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Melting Behavior in Binary Compounds: Inclusion Compounds as Examples of Congruent vs Incongruent Melting

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The melting behaviors of three inclusion compounds (ethanol–Dianin's compound, CCl_4–Dianin's compound, and CBr_4–hexakis(phenylthio)benzene) and their parent compounds (Dianin's compound and hexakis(phenylthio)benzene) have been examined by differential scanning calorimetry. All three inclusion compounds were found to melt incongruently, at temperatures slightly less than the melting points of the parent compounds. To examine factors that determine whether melting takes place congruently or incongruently, Gibbs energies of these and two other inclusion and their parent (host) compounds were calculated. The most important factor in melting behavior of inclusion compounds is the relative Gibbs energy of the pure host lattice compared with the inclusion compound: lower Gibbs energy of the inclusion compound leads to congruent melting, and lower Gibbs energy of the host lattice leads to incongruent melting. This is discussed in terms of guest–host interactions and structural considerations in these systems. These considerations are generally applicable to melting behavior of any binary compound.

Introduction

Knowledge of melting behavior of a binary compound material can be important in several ways. For preparation, it is important to know whether or not it will be possible to produce the compound directly from the melt. A related consideration is whether or not the material decomposes on melting. If so, it is important to consider how temperature excursions in excess of the melting point will affect the material integrity. Furthermore, knowledge of melting behavior may provide qualitative structural information about the material.

The melting behavior of a binary compound material can be categorized in terms of congruency or incongruency. In the former case, melting the binary compound leads directly to a liquid region, with solid–liquid coexistence at a single temperature (the melting point); consequently, the liquid has the same composition as the solid. A binary compound melts incongruently if, at a temperature below the melting point of one (or both) of the constituent components, the compound decomposes to give both a liquid (containing one or both of the components), and a solid (usually one of the pure components). On further heating of an incongruently melting compound, there is a temperature range of liquid–solid coexistence before melting is complete. Schematic melting point diagrams for binary systems with no compound formation, and with congruent- and incongruent-melting compounds (all with miscible liquid components) are shown in parts a–c of Figure 1, respectively.

Clearly, an incongruently melting compound cannot easily be prepared directly from the melt, since the kinetics of rearrangement of the pure solid component (which solidifies first) will not favor compound formation. (Similarly, an incongruently melting compound cannot easily be recovered on resolidification.) However, it can be seen from Figure 1b that cooling a liquid of appropriate composition can directly produce a congruently melting compound.

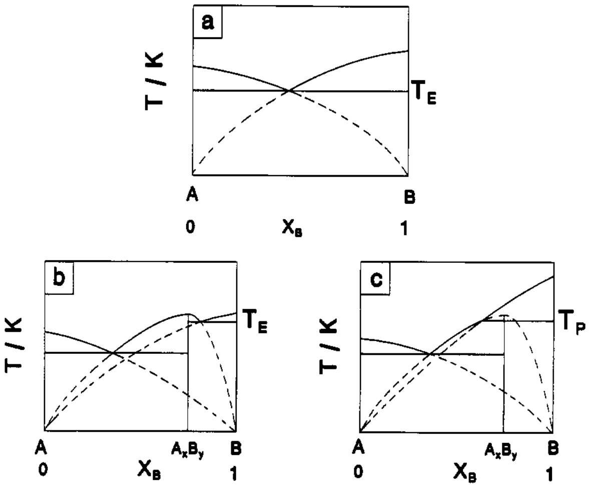

Figure 1. Schematic melting point diagrams showing temperature as a function of mole fraction of component B for (a) no compound formation, (b) a congruently melting binary compound, and (c) an incongruently melting binary compound. T_E is an eutectic temperature; T_P is a peritectic temperature.

Whether a material melts congruently or incongruently depends on a number of factors, especially relative thermodynamic stabilities of the compound and its constituent components. In particular, an incongruently melting compound must melt at a lower temperature than at least one of its pure components, whereas a congruently melting compound can melt at a lower or higher temperature than its pure components. However, even a rigorous thermodynamic treatment does not *per se* show why melting is congruent or incongruent. To understand the driving force for melting behavior, it is useful to have a microscopic approach that includes relevant structural information. It is our purpose here to use a particular

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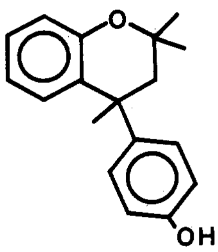

Figure 2. Molecular structure of Dianin's compound, 4-(3,4-dihydro-2,2,4-trimethyl-2*H*-1-benzopyran-4-yl)phenol.

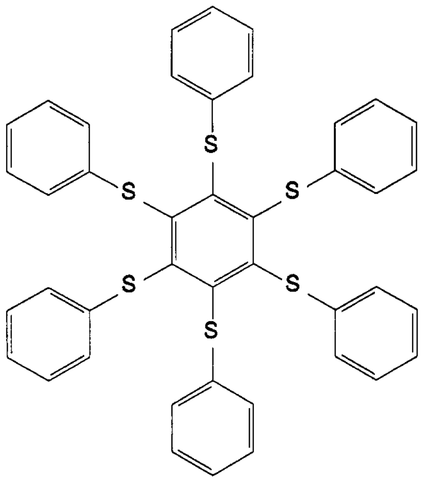

Figure 3. Molecular structure of hexakis(phenylthio)benzene (abbreviated HPTB).

family of binary compounds—inclusion compounds—to delineate structural stability–melting relations, in order to make general predictions concerning melting behavior.

