Solid−Liquid Equilibria in Binary Mixtures of 1,8-Cineole with *p*-Cymene, *β*-Pinene, and Camphene

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Solid−liquid equilibria have been measured for binary mixtures of 1,8-cineole with *p*-cymene, *β*-pinene, and camphene, respectively, using differential scanning calorimetry (DSC) over the whole composition concentration range. All three are simple eutectic systems. The eutectic point of the (1,8-cineole (1) + *p*-cymene (2)) mixture is at 200.0 K and $x_1 = 0.124$, the (1,8-cineole (1) + *β*-pinene (2)) mixture at 205.6 K and $x_1 = 0.154$, and the (1,8-cineole (1) + camphene (2)) mixture at 251.8 K and $x_1 = 0.582$. An empirical equation of Ott and Goates was used for correlating the experimental data.

Introduction

1,8-Cineole, also known as eucalyptol, is a natural constituent of the essential oil fraction from several natural sources.[1] It is widely used in medicinal, perfumery, and flavor preparations.[2] Furthermore, recent clinical research has shown that 1,8-cineole also presents anti-inflammatory and pain release properties and may promote leukemia cell death.[3−5] It is reported to be particularly abundant in leaves, and its content in the essential oil of different eucalyptus species varies between 25 % and 90 %. In addition to the 1,8-cineole compound, the essential oil of leaves from eucalyptus species contains, in relatively high amounts, several monoterpene hydrocarbons: α-pinene, *β*-pinene, limonene, *p*-cymene, camphene, and so forth, with the first three in major amounts.[6] To study the separations of 1,8-cineole from the rectified eucalyptus oil by batch crystallization, the solid−liquid equilibria for the binary systems (1,8-cineole + α-pinene), (1,8-cineole + limonene), and (α-pinene + limonene) and for the ternary system (1,8-cineole + α-pinene + limonene) have been published by Gomes et al.[7] The phase diagrams for (1,8-cineole + phenol, + cyclohexanol, + methanol, + ethanol, + 1-propanol, and + 1-butanol) have been studied by Huang et al.[8] In the present study, complete data obtained by differential scanning calorimeter (DSC) for the solid−liquid equilibria binary systems of 1,8-cineole with *p*-cymene, *β*-pinene, and camphene, respectively, have been measured. The solid−liquid equilibrium data are one of the most important process parameters and are of scientific interest for the development of the solution theory.

Experimental Section

Chemicals. 1,8-Cineole ($w = 0.995$), *p*-cymene ($w = 0.98$), *β*-pinene ($w = 0.98$), and camphene ($w = 0.98$) were purchased from Aladdin Reagent Database, Inc. Their melting temperatures were measured using a DSC (Mettler DSC 30) and are compared in Table 1. The melting temperatures of the substances are in good agreement with literature data, and all of them were used without further purification. The chemical structure of each constituent compound involved in this study is shown in Figure 1. Prior to use, these materials were kept in a desiccator with dry silica gel for at least 24 h at room temperature.

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Apparatus and Procedure. The solid−liquid equilibria of the binary systems were determined using a Mettler DSC apparatus (model DSC 30) that was equipped with a heating system under nitrogen circulation and a cooling accessory using liquid nitrogen as the cooling agent. The experimental procedure was described in detail in our previous work.[12] During the scanning operation, high purity nitrogen gas was purged through the DSC chamber at 50 mL·min^{-1}. The measurements were carried out under fixed conditions of a constant heating rate of 2 K·min^{-1}. The uncertainties of the measurements are estimated to be ± 0.2 K for the temperature.

To obtain a uniform material, each mixture sample (about 1 g) was prepared by weighing the pure compounds with an accuracy of ± 0.1 mg and sealing them in a tiny glass vial. The liquefied sample was then shaken vigorously. Then, a small amount of sample about 5 mg was taken and sealed in a Mettler sample crucible for the analysis. The experimental uncertainties for the mole fraction are estimated to be ± 0.0005.

