Solid–Liquid Equilibrium for Mixtures Containing Cresols, Piperazine, and Dibutyl Ether

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The solid–liquid phase diagrams have been determined for six binary and one ternary system composed of *m*-cresol, *p*-cresol, piperazine, and dibutyl ether. The results indicate the existence of 1–2 complexes in the *p*-cresol + *m*-cresol, piperazine + *m*-cresol, and piperazine + *p*-cresol systems. The observed melting points were correlated with composition by an empirical equation.

Introduction

Dissociation extractive crystallization is one of the potential methods for separating a compound from close boiling point mixtures such as *p*-cresol + 2,6-xylenol (*1*) and *m*-cresol + *p*-cresol systems (*2*). Gaikar et al. (*2*) reported that using piperazine as a neutralizing agent and dibutyl ether as a solvent enables the recovery of 91% of *p*-cresol from a *m*-cresol + *p*-cresol mixture. This attractive method is of interest for further investigations. To obtain better insight into this separation process, we measured the melting points of the mixtures composed of *m*-cresol, *p*-cresol, piperazine, and dibutyl ether by the solid-disappearance method over a temperature range from 246 to 382 K and at atmospheric pressure. The melting temperatures obtained from the present study were correlated with composition by an empirical equation proposed by Ott and Goates (*3*).

Experimental Section

m-Cresol (99 mass %), *p*-cresol (99 mass %), piperazine (anhydrous, 99 mass %), and dibutyl ether (99 mass %) were purchased from Aldrich. All those substances were used without further purification.

The samples were prepared by mass with an accuracy better than ±0.5 mg, and the typical mass of the samples was about 2–3 g. To minimize the errors in composition that arise from evaporation during the preparation, we loaded the heavier component into a sample vial first. If the prepared mixture still had undissolved solid, the sample was heated in a high-temperature bath till dissolution. The vial was then placed in a low-temperature bath to yield a stable solid. If the prepared sample was a homogeneous solution, the sample vial was immersed alternatively into a liquid nitrogen bath with a low-temperature thermostat accompanied by vigorous agitation until a stable solid was formed.

For the solid whose melting point was higher than 273 K, the sample was observed in a visual high-temperature thermostat (Neslab, TV-4000, stability ±0.03 K, temperature range ambient to 503 K), which was connected with an external refrigeration circulator (Neslab, RTE-110A, stability ±0.01 K, temperature range 248–373 K) to operate the visual bath at temperatures from 273 K up to the ambient. Another visual low-temperature bath (Neslab, LTV-70, stability ±0.05 K, temperature range 203–288 K) was employed, if the melting point of the solid was below 273 K.

The sample was heated gradually with vibration to keep the uniformity of temperature in the vial. As the melting

Table I. Melting Temperatures T_m for *p*-Cresol (1) + *m*-Cresol (2)

	this work		Chivate and Shah (5)		Dawson and Mount Ford (4)	
x_2	T_m/K	$\delta T_m{}^a$/K	x_2	T_m/K	x_2	T_m/K
0.0	307.95	0.00	0.0	307.65	0.0	307.30
0.0281	305.21	0.00				
0.0962	301.15	−0.07				
0.1632	296.46	0.19				
0.2166	292.18	−0.01				
0.2464	289.69	−0.20				
0.3564	279.88	0.16				
0.3929	276.43	0.00				
0.4093	274.46^b	−0.06^c, 0.25^d	0.405	274.65^b	0.430	274.35^b
0.4206	275.18	0.08				
0.4475	277.15	−0.55				
0.5381	280.75	0.25				
0.5893	282.81	−0.01				
0.6416	283.75	0.05				
0.6755	283.91^e	0.04	0.670	283.75^e	0.667	282.85^e
0.7122	283.76	−0.10				
0.7593	282.64	−0.02				
0.8607	278.51	−0.05				
0.8903	276.89^b	0.06^c, 0.00^d	0.890	276.95^b	0.880	275.15^b
0.9183	278.34	0.00				
0.9625	281.09	0.00				
1.0	284.16	0.00	1.0	284.65	1.0	284.15

