Optimization of Solvent Crystallization Process in Obtaining High Purity Anthracene and Carbazole from Crude Anthracene

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Solvent crystallization is the main method used for preparing anthracene and carbazole from the crude anthracene. The key to the optimization of this method is improving the solubility selectivity of the solvent by means of solvent modulating and process optimization. In this study, the solubility of anthracene, phenanthrene, and carbazole in xylene, dimethylformamide (DMF), DMF with amine/amide, isopropanolamine, and chlorobenzene is examined and the solid-liquid ternary anthracene–carbazole–DMF/(DMF+19.96% isopropanolamine) system phase diagram is determined and applied in the solvent crystallization process. The results showed that the solubility selectivity of xylene increases with increased temperature. Also, selectivity increases with an increase of the amount of isopropanolamine in the mixture of DMF and isopropanolamine, while decreases with increased temperature. Through multiple washings of crude anthracene with xylene, DMF+19.96% isopropanolamine, and chlorobenzene, it was possible to obtain anthracene and carbazole of purity higher than 98 wt %. © 2013 American Institute of Chemical Engineers *AIChE J*, 60: 275–281, 2014

Keywords: solvent crystallization process, anthracene, carbazole, solvent selectivity, ternary system phase diagram

Introduction

Coal tar, one of the products from the coal thermal process, is a major source of chemicals, fuels, and other nonfuel products. Among the chemicals derived from coal tar are anthracene and carbazole, which compose more than 1 wt % of the coal tar and are important nonrenewable chemical resources for many types of dyes, pharmaceuticals, and photoelectric materials, etc.[1–5] Anthracene is an important raw material in making bactericide and dyes.[6–9] Its derivatives also usually have a high fluorescence quantum yield, wide energy gap, and good thermal stability. Thus, they have been widely used as deep-blue emitting materials in organic light emitting diodes.[1,10] Carbazole-based polymeric materials have unique electrical, electrochemical and optical properties,[3,11] and using different synthetic strategies and substitution patterns, the physicochemical properties can be fine-tuned, leading to high performance materials for a large number of electronic applications.[2,12,13] It is also used as bactericide.[14–16] With such a wide range of applications, demand increases annually, especially for carbazole. For fine chemicals manufacturing, anthracene and carbazole with purity of higher than 98 wt % is required. Although carbazole can now be chemically synthesized,[17] due to issues of cost and waste, more than 90 wt % of carbazole currently used in manufacturing is still obtained by separation and purification from crude anthracene oil. The separation and collection of high purity products is a challenging task as the concentrations of the main components of crude anthracene vary with the coal and the coal processing. The most commonly used techniques for producing anthracene and carbazole are the solvent crystallization method, the rectification method and the chemical method and are based on the physicochemical properties of solubility,[18,19] boiling point and chemical reactivity, respectively. Further refining methods include recrystallization, sublimation, and crystal fusing. As a result of these treatments, anthracene and carbazole of different degrees of purity are obtained, but the maximum purity of anthracene and carbazole obtained is usually only about 97 wt %. For purity higher than 97 wt %, a combination of evaporation and sublimation of carbazole is used.

In the solvent crystallization method, the separating and refining of anthracene, carbazole, and phenanthrene is carried out according to their solubility in different solvents. The disadvantages of this method are the length of the process and the large amounts of solvents required due to the fact that the similarity in the structure of anthracene and carbazole, standard extraction systems cannot assure a great enough distribution coefficient. Also, in the current practices, the purity of anthracene and carbazole typically only reaches about 90–95 wt %, with a total yield of about 70–80 wt % and 40–50 wt %, respectively.[20]

Since phenanthrene has a higher solubility than either anthracene or carbazole in most solvents, it is easier to remove. The solubility of anthracene is particularly low in almost all of

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solvent used, while the solubility of carbazole is high in solvents containing nitrogen and oxygen, such as pyridine, dimethylformamide (DMF), and N-methyl-2-pyrrolidone, but low in solvents containing benzene and its derivatives. The common processing steps use xylene or solvent oil to first remove phenanthrene, and then DMF is used to separate the anthracene and carbazole. The resulting crude carbazole is refined by xylene. However, the problem is the poor solubility selectivity of the solvent, and a large portion of carbazole is lost during the anthracene and carbazole separation and refining, so the use of DMF and xylene as the primary solvents is not optimal. It is therefore necessary to develop a new solvent system and to further optimize the process. The solvent type, liquid-solid ratio and operational temperature all significantly affect crystal forms and purity during processing.[21–25] Solubility data and phase diagram determination are necessary and helpful for solvent screening and operational condition optimizing in the solvent crystallization process.[26,27] So far, however, little has been published regarding the systematic determination of the solubility of anthracene and carbazole in different solvents, not to mention a ternary system phase diagram of anthracene-carbazole-solvent.

