

Binary Solid–Liquid Phase Diagrams of Selected Organic Compounds

A Complete Listing of 15 Binary Phase Diagrams

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The investigation of multicomponent solid–liquid equilibria is of considerable importance in chemistry and materials science. Binary solid–liquid phase diagrams, as the simplest representatives of these equilibria, are determined in most undergraduate physical chemistry laboratory courses because they provide a variety of thermodynamic quantities and information about the system (1–4). A large educational benefit results from the thermal analysis using even basic instrumentation. However, the almost infinite number of combinations of substances is in practice limited by several factors—for example, the temperature range of melting points or the toxicity or price of the chemicals. The main purpose of our work was to find a useful but limited number of compounds that can be combined to give a large number of binary systems suitable to work in an undergraduate laboratory course.

This work presents the results of a laboratory project in which a set of six substances were combined to yield a total of 15 binary phase diagrams. The six compounds are biphenyl, durene, diphenylmethane, naphthalene, phenanthrene, and triphenylmethane. These substances are stable and without any special functional groups, easily accessible, and inexpensive. Their melting points vary between 20 and 100 °C, which allows easy melting and freezing.

Further, an experimental setup especially created for the investigation of solid–liquid phase transitions is presented. This apparatus has been successfully used for many years

in our undergraduate physical chemistry laboratory course and has provided us with results of reasonable accuracy and reproducibility.

Some of the investigated phase diagrams are mentioned in different (mainly older) publications (5–11); some are, as far as we know, presented for the first time in this article.

Solid–Liquid Phase Equilibrium

The theoretical background for solid–liquid binary phase diagrams with no solid solubilities is quite simple. A system with one or more compounds A_i in two phases (s) and (l) that are in mutual contact is in thermodynamic equilibrium if the chemical potentials μ_i are the same in both phases:

$$\mu_i(s)(p, T) = \mu_i(l)(p, T, x_i(l)) \quad (1)$$

In the following, we consider the compounds to be completely insoluble in the solid phase

$$\mu_i(s)(p, T) = \mu_i^*(s)(p, T) \quad (2)$$

where $\mu_i^*(s)(p, T)$ is the chemical potential of the pure solid compound A_i at pressure p and temperature T . Complete miscibility in the liquid phase leads to

$$\mu_i(l)(p, T, x_i(l)) = \mu_i^*(l)(p, T) + RT \ln(f_i(l)x_i(l)) \quad (3)$$

where $\mu_i^*(l)(p, T)$ represents the chemical potential of the pure liquid compound A_i . While the activity coefficients $f_i(l)(p, T, x_i(l))$ in real systems depend on the composition of the liquid phase, in systems exhibiting nearly ideal behavior $f_i(l) \approx 1$, which, as a result of the experimental findings, can be considered fulfilled in the following. The temperature T at which the two coexisting phases are in equilibrium at constant pressure is then related to the mole fraction $x_i(l)$ of the liquid melt by

$$T = \left(\frac{1}{T_i^*} - \frac{R}{\Delta_m H_i^*} \ln x_i(l) \right)^{-1} \quad (4)$$

where $\Delta_m H_i^* = h_i(l) - h_i(s)$ is the molar heat of fusion and T_i^* is the melting point of the pure substance A_i . In deriving eq 4, $\Delta_m H_i^*$ is considered to be constant in the temperature range investigated. The coexistence curve between the liquid mixture and the pure solid A_i in the $(T, x_i(l))$ diagram extends from the pure substance to the eutectic composition; that is, $1 \leq x_i(l) \leq x_{i,E}(l)$ for $i = \{1, 2\}$.

The eutectic point $(x_{i,E}(l), T_E)$ in an ideal binary system (where $x_1(l) + x_2(l) = 1$) with given quantities T_i^* and $\Delta_m H_i^*$ can be obtained by numerical analysis (e.g. using Maple or Mathematica) or by a simple iterative approximation (Fig. 1).

