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Process parameters influence on zone refining and thermodynamics analysis of 1,2-diphenylethane

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ABSTRACT

Effective distribution coefficients of 9 impurities in 1,2-diphenylethane have been calculated by directional crystallization under different ambient frozen temperature. The effect of varied zone size, temperature difference between the melt and ambient frozen environment, number of zone on purity of 1,2-diphenylethane have been also investigated during the process of zone refining. The results indicate that the product purity in the intermediate purified region with varied zone size is higher 0.04%–0.2% than that with constant zone size. The product purity increases with temperature difference between the melt and ambient frozen environment. The appropriate temperature difference is adopted 50 °C. The product purity in the intermediate region of sample bar with 2 molten zones is higher 0.05%–0.43% than that with 1 molten zone. In addition, the change of enthalpy and entropy between impurities and 1,2-diphenylethane have been determined.

1. Introduction

In recent years, zone refining has been considered as an exceptional method for preparing high or ultrahigh pure materials [1–10] since it was first outlined by Pfann [11,12]. As is shown in Fig. 1, there are two solid-melt interfaces containing the freezing interface and melting interface. When the molten zone traverses the solid bar, at the melting interface, solid materials are merely melted and mixed with the material in molten zone; at the freezing interface, solid material are recrystallized from the melt. If the presence of impurity lowers the melting point of the material, the impurity concentration will decrease in the refrozen section of the material bar. However, if the impurity raises the melting point of the material, its concentration will increase in the solidified section of the material bar. Therefore, the freezing interface can reject or attract impurities in the molten zone. When the material contains several impurities which lower or raise the melting point of the main component, the former will travel against the mobile direction of molten zone and the latter will travel along the moving direction of molten zone during the process of molten zone passing through the material bar. As a result, the impurities will be pushed to the two ends of material bar. The similar process of zone refining will be repeated until the desired purity is realized. Then the two ends of the material bar are removed, the intermediate section of the material bar are the purified product [13–16].

1,2-Diphenylethane ($C_{14}H_{14}$; Molecular Weight 182.26; Melting Point 52 °C; Boiling Point 284 °C; CAS Registry No.103-29-7; Fig. 2) is known as an important aromatic compound that can be considered the derivative of ethane, substituting two phenyl groups for two hydrogen atoms from different carbons respectively. As it has special molecular structure, 1,2-diphenylethane is liable to undergo substitution, sulfonation, oxidation, and dehydrogenation reactions. The particular structure has aroused considerable interest in organic synthesis field and makes 1,2-diphenylethane become a significant intermediate of organic synthesis. It is used for synthesizing flame retardant named 1,2-bis(pentabromophenyl) ethane, fluorescent brightening agents, and forming the central core of some stilbenoid natural products and isoquinoline alkaloids, *etc*. [18,19]. At present, the purity of raw industrial 1,2-diphenylethane is less than 98%. In order to realize the higher purity of 1,2-diphenylethane, the traditional purification methods, distillation and solvent crystallization are used for purification of raw 1,2-diphenylethane. However, both methods are hard to produce high or ultrahigh pure 1,2-diphenylethane. The distillation separation of 1,2-diphenylethane consumes excessive energy, needs heavy tower equipment, wastes

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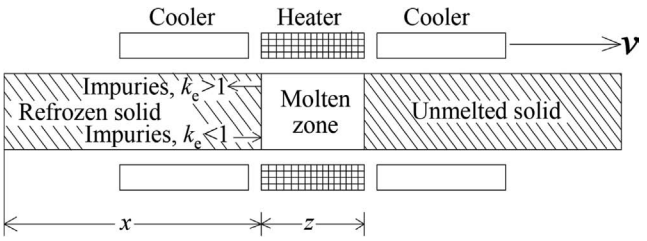

Fig. 1. The sketch of zone refining.

many money, is not easy to remove the impurities of high boiling point and is very difficult to realize the purity of 1,2-diphenylethane excess 99.5%. The solvent crystallization of 1,2-diphenylethane consumes a lot of organic solvents, recycling of organic solvents exhausts many energies and causes problems of environmental pollution. Aiming at realizing high pure 1,2-diphenylethane, saving energy, and reducing the use of organic solvents, zone refining is borrowed to purify 1,2-diphenylethane. The obvious advantages of zone refining are no using solvents and achieving high purity. In order to investigate the process of zone refining of 1,2-diphenylethane, the effective distribution coefficients of a several main impurities have been calculated by directional crystallization. The impacts of varied zone size, temperature difference, and molten zone number on product purity have been also investigated. Finally, the change of thermodynamic property have been calculated.

