Solid−Liquid Equilibria for Hexanedioic Acid + Benzoic Acid, Benzoic Acid + Pentanedioic Acid, and Hexanedioic Acid + Pentanedioic Acid

Tzu-Chi Wang,[†] Tzu-Yu Lai,[†] and Yan-Ping Chen*,[‡]

Department of Chemical and Materials Engineering and Master Program of Nanomaterials, Chinese Culture University, Taipei, Taiwan, Republic of China, and Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Solid−liquid equilibria for three organic binary mixtures of hexanedioic acid (1) + benzoic acid (2) (eutectic temperature $T_E = 378.17$ K, eutectic composition $x_{1E} = 0.249$), benzoic acid (1) + pentanedioic acid (2) ($T_E = 343.50$ K, $x_{1E} = 0.402$), and hexanedioic acid (1) + pentanedioic acid (2) ($T_E = 355.87$ K, $x_{1E} = 0.205$) were measured using differential scanning calorimetry (DSC). Simple eutectic behaviors for these systems were observed. The experimental results were correlated using the Wilson and nonrandom two-liquid (NRTL) activity coefficient models with satisfactory results.

Introduction

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

Conventionally, the SLE data are 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 this method, there have been several reported data dealing with systems of metals, polymers, and organic compounds.[2−5] In brief, the DSC method measures the heat effect during phase transformation and evaluates the phase boundaries.[6] Several mathematical models have been presented in literature[4,7] by using DSC data.

In this study, we focused on the experimental SLE measurements of three binary organic mixtures: hexanedioic acid ($C_6H_{10}O_4$) + benzoic acid ($C_7H_6O_2$), benzoic acid + pentanedioic acid ($C_5H_8O_4$), and hexanedioic acid + pentanedioic acid. To our knowledge, these SLE data have not been shown yet in literature. The Wilson[8] and nonrandom two-liquid (NRTL)[9] activity coefficient models were also used to correlate the experimental data. Finally, we demonstrated that the estimated eutectic conditions of all binary systems from both activity coefficient models agreed well with those from direct experimental observations.

Experimental Section

Hexanedioic acid was purchased from Fluka, and the other chemicals were bought from Aldrich. The purity of each chemical was greater than mass fraction $w = 0.99$, and they were used without further purification. Their melting temperatures and enthalpies of fusion were measured using DSC (Perkin-Elmer DSC 4000). Table 1 lists the measured pure component properties and the comparison of our experimental data 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.

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

	T_m/K		$\Delta_{fus}H_m^0$/kJ·mol^{-1}	
compound	this study	literature	this study	literature
benzoic acid	396.08	395.52[12]	18.71 ± 0.02	18.07[12]
pentanedioic acid	369.13	370.05[13]	21.53 ± 0.13	20.9[14]
hexanedioic acid	426.31	425.50[15]	35.20 ± 0.17	34.85[15]

The SLE data were measured using the DSC equipment in this study. For each binary system, about 5 mg of the sample at a specific composition was sealed in a high-pressure aluminum container made by Perkin-Elmer. The accuracy of the balance (Shimadzu C9AS-AUW220D) is ± 0.01 mg. The DSC was first purged with nitrogen gas, cleaned by heating to 713.15 K, and was 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 submitted to a first heating run at 20 K·min^{-1} to a state that was above the higher pure component melting temperature of the binary mixture. After being kept for 1 min at this temperature, the samples were then cooled to 303.15 K at a cooling rate of 10 K·min^{-1} and were allowed to stay at this temperature for 20 min. After these pretreatments, each sample for hexanedioic acid + benzoic acid and hexanedioic acid + pentanedioic acid was then heated at the rate of 1 K·min^{-1}. Samples of benzoic acid + pentanedioic acid were heated at the rate of 0.2 K·min^{-1}. The eutectic temperatures were determined from the onset 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.

Model and Correlation

The thermodynamic relationship for SLE,[10] neglecting the difference in heat capacities of the liquid and solid phases, gives

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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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$$\ln(\gamma_i x_i) = -\frac{\Delta_{fus}H^0_{m,i}}{RT_{m,i}}\left(\frac{T_{m,i}}{T} - 1\right) \tag{1}$$

where T_m is the melting temperature, $\Delta_{fus}H^0_m$ is the molar enthalpy of fusion, γ is the activity coefficient, and x is the equilibrium liquid composition in mole fraction. The activity coefficient shown in eq 1 represents the nonideal solution behavior and was correlated by the Wilson and NRTL models in this study. The Wilson equations are:

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

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

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

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

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

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

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

$$\ln G_{12} = -\alpha_{12}\tau_{12} \qquad \ln G_{21} = -\alpha_{12}\tau_{21} \tag{8}$$

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

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 set to be 0.3 in this study. The other two parameters of either the Wilson or NRTL model for each binary mixture were evaluated by minimizing the following objective function (obj) between the calculated and experimentally determined liquidus temperatures:

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

The subscript k denotes the kth data point. The calculated SLE phase boundaries form these models are then compared with the experimentally measured results.