In this article, the solubility of anthracene, phenanthrene, and carbazole in xylene, chlorobenzene, isopropanolamine, DMF, and DMF with different amine/amide mixtures are determined in a temperature range of 30 to 80°C at intervals of 10°C and the differences in the solvents used in the experiment are discussed. The ternary system diagrams of anthracene-carbazole-DMF and anthracene-carbazole-DMF + 19.96% isopropanolamine at 30°C are also measured. The traditional process of solvent crystallization method was improved by means of using new solvents and optimizing process conditions. The processing of crude anthracene could be shortened to 5–6 washes with a resulting purity of anthracene and carbazole higher than 98 wt %.

Experimental

Determination of the solubility and phase diagram of anthracene and carbazole

The reagents examined are DMF, xylene (the mixture of 10–15% *o*-xylene, 45–70% *m*-xylene, and 15–25% *p*-xylene), chlorobenzene, tripropylamine, isopropanolamine, and urea (analytical grade). The solubility of anthracene, phenanthrene, and carbazole was measured by equilibrium method.[28] Anthracene, phenanthrene, and carbazole were purified with xylene or DMF before use, and the purity is higher than 99 wt %. Anthracene (8 × 2 g) was dissolved in 15 mL solvent of DMF, xylene, chlorobenzene, isopropanolamine, DMF + 19.96% isopropanolamine, DMF + 34.94% isopropanolamine, DMF + 3.4% tripropylamine, and DMF + 9.34% urea, respectively. Carbazole was weighed at 10 g, 2 g, 2 g, 2 g, 5 g, and 5 g and dissolved in 15 mL solvent of DMF, xylene, chlorobenzene, isopropanolamine, DMF + 19.96% isopropanolamine, DMF + 34.94% isopropanolamine, respectively. Phenanthrene (50 g) was dissolved in 15 mL xylene. The tubes were then placed in an oil bath at a temperature of 90°C for 2 h. The system temperature was then gradually reduced by intervals of 10 degrees to a temperature of 30/35°C respectively, and then maintained at that temperature for 3 days. The samples (saturated solution) were transferred by pipettor and diluted with acetonitrile and analyzed by gas chromatography (GC).

Determination of anthracene-carbazole-DMF/(DMF + 19.96% isopropanolamine) solid-liquid ternary system phase diagrams is as follows: anthracene was weighed at 0.02 g, 0.04 g, 0.08 g, 0.2 g, 0.3 g, 0.3 g, 0.3 g, 0.3 g and placed in eight different test tubes, and then 4.0 g, 4.0 g, 4.0 g, 4.0 g, 2.0 g, 1.5 g, 1.0 g, 0.5 g of carbazole was added, respectively. 15 mL of DMF or DMF + 19.96% isopropanolamine was added to each tube. The tubes were then placed in oil bath at a temperature of 100°C for 2 h, and then gradually cooled to 30°C and maintained for 3 days. The saturated solutions of anthracene and carbazole were also transferred by pipettor and diluted with acetonitrile and analyzed by GC.