2. Experimental

2.1. Apparatus and materials

The experimental apparatus are shown in Fig. 3. The zone refiner of 1,2-diphenylethane consists of driving motors, mobile structure, speed regulators, heaters, coolers, and quartz glass tube, and so on. The raw material and solvent are 1,2-diphenylethane and chromatographic grade dichloromethane respectively. GC–MS is used for analyzing the purity of 1,2-diphenylethane and impurity concentration. HP-5 (30 m × 0.32 mm × 0.25μmm) is designated as the pattern of chromatographic column.

2.2. Experimental and analytical methods

Experimental procedures: Firstly, the raw 1,2-diphenylethane was loaded into the quartz glass tube, then, the nitrogen was filled in the quartz glass tube, and finally the quartz glass tube was sealed with an airtight cork. The cooling temperature was controlled by the low temperature thermostatic bath while the heating temperature was controlled by the digital temperature controller. The molten zone moved at a specific rate with the help of driving units. When it ended one motion, the molten zone returned to the initial position and started another motion. After the process ended, the different samples were removed with the sampler.

Analytical method: First of all, the operator accurately weighed 0.1 g 1,2-diphenylethane and added it into a volumetric flask. Then the operator added chromatographic grade dichloromethane into the volumetric flask and made 1,2-diphenylethane dissolve completely. Finally, the operator started analytical experiment with GC–MS. The temperature program was that the starting column temperature was 120 °C, then the column temperature was kept for 3 minutes and finally increased to 280 °C at the rate of 10 °C·min^{-1}, the holding time was 15 minutes, the temperature of vaporizing chamber was 290 °C, and the connection tube temperature was 280 °C. The injection volume was 0.2 μl [17,18].

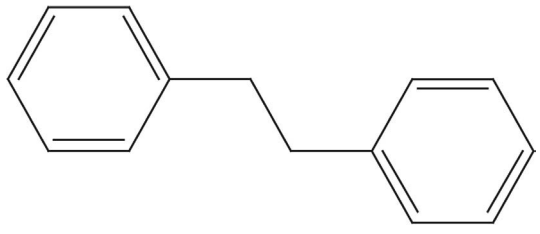

Fig. 2. Chemical structure of 1,2-diphenylethane.

3. Therodynamics Analysis

Under the constant pressure, the Gibbs free energy of impurity in liquid is equal to that in solid when the impurity diffusion equilibrium is reached at the solid–liquid interface [6,9].

$$G^l = G^s \tag{1}$$

$$G^l = \sum X_i^l H_i^l + X_{mc}^l H_{mc}^l - T\left(X_{mc}^l S_{mc}^l + \sum X_i^l S_i^l\right) + RT\left(\sum X_i^l \ln X_i^l + X_{mc}^l \ln X_{mc}^l\right) \tag{2}$$

$$G^s = \sum X_i^s H_i^s + X_{mc}^s H_{mc}^s - T\left(X_{mc}^s S_{mc}^s + \sum X_i^s S_i^s\right) + RT\left(\sum X_i^s \ln X_i^s + X_{mc}^s \ln X_{mc}^s\right) \tag{3}$$

