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Crystal–plastic and plastic–liquid phase transitions, and purity determination

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Abstract

Six environmental standards, Heptachlor, Heptachlor epoxide, β-Endosulphan, Dieldrin, Endrin and Endrin ketone, have been investigated by DSC. The temperature, enthalpy and entropy of the phase transitions were determined. The plastic–liquid and normal crystal–plastic phase equilibria were used for the determination of eutectic purity by the cryometric method. The plastic phase–liquid equilibrium is not useful for the purity determination. The eutectic purity calculated on the basis of the normal crystal–plastic phase transition is consistent with GC and HPLC results.

Keywords: Pesticide; Phase transition; Plastic phase; Purity

1. Introduction

Fundamental research experimental works require high purity materials. Analytical methods such as gas chromatography (GC), liquid chromatography (HPLC) and spectrophotometry are frequently used to determine the purity of organic compounds. Pure compounds possess well-determined boiling temperatures and melting temperatures, which are very sensitive to the degree of purity. In ebulliometric methods, the change in the boiling temperature is used to estimate the purity

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of thermally stable compounds. Changes in the melting temperature of the compound determine the purity characterized by the cryometric method, which is commonly used because the melting temperature is significantly lower than the boiling temperature and more sensitive to the level of impurities. We often have no information on the thermodynamic properties of impurities existing in studied compounds. For this reason it is assumed that impurities which form ideal solutions are insoluble in the solid state and soluble in the liquid phase. The molecular interactions between the impurities and compound molecules determine the formation of solid solutions or pure crystals. The probability of the formation of the solid solution is greater for disordered crystals. Condis crystal, plastic crystal and liquid crystal are increasingly less ordered (more disordered state) [1,2]. An approximate measure of the disorder in the solid state is the melting entropy, which for the (ordered) normal crystal is several times greater than for the plastic phase [2]. Sometimes the plastic phase is better described as a "crystal liquid", in which the crystal shape is retained but the molecules possess considerable translational motion.

As observed by Donnelly et al. [3], the experimental eutectic purity determined by the cryometric method could be higher than the true purity for melting compounds with entropy values lower than 8 cal mol^{-1} K^{-1}. They explained that such compounds may easily form solid solutions with impurities.

Assuming that impurities are completely soluble in the plastic phase and insoluble in the normal crystal phase, the transition normal crystal–plastic phase can be used to approximate the purity in the same manner for crystal–liquid equilibrium using the cryometric method. The aim of this study is to determine whether the normal crystal–plastic phase equilibrium can be applied to the approximation of eutectic purity, and the results obtained will be compared with those from other analytical methods.

2. Experimental

Samples of environmental standards were purified and their purity was determined in the Department of Analytical Chemistry at the Institute of Organic Industrial Chemistry, Warsaw. The purities (P_A) of the investigated compounds, characterized by GC and HPLC, are collected in Table 1.

The measurements were performed on the heat-flux DSC 605M UNIPAN calorimeter coupled with an IBM AT computer. Calorimetric measurements of the melting processes were performed using hermetic aluminium pans. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene, benzoic acid. The purity of the metals used was greater than 99.999%, and that of the organic compounds greater than 99.95%. The temperature calibration was made using the melting temperature of the calibrants determined by cryometric analysis.

For the cryometric determination of the eutectic purity the starting part of the equilibrium was taken. The upper limit of the transition fraction was $F \approx 0.25$, the same as in our earlier publication [4].

Table 1
The purity of environmental standards determined by GC or HPLC

Compound	P_A in mol%
2,3-Epoxy-1,4,5,6,7,8,8-heptachloro-3*a*,4,7,7*a*-tetrahydro-4,7-methano-indene (Heptachlor epoxide)	99.1
(1*R*,4*S*,4*aS*,5*R*,6*R*,7*S*,8*S*,8*aR*)-1,2,3,4,10,10-Hexachloro-1,4,4*a*,5,6,7,8,8*a*-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene (Dieldrin)	99.5
(1,4,5,6,7,7-Hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene)sulphite-(3α,5*a*α,6β,9β,9*a*β) (β-Endosulphan)	99.7
2,5,7-Metheno-3*H*-cyclopenta(α)-pentalen-3-one-3*b*,4,5,6,6,6*a*-hexachlorodecahydro-(2α,3αβ,3*b*β,4β,5β,6*a*β,7α,7αβ,8*R**) (Endrin ketone)	99.1
(1*R*,4*S*,4*aS*,5*S*,6*S*,7*R*,8*R*,8*aR*)-1,2,3,4,10,10-Hexachloro-1,4,4*a*,5,6,7,8,8*a*-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene (Endrin)	99.6
1,4,5,6,7,8,8-Heptachloro-3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene (Heptachlor)	99.7