^{a} $\delta T_m = T_m{}^{calcd} - T_m{}^{exptl}$, where $T_m{}^{calcd}$ is calculated from eq 1. ^{b} Eutectic point. ^{c} Deviation of the calculated T_m from eq 1 for x_2 smaller than the eutectic composition. ^{d} Deviation of the calculated T_m from eq 1 for x_2 larger than the eutectic composition. ^{e} Congruent point.

point was approached, the bath was controlled at a constant temperature in a period of time of about 20–30 min. Provided that the solid did not melt completely, the set point of the bath was elevated by 0.1 K each time until the disappearance of the last trace of solid was observed. Then the bath temperature was recorded from the reading of a Hart Scientific Microtherm 1006 with a platinum RTD probe (accuracy ±0.02 K). The average of two or three replications was taken as the melting point (T_m) of the sample. In general, the measurements were reproduced with ±0.1 K.

Results and Discussion

The measured T_m's of the *p*-cresol (1) + *m*-cresol (2) system are listed in Table I and compared with the literature values reported by Dawson and Mount Ford (*4*) and by Chivate and Shah (*5*) as illustrated in Figure 1. Our results generally agree with those of Chivate and Shah (*5*) except for 0 < x_2 < 0.15
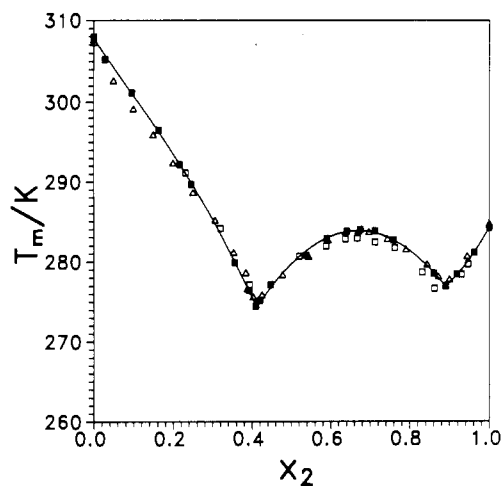
Figure 1. Comparison of melting point measurements for p-cresol (1) + m-cresol (2): ■, this work; □, Dawson and Mount Ford (4); △, Chivate and Shah (5); —, calculated from eq 1.

Table II. Melting Temperatures T_m for Dibutyl Ether (1) + Piperazine (2)

x_2	T_m/K	$\delta T_m/K$	x_2	T_m/K	$\delta T_m/K$
0.0313	290.38	3.94	0.4576	359.48	-0.99
0.0450	302.58	-0.92	0.5065	361.16	-0.26
0.0597	309.23	-0.66	0.5586	363.73	-0.44
0.0717	314.41	-0.86	0.6032	365.29	-0.17
0.0806	319.04	-2.14	0.6449	366.61	0.01
0.1049	326.91	-2.21	0.6965	367.42	0.79
0.1303	331.22	-0.11	0.7763	369.46	0.92
0.1507	334.34	0.87	0.8087	371.27	0.04
0.1851	339.65	0.87	0.8527	374.03	-1.22
0.2408	345.35	0.90	0.9001	374.74	0.18
0.2813	347.49	1.65	0.9281	376.27	0.21
0.3417	351.95	0.63	0.9696	379.34	-0.13
0.4044	356.82	-1.02	1.0	381.78	0.00

Table III. Melting Temperatures T_m for Dibutyl Ether (1) + p-Cresol (2) and Dibutyl Ether (1) + m-Cresol (2)

dibutyl ether (1) + p-cresol (2)			dibutyl ether (1) + m-cresol (2)		
x_2	T_m/K	$\delta T_m/K$	x_2	T_m/K	$\delta T_m/K$
0.6309	253.66	0.15	0.7171	245.94	0.06
0.6532	260.93	0.10	0.7421	251.27	0.02
0.6826	269.52	-0.64	0.7658	255.91	-0.29
0.7183	276.22	0.19	0.8047	261.28	0.22
0.7512	281.72	0.20	0.8239	263.81	0.19
0.7961	287.63	0.27	0.8653	269.20	-0.29
0.8315	291.78	0.03	0.9106	274.11	0.10
0.8622	295.32	-0.47	0.9528	279.28	-0.01
0.9248	300.38	0.20	0.9825	282.58	0.00
0.9691	304.77	-0.03	1.0	284.16	0.00
1.0	307.95	0.00			