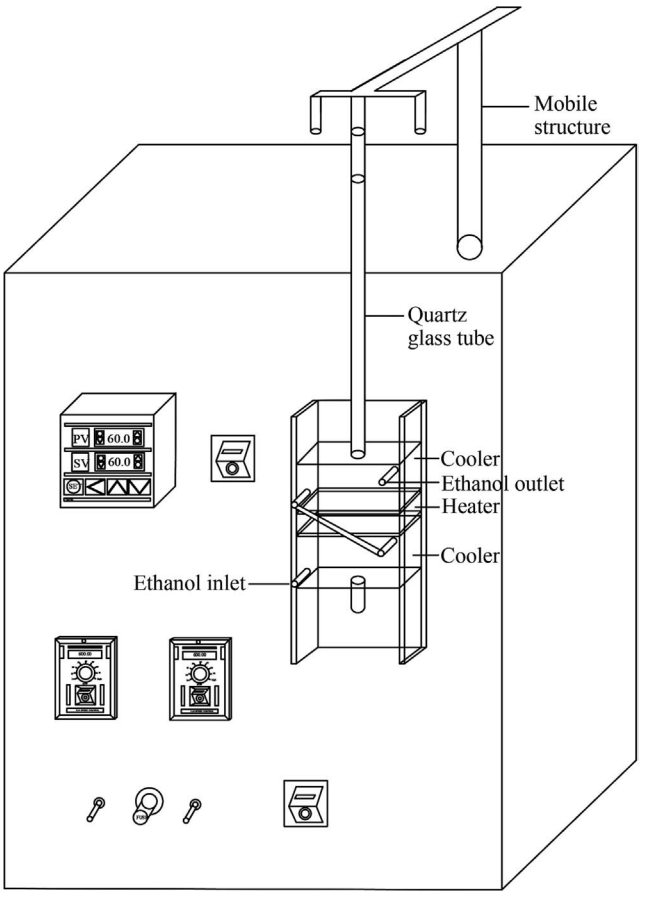

Fig. 3. The sketch of zone refiner.

Where X_i^l and X_{mc}^l are mole fractions of impurity and main component in liquid respectively.

X_i^s and X_{mc}^s are mole fractions of impurity and main component in solid respectively. H_i^l and H_{mc}^l represent the enthalpy of impurity and main component in liquid respectively. H_i^s and H_{mc}^s represent the enthalpy of impurity and main component in solid respectively. S_i^l and S_{mc}^l are entropy of impurity and main component in liquid respectively. S_i^s and S_{mc}^s are entropy of impurity and main component in solid respectively. G^l and G^s are Gibbs free energy of the system in liquid and solid respectively. T is the ambient frozen temperature, R is 8.314 J·mol^{-1}·K^{-1}. Eq. (4) and Eq. (5) can be derived from Eq. (2) and Eq. (3).

$$\left(\frac{\partial G_i^l}{\partial X_i^l}\right)_{T,P,X_j} = \left(H_i^l - H_{mc}^l\right) - T\left(S_i^l - S_{mc}^l\right) + RT\ln\frac{X_i^l}{X_{mc}^l} \tag{4}$$

$$\left(\frac{\partial G_i^s}{\partial X_i^s}\right)_{T,P,X_j} = \left(H_i^s - H_{mc}^s\right) - T\left(S_i^s - S_{mc}^s\right) + RT\ln\frac{X_i^s}{X_{mc}^s} \tag{5}$$

Neglecting the difference between X_{mc}^l and X_{mc}^s, by rearranging Eq. (1), Eq. (4) and Eq. (5), it can been obtained as follows:

$$\Delta H_i - \Delta H_{mc} - T(\Delta S_i - \Delta S_{mc}) = RT\ln\frac{X_i^s}{X_i^l} \tag{6}$$

Where ΔH_i, ΔH_{mc}, ΔS_i and ΔS_{mc} are the variations of enthalpy and entropy between the liquid and solid phases during the process of solidification, respectively.

$$X_i^s = \frac{C_S/M_i}{1/M_S} \tag{7}$$

$$X_i^l = \frac{C_L/M_i}{1/M_l} \tag{8}$$

Where C_S and C_L are mass fraction of impurity in solid and liquid respectively. M_i is molar mass of every impurity. M_S and M_l are molar mass of solid and liquid respectively. From Eq. (7) and Eq. (8), it can been obtained as follows:

$$\frac{X_i^S}{X_i^l} = \frac{M_S}{M_l} \times \frac{C_S}{C_L} \tag{9}$$

Neglecting the difference between M_S and M_l, it can be gotten that:

$$M_S = M_l \tag{10}$$

By rearranging Eq. (9) and Eq. (10), it can been obtained as follows:

$$\frac{X_i^S}{X_i^l} = \frac{C_S}{C_L} \tag{11}$$

The X_i^s/X_i^l is just the effective distribution coefficient k_e. So that:

$$\ln k_e = \frac{1}{T}\left(\frac{\Delta H_i - \Delta H_{mc}}{R}\right) - \frac{\Delta S_i - \Delta S_{mc}}{R} \tag{12}$$

