Thermodynamic Studies of Two Different Inclusion Compounds with the Same Guest: Toward a General Understanding of Melting Behavior in Binary Compounds

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Melting behaviors of the hexadecane channel inclusion compounds of urea and of perhydrotriphenylene (PHTP) have been investigated by differential scanning calorimetry and hot-stage microscopy. Urea−hexadecane melts incongruently to give solid urea and liquid hexadecane, whereas PHTP−hexadecane melts congruently, i.e., giving liquid directly. Through examination of Gibbs energies, determined from adiabatic calorimetry, it is concluded that both inclusion compounds are stable with respect to their components, and melting behavior can be considered to be dictated by the stability of the host lattice at the melting point. Generalizations concerning factors influencing congruency of melting behavior in binary systems are presented.

Introduction

Inclusion compounds—multicomponent materials in which one component forms a host lattice in which other component(s) reside as guests—provide an unusual opportunity to investigate structure−property relations, especially since their structures and intermolecular interactions can be modified in many ways. We have been studying inclusion compounds to add to the understanding of thermal properties of molecular solids, viz., thermal conductivity[1−5] and heat capacity and related lattice dynamical properties.[6−15] In addition, through examination of relative Gibbs energies of inclusion compounds and their pure components, we have been able to reach some general conclusions concerning melting behavior.[16]

A binary compound can melt congruently, i.e., solid-to-liquid at a fixed temperature, or incongruently, i.e., solid to give liquid and solid (with a composition different from that of the compound) coexisting over a temperature range before melting is complete. The matter of the melting behavior can be of considerable importance in preparation of a binary compound: solidification of a solution of the appropriate composition will produce a congruently melting compound, but the situation can be hampered by the production of the first-solidifying solid in the case of an incongruently melting compound. Thus, from the points of view of materials preparation and/or use of materials near the melting point, it is important to understand the forces responsible for congruency/incongruency of melting.

In a previous investigation,[16] we looked at what could be termed “ideal inclusion compounds”, i.e., those in which the interaction enthalpy was assumed to be negligible with respect to entropic considerations ($\Delta_{\text{mix}}G$ could be considered to be ideal). However, the enthalpy of the guest−host interaction could be an important factor in the thermodynamic properties of an inclusion compound. The wide variety of known inclusion compounds allows one to choose systems in which rather direct comparisons can be made. Here we present the results of investigations of the melting behavior of inclusion compounds with the same guest in two different channel compounds: *n*-hexadecane inclusion compounds with urea (a polar host lattice) and with perhydrotriphenylene (PHTP, a nonpolar host lattice). The purpose is to answer the following question: *How does the guest−host interaction affect melting congruency*? We address this question through use of experimental data for the relative Gibbs energies of the inclusion compounds and their constituents. The low vapor pressure of the *n*-hexadecane guest allows the assumption that only liquid−solid equilibria need be considered, and the systems chosen help answer what has been called[17] “an intriguing and long unsolved problem”, the different melting behaviors of PHTP and urea inclusion compounds with the same hydrocarbon guest.

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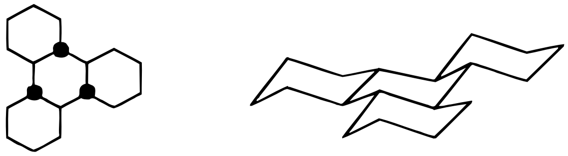

Figure 1. Two views of the structure of perhydrotriphenylene, PHTP. The material studied here is a racemic mixture of this stereoisomer and its enantiomer.

Urea inclusion compounds have been known since 1940, when Bengen reported the accidental discovery of needlelike crystals from a mixture of urea and milk due to the formation of the urea−1-octanol inclusion compound.[18] Through X-ray crystallography, Smith[19] showed that urea molecules hydrogen bond in helical ribbons, forming hexagonal channels in which guest molecules can reside. The urea repeat distance along the channel is 11.01 Å, the channel width is 5.5−5.8 Å,[20] sufficient to accommodate linear alkanes and analogous guest molecules, including alcohols, aldehydes, ketones, esters, ethers, and carboxylic acids, with little branching and (usually) at least six carbons in the chain. Urea−*n*-alkane inclusion compounds are known to melt incongruently.[21] Like many host compounds, pure urea does not have open channels; it has a closer-packed tetragonal structure.[19] Many of the interesting properties of urea, thiourea, and selenourea have been summarized recently.[22]