Inclusion compounds are multicomponent materials in which one component forms a host lattice in which molecules of the other component(s) reside. The topology of the host lattice and the resulting locations of the guest molecules determine the type of inclusion compound—e.g., channel compounds (guests reside in the open channels of the host lattice), intercalates (guests reside between host lattice layers), and clathrates (guests reside in closed cages formed by host lattice). Inclusion compounds can melt congruently or incongruently, depending on the host and guest and also on the pressure. The availability of structural, dynamic, and thermodynamic information concerning inclusion compounds allows an investigation of these materials to make the links between melting behavior, stability, and structure.

In this paper we report melting behavior in two inclusion compound families (including the empty host lattices), *viz.*, Dianin's compound (4-(3,4-dihydro-2,2,4-trimethyl-2*H*-1-benzopyran-4-yl)phenol, abbreviated DC; see Figure 2 for molecular structure) and hexakis(phenylthio)benzene (abbreviated HPTB; molecular structure in Figure 3). These inclusion compounds are both known to form trigonal crystals of $R\bar{3}$ space group.[1,2] The crystal structures are shown schematically in Figures 4 and 5.

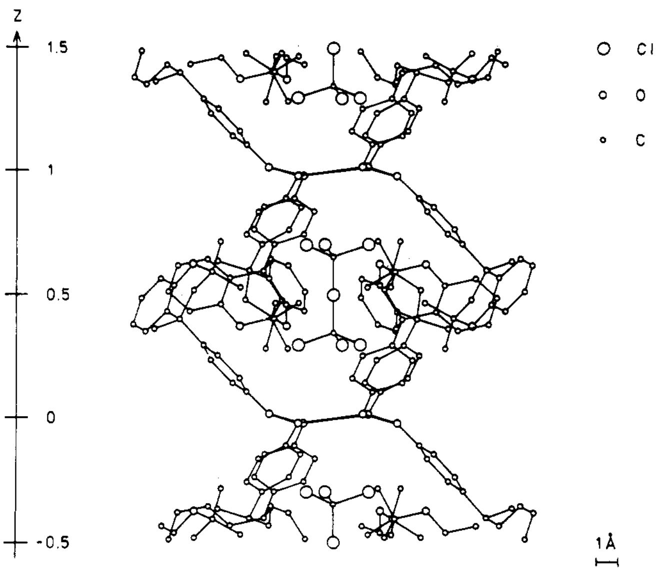

Figure 4. Structure of CCl_4–Dianin's compound.[31] There is one CCl_4 molecule in each cage, either in the upper or lower half, with a Cl at the middle of the cage in either case. Both CCl_4 positions are shown.

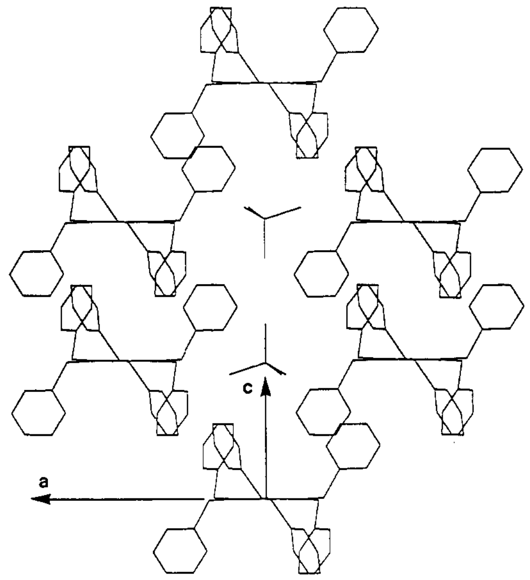

Figure 5. Structure of CBr_4–HPTB.[8] Two HPTB molecules (one above and one below the plane) are omitted for clarity.

In addition, we calculate the relative thermodynamic stabilities of these and other inclusion compounds, compared with the pure host component, in order to deduce the thermodynamic driving force for congruent or incongruent melting. This information is used to correlate structural information with melting behavior.

Experimental Methods

The melting behavior of three inclusion compounds (ethanol clathrate of Dianin's compound, CCl_4 clathrate of Dianin's compound, CBr_4 clathrate of HPTB) and the two pure host compounds were investigated by differential scanning calorimetry.

Ethanol–Dianin (hereafter abbreviated as EtOH–DC) and CCl_4–Dianin (abbreviated CCl_4–DC) were prepared by a literature route.[3] The host–guest mole ratios, from density measurements,[4] are 3:1 and 6:1, respectively. Pure Dianin's compound was prepared from recrystallization from decanol, a solvent too large

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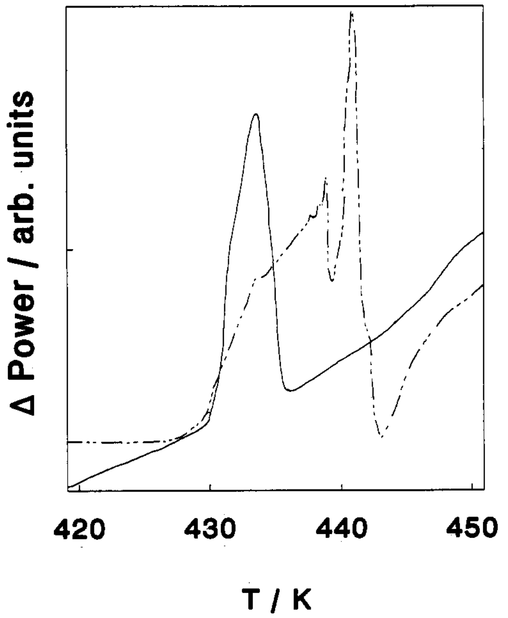