4. Results and Discussion

4.1. Effective distribution coefficients

The effective distribution coefficient is expressed as $k_e = C_S/C_L$. According to the related theory [19], the directional crystallization equation is shown as follows:

$$C_S/C_0 = k_e(1-x)^{k_e-1} \tag{13}$$

Where C_0 is the initial impurity concentration of the sample, x is the normalized distance from the starting end. Eq. (14) is gotten by Eq. (13)

$$\ln(C_S/C_0) = \ln k_e + (k_e - 1)\ln(1-x) \tag{14}$$

$\ln(1-x)$ is set as abscissa, $\ln(C_S/C_0)$ is taken as vertical coordinate and a straight line is plotted. k_e is gained from the slope of the straight line. With the help of directional crystallization, the effective distribution coefficients of nine main impurities in 1,2-Diphenylethane have been shown in Table 1. The conditions of directional crystallization is that the temperature of melt is 60 °C, and the ambient frozen temperature is T_{frozen}, °C. From Table 1, it can be seen that the effective distribution coefficients depend on ambient frozen temperature, $T_{frozen.}$ k_e which is less than 1.0 increases with T_{frozen} while k_e which is more than 1.0 deceases with T_{frozen}. Lowering ambient frozen temperature can enlarge the difference between k_e and 1.0. It means that low ambient frozen temperature is helpful to the impurities segregation.

4.2. Effect of varied zone size on product purity

Fig. 4 shows the profiles of product purity with different zone sizes after 15 zone passes. The experiments adopt two programs. The first one is constant zone size with normalized zone size of 0.21. The other is varied zone size that is 1.0 for the first zone pass, 0.333 for the second to third zone pass, 0.200 for the fourth to fifth zone pass, and 0.133 for the sixth to fifteenth zone pass. It can be seen that the product purity in the intermediate region of the sample bar with varied zone size is higher 0.04%–0.2% than that with constant zone size. It also provides an idea that varied zone size is better than constant zone size during zone refining process of 1,2-Diphenylethane. It also matches the results of the previous literature [18] about zone refining. In the literature [18], through numerical modeling and calculation, it is proved that the refining efficiency with varied zones from large molten zones at primary

Table 1
The effective distribution coefficients under different experimental conditions

Chemical substances	Effective distribution coefficient/k_e			
	T_{frozen} = 20 °C	T_{frozen} = 15 °C	T_{frozen} = 10 °C	T_{frozen} = 5 °C
1,1-Diphenylethane	0.475	0.435	0.361	0.308
2,3-Dimethyl-2,3-diphenylbutane	0.436	0.358	0.332	0.264
1,2-Diphenylpropane	2.452	2.572	2.653	2.795
Diphenylmethane	0.551	0.474	0.429	0.378
5-Phenylvaleric acid	1.171	1.305	1.373	1.401
1,1-Diphenylpropane	0.102	0.087	0.078	0.073
1,1′-Butane-2,3-diyldibenzene	0.840	0.815	0.794	0.757
m-Phenoxyphenol	0.282	0.267	0.208	0.167
Cyclohexybenzene	0.686	0.516	0.470	0.455

