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Solid−Liquid Phase Equilibria of Binary and Ternary Mixtures for 2,6-Dimethylnaphthalene and 2,7-Dimethylnaphthalene with Ethanol or Methanol

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Experimental data of the solid−liquid equilibrium in the binary systems 2,6-dimethylnaphthalene (2,6-DMN) + 2,7-dimethylnaphthalene (2,7-DMN), 2,7-DMN + methanol, and 2,7-DMN + ethanol and solubility data in the ternary systems 2,6-DMN + 2,7-DMN + methanol and 2,6-DMN + 2,7-DMN + ethanol are presented.

Introduction

2,6-Dimethylnaphthalene (DMN) is a starting material for the manufacture of polyethylene naphthalate (PEN). PEN has received much attention because it has better heat resistance, elasticity, chemical stability, and gas barrier properties than poly(ethylene terephthalate). Such better performance properties make it possible to be used in applications such as special films, fibers, reaction containers, and packings.

In the present work, we carried out the separation of 2,6-DMN from 2,6-DMN + 2,7-DMN mixtures by extractive crystallization.[1] It is difficult to separate 2,6-DMN from 2,7-DMN by melt crystallization because they form a eutectic point (mole fraction of 2,6-DMN = 0.41). Extractive crystallization[2−6] was one possible method of purifying 2,6-DMN from 2,6-DMN + 2,7-DMN mixtures. The solid−liquid phase equilibria (SLE) data for the extractive crystallization processes are used for the separation of isomers. An extractive solvent that can improve the crystal quality must be selected. From these points of view, methanol and ethanol are recommended as suitable extractive solvents in an extractive crystallizer. The solubility of 2,6-DMN and 2,7-DMN must be known to interpret the kinetics of extractive crystallization. In previous work, the solubility of 2,6-DMN in C_1 to C_7 1-alkanols was measured.[7]

In this work, solid solubility data in the binary systems 2,7-DMN + methanol and 2,7-DMN + ethanol and in the ternary systems 2,6-DMN + 2,7-DMN + methanol and 2,6-DMN + 2,7-DMN + ethanol have been measured over the temperature range from 245 K to 350 K at the operating conditions of the separation of 2,6-DMN by extractive crystallization. The SLE behavior was also investigated for mixtures of 2,6-DMN + 2,7-DMN.

Experimental Section

Materials. Reagent-grade 2,6-DMN and 2,7-DMN (Aldrich Chemical Co., +99%) were used. Before use, 2,6-DMN and 2,7-DMN were purified further by recrystallization using methanol. After recrystallization, the purities were greater than 99.9% and 99.5%, respectively. The materials were analyzed with a flame-ionization detection gas chromatograph (FID DONAM GC 6200) equipped with capillary columns (Shinwa, GC-8A capillary column ULBON HR-1). Methanol (Hayman Ltd., +99.5%) and ethanol (Jin Chemical Pharmaceutical Co., +99.5%) as extractive solvents were used. Methanol and ethanol were used without further purification. The properties of the pure components are listed in Table 1.

Table 1. Physical Properties of 2,6-DMN, 2,7-DMN, Ethanol, and Methanol

compound	T_{fus}/K	T_b/K	ρ/g cm^{-3}	$\Delta_{fus}H$/kJ mol^{-1}
2,7-DMN	371.15[8]	535.15[8]	1.010[9]	23.35[9]
2,6-DMN	385.15[8]	535.15[8]	1.020[9]	25.06[9]
methanol[10]	176.00	337.00	0.786	2.196
ethanol[10]	159.00	351.50	0.785	4.962

Measurement of Solid−Liquid Equilibrium. The mixtures were prepared with a Metter AG 204 balance with an accuracy of ±0.0001 g. The estimated error in the mass fraction is less than $\pm 2 \times 10^{-4}$. The solid−liquid equilibrium temperature of the 2,6-DMN + 2,7-DMN system was measured under atmospheric pressure with a differential scanning calorimeter (DSC, TA Instruments). Inert gas (He or N_2) was flushed throughout the DSC furnace to avoid condensation at purge rates of 7 to 30 mL min^{-1}. The experimental temperature was 320 K to 400 K. A small amount of sample was weighed in a sample pan. The sample was then heated at a fixed rate of 1 K min^{-1} to reach the final temperature, which is much higher than the expected solubility temperature.

