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Vapor−Liquid−Solid Equilibria for the System Propane or 2-Methylpropane + Dodecanoic Acid + Tetradecanoic Acid

Hiroyuki Enomoto, Kouji Maeda,* Keisuke Fukui, and Syouji Hirota

Department of Chemical Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-22, Japan

Vapor−liquid−solid equilibria for the propane + dodecanoic acid + tetradecanoic acid and 2-methylpropane + dodecanoic acid + tetradecanoic acid systems have been measured. The relationship between the temperature and the pressure of the three-phase equilibria is described. The liquefied gases (propane or 2-methylpropane) decreased the temperatures of solid−liquid equilibrium (SLE) for the dodecanoic acid + tetradecanoic acid system. The effect of the liquefied gas on the SLE for the binary fatty acids system was presented. The three-phase equilibria could be well correlated by an associated solution model combined with the NRTL equation.

1. Introduction

Soaps, surfactants, paints, candles, and medicine are made from fatty acids, and crystallization is an effective method to separate fatty acid mixtures. Hence, data for crystallization is required on the solid−liquid equilibria (SLE) of fatty acid mixtures. Many crystallization processes of fatty acids use large amounts of solvent in order to reduce the slurry density. Liquefied gases could be useful for the solvent crystallization, because the liquefied gases are easily recovered from the solution (Hasenhuettl, 1993).

In this study, we report vapor−liquid−solid equilibria (VLSE) for the system liquefied gas (2-methylpropane and propane) + dodecanoic acid + tetradecanoic acid. The effect of the liquefied gases on the solubility of saturated fatty acids was discussed.

2. Experimental Section

2.1. Materials. Dodecanoic acid and tetradecanoic acid from Nacalai Tesque Co. were used without purification. Purities were more than 99%, as analyzed by gas chromatography. 2-methylpropane and propane were from Sumitomo Seika Co., and their purities were more than 99.9%, as analyzed by gas chromatography.

2.2. Experimental Procedures. The experimental apparatus previously reported (Nagahama et al., 1991) was used. First, 0.02 kg of the fatty acids of known mole fraction of dodecanoic acid was fed to a glass cell (TAIATSU glass V100) capable of withstanding a pressure of 0.2 MPa. Air in the cell was removed after the fatty acids were frozen at liquid nitrogen temperature. Next, the liquefied gas was fed into the glass cell from the liquefied gas reservoir. The mass of liquefied gas in the solution was determined by the change of mass of the liquefied gas reservoir. All mole fractions in the solution were calculated by all mass in the feed.

The solution in the glass cell was agitated at 350 revolutions per minute (rpm), and the temperature of the solution was controlled by a thermostat bath. The solution was heated to 333 K to dissolve the saturated fatty acids completely. After vapor−liquid equilibrium (VLE) was established, the solution was slowly cooled at 0.5 K/min. The variation of the temperature and pressure with time
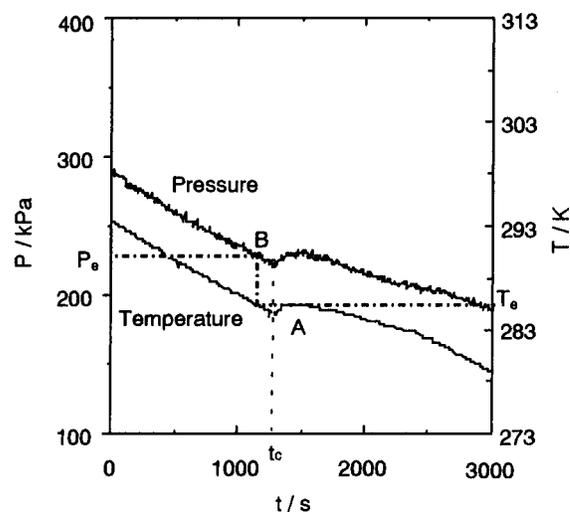
* Author to whom correspondence should be addressed. E-mail: maeda@mech.eng.himeji-tech.ac.jp.

