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Solid−Liquid Equilibria for 3-Aminophenol + 2-Aminophenol, 4-(Acetylamino)toluene + 2-(Acetylamino)toluene, and 3,4,5-Trimethoxybenzoic Acid + 2,4,5-Trimethoxybenzoic Acid

Chih-Yung Huang,[†] Muoi Tang,[†] and Yan-Ping Chen*,[‡]

Department of Chemical Engineering, Chinese Culture University, and Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

Solid−liquid equilibria for three isomeric binary mixtures of 3-aminophenol (1) + 2-aminophenol (2) (eutectic temperature T_E = 376.5 K, eutectic composition x_{1E} = 0.86), 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) (T_E = 357.2 K, x_{1E} = 0.30), and 3,4,5-trimethoxybenzoic acid (1) + 2,4,5-trimethoxybenzoic acid (2) (T_E = 395.8 K, x_{1E} = 0.33) were measured using differential scanning calorimetry (DSC). Simple eutectic behaviors for these systems were observed. The experimental results were correlated using the Wilson activity coefficient model. The eutectic compositions were also determined using Gray's model and the fractional transformation method.

Introduction

On purifying the isomeric compounds where traditional methods are inapplicable, solid−liquid separation may suggest a feasible solution. Solid−liquid equilibrium (SLE) data are thus important to such process design. SLE is conventionally determined by a cooling curve or visual measurement.[1] An alternative approach is the application of differential scanning calorimetry (DSC) where many systems of metal, polymer, and organic compounds were reported.[2,3] The DSC method measures the heat effect during the phase transformation, and the phase boundaries are evaluated.[4] Several mathematical models for DSC were presented in the literature.[3,5] Using these models and the experimentally measured SLE data, the eutectic-point temperature and composition are more accurately determined than those from traditional methods.

In this study, SLE data for three isomeric organic systems of 3-aminophenol (C_6H_7NO) + 2-aminophenol, 4-(acetylamino)toluene ($C_9H_{11}NO$) + 2-(acetylamino)toluene, and 3,4,5-trimethoxybenzoic acid ($C_{10}H_{12}O_5$) + 2,4,5-trimethoxybenzoic acid were measured using DSC. The eutectic points for these systems were determined by employing the fractional transformation model. The experimental data were also correlated by applying the thermodynamic activity coefficient model.

Experimental Section

2-Aminophenol and 3-aminophenol were purchased from Merck, and the other chemicals were bought from Acros. The purity of each chemical was greater than 99%, and they were used without further purification. Their melting temperatures and enthalpies of fusion were measured using DSC (DuPont TA2010). Table 1 lists the results and the comparison with available literature data. The measured melting temperatures for all pure compounds are in satisfactory agreement with literature data.

Table 1. Comparison of the Measured Melting Temperatures with Literature Data for Pure Compounds

compound	T_m/K exptl	T_m/K lit[9]	$|\Delta T|$/K[a]
2-aminophenol	447.6	447.2	0.4
3-aminophenol	396.8	396.2	0.6
2-(acetylamino)toluene	382.7	383.2	0.5
4-(acetylamino)toluene	424.0	425.2	1.2
2,4,5-trimethoxybenzoic acid	417.9	418.2	0.3
3,4,5-trimethoxybenzoic acid	444.5	445.5	1.0

[a] $\Delta T = T_m(\text{exptl}) - T_m(\text{lit})$.

The SLE data were measured using the DSC equipment. For each binary system, the samples were prepared in a total amount of 10 g at a specific composition. The sample was ground to a uniform mixture, and 5 mg of it was sealed in a high-pressure copper container made by DuPont Co. The accuracy of the balance (Precisa XB-120A) is ±0.1 mg. The DSC was first purged with nitrogen gas and was heated to 773 K at a scanning rate of 10 K/min. The straight baseline was obtained at a scanning rate of 1 K/min from room temperature to 523 K by adjusting the power output ratio of the microfurnaces. The DSC was calibrated using high-purity indium and zinc at a scanning rate of 1 K/min.

Each binary organic sample was initially melted by heating in the DSC to 473 K, that is, over its melting temperature. It was then cooled to room temperature and maintained at this state for 30 min. The DSC experiments were finally carried out at a heating rate of 1 K/min, and the measured curves were analyzed for SLE. The uncertainty in the temperature measurement is estimated to be ±0.2 K.

