Solid and Liquid Phase Equilibria in Mixtures of 1,8-Cineole with Phenol, Cyclohexanol, and an *n*-Alkanol

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Solid−liquid phase diagrams have been constructed for 1,8-cineole with phenol or cyclohexanol or an *n*-alkanol. Solid addition compounds with the empirical formulas $C_{10}H_{18}O{\cdot}C_6H_5OH$ and $C_{10}H_{18}O{\cdot}C_6H_{11}OH$ were formed. Compound formation is attributed to hydrogen bonding. No solid addition compounds form in (1,8-cineole + methanol, + ethanol, + 1-propanol, or + 1-butanol).

Introduction

1,8-Cineole is a chemical with several pharmaceutical applications and is obtainable from rectified eucalyptus oil by batch crystallization. To study the separations of 1,8-cineol from the eucalyptus oil, we have measured the solid and liquid phase diagrams for (1,8-cineole + phenol, + cyclohexanol, + methanol, + ethanol, + 1-propanol, + 1-butanol).

Experimental Section

All the chemicals, 1,8-cineole (Aldrich, >99%), phenol (Guangzhou Chem. China, >99.5%), cyclohexanol (Guangzhou Chem. China, >99.5%), methanol (Guangzhou Chem. China, >99.5%), ethanol (Guangzhou Chem. China, >99.5%), 1-propanol (Guangzhou Chem. China, >99.5%), and 1-butanol (Guangzhou Chem. China, >99.5%), were purified by distillation in a vacuum or distilled in a 2.5 m distillation column. The center cuts were retained in a dryer for use. The mole-fraction purities determined by PE Autosystem XL GC analysis were (0.9972, 0.9967, 0.9975, 0.9995, 0.9997, 0.9998, and 0.9999) for (1,8-cineole, phenol, cyclohexanol, methanol, ethanol, 1-propanol, and 1-butanol), respectively.

The freezing temperature apparatus is that described in ref 1. Temperatures were measured with a model 5614 platinum resistance thermometer which was calibrated to the ITS-90 scale over the range 73 to 373 K, and they were estimated to be accurate to 0.03 K. Before starting the measurements, we checked the calibration at the ice-point temperature (T = 273.15 K), the freezing temperature of mercury (T = 234.29 K), and the transition temperature of sodium sulfate decahydrate (T = 305.53 K). Their freezing temperatures according to our determination were respectively (274.42, 313.65, 298.30,175.49, 159.12, 147.09, and 184.43) K. The values from the literature[2] are (274.45, 314.05, 298.35, 175.45, 159.15, 146.95, and 184.55) K, respectively. Binary mixtures were prepared by mass in airtight stoppered glass bottles with a precision of 0.1 mg. Transfer of materials was made with hypodermic syringes to reduce evaporation. Melting temperatures were obtained principally from time against temperature warming curves with the accuracy of 0.05 K. The precision of the melting

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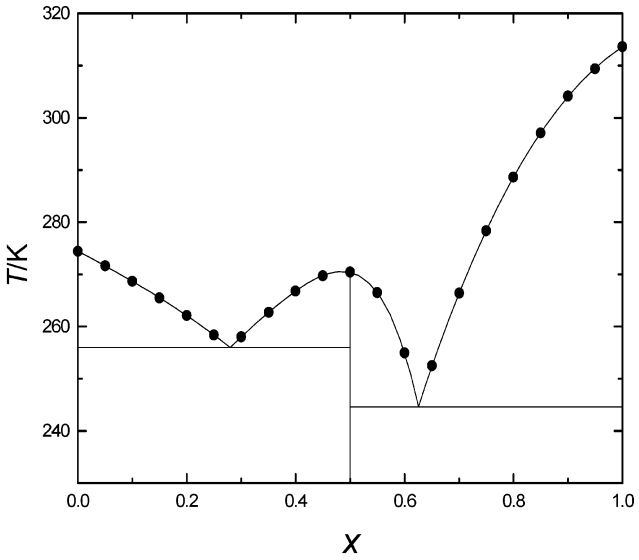

