Solid–Liquid Equilibria in the Systems Thianthrene + Phenanthrene, Salicylic Acid + Phenanthrene, and 3-Hydroxybenzoic Acid + Phenanthrene

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Solid–liquid equilibria (SLE) phase diagrams have been determined for the binary systems of thianthrene, salicylic acid, and 3-hydroxybenzoic acid with phenanthrene. Compounds of this type are commonly used as model compounds for demonstrating the capabilities of supercritical fluid extraction (SFE), yet little is known about their thermodynamic properties. SLE provides a simple method for qualitative examination of some basic properties in these systems.

Introduction

SLE phase diagrams provide valuable information with regard to the nature and type of interactions occurring in the solid and liquid phases and provide a route whereby various thermodynamic properties can be interrelated (*1*). In this paper we report the results of a study to measure the SLE for three binary systems (thianthrene, salicylic acid, and 3-hydroxybenzoic acid with phenanthrene) and demonstrate a method for estimating thermodynamic properties from these data.

The impetus for the present work is in the development of mathematical models for phase equilibria of representative compounds in supercritical fluid extraction (SFE). Phenanthrene and thianthrene (a sulfur heterocycle of anthracene) are commonly used as model compounds in coal-related studies. The benzoic acids have importance both in terms of environmental cleanup and specialty separations, in addition to having functional groups that could exhibit interactions even in the solid phase. However, even though the solubilities of these compounds have been determined in supercritical fluids (*2–5*), many other physical properties are not known.

Corresponding-states theory is a most powerful tool for engineers forced to estimate thermodynamic properties for mixtures where no data or only limited data exist. Critical properties are normally used as reducing parameters, but for many very heavy compounds these either are not known or are inaccessible experimentally. Although many estimation techniques exist (*6*), their use has three drawbacks: First, there are errors in these methods, especially for critical pressures and volumes. Next, for complex molecules, many methods are completely inapplicable. But finally, and perhaps most important, the critical properties themselves are of no importance; what is really needed is a convenient reducing parameter. Many other reducing parameters have been used successfully, as for example the Lennard-Jones force constants σ and ϵ for small molecules (*7*). In working with very heavy molecules, a measure for intermolecular force that we have found useful previously (*8*) is the heat of sublimation, often available experimentally for solids by the Clapeyron equation from vapor pressure data.

The heat of vaporization has benefits also as a reducing parameter in systems combining heavy and light components and could be inferred from solid vapor pressure data along with the heat of fusion. It is easier to determine properties around the triple point or melting point, especially the enthalpies of phase changes that are relatively insensitive to temperature in this region. The vapor pressures of several very nonvolatile solids have recently been measured accurately as another facet of this work (*9*, *10*). These data coupled with a heat of fusion measurement could provide good estimates of heats of vaporization, which may be inaccessible experimentally.

We suggest a reasonably accessible measure of intermolecular forces might be given by the heat of fusion. For many heavy compounds the melting point may be the only physical property known, and a thermodynamic property would be very useful for examining solution behavior in SFE. A fairly good measure of the heat of fusion can be obtained from relatively straightforward freezing point measurements on mixtures, or mixture solid–liquid equilibria (SLE), by making some reasonable assumptions about the solution behavior. In this paper we describe such an application and show examples of three such measurements.

Experimental Section

All the chemicals used in this investigation were obtained from Aldrich Chemical Co. with a purity of 99.5%. The purity of the chemicals was increased further by recrystallization and verified by measuring the pure-component melting temperature.

The freezing point apparatus used in this investigation is similar to the apparatus used by Ott and co-workers (*11*). Essentially it consists of a 20-mm-o.d. × 30-cm-length Pyrex tube sealed inside a 38-mm-o.d. × 29-cm-length tube that was connected to a Sargent-Welch DuoSeal 1405 vacuum pump. A Teflon micrometering valve was also connected to the outer tube to allow introduction of varying amounts of nitrogen into the jacket to act as a heat-transfer medium, as desired. The vacuum pump was isolated from the jacket by means of a liquid nitrogen trap. The pressure in the jacket was monitored with a Varian 531 Thermocouple Gauge.

The temperature of the sample was monitored with an Omega RTD probe inside a stainless steel tube that went down through the center of the inner Pyrex tube. The stainless steel temperature probe was sealed into a ground-glass Pyrex cap at the top of the apparatus with use of a silicon sealant. The RTD probe was connected to both an Omega digital thermometer and a chart recorder to record time–temperature curves. The accuracy of the freezing points reported in this paper are estimated to be ±0.5 °C.

