J. Chem. Eng. Data **2001,** *46,* 47−50

Solid−Liquid Equilibrium for 2,4-Dinitrophenol + Naphthalene

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Phase diagram studies have shown that 2,4-dinitrophenol forms a 1:1 addition compound with naphthalene. There is a formation of two eutectics, one between naphthalene and a congruent melting compound and the other between the congruent melting compound and 2,4-dinitrophenol. The linear velocity of crystallization and the flow time measurements of the molten material have shown some sort of molecular association between the components in the eutectics, and also there is a weak molecular interaction between 2,4-dinitrophenol and naphthalene in the addition compound. The interaction may be a dipole−induced dipole interaction. Microstructures of the addition compound are changed considerably in the presence of impurities.

Introduction

Properties required for a specific purpose are not generally achieved by a single material and hence composite materials are required. To control various properties of the materials, solidification behavior and microstructures have been studied.[1,4] For many materials, melting temperatures are high, and as such the experimental setup for the study of solidification behavior becomes complicated. Organic compounds have low melting temperatures and form composite materials (eutectics) similar to metallic systems. As such these systems can be studied as model systems. In the present paper solid−liquid equilibrium data of 2,4-dinitriphenol + naphthalene, solidification behavior of eutectics, and their microstructures have been studied.

Materials and Purification

2,4-Dinitrophenol was purified by repeated crystallization from hot water. The purified sample melts at 387.0 ± 0.1 K. Naphthalene was purified by distillation under reduced pressure. The melting point of the pure sample of naphthalene was 353.0 ± 0.1 K.

Phase Diagram Studies. Phase diagram studies were made by using the thaw melt method.[3] Known masses of both components were taken in well cleaned glass test tubes in order to prepare mixtures of different compositions. The tubes were sealed to prevent evaporation of the materials on heating. The mixtures were homogenized by melting at a temperature slightly above the melting points of the components and then chilled in ice cold water. The process of heating and cooling was repeated for each mixture at least three times. Finally the test tubes were broken and the solidified materials were ground into fine powders in glass mortar. The thaw point and melting points of the mixtures were determined.

Undercooling Measurements. The undercooling study was made by the procedure of Rastogi and Verma.[3] About 5 g of the mixtures was taken in clean glass test tubes which were then sealed. The tubes were kept in an oil bath at a temperature 20.0 °C higher than the melting points of the mixtures. The bath was allowed to cool slowly, and the temperature at which the first crystal nuclei were observed was noted with the help of a precision thermometer. The difference between the melting temperature and the temperature of the first observable nuclei (seen by the magnifying glass) gave the undercooling value for a particular mixture.

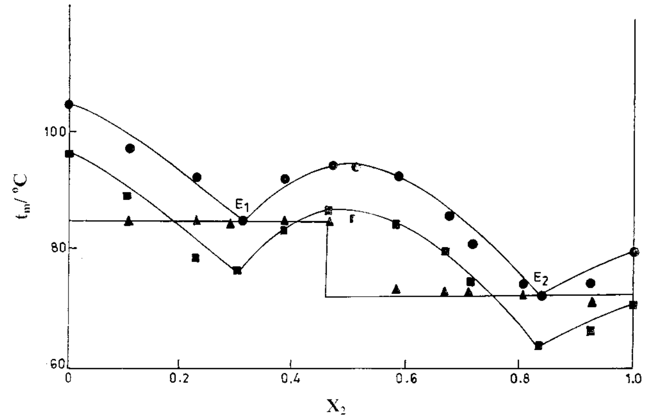

Figure 1. Solid−liquid equilibrium data for 2,4-dinitrophenol (1) + naphthalene (2).

Linear Velocity of Crystallization. The linear velocity of crystallization was determined by the method described earlier.[2] The molten mixtures were placed in Pyrex glass U-tubes kept horizontally and vertically in an oil thermostat maintained at temperatures a few degree below the melting temperature. When the tube attained the temperature of the bath, a seed crystal of the same compound was added from one side of the tube to start nucleation. As soon as the seed crystal was added, nucleation started and the crystallization occurred linearly in the tube. The time for the crystallization of a definite length in the tube was noted with a stopwatch.

Flow Time Measurements. An Ostwald viscometer was filled with molten 2,4-dinitrophenol, naphthalene, the eutectics, and the addition compound separately. The viscometers were placed at 388.0 ± 0.1 K in a thermostat, and the time of flow from one point to another was recorded in each case.