Figure 1. Determination of vapor−liquid−solid equilibrium from the cooling curve.

in the cell were measured by the platinum resistance (Shimaden) and a pressure gauge (Setra Systems, Inc. Acton, MA). The temperature and pressure data were entered automatically into the personal computer. The platinum resistance previously was calibrated using the melting temperature and the boiling temperature of distilled water (based on ITS-90). The pressure gauge was calibrated using the vapor pressure of pure 2-methylpropane represented by the Wagner equation (Prausnitz, 1987). Temperature and pressure were measured within accuracies of 0.1 K and 0.5 kPa respectively. Typical temperature and pressure plots for the solution during cooling are shown in Figure 1. After the solution was cooled to t_c, the temperature and pressure suddenly increased. Point A on the cooling curve was cited as the equilibrium temperature (T_e). Point A remained at a constant temperature for a few minutes after the release of supercooling. The equilibrium pressure (P_e) was considered as point B, which had been the VLE on the cooling curve before the fatty acid crystallized. The cooling curves were measured more than twice for each solution. The equilibrium temperatures were reproducible to within 0.1 K. The equilibrium pressures were reproduced to within 1 kPa. Accuracy of the mole fractions in the solution was ±0.001.

Table 1. Vapor−Liquid−Solid Equilibrium Data for Propane (1) + Dodecanoic Acid (2) + Tetradecanoic Acid (3)

x_1	x_2	x_3	T_e/K	P_e/kPa
0.104	0.896	0	316.1	94
0.178	0.822	0	314.9	175
0.405	0.595	0	309.5	473
0.533	0.468	0	305.5	645
0.693	0.307	0	301.9	709
0.121	0.615	0.264	306.2	96
0.205	0.556	0.239	304.6	173
0.423	0.404	0.173	299.7	392
0.537	0.324	0.139	295.9	509
0.711	0.202	0.086	289.5	608
0.129	0.436	0.435	308.2	105
0.205	0.398	0.397	307.0	181
0.448	0.276	0.276	301.8	454
0.552	0.224	0.224	298.2	568
0.732	0.134	0.134	295.4	635
0.103	0.269	0.623	316.4	91
0.195	0.242	0.563	314.9	183
0.422	0.174	0.404	310.5	480
0.555	0.134	0.311	307.7	663
0.721	0.084	0.195	304.6	736
0.136	0	0.864	324.9	132
0.230	0	0.770	323.5	241
0.431	0	0.569	322.2	380
0.577	0	0.423	317.5	718
0.739	0	0.261	315.2	890

Table 2. Vapor−Liquid−Solid Equilibrium Data for 2-Methylpropane (1) + Dodecanoic Acid + (2) Tetradecanoic Acid (3)

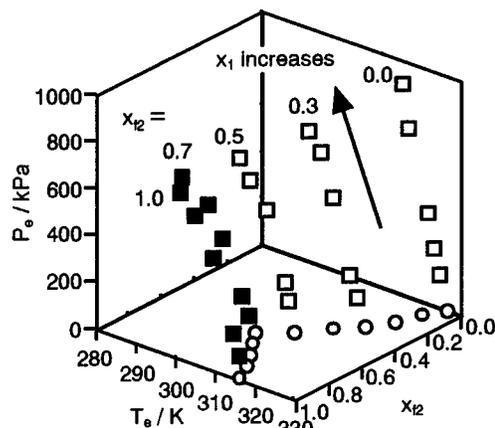| x_1	x_2	x_3	T_e/K	P_e/kPa
0.085	0.915	0	315.5	65
0.203	0.797	0	313.0	135
0.341	0.659	0	309.7	215
0.460	0.540	0	306.0	267
0.772	0.228	0	295.0	305
0.082	0.642	0.276	306.3	50
0.155	0.591	0.254	304.5	87
0.360	0.448	0.192	299.5	176
0.500	0.350	0.150	295.5	216
0.781	0.153	0.066	285.8	234
0.102	0.449	0.449	307.6	60
0.149	0.426	0.425	307.1	82
0.370	0.315	0.315	301.9	185
0.500	0.250	0.250	298.2	226
0.787	0.106	0.106	288.3	257
0.080	0.276	0.644	315.9	49
0.155	0.254	0.591	314.6	91
0.410	0.177	0.413	309.3	234
0.483	0.155	0.362	307.1	268
0.792	0.063	0.145	298.2	317
0.101	0	0.899	324.9	66
0.171	0	0.829	323.7	113
0.372	0	0.628	319.8	259
0.504	0	0.496	315.8	324
0.799	0	0.201	307.3	396

Figure 2. Vapor−liquid−solid equilibrium for propane (1) + dodecanoic acid (2) + tetradecanoic acid (3): ○ I.C.T. (1928); ■ dodecanoic acid crystallizing; □ tetradecanoic acid crystallizing.

Figure 3. Vapor−liquid−solid equilibrium for 2-methylpropane (1) + dodecanoic acid (2) + tetradecanoic acid (3): ○ I.C.T. (1928); ■ dodecanoic acid crystallizing; □ tetradecanoic acid crystallizing.