The temperatures of the samples for this investigation were varied by wrapping the freezing apparatus in heating tape connected to a Variac to control the heat input. In these

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Table I. Comparison with Literature Data for CCl_4 + Furan

mole fraction of CCl_4	T_m, K measured	T_m, K literature[a]
0.18	172	173.8
0.28	179	179.7
0.91	236	237.1

[a] Reference 12.

experiments the annular region was evacuated to the lowest pressure attainable by the vacuum pump (approximately 10^{-2}–10^{-3} Torr). The samples were heated above their melting points, and time–temperature cooling curves were measured.

Stirring was accomplished with a magnetically driven chromel stirring rod that moved vertically in the freezing tube. The top of the stirring rod extends into a 9-mm-i.d. × 10-cm-length Pyrex tube connected to the cap at the top of the apparatus. The top of this tube was sealed with a septum cap to prevent sample contamination. An 8-mm-o.d. × 3-cm-length piece of iron was connected to the top of the stirring rod. Outside this tube, a pair of magnets, oscillating vertically, were used to move the stirring rod.

The composition of the samples was changed by adding a known amount of solid sample through a port in the cap connected to a line flushed with nitrogen. Sample additions were introduced into the freezing chamber by first placing them in the nitrogen flush line for approximately 1 h and then opening the line to the freezing chamber and letting the sample fall into the chamber. A nitrogen blanket was maintained over the sample in the freezing chamber throughout the experiment to minimize sample evaporation and moisture contamination.

The liquidus curve was determined by charging a known weight of one of the pure components into the freezing chamber and measuring its freezing temperature. A known weight of the second component was added to the sample in the chamber, and the freezing point was again measured. This process of incremental additions was continued until a 50–50 composition was obtained. The process was then repeated by starting with the other pure component.

The apparatus and procedure were verified by measuring the melting points at selected compositions for the carbon tetrachloride + furan and carbon tetrachloride + pyridine systems for which accurate liquidus curves have been determined (*12*). As seen in Table I, all the measurements were within 1.1% of the reported temperatures.

Development

If some well-defined assumptions are made about the nature of the solution in the liquid state, straightforward thermodynamic relations allow the extraction of physical property data from SLE curves. We will not consider the possibility of solid-phase miscibility but instead assume that both solids in equilibrium with the liquid solution are pure. Following strict phase equilibria thermodynamics (*13*)

$$\ln (x_i \gamma_i) = \ln \left(\frac{f_i(\text{pure solid})}{f_i^\circ} \right) \quad (1)$$

where f_i° is the standard-state fugacity of component i, which is usually chosen as the pure subcooled liquid, denoted f_i^L. The ratio of fugacities is found from a straightforward thermodynamic cycle and leads to the familiar expression

$$\ln \frac{f^L}{f^S} = \frac{\Delta h_f}{RT_t}\left(\frac{T_t}{T} - 1\right) - \frac{\Delta C_p}{R}\left(\frac{T_t}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_t}{T} \quad (2)$$

The last two terms in eq 2 largely cancel each other, and their combined contribution is negligible compared to the first term.

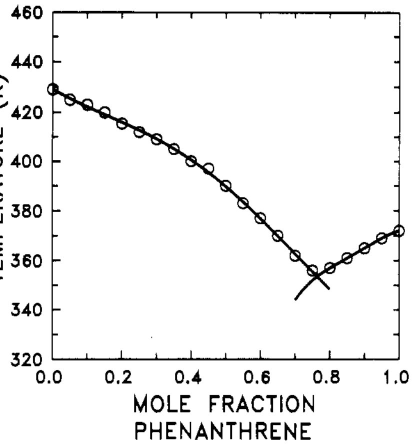

Figure 1. Experimental freezing point data for thianthrene–phenanthrene. Curves are least-squares fits.

In addition, the melting temperature (T_m) may be substituted for the triple point temperature (T_t) without introducing much error. This leads to a useful equation for estimating the heat of fusion of a compound from its activity coefficient in a solution of known composition:

$$\ln (x_i \gamma_i) = -\frac{\Delta h_f}{RT_m}\left(\frac{T_m}{T} - 1\right) \quad (3)$$

If the chemical nature of the two components in solution are similar, we would expect the solution to be nearly ideal and γ to be near unity. However, even in cases where slightly dissimilar molecules are mixed, the activity coefficient can be determined from any one of a number of solution models. We chose regular solution theory for this purpose (eq 4), substituting

$$\ln \gamma_2 = \frac{V_2 \Phi_1 (\delta_2 - \delta_1)^2}{RT} \quad (4)$$

the expression for γ into eq 3. A least-squares fit of the SLE curve using this method generates a value for the pure-component heat of fusion.