Figure 6. Differential scanning calorimetry results for pure Dianin's compound (—) and the ethanol clathrate of Dianin's compound (- - — - -).

to be included in the cavities of the host lattice;[5] its structure is the same as that of its clathrates.[6]

HPTB was prepared by a literature route[7] involving the reaction of C_6Cl_6 with C_6H_5SNa. CBr_4–HPTB was prepared from HPTB dissolved in chloroform with excess CBr_4. The structure[8] of CBr_4–HPTB involves cages of HPTB molecules each containing two guest molecules; the 3-fold symmetry axis of the CBr_4 guest is collinear with the *c* axis. The host–guest mole ratio of CBr_4–HPTB was found, by density measurement, to be 1:2.

Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC-1, modified as described elsewhere.[9] Typical sample masses were about 20 mg (known to three significant figures). The samples were in aluminum pans, sealed in air. Heating rates were 5 K min^{-1}. Temperature and enthalpy calibrations were carried out using the melting point of indium (at $T = 429.76$ K; $\Delta_{\mathrm{fus}}H = 28.45$ J g^{-1}).[10]

Experimental Results

The DSC traces for melting of pure Dianin's compound, EtOH–DC, CCl_4–DC, pure HPTB, and CBr_4–HPTB are shown in Figures 6–8. The melting points (onset temperatures in the DSC) were determined to be 430.2, 428.5, 429.2, 453.2, and 438.6 K, respectively, with uncertainties of 0.5 K.

For the DSC experiments, the enthalpy changes on fusion of Dianin's compound and HPTB were found to be 143 ± 5 and 88 ± 3 J g^{-1}, respectively.

Observation of morphological changes and the temperature range of coexistence of solid and liquid above the temperature at which melting initiated on a hot-stage microscope showed that all three inclusion compounds (EtOH–DC, CCl_4–DC, CBr_4–HPTB) melt incongruently. Due to the temperature range of fusion and interference due to decomposition, the enthalpies of fusion of the inclusion compounds could not be quantified reliably. The binary phase diagrams (EtOH/DC, CCl_4/DC, CBr_4/HPTB) are discussed below.

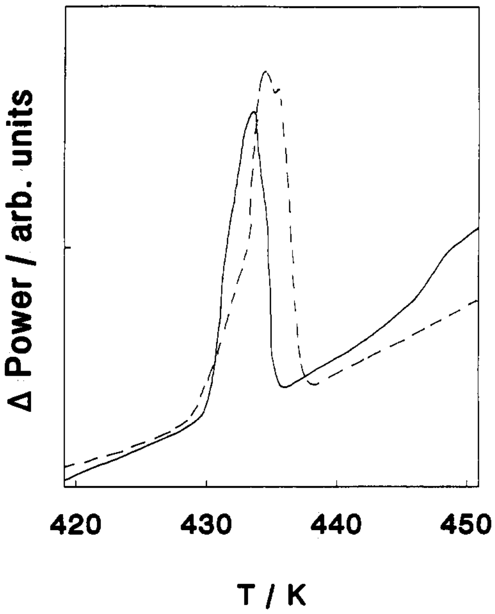

Figure 7. Differential scanning calorimetry results for pure Dianin's compound (—) and the CCl_4 clathrate of Dianin's compound (- - -).

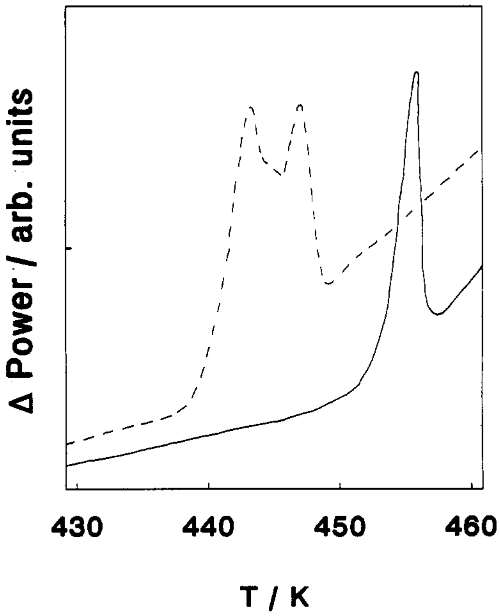

Figure 8. Differential scanning calorimetry results for pure HPTB (—) and CBr_4–HPTB (- - -).

Discussion

T vs X Relations in Binary Melting Point Diagrams. From the relationships in a T vs X (i.e., temperature vs composition) phase diagram, a partial explanation of congruent/incongruent melting behavior can be found.

Reisman[11] discusses binary phase diagrams in some detail, and those results are summarized here in order to provide context for discussion of factors that determine melting behavior. For a simple binary system, with no

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[5] McConnell, A. A.; MacNicol, D. D.; Porte, A. L. *J. Chem. Soc. A* 1971, 3516.