PHTP (see Figure 1) was first synthesized in 1963 as a model to study optically active polymers.[23] There are 10 stereoisomers of PHTP;[24] only the ATATAT (A = anti in the exocyclic bonds, T = trans in the endocyclic bonds; see Figure 1) compound (racemic mixture) was studied here. Pure PHTP has two monoclinic forms (both different from PHTP inclusion compounds): a metastable form can be obtained from rapid cooling of the melt, but over a few hours it converts to the stable form.[25] In PHTP inclusion compounds, six PHTP molecules orient themselves along a cavity, and these stack on top of other PHTP molecules, leaving channels 5.7−6.7 Å wide,[26] with a distance of about 14.3 Å between centers of adjacent channels.[27] The weaker van der Waals host binding force (compared with hydrogen bonding in urea) allows greater flexibility of the PHTP host lattice toward guests, and this allows inclusion of a wide variety of guest molecules, e.g., linear hydrocarbons, branched hydrocarbons, planar molecules, polymers, and organic acids.[17] Since the finding that PHTP could include polymers[28] and that monomer guests can be polymerized in situ by X-rays or γ-rays,[29] PHTP−polymer inclusion compounds have been studied both experimentally[30−33] and by molecular dynamic simulations.[34−39] PHTP inclusion compounds have been used to study the crystal-forming interactions of a variety of functional groups.[40] PHTP also can be used to include polar molecules to make nonlinear optical materials.[41−43] For these materials to be useful, it is especially important to understand their melting behavior. PHTP−*n*-alkane inclusion compounds are known to melt congruently.[44]

Experimental Methods

Urea−hexadecane was prepared by the addition of hexadecane (Aldrich, 99%) to powdered urea (Fisher, 98%) in hot methanol. The composition of the resulting inclusion compound has been found[45] to be 12.4 urea:$C_{16}H_{34}$; from melting enthalpy (determined by differential scanning calorimetry), we determined the urea:$C_{16}H_{34}$ ratio to be 12.25 ± 0.45.

PHTP was prepared by the hydrogenation of dodecahydrotriphenylene (DHTP),[23] which had been prepared by the Friedel−Crafts alkylation of benzene: 950 g of dichlorobutane (Aldrich, 99%) was reacted with 500 mL of benzene (Aldrich, 99%) and 500 g (in small portions) of water-free $AlCl_3$ (Aldrich, 98%) over 48 h at 20 °C. This produced a viscous reddish-brown mixture that was then stirred for 12 h. The mixture was then hydrolyzed with ice, and the fine yellow crystals of DHTP were filtered, washed with acetone, and air-dried. The capillary tube melting point of the DHTP crystals was 230 °C, compared with the literature[46] value of 232−3 °C. Hydrogenation of DHTP to PHTP was carried out at 300 °C at 200 atm of H_2 ($\sim$25 g of DHTP/run gave $\sim$50% PHTP by mass, $\sim$5 g of pure PHTP), with Pd/C catalyst (Aldrich, 10% Pd) in heptane. The product was filtered to remove the catalyst, and the solvent was pumped off, leaving behind white crystals of the PHTP−heptane inclusion compound. To recover pure PHTP, the material was recrystallized from 2-butanone (Aldrich, >99%, 500 mL for 5 g). The PHTP crystals were allowed to air-dry, and they had a melting point (capillary tube) of 126.4 °C, compared with a literature value[17] of 125.2 °C. PHTP was dissolved in methyl ethyl ketone (Aldrich, >99%, $\sim$30 mL) and $\sim$5 mL of hexadecane (Aldrich, 99%) was added directly over 7−10 days to produce needlelike crystals of PHTP−hexadecane.

Melting behavior was investigated by differential scanning calorimetry, using a Perkin-Elmer Pyris-1 DSC. Samples of approximate mass 15 mg were loaded in air and heated (or

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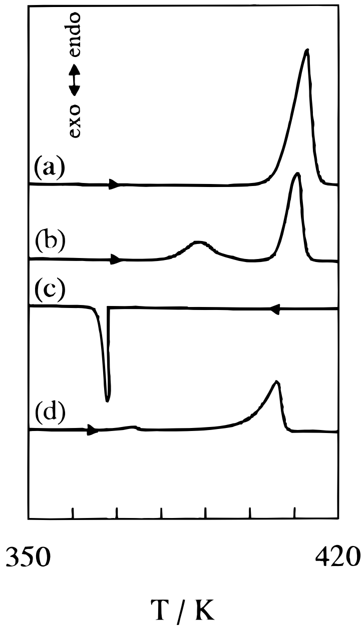

Figure 2. DSC scans of urea and urea−hexadecane. (a) Pure urea on heating at 10 K/min. (b) Urea−hexadecane on first heating to $T = 433$ K at 10 K/min, then (c) cooling to $T = 343$ K at 10 K/min, and, after waiting at $T = 343$ K for 60 min, (d) heating at 10 K/min. Note that urea−hexadecane is not recovered after melting.