Refining of crude anthracene

In order to minimize the loss of solvent and maximize the dissolution of anthracene, phenanthrene, and carbazole in the solvent crystallization process, heating temperatures of 120°C, 120°C, and 100°C selected for xylene, DMF, and chlorobenzene, respectively. This allows phenanthrene and other components with a melting point below 100°C to be partially removed during processing without impacting the yield of anthracene and carbazole. Crude anthracene used in this experiment is a distillation fraction from coal tar with the boiling point range of 300–360°C, was obtained from the One Steel factory, Wuhan, China. The amounts of anthracene, phenanthrene, and carbazole in crude anthracene are 43.17 wt %, 21.96 wt %, and 14.94 wt % accordingly. Typically, 100 g crude anthracene and 100 mL xylene (solvent-solid ratio of 1:1) were added to a three-neck flask equipped with a blender, a reflux condenser pipe and thermometer tubes equipped with a mixer, stirred and heated to 120°C and then maintained for 30 min. The mixture was then filtered under vacuum at 50°C, and the resulting cake (cake 1) was washed by 10 mL xylene and dried at room temperature. The filtrate was placed in a rotary evaporator (Buchi R-200, Switzerland) under vacuum until completely dry.

Then, using cake 1 as raw material and xylene as solvent, the first step was repeated using liquid-solid ratio of 1.5:1. The resulting cake (cake 2) was then dissolved in DMF, DMF + 19.96% isopropanolamine, and DMF + 11.42% urea at 120°C for 30 min with the liquid-solid ratio of 1.5:1 followed by filtration at 30°C. The resulting cake was named cake 3 and the residue named residue 3. Cake 3 was refined with DMF as the solvent at 120°C for 30 min with a liquid-solid ratio of 1.5:1, and the resulting cake named cake 3–1. Residue 3 was refined by chlorobenzene 2–3 times with the liquid-solid ratio varying from 5:1 to 2.5:1 according to the content of anthracene in residue 3, at a temperature of 100°C and maintained 30 min, then filtered at 60°C. The resulting cakes were named cake 4, cake 5, and cake 6, respectively.

Gas chromatographic analysis

GC analysis was performed on a Shimadzu GC 2014 (Japan) with an Rtx®−5 (USA) capillary column (0.32 mm × 30 m × 0.25 μm), wall-coated with 5% dipheny/95% dimethyl polysiloxane. A flame ionization detector was used as the detector. The temperature program was as follows: 170°C (0.4 μL injection volume) for 1 min, then increased by 3.5°C/min to 200°C, held for 1 min, then further increased by 10°C/min to 250°C. The internal standard curves method with 9-fluorenone as the internal standard substance was used for quantitative analysis. The standards

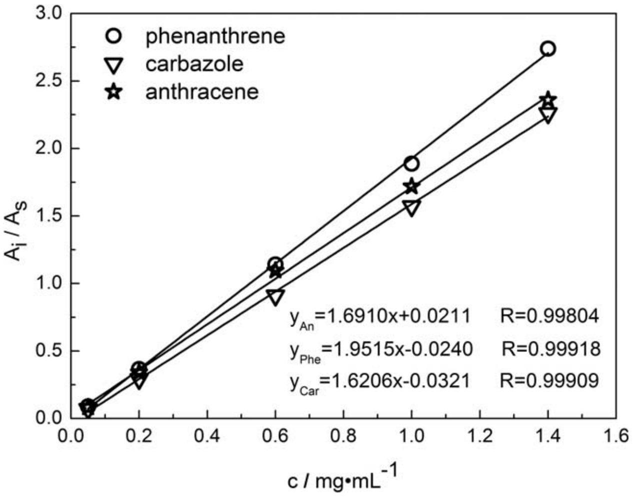

Figure 1. Calibration curves of anthracene, phenanthrene and carbazole using 9-fluorenone as the internal standard substance.

used in the experiment were of purity higher than 99 wt %. The calibration curves are shown in Figure 1.