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[8] Michalski, D.; Cameron, T. S.; White, M. A., unpublished work.

[9] Millier, B.; Van Oort, M.; White, M. A. *J. Chem. Educ.* **1985**, *62*, 64.

[10] Handbook of Chemistry and Physics, 61st ed.; CRC Press: Boca Raton, FL, 1980.

[11] Reisman, A. *Phase Equilibria*; Academic Press: New York, 1970.

compound formation, the liquidus lines represent the solubilities of the respective components (since upon cooling a certain composition, precipitation first occurs at the temperature of the liquidus line). The theoretical liquidus line of component B, assuming the solution to be ideal, is given by the equation for melting point depression:

$$\ln X_B = \frac{\Delta_{fus}H_B}{R}\left[\frac{1}{T_B} - \frac{1}{T}\right] \qquad (1)$$

where X_B is the molar fraction of B at the liquidus composition at temperature T, $\Delta_{fus}H_B$ is the molar heat of fusion of pure component B, T_B is its melting temperature, and R is the gas constant. Although nonideal interactions may require replacement of X_B in eq 1 by activity (a_B), $\Delta_{fus}H_B$ and T_B are always prevalent, and it is this relationship which is primarily responsible for the liquidus slope. With miscible components and no compound formation, the liquidus lines meet at the eutectic temperature, T_E, and extend metastably to $T = 0$ K, as in Figure 1a.

For a binary system with the formation of a compound A_xB_y that melts congruently, the melting point of the compound exceeds the temperature of the A and B liquidus lines at intermediate compositions on either side of the composition of the compound (Figure 1b). The A_xB_y liquidus intersects the A liquidus (at compositions of A greater than in A_xB_y) and the B liquidus (at compositions of B greater than in A_xB_y), as in Figure 1b, and two eutectics result.

If A_xB_y melts incongruently, the liquidus lines of one component (A in Figure 1c) and of A_xB_y (where the heat of fusion and melting temperature are from the metastable extensions) will intersect at the peritectic temperature, T_P. In this case, the intermediate compound will not be stable above T_P. The compound melts incongruently because its (metastable) melting point is below the liquidus temperature at the composition of the compound. This can come about if the liquidus slope of one of its components (determined largely by the heat of fusion of the component, assuming ideality) results in a temperature (for the liquidus) at the compound composition that exceeds the (metastable) melting point of the compound.

On cooling, the incongruently melting compound will precipitate from the liquid as the system is cooled from T_P to T_E. The major difference between preparation of a congruent- and incongruent-melting compound is that in the former the entire liquid at the composition of the compound can be solidified to a single phase, whereas in cooling the latter one can convert only a portion of the liquid to the compound.

In principle, on the basis of eq 1, the binary melting point diagrams of the three systems investigated here (ethanol–Dianin's compound, CCl_4–Dianin's compound, CBr_4–HPTB) could be calculated. However, the use of eq 1 gives such steep liquidus lines starting from the pure components that it leads to melting points of the compounds far below the melting points of the pure host lattice, contrary to what is observed experimentally. The failure of eq 1 to produce the observed binary phase diagrams shows that these solutions are quite nonideal. To have liquidus lines less steep than the ideal case, as is observed experimentally, host activities must be in excess of mole fractions, as this will lead to less freezing-point depression of the host lattice on addition of the guest species. This implies that the EtOH–DC, CCl_4–DC, and CBr_4–HPTB interactions must be slightly more repulsive than interactions within the pure components, which is reasonable, considering guest and host polarities in each inclusion compound. However, as the required activity coefficients are not known, we are not able to calculate the full phase diagrams for these systems.

In the context of the discussion in this section, it is clear that thermodynamic stabilities of the compound, the liquid, and the pure constituent solids are important in defining melting behavior, and we turn our attention to this next.

***G* vs *X* Relations in Binary Melting Point Diagrams.** Discussion of whether melting is congruent or incongruent leads to consideration of relative Gibbs energies of the liquid phase, the solid compound, and the pure solid components.

In a G vs X (Gibbs energy vs composition) phase diagram for a simple A,B binary system, the Gibbs energy of the liquid phase, G_{liq}, is given by

$$G_{liq} = \sum_{i=A,B} n_i(\mu_i^\circ + RT\ln X_i) \qquad (2)$$

where n_i is the number of moles of component i and μ_i° is the chemical potential of pure component i, and the solution is assumed to be ideal (otherwise $\ln a_i$ would replace $\ln X_i$). With $n_A + n_B = 1$ mol, eq 2 gives the molar Gibbs energy, $G_{m,liq}(X)$, as a curve with its minimum at a composition intermediate between pure A and pure B (at $X = 0.5$ for an ideal case with $\mu_A^\circ = \mu_B^\circ$).