Table 1. Melting Behavior of Urea and the Urea−Hexadecane Inclusion Compound, As Determined by DSC[a]

	T_m/K	$\Delta_{fus}H$/(kJ (mol of urea)$^{-1}$)
urea	406.7 ± 1.0 (405.9)[21]	14.4 ± 1.0 (14.5)[63]
urea−hexadecane	383.6 ± 1.0 (374 ± 6)[21]	7.0 ± 0.3 (7.7)[21]

[a] Uncertainties are based on triplicate runs. Literature values are given in parentheses.

cooled) at a rate of 10 K/min. Temperature and enthalpy calibrations were carried out with high-purity indium.[47]

Heat capacities for PHTP and PHTP−hexadecane were determined by adiabatic calorimetry; the apparatus is described in detail elsewhere.[48] Sample masses were 1.1157 g (PHTP) and 0.4773 g (PHTP−hexadecane), contributing ~15% and ~10% to the total heat capacity, respectively, over the temperature range 30−320 K. For urea[49] and urea−hexadecane,[50] literature values of heat capacities were available over the temperature ranges 15−310 and 12−300 K, respectively.

Characterization of Materials

DSC scans of urea and urea−hexadecane are shown in Figure 2; melting temperatures (as DSC onset temperatures, compared with literature values) and corresponding enthalpy changes are given in Table 1. Similarly, DSC scans of PHTP and PHTP−hexadecane are shown in Figures 3 and 4, respectively; melting temperatures (as DSC onset temperatures, compared with literature values) and corresponding enthalpy changes are presented in Table 2.

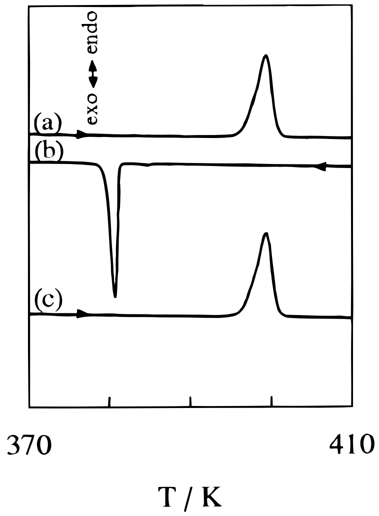

Figure 3. DSC scans of pure PHTP, on (a) first heating, (b) cooling, and (c) second heating, all at 10 K/min.

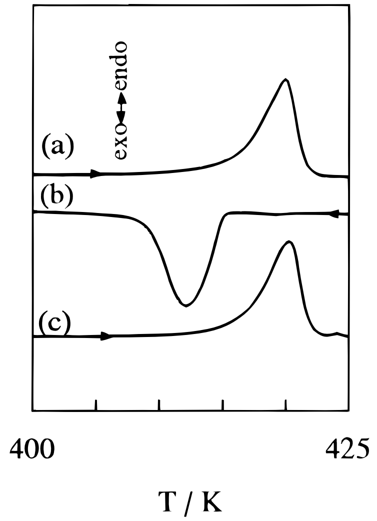

Figure 4. DSC scans of PHTP−hexadecane, on (a) first heating, (b) cooling, and (c) second heating, all at 10 K/min. Note that PHTP−hexadecane is recovered on melting.

Table 2. Melting Behavior of PHTP and the PHTP−Hexadecane Inclusion Compound, As Determined by DSC[a]

	T_m/K	$\Delta_{fus}H$/(kJ (mol PHTP)$^{-1}$)
PHTP	399.2 ± 0.5 (398.4)[17]	26.4 ± 0.5
PHTP−hexadecane	416 ± 2 (421)[64]	22.2 ± 1.0

[a] Uncertainties are based on triplicate runs. Where available, literature values are given in parentheses.

Results

Melting Behavior. From the DSC results of Figure 2, it can be seen that urea−hexadecane melts in two steps, where the higher-temperature step is melting of pure urea. This is consistent with the known incongruent melting of urea−hexadecane[21] and as shown in hot-stage microscopy results in Figure 5. A second heating DSC run on the previously melted sample (Figure 2d) shows that urea−hexadecane is not recovered under these solidification conditions, reflecting the problem of preparation of an incongruently melting compound from the melt.

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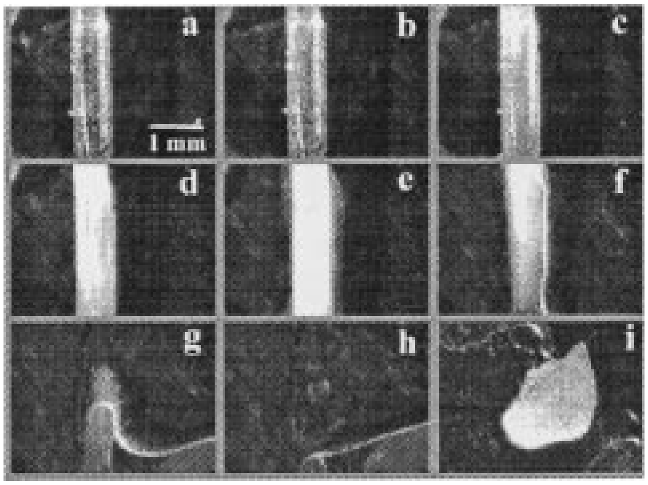

Figure 5. Hot-stage microscopy of a needle of urea–hexadecane (a) at room temperature, (b) at the onset of incongruent melting, (c)–(e) at various temperatures during which solid urea and liquid hexadecane coexist, (f) at the onset of melting of urea, (g) and (h) after melting is complete, resulting in two immiscible liquids, urea and hexadecane, and (i) after cooling, resulting in solid urea and liquid hexadecane.