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
Hexanedioic Acid (1) + Benzoic Acid (2)					
0.00	NA[a]	396.08	59.96	377.86	406.55
4.93	378.03	391.84	64.95	378.22	408.33
10.30	378.26	387.53	69.79	378.18	411.77
15.29	378.18	384.07	75.14	378.00	414.34
29.78	378.08	382.85	80.17	377.99	416.55
35.40	378.16	389.04	85.29	377.70	419.34
39.01	378.06	393.17	89.86	377.67	420.97
44.92	377.88	397.05	95.04	378.12	423.94
50.03	377.95	400.12	100.00	NA	426.31
55.62	377.67	402.99			
Benzoic Acid (1) + Pentanedioic Acid (2)					
0.00	NA	369.13	60.58	345.92	363.85
4.95	342.39	365.56	64.66	345.75	367.39
10.11	343.12	362.89	69.75	345.99	371.93
15.19	342.53	360.64	74.87	345.47	375.71
20.55	343.68	356.64	80.10	345.27	380.07
25.11	344.44	353.75	85.12	346.09	384.15
29.97	344.15	350.94	89.83	345.15	387.46
34.97	344.97	347.47	94.83	344.74	391.63
50.09	344.40	353.98	100.00	NA	396.08
55.24	345.71	358.31			
Hexanedioic Acid (1) + Pentanedioic Acid (2)					
0.00	NA	369.13	59.72	356.28	403.23
5.17	355.79	366.44	65.41	357.12	406.62
10.15	358.25	363.18	69.98	356.78	409.60
25.23	357.13	365.31	74.90	356.33	412.30
30.00	357.14	372.34	80.15	357.90	414.51
34.80	357.60	380.14	84.97	356.31	418.23
39.85	356.97	387.14	89.75	357.88	420.45
45.32	357.66	391.20	94.97	356.36	423.55
49.15	356.13	395.08	100.00	NA	426.31
54.11	356.80	398.18			

[a] NA: not available.

Table 3. Optimally Fitted Binary Parameters and Deviations of Regression from the Wilson and NRTL Models

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
Hexanedioic Acid (1) + Benzoic Acid (2)			
10.39/57.97	−38.85/110.04	0.13	0.13
Benzoic Acid (1) + Pentanedioic Acid (2)			
−86.1664/124.6890	167.99/−126.36	0.12	0.12
Hexanedioic Acid (1) + Pentanedioic Acid (2)			
45.7693/−190.2406	−367.16/257.06	0.18	0.18

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

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 ± 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 parameters of these models and the absolute average deviations in the calculated liquidus temperatures (AADT) are shown in Table 3. With the optimally fitted binary parameters, it is depicted that the experimental data were satisfactorily correlated using either the Wilson or NRTL model. The AADT values listed in Table 3 are within the experimental uncertainty for all three systems. Both of these two models show nearly the same absolute average deviation of less than 0.2 % of liquidus temperatures. The eutectic compositions and temper-

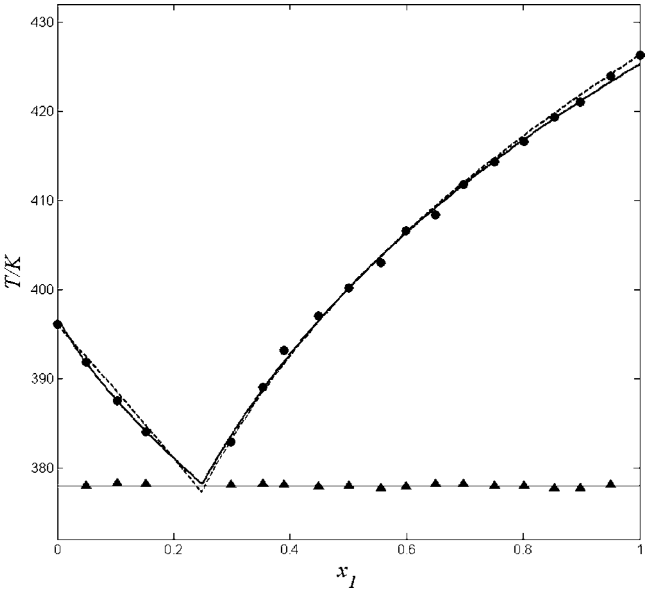

Figure 1. Comparison of the experimental and calculated liquidus temperature for the binary mixture of hexanedioic acid (1) + benzoic acid (2) (●, liquidus temperature; ▲, eutectic temperature; ---, Wilson model; —, Clarke−Glew equation).

