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Solid−Liquid Equilibria for Three Binary Mixtures of Benzoic Acid with Heptanedioic Acid, 3-Methylpentanedioic Acid, and 2,3-Dimethylbutanedioic Acid

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ABSTRACT: Solid−liquid equilibria for three organic binary mixtures of benzoic acid (1) + heptanedioic acid (2) (eutectic temperature T_E = 350.20 K, eutectic composition x_{1E} = 0.498), benzoic acid (1) + 3-methylpentanedioic acid (3) (T_E = 340.03 K, x_{1E} = 0.427), and benzoic acid (1) + 2,3-dimethylbutanedioic acid (4) (T_E = 352.71 K, x_{1E} = 0.462) were measured using differential scanning calorimetry (DSC). We observe simple eutectic behaviors for all three binary mixtures. The experimental results were further correlated using the Wilson and nonrandom two-liquid (NRTL) activity coefficient models. The optimally fitted binary interaction parameters are reported, and satisfactory correlation results are depicted.

INTRODUCTION

Solid−liquid equilibrium (SLE) measurements are important to separation processes such as crystallization operated at relatively low temperatures. This process is appropriate to the separation of isomeric components or thermolabile compounds where traditional methods such as distillation are not applicable. The SLE data of various systems are an essential part of the design concerning such processes.

The SLE data are usually determined by a cooling curve or visual measurement.[1] However, owing to assorted difficulties accompanying this method, an alternative approach has been developed by the application of differential scanning calorimetry (DSC). Applying the DSC method, there have been reported references for systems of metals, polymers, and organic compounds.[2−5] The DSC method basically measures the heat effect during phase transformation. The measured onset or peak temperatures are then used to evaluate the phase boundaries.[6] Several mathematical models have been presented in literature[4,7,8] to describe the DSC measurement system.

In this study, we measured SLE data for three binary organic mixtures: benzoic acid ($C_7H_6O_2$) + heptanedioic acid ($C_7H_{12}O_4$), benzoic acid + 3-methylpentanedioic acid ($C_6H_{10}O_4$), and benzoic acid + 2,3-dimethylbutanedioic acid ($C_6H_{10}O_4$). To our knowledge, these SLE data have not been shown in literature. The Wilson[9] and nonrandom two-liquid (NRTL)[10] activity coefficient models were also used to correlate the experimental data. Finally, the optimal binary interaction parameters for each model are presented. A comparison between the model calculated results with those from direct experimental observations is demonstrated.

EXPERIMENTAL SECTION

All chemicals were bought from Aldrich. The purity of each chemical was greater than mass fraction w = 0.99, and no further purification was made before using in the experiments. Their melting temperatures and enthalpies of fusion for pure compounds were measured using DSC (Perkin-Elmer DSC 4000).

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

	T_m/K		$\Delta_{fus}H^o_m$/kJ·mol^{-1}	
compound	this study	lit.	this study	lit.
benzoic acid	396.08	395.52[14]	18.7 ± 0.3	18.07[14]
heptanedioic acid	377.40	379.15[15]	28.8 ± 0.5	27.62[16]
3-methylpentanedioic acid	358.61	NA[a]	31.0 ± 0.6	NA
2,3-dimethylbutanedioic acid	392.48	NA	16.9 ± 0.3	NA

[a] NA: not available.

Table 1 lists the measured pure component properties and the comparison with those from available literature. It is shown that our measured melting temperatures and enthalpies of fusion are in satisfactory agreement with literature data for all pure compounds.

The SLE data were measured using the DSC equipment in this study. For each binary system, about (4 to 5) mg of the sample at a specific composition was sealed in a high-pressure aluminum container purchased from Perkin-Elmer. The accuracy of the balance (Shimadzu C9AS-AUW220D) is ± 0.01 mg. The DSC equipment was first purged with nitrogen gas, cleaned by heating to 673.15 K, and then calibrated using high-purity indium and zinc before the SLE measurements. To delete the previous thermal histories and to homogenize the mixtures, each sample was first heated at a rate of 10 K·min^{-1} to a state that was above the higher pure component melting temperature of the binary mixture. After keeping at this temperature for 1 min, the samples were then cooled to 303.15 K at a cooling rate of 10 K·min^{-1}. The samples were allowed to stay at this temperature for 30 min