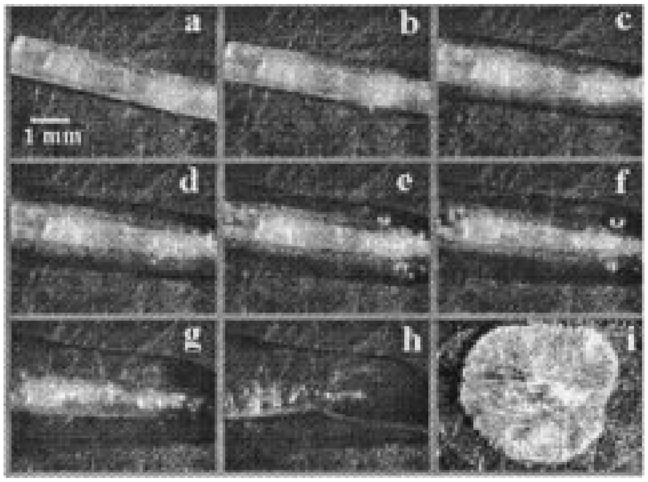

Figure 6. Hot-stage microscopy of a needle of PHTP–hexadecane, (a) at room temperature, (b) at the onset of melting, (c)–(h) during congruent melting, and (i) after cooling, resulting in needles of PHTP–hexadecane.

DSC of PHTP–hexadecane shows that it melts at a higher temperature than pure PHTP (Figure 3), so melting must be congruent, as has been observed previously for many PHTP–alkane inclusion compounds.[25,44] Heating of PHTP–hexadecane on a hot-stage microscope confirms this (Figure 6). A second heating of the previously melted PHTP–hexadecane sample (DSC scan of Figure 4c) shows that the inclusion compound is recovered on solidification.

Thermodynamic Analysis. Differential scanning calorimetric determinations of urea and urea–hexadecane from 300 K to the melting point show no unusual features, which makes smooth extrapolation of the lower-temperature data[49,50] reasonable for the thermodynamic analysis that follows.

Thermal studies of PHTP (adiabatic calorimetry[51] and DSC) show that PHTP has no solid–solid phase transitions in the temperature range 30 K to the melting point. One small thermal anomaly was observed in PHTP–hexadecane, but its temperature (T = 291 K) and its absence in DSC runs on some samples indicated that it is a eutectic due to slight excess (calculated to be 3.5 mass % on the basis of the associated enthalpy change) of n-hexadecane in the adiabatic calorimetry sample. Heat capacity data were for PHTP–hexadecane were corrected by assuming additivity with that of hexadecane.[52] The small sample masses lead to a scatter in heat capacity results of ~5% for PHTP (Figure 7) and ~10% for PHTP–hexadecane (Figure 8), with estimated accuracies of smoothed heat capacity (Table 3) within 2% and 4%, respectively.

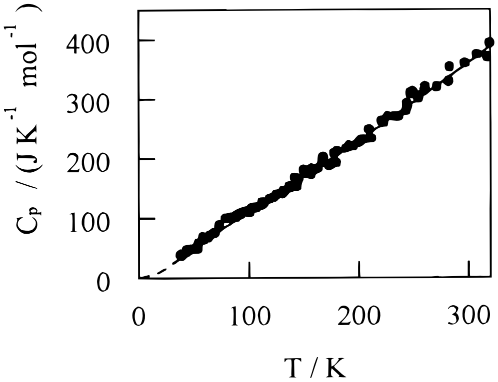

Figure 7. Heat capacity at constant pressure, C_p, for PHTP. The circles are the experimental data, and the line represents the smoothed data.

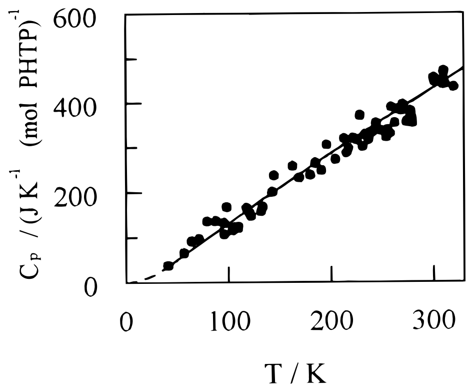

Figure 8. Heat capacity at constant pressure, C_p, for PHTP–hexadecane. The circles are the experimental data, and the line represents the smoothed data.