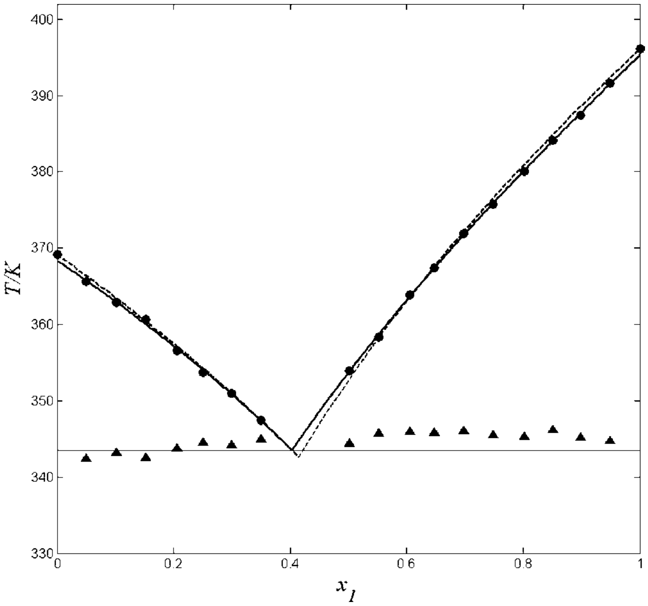

Figure 2. Comparison of the experimental and calculated liquidus temperature for the binary mixture of benzoic acid (1) + pentanedioic acid (2) (●, liquidus temperature; ▲, eutectic temperature; ---, Wilson model; —, Clarke−Glew equation).

atures for three binary systems investigated in this study are shown in Table 4 from either the smoothed curves using the Clarke−Glew equation[16,17] or the calculated results from the Wilson and NRTL models. It is demonstrated in Table 4 that the model calculated and experimentally measured results are in satisfactory agreement. Graphical presentations for the calculated phase boundaries from the Wilson model and the Clarke−Glew equation for three binary systems of hexanedioic acid (1) + benzoic acid (2), benzoic acid (1) + pentanedioic acid (2), and hexanedioic acid (1) + pentanedioic acid (2) are shown in Figures 1 to 3, respectively. The eutectic composition and temperature for hexanedioic acid (1) + benzoic acid (2) are determined as $x_{1E} = 0.249$ and $T_E = 378.17$ K. Those for benzoic acid (1) + pentanedioic acid (2) are $x_{1E} = 0.402$ and $T_E = 343.50$ K, and those for hexanedioic acid (1) + pentanedioic acid (2) are $x_{1E} = 0.205$ and $T_E = 355.87$ K.

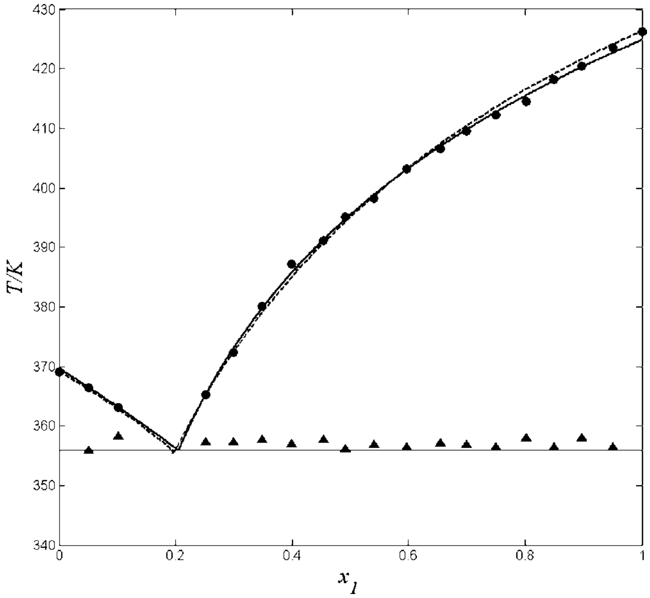

Figure 3. Comparison of the experimental and calculated liquidus temperature for the binary mixture of hexanedioic acid (1) + pentanedioic acid (2) (●, liquidus temperature; ▲, eutectic temperature; ---, Wilson model; —, Clarke−Glew equation).

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

method	eutectic composition, x_1	T_E/K
Hexanedioic Acid (1) + Benzoic Acid (2)		
Wilson model	0.247	377.27
NRTL model	0.248	377.32
Clarke−Glew equation	0.249	378.17
Benzoic Acid (1) + Pentanedioic Acid (2)		
Wilson model	0.415	342.61
NRTL model	0.415	342.61
Clarke−Glew equation	0.402	343.50
Hexanedioic Acid (1) + Pentanedioic Acid (2)		
Wilson model	0.196	355.58
NRTL model	0.196	355.64
Clarke−Glew equation	0.205	355.87

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