The solubilities of 2,6-DMN + 2,7-DMN, 2,7-DMN + methanol or ethanol, and 2,6-DMN + 2,7-DMN + methanol or ethanol were measured with a polythermal method using a previously published method.[7] The equilibrium cell and a cylindrical glass vessel (50 mm inside diameter, 120 mm long) was placed in a triple-jacketed vessel by a ground-glass joint. The outer jacket was evacuated. Either a heated or cooled medium from a thermostated bath could be circulated through the middle jacket. The ethylene glycol

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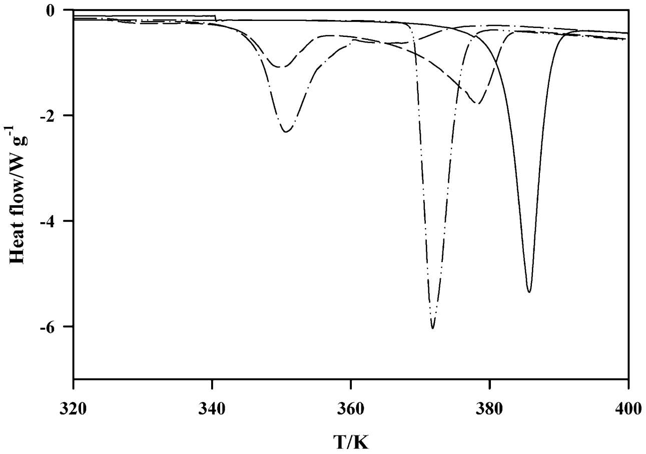

Figure 1. DSC curves of different mixtures for the 2,6-DMN (x_1) + 2,7-DMN system: –, x_1 = 1.0; - - -, x_1 = 0.8; -·-, x_1 = 0.2; -··-, x_1 = 0.0.

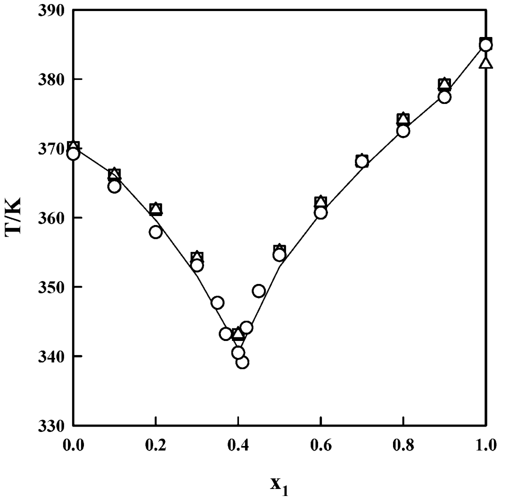

Figure 2. Binary phase diagram of 2,6-DMN + 2,7-DMN mixtures: ○, DSC measurement; □, polythermal method; △, Iwai Y. et al.;[14] –, Ott and Goates' fitting.

Table 2. Experimental Solid−Liquid Equilibrium of the 2,6-DMN (1) + 2,7-DMN (2) System

	T/K	
x_1	DSC	polythermal method
0.00	369.1	370
0.10	364.4	366
0.20	357.8	361
0.30	353.0	354
0.35	347.6	
0.37	343.1	
0.40	340.4	343
0.41	339.0	
0.42	344.0	
0.45	349.3	
0.50	354.5	355
0.60	360.6	362
0.70	368.0	368
0.80	372.4	374
0.90	377.3	379
1.00	384.8	385

