest, and the degree of saturation of anthracene in the feed solution was the highest. Therefore, supersaturation can be created for anthracene, and the separation of pure anthracene from crude anthracene solution can be achieved. Figure 8 shows the total yields

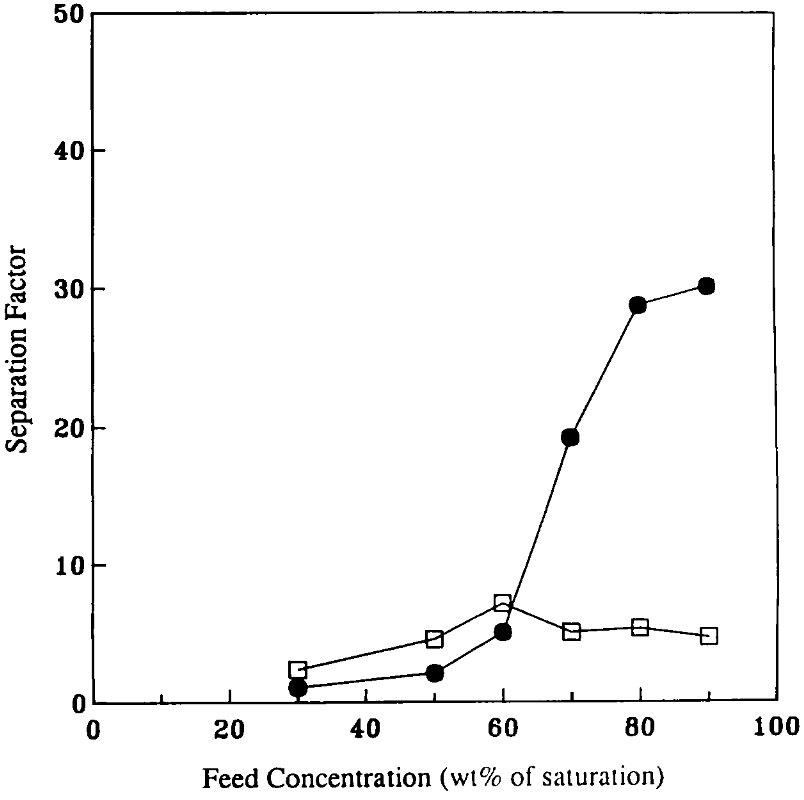


FIG. 9. Separation factor of anthracene versus phenanthrene (●) and anthracene versus carbazole (□) at 52 atm and 27°C.

of purified solids at 52 and 103 atm. It is evident that separation at 103 atm gave a higher yield because of larger solvent expansion. The purity and the yield of anthracene are relatively high at high pressure. It is possible that liquid carbon dioxide dissolves some impurities and phenanthrene, which has a lower melting point than anthracene, during washing and drying at 103 atm. The efficiency of separation using GAS crystallization was evaluated by the separation factor, which is defined as the ratio of the product composition to the feed composition, i.e.,

$$\text{Separation factor} = \frac{\left\{\dfrac{W_{\text{desired}}}{W_{\text{undesired}}}\right\}_{\text{product}}}{\left\{\dfrac{W_{\text{desired}}}{W_{\text{undesired}}}\right\}_{\text{feed}}}$$

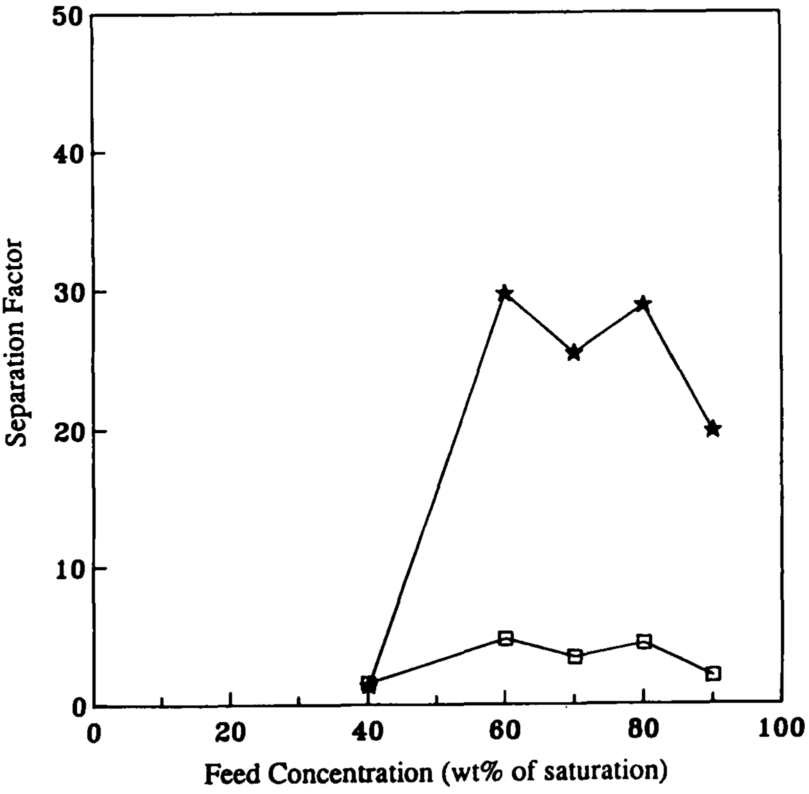


FIG. 10. Separation factor of anthracene versus phenanthrene (★) and anthracene versus carbazole (☐) at 103 atm and 27°C.

The separation factors of anthracene versus phenanthrene and anthracene versus carbazole are shown in Figs. 9 and 10 for both pressure tests. They illustrate that the separation of anthracene versus phenanthrene is always better than anthracene versus carbazole, and a high feed concentration also gives a large separation factor for anthracene versus phenanthrene, especially in the 52-atm test. It is interesting to note that the separation factor for anthracene versus phenanthrene is lower than that for anthracene versus carbazole as the feed concentration goes down below 60% saturation in the 52-atm test, but this is not true for the test run at 103 atm.

CONCLUSIONS

The separation of anthracene from crude anthracene was examined by using gas antisolvent crystallization. We obtained greater than 20% total yield of crude anthracene close to the saturated feed concentration for both pressure tests. GAS crystallization yields 90% purity anthracene in the purified product. The highest separation factor is 30.07 for anthracene versus phenanthrene. Both purity and yield could be improved at high feed concentration, but the separation factor may not improve. Our results show that the complete separation of anthracene versus phenanthrene is possible at a suitable operating pressure and feed concentration.

Acknowledgments

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