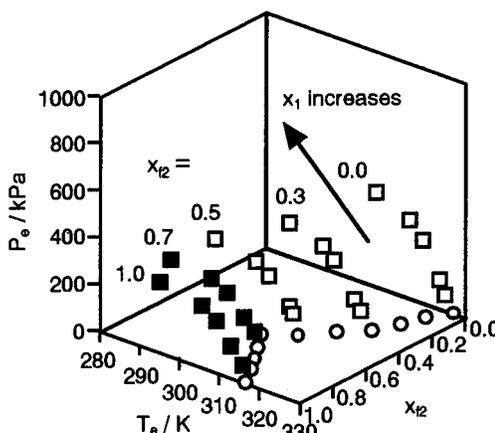where tetradecanoic acid crystallized. Dodecanoic acid crystallized in the region 0.6−1.0. The eutectic point appeared near $x_{f2} = 0.6$.

3. Experimental Results

VLSE data (25 points) for the system propane (1) + dodecanoic acid (2) + tetradecanoic acid (3) and VLSE data (25 points) for the system 2-methylpropane (1) + dodecanoic acid (2) + tetradecanoic acid (3) are listed in Tables 1 and 2 respectively. The VLSE phase diagrams for the two ternary systems are shown in Figures 2 and 3. As the mole fraction of liquefied gas (x_1) increased, the equilibrium temperature (T_e) decreased and the equilibrium pressure (P_e) increased. When the liquefied gas-free mole fraction of dodecanoic acid (x_{f2}) increased from 0 to 0.6, the equilibrium temperature (T_e) and the pressure (P_e) decreased. When the liquefied gas-free mole fraction of dodecanoic acid (x_{f2}) increased to more than 0.6, the equilibrium temperature (T_e) and the pressure (P_e) increased. The range between 0 and 0.6 was the region

4. Correlation

The saturated fatty acid dissolved in the liquefied gas will generally form a complex by two carboxyl functional groups (Maeda, 1996). The equilibrium reaction of solvation for the binary fatty acid mixture is given by the following formula. For dodecanoic acid + dodecanoic acid

$$A + A = A_2 \tag{1}$$

$$k_A = x_{A2}/(x_A{}^2) \tag{2}$$

where x_A is the mole fraction of dimer dodecanoic acid and x_{A2} is the mole fraction of dimer dodecanoic acid. k_A is the dimerization constant (dodecanoic acid + dodecanoic acid). For tetradecanoic acid + tetradecanoic acid

$$B + B = B_2 \tag{3}$$

$$k_B = x_{B2}/(x_B{}^2) \tag{4}$$

where x_B is the mole fraction of monomer tetradecanoic acid and x_{B2} is the mole fraction of dimer tetradecanoic acid. k_B is the dimerization constant (tetradecanoic acid + tetradecanoic acid). For dodecanoic acid + tetradecanoic acid

$$A + B = AB \tag{5}$$

$$k_{AB} = x_{AB}/(x_A)(x_B) \tag{6}$$

where x_{AB} is the mole fraction of solvate of dodecanoic acid and tetradecanoic acid and k_{AB} is the solvation constant (dodecanoic acid + tetradecanoic acid).

If the dimers and the solvates are taken into consideration, the solution will consist of six components (liquefied gas, dodecanoic acid, tetradecanoic acid, dimer dodecanoic acid, dimer tetradecanoic acid, solvate dodecanoic acid + tetradecanoic acid). Using the mole fraction of liquefied gas (x_g), mole fraction of dodecanoic acid ($x_{A,T}$) and mole fraction of tetradecanoic acid ($x_{B,T}$) of nonassociated solution, the mole fraction (x_A) of dodecanoic acid and the mole fraction (x_B) of tetradecanoic acid in solvation equilibrium can be given by the following equations.

$$x_g = (1 - x_A - x_B - (k_A x_A{}^2 + k_B x_B{}^2 + k_{AB} x_A x_B))/S \tag{7}$$

$$x_{A,T} = (x_A + 2k_A x_A{}^2 + k_{AB} x_A x_B)/S \tag{8}$$

$$x_{B,T} = (x_B + 2k_B x_B{}^2 + k_{AB} x_A x_B)/S \tag{9}$$

where

$$S = 1 + k_A x_A{}^2 + k_B x_B{}^2 + k_{AB} x_A x_B \tag{10}$$

VLE of six components can be given by

$$P_e = P^{\circ}_g x_g \gamma_g + P^{\circ}_A x_A \gamma_A + P^{\circ}_B x_B \gamma_B + P^{\circ}_{A2} x_{A2} \gamma_{A2} + P^{\circ}_{B2} x_{B2} \gamma_{B2} + P^{\circ}_{AB} x_{AB} \gamma_{AB} \tag{11}$$

where P_e is the total equilibrium pressure, P°_i is the vapor pressure of the i pure substance, and γ is an activtiy coefficient in the solution. Since the partial pressures of dodecanoic acid and tetradecanoic acid are considerably lower than for the liquefied gas, the total equilibrium pressure can be calculated by the following equation.

$$P_e = P^{\circ}_g x_g \gamma_g \tag{12}$$

However, activity is still important for the equilibrium constant.