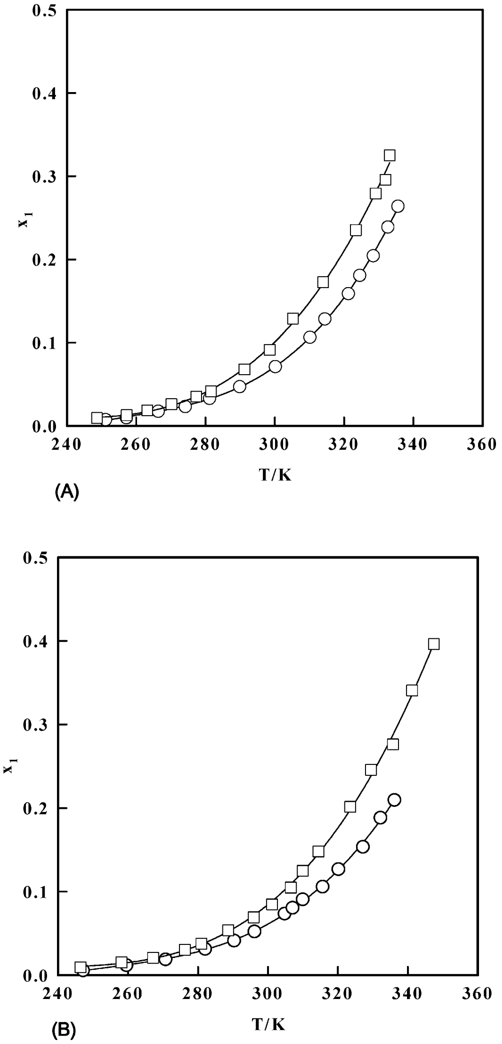

Figure 3. Solubility of 2,6-DMN (○) and 2,7-DMN (□) in (A) methanol and (B) ethanol.

Table 3. Coefficients of Equation 1

x_1^*	T^*/K	a_1	a_2	a_3	a_4	a_5	σ/K
0.0	371.15	0.5341	1.0057	0.4719			0.05
1.0	385.15	0.2100	0.9016	4.3427	8.7613	6.4957	0.27

Table 4. Experimental Solubilities and Activity Coefficients of 2,7-DMN in Methanol or Ethanol

2,7-DMN (1) + methanol (2)			2,7-DMN (1) + ethanol (2)		
T/K		$x_1^L\gamma_1^L$	*T*/K	x_1^L	γ_1^L
248.5	0.0094	2.5527	246.3	0.0094	2.3027
257.1	0.0130	2.7090	258.0	0.0153	2.3872
263.0	0.0187	2.3946	267.0	0.0208	2.5245
270.0	0.0261	2.2618	276.1	0.0303	2.4536
277.2	0.0353	2.1931	280.8	0.0378	2.3312
281.4	0.0414	2.1730	288.5	0.0537	2.1433
291.1	0.0680	1.8452	295.8	0.0693	2.1086
298.4	0.0912	1.7414	301.0	0.0846	2.0361
305.1	0.1291	1.5123	306.4	0.1047	1.9380
313.8	0.1727	1.4591	309.8	0.1249	1.7965
323.3	0.2353	1.3921	314.3	0.1480	1.7260
329.0	0.2792	1.3637	323.4	0.2014	1.6308
331.8	0.2959	1.3829	329.3	0.2458	1.5610
333.0	0.3249	1.2984	335.6	0.2762	1.6302
			341.1	0.3407	1.5126
			347.3	0.3963	1.5049

+ water mixture was thermostated and controlled by a thermoelectric Eurotherm 808 PID controller with ±0.1 K accuracy. The cell had a perforated rubber stopper through which a copper−constantan thermocouple was inserted. The contents were stirred with a magnetic spin bar. The cell was tightly sealed to protect the system from dust and moisture condensation. Mixtures of solute and solvent were cooled in a batch until an abundant amount of crystals were formed and then heated very slowly at less than 0.001 K min^{-1} near the equilibrium temperature. The crystal