3. Results and discussion

The melting enthalpies and temperatures of the crystal–plastic and plastic–liquid phase transitions for six compounds are listed in Table 2. For comparison, the results of Plato [6] are placed in parentheses. The melting enthalpy (ΔH_m), melting entropy (ΔS_m), normal crystal–plastic phase transition (ΔS_{tr}) and ratio of crystal–plastic to plastic–liquid transitions ($\Delta S_{tr}/\Delta S_m$) are calculated. The melting entropies of the plastic phases are very low ($\Delta S_m \approx R$). These results indicate that the investigated plastic phases are less solid (more liquid) and the formation of solid solutions with impurities is highly possible. The ratio of the entropy of the crystal–plastic transition to the plastic phase–liquid transition ($\Delta S_{tr}/\Delta S_m$) is very high and indicates the significant contribution of orientational factors to the entropy value of normal crystals.

Fig. 1 shows the two consecutive DSC curves for the same sample of β-Endosulphan at the heating rate $\beta = 2$ K min^{-1}. The first endothermic peak relates to the crystal (I)–crystal (II) transition at $T_{tr(C_I-C_{II})} = 389.0$ K, for which the transition enthalpy $\Delta H_{tr(C_I-C_{II})} = 2.94$ kJ mol^{-1}; the second peak presents the crystal–plastic phase transition at $T_{tr(c\rightarrow p)} = 425.3$ K; the third peak is due to the melting process of the plastic phase at $T_m = 486.2$ K. The transition crystal (I)–crystal (II) was not observed in the second scan.

Two consecutive scans for the same sample of Dieldrin taken at a heating rate of $\beta = 5$ K min^{-1} are presented in Fig. 2. The large first peak shows the crystal–plastic phase transition, and the second peak indicates the melting process of the plastic phase. The peaks in the second scan are shifted to lower temperatures. The enthalpies of transitions are lower than in the first scan. These results indicate that Dieldrin is thermally unstable in the region of phase transitions. The plastic phase melting peak disappears faster than the peak related to the crystal–plastic phase transition.

Table 2
Crystal–plastic and plastic–liquid transitions and purity determinations

Compound	T_{trs} in K	ΔH_{tr} in J mol^{-1}	P_{c-p} in %	ΔP in %	T_m in K	ΔH_m in J mol^{-1}	$\Delta S_m/R$	$\Delta S_{tr}/\Delta S_m$	P_{p-l} in %
Heptachlor epoxide	385.2 (392) [a]	18.9	99.4	0.3	434.9	2.85 (3.01) [a]	0.79	7.50	99.96
Dieldrin	405.6 (403) [a]	19.33 (18.41) [a]	99.5	0.0	452.9 (453) [a]	3.04 (2.89) [a]	0.81	7.09	99.80
β-Endosulphan	425.3	21.10	99.6	−0.1	486.2	4.13	1.02	5.84	99.96
	389 [b]	2.94 [b]							
Endrin ketone	498.4	28.25	99.4	0.3	562.4	4.15	0.89	7.68	99.84
Endrin	383.7	16.59	99.6	0.0					
Heptachlor	358.2 (356) [a]	23.40 (22.97) [a]	99.5	−0.2	371.0	2.09 (1.88)	0.68	13.9	99.96

[a] The results of Plato [6] are in parentheses. [b] Crystal I–crystal II transition.