In an isothermal G vs X plot, the solid compounds (pure components or intermediate compounds; solid state immiscibility assumed here) are represented by points (at their compositions) which correspond to their Gibbs energies (relative, say, to $G_0 = 0$ at $T = 0$ K, i.e., $G(T) = G_T - G_0$) at a given temperature. Since minimum Gibbs energy indicates stability, the points (for the fixed-composition solids) will be above the liquidus curve at temperatures above their melting points. Decreasing temperature results in the solid points (eventually) having lower Gibbs energy than the liquid curve at their compositions, which results in solidification. Tangent lines, $\partial G/\partial X_B$ ($=\partial G/\partial n_B$ for $n_A + n_B = 1$ mol), represent the chemical potentials of components at given compositions; equivalency of chemical potentials of a component in the liquid and solid phases defines liquid–solid phase equilibrium for that component. The composition region of coexistence of liquid and solid stable phases at a given temperature is given by a tangent line to the liquid curve through the solid point(s).[12]

We now consider how Gibbs energies for the liquid and solid phases change with temperature. Figures 9 and 10 show $G(X_B)$ isotherms at six different temperatures, corresponding to systems with compound AB melting congruently and incongruently, respectively. For simplicity in this analysis, we have chosen melting points of A and B, and temperatures T_1–T_6 to correspond for the two-phase diagrams, in order to focus on the differences that determine whether melting is congruent or incongruent.

The greatest difference in the $G(X)$ diagrams for the two cases (congruently and incongruently melting compound) occurs at temperature T_3, the eutectic (congruent)

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(12) For a general discussion of these matters see, for example: Oonk, H. A. J. *Phase Theory. The Thermodynamics of Heterogeneous Equilibria*; Elsevier: Amsterdam, 1981.

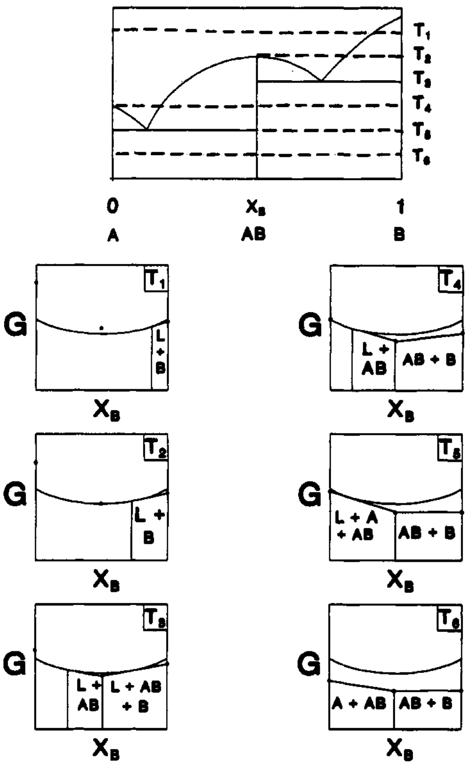

Figure 9. Melting point diagram for the A–B binary system with congruently melting compound AB, including Gibbs energy as a function of composition at six different temperatures.

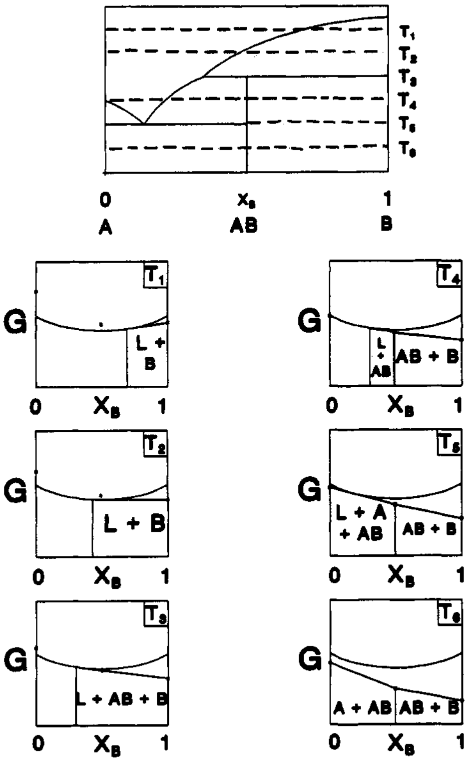

Figure 10. Melting point diagram for the A–B binary system with incongruently melting compound AB, including Gibbs energy as a function of composition at six different temperatures.

or peritectic (incongruent) temperature. The important difference at T_3 is in the Gibbs energy of the compound AB relative to that of component B. In the case of a congruently melting compound, the Gibbs energy of the compound is less than that of pure component B, and therefore heating a congruently melting compound causes it to go directly to the liquid phase. For an incongruently melting compound, the Gibbs energy is lower for the pure component, and heating causes it to transform to liquid and the more stable pure solid component (B in this case).

The discussion provides a framework for understanding the driving force which determines whether the melting is congruent or incongruent; in the next section we test the relationship between relative Gibbs energies and melting behavior.

Gibbs Energies and Melting Behavior of Inclusion Compounds. Since the molar Gibbs energy can be used to determine the stabilities of phases at a given temperature (assuming that equilibrium is attained), studies of G vs T for a given composition could indicate that an inclusion compound melts incongruently because, at the peritectic temperature, the stability of the empty lattice exceeds that of the compound. This would be reflected in Gibbs energies: incongruent melting would result when the Gibbs energy of the empty lattice is lower than that of the compound; congruent melting would take place in the opposite case. (This also fits with the finding that incongruently melting compounds must melt at lower temperatures than the pure component which is produced in this incongruent melting.)