Table 5. Experimental Data for the Ternary System of 2,6-DMN (1) + 2,7-DMN (2) + Methanol (3)

x_1	x_2	x_3	x_1	x_2	x_3
T = 273.15 K			T = 283.15 K		
0.00000	0.00699	0.99301	0.00000	0.01091	0.98909
0.00090	0.00812	0.99098	0.00133	0.01199	0.98668
0.00451	0.01050	0.98499	0.00622	0.01452	0.97926
0.01234	0.01851	0.96916	0.01692	0.02538	0.95770
0.00839	0.00840	0.98321	0.01209	0.01209	0.97583
0.00728	0.00313	0.98959	0.01062	0.00455	0.98483
0.00592	0.00058	0.99350	0.00906	0.00090	0.99004
0.00488	0.00000	0.99512	0.00760	0.00000	0.99240
T = 293.15 K			T = 303.15 K		
0.00000	0.01678	0.98322	0.00000	0.02581	0.97419
0.00196	0.01769	0.98035	0.00290	0.02610	0.97100
0.00860	0.02007	0.97133	0.01189	0.02774	0.96037
0.02321	0.03481	0.94198	0.03183	0.04774	0.92043
0.01719	0.01719	0.96562	0.02474	0.02474	0.95052
0.01568	0.00672	0.97760	0.02285	0.00979	0.96736
0.01372	0.00136	0.98492	0.02076	0.00205	0.97719
0.01168	0.00000	0.98832	0.01795	0.00000	0.98205
T = 313.15 K			T = 323.15 K		
0.00000	0.03970	0.96030	0.00000	0.06195	0.93805
0.00428	0.03852	0.95720	0.00632	0.05685	0.93683
0.01643	0.03834	0.94523	0.02271	0.05300	0.92429
0.04366	0.06548	0.89086	0.05987	0.08981	0.85031
0.03561	0.03561	0.92877	0.05065	0.05065	0.89871
0.03374	0.01446	0.95181	0.04982	0.02135	0.92883
0.03182	0.00315	0.96503	0.04814	0.00477	0.94709
0.02798	0.00000	0.97202	0.04298	0.00000	0.95702
T = 328.15 K			T = 333.15 K		
0.00000	0.07683	0.92317	0.00000	0.09529	0.90471
0.00762	0.06860	0.92378	0.00920	0.08278	0.90802
0.02685	0.06266	0.91049	0.03139	0.07325	0.89535
0.07050	0.10576	0.82374	0.08212	0.12318	0.79470
0.06076	0.06076	0.87847	0.07202	0.07202	0.85596
0.06013	0.02577	0.91410	0.07258	0.03111	0.89631
0.05922	0.00586	0.93492	0.07191	0.00711	0.92098
0.05328	0.00000	0.94672	0.06604	0.00000	0.93396

Table 6. Experimental Data for the Ternary System of 2,6-DMN (1) + 2,7-DMN (2) + Ethanol (3)