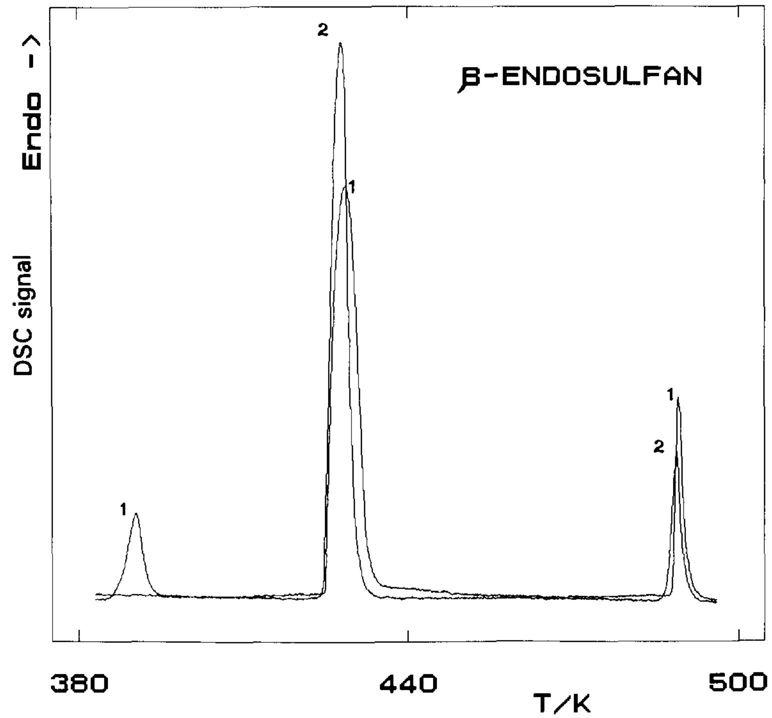

Fig. 1. Comparison of the first (1) and second (2) DSC curves of the transition processes performed using the same sample of β-Endosulphan with $\beta = 2$ K min^{-1}. The first peak is due to the normal crystal–plastic crystal transition, and the second one to the melting process of the plastic crystal.

Two consecutive scans of Heptachlor are presented in Fig. 3. The second scan was taken after 3 h. In the second scan, the value of the energy of the crystal–plastic transition is smaller and shifted to lower temperatures. The same energy value of the phase transition for two consecutive measurements was obtained when the period between two consecutive measurements was longer than 6 h. These results suggest that the rate of transition from plastic phase to normal crystal is low.

Endrin exhibits only one crystal–plastic phase transition. The baseline after the peak shifts in the direction of an exothermic process. Three consecutive scans for the same sample are shown in Fig. 4. The temperature of the baseline shift for three consecutive scans decreases as a result of decomposition processes within the solid [5]. For this reason, melting of the plastic phase was impossible to investigate. The shift in transition temperature is caused by impurities produced during the decomposition process, which act in the same manner as those influencing the crystal–liquid equilibrium [4].

The purities approximated on the basis of the plastic phase–liquid equilibria by the cryometric method ($P_{(p-l)}$) are collected in the last column of Table 2. These purity values are unrealistically high compared with those determined by GC or HPLC (Table 1). The presented results are consistent with the conclusions of