From the heat capacity (C_p) data for urea–hexadecane,[50] hexadecane,[52] PHTP,[51] and PHTP–hexadecane,[51] their enthalpies, H (relative to $H(T{=}0\ \text{K})$), entropies, S (relative to $S(T{=}0\ \text{K})$) and Gibbs energies, G (relative to $G(T{=}0\ \text{K})$) have been determined as follows:

$$H(T) \equiv H(T) - H(T{=}0\ \text{K}) = \int_{T=0\text{K}}^{T} C_p\, \mathrm{d}T \qquad (1)$$

$$S(T) \equiv S(T) - S(T{=}0\ \text{K}) = \int_{T=0\text{K}}^{T} \frac{C_p}{T}\, \mathrm{d}T \qquad (2)$$

$$G(T) \equiv G(T) - G(T{=}0\ \text{K}) = H(T) - TS(T) \qquad (3)$$

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[51] For raw data, see: Harnish, R. S. MSc Thesis, Dalhousie University, Halifax, Canada, 1997.

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Table 3. Thermodynamic Data for PHTP, PHTP–Hexadecane Inclusion Compound, and Its Constituent Components (PHTP + 1/9.03 Hexadecane); Extrapolated Data in Parentheses, Hexadecane Data from the Literature[52]

	C_p/(J K^{-1} (mol of PHTP)$^{-1}$)		G/(J (mol of PHTP)$^{-1}$)[a]		
T/K	PHTP	PHTP–$C_{16}H_{34}$	PHTP[b]	PHTP–$C_{16}H_{34}$[c]	PHTP[b] + 0.111 $C_{16}H_{34}$[b,52]
0	0	0	0	0	0
20	(11)	(17)	(−52)	(0)	(−56)
40	36	35	−327	−340	−372
60	61	72	−957	−1030	−1113
80	87	101	−1991	−2200	−2340
100	110	132	−3457	−3875	−4080
120	134	166	−5366	−6078	−6341
140	158	197	−7721	−8834	−9123
160	182	232	−10528	−12153	−12426
180	205	262	−13789	−16052	−16252
200	229	287	−17508	−20534	−20600
220	255	319	−21685	−25590	−25469
240	283	357	−26325	−31224	−30862
260	312	378	−31436	−37455	−36789
280	337	409	−37026	−44267	−43256
300	361	434	−43098	−51663	−50444
320	392	462	−49653	−59638	−58418
340	(417)	(499)	(−56697)	(−68190)	(−66953)
360	(450)	(529)	(−64234)	(−77330)	(−76049)
380	(477)	(555)	(−72268)	(−87057)	(−85710)
400	(503)	(583)	(−80804)	(−97369)	(−95901)
416	(524)	(605)	(−87633)	(−105619)	(−104079)

[a] Two (below ca. 50 K) or three (above ca. 50 K) figures in G can be considered to be significant. [b] G relative to $G(T{=}0$ K). [c] G relative to $G(T{=}0$ K). To make comparisons with the PHTP and hexadecane for stability discussions, subtract 6.0 kJ/(mol PHTP) (=$\Delta_f H(T{=}0$ K)).

(Note that heat capacity data have been extrapolated to $T = 0$ K by Debye analysis for a polyatomic molecular solid with nearly linear heat capacity;[11] uncertainty in G would be less than 5 J (mol PHTP)$^{-1}$, i.e., less than 0.01% at the melting point. Extrapolation to temperatures higher than the measurement temperature was by smooth polynomial fit to the high-temperature data; extrapolation leads to uncertainty of ±2% in G at the melting point.) Calculation of H, S, and G for urea has been given elsewhere.[49]

To compare the Gibbs energies of the inclusion compounds with the host and guest, a common reference point was required, and this was taken to be $G(T{=}0$ K). $\Delta_f G(T{=}0$ K), i.e. the Gibbs energy change for the formation of each inclusion compound from the solid host and solid guest at $T = 0$ K was determined from a thermodynamic cycle (host + guest at $T = 0$ K $\rightarrow$ host + guest just above the melting point $\rightarrow$ solidification of inclusion compound $\rightarrow$ cooling to $T = 0$ K), making use of the experimental heat capacities and enthalpies of fusion. (Note that $\Delta_f G(T{=}0\text{ K}) = \Delta_f H(T{=}0\text{ K})$.) On this basis, $\Delta_f G(T{=}0$ K) was determined to be −1.5 kJ (mol urea)$^{-1}$ for urea–hexadecane and −6.0 kJ (mol of PHTP)$^{-1}$ for PHTP–hexadecane.