Calculation of $G(T)$ for a material requires knowledge of the enthalpy, H, and entropy, S, as functions of temperature:

$$G(T) \equiv G_T - G_0 \equiv G = H - TS \tag{3}$$

and these can be derived from heat capacity, C_p, as a function of temperature:

$$H(T) \equiv H_T - H_0 = \int_0^T C_p \, dT \tag{4}$$

$$S - S_0 = \int_0^T C_p \, d\ln T \tag{5}$$

(The residual entropy, S_0, if present in the system, must also be considered.)

The required heat capacity data (for the inclusion compound and its pure host) and definitive information concerning melting behavior are available for five inclusion compounds: EtOH–DC,[13] CCl_4–DC,[13] CBr_4–HPTB,[14] ethylene oxide (EO) clathrate hydrate,[15,16] tetrahydrofuran (THF) clathrate hydrate.[17,18] Their melting behaviors, compositions, and data sources are summarized in Table 1.

$G(T)$ was calculated for each of these five inclusion compounds (per mole of constituent component, e.g., for THF·$17H_2O$ it was calculated from $G(\text{THF}\cdot 17H_2O)/18$), in comparison with $G(T)$ for the pure host component. The results are summarized in Table 2. In Figures 11–13 $\Delta G = G_{\text{host}} - G_{\text{inclusion}}$, the difference between Gibbs energies of the inclusion compound and the corresponding host lattice are shown explicitly. It can clearly be seen from these figures that EtOH–DC, CCl_4–DC, and CBr_4–HPTB are driven by Gibbs energy considerations to melt incon-

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Table 1. Melting Behavior and Heat Capacity Data for Various Inclusion Compounds and Their Corresponding Host Lattices

inclusion compound	composition	melting temp/K	melting type[a]	C_p ref	S_0/R value[b]	S_0/R ref	host lattice type	host lattice C_p ref
ethanol clathrate of Dianin's compound	2EtOH + 6DC	428.5	ic	13			DC	13
CCl_4 clathrate of Dianin's compound	CCl_4 + 6DC	429.2	ic	13			DC	13
CBr_4 clathrate of hexakis(phenylthio)benzene	$2CBr_4$ + HPTB	438.6	ic	14			HPTB	14
ethylene oxide clathrate hydrate	EO + $6.8H_2O$	284	c	16	0.4125	29	ice Ih	30
tetrahydrofuran clathrate hydrate	THF + $17H_2O$	278	c	18	0.4125	29	ice Ih	30

[a] c = congruently melting; ic = incongruently melting. [b] Expressed per mole of host lattice; same value assumed for inclusion compound (scaled for stoichiometry) and host lattice; R = 8.314 51 J K^{-1} mol^{-1}.

Table 2. Values of Gibbs Energies (Relative to T = 0 K) for Various Inclusion Compounds and Their Corresponding Host Lattices, Expressed per Mole of Host Lattice

T/K	G/J mol^{-1} Dianin's compound	ethanol–Dianin compound	CCl_4–Dianin compound
50	−595.84	−803.03	−823.19
100	−3685.4	−4174.8	−4290.3
150	−9719.1	−10160	−10527
200	−18672	−18691	−19471
250	−30579	−29741	−31129
300	−45447	−43288	−45491
350	−63239	−59310	−62550
400	−83923	−77812	−82315

T/K	G/J mol^{-1} H_2O	THF clathrate hydrate	ethylene oxide clathrate hydrate
50	−258.36	−293.46	−317.23
100	−879.32	−1075.9	−1223.0
150	−1891.0	−2340.3	−2658.1
200	−3258.0	−4020.0	−4532.1
250	−4988.1	−6085.9	−6807.6

T/K	G/J mol^{-1} HPTB	CBr_4-HPTB
50	−2239.0	−1985.8
100	−12595	−9027.7
150	−30787	−20241
200	−56077	−34962
250	−88149	−52872

gruently to give their pure solid host lattices. On the other hand, THF clathrate hydrate and EO clathrate hydrate melt congruently because, at their respective melting points, the clathrate is more stable (lower G) than the pure host, ice Ih. From Figures 11–13 it can be seen that the gap in Gibbs energy between the host lattice and the clathrate also reflects the relative melting points: the closer they are, the closer their melting points (e.g., they are close for CCl_4–DC and DC [respective melting points 429.2 and 430.2 K] and farther apart for HPTB–CBr_4 and HPTB [respective melting point 438.6 and 453.2 K]).

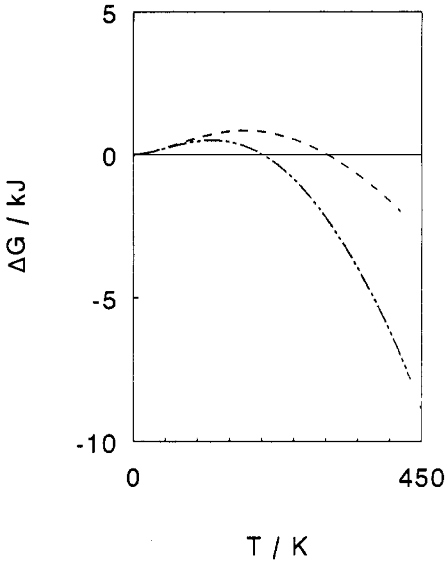

Figure 11. Molar Gibbs energy of the host lattice relative to the inclusion compound ($\Delta G = G_{host} - G_{incl}$) as a function of temperature for the ethanol clathrate of Dianin's compound (- - — - -), and the CCl_4 clathrate of Dianin's compound (- - -). EtOH–DC melts incongruently at 428.5 K, and CCl_4–DC melts incongruently at 429.3 K.