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before our SLE measurements. After these pretreatments, samples for benzoic acid + heptanedioic acid and benzoic acid + 3-methylpentanedioic acid were then heated at a rate of 1 K·min^{-1}. Samples of benzoic acid + 2,3-dimethylbutanedioic acid were heated at a slower rate of 0.5 K·min^{-1} to clearly identify the peak temperatures during DSC experiments. The eutectic temperatures were determined from the onset temperatures or peak temperatures from the DSC measurement. The liquidus temperatures were determined from the modified peak temperatures from the DSC results, as we have presented in our previous study.[5] The uncertainty in the temperature measurement was estimated to be ± 0.2 K.

Table 2. Measured SLE Data for Three Binary Systems

100 x_1	T_E/K	T_L/K	100 x_1	T_E/K	T_L/K
Benzoic Acid (1) + Heptanedioic Acid (2)					
0.00		377.40	60.03	350.82	359.28
5.02	348.09	376.20	64.99	350.97	364.54
9.98	348.82	373.23	70.08	350.69	368.73
14.97	349.54	369.88	75.04	350.58	373.71
19.97	349.85	367.39	80.04	350.59	378.29
25.01	350.18	365.51	85.03	350.53	382.33
29.86	350.22	362.78	90.00	350.39	386.72
34.91	350.48	359.51	94.94	350.14	391.73
40.04	350.60	355.28	100.00		396.08
44.87	350.85	353.52			
Benzoic Acid (1) + 3-Methylpentanedioic Acid (3)					
0.00		358.61	59.23	340.21	361.41
4.96	338.34	356.59	64.99	340.44	365.54
10.32	338.76	353.97	69.60	340.40	369.75
14.88	339.85	351.34	75.31	339.47	374.25
19.64	340.37	349.66	80.13	340.21	376.87
24.60	340.63	348.48	84.88	340.45	383.86
30.01	340.75	345.43	90.42	340.13	387.21
44.43	340.11	347.18	95.14	339.75	387.96
49.70	340.41	350.25	100.00		396.08
54.72	340.27	354.55			
Benzoic Acid (1) + 2,3-Dimethylbutanedioic Acid (4)					
0.00		392.48	59.85	353.64	362.94
5.06	350.85	385.62	64.74	353.55	367.02
9.81	352.34	382.08	69.90	352.56	370.89
14.92	352.00	379.34	75.57	353.33	375.75
20.24	350.22	374.85	80.01	351.55	378.06
24.72	353.91	370.00	85.01	353.29	383.53
30.41	352.63	365.09	90.23	353.95	388.57
34.82	352.46	362.62	94.71	353.34	391.31
54.97	353.68	359.90	100.00		396.08

MODEL AND CORRELATION

We correlated our experimental results using the equal fugacity criterion for SLE.[11] Upon neglecting the difference in heat capacities of the liquid and solid phases, the thermodynamic relation gives

$$\ln(\gamma_i x_i) = -\frac{\Delta_{fus}H^o_{m,i}}{RT_{m,i}}\left(\frac{T_{m,i}}{T} - 1\right) \quad (1)$$

where $T_{m,i}$ is the melting temperature, $\Delta_{fus}H^o_{m,i}$ is the molar enthalpy of fusion, γ_i is the activity coefficient, and x_i is the equilibrium liquid composition in mole fraction. The activity coefficient shown in eq 1 represents the nonideal solution behavior of the mixture. We correlated the γ_i values by employing the Wilson and NRTL models in this study. The Wilson equations are:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (2)$$

Table 4. Comparison of the Eutectic Point Results from Different Methods for the Three Binary Mixtures

method	eutectic composition, x_1	T_E/K
Benzoic Acid (1) + Heptanedioic Acid (2)		
Wilson model	0.506	347.80
NRTL model	0.505	347.31
DSC measurement	0.498	350.20
Benzoic Acid (1) + 3-Methylpentanedioic Acid (3)		
Wilson model	0.412	340.47
NRTL model	0.412	339.63
DSC measurement	0.427	340.03
Benzoic Acid (1) + 2,3-Dimethylbutanedioic Acid (4)		
Wilson model	0.459	348.32
NRTL model	0.459	348.45
DSC measurement	0.462	352.71