Values of G for PHTP and PHTP–hexadecane are given at regular temperature intervals in Table 3; reference points for G are indicated in the heading. Included in the table are values of G for the inclusion compound constituents, i.e., PHTP + 1/9.03 hexadecane; *n*-hexadecane heat capacity data were from the literature.[52]

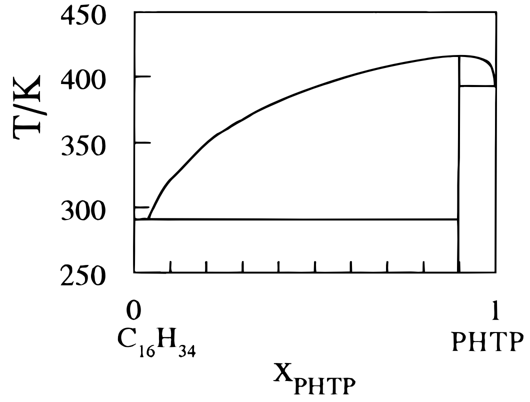

Figure 9. Calculated PHTP–*n*-hexadecane phase diagram. Note that the inclusion compound melts congruently.

Discussion

Calculated Phase Diagrams. Farina and co-workers[44,53,54] have developed a methodology to calculate binary phase diagrams, especially for inclusion compounds. Briefly, the method considers the melting point depression of each end member in the binary phase diagram and also for a binary compound, with the interaction parameter, W (the repulsive term from regular solution theory; $W = 0$ for an ideal system), assumed to be independent of temperature and composition, and the host and inclusion compound assumed to be immiscible. (The latter assumption likely is valid for the two systems studied here because the hosts and their inclusion compounds have very different structures.) It has been shown that PHTP–hexane behaves ideally,[44] and that making the interaction parameter W more positive can lead to immiscibility. Explanation of the trends associated with guests of increasing incompatibility with PHTP on the PHTP–guest binary phase diagram is one of the successes of this theory,[54] although one should be cautious in that the melting point of the guest also can vary considerably and this also can be influential (vide infra).

On the basis of the Farina method and the present thermodynamic data (Table 2), we have calculated the PHTP–hexadecane phase diagram (assuming ideality, i.e., $W = 0$); it is shown in Figure 9. On the same basis, we have calculated the urea–hexadecane phase diagram (Figure 10); the guest–host interaction would be nonideal in this system, so we have tried a range of W values; we find that $W = 18$ kJ/mol agrees best with the observed melting behavior. This value of W is in line with the finding[55] that liquid–liquid phase separation is favored for $W > 2RT$, and W is comparable to the value found for the $C_{24}F_{50}$–PHTP phase diagram.[17]

Thermodynamic Considerations. For the materials investigated here, we have the opportunity to explore Gibbs energy–composition space, with experimental data, and we use it to answer the question, *Why does PHTP–hexadecane melt congruently whereas urea–hexadecane melts incongruently*? Thermodynamic considerations of the stabilities of binary compounds relative to their components and liquid phase have been

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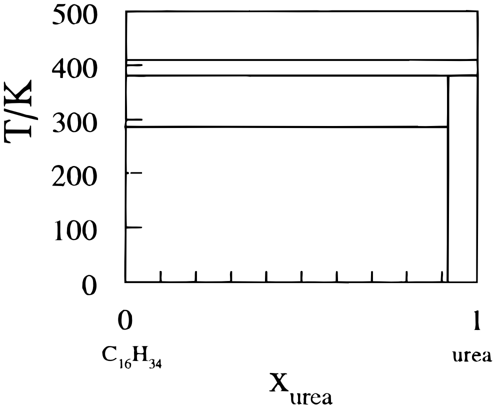

Figure 10. Calculated urea–*n*-hexadecane phase diagram. Note that the inclusion compound melts incongruently, to give solid urea and liquid hexadecane.