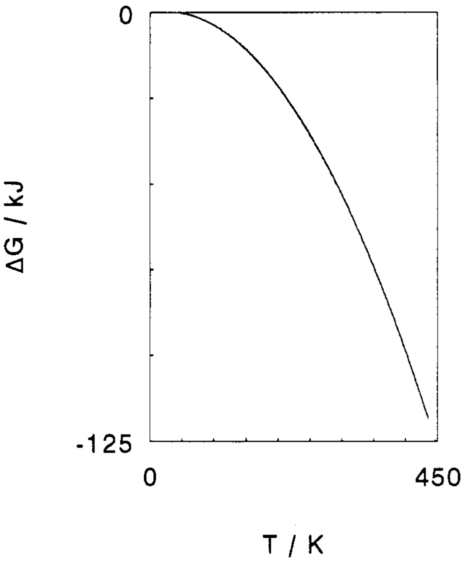

Figure 12. Molar Gibbs energy of the host lattice relative to the inclusion compound ($\Delta G = G_{host} - G_{incl}$) as a function of temperature for the CBr_4 clathrate of HPTB. CBr_4–HPTB melts incongruently at 438.6 K.

It is interesting to consider the enthalpic and entropic contributions to G and how these may affect melting behavior. From the shapes of the $\Delta G(T)$ curves, it appears that the more stable structure (compound or host lattice) may gain its stability by greater curvature in the $G(T)$ curve. From thermodynamic relations, $(\partial G/\partial T)_p$, is given by

$$[\partial G/\partial T]_p = -S \qquad (6)$$

which indicates that, especially in the absence of specific guest–host bonding, entropy considerations may be very important in determining which structure has lower G and hence whether melting is congruent or incongruent. Since S is always positive, $(\partial G/\partial T)_p$ must always be negative, and a more entropic solid, enthalpy factors being equal, will be more stable. When the temperature of a solid is sufficiently high, the lattice vibrations disrupt the lattice and cause melting (Lindemann's law states that this occurs when the volume is about 10% greater than

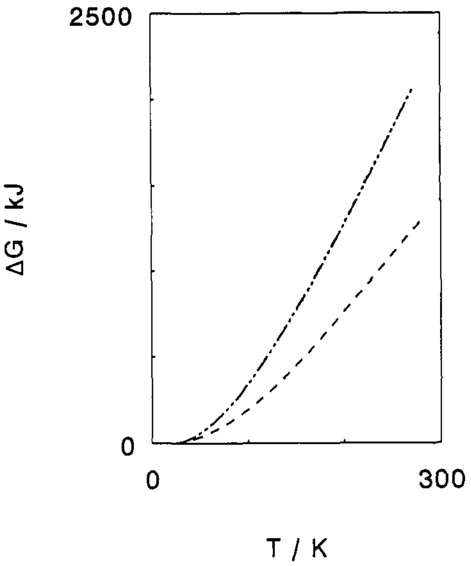

Figure 13. Molar Gibbs energy of ice Ih relative to the clathrate hydrate inclusion compounds ($\Delta G = G_{ice} - G_{incl}$) as a function of temperature for tetrahydrofuran clathrate hydrate (- - -) and ethylene oxide clathrate hydrate (- - — - -). THF clathrate hydrate melts congruently at 278 K, and EO clathrate hydrate melts congruently at 284 K.

that at absolute zero, i.e., the average displacement from the lattice site is about 3% of the lattice spacing). Whether melting occurs congruently to give a liquid only or incongruently to give a liquid coexisting with one solid component can depend largely on the relative entropies of the compound and the pure component.

Structural Considerations. If enthalpy is not a dominant factor, then the more entropic solid (host component or inclusion compound) will be the one that is more stable at the melting/decomposition temperature: an inclusion compound that is more disordered than its pure host component will melt congruently; an inclusion compound that is less disordered than its pure host component will melt incongruently. This analysis provides links between structure, thermodynamic considerations and melting behavior.

That thermodynamic stability and melting behavior are consistent with structural considerations can be seen here as follows. First, we consider the incongruently melting compounds, EtOH–DC, CCl_4–DC, and CBr_4–HPTB. In Dianin clathrates and CBr_4–HPTB, the guests are relatively ordered; since the host lattice is somewhat flexible (vide infra), the presence of the guest makes the structure more rigid and lowers the molar entropy.

In the Dianin clathrates, the host lattice has essentially the same structure as the inclusion compound, except for the existence of the guest species in the voids. The host lattice is not rigid; its flexibility is observable by ^{13}C NMR,[19] by its large number of low-frequency internal vibrations,[20] and by its resultant (nearly) linear heat capacity.[13] (The linear heat capacity results from a large number of optic modes with a wide range of energies, each well-represented by the Einstein model and each "turning on" at a different temperature such that the sum is essentially linear.) In addition, these low-frequency internal modes resist heat flow, resulting in "glasslike" thermal conductivity of the pure host component.[21] It is these motions that make the pure Dianin host component high in molar entropy, resulting in a low Gibbs energy relative to its inclusion compounds, and concomitant incongruent melting.

Although there is somewhat less information concerning the HPTB system, the heat capacity of pure HPTB is again very nearly linear,[14] indicating many low-frequency internal modes, a high molar entropy, and consequent incongruent melting of CBr_4–HPTB.