Results and Discussion

Solvent modulation for anthracene and carbazole refining

The key to the solvent crystallization method is in choosing the most suitable solvent for the process. Xylene is used for phenanthrene removal due to its high efficiency. In order to improve the selectivity of the solvent used in the separation process, the solubility of anthracene, phenanthrene, and carbazole in chlorobenzene and xylene are measured and determined. The solubility of a compound will decrease with decreasing temperature, increasing melting temperature (T_m), increasing enthalpy of fusion(Δh_m).[29] Among the anthracene ($T_m = 489.6$ K, $\Delta h_m = 28860$ J/mol), phenanthrene ($T_m = 369.4$ K, $\Delta h_m = 186404$ J/mol), and carbazole ($T_m = 517.95$ K, $\Delta h_m = 29400$ J/mol), the T_m and Δh_m of carbazole is the highest, so the solubility of carbazole in xylene or chlorobenzene as shown in Table 1 is the lowest. In addition, Table 1 shows that the solubility of anthracene and carbazole increases when using chlorobenzene as the solvent, especially for anthracene. Xylene might form van der Waals complexes with anthracene like benzene,[30] or the most likely interaction of xylene and anthracene is π-π interaction, and xylene could possibly form N—H…π with carbazole. In chlorobenzene, the Cl substituent plays two roles, one is the conjugation effect of the *p* orbital of Cl atom and π orbital of phenyl ring, the other is the inductive effect between the Cl atom and the charge of benzene ring, with the latter being dominant. These two effects cause the Cl atom to present both positive and negative charges. With the conjugation effect, the association is occurring because of the interaction of the positive fractional charge at the site of Cl atom in chlorobenzene and π-delocalized electron cloud in the benzene ring of the anthracene molecule at sites 9 and 10.[31] The N atom of carbazole is the positively charged center, and because of the inductive effect, it is possible that an N—H…Cl hydrogen bond is formed between the Cl atom of chlorobenzene and the N—H of carbazole.

Based on GC analysis results, the main impurities of crude carbazole (residue 3) are anthracene and phenanthrene, so the key to the carbazole refining process is removing of anthracene, phenanthrene and other impurities from crude carbazole, therefore, chlorobenzene is better than xylene for carbazole refining.

The influence of the types of amine/amide additives on the solubility of anthracene and carbazole in DMF is also investigated. The resulting data is shown in Tables 2 and 3. For comparison, Tables 1–3 also present the solubility of anthracene and carbazole which reported in the literatures at 20/25/30°C. Analysis of the experimental data for carbazole and anthracene in DMF and xylene is in agreement with data reported in literatures.[20,30,32–37]

Here, isopropanolamine, urea, and tripropylamine are used as additives to DMF, and the solubility data for anthracene is listed in Table 2. Regardless of the type of amine/amide added to the DMF, the solubility of anthracene decreases to a certain extent, especially at higher temperatures, although this decrease is more significant when using either urea or isopropanolamine as the additive as opposed to tripropylamine. The influence of the addition of isopropanolamine on solubility was also investigated. It was found that at 30°C, when the isopropanolamine increased from 0 to 100%, the solubility of anthracene decreased sharply from 0.0113 to 0.00096. A similar trend was observed for carbazole when adding isopropanolamine to DMF (Table 3). Compared to anthracene, there is more obviously an effect on the solubility of carbazole with the addition of isopropanolamine and

Table 1. Mole Fraction Solubility of Anthracene, Carbazole, and Phenanthrene in Chlorobenzene and Xylene

		Solubility						
Solvents	Samples	25°C	30°C	40°C	50°C	60°C	70°C	80°C
Chlorobenzene	Anthracene		0.01336	0.0175	0.02551	0.03544	0.04392	0.0649
	Carbazole		0.00415	0.0077	0.0098	0.01335	0.0178	0.02074
Xylene	Phenanthrene		0.1745	0.2385	0.318	0.4105	0.5306	0.6248
	Anthracene	0.007142 0.00762[a]/0.00662[b]/0.00625[c,36] (20°C) 0.01101[a]/0.00989[b]/0.01053[c,35] 0.00733[c]/0.007956[b,37]	0.00987	0.0159	0.02116	0.031925	0.04099	0.05783
	Carbazole	0.00485 0.00434[a]/0.00368[b]/0.00430[c,36](20°C)	0.00588	0.00704	0.00965	0.01283	0.01633	0.02132

[a] Data in *o*-xylene.
[b] Data in *m*-xylene.
[c] Data in *p*-xylene.
Note: the solubility of phenanthrene in chlorobenzene was not determined. Xylene that we used is a mixture of 10–15% *o*-xylene, 45–70% *m*-xylene and 15–25% *p*-xylene.