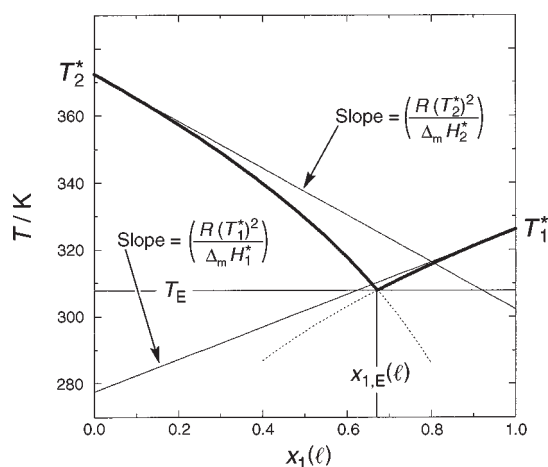


Figure 1. Calculated liquidus curves (bold lines) in an ideal binary solid–liquid phase diagram assuming no solid solubility. The two curves (dotted lines) described by eq 4 intersect at the eutectic point at $x_{1,E}(l)$. The light solid straight lines show the asymptotic freezing point depression near the pure components. This diagram represents the binary system *p*-dichlorobenzene (1)–phenanthrene (2).

Table 1. Properties of Compounds Used in This Work

Compound A_i	Molecular Mass $M_i/(\text{g mol}^{-1})$	Melting Point ^a T_i^*/K	Enthalpy of Fusion ^a $\Delta_m H_i^*/$ (kJ mol^{-1})	Cryoscopic Constant $R(T_i^*)^2/$ $\Delta_m H_i^*/\text{K}$
Biphenyl	154.21	342.1	18.57	52.4
Durene	134.22	352.4	21.0	49.2
Naphthalene	128.17	353.4	19.01	54.6
Phenanthrene	178.23	372.4	16.46	70.1
Diphenylmethane	168.24	298.5	18.57	39.9
Triphenylmethane	244.34	365.5	21.5	51.7

^aSelected values (12, 13).

The two liquidus curves described by eq 4 cross at the eutectic composition when $T(x_1(\ell)) = T(x_2(\ell))$. Table 2 lists eutectic compositions and temperatures that have been calculated for our binary systems using the data of the pure components as given in Table 1. The cryoscopic constant $R(T_i^*)^2/\Delta_m H_i^*$ is the slope of the liquidus curve $T(x_i(\ell))$ at $x_i(\ell) = 1$.

Experimental Method

Apparatus

Phase transition temperatures of mixtures with pre-defined compositions were obtained from cooling curves measured with the apparatus shown in Figure 2. The apparatus consisted of a home-built mechanical stirrer, a 0.5-L stainless steel Dewar containing an appropriate cooling liquid, and a sample compartment, attached to a clamp-mounted cell holder with a polyester screw cap for quick assembly. All parts with contact to the sample were made from glass or stainless steel. The sample cell was thermally shielded from the environment by an outer wide glassy isolation tube, thereby decreasing the cooling rate of the molten sample. The mount contained two narrow tubes, one guiding a stirring wire that moved up and down by means of a stirring device (small servo motor with gearing) to mix the melt thoroughly and to avoid supercooling of the melt. One junction of a K-type thermocouple entered through the other pipe down into the sample.

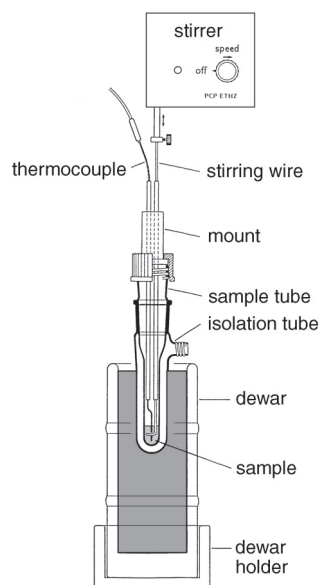


Figure 2. Schematic drawing of experimental assembly.

The reference junction was held in an ice–water mixture in an external Dewar. The thermocouple voltage (ca. $40 \mu\text{V K}^{-1}$) was measured and plotted as thermograms with a W+W 600 strip-chart recorder while the sample cooled and solidified.

Procedure

The solid samples were liquefied by heating the sample tube (with the isolation tube removed) with a hair dryer. Regular cooling of the probe could be achieved by immersing the sample cell in an ice bath with the aid of a laboratory jack supporting the bath. Applying vacuum isolation between the sample tube and the outer tube was not necessary but could be used in cases where a lower cooling rate was appropriate. A sample mass of typically 1–3 g was enough for a run. Therefore, a top-loading balance with a readability of ± 0.01 g was convenient to weigh the components directly into the sample tube with sufficient precision.