On the other hand, THF clathrate hydrate and EO clathrate hydrate both melt congruently at normal pressures. We have seen above that this is driven by lower Gibbs energy of the clathrate than for pure H_2O at the melting point of the clathrate, and this follows from the molar entropy of the clathrate being higher than for ice. In the microdomain of the H_2O molecule, the local structures of the clathrate hydrate and of ice are known to be similar[22] and relatively rigid (aside from hydrogen-bonding dynamics, which are quite similar in ice and the clathrate hydrates). Therefore, the main entropic difference between ice and these clathrate hydrates is in the presence (and disorder) of the guest. It is known that the THF guest molecule is dynamically disordered even at very low temperature;[18] apparently this contributes considerably to the entropic stabilization of the inclusion compound.

Effect of Applied Pressure on Melting Behavior. It is known for THF clathrate hydrate that an increase in pressure from 1 bar to 1 kbar causes the melting behavior to change from congruent to incongruent.[17] From the thermodynamic relation

$$[\partial G/\partial P]_T = V \qquad (7)$$

the structure (pure solid host or inclusion compound) with the larger molar volume will have its Gibbs energy raised more by an increase in pressure. The open structure of THF clathrate hydrate, compared with ice Ih, leads to a greater increase in G with increasing pressure for the clathrate hydrate. Apparently this increase is sufficient, at the melting point and 1 kbar, to reverse the order of the relative stability of THF clathrate hydrate and ice from the values at 1 bar; THF clathrate hydrate melts incongruently at 1 kbar. Again, since pressure could cause ordering of the inclusion compound, this fits with the microscopic picture of the pure host lattice being produced from the melt (i.e., incongruent melting) when the inclusion compound is more ordered than the solid host lattice.

Other Inclusion Compound Systems. Although melting behavior is known for some other inclusion compound systems, the discussion above appears to include all systems for which there is both definitive melting information and the required thermodynamic data to assess Gibbs energies. Nevertheless, there are some other systems for which pertinent information is known, and these are discussed briefly here.

PHTP, or perhydrotriphenylene, is a saturated tetracyclic hydrocarbon that is capable of forming inclusion compounds with straight-chain hydrocarbons. Alkane–PHTP inclusion compounds have channels in which the guest molecules can reside.[23] Many *n*-paraffin (chain

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lengths >8 carbons) PHTP inclusion compounds are known to melt congruently above the melting point of pure PHTP.[24,25]

Urea forms rather similar inclusion compounds; the lattice is hexagonal and consists of interpenetrating helices which form channels that can theoretically hold guest molecules of infinite length.[26] The most common urea inclusion compounds contain *n*-paraffins or their monosubstituted derivatives as guests. Series of *n*-paraffin–urea inclusion compounds have been studied, and the results indicate that the nature of their thermal decomposition is incongruent melting.[27,28]

Although urea and PHTP are similar in that they form inclusion compounds with straight-chain alkanes, they are very different structurally: the extensive hydrogen bonding in urea is not present in either PHTP or the guest alkanes. Farina et al.[24] used regular solution theory and the difference between host and guest polarity to explain why PHTP systems melt congruently and the urea systems incongruently. With W as an interaction parameter that is a measure of the tendency of the two components to segregate (as liquids), higher values of W indicate increased nonideality of the solution. Since both the PHTP and alkane guest are hydrocarbons (and would therefore make nearly ideal solutions), W for the alkane–PHTP system is low; since urea ($O{=}C(NH_2)_2$) is more polar than its hydrocarbon guest (and would therefore not mix well with the guest in solution), W would be high for alkane–urea compounds and a miscibility gap in the liquid region of the T vs X phase diagram results. It is this miscibility gap (reciprocal insolubility) that prevents congruent melting of these urea inclusion compounds above the melting point of pure urea.

The difference in melting of PHTP and urea paraffin inclusion compounds can be understood from the point of view of the present analysis. Other factors (especially entropy considerations) being similar for the two systems, the order of Gibbs energies of the inclusion compound and pure host lattice could be opposite for the two systems due to guest–host enthalpy terms. In alkane–PHTP, the interaction is favorable due to like (nonpolar) components; this could decrease the Gibbs energy of the inclusion compound relative to the pure host lattice and lead to congruent melting (as observed). In alkane–urea, the same unfavorable guest–host interactions that lead to immiscibility in the liquidus region could cause the pure host lattice to have a lower Gibbs energy than the inclusion compounds; this would lead to the observed incongruent melting. Further thermodynamic information (especially heat capacity data, in order to determine Gibbs energies) would allow a test of this conjecture in these systems.

Conclusions

Melting behavior of compounds formed in binary systems has been examined, with emphasis on inclusion compounds. These systems allowed consideration of thermodynamic factors influencing melting behavior. In particular, it is found that lower Gibbs energy of the pure host compound relative to the inclusion compound leads to incongruent melting. Conversely, lower Gibbs energy of the inclusion compound relative to the pure host lattice leads to congruent melting. Gibbs energy can be raised either by low entropy or by unfavorable guest–host interactions. Enthalpy contributions may be deduced by consideration of guest–host interactions; entropy considerations can be linked to structural features. Although deduced for the specific case of inclusion compounds in order to test their veracity, these considerations would appear to be generally applicable to melting in any binary compound.

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