where our observed T_m's are higher by about 2 K. Meanwhile, the melting points determined by this work are consistent with those by Dawson and Mount Ford, but the results of Dawson and Mount Ford are lower by about 1 K in the range of x_2 from 0.6 to 0.85. The comparison of the observed values from the different works is made in Table I for the pure components, eutectic compounds, and congruent compound.

Employing a similar procedure, we also determined the melting temperatures for the five binary systems including dibutyl ether + piperazine, dibutyl ether + p-cresol, dibutyl ether + m-cresol, piperazine + p-cresol, and piperazine + m-cresol. Those results are presented, respectively, in Tables II–V. From Figure 2, the melting curves of the mixtures containing dibutyl ether increase monotonically with x_2, indicating no complex formation between those two unlike pair molecules. Figure 2 shows that the melting points of the dibutyl ether + piperazine system increase markedly when

Table IV. Melting Temperatures T_m for Piperazine (1) + p-Cresol (2)

x_2	T_m/K	$\delta T_m/K$	x_2	T_m/K	$\delta T_m/K$
0.0	381.78	0.00	0.6703	362.33[b]	0.02
0.0607	376.91	0.02	0.7018	361.63	-0.30
0.1238	372.23	-0.16	0.7202	360.39	-0.59
0.2038	364.02	0.54	0.7386	357.54	-0.08
0.2697	357.64	-0.70	0.7861	346.97	0.02
0.3177	351.08	-0.14	0.8129	337.65	0.03
0.3515	346.03	0.74	0.8429	323.34	0.40
0.3912	342.63[a]	-0.31, -0.21	0.8555	314.85	1.79
0.4470	344.94	-0.52	0.8820	297.58	1.40
0.4840	346.77	0.77	0.8910	294.84[a]	-2.74, 0.00
0.5320	351.58	0.98	0.9264	298.46	0.00
0.5881	358.68	-0.40	0.9577	302.71	0.00
0.6278	361.73	-0.54	1.0	307.95	0.00

[a] Eutectic point. [b] Congruent point.

Table V. Melting Temperatures T_m for Piperazine (1) + m-Cresol (2)

| x_2	T_m/K	$\delta T_m/K$	x_2	T_m/K	$\delta T_m/K$
0.0	381.78	0.00	0.6250	329.74	-0.55
0.0591	376.70	0.02	0.6658	331.32[b]	0.06
0.1082	373.22	-0.09	0.6882	330.83	0.31
0.2222	363.23	0.75	0.7095	328.90	0.73
0.2786	356.75	0.31	0.7526	322.25	0.02
0.3116	352.76	-0.78	0.7877	312.50	-0.51
0.3429	347.55	0.46	0.8058	305.59	-0.12
0.3947	339.24	-0.55	0.8328	293.79	1.14
0.4278	331.43	-0.07	0.8768	281.10	-2.71
0.4438	327.30	-0.01	0.8986	272.87[a]	1.22, 0.06
0.4594	321.63	-1.32	0.9172	274.03	-0.18
0.4839	316.04[a]	-0.80, -0.63	0.9345	275.62	0.16
0.5160	317.41	0.81	0.9539	278.62	-0.05
0.5454	320.00	1.00	0.9673	280.55	0.00
0.5908	327.23	-1.40	1.0	284.16	0.00