Table 2. Mole Fraction Solubility of Anthracene in DMF, DMF+9.34% urea, DMF+19.96% Isopropanolamine, DMF+34.94% Isopropanolamine, Isopropanolamine, and DMF+3.4% Tripropylamine

	Solubility						
Solvents	25°C	30°C	40°C	50°C	60°C	70°C	80°C
DMF	0.00568 0.0054[33] 0.007839[37] 0.00733[30]	0.0113 0.0091[18]	0.01565	0.02088	0.0284	0.04063	0.05172
DMF+19.96% isopropanolamine		0.00493	0.00719	0.00985	0.013	0.0178	0.0237
DMF+34.94% isopropanolamine		0.00235	0.00338	0.00485	0.0066	0.00913	0.01255
isopropanolamine		0.00096	0.00144	0.0021	0.00283	0.00455	0.00678
DMF+ 3.4% tripropylamine		0.0134 (35°C)	—	0.02083	0.0251	0.0241	—
DMF+ 9.34% urea		0.00754 (35°C)	—	0.0114	0.01497	0.01638	—

the solubility of carbazole is decreased from 0.1667 to 0.02607 at 30°C.

DMF and anthracene could form C—H…π interactions between the N-methyl group of DMF and the benzene ring of anthracene.[38] Also, the high solubility of carbazole in DMF is considered due to the hydrogen bonding between DMF and carbazole.[39] When adding urea, tripropylamine, or isopropanolamine to DMF, due to the intermolecular hydrogen bond formation between DMF and amine/amide,[40] steric hindrance plays a key role in limiting the dissolution of anthracene and carbazole in the mixed solvent. The effect of steric hindrance is obvious more clear with urea and isopropanolamine than with tripropylamine.

Since the association of anthracene and chlorobenzene is stronger than the π-π interaction of anthracene and xylene, and the hydrogen bond force of N—H…Cl is stronger than N—H…π, the solubility of anthracene and carbazole in chlorobenzene is improved.

Solubility selectivity and ternary phase diagram

The crystallization temperature and liquid-solid ratios used in the process have significant influence on the processing results, so the solvent selectivity and ternary phase diagram of anthracene-carbazole-DMF/(DMF + 19.96% isopropanolamine) are determined in order to obtain the appropriate crystallization temperature and liquid-solid ratios.

The solubility selectivity varies with solvent type and class and is also affected by temperature. The definition of solubility selectivity is as follows

$$SS_{CAR/AN}=\frac{S_{CAR}}{S_{AN}}, SS_{PHEN/AN}=\frac{S_{PHEN}}{S_{AN}},\ \text{and}\ SS_{PHEN/CAR}=\frac{S_{PHEN}}{S_{CAR}}$$

where $SS_{CAR/AN}$ is the solubility selectivity of carbazole over anthracene, $SS_{PHEN/AN}$ is the solubility selectivity of phenanthrene over anthracene, $SS_{PHEN/CAR}$ is the solubility selectivity of phenanthrene over carbazole, and S_{PHEN}, S_{CAR}, and S_{AN} represent the solubility of carbazole, phenanthrene, and anthracene, mole fraction.

According to the solubility data of phenanthrene, anthracene, and carbazole in xylene (Table 1), the solubility selectivity of xylene is calculated and shown in Figure 2. The selectivity of xylene is very high for phenanthrene and decreases as a function of temperature. It is apparent that crystallization at lower temperatures favors phenanthrene removal. So the crystallizing temperature was selected at 30°C. Due to the high solubility of phenanthrene and $SS_{PHEN/CAR}$ of xylene, low liquid-solid ratios are needed to insure the removal efficiency of phenanthrene and the high yields of anthracene and carbazole. Here, the liquid-solid ratio of 1:1–1.5:1 was selected for practical operation.

The solubility selectivity of DMF, isopropanolamine and the mixed solvent (DMF + isopropanolamine) on carbazole over anthracene from 30°C to 80°C was also calculated (Figure 3). The $SS_{CAR/AN}$ of isopropanolamine is higher than that of DMF in the determined temperature range (about 27.2 for isopropanolamine and 16.9 for DMF at 30°C), although the absolute solubility of isopropanolamine is very low for both anthracene and carbazole. The $SS_{CAR/AN}$ is improved as the amount of isopropanolamine increases in the mixture while decreasing sharply as the temperature increased. Therefore, it is beneficial for the effective separation of carbazole and anthracene to conduct crystallization at lower temperatures. Taking practical operation into consideration, 30°C was selected.