x_1	x_2	x_3	x_1	x_2	x_3
T = 273.15 K			T = 283.15 K		
0.00000	0.00938	0.99062	0.00000	0.01413	0.98587
0.00109	0.00989	0.98902	0.00170	0.01528	0.98302
0.00387	0.00904	0.98709	0.00639	0.01492	0.97869
0.00795	0.01193	0.98012	0.01195	0.01793	0.97011
0.00632	0.00633	0.98735	0.00999	0.00998	0.98003
0.00655	0.00282	0.99063	0.01044	0.00447	0.98509
0.00594	0.00066	0.99340	0.00934	0.00104	0.98962
0.00601	0.00000	0.99399	0.00934	0.00000	0.99066
T = 293.15 K			T = 303.15 K		
0.00000	0.03160	0.96840	0.00000	0.04758	0.95242
0.00344	0.03136	0.96520	0.00489	0.04375	0.95136
0.01420	0.03398	0.95182	0.02398	0.04995	0.92607
0.02601	0.03902	0.93497	0.03861	0.05792	0.90346
0.01888	0.01888	0.96223	0.02523	0.02523	0.94953
0.01894	0.00804	0.97302	0.02524	0.01225	0.96251
0.01801	0.00212	0.97987	0.02108	0.00360	0.97532
0.01885	0.00000	0.98115	0.02502	0.00000	0.97498
T = 313.15 K			T = 323.15 K		
0.00000	0.07065	0.92935	0.00000	0.08609	0.91391
0.00719	0.06263	0.93018	0.00849	0.07470	0.91681
0.03792	0.07784	0.88423	0.04653	0.09208	0.86139
0.05806	0.08709	0.85485	0.07029	0.10544	0.82427
0.03491	0.03491	0.93019	0.04138	0.04138	0.91724
0.03488	0.01633	0.94879	0.04133	0.01886	0.93981
0.02955	0.00542	0.96503	0.03498	0.00652	0.95850
0.03447	0.00000	0.96553	0.04062	0.00000	0.95938
T = 328.15 K			T = 333.15 K		
0.00000	0.10640	0.89360	0.00000	0.13043	0.86957
0.01019	0.09260	0.89721	0.01228	0.11053	0.87719
0.05773	0.10763	0.83464	0.05410	0.12623	0.81967
0.08619	0.12929	0.78452	0.11429	0.17143	0.71429
0.04902	0.04902	0.90196	0.05357	0.05357	0.89286
0.04901	0.02099	0.93000	0.05780	0.02477	0.91743
0.04142	0.00773	0.95085	0.05094	0.00566	0.94340
0.04597	0.00000	0.95403	0.05213	0.00000	0.94787

disappearance temperature by visual detection was measured with a calibrated thermocouple connected to a recorder (Yokogawa, 180 micro R). The thermocouples were calibrated with a calibrated thermometer from Fisher Scientific (no. 15-078-7) with an accuracy of ±0.05 K. The accuracy of the thermocouple measurements is believed to be ±0.1 K. Some experiments were conducted three times to check the reproducibility. The saturation temperature for a given mixture was reproducible to within ±0.1 K.

Results and Discussion

Binary Phase Diagram of the 2,6-DMN + 2,7-DMN System. The solid−liquid equilibrium temperature of the 2,6-DMN + 2,7-DMN system was measured under the atmospheric pressure by DSC and polythermal methods. Figure 1 shows the DSC curves for 2,6-DMN mole fraction (x_1) of 0, 0.2, 0.8, and 1 in the mixture 2,6-DMN + 2,7-DMN. The experimental results are shown in Figure 2 and listed in Table 2. Figure 2 shows that the present system is a simple eutectic mixture and that the experimental results are similar to the Iwai et al.[11] experimental results.

The experimental melting temperatures obtained in this study were fit by the empirical equation of Ott and Goates,[12] expressed as

$$T = T^*[1 + \sum_{j=1}^{n} a_j(x_i - x_i^*)^j] \tag{1}$$

where T^* is the solid-disappearance temperature of a pure compound or congruent complex at composition x_i^*, T is the melting point at composition x_i, and a_j represents the coefficients to be regressed to the experimental data. Table 3 gives the best-fit coefficients, and the fitting result is plotted in Figure 2.

The average absolute deviations σ of the equilibrium temperatures are given by

$$\sigma/\mathrm{K} = \left(\frac{1}{N}\right)\sum_{i=1}^{N} |T_{\mathrm{calcd},i} - T_{\mathrm{exptl},i}| \tag{2}$$

where N is the number of experimental points. The subscripts calcd and exptl stand for the calculated values and the experimental values. The σ between the measured solubility data and the data calculated from eq 1 are listed in Table 3.