We adopted the method in which liquidus and solidus curves were estimated from the onset and peak temperatures obtained from the measured DSC curves.

Results and Discussion

The experimental data, reported in Table 2 and Figures 2, 3, and 4, clearly show that all of the systems can be considered as the simple eutectic system. The compositions of the liquid phase in the eutectic points were determined by extrapolation. For the (1,8-cineole (1) + *p*-cymene (2)) system we observe an eutectic point at 200.0 K and $x_1 = 0.124$. The (1,8-cineole (1) + *β*-pinene (2)) and (1,8-cineole (1) + camphene (2)) systems show the eutectic point at 205.6 K and $x_1 = 0.154$ and 251.8 K and $x_1 = 0.582$, respectively.

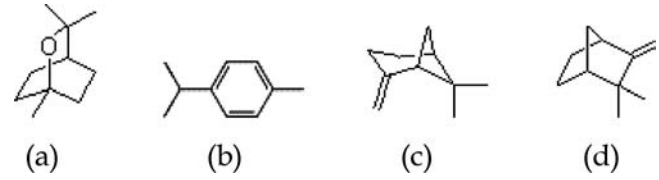

Figure 1. Chemical structures of (a) 1,8-cineole, (b) *p*-cymene, (c) *β*-pinene, and (d) camphene.

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Table 1. Characteristics of Pure Compounds

substance	IUPAC name	CAS RN	formula	mol wt	T_m/K this work	T_m/K lit.
1,8-cineole	1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane	470-82-6	$C_{10}H_{18}O$	154.25	274.4	273.9[9] 274.1[10] 274.6[11]
p-cymene	1-methyl-4-(1-methylethyl)benzene	99-87-6	$C_{10}H_{14}$	134.22	204.6	205.21[9,11] 204.2[10]
β-pinene	6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane	18172-67-3	$C_{10}H_{16}$	136.24	211.6	211.6[9] 212[10]
camphene	2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane	79-92-5	$C_{10}H_{16}$	136.24	324.2	325[9] 324 to 325[10]

Table 2. Experimental (Solid + Liquid) Phase Equilibrium Temperatures, *T*, for the Binary Systems[a]

x_1	T/K	$T_{(calc)}$/K	δT/K[b]	x_1	T/K	$T_{(calc)}$/K	δT/K[b]
1,8-Cineole (1) + *p*-Cymene (2)							
0	204.6	204.6	0.0	0.5208	247.1	247.2	0.1
0.0112	204.5	204.3	−0.2	0.5400	248.4	248.6	0.2
0.0251	204.1	203.9	−0.2	0.5682	249.9	250.5	0.6
0.0497	202.9	203.1	0.2	0.5811	252.1	251.3	−0.8
0.0732	202.1	202.2	0.1	0.6326	254.0	254.6	0.6
0.2041	213.7	213.5	−0.2	0.7050	259.0	258.9	−0.1
0.2486	220.0	219.9	−0.1	0.8001	264.6	264.2	−0.4
0.2781	223.5	223.8	0.3	0.8545	266.7	267.1	0.4
0.3191	228.7	228.8	0.1	0.9258	270.8	270.7	−0.1
0.3422	231.9	231.4	−0.5	0.9641	272.6	272.7	0.1
0.3601	233.4	233.2	−0.2	0.9759	273.3	273.2	−0.1
0.3831	234.9	235.6	0.7	0.9880	273.8	273.8	0.0
0.4109	238.3	238.2	−0.1	0.9910	274.1	274.0	−0.1
0.4983	246.2	245.5	−0.7	1.0000	274.4	274.4	0.0
1,8-Cineole (1) + *β*-Pinene (2)							
0	211.6	211.6	0.0	0.4422	242.3	241.8	−0.5
0.0125	210.9	211.1	0.2	0.4704	244.1	244.1	0.0
0.0256	210.7	210.7	0.0	0.5011	245.7	246.4	0.7
0.0507	210.2	210.0	−0.2	0.5578	250.1	250.5	0.4
0.0816	209.0	209.2	0.1	0.6092	253.7	253.9	0.2
0.2209	216.0	216.8	0.8	0.6513	256.9	256.5	−0.4
0.2491	221.8	221.0	−0.8	0.6972	259.8	259.2	−0.6
0.2699	223.5	223.8	0.3	0.7695	262.9	263.1	0.2
0.3015	227.7	227.7	0.0	0.8681	267.4	268.0	0.6
0.3212	230.5	230.0	−0.5	0.8999	269.9	269.6	−0.3
0.3503	232.4	233.2	0.8	0.9633	272.7	272.6	0.1
0.3777	236.8	235.9	−0.9	0.9823	273.8	273.5	−0.3
0.3998	238.0	238.0	0.0	1.0000	274.4	274.4	0.0
1,8-Cineole (1) + Camphene (2)							
0	324.2	324.2	0.0	0.4772	268.6	268.6	0.0
0.0566	319.1	319.0	−0.1	0.7165	259.8	259.8	0.0
0.1146	312.9	312.7	−0.2	0.8072	265.1	265.2	0.1
0.1555	307.9	308.1	0.2	0.8563	267.8	267.9	0.1
0.1976	302.9	303.1	0.2	0.9008	270.7	270.2	−0.5
0.2816	293.2	293.1	−0.1	0.9489	271.9	272.4	0.5
0.3632	283.5	283.3	−0.2	0.9666	273.3	273.2	−0.1
0.4291	274.8	275.0	0.2	1.0000	274.4	274.4	0.0