Based on the solubility selectivity results, the equilibrium phase diagrams of the ternary anthracene–carbazole–DMF and anthracene–carbazole–(DMF + 19.96% isopropanolamine) systems are measured at 30°C to determine and optimize the liquid-solid ratio of the solvent crystallization process. As shown in Figures 4 and 5, there are three crystallization regions in the phase diagram: anthracene (I), carbazole (III), mixture of anthracene, and carbazole (II). A (A′),

Table 3. Mole Fraction Solubility of Carbazole in DMF, Isopropanolamine, DMF+19.96% Isopropanolamine, DMF+34.94% Isopropanolamine

	Solubility						
Solvents	25°C	30°C	40°C	50°C	60°C	70°C	80°C
DMF	0.1145 0.14[17]	0.1667	0.1811	0.1925	0.21438	0.2322	0.2399
Isopropanolamine		0.02607	0.0302	0.03548	0.04365	0.05286	0.06715
DMF+19.96% isopropanolamine		0.0.08596	0.1027	0.11485	0.11823	0.13538	0.1466
DMF+34.94% isopropanolamine		0.05354	0.06042	0.06615	0.07465	0.0776	0.0794

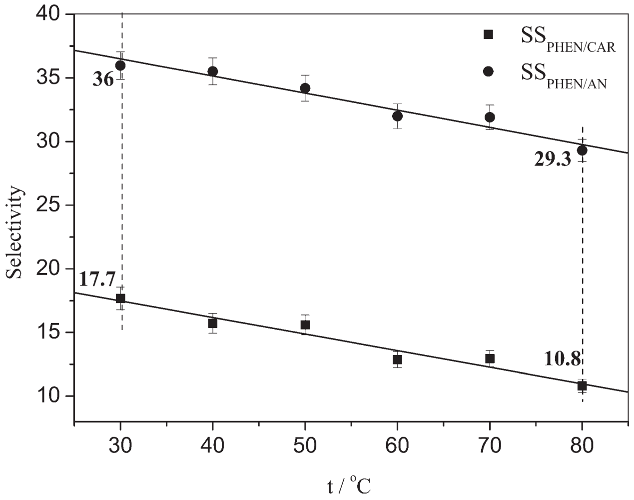

Figure 2. Selectivity of xylene at 30–80°C.

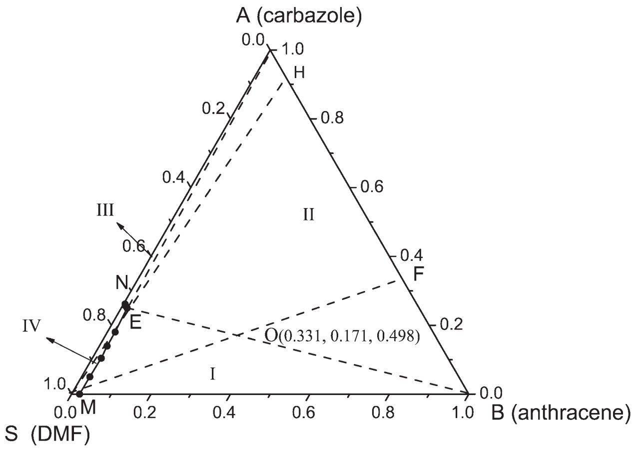

Figure 4. Equilibrium phase diagram of the ternary anthracene- carbazole-DMF system at 30°C; I- crystalline region of anthracene; II - crystalline region both of anthracene and carbazole; III - crystalline region of carbazole, IV - homogeneous region.

