



# Phase behavior and solid–liquid equilibria of aliphatic and aromatic carboxylic acid mixtures



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## ABSTRACT

We newly developed an apparatus for the solid–liquid equilibrium measurements to examine the phase equilibria of carboxylic acid mixtures. The equilibrium freezing temperatures obtained from the cooling curve of the liquid state to solid were measured for the stearic acid + benzoic acid, adipic acid + benzoic acid, and p-toluic acid + benzoic acid systems. The experimental results were correlated successfully by Wilson, NRTL, and UNIQUAC models. Moreover thermodynamic approach of Slaughter and Doherty was applied to represent the solid–liquid equilibria of peritectic and eutectic compound exists in the solid phase due to the reaction of complex formation. Good agreement between the experimental and calculated values for the binary carboxylic acid mixtures was obtained.

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## 1. Introduction

Pharmaceutical, cosmetic, and food industries make good use of fatty acids and their mixture as addition ingredients to the products. The fatty acid mixtures act as a surface and viscosity modifier and stabilizer additive by adjusting fusion characteristics in accordance with the melting temperature of fatty acids. The phase behavior and transition phenomena of fatty acid mixtures have been examined intensively by differential scanning calorimetry (DSC) and complemented by different types of X-ray, NMR, and IR and FT-Raman spectroscopy analyses [1,2]. It was revealed that the phase diagram for the fatty acid mixtures is quite complicated and exhibits eutectic and peritectic points, where a new solid compound forms in solid phase due to the difference in the molecular interactions between like and unlike molecules. Besides fatty acid and their methyl ester as major components in biodiesel fuel made from natural vegetable oils attracts a current interest in renewable energy sources as energy alternatives of fossil fuel. In the upstream and downstream processing, it is important to understand the phase behavior of mixtures containing fatty acids. So the precise and reliable phase equilibrium data are necessary for a proper design of the refinery process as well as for a further development of thermodynamic predictive models. Solid–liquid equilibrium

measurements have been carried out using several different kinds of techniques [3–8]; analytical, synthetic, and visual methods, dynamic determination of melting and cooling curves, and pour/cloud test.

In the present work we newly made an apparatus for solid–liquid equilibrium measurements to examine the phase equilibria of carboxylic acid mixtures. The apparatus consists of heating and cooling systems for the measurements of equilibrium temperature and light scattering intensity measurement system that can detect a change from liquid mixture to solid-state formation. The light scattering intensity measurement was secondarily performed to observe the solid formation. We aim to study the phase and solid–liquid equilibria for aliphatic and aromatic carboxylic acid mixtures. The equilibrium freezing temperatures and eutectic and peritectic points for stearic acid + benzoic acid, adipic acid + benzoic acid, and p-toluic acid + benzoic acid mixtures were measured from the cooling temperature profiles of the liquid state to solid. The experimental results of the binary mixtures were correlated by the Wilson [9], NRTL [10], and UNIQUAC [11] models. Moreover the experimental data were examined by comparing with those calculated from the thermodynamic approach [12–14] for a peritectic and eutectic compound exists in the solid phase due to the reaction of complex formation.

## 2. Experimental

Adipic acid, and benzoic acid, and naphthalene were purchased

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from Wako Chemicals, stearic acid and p-toluic acid were from Tokyo Chemical Industry, and phenanthrene from Sigma–Aldrich Co. The purity and melting point of the chemicals were given in Table 1. The melting temperatures of the materials were in good agreement with literature [1,15–18] and they were used without further purification.

A schematic diagram of the calorimeter is illustrated in Fig. 1 (a). The apparatus was designed for the determination of equilibrium freezing and eutectic points from the cooling temperature curve. Additionally the measuring system equipped a laser light source with a light detector to observe the solid-state formation from the change of light scattering intensity, as shown in Fig. 1 (b). The apparatus consists of an equilibrium cell with the capacity about 8 cm<sup>3</sup>. Solidus binary sample prepared gravimetrically at a specified composition was loaded in the cell and heated to melt above a higher melting temperature of every pure component. The resultant liquid sample mixture was homogenized by stirring with a magnetic stirrer vigorously. Then the melting mixture was cooled to 303.15 K at a cooling rate of 1.0 K/min. The rate of temperature change in the vicinity of the phase transition was controlled within 0.1 K/min by data acquisition and control system (Keyence, KV-300, KVTP40). The temperature in the cell was measured every second by a platinum temperature-sensing probe within  $\pm 0.01$  K. The equilibrium temperature was obtained from the cooling curve of the liquid state to solid as well as the derivative of the temperature with respect to time. Fig. 2 depicts practical exemplification in determination of the freezing temperature from the cooling temperature profiles of pure component and binary mixtures. The measurements were triplicated to ensure reproducibility in the determination of equilibrium liquid temperature. The experimental uncertainties in the temperature were estimated as not larger than 0.5 K.