[a] x_1, $T_{(calc)}$, and δT denote the mole fraction of 1,8-cineole, the calculated temperature, and the deviation of the experimental temperature from the value calculated from eq 1, respectively. [b] $\delta T = T_{(calc)} - T_{(xpt)}$.

For interpolation purposes, the liquidus lines were correlated by the semiempirical equation of Ott and Goates[13]

$$T = T^*[1 + \sum_{j=1}^{n} a_j(x_1 - x_1^*)^j] \quad (1)$$

where x_1 is the mole fraction of component 1, T is the solid−liquid equilibrium temperature of the binary mixture, T^* is the melting temperature of the pure substance, x_1^* is the value of x_1 at $T = T^*$, and a_j's are the coefficients to be determined by regression to the experimental solid−liquid equilibrium data.

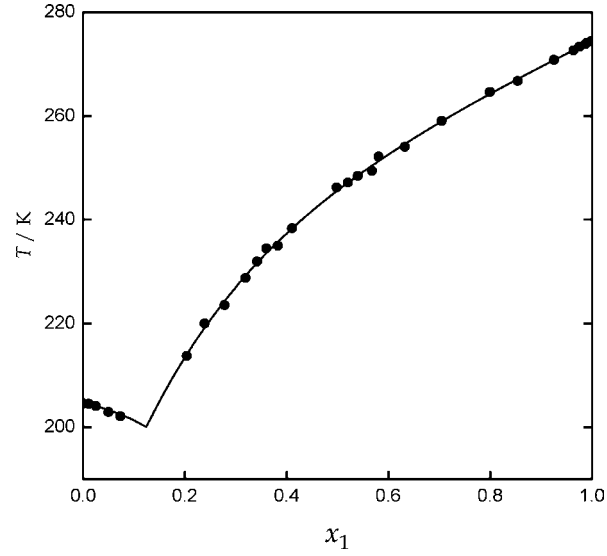

Figure 2. Solid−liquid phase equilibrium diagram for 1,8-cineole (1) + *p*-cymene (2).