B (B′), and S (S′) are carbazole, anthracene, and solvent respectively. E (E′) is the cosaturated point, which represents the equilibrium of the two solid-phase anthracene and carbazole. ME (M′E′) is the saturation curve corresponding to the solid-phase anthracene and NE (N′E′) is the saturation curve corresponding to the solid-phase carbazole. Point F (F′) is the solid-phase composition point of anthracene and carbazole in the raw material after phenanthrene removal, connecting line SF (S′F′), and intersecting the anthracene crystal line BE (B′E′) at O (O′). Point O (O′) corresponds to the optimal separation liquid-solid ratio for anthracene and carbazole at 30°C. And, according to the phase diagram, the optimum liquid-solid ratios are 1.05:1 and 1.5:1 for DMF and DMF with 19.96% isopropanolamine (IPA), respectively. Therefore, it is necessary to improve the liquid-solid ratio to assure the refining effect after adding isopropanolamine to DMF due to the lower solubility of the mixture. In the anthracene-carbazole-DMF ternary phase diagram, the anthracene and carbazole mixed crystal region (II) accounted for about 80% of the whole region. The crystalline region of anthracene (I) is larger than that of carbazole (III), and the crystallization process of anthracene is relatively simple. Adding isopropanolamine to DMF reduced the crystalline region of anthracene (I), while the crystalline region of the mixed region (II) improved, so this appears to be beneficial in improving the yield of carbazole. Line SE (S′E′) connects to the Y axis at H (H′), which indicates the maximum amount of carbazole obtainable, and the corresponding amounts of carbazole are 92.35 wt % and 90.87 wt % respectively. In other words, it is the upper limit of the purity of carbazole with DMF/DMF with 19.96% isopropanolamine as solvent in the solvent crystallization method, so further refining for high purity products would be necessary.

The refining resulting of crude anthracene

To ensure the complete removal of phenanthrene, a two-step washing process with xylene was used with the liquid-

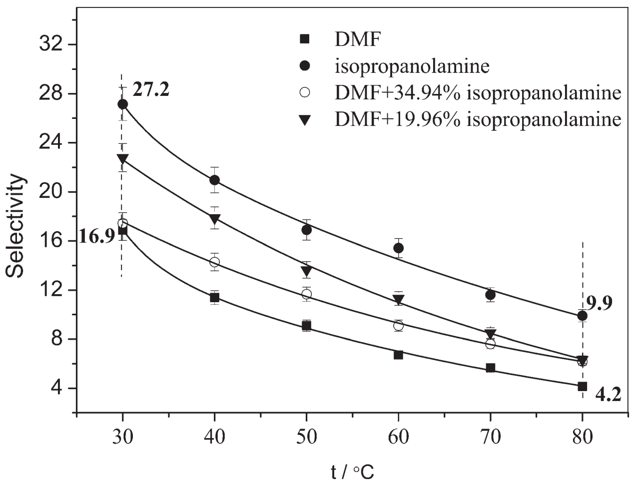

Figure 3. Selectivity of DMF, isopropanolamine, DMF+19.96% isopropanolamine and DMF+34.94% isopropanolamine mixed solvent of carbazole over anthracene at 30–80°C.

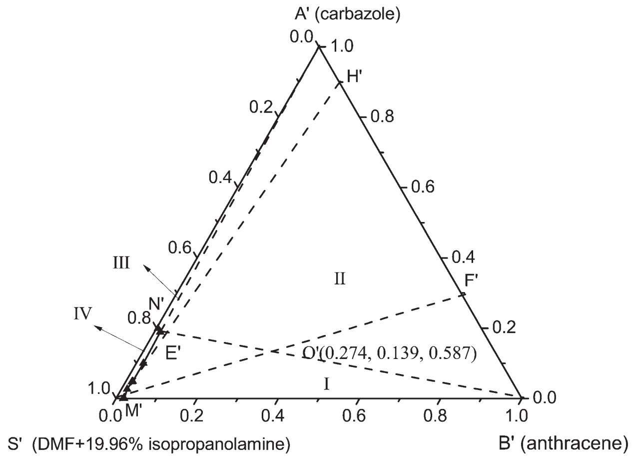

Figure 5. Equilibrium phase diagram of the ternary anthracene-carbazole-DMF with 19.96% isopropanolamine system at 30°C; I- crystalline region of anthracene; II - crystalline region both of anthracene and carbazole; III - crystalline region of carbazole; IV - homogeneous region.

Table 4. Phenanthrene Removal Results by Xylene

Sample	Content/wt %			Yield/wt %	
	Phenanthrene	Anthracene	Carbazole	Anthracene	Carbazole
Crude anthracene	21.96	43.17	14.94		
Cake 1	12.30	58.05	19.31	89.87	86.39
Cake 2	3.61	69.09	23.07	94.57	94.94
Total yield/wt %				84.99	82.02

solid ratios of 1:1 and 1.5:1, respectively, in the new process. This ensured a removal yield of phenanthrene higher than 90 wt %. Results are shown in Table 4. The amount of phenanthrene in cake 2 is reduced to 3.61 wt % and the yields of anthracene and carbazole are 84.99 wt % and 82.02 wt %, respectively after two-step washing with xylene.