Solubility of 2,6-DMN and 2,7-DMN with Methanol or Ethanol. The solubility of 2,7-DMN in ethanol and methanol was measured over the temperature range from 246.45 K to 347.42 K, and the values are listed in Table 4. The solubility of 2,7-DMN increases with the temperature. The temperature dependence on solubility is higher. The solubility of 2,7-DMN in methanol is lower than in ethanol. This means that the solubility of 2,7-DMN in methanol and ethanol increases with increasing polarity of the solvent.

Solubility data can be used to estimate the activity coefficient through the equilibrium relationship. If no solid−solid transition occurs in the experimental temperature range, then solid−liquid equilibria of binary systems can be calculated by the following simplified thermodynamic relation[13,14]

$$\ln x_i^{\mathrm{L}}\gamma_i^{\mathrm{L}} = -\frac{\Delta_{\mathrm{fus}}H_i}{RT}\left(1 - \frac{T}{T_{\mathrm{fus},i}}\right) \tag{3}$$

where x_i^{L} is the mole fraction of component i in the liquid

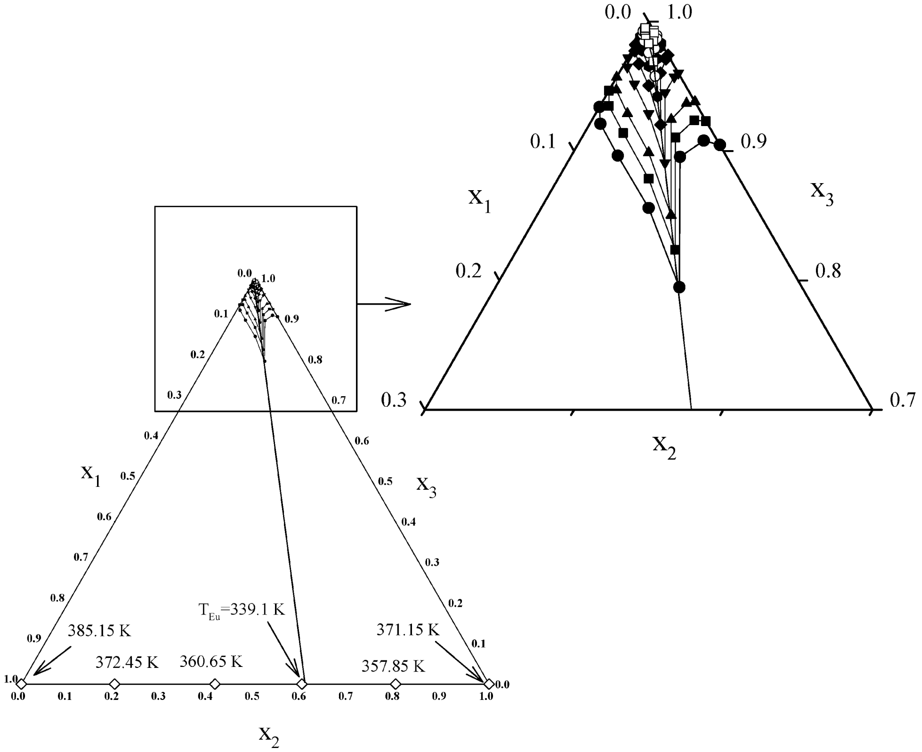

Figure 4. Ternary phase diagram of the 2,6-DMN (1) + 2,7-DMN (2) + methanol (3) system: ●, 333.15 K; ■, 328.15 K; ▲, 323.15 K; ▼, 313.15 K; ♦, 303.15 K; ○, 293.15 K; □, 283.15 K; △, 273.15 K.