Model and Correlation

A heat-transfer model was proposed by Gray[6] for the heat flow in DSC cells. Upon eliminating the baseline effect, Gray's model is written as[3]

$$\frac{\mathrm{d}h(t)}{\mathrm{d}t} = -\frac{\mathrm{d}q(t)}{\mathrm{d}t} RC_S \frac{\mathrm{d}^2 q(t)}{\mathrm{d}t^2} \tag{1}$$

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* Corresponding author. E-mail: ypchen@ntu.edu.tw. Fax: +886-2-2362-3040.

[†] Chinese Culture University.

[‡] National Taiwan University.

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Table 2. Measured Solid−Liquid Equilibrium Data for the 3-Aminophenol (1) + 2-Aminophenol (2) Binary System

x_1	T_E/K	T_L/K	f_E	γ_1	γ_2
0.000		447.6	0.000	2.407	1
0.050	376.8	442.1	0.029	2.191	1.003
0.100	376.8	439.2	0.086	2.002	1.01
0.150	376.5	435.8	0.152	1.843	1.023
0.200	376.4	433.7		1.706	1.041
0.251	376.2	431.1	0.253	1.589	1.064
0.301	376.5	428.2	0.336	1.491	1.091
0.318	376.8	426.3	0.369	1.462	1.102
0.401	377.0	422.9	0.410	1.335	1.163
0.513	376.5	413.7	0.574	1.209	1.273
0.550	377.0	407.1	0.652	1.177	1.32
0.650	376.8	399.7	0.757	1.103	1.466
0.701	377.2	396.0	0.802	1.074	1.556
0.750	376.6	389.0	0.867	1.052	1.661
0.899	376.7	384.2	0.825	1.008	2.041
0.950	376.2	391.6	0.288	1.002	2.177
1.000		396.8	0.000	1	2.332

Table 3. Measured Solid−Liquid Equilibrium Data for the 4-(Acetylamino)toluene (1) + 2-(Acetylamino)toluene (2) Binary System

x_1	T_E/K	T_L/K	f_E	γ_1	γ_2
0.000		382.7	0.000	0.396	1
0.050	357.7	378.5	0.161	0.449	0.996
0.101	356.9	375.2		0.505	0.986
0.151	357.6	370.5	0.496	0.557	0.971
0.200	357.4	367.6	0.667	0.608	0.951
0.399	357.1	372.9	0.852	0.796	0.854
0.450	357.0	380.3	0.780	0.836	0.83
0.499	357.2	384.8	0.708	0.869	0.806
0.547	357.5	388.8	0.660	0.896	0.782
0.600	357.2	394.6	0.556	0.922	0.758
0.650	357.1	397.3	0.512	0.942	0.733
0.699	357.0	401.3	0.411	0.959	0.711
0.799	357.1	409.1	0.250	0.983	0.667
0.850	357.4	412.5	0.197	0.991	0.645
0.898	357.5	415.8		0.996	0.625
0.949	357.1	418.4	0.091	0.999	0.604
1.000		424.0	0.000	1	0.586

Table 4. Measured Solid−Liquid Equilibrium Data for the 3,4,5-Trimethoxybenzoic Acid (1) + 2,4,5-Trimethoxybenzoic Acid (2) Binary System

x_1	T_E/K	T_L/K	f_E	γ_1	γ_2
0.000		417.9	0.000	1.189	1
0.050	395.6	414.6	0.092	1.178	1
0.100	396.2	412.1	0.228	1.168	1.001
0.150	396.3	408.7	0.415	1.157	1.002
0.200	395.8	406.0	0.662	1.146	1.004
0.250	395.9	402.5		1.135	1.007
0.401	396.0	405.7		1.101	1.022
0.451	396.1	408.6	0.826	1.089	1.03
0.500	396.2	412.7	0.743	1.078	1.04
0.600	396.1	421.6	0.576	1.055	1.067
0.650	396.0	424.2	0.493	1.045	1.084
0.699	395.7	428.1	0.432	1.035	1.105
0.800	395.9	433.3		1.017	1.162
0.850	395.4	435.5	0.191	1.01	1.199
0.900	395.8	438.0	0.132	1.005	1.255
0.950	395.4	441.4		1.001	1.299
1.000		444.5	0.000	1	1.366

where dg/dt is the enthalpy generation rate in the phase transformation, dq/dt is the experimentally measured power difference (or heat flow) between the sample and reference cells, R is the thermal resistance between the cells, and C_S is the specific heat of the sample.