After using xylene for the first and second steps, the effect of utilizing DMF, DMF + 19.96% isopropanolamine, and DMF + 11.42% urea mixed solvent with liquid-solid ratios of 1.5:1 in the third step were investigated. And the liquid-solid ratio varied from 2.5:1 to 5:1 for carbazole refining by chlorobenzene according to the amount of the anthracene in the products (residue 3, cake 4, and cake 5). The liquid-solid ratio was 5:1 for the fourth and fifth steps, and reduced to 2.5:1 for the sixth step, filtered at 60°C, and the results are as follows (Table 5).

The addition of isopropanolamine and urea to DMF strongly restricted the dissolution of anthracene, although the change of amount and yield is not obvious in cake 3. The anthracene amount in the residue 3 reduced from 11.42 wt % with pure DMF to 8.19 wt % and 9.43 wt % with DMF + 19.96% isopropanolamine and DMF + 11.42% urea as the solvent, respectively. In comparison, the subsequent carbazole refining process is relatively easy. Whatever the additive, either isopropanolamine or urea, only two washings of residue 3 by chlorobenzene were required to increase the amount of carbazole (cake 5) from 90–95 wt % as obtained by the original process to 98.69 wt % and 98.57 wt % respectively. Also, the total yield is nearly 50 wt % without mother liquor recycling. However, when pure DMF was used in the third step, even after three washings with chlorobenzene, the amount of carbazole only reached 97.85 wt %. Moreover, the carbazole amount in residue 3 is the highest when using DMF + 19.96% isopropanolamine in the third step. Since urea is a solid at room temperature, it is not feasible for practical operation, so isopropanolamine was selected for further study. Cake 3 was refined by DMF one time and a high purity product of anthracene (cake 3-1) was obtained. The purity was improved from 95 wt % to 98.93 wt % with a total yield of anthracene of about 74.8 wt % without mother liquor recycling.

Conclusions

Through determination by solubility data and phase diagram analysis, the solvent crystallization process in obtaining high purity anthracene and carbazole from crude anthracene was optimized. New solvents, DMF with 19.96% isopropanolamine mixture and chlorobenzene, were introduced in the solvent crystallization processing for crude anthracene resulting in improvement of solubility selectivity of the solvent on carbazole over anthracene. The separation of anthracene and carbazole became markedly more straightforward in comparison with the original process. The whole process was reduced significantly from washing 9–10 times to 5–6 times with less solvent consumption. The purity was improved from 95 wt % for anthracene and from 90–95 wt % for carbazole to higher than 98 wt %, and the total yield of anthracene and carbazole was more than 74 wt % and 50 wt %, respectively without mother liquor recycling.

Table 5. Refining Results of Crude Anthracene

Solvents	Samples	Content and yield (Y)/wt %			
		Anthracene	$Y_{anthracene}$	Carbazole	$Y_{carbazole}$
DMF	cake 3	94.18	86.46	3.73	—
	residue 3	11.42	—	62.37	99.80
Chlorobenzene	cake 4	6.46	—	88.85	86.90
Chlorobenzene	cake 5	2.98	—	96.22	83.82
Chlorobenzene	cake 6	2.15	—	97.85	88.91
Total yield/wt %			73.48		53.01
DMF+19.96% Isopropanolamine	cake 3	92.44	91.08	5.77	—
	cake 3-1[a]	98.93	96.65	1.07	
	residue 3	8.19	—	68.32	95.89
Chlorobenzene	cake 4	2.74	—	93.54	75.99
Chlorobenzene	cake 5	1.31	—	98.69	83.61
Total yield/wt %			74.82		49.97
DMF+11.42% urea	cake 3	94.33	86.68	4.03	—
	residue 3	9.43	—	59.18	97.72
Chlorobenzene	cake 4	4.15	—	92.62	73.21
Chlorobenzene	cake 5	1.43	—	98.57	85.14
Total yield/wt %			73.67		49.96

[a] The solvent used is DMF.

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