Microscopic and Microphotographic Studies. Small amounts of 2,4-dinitrophenol, the eutectics, and the addi-

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10.1021/je000179t CCC: $20.00

Table 1. Phase Equilibrium Data for 2,4-Dinitrophenol (1) + Naphthalene (2)

mole fraction of x_2	thaw point/°C	melting point t_m/°C	undercooling ΔT/K
1.0000		80.0	9.0
0.9251	71.0	74.5	8.2
0.8383		71.0	8.0
0.7140	71.2	82.0	8.0
0.6666	71.2	86.1	6.8
0.5740	71.5	93.6	9.2
0.5000		94.0	8.7
0.4644	84.5	93.9	7.5
0.3834	84.0	91.1	7.1
0.3158		84.5	8.5
0.2825	84.2	86.8	8.8
0.2241	84.5	93.0	7.1
0.1056	84.5	98.2	8.4
0.0000		105.0	8.0

Table 2. Time Intervals after which Crystallization Starts in a U-Tube and a Vertical Tube for the Eutectic Melts of a 2,4-Dinitrophenol−Naphthalene System on the Addition of Seed Crystal

	time interval when seed crystal is from the same mixture, S	
undercooling ΔT/K	time interval in U−tube	time interval in vertical tube
8	6	5
6	11	8
4	14	10
2	17	14

Table 3. Linear Velocity of Crystallization

	linear velocity of crystallization, v/mm·s^{-1}				
undercooling ΔT/K	2,4-DNP[a]	N[b]	eutectic I	eutectic II	1:1addition compound
8	0.995	1.019	0.976	1.057	0.188
6	0.646	0.845	0.576	0.862	0.145
4	0.496	0.574	0.468	0.594	0.093
2	0.357	0.382	0.329	0.397	0.083

[a] DNP = dinitrophenol. [b] N = naphthalene.

Table 4. Test of the Equation $V = x_1v_1 + x_2v_2$ for the Eutectics of the 2,4-Dinitrophenol−Naphthalene System

	linear velocity of crystallization, v/mm·s^{-1}			
	eutectic I		eutectic II	
undercooling ΔT/K	exp value	mixture rule	exp value	mixture rule
8.0	0.976	1.003	0.091	1.015
6.0	0.576	0.709	0.062	0.814
4.0	0.478	0.521	0.054	0.562
2.0	0.329	0.402	0.037	0.386

Table 5. Test of the Equation $V = x_1v_1 + x_2v_2$ for the 1:1 Addition Compound of the 2,4-Dinitrophenol + Naphthalene System

	linear velocity of crystallization, v/mm·s^{-1}	
undercooling ΔT/K	exp value	mixture rule
8.0	0.188	1.000
6.0	0.145	0.745
4.0	0.093	0.534
2.0	0.083	0.396

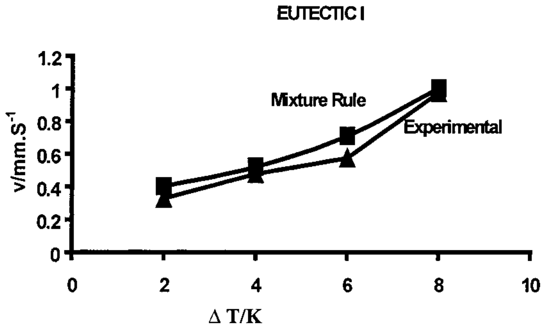

Figure 2. Linear velocity of crystallization for eutectic I of 2,4-dinitrophenol (1) + naphthalene (2).

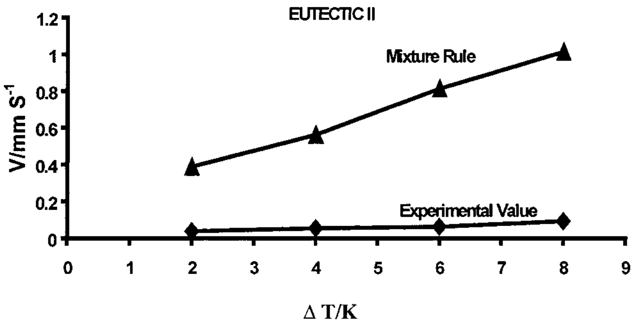

Figure 3. Linear velocity of crystallization for eutectic II of 2,4-dinitrophenol (1) + naphthalene (2).

tion compound were placed separately on a glass slide and placed at a temperature slightly higher than the melting points and allowed to melt. The cover slip was glided over the melt and allowed to undercool. Nucleation started from one side, and care was taken to have unidirectional freezing. The microphotographs were taken with the help of a camera attachment with the microscope at a suitable magnification.

Results and Discussion

The phase diagram of the system 2,4-dinitrophenol and naphthalene is shown in Figure 1, and the solid−liquid equilibrium data are given in Table 1. From the phase diagram it is inferred that a 1:1 addition compound is formed. Since the maxima are flat, it appears that the addition compound is stable in the solid state and dissociated in the solution or molten state. There are two eutectic points which are designated as E_1 and E_2. The eutectic E_1 is formed between the addition compound and 2,4-dinitrophenol whereas the eutectic E_2 is formed between the addition compound and naphthalene.