Figure 1. (Solid + liquid) phase diagram for $\{(1 - x)C_{10}H_{18}O + (x)C_6H_5OH\}$

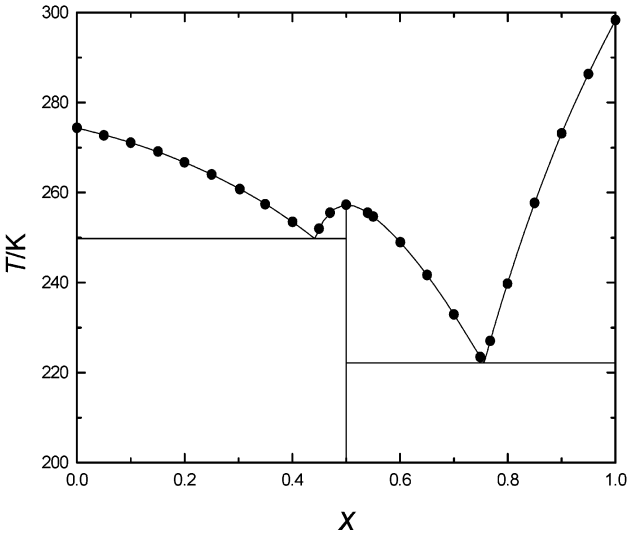

Figure 2. (Solid + liquid) phase diagram for $\{(1 - x)C_{10}H_{18}O + (x)C_6H_{11}OH\}$

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Table 1. (Solid + Liquid) Phase Equilibria with T Denoting the Melting Temperature and δT Denoting the Deviation of the Experimental Temperature from the Value Calculated from Eq 1