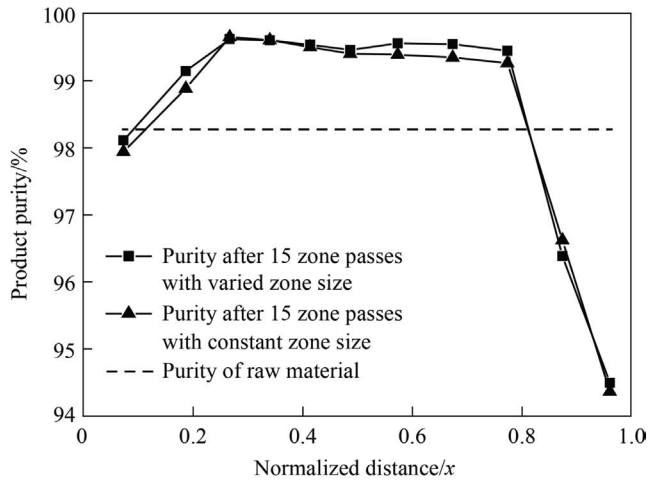

Fig. 4. Effect of varied zone size on the product purity (v = 12.35 mm·h^{-1}, T_{melt} = 60 °C, T_{frozen} = 20 °C).

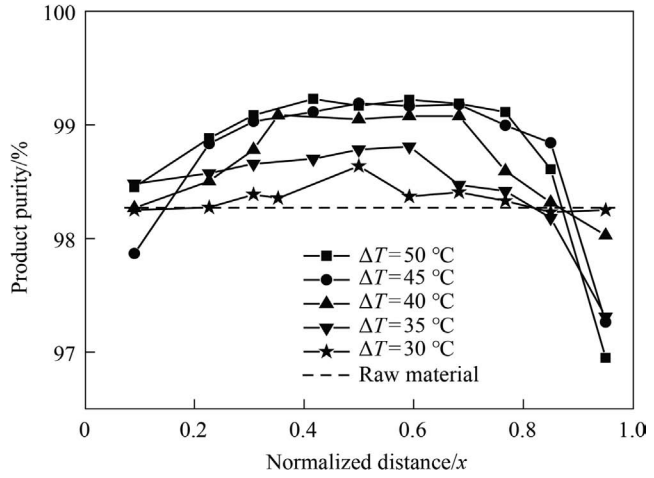

Fig. 5. Effect of temperature difference on product purity (v = 12.35 mm·h^{-1}, N = 1, z = 0.21).

stage to small molten zones at final stage is higher that with constant zones after many zone passes.

4.3. Effect of temperature difference on product purity

From Fig. 5, it indicates that the product purity in the intermediate purified region increases with ΔT, which is temperature difference between the melt and ambient frozen environment after 1 zone pass. When the temperature difference ΔT is smaller, the product purity is lower but the increase of product purity is larger in the intermediate purified region. When the temperature difference ΔT is bigger, the product purity is higher and the increase of product purity becomes smaller in the intermediate purified region. When temperature difference ΔT increase to 50 °C, the product purity in the intermediate purified region reach stability. However, bigger temperature difference is helpful to zone refining of 1,2-diphenylethane. In fact, the influence of temperature difference on product purity are due to two aspects. The one is free convection which is positive factor and the other is constitutional subcooling which is negative factor. On one hand, a larger temperature difference means stronger free convection and it strengthens the mixture of material in the melting zone and reduces the mass transfer resistance between the freezing and melt interface. On the other hand, a larger temperature difference inevitably intensifies constitutional subcooling, makes the freezing interface become rough, and rough freezing interface hinders the mass transfer between the freezing and melt interface to some extent. Within the range of experimental conditions, a larger temperature difference between the melt and frozen environment is prone to improving the product purity. Hence, the temperature difference of 50 °C is adopted.

4.4. Effect of number of zone on product purity

The effect of number of zone on product purity is shown in Fig. 6. It can be seen that the product purity in the intermediate region of sample bar with 2 molten zones is higher 0.05%–0.43% than that with 1 molten zone. It can be concluded that increasing number of zone promotes the zone refining efficiency. But when the molten zone number is more than 2, it can hardly realize steady and smooth zones, and the zone refining process is out of control. Therefore, during zone refining of 1,2-Diphenylethane, two molten zones are recommended.