At the end of the phase transformation, dq/dt has its maximum value, and dh/dt is zero. The DSC curve returns to its baseline according to an exponential curve

$$\frac{\mathrm{d}q(t)}{\mathrm{d}t} = \left(\frac{\mathrm{d}q(t)}{\mathrm{d}t}\right)_{\max} \exp\left(-\frac{t}{RC_S}\right) \tag{2}$$

where RC_S is taken as a time constant in the DSC experiment and is evaluated from the measured results from the standards.

To determine the eutectic temperatures and compositions accurately, we employed the fractional transformation method in this study. The fractional transformation is the fraction of a mixture that is liquefied. The mathematical expression for the fractional transformation f_L is

$$f_L(t) = \frac{\int_0^t \frac{\mathrm{d}h(t)}{\mathrm{d}t}\mathrm{d}t}{\Delta H} \tag{3}$$

The numerator is the enthalpy generated at time t, and the denominator is the total enthalpy of the phase transformation

$$\Delta H = \int_0^\infty -\frac{\mathrm{d}h(t)}{\mathrm{d}t}\mathrm{d}t \tag{4}$$

Using the experimentally measured results, we determined the fractional transformation values at each time and the corresponding temperatures by using eqs 3 and 4.

The thermodynamic relationship for SLE,[7] neglecting the difference in heat capacities of the liquid and solid phases, gives

$$\ln(\gamma_i x_i) = -\frac{\Delta H_i^{\mathrm{f}}}{RT_{\mathrm{m},i}}\left(\frac{T_{\mathrm{m},i}}{T} - 1\right) \tag{5}$$

where T_m is the melting temperature, ΔH^f is the molar enthalpy of fusion, γ is the activity coefficient, and x is the equilibrium liquid composition. The activity coefficient γ shown in eq 5 represents the nonideal solution behavior and is correlated by the Wilson[8] model in this study. The Wilson model has two parameters (as listed in Table 5) for each binary mixture that are evaluated by minimizing the following objective function between calculated and experimentally determined liquidus temperatures:

$$\mathrm{obj} = \sum_{k=1}^{N}\left(\frac{1}{N}\right)\left\{\frac{T_L^{\mathrm{calcd}} - T_L^{\mathrm{exptl}}}{T_L^{\mathrm{exptl}}}\right\}_k \tag{6}$$

The subscript k denotes the kth data point. The calculated SLE phase boundaries from the Wilson model are then compared with the experimentally measured results.

Results and Discussion

The experimentally measured eutectic temperatures (T_E) and liquidus temperatures (T_L) for three binary systems of isomeric compounds at various compositions are presented in Tables 2 to 4, respectively. The uncertainties in the experimental temperatures and compositions are ±0.2 K and ±0.002 mole fraction, respectively. For each binary system, the fractional transformation data are calculated using eq 3, and a typical plot is shown in Figure 1 for 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) at x_1 = 0.05. All three binary systems in this study show simple eutectic behavior. A sharp transition point is observed in Figure 1 where the eutectic temperature and the fractional transformation value at the eutectic temperature f_E (eutectic fraction) are easily determined. Plots of the f_E values at various compositions for each binary

Table 5. Optimally Fitted Binary Parameters of the Wilson Model and the Deviations of Regression

binary systems	Wilson parameters[a] $\frac{\lambda_{12}-\lambda_{11}}{R}/\frac{\lambda_{21}-\lambda_{22}}{R}$ (K)	AADT(%)[b]
3-aminophenol (1) + 2-aminophenol (2)	274.4/137.9	0.37
4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2)	55.0/−278.3	0.41
3,4,5-trimethoxybenzoic acid (1) + 2,4,5-trimethoxybenzoic acid (2)	−149.5/316.3	0.24

[a] The Wilson equations are

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{\Lambda_{12}x_2 + x_1}\right]$$

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right)$$

where V_1 and V_2 are the liquid molar volumes. For isomers, the ratios of liquid molar volumes are assumed to be unity.