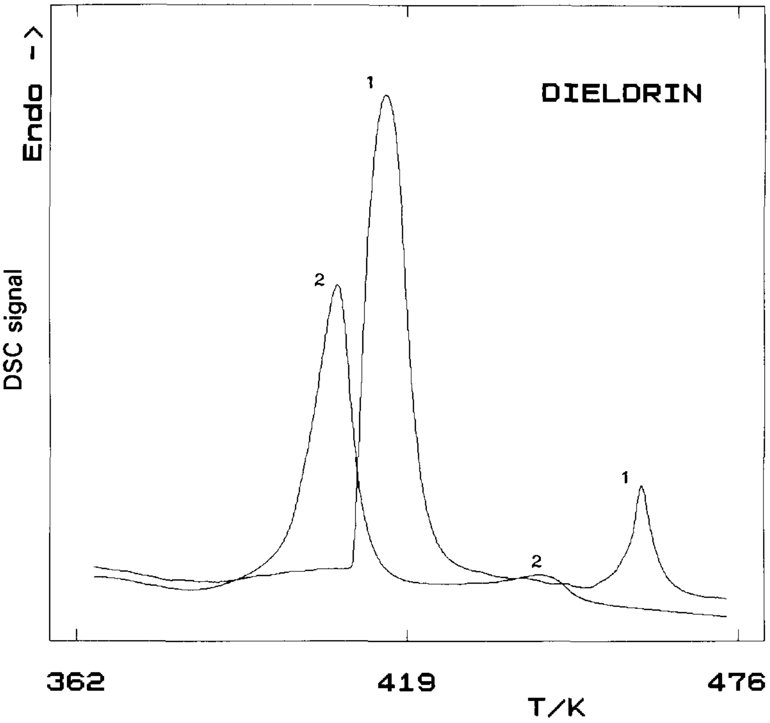

Fig. 2. Two thermoanalytical curves (1,2) of transitions performed with the same sample of Dieldrin scans. The first peak is due to the normal crystal-plastic crystal transition, and second one to the melting process of the plastic crystal.

Donnelly et al. [3] and Plato [6]. The plastic phase-liquid equilibrium is not useful for purity approximations. The purities calculated on the basis of crystal-plastic equilibria by application of the same cryometric theory (P_{c-p}) are presented in Table 2, column 5. These values are consistent with the results obtained by GC or HPLC listed in Table 1. Positive and negative deviations ($\Delta P = P_A - P_{c-p}$) are obtained. The mean deviation is 0.15 mol%.

The eutectic purities of Endrin were calculated from consecutive scans performed on the same sample with different final temperatures, and the results are collected in Table 3. Sample I was heated five times to the final temperature $T_f = 445.7$ K. The small increase in purity during the second scan is probably due to the evaporation of a trace amount of solvent used for crystallization. A decrease in purity was observed for the higher final temperature (475.3 K). Comparison of the two last purity values allows the conclusion to be drawn that the thermal decomposition reaction is catalyzed by the decomposition products. The initial heating to the final temperature $T_f = 495.0$ K causes a purity decrease of about 0.5 mol%, and the next heating one of about 5.9 mol%. The last approximation of the purity is doubtful since the total amount of impurities is beyond the range of applications of the cryometric

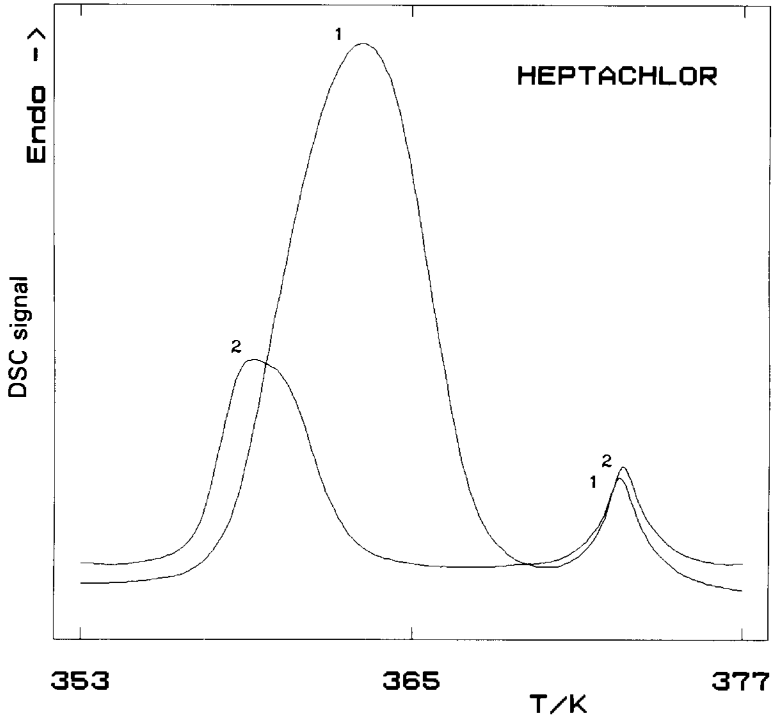

Fig. 3. Comparison of the first (1) and second (2) thermoanalytical curves of phase transitions performed with the same sample of Heptachlor. The period between two consecutive measurements was 3 h. The first peak is due to the normal crystal–plastic crystal transition, and the second one to the melting process of the plastic crystal.