Note that the most ambiguous term in this analysis is the activity coefficient in the liquid solution. The assumption of pure-solid phases in equilibrium with the liquid (i.e. very steep phase boundaries at the pure-component ends) is a good assumption and can be relaxed without having a large effect on the calculated phase equilibria. By far the biggest assumption is that the liquid solution can be described by regular solution theory. These compounds are polar, and the benzoic acids have hydrogen-bonding capabilities. However, there is no generally accepted method for calculating the activity coefficients of compounds such as these, and we are taking advantage of the recognized ability of regular solution theory to give an estimate for γ that is not unreasonable. Therefore, any deviations and errors in the calculated heats of fusion should be attributed directly to the inability to calculate the liquid-phase activity coefficients.

Finally, it should be recognized that this technique is not as good as a direct measurement of the heat of fusion (e.g. by differential scanning calorimetry) but can be useful when only SLE data are available.

Results

Solid–liquid equilibria data were obtained over the entire composition range for the three binary systems thianthrene, salicylic acid, and 3-hydroxybenzoic acid with phenanthrene. The freezing point data are compiled in Table II, and the phase diagrams for the systems are shown in Figures 1–3. The solid

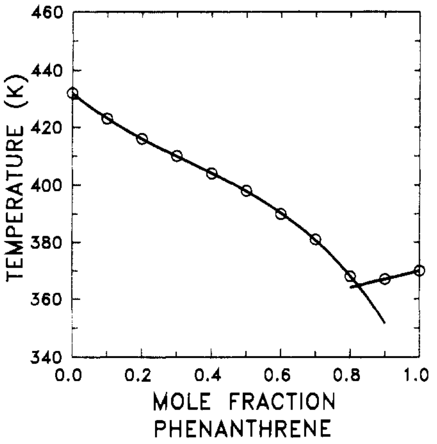

Figure 2. Experimental freezing point data for salicylic acid-phenanthrene. Curves are least-squares fits.

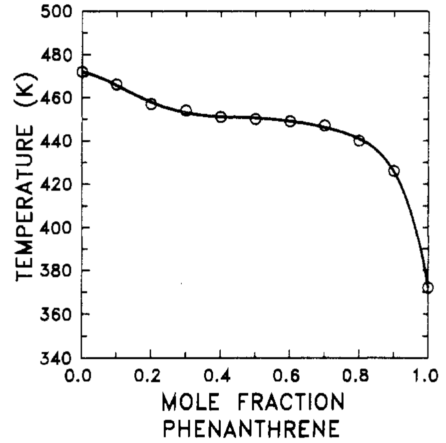

Figure 3. Experimental freezing point data for 3-hydroxybenzoic acid-phenanthrene. Curves are least-squares fits.

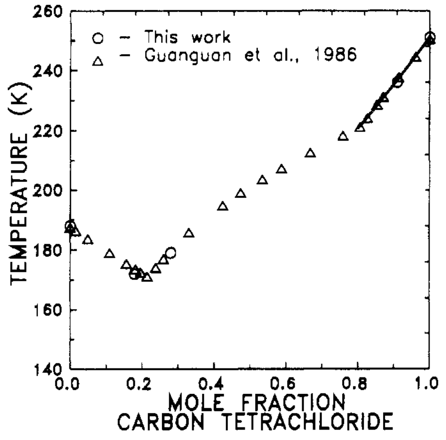

Figure 4. Determination of heat of fusion from SLE data for the system CCl_4-furan.

curves in the figures were determined from the least-squares fit of the data points. The thianthrene + phenanthrene and salicylic acid + phenanthrene exhibit simple eutectic behavior while the 3-hydroxybenzoic acid + phenanthrene system exhibits behavior indicative of either compound formation or a solid solution.

Table II. Equilibrium Temperatures for SLE Phase Changes in Three Systems

mole fraction of phenanthrene	freezing point, K	mole fraction of phenanthrene	freezing point, K
Thianthrene + Phenanthrene			
0.00	429	0.55	383
0.05	425	0.60	377
0.10	423	0.65	370
0.15	420	0.70	362
0.20	416	0.75	356
0.25	412	0.80	357
0.30	409	0.85	361
0.35	405	0.90	365
0.40	400	0.95	369
0.45	397	1.00	372
0.50	390		
Salicylic Acid + Phenanthrene			
0.00	432	0.60	390
0.10	423	0.70	381
0.20	416	0.80	368
0.30	410	0.90	367
0.40	404	1.00	370
0.50	398		
3-Hydroxybenzoic Acid + Phenanthrene			
0.00	472	0.60	449
0.10	466	0.70	447
0.20	457	0.80	440
0.30	454	0.90	426
0.40	451	1.00	372
0.50	450		

Table III. Heats of Fusion and Properties of the Compounds Used

compound	v_L, cm^3/mol	δ_L, $(J/cm^3)^{1/2}$	Δh_f, J/mol	
			regressed	literature
phenanthrene	168	20.3	17400	18600[a] 16600[b] 16700[c]
thianthrene	195		23200	25440[d]
salicylic acid	122		14200	
3-hydroxybenzoic acid	121		55400	
carbon tetrachloride	96.5	17.6	3120	3280[a]

[a] Reference 14. [b] Reference 16. [c] Reference 17. [d] Reference 18.