[b] $\mathrm{AADT}(\%) = \frac{100}{N}\sum_{k=1}^{N}\left|\frac{T_L^{\mathrm{calcd}} - T_L^{\mathrm{exptl}}}{T_L^{\mathrm{exptl}}}\right|_k$

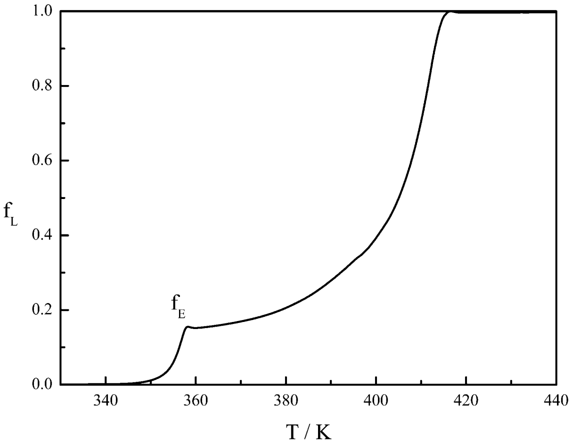

Figure 1. Fraction transformation f_L for the 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) binary system at $x_1 = 0.05$.

system are shown in Figures 2 to 4. At the eutectic point of a binary mixture, the f_E value approaches unity. The eutectic composition for each binary system is thus easily determined from Figures 2 to 4. As indicated in our previous study,[3] one advantage of the eutectic fraction plot in determining the eutectic composition is to avoid the error due to small samples in the DSC experiments. The DSC experiments are difficult for mixtures near the eutectic composition, owing to the overlap of the DSC peaks. The fractional transformation method, however, provides a convenient way to locate the eutectic point without experimental data near the eutectic composition. The f_E data at various compositions for each binary mixture are also shown in Tables 2 to 4, respectively.

Table 5 presents the optimally fitted binary parameters of the Wilson model as well as the calculated deviation in liquidus temperatures. It is observed that with the optimal binary parameters the Wilson model correlates the experimental data satisfactorily. The absolute average percentage deviations for the calculation of liquidus temperatures are all less than 0.4%. Graphical presentations for the calculated phase boundaries of a typical binary system of 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) and

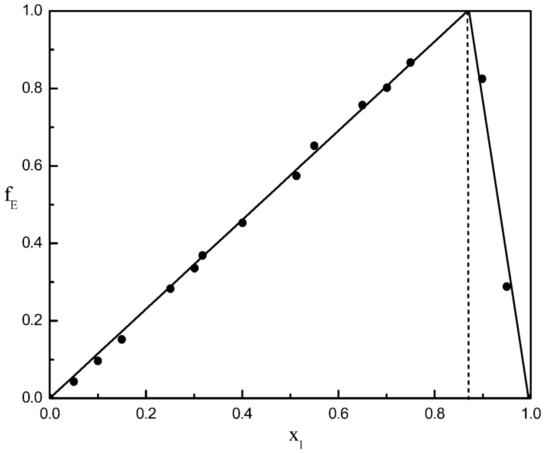

Figure 2. Eutectic fraction f_E for the binary mixture of 3-aminophenol (1) + 2-aminophenol (2); the eutectic composition is at $x_{1E} = 0.865$.

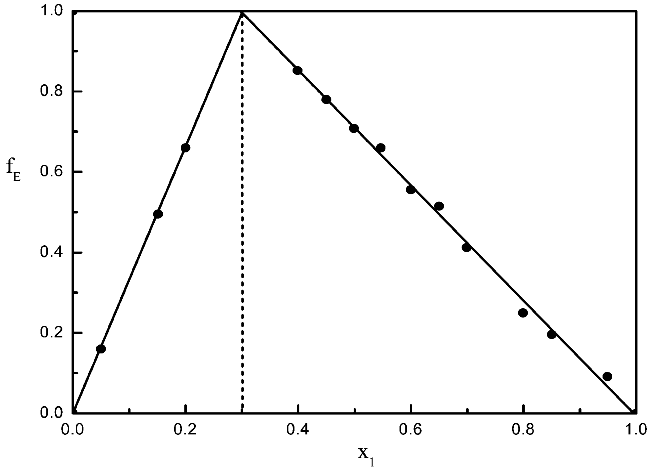

Figure 3. Eutectic fraction f_E for the binary mixture of 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2); the eutectic composition is at $x_{1E} = 0.300$.