Table 2. Compositions and Temperatures of All 15 Eutectic Binary Systems

	Durene		Triphenylmethane		Diphenylmethane		Biphenyl		Phenanthrene	
	$x_{1,E}(\ell)$	$T_E/^\circ\text{C}$	$x_{1,E}(\ell)$	$T_E/^\circ\text{C}$	$x_{1,E}(\ell)$	$T_E/^\circ\text{C}$	$x_{1,E}(\ell)$	$T_E/^\circ\text{C}$	$x_{1,E}(\ell)$	$T_E/^\circ\text{C}$
Naphthalene	0.49	47.7	0.46	52.4	0.66^a	12.8^a	0.54^b	41.7^b	0.47^c	48.6^c
	0.49	47.2	0.42	52.6	0.77	15.2	0.56	40.8	0.45	50.5
Phenanthrene	0.54	55.0	0.47	56.3	0.82	16.5	0.61	54.3		
	0.54	51.5	0.48	58.2	0.78	15.9	0.60	44.3		
Biphenyl	0.42	44.8	0.40	43.8	0.61	10.2				
	0.43	42.0	0.36	46.7	0.72	12.9				
Diphenylmethane	0.20	16.6	0.20	13.7						
	0.21	16.2	0.17	18.3						
Triphenylmethane	0.55	55.2								
	0.57	53.5								

NOTE: Values set in boldface type were obtained from experimental data; other values were calculated using data from Table 1. Components in the column headings are assigned the index 1.

^a0.74; 15.4 °C (10).

^b0.555; 39.4 °C (9).

^c0.45; 48.0 °C (10) and 0.46; 47.5 °C (11).

Transition temperatures (freezing/melting) of eutectic and other mixtures were determined as break and arrest temperatures in the cooling curves, as described in standard laboratory textbooks (1–3) and shown elsewhere in this *Journal* (6, 14).

Chemicals

Biphenyl, diphenylmethane, naphthalene, phenanthrene, and triphenylmethane were purchased from Fluka in purum grade quality and used without further purification; durene was purchased from Fluka in puriss. grade and used as received.

Hazards

The polyaromatics used in these experiments are known to be toxic or irritant. It is strongly recommended that the

most recent material safety data sheets (MSDSs) and the risk and safety phrases (RS phrases) of all compounds be consulted before handling them. Contamination of skin and eyes and inhalation of dust particles must be avoided. Students should therefore wear protective gloves and preferably place the apparatus in a hood. We used an essentially closed sample compartment (Fig. 2) to minimize the release of gaseous probe material into the laboratory environment.

Experimental Results

The solid–liquid phase diagrams of all 15 binary systems are presented in Figure 3. Experimental points are drawn with error bars that result from estimated uncertainties of the determined break and arrest temperatures in the thermograms.