x	T/K	δT/K	x	T/K	δT/K	x	T/K	δT/K
			$(1-x)C_{10}H_{18}O + (x)C_6H_5OH$					
0	274.42	0.00	0.3505	262.71	0.03	0.7003	266.39	0.07
0.0504	271.63	−0.03	0.3996	266.83	−0.06	0.7496	278.35	0.00
0.0998	268.68	0.01	0.4498	269.73	0.08	0.7996	288.63	−0.04
0.1497	265.49	0.04	0.5002	270.44	0.01	0.8497	297.12	−0.00
0.2002	262.13	−0.05	0.5499	266.49	0.03	0.8999	304.15	0.08
0.2497	258.37	0.02	0.5998	254.98	−0.00	0.9499	309.40	0.13
0.3002	258.01	−0.00	0.6504	252.51	0.04	1	313.65	0.00
			$(1-x)C_{10}H_{18}O + (x)C_6H_{11}OH$					
0	274.42	0.00	0.4003	253.50	−0.03	0.7000	232.95	0.00
0.0504	272.73	0.11	0.4496	252.00	−0.04	0.7490	223.47	0.00
0.1002	271.07	0.01	0.4700	255.50	0.11	0.7675	227.05	−0.04
0.1507	269.11	−0.08	0.4999	257.33	−0.00	0.7995	239.76	0.09
0.2002	266.71	0.00	0.5400	255.50	0.08	0.8497	257.71	−0.04
0.2503	264.06	−0.03	0.5503	254.68	0.01	0.9001	273.18	−0.06
0.3024	260.78	0.04	0.6005	248.98	−0.04	0.9499	286.34	0.08
0.3498	257.45	0.01	0.6502	241.67	0.01	1	298.30	0.00
			$(1-x)C_{10}H_{18}O + (x)CH_3OH$					
0	274.42	0.00	0.4026	261.03	−0.04	0.8003	244.59	−0.06
0.0512	271.90	−0.07	0.4519	259.32	−0.05	0.8501	236.12	−0.08
0.1050	270.17	−0.01	0.5017	257.74	0.01	0.9000	222.51	−0.10
0.1512	268.98	0.06	0.5515	256.42	0.05	0.9500	201.65	−0.13
0.2063	267.59	0.08	0.6017	255.29	0.05	0.9701	190.56	−0.04
0.2532	266.28	0.03	0.6513	254.11	0.04	1	175.49	0.00
0.3172	264.15	−0.01	0.7004	252.46	0.01			
0.3568	262.76	−0.07	0.7447	250.01	−0.01			
			$(1-x)C_{10}H_{18}O + (x)CH_3CH_2OH$					
0	274.42	0.00	0.4019	261.47	−0.04	0.8011	246.96	−0.04
0.0507	272.02	−0.14	0.4541	259.85	−0.09	0.8502	237.37	−0.04
0.1019	270.50	−0.10	0.5008	258.59	−0.00	0.9002	221.18	−0.01
0.1531	269.30	−0.03	0.5546	257.72	−0.08	0.9498	196.26	−0.07
0.2082	267.88	0.08	0.5994	257.16	−0.07	0.9748	179.34	−0.08
0.2601	266.40	0.05	0.6509	256.41	−0.01	1	159.12	0.00
0.3063	264.88	0.00	0.7002	255.22	−0.06			
0.3511	263.27	−0.02	0.7514	252.43	−0.07			
			$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_2OH$					
0	274.42	0.00	0.4018	259.70	−0.08	0.8001	237.34	−0.09
0.0529	271.91	−0.12	0.4516	257.52	−0.02	0.8504	226.22	−0.10
0.1017	270.34	−0.06	0.5010	255.6	−0.01	0.9000	209.01	−0.08
0.1521	268.93	0.06	0.5414	254.21	−0.01	0.9501	182.90	−0.09
0.2007	267.56	0.10	0.6009	252.32	−0.01	0.9739	166.65	−0.18
0.2510	266.02	−0.02	0.6498	250.62	−0.04	1	147.09	0.00
0.3027	264.01	−0.03	0.7002	248.11	−0.04			
0.3525	261.88	−0.06	0.7513	244.01	−0.11			
			$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_3OH$					
0	274.42	0.00	0.4017	259.64	−0.02	0.7982	234.71	−0.09
0.0592	271.67	0.04	0.4508	257.64	−0.07	0.8504	225.61	−0.20
0.1028	270.15	0.04	0.5011	255.47	−0.02	0.8998	213.19	−0.18
0.1531	268.62	0.01	0.5513	253.27	0.01	0.9483	196.20	−0.11
0.2011	267.06	0.07	0.6002	251.00	0.02	1	184.43	0.00
0.2508	265.44	0.03	0.6506	248.26	0.08			
0.3035	263.63	−0.08	0.7006	245.01	−0.00			
0.3517	261.71	−0.05	0.7505	240.61	−0.07			

temperature is 0.1 K for a few points in the steeper regions of the phase diagram near the eutectics.

Results and Discussion

Melting temperatures were obtained over the entire composition range for {(1 − x)1,8-cineole + (x)phenol, + (x)cyclohexanol, + (x)methanol, + (x)ethanol, + (x)1-propanol, and + (x)1-butanol}. The melting temperatures are recorded in Table 1, and the invariant points in Table 2. The phase diagrams are shown in Figures 1−6. The melting temperatures T were fitted by least squares with the equation[3]

$$T = T^*[1 + \sum_{j=1}^{n} A_j(X - X^*)^j] \qquad (1)$$

Table 2. Summary of Invariant Points

type	x	T/K
	$(1-x)C_{10}H_{18}O + (x)C_6H_5OH$	
eutectic	0.280	256.0
compound $C_{10}H_{18}O{\cdot}C_6H_5OH$	0.5000	270.5
eutectic	0.625	244.6
	$(1-x)C_{10}H_{18}O + (x)C_6H_{11}OH$	
eutectic	0.442	249.0
compound $C_{10}H_{18}O{\cdot}C_6H_{11}OH$	0.5000	257.3
eutectic	0.756	222.2
	$(1-x)C_{10}H_{18}O + (x)CH_3OH$	
eutectic	0.995	175.5
	$(1-x)C_{10}H_{18}O + (x)CH_3CH_2OH$	
eutectic	0.999	159.1
	$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_2OH$	
eutectic	0.999	147.1
	$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_3OH$	
eutectic	0.987	184.4