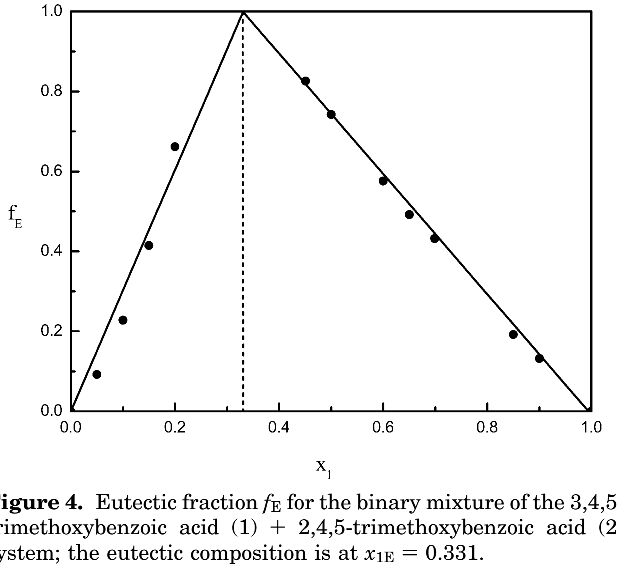

Figure 4. Eutectic fraction f_E for the binary mixture of the 3,4,5-trimethoxybenzoic acid (1) + 2,4,5-trimethoxybenzoic acid (2) system; the eutectic composition is at $x_{1E} = 0.331$.

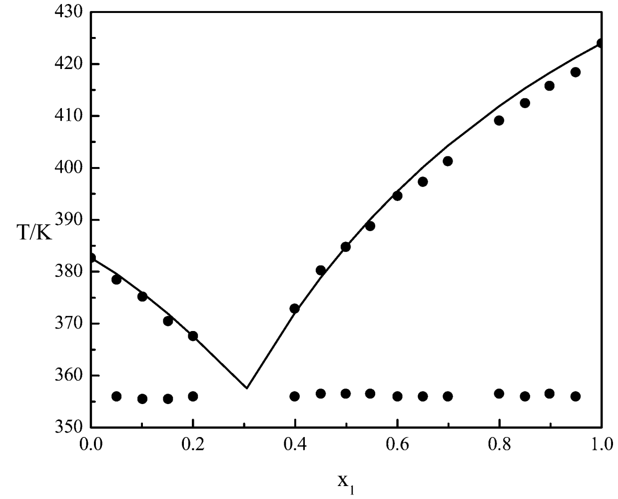

Figure 5. Measured data and calculated SLE results for the binary mixture of the 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) system. (● DSC; −, Wilson equation).

Table 6. Comparison of the Eutectic Point Results from Various Methods for Three Binary Mixtures

method	eutectic composition, x_{1E}	T_E/K
3-Aminophenol (1) + 2-Aminophenol (2)		
Wilson equation	0.777	384.6
DSC experiment	0.855	376.5
fractional transformation method	0.865	
4-(Acetylamino)toulene (1) + 2-(Acetylamino)toulene (2)		
Wilson equation	0.305	357.6
DSC experiment	0.301	357.2
fractional transformation method	0.300	
3,4,5-Trimethoxybenzoic Acid (1) + 2,4,5-Trimethoxybenzoic Acid (2)		
Wilson equation	0.357	399.0
DSC experiment	0.326	395.8
fractional transformation method	0.331	

the comparisons with experimental data are shown in Figure 5.

The eutectic-point compositions and temperatures for three binary systems in this study are shown in Table 6 on the basis of the experimental observations and various calculations. The eutectic composition and temperature for 3-aminophenol (1) + 2-aminophenol (2) are $x_{1E} = 0.86$ and $T_E = 376.5$ K. Those for 4-(acetylamino)toluene (1) + 2-(acetylamino)toluene (2) are $x_{1E} = 0.30$ and $T_E = 357.2$ K, and those for 3,4,5-trimethoxybenzoic acid (1) + 2,4,5-trimethoxybenzoic acid (2) are $x_{1E} = 0.33$ and $T_E = 395.8$ K. The calculated eutectic compositions for all three binary systems using the fractional transformation method are in good agreement with the experimentally measured DSC data. It is again shown as a simple and reliable method to determine the eutectic points for binary mixtures.

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