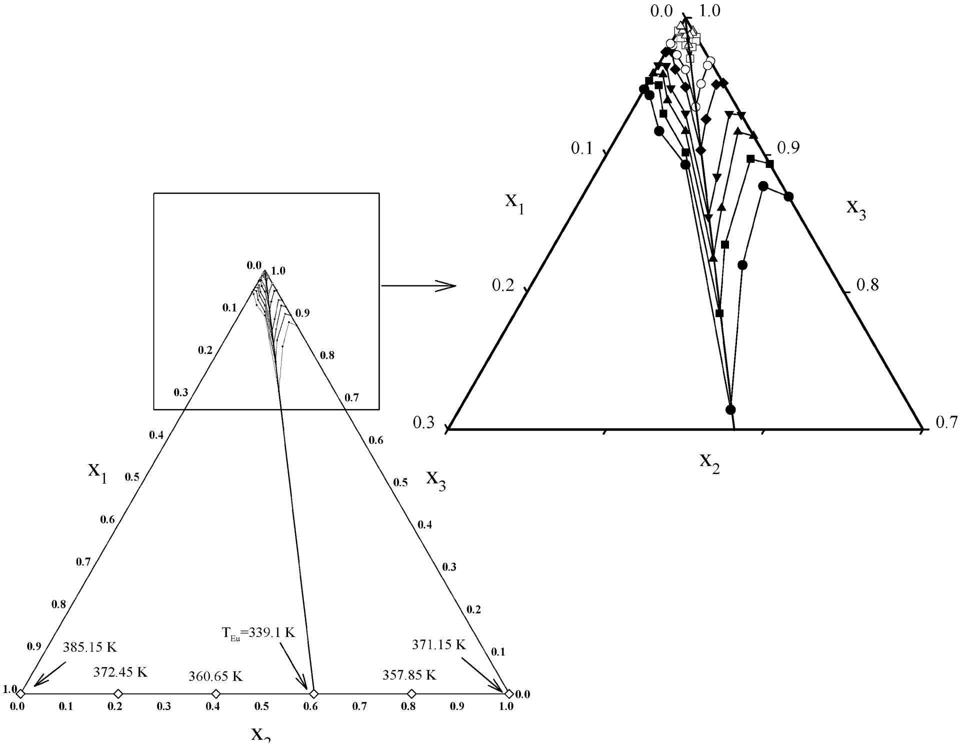

Figure 5. Ternary phase diagram of the 2,6-DMN (1) + 2,7-DMN (2) + ethanol (3) system: ●, 333.15 K; ■, 328.15 K; ▲, 323.15 K; ▼, 313.15 K; ♦, 303.15 K; ○, 293.15 K; □, 283.15 K; △, 273.15 K.

phase, γ_i^L is the activity coefficient in the liquid phase, $\Delta_{fus}H_i$ is the molar enthalpy of fusion, $T_{fus,i}$ is the melting temperature of pure component i, T is the absolute temperature of the mixture, and R is the universal gas constant. In this work, the activity coefficient was calculated using eq 3 from the experimentally determined solution composition and temperature. The activity coefficients are given in Table 4. The solubility of 2,7-DMN in methanol or ethanol was lower than the solubility expected from ideal solution behavior. The solution showed positive deviations from ideality ($\gamma_1 \gg 1$).

In previous work,[10] the solubility of only 2,6-DMN in methanol and ethanol was measured. Figure 3 shows the comparison of the solubility of 2,6-DMN and 2,7-DMN in methanol and ethanol. As shown in Figure 3, the difference in the solubility of 2,6-DMN and 2,7-DMN is larger. Therefore, a combination of cooling and extractive crystallization can be recommended for the separation of 2,6-DMN from 2,6-DMN + 2,7-DMN mixtures using extractive solvents such as methanol and ethanol.

Ternary Phase Diagram of 2,6-DMN + 2,7-DMN with Methanol or Ethanol. The solubility of ternary systems for 2,6-DMN + 2,7-DMN in ethanol or methanol was measured over the temperature range from 273.15 K to 333.15 K. The values are listed in Tables 5 and 6 and plotted in Figures 4 and 5. These solid−liquid phase equilibria (SLE) from the basis of the cooling and extractive crystallization processes can used in the chemical industry for the separation of 2,6-DMN from 2,6-DMN + 2,7-DMN mixtures.

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