A demonstration of the technique for extracting Δh_f from SLE curves is shown in Figure 4, where our data are compared to those of Guanquan and co-workers (*12*) for the system carbon tetrachloride + furan. The least-squares fit included all points above 0.82 mole fraction of CCl_4 and is shown as the solid line in this figure. The value of Δh_f obtained for CCl_4 is 3120 J/mol, which is within 5% of the literature value of 3280 J/mol (*14*).

The calculated heats of fusion are given in Table III, along with the literature values when available. We show the calculated value for phenanthrene from the phenanthrene + thianthrene system to be in excellent agreement with the literature values, which themselves are relatively disparate. The uncertainty in the freezing point measurement results in an uncertainty in the regressed Δh_f of approximately 10%. The phenanthrene heat of fusion could not be calculated from the benzoic acid systems due to the location of the eutectic point and the lack of data near the pure phenanthrene end of the diagram. The regressed value for thianthrene is in good agreement (within 10%) with a recently reported experimental value.

In the hydroxybenzoic acid (HBA) systems, one would expect the heat of fusion to increase as 2-HBA < 3-HBA < 4-HBA based on melting points and solid-phase packing. The regressed value for 2-HBA is much less than the literature value for 4-HBA of 30 900 J/mol (*15*), but the 3-HBA value does not fall between these two. Indeed, the phase diagram for the 3-HBA system is consistent with nonideal behavior in the liquid phase. Therefore, these values may be less reliable due to the possibility of compound formation and liquid-phase nonideality in these systems, but the data are not sensitive enough to draw any conclusions.

Conclusions

The SLE phase diagrams have been measured for three binary systems of heavy aromatics. These data have been used in a novel method for generating previously unknown heat of fusion data. The method can give excellent estimates for compounds forming relatively ideal solutions but is less reliable when used for systems exhibiting complex phase behavior. The experiment is relatively simple and straightforward and provides an easy evaluation of properties for unusual or difficult compounds.

Acknowledgment

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Registry No. Thianthrene, 92-85-3; salicylic acid, 69-72-7; 3-hydroxybenzoic acid, 99-06-9; phenanthrene, 85-01-8.

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Liquid–Liquid Phase Equilibria in the Methanol + 2,2,4-Trimethylpentane and Methanol + Methylcyclopentane Systems at Pressures from 5 to 120 MPa

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Liquid–liquid phase equilibria of the mixtures methanol + 2,2,4-trimethylpentane (isooctane) and methanol + methylcyclopentane were investigated by using the synthetic method. The phase coexistence curves were determined over a pressure range from 5 to 120 MPa and a methanol mole fraction range from approximatively 0.25 to 0.85. Empirical equations were used to correlate the experimental data and to obtain the critical lines.

Introduction

The thermodynamic properties of mixtures of alcohols with hydrocarbons are of considerable theoretical interest, because they reflect effects of hydrogen bonds in a nonpolar medium. Such mixtures usually show large deviations from ideality, and hence positive azeotropy or liquid–liquid phase separations are often observed.

Phase equilibrium data for the liquid–liquid phase splitting at elevated pressures have been reported for methanol + normal alkane mixtures, as well as for ethanol + normal alkane mixtures, with the alkane carbon number ranging from 2 to 10 (*1–4*). Here, phase equilibrium data are presented for mixtures of methanol with two branched hydrocarbons in order to show the influence of molecular shape on phase behavior.

Experimental Section

The measurements were performed in a high-pressure vessel equipped with sapphire windows, as described by Liphard and Schneider (*5*), but with some modifications concerning pressure transmission, temperature regulation, and cell sealing (*6–8*). The pressure vessel was made of nonmagnetic material (Nimonic 90) in order to permit mixing with a magnetic stirrer. The vessel was filled with mixtures of known composition in the homogeneous state; then demixing was brought about by cooling at a fixed rate at constant pressure. The temperature at which the phase separation started was recorded.

The pressure was generated with a screw press and transmitted to the cell by a moving O-ring-sealed piston. Two Heise gauges, calibrated against a dead-weight gauge, were connected to the screw press. The pressure readings are estimated to be accurate to ±0.1 MPa in the range 5–80 MPa and to ±0.5 MPa above 80 MPa.

Temperatures were measured with a chromel/alumel thermocouple. Calibration of this thermocouple showed that temperature readings were accurate to ±0.03 K. The values of demixing temperatures, however, depend on the reliability of the visual detection of the phase splitting. Because the detection of a very small amount of a new phase is difficult, the accuracy of demixing temperatures is estimated to be ±0.1 K near a

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