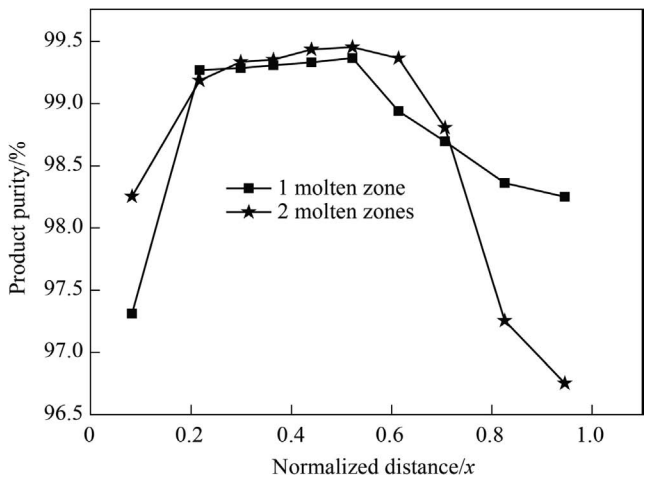

Fig. 6. Effect of molten zone number on the product purity (N = 1, T_{melt} = 60 °C, T_{frozen} = 20 °C, v = 4.97 mm·h^{-1}).

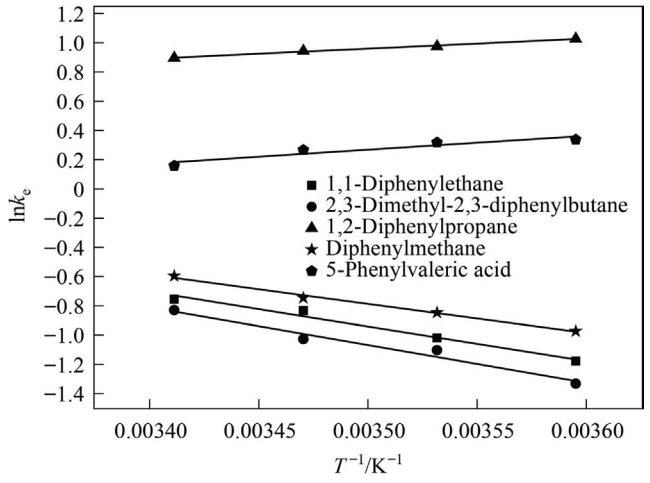

Fig. 7. The plots of lnk_e *versus* 1/T for 5 impurities.

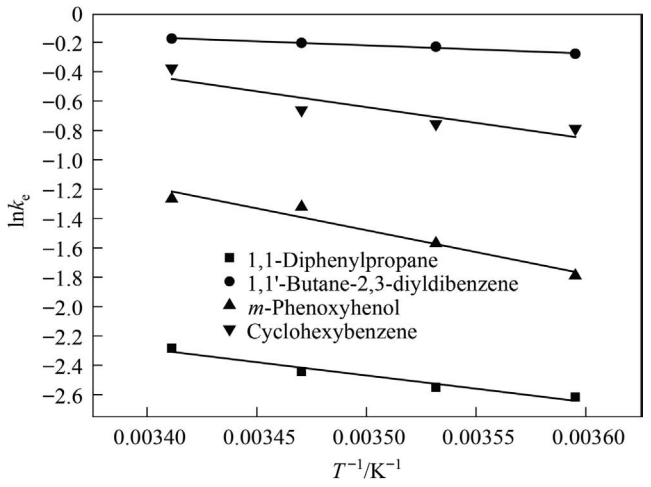

Fig. 8. The plots of lnk_e *versus* 1/T for 4 impurities.

Table 2
Change of enthalpy and entropy between impurities and 1,2-Diphenylethane

Chemical substances	$\Delta H_i - \Delta H_{mc}$/ J·mol^{-1}	$\Delta S_i - \Delta S_{mc}$/ J·mol^{-1}·K^{-1}	R^2
1,1-Diphenylethane	−19,753	−61.31	0.9796
2,3-Dimethyl-2,3-diphenylbutane	−21,441	−66.17	0.9698
1,2-Diphenylpropane	5747	12.14	0.992
Diphenylmethane	−16,666	−51.8	0.9926
5-Phenylvaleric acid	7940	25.56	0.8879
1,1-Diphenylpropane	−15,040	−32.11	0.9605
1,1′-Butane-2,3-diyldibenzene	−4593	−14.24	0.9845
m-Phenoxyphenol	−24,769	−74.39	0.9525
Cyclohexybenzene	−17,844	−57.13	0.8283