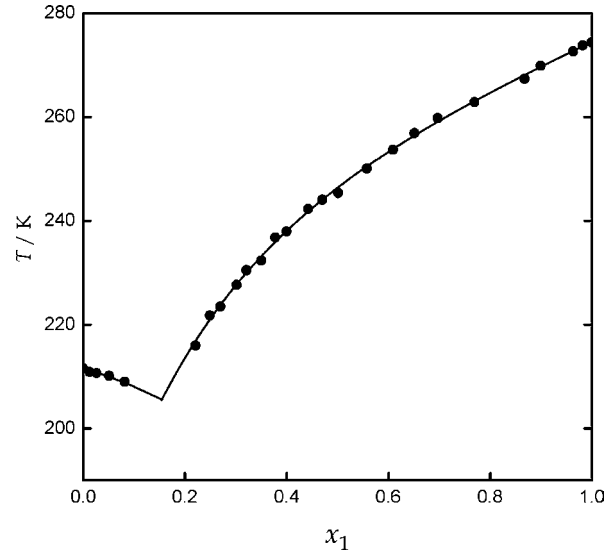

Figure 3. Solid−liquid phase equilibrium diagram for 1,8-cineole (1) + *β*-pinene (2).

The root-mean-square deviation (rmsd) in temperature defined by eq 2 was used as a measure of the goodness-of-fit of the liquidus curves.

$$\text{rmsd} = \left\{\frac{1}{n - m - 1}\sum_{j=1}^{n}(T_{(calc),j} - T_{(expt),j})^2\right\}^{1/2} \quad (2)$$

where the subscript (calc) stands for the calculated values and (expt) for the experimental values, m is the number of

Table 3. Coefficients for Equation 1 with Columns 1 and 2 Giving the Mole Fraction Range over Which the Equation Applies

$x_{1,min}$	$x_{1,max}$	x_1*	T*/K	a_1	a_2	a_3	a_4	a_5	rmsd/K[a]
1,8-Cineole (1) + *p*-Cymene (2)									
0.0	0.124	0.0	204.6	−0.1318	−0.4120				0.3
0.124	1.0	1.0	274.4	0.1723	−0.1150	−0.3144	−0.5399	−0.1446	0.4
1,8-Cineole (1) + β-Pinene (2)									
0.0	0.154	0.0	211.6	−0.1939	1.3417	−8.3092			0.3
0.154	1.0	1.0	274.4	0.1806	0.0924	0.4983	0.6832	0.4919	0.6
1,8-Cineole (1) + Camphene (2)									
0.0	0.582	0.0	324.2	−0.2534	−0.6432	1.6166	−1.5398		0.2
0.582	1.0	1.0	274.4	0.1248	−0.3285	−0.3726			0.4

[a] rmsd = $[(1/(n - m - 1))\sum_{j=1}^{n}(T_{(calc),j} - T_{(xpt),j})^2]^{1/2}$.

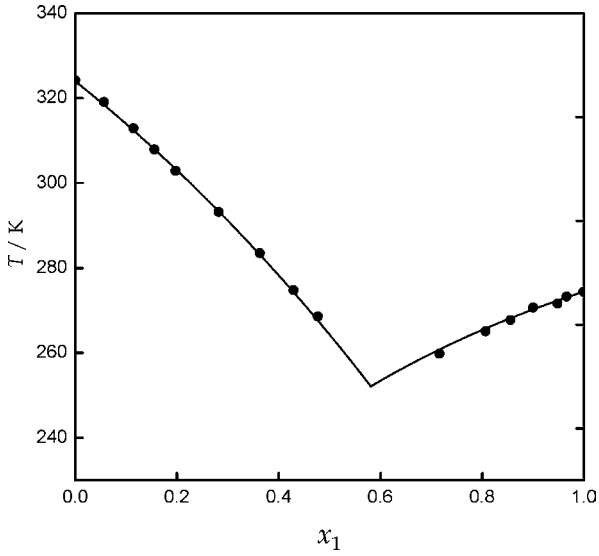

Figure 4. Solid−liquid phase equilibrium diagram for 1,8-cineole (1) + camphene (2).

coefficients in eq 1, and n is the number of data points, which includes the melting point of the pure substance and the eutectic point of the mixture.

The best-fitted coefficients and corresponding rmsd's of the correlation for each mixture are presented in Table 3. The deviations of the calculated temperatures from the experimental values, δT, are listed in Table 2.

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