The experimental setup was validated by comparing the freezing temperature measured for naphthalene and phenanthrene mixture with the literature [19]. Table 2 lists the experimental data for the naphthalene and phenanthrene system measured in this work. Fig. 3 shows the freezing temperature of naphthalene and phenanthrene mixture was in good agreement with the literature values within average temperature deviation of 1.5 K. Table 3 summarized the experimental freezing temperatures ( $T_i$ ) and eutectic temperatures ( $T_E$ ) in the solid–liquid equilibria for the carboxylic acid mixtures. As shown in Fig. 4, it was found that the stearic acid + benzoic acid, adipic acid + benzoic acid, and p-toluic acid + benzoic acid systems exhibited the eutectic and peritectic points in phase behavior. Besides the freezing temperatures of the adipic acid + benzoic acid mixture at the mole fraction range of adipic acid up to 0.2 was lower than those of Wang et al. [16] obtained from the differential scanning calorimetry (DSC) and a peritectic point of the stearic acid + benzoic acid system appears

around the adipic acid mole fraction of 0.2 was observed in this work.

### 3. Calculated results

The experimental results were analyzed by thermodynamic framework of solid–liquid equilibria [20]. The thermodynamic criteria of solid–liquid equilibria is described by

$$\ln\left(z_i\gamma_i^S/x_i\gamma_i^L\right) = \frac{\Delta H_i}{RT_{m,i}}\left(\frac{T_{m,i}}{T} - 1\right) \quad (1)$$

where  $z_i$  and  $x_i$  are the mole fraction of component  $i$  in solid and liquid phases,  $\gamma_i^S$  and  $\gamma_i^L$  the activity coefficients in solid and liquid phases,  $\Delta_{fus}H_i$  the enthalpy of fusion,  $T_{m,i}$  the melting temperature. For the system with the pure immiscible solids exist in the solid phase, as known eutectic solid mixture, the term  $z_i\gamma_i^S$  in Eq. (1) equals to unity. The equilibrium liquidus temperature of the mixture can be expressed by

$$T = \Delta_{fus}H_i \left/ \left[ \frac{\Delta_{fus}H_i}{T_{m,i}} - R \ln(x_i\gamma_i^L) \right] \right. \quad (2)$$

The experimental results measured in the present work were correlated using the Wilson model [9], NRTL model ( $\alpha_{ij} = 0.3$ ) [10], and UNIQUAC model [11]. Table 4 lists the physical properties of carboxylic acids and the UNIQUAC volume and surface parameters estimated by the group contribution method of Fredenslund et al. [21]. The binary interaction parameters in the activity coefficient models were obtained fitting the model to the experimental data by minimizing the objective function:

$$F = \sum_{i=1}^N \left( \frac{T_{exp,i} - T_{calc,i}}{T_{exp,i}} \right)^2 \quad (3)$$

The absolute arithmetic mean deviation AAD was defined by

$$AAD = 100 \sum_{i=1}^N \frac{|T_{exp,i} - T_{calc,i}|}{T_{exp,i}} \bigg/ N \quad (4)$$

where  $N$  is the number of experimental data. The binary energy parameters ( $\lambda_{ji} - \lambda_{ii}$ ), ( $g_{ji} - g_{ii}$ ), ( $u_{ji} - u_{ii}$ ) in the Wilson model, NRTL model ( $\alpha_{ij} = 0.3$ ), and UNIQUAC model were determined as fitting parameters by a numerical iterative procedure available from Refs. [10,20]. Table 5 presents the binary parameters along with the absolute arithmetic mean deviation AAD between the experimental and calculated values. Compared with the UNIQUAC model, the Wilson and NRTL models exhibited the higher AAD of 1% in reproducing the freezing temperatures for the stearic acid + benzoic acid system. As can be seen in Fig. 5, a peritectic point of the stearic acid + benzoic acid system appears around the mole fraction of stearic acid, 0.6 and an inflection on the freezing temperature curve were observed. As the same reported previously for fatty acid mixtures in the solid phase [1,2], this phase behavior could be related to the formation of peritectic compound and phase transition. The peritectic solid mixture is the system that perfectly miscible solids exist in the solid phase to form a new solid compound due to the molecular interactions between unlike molecules.

In the representation for the peritectic system, Slauter and Doherty [12] suggested the chemical reaction between pure solid components A and B in the solid phase. The equilibrium constant  $K$  was defined by the activity of chemical species as

**Table 1**  
Purity of chemicals used and melting temperatures.

Compound	Purity, mass fraction	$T_m$ /K	
		This work	Literature
Adipic acid	>0.995	426.35	425.65 <sup>a</sup> , 426.31 <sup>b</sup> , 426.35 <sup>c</sup>
Benzoic acid	>0.995	395.50	395.50 <sup>a</sup> , 396.08 <sup>b</sup>
Naphthalene	>0.98	353.41	352.41 <sup>a</sup> , 353.4 <sup>d</sup>
Phenanthrene	>0.98	372.39	372.39 <sup>a</sup> , 372.4 <sup>d</sup>
Stearic acid	>0.98	342.95	342.45 <sup>a</sup> , 342.95 <sup>e</sup>
p-toluic acid	>0.98	452.75	452.75 <sup>a,c</sup>

<sup>a</sup> [15].

<sup>b</sup> [16].

<sup>c</sup> [17].

<sup>d</sup> [18].

<sup>e</sup> [1].

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