Some investigations have suggested that the crystals of fatty acids are constructed by dimer unit (Goto et al, 1978a,b). It is a natural consideration that only the dimers of fatty acids can transform from a liquid state to a crystal state. When the dimers of fatty acids in the solution form a crystal state, the SLE of the dodecanoic acid and tetradecanoic acid should be calculated by

$$\ln(x_{A2}\gamma_{A2}) = 2\Delta_{fus}H_{mA}/R\,(1/T_{mA} - 1/T_e) \tag{13}$$

$$\ln(x_{B2}\gamma_{B2}) = 2\Delta_{fus}H_{mB}/R\,(1/T_{mB} - 1/T_e) \tag{14}$$

where H_m is a fusion enthalpy and T_m is a melting temperature. Those values are listed in Table 3. R is the gas constant, and T_e is the equilibrium temperature. The activity coefficients of eqs 12–14 are calculated by the NRTL equation (Poling et al., 1987). Simulating eqs 12 and 13 or 14, the three-phase equilibria can be represented. The nonlinear least-squares method was used for fitting parameters (2 dimerization constants, 1 solvation constant, and 20 NRTL parameters for the two ternary systems in Table 4). The nonrandomness parameter of NRTL was fixed at 0.3. The *P-T* diagrams of the correlated results are described in Figures 4 and 5. Average deviations of the equilibrium temperature and the equilibrium pressure

Table 3. Enthalpies of Fusion and Melting Temperatures of Pure Fatty Acids (Landolt-Bornstein, 1996)

	$\Delta_{fus}H$/J·mol^{-1}	T_m/K
dodecanoic acid	36300	317.0
tetradecanoic acid	45100	327.3

Table 4. Correlated Dimerization and Solvation Constants and NRTL Parameters[a]

	k_{22} 800	k_{33} 500	k_{23} 2200		
dodecanoic acid	Δg_{1-2} −14230	Δg_{1-3} −17825	Δg_{1-22} −420	Δg_{1-33} −764	Δg_{1-23} 1912
tetradecanoic acid	Δg_{1-2} −5132	Δg_{1-3} −9005	Δg_{1-22} −100	Δg_{1-33} −424	Δg_{1-23} 1090
		Δg_{2-3} 10590	Δg_{2-22} 660	Δg_{2-33} −15900	Δg_{-2-23} 10054
			Δg_{3-22} −50	Δg_{3-33} −6321	Δg_{3-23} −6003
				Δg_{22-33} 7333	Δg_{22-23} −824
					Δg_{33-23} 942

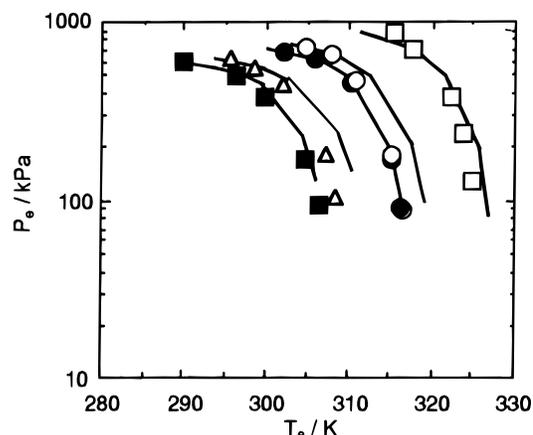[a] $\Delta g_{i-j} = \Delta g_{j-i}$ (J·mol^{-1}), nonrandomness parameter $\alpha = 0.3$.