[a] Eutectic point. [b] Congruent point.
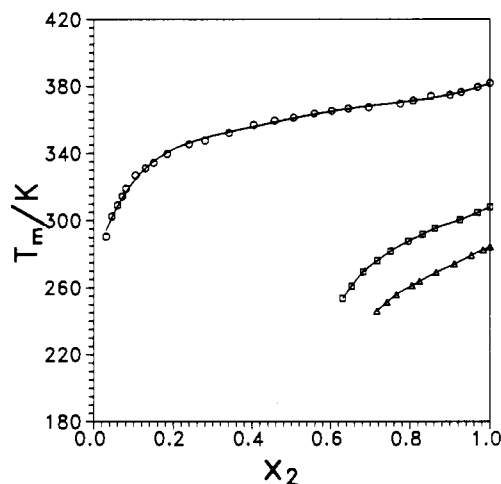
Figure 2. Solid–liquid phase diagram for dibutyl ether (1) + piperazine (2) (O), dibutyl ether (1) + p-cresol (2) (□), and dibutyl ether (1) + m-cresol (2) (△): —, calculated from eq 1.

a small amount of piperazine is added to dibutyl ether. However, this effect levels off as $x_2 > 0.4$. Furthermore, the solid–liquid phase boundaries of dibutyl ether + p-cresol and dibutyl ether + m-cresol have a similar shape, and the variation of melting points with the amount of dibutyl ether is more sensitive for these two systems than for the dibutyl ether (1) + piperazine (2) for x_2 ranging from 0.6 to 1.0.

Figure 3 illustrates the solid–liquid phase diagrams of the piperazine (1) + p-cresol (2) and piperazine (1) + m-cresol (2) systems. Each system exhibits two eutectic points and one congruent point. The first eutectic points are located at
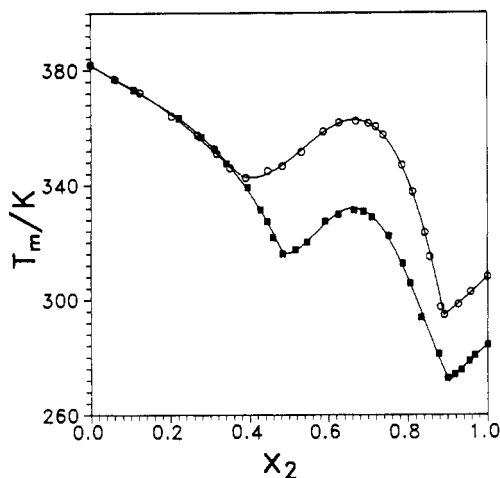
Figure 3. Solid–liquid phase diagram for piperazine (1) + p-cresol (2) (O) and piperazine (1) + m-cresol (2) (■): —, calculated from eq 1.

Table VI. Melting Temperatures T_m for the Piperazine (1') + Cresols (2')[a] Ternary System

x_2'	T_m/K	δT_m/K	x_2'	T_m/K	δT_m/K
0.0	381.78	0.00	0.6224	316.35	0.01
0.0549	379.34	−0.02	0.6348	316.72	0.50
0.1390	372.43	0.24	0.6728	317.96[c]	0.11
0.1950	367.54	−0.49	0.7050	316.27	−0.19
0.2342	362.70	−0.12	0.7150	315.24	−0.34
0.2789	356.09	0.76	0.7364	311.52	0.03
0.3266	349.95	−0.12	0.7643	305.37	0.51
0.3686	343.39	−0.56	0.7788	302.99[d]	−0.29, −0.02
0.4264	332.22	−0.18	0.8218	300.89	−0.18
0.4474	327.10	0.78	0.8408	297.53	−0.25
0.4682	323.53	0.18	0.8604	291.44	0.91
0.5232	314.09	−1.09	0.8945	281.21	−0.54
0.5486	307.96[b]	0.62, 0.18	0.9136	272.52[b]	0.08, 0.00
0.5710	311.21	−0.21	0.9493	277.94	0.00
0.5994	314.53	−0.30	1.0	283.85	0.00

[a] Constant cresol composition, m-cresol:p-cresol = 70 mol %:30 mol %. [b] Eutectic point. [c] Congruent point. [d] Meritectic point.