Table 3. Wilson and NRTL Parameters and Deviations of Regression for the Three Binary Mixtures

Wilson parameters	NRTL parameter (α_{12} is 0.3 in this study)	AADT[a]/%	
$[(\lambda_{12} - \lambda_{11})/R]$/K, $[(\lambda_{21} - \lambda_{22})/R]$/K	$[(g_{12} - g_{22})/R]$/K, $[(g_{21} - g_{11})/R]$/K	Wilson	NRTL
Benzoic Acid (1) + Heptanedioic Acid (2)			
−182.77/172.13	249.19/−290.57	0.18	0.19
Benzoic Acid (1) + 3-Methylpentanedioic Acid (3)			
−30.7302/16.3110	−246.89/210.49	0.32	0.32
Benzoic Acid (1) + 2,3-Dimethylbutanedioic Acid (4)			
323.96/−205.68	−222.41/347.73	0.26	0.25

[a] AADT = $(100/N)\sum_{k=1}^{N}|[T_L(\text{calc}) - T_L(\text{expt})]/T_L(\text{expt})|_k$.

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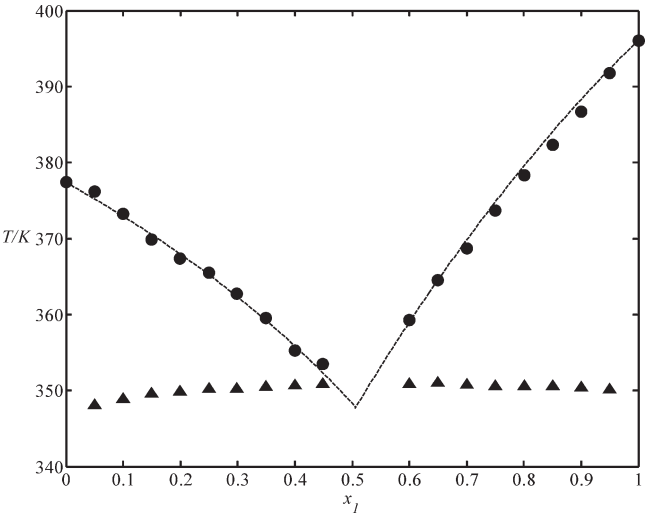

Figure 1. Comparison of the experimental and calculated liquidus temperature for the binary mixture of benzoic acid (1) + heptanedioic acid (2) (●, liquidus temperature; ▲, eutectic temperature; - - -, Wilson model).

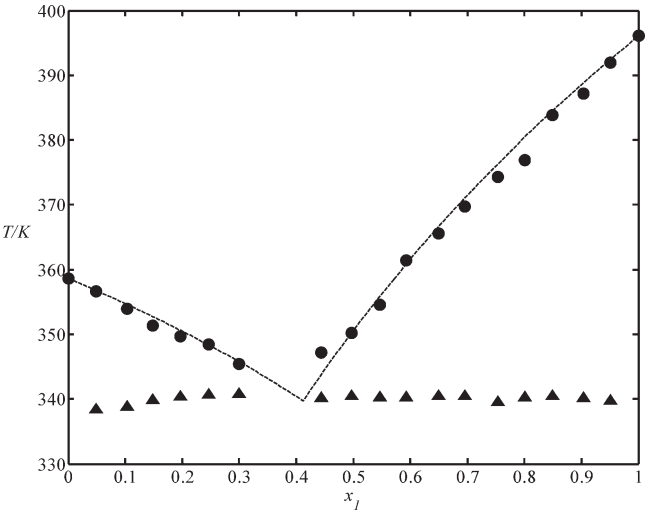

Figure 2. Comparison of the experimental and calculated liquidus temperature for the binary mixture of benzoic acid (1) + 3-methylpentanedioic acid (3) (●, liquidus temperature; ▲, eutectic temperature; - - -, Wilson model).