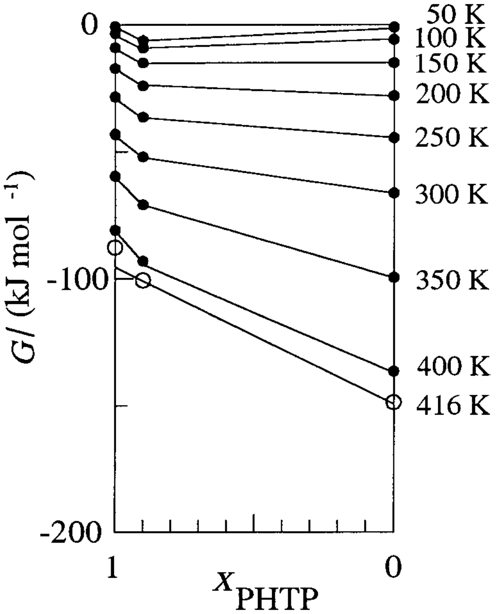

Figure 11. Gibbs energy, *G*, as a function of mole fraction of PHTP, x_{PHTP}, at different temperatures. Note: $T = 416$ K is the melting point of PHTP–hexadecane. Circles represent Gibbs energies for pure *n*-hexadecane[52] ($x_{PHTP} = 0$, liquid or solid depending on whether above or below its melting point of 291 K), the solid inclusion compound ($x_{PHTP} = 0.900$) and pure solid PHTP ($x_{PHTP} = 1$, data extrapolated above its melting point of 399 K); (●) below inclusion compound melting point; (○) at inclusion compound melting point. Lines indicate the stable phase(s) in a given region at the temperature indicated. Note that at $T = 416$ K, the melting point of the inclusion compound, *G*(PHTP), lies above the hexadecane–inclusion compound liquid line, i.e., solid PHTP is not stable, and PHTP–hexadecane melts congruently. The reference point for *G* for PHTP and hexadecane is $G = 0$ at $T = 0$ K; $\Delta_f H(T{=}0$ K) is taken into account for *G* of the inclusion compound.

given in the abstract, for example, in textbooks and monographs,[56,57] but here we shall use experimental data.

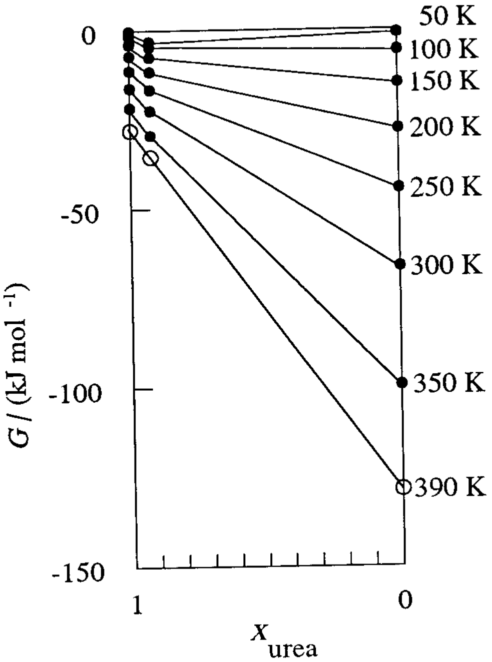

Figure 12. Gibbs energy, *G*, as a function of mole fraction of urea, x_{urea}, at different temperatures. Note: $T = 390$ K is the melting point of urea–hexadecane. Circles represent Gibbs energies for pure *n*-hexadecane[52] ($x_{urea} = 0$, liquid or solid depending on whether above or below its melting point of 291 K), the solid inclusion compound[50] ($x_{urea} = 0.925$) and pure solid urea[49] ($x_{urea} = 1$); (●) below inclusion compound melting point; (○) at inclusion compound melting point. Lines indicate the stable phase(s) in a given region at the temperature indicated. Note that at $T = 390$ K, the melting point of the inclusion compound, *G*(urea), lies on the hexadecane–inclusion compound liquid line, i.e., solid urea is stable, and urea–hexadecane melts incongruently. The reference point for *G* for urea and hexadecane is $G = 0$ at $T = 0$ K; $\Delta_f H(T{=}0$ K) is taken into account for *G* of the inclusion compound.

The Gibbs energies for the pure components and the inclusion compounds, at various temperatures, are shown in Figures 11 (PHTP–hexadecane) and 12 (urea–hexadecane); the former makes use of the present results and literature data for *n*-hexadecane[52] and the latter makes use only of literature data.[49,50,52] Two conclusions are apparent.

First, the Gibbs energy of the PHTP–hexadecane inclusion compound is less than that of the appropriate proportions of guest and host: for example, at $T = 300$ K, PHTP–hexadecane is 7.2 kJ/(mol of PHTP) lower. The lower Gibbs energy of the compound shows that it is stabilized with respect to its constituent components. On the other hand, urea–hexadecane is closer in Gibbs energy to its components (stabilized by 1.3 kJ/(mol of urea) at $T = 300$ K), showing that this inclusion compound is less stable at room temperature with respect to its components than is PHTP–hexadecane.