$x_2 = 0.3912$, $T_m = 342.63$ K and $x_2 = 0.4839$, $T_m = 316.04$ K for the piperazine (1) + p-cresol (2) and piperazine (1) + m-cresol (2) systems, respectively, and the respective second eutectic points are located at $x_2 = 0.8910$, $T_m = 294.84$ K and $x_2 = 0.8986$, $T_m = 272.87$ K. Also, their congruent points appear at $x_2 = {}^2/_3$, indicating a 1–2 complex between piperazine and cresol. As compared in Figure 3, the congruent tem-
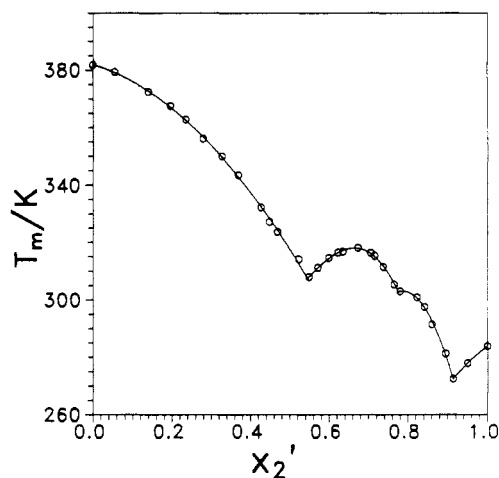

Figure 4. Solid–liquid phase diagram for the ternary mixtures of piperazine (1') + (70 mol % m-cresol + 30 mol % p-cresol) (2'): O, experimental value; —, calculated from eq 1.

perature of the piperazine + p-cresol mixture (362.33 K) is substantially higher than that of the piperazine + m-cresol mixture (331.32 K) by about 31 K. This suggests that the piperazine + (p-cresol)₂ complexes should be preferentially crystallized from the solution of piperazine + p-cresol + m-cresol.

The solid–liquid equilibrium behavior of the ternary system piperazine (1) + p-cresol (2) + m-cresol (3) investigated in this work had $x_2/x_3 = {}^3/_7$ since the typical composition of the commercial grade of cresols (p-cresol:m-cresol) is about 3:7 in mole ratio. The mixtures studied are listed in Table VI. Figure 4 illustrates the results as a pseudobinary system. It shows that there are two eutectic points ($x_2' = 0.5486$, $T_m = 307.96$ K and $x_2' = 0.9136$, $T_m = 272.52$ K), one congruent point ($x_2' = 0.6728$, $T_m = 317.96$ K), and one meritectic point at $x_2' = 0.7788$, $T_m = 302.99$ K. If the mole ratio of piperazine to p-cresol is 1:2, the corresponding x_2' is about 0.8695. For this mixture, a solid of piperazine + (p-cresol)₂ complexes may form at the temperatures below 293 K as indicated in Figure 4.

Correlation

Ott and Goates (3) reported that each piece of smooth melting curves for the systems with or without a congruent compound can be expressed well by the following empirical

Table VII. Correlation of Melting Temperatures T_m by Equation 1

mixture[a]	$x_{2,min}$	$x_{2,max}$	x_2^*	T_m^*/K	a_1	a_2	a_3	a_4	a_5	AAD[b]
A	0.6309	1	1	307.95	0.3584	0.7863	3.8838	7.6359	14.1716	0.23
B	0.7171	1	1	284.16	0.2750	−2.8335	−23.7303	−82.5119	−89.1184	0.13
C[c]	0.0313	1	1	381.78	0.2264	0.4362	−0.7637	−5.5033	−8.3687	0.88
D	0	0.4093	0	307.95	−0.3909	3.2349	−21.3660	56.2877	−52.7171	0.09
	0.4093	0.8903	0.667	283.95	0.0050	−0.6221	0.0232	2.1795	−0.7493	0.13
	0.8903	1	1	284.16	0.3291	1.2039	3.0062			0
E	0	0.3912	0	381.78	−0.2349	0.6452	−4.0119	5.9843	−1.1063	0.37
	0.3912	0.8910	0.667	362.35	0.0037	−2.2195	−6.1100	−4.2565	−7.0865	0.68
	0.8910	1	1	307.95	0.3197	−2.7847	−19.5852			0
F	0	0.4839	0	381.78	−0.2661	0.9896	−5.3814	10.9196	−10.0338	0.42
	0.4839	0.8986	0.667	331.40	0.0398	−3.3958	−12.5929	21.7924	140.6404	0.75
	0.8986	1	1	284.16	0.2115	−7.1030	−52.7126			0.09
G	0	0.5486	0	381.78	−0.0606	−1.2447	4.5008	−10.5375	8.6023	0.43
	0.5486	0.7788	0.667	318.15	−0.0190	−3.7491	−9.1519	52.5186	286.3131	0.24
	0.7788	0.9136	0.790	303.15	−0.0279	−7.3566	7.9795			0.33
	0.9136	1	1	283.85	0.3383	−1.4316				0