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (3)$$

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \quad (4)$$

$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \quad (5)$$

where R is the gas constant, V_1 and V_2 are the liquid molar volumes determined from DIPPR[12] or Elbro's group contribution method,[13] and $(\lambda_{12} - \lambda_{11})/R$ and $(\lambda_{21} - \lambda_{22})/R$ are two parameters. The NRTL equations are:

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \quad (6)$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \quad (7)$$

$$\ln G_{12} = -\alpha_{12}\tau_{12} \qquad \ln G_{21} = -\alpha_{12}\tau_{21} \quad (8)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (9)$$

where $(g_{12} - g_{22})/R$, $(g_{21} - g_{11})/R$, and α_{12} are three parameters. The nonrandomness factor α_{12} in the NRTL model was fixed as 0.3 in this study. The other two parameters of either the Wilson or NRTL model for each binary mixture were determined by minimizing the following objective function (obj) between the calculated and experimentally determined liquidus temperatures T_L:

$$\text{obj} = \sum_{k=1}^{N}\left(\frac{1}{N}\right)\left\{\frac{T_L(\text{calc}) - T_L(\text{expt})}{T_L(\text{expt})}\right\}_k \quad (10)$$

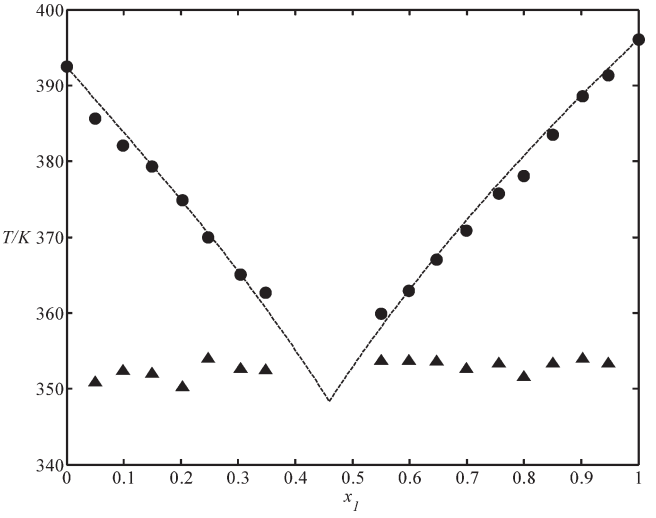

Figure 3. Comparison of the experimental and calculated liquidus temperature for the binary mixture of benzoic acid (1) + 2,3-dimethylbutanedioic acid (4) (●, liquidus temperature; ▲, eutectic temperature; - - -, Wilson model).

The subscript k represents the kth data point. The calculated phase boundaries for SLE from these models 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 organic compounds at various compositions (mole fraction) are presented in Table 2. The uncertainties in the experimentally measured temperatures and compositions are estimated as ± 0.2 K and ± 0.002 mole fraction, respectively. The liquidus phase boundaries were calculated using the Wilson and NRTL models. The optimally fitted binary interaction parameters of these models and the absolute average deviations in the calculated

liquidus temperatures (AADT) are presented in Table 3. With the optimally fitted binary parameters, it is depicted that the experimental data agree well with the correlated results using either the Wilson or NRTL model. The AADT values listed in Table 3 are approximately within the experimental uncertainty for all three systems. Both of these two models yield nearly the same absolute average deviation less than 0.3 % of liquidus temperatures. The eutectic compositions and temperatures for three binary systems investigated in this study are shown in Table 4 from either the smoothed curves using the DSC measurement or the calculated results from the Wilson and NRTL models. Graphical presentations for the calculated phase boundaries from the Wilson model for three binary systems of benzoic acid (1) + heptanedioic acid (2), benzoic acid (1) + 3-methylpentanedioic acid (3), and benzoic acid (1) + 2, 3-dimethylbutanedioic acid (4) are shown in Figures 1 to 3, respectively. The eutectic composition and temperature for benzoic acid (1) + heptanedioic acid (2) are determined as x_{1E} = 0.498 and T_E = 350.20 K. Those for benzoic acid (1) + 3-methylpentanedioic acid (2) are x_{1E} = 0.427 and T_E = 340.03 K, and those for benzoic acid (1) + 2,3-dimethylbutanedioic acid (2) are x_{1E} = 0.462 and T_E = 352.71 K.

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