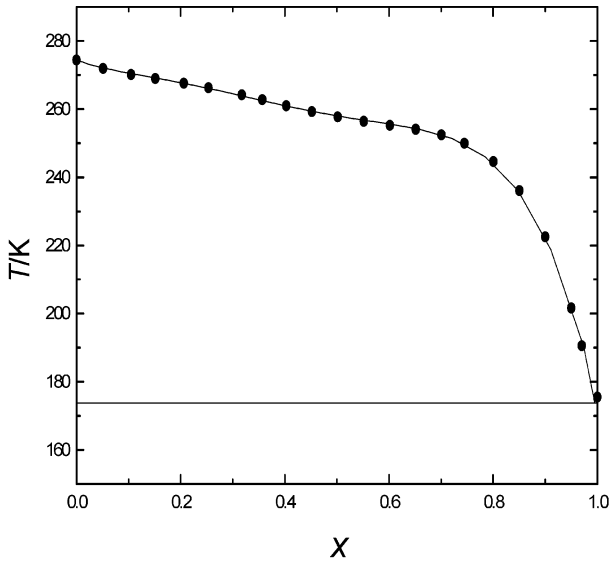

Figure 3. (Solid + liquid) phase diagram for {(1 − x)$C_{10}H_{18}O$ + (x)CH_3OH}

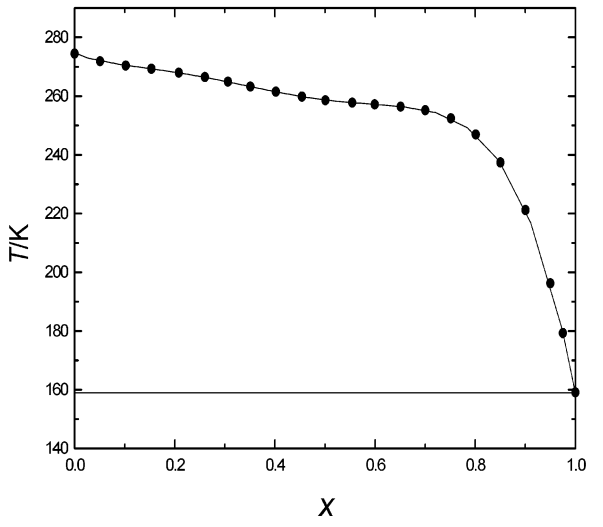

Figure 4. (Solid + liquid) phase diagram for {(1 − x)$C_{10}H_{18}O$ + (x)CH_3CH_2OH}

There T^* is the melting temperature of the pure substance, and x^* is the value of x at $T = T^*$. The parameters for the fitting equation, along with the standard deviations, are given in Table 3. Deviations of the experimental melting

Table 3. Coefficients for Eq 1 with Columns 1 and 2 Giving the Mole Fraction Range over Which the Equation Applies, *s* Being the Standard Deviation of *T*, and *x Being the Value of *x* at *T* = *T****

x_{min}	x_{max}	x^*	T^*/K	A1	A2	A3	A4	A5	*s*/K
				$(1-x)C_{10}H_{18}O + (x)C_6H_5OH$					
0	0.280	0	274.42	−0.1994	−0.0736	−0.2599			0.043
0.280	0.625	0.5000	270.45	−0.0905	−3.3303	−12.9011	−21.8261	−2.2891	0.078
0.625	1	1	313.65	0.2221	−0.7746	0.5316			0.077
				$(1-x)C_{10}H_{18}O + (x)C_6H_{11}OH$					
0	0.442	0	274.42	−0.1071	−0.1222	−0.2166			0.066
0.442	0.756	0.5000	257.33	0.0129	−5.7949	35.6925	−133.054	193.240	0.075
0.756	1	1	298.30	0.7548	−0.7002	2.0422			0.086
				$(1-x)C_{10}H_{18}O + (x)CH_3OH$					
0	0.995	0	274.42	−0.2396	1.3161	−4.9676	7.7228	−4.2092	0.066
				$(1-x)C_{10}H_{18}O + (x)CH_3CH_2OH$					
0	0.999	0	274.42	−0.2438	1.4827	−5.8248	9.3298	−5.1658	0.072
				$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_2OH$					
0	0.999	0	274.42	−0.2399	1.3708	−5.4763	8.7180	4.8379	0.088
				$(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_3OH$					
0	0.987	0	274.42	−0.2034	0.7683	−2.8311	4.3351	−2.4448	0.093