[a] Key: A, dibutyl ether (1) + p-cresol (2); B, dibutyl ether (1) + m-cresol (2); C, dibutyl ether (1) + piperazine (2); D, p-cresol (1) + m-cresol (2); E, piperazine (1) + p-cresol (2); F, piperazine (1) + m-cresol (2); G, piperazine (1') + (70 mol % m-cresol + 30 mol % p-cresol) (2'). [b] AAD/K = $(1/n_p)\sum_{k=1}^{n_p} (|T_m^{calcd} - T_m^{exptl}|)_k$. [c] An additional coefficient, $a_6 = -4.1218$.

equation:

$$T_m = T_m^*[1 + \sum_{i=1}^{n} a_i(x_2 - x_2^*)^i] \qquad (1)$$

where x_2 is the mole fraction of component 2, T_m is the melting point, a_i's are the coefficients to be determined from experimental data, and x_2^* and T_m^* are the mole fraction of component 2 and the melting temperature for the congruently melting compounds or for the pure substances. This empirical model was employed to fit the results of this investigation. The optimal coefficients a_i's for each piece of smooth melting curves were determined by a linear regression algorithm. Table VII lists the respective optimal coefficients and the average of absolute deviations (AAD) of the correlation, where

$$(AAD/K) = \frac{1}{n_p}\sum_{k=1}^{n_p}(|T_m^{calcd} - T_m^{exptl}|)k \qquad (2)$$

In general, a fifth-order polynomial of eq 1 is adequate for most systems, except a sixth-order polynomial is needed for the dibutyl ether + piperazine system. The calculated results have been illustrated as smooth curves in the corresponding graphs, and the deviations of the melting temperature ($\delta T_m = T_m^{calcd} - T_m^{exptl}$) have also been given in Tables I–VI. It appears that eq 1 is satisfactory for interpolation purposes.

Conclusion

The melting points have been observed for mixtures composed of cresols, piperazine, and dibutyl ether at temperatures ranging from 246 to 382 K and at atmospheric pressure. It is indicated that 1–2 complexes (m-cresol + (p-cresol)$_2$, piperazine + (m-cresol)$_2$, and piperazine + (p-cresol)$_2$) form in the corresponding systems. Also, a congruent locus for the ternary system of piperazine + m-cresol + p-cresol passes through the point at about $x_2' = {}^2/_3$ and $T_m = 317.96$ K, and the melting point of the mixture (13.05 mol % piperazine + 26.1 mol % p-cresol + 60.85 mol % m-cresol) is at about 293 K. Furthermore, the empirical equation proposed by Ott and Goates correlates well the melting temperatures determined in this study.

Glossary

AAD	average of absolute deviations defined in eq 2
a_i	coefficients in eq 1
n_p	total number of data points
T_m	melting temperature
T_m^*	characteristic temperature (in eq 1)
δT_m	$T_m^{calcd} - T_m^{exptl}$
x	mole fraction
x'	mole fraction for a pseudobinary mixture
x_2^*	characteristic mole fraction (in eq 1)

Superscripts

calcd	calculated value from eq 1
exptl	experimental value

Subscripts

2	component 2
max	maximum
min	minimum

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