Second, the present analysis provides information concerning melting behavior. The most distinguishing feature of the *G*(*x*) diagrams of PHTP–hexadecane (Figure 11) and urea–hexadecane (Figure 12) relates to melting behavior in PHTP–hexadecane compared with urea–hexadecane. In both diagrams, the Gibbs energies of the inclusion compounds at temperatures below the melting point lie below a line between the host and guest lattice, indicating inclusion compound stability with respect to the host and guest, as discussed above. However, the behaviors at the melting points ($T = 416$ K for PHTP–hexadecane and $T = 390$ K for urea–hexadecane) are quite different. At the inclusion compound melting point, G_{host} falls *above* the $G_{guest} \rightarrow$

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Table 4. Factors Influencing Congruent/Incongruent Melting Behavior in Binary Compounds, Generalized as A_xB_y Where the Components Are A and B

factor	congruent melting favored	incongruent melting favored	nature of condition
$A_xB_y \rightarrow$ liq + A(s) or B(s)	$\Delta G > 0$	$\Delta G = 0$	necessary
$S(A_xB_y)$	large $S(A_xB_y)$	small $S(A_xB_y)$	influential
$S(A)$, $S(B)$	small $S(A)$ or $S(B)$	large $S(A)$ or $S(B)$	influential
A−B interaction	like−like (e.g., polar−polar)	like−unlike (e.g., polar−nonpolar)	influential
A−B enthalpy considerations	ideal solution	immiscible constituents	influential
relative melting temperatures	$T_{fus}(A_xB_y) > T_{fus}$(A or B)	$T_{fus}(A_xB_y) < T_{fus}$(A or B)	influential

$G_{\text{inclusion compound}}$ liquid line for PHTP−hexadecane (Figure 11), and *on the line* for urea−hexadecane (Figure 12).

Binary compounds can be entropically stabilized,[16,58] and although a pair of solid−solid phase transitions in urea−hexadecane (T_{trs} = 135.3 and 151.8 K, $\Delta_{trs}S^{total}$ = 1.46 R [expressed per mole of hydrocarbon guest][50]) associated with changes in motional freedom of the guest[59] probably help stabilize the inclusion compound with respect to the guest and host at temperatures below the melting point, apparently this is not sufficient to prevent incongruent melting. (That is, the stability of the solid host wins at the melting point.) The main competition is the increase in entropy (and hence more rapid lowering of G) beyond the melting of the hexadecane guest component (T_{fus} = 291.34 K); apparently this helps tip the balance in favor of stability of a solid constituent (urea), which favors incongruent melting.

For PHTP−hexadecane, the Gibbs energy of the host lattice is about 7.6 kJ/(mol of PHTP) higher than the liquidus line at the melting point of the inclusion compound (Figure 11), consistent with the finding of congruent melting. Although the difference in Gibbs energies is significant (propagation of uncertainties in C_p and extrapolation lead to ±4% in G at the melting point), it is largely attributable to the enthalpy of formation of the inclusion compound (recall that the compound is more stabilized by 6.0 kJ/(mol of PHTP) at $T = 0$ K). Therefore one could expect less stabilization in other PHTP inclusion compounds with less favorable guest−host interaction enthalpies; less stability has been observed for PHTP−4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene.[60] Even more destabilization could lead to incongruent melting behavior in other PHTP inclusion compounds, as has been observed recently.[61]

Farina and co-workers have suggested[44] that incongruent melting in urea−alkanes results from immiscibility of the liquid components, which leads to the following question: *How influential is liquid-state immiscibility in determining melting of a binary compound*? From Figures 11 and 12, the dominant factor in the form of the $G_{liquid}(x)$ function (and hence the melting behavior) is the relative Gibbs energies of the liquid components; the curvature of $G_{liquid}(x)$, which would be determined by solution ideality, i.e., miscibility, is of secondary importance, especially since $G_{liquid,host}$ and $G_{liquid,guest}$ are so different. (For PHTP, which is nearly an ideal solution, concavity in $G_{liquid}(x)$ due to $\Delta_{mix}G$ is not visible on the scale of Figure 11.) Therefore, although immiscibility of the liquids plays a role in melting products, when $G_{liquid}(x)$ has a steep slope, the dominant factor concerning congruency resides with relative Gibbs energies of the compound, its constituents and the liquid phase. This conclusion does not contradict the finding that immiscibility favors incongruent melting;[44] however, that generalization was based on models in which changes in melting points (i.e., thermodynamic stabilities) of the two components (inclusion compound and guest) were neglected, and we now have shown that this is an important consideration. Nevertheless, miscibility is a reflection of guest−host interactions, and it is clear that an unfavorable value of $\Delta_fH(T{=}0\ \text{K})$, which would lead to guest−host immiscibility, could also be responsible for incongruent melting.

Conclusions

On the basis of this comparative study of inclusion compounds composed of two different host materials with the same guest species, we conclude that melting behavior of a binary compound can be influenced by a number of factors, as summarized in Table 4. The most important factor is the relative stability of the compound compared with its constituents. (Similarly, it has been concluded that lattice stability influences melting behavior in binary alloys.[62]) Stability, and hence melting behavior, can be influenced by entropic factors in the binary compound or in its components. Enthalpic interactions also can be influential, although, like entropy, enthalpy alone is not the determinant of melting behavior. However, enthalpy can influence the formation of the compound (perhaps even to the point of stabilization or destabilization with respect to the components) and the nature of the liquid formed after melting.

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