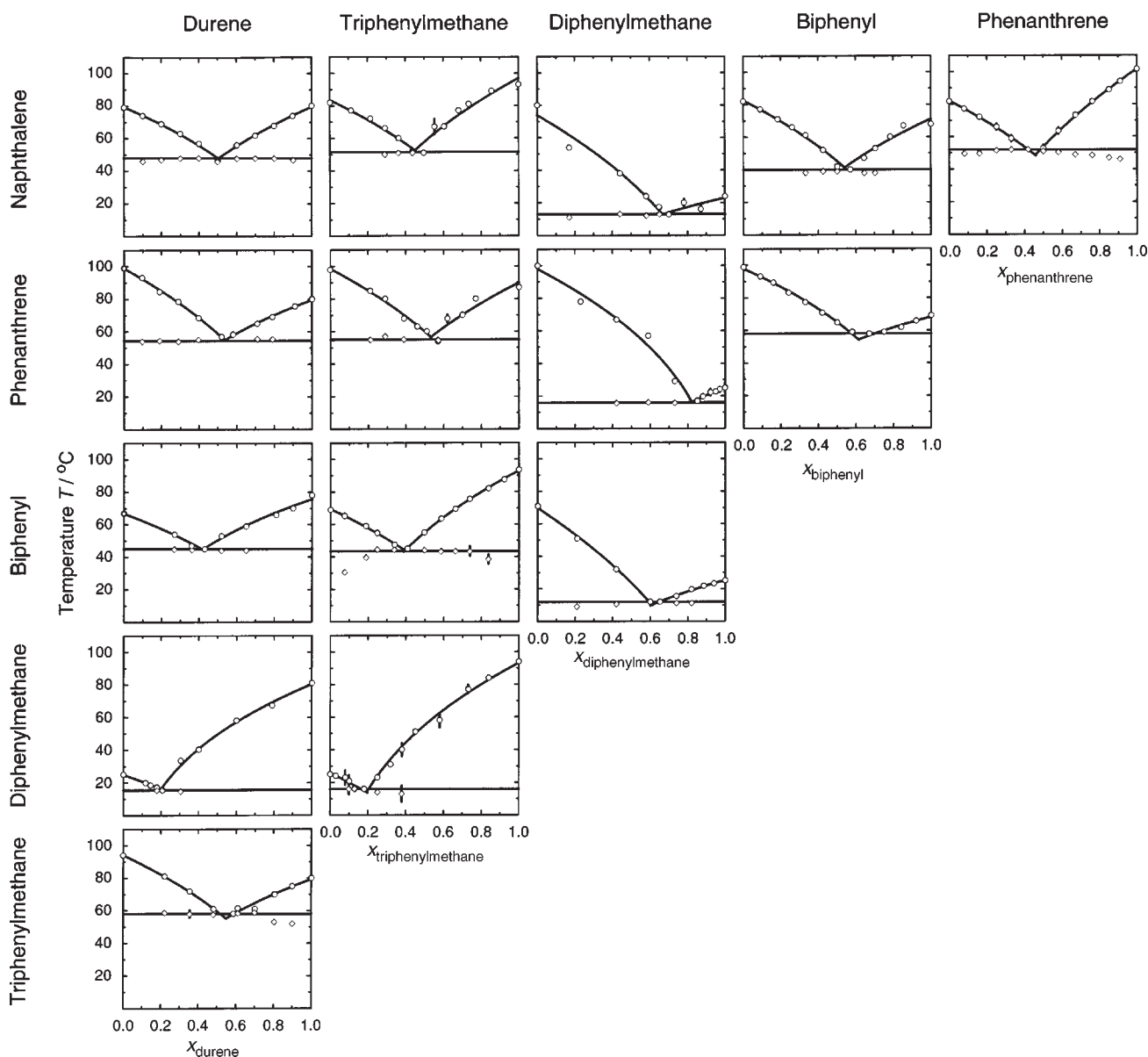


Figure 3. Experimental phase diagrams of all 15 binary systems. Break and arrest temperatures obtained from thermograms are shown with open circles and diamonds, respectively. Liquidus curves result from least-squares fits of eq 4 to the experimental data. Horizontal lines indicate the maximum arrest temperatures corresponding to the extrapolated melting temperature of the eutectic.

The liquidus curves were calculated by fitting eq 4 to the experimental data using a nonlinear least-squares procedure (15) with unknown parameters $\Delta_m H_i^*$ and T_i^* . Alternatively, linear regression can be applied to the data after adequate transformation. From the two branches, eutectic compositions and melting temperatures were calculated, giving the data in Table 2.

Our results agree to within a few percent with predicted values on the basis of ideal behavior (that is, assuming temperature-independent enthalpies of fusion and negligible solid solubility). Each system showed a simple phase diagram with clear freezing-point depression and one single eutectic point. All phase transition temperatures lay well within the small range of 0 to 100 °C, which means that the use of a water bath would be a convenient way to melt the samples, as was recommended recently in this *Journal* (6).

The largest deviations between measured and calculated eutectic data were observed in systems involving diphenylmethane (see Table 2), although their phase diagrams were still reasonable (Fig. 3, column 3). The low melting point of diphenylmethane (25.3 °C) and its mixtures facilitates supercooling effects. A 1:3 sodium chloride–ice freezing mixture (–17 °C) was used in these cases.

Conclusions

This work presents a systematic investigation of solid–liquid equilibria of 15 binary systems from the combination of only 6 selected aromatic hydrocarbons.¹ These compounds are readily available and inexpensive, they melt in a convenient temperature range, and need no further purification. For undergraduate physical chemistry laboratory courses, this material provides a variety of suitable systems illustrating the concepts of heterogeneous equilibrium. We believe that students will benefit from the qualitative behavior and quantitative data resulting from these experiments.

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Note

1. Further experiments have shown that our set of compounds can be extended by, for example, the aromatic hydrocarbons fluorene and *trans*-stilbene, which both give eutectics with compounds described in the article.

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