4.5. Change of thermodynamics property

The plots of lnk_e *versus* 1/T for 9 impurities are shown in Figs. 7 and 8. The slope of the straight line is $(\Delta H_i - \Delta H_{mc})/R$ and the intercept of line is $-(\Delta S_i - \Delta S_{mc})/R$. After calculating, the change of enthalpy and entropy between impurities and 1,2-diphenylethane are listed in Table 2. The square of linearly correlation coefficients, R^2 are also given in Table 2. R^2 of 7 impurities is above 0.95 and just R^2 of 2 impurities is below 0.9. For impurities of 1,2-diphenylpropane and 5-phenylvaleric acid, $\Delta H_i - \Delta H_{mc} > 0$, but for the rest of 7 Impurities, $\Delta H_i - \Delta H_{mc} < 0$, so that 1,2-diphenylethane freezing from melt needs removing more energy than most impurities freezing from melt. Lower temperature of ambient frozen environment is helpful to separation. For all the impurities, the values of ΔS_i and ΔS_{mc} are positive in process of melting. For the most of impurities, $\Delta S_i - \Delta S_{mc} < 0$ represents the entropy production of impurity from solid into melt is less than the entropy production of 1,2-diphenylethane from solid into melt.

5. Conclusions

The effective distribution coefficients of 9 impurities in 1,2-diphenylethane have been obtained by directional crystallization. The majority of effective distribution coefficients are below 1.0 and the minority of effective distribution coefficients are above 1.0. The product purity in the intermediate purified region with varied zone size is higher 0.04%−0.2% than that with constant zone size. The purity of 1,2-diphenylethane in the intermediate purified region increases as temperature difference decreases, but the increasing range decreases as temperature difference increases. The temperature difference between the melt and ambient frozen environment of 50 °C is preferred. The product purity in the intermediate region of sample bar with 2 molten zones is higher 0.05%–0.43% than that with 1 molten zone. The change of enthalpy and entropy between impurities and 1,2-diphenylethane are determined.

Nomenclature

C_0	initial impurity concentration of the sample, g·g^{-1}
C_L	impurity concentration in liquid phase, g·g^{-1}
C_S	initial concentration in solid phase, g·g^{-1}
G^l	Gibbs free energy of the system in liquid, J·mol^{-1}
G^s	Gibbs free energy of the system in solid, J·mol^{-1}
H_i^l	enthalpy of impurity in liquid, J·mol^{-1}
H_i^s	enthalpy of impurity in solid, J·mol^{-1}
ΔH_i	variations of enthalpy of impurity between the liquid and solid phases, J·mol^{-1}
H_{mc}^l	enthalpy of main component in liquid, J·mol^{-1}
H_{mc}^s	enthalpy of main component in solid, J·mol^{-1}
ΔH_{mc}	variations of enthalpy of main component between the liquid and solid phases, J·mol^{-1}
k_e	effective distribution coefficient
N	number of zone passes
R	gas constant, 8.314 J·mol^{-1}·K^{-1}
R^2	square of linearly correlation coefficients
ΔS_i	variations of entropy of impurity between the liquid and solid phases, J·mol^{-1}·K^{-1}
ΔS_{mc}	variations of entropy of main component between the liquid and solid phases, J·mol^{-1}·K^{-1}
T	the ambient frozen temperature, K
ΔT	temperature difference between the melt and ambient frozen environment, °C
T_{frozen}	the ambient frozen temperature, °C
T_{melt}	The temperature of melt, °C
v	translation rate of molten zone, mm·h^{-1}
X_{mc}^l	mole fraction of main component in liquid
X_{mc}^s	mole fraction of main component in solid
X_i^l	mole fraction of impurity in liquid
X_i^s	mole fraction of impurity in solid
x	normalized distance along the sample bar
z	normalized size of molten zone

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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