Figure 4. Vapor−liquid−solid equilibrium for propane (1) + dodecanoic acid (2) + tetradecanoic acid (3): x_{f2} ● = 1.0, = 0.7, ■ = 0.5, △ = 0.3, ○ = 0.1, □ = 0.0, − = calcd.
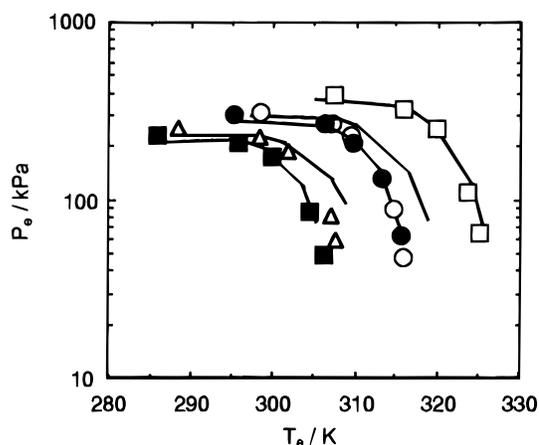

Figure 5. Vapor−liquid−solid equilibrium for 2-methylpropane (1) + dodecanoic acid (2) + tetradecanoic acid (3): x_{f2} ● = 1.0, = 0.7, ■ = 0.5, △ = 0.3, ○ = 0.1, □ = 0.0, − = calcd.

for system containing 2-methylpropane were $\Delta T = 0.5$ K and $\Delta P = 14$ kPa. Average deviations of the equilibrium temperature and the pressure for the system containing propane were $\Delta T = 0.9$ K and $\Delta P = 21$ kPa. The correlations seems to be well satisfied, even if the solutions include strong hydrogen-bonding substances. We have examined the nonassociated solution model for the cor-
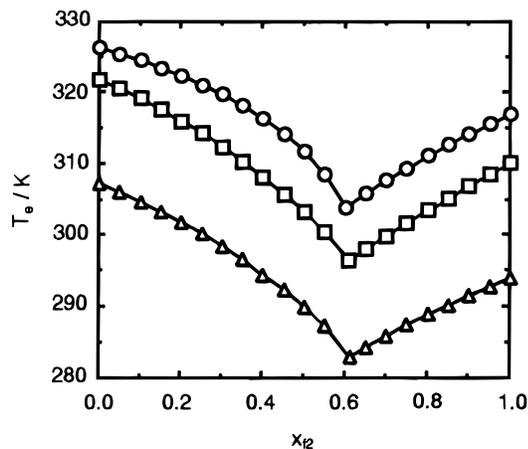
Figure 6. Solid−liquid equilibrium for propane (1) + dodecanoic acid (2) + tetradecanoic acid (3): x_1 −○− = 0.0, −□− = 0.4, −△− = 0.8.
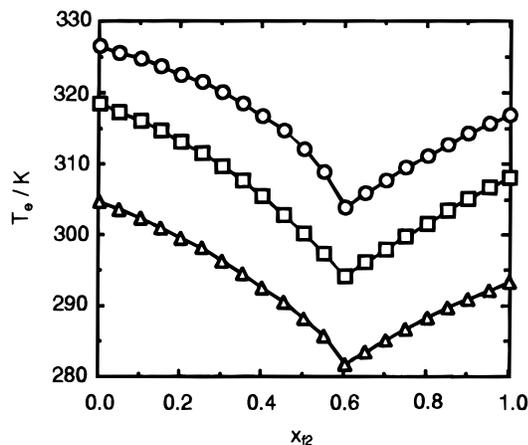

Figure 7. Solid−liquid equilibrium for 2-methylpropane (1) + dodecanoic acid (2) + tetradecanoic acid (3): x_1 = −○− = 0.0, −□− = 0.4, −△− = 0.8.

relation of VLSE, and the average deviations were 0.9 K for ΔT, 21 kPa for ΔP for the system containing 2-methylpropane and 1.3 K for ΔT, 138 kPa for ΔP for the system containing propane. The associated solution for fatty acids improved the correlation of VLSE data significantly.

Liquefied gas free-SLE for the dodecanoic acid + tetradecanoic acid system are shown in Figures 6 and 7. Both liquefied gases show little influence on the relative SLE for the dodecanoic acid + tetradecanoic acid system, but the eutectic composition changed a little toward high dodecanoic acid concentration. The equilibrium pressures containing propane were higher than those containing 2-methylpropane; however, the equilibrium temperature effectively decreased with addition of 2-methylpropane.

5. Conclusions

Vapor−liquid−solid equilibria for the system liquefied gas + dodecanoic acid + tetradecanoic acid were measured. If the association of fatty acids is considered, the three-phase equilibria can be well correlated with the experimental values. Even if the liquefied gases were added to the solution, the solid−liquid equilibria were barely changed, only in a parallel manner. It was found that only the liquefied gases played the role of inert solvent to decrease the melting temperature.

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