Table 3
Melting enthalpy and eutectic purity of Endrin for consecutive scans performed with the same sample

n_S	ΔH_m in J mol^{-1}	P in mol%	T_f in K
Sample I, $\beta = 2$ K min^{-1}			
1	16.59	99.72	383.7
2	16.78	99.89	445.7
3	16.79	99.83	445.7
4	16.66	99.84	445.7
5	16.75	99.81	445.7
6	16.68	99.82	445.7
7	16.46	99.57	475.3
8	16.21	99.08	495.0
9	13.81	93.20	495.0
Sample II, $\beta = 5$ K min^{-1}			
1	16.58	99.62	383.8
2	14.35	96.23	506.0
3	12.58	93.70	472.5

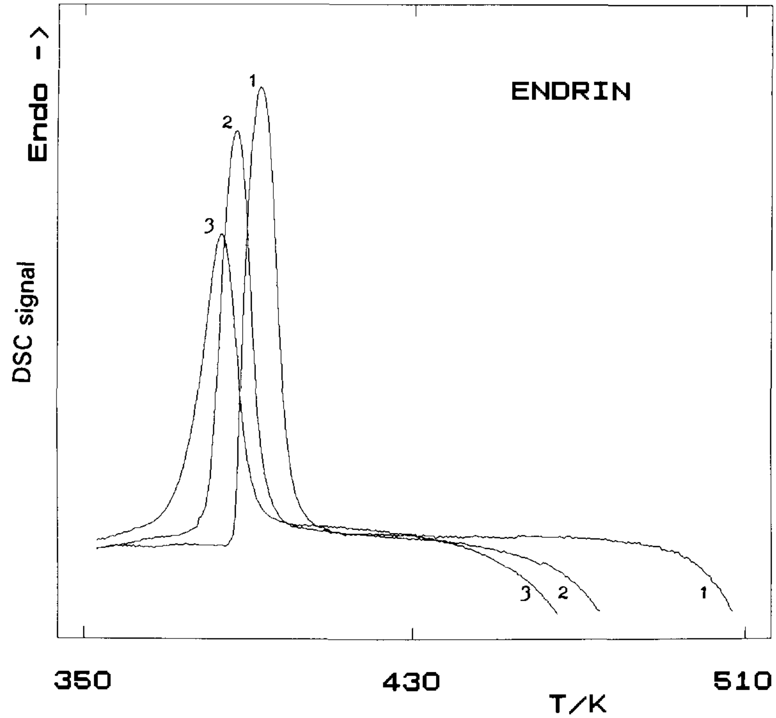

Fig. 4. Comparison of the first (1), second (2) and third (3) DSC curves of the normal crystal–plastic crystal transition performed with the same sample of Endrin.

method. Similar relationships were received for sample II with a heating rate of $\beta = 5$ K min^{-1}. The transition enthalpy decreases if the purity of the used sample decreases. The purity of Dieldrin decreases by about 5% during the heating process to the final temperature $T_f = 542$ K at a heating rate of $\beta = 5$ K min^{-1}.

4. Conclusions

The presented results indicate that the equilibrium plastic phase–melt is not useful for purity estimation by the cryometric methods. The purity values are always greater than the values calculated by GC or HPLC methods. Results suggest that the investigated compounds form solid solutions with impurities in the plastic phase. The values of the melting entropies are small ($\Delta S \approx R$), and the plastic crystals are less solid (more liquid-like). Application of the normal crystal–plastic phase equilibrium to purity determination by the cryometric method gives results in good agreement with those from GC or HPLC methods. This indicates that the transitional motion in the plastic crystal is extensive enough to deteriorate the equilibrium between pure crystals and the solid plastic solution, as it takes place in the normal crystal–liquid solution for which cryometric methods were developed.

The equilibrium between normal crystal and plastic solid solution requires great transitional motion in the plastic crystal, as in liquids. In our earlier publications [7–9] the mechanism of this transition was presented; the transition between the solid phases of pure substances occurs at the melting temperature of the phase which is stable at lower temperatures. The melting of normal crystals causes relaxation of the packing and translational motion that facilitates reorganization and formation of a new solid form. The transition between two solid phases probably proceeds via a transitional liquid state that ensures an equilibrium between the normal crystal and the plastic solid solution.

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