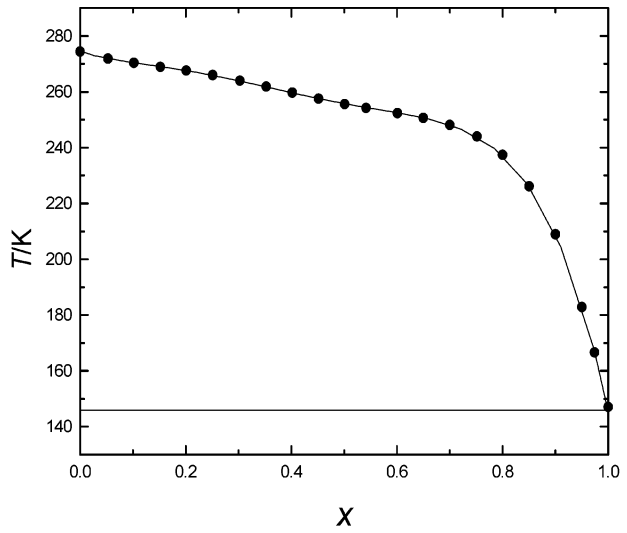

Figure 5. (Solid + liquid) phase diagram for $\{(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_2OH\}$

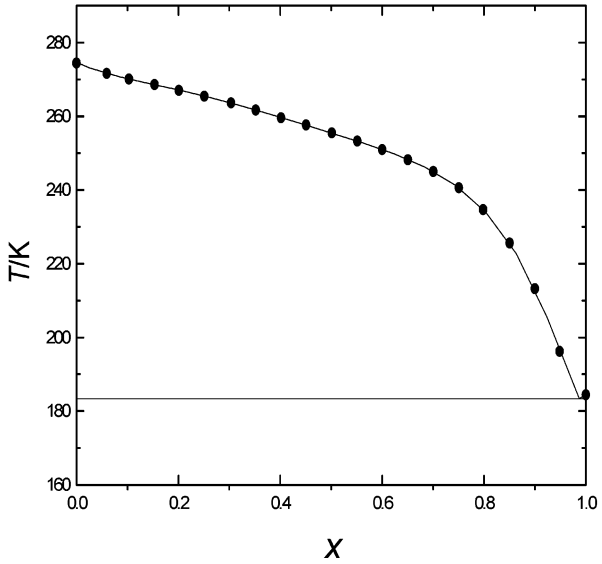

Figure 6. (Solid + liquid) phase diagram for $\{(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_3OH\}$.

temperatures from the fitting equation are given in Table 1.

It is evident from the phase diagrams that 1:1 congruently melting solid addition compounds form in $\{(1-x)C_{10}H_{18}O + (x)C_6H_5OH\}$ and $\{(1-x)C_{10}H_{18}O + (x)C_6H_{11}OH\}$. Since the maximum in the diagrams occurs at the midpoint on the composition axis, we conclude that the complex has a 1:1 stoichiometric ratio. The existence of such a compound is excellent evidence for strong interaction between the two dissimilar molecules. Compound formation between $C_{10}H_{18}O$ and HOC_6H_5 or $C_{10}H_{18}O$ and HOC_6H_{11} is attributed to hydrogen bonding between the oxygen in 1,8-cineole and the hydrogen in phenol or cyclohexanol. The phase diagrams for $\{(1-x)C_{10}H_{18}O + (x)CH_3OH$, $(1-x)C_{10}H_{18}O + (x)CH_3CH_2OH$, $(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_2OH$, and $(1-x)C_{10}H_{18}O + (x)CH_3(CH_2)_3OH\}$ given in Figures 3−6 show no solid compound formation. They are simple eutectic systems.

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