For the study of the crystallization process, experiments were performed in U-shaped and vertical tubes using seed crystals of the same material. When a seed crystal of the same material was introduced into the U-tube and the vertical tube, the time required for the start of crystallization was noted and is given in Table 2. The results indicate that the time required for crystallization was lower in the vertical tubes than that in the U-tube. This may be due to the gravitational force acting on the vertical tubes. The values of linear velocity of crystallization for the components, the eutectics, and the addition compound with undercooling are given in Table 3.

The linear velocity of crystallization calculated from the mixture rule (eq 1) for the eutectic and the addition compound is given in Tables 4 and 5.

$$V = x_1v_1 + x_2v_2 \tag{1}$$

where v_1 and v_2 are the linear velocity of crystallization and x_1 and x_2 are the mole fractions of components 1 and 2, respectively. The variations of the velocity of crystallization (v) with undercooling for experimental data and those calculated from eq 1 for eutectic I and eutectic II are shown in Figures 2 and 3. These figures show that the values calculated from the mixture rule are higher than the experimental values, indicating that the eutectics are

Table 6. Flow Time *t* (Experimental and Mixture Rule) for the 2,4-Dinitrophenol−Naphthalene System

system	*t*/s	
	exp value	mixture rule
eutectic I	46.0	9.6
eutectic II	44.0	16.7
1:1 addition compound	54.0	14.2

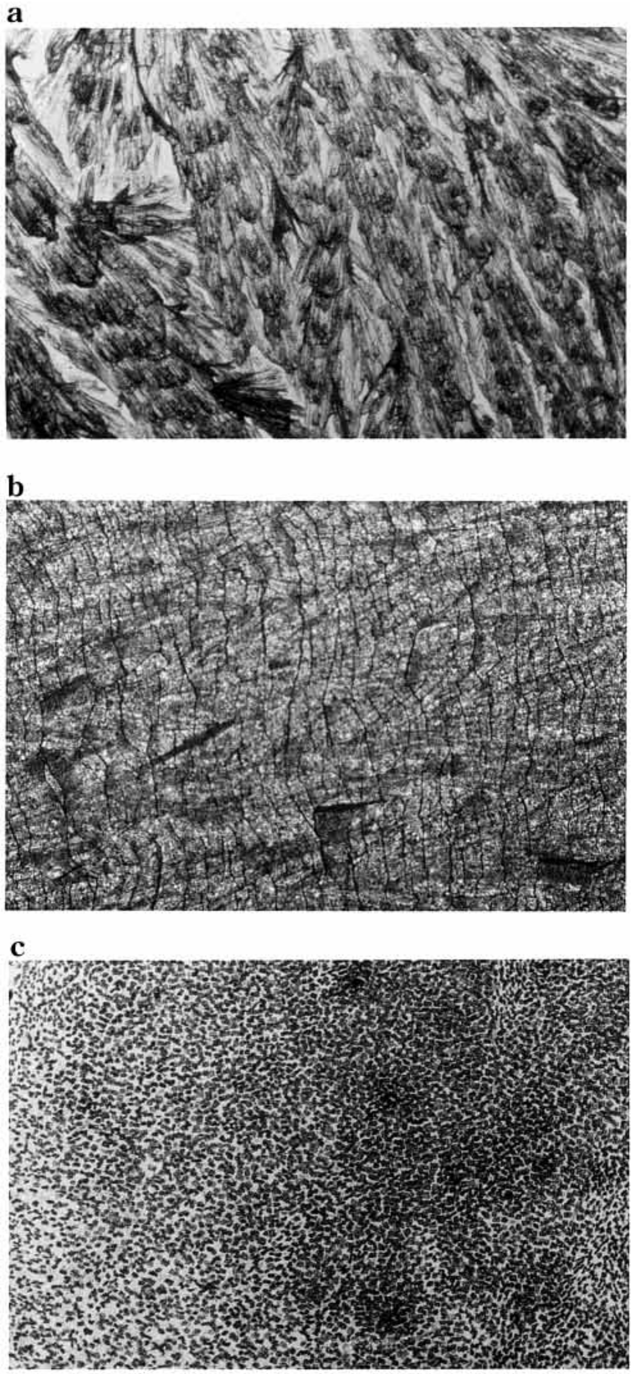

Figure 4. (a) Microstructure of 2,4-dinitrophenol × 150. (b) Microstructure of 2,4-dinitrophenol exposed to the vapors of naphthalene for 10 min at 60 °C × 150. (c) Microstructure of 2,4-dinitrophenol exposed to the vapors of naphthalene for 1 h at 60 °C × 150.

Figure 5. Microstructure of eutectic I of 2,4-dinitrophenol (1) + naphthalene (2) × 150.

Figure 6. Microstructure of eutectic II of 2,4-dinitrophenol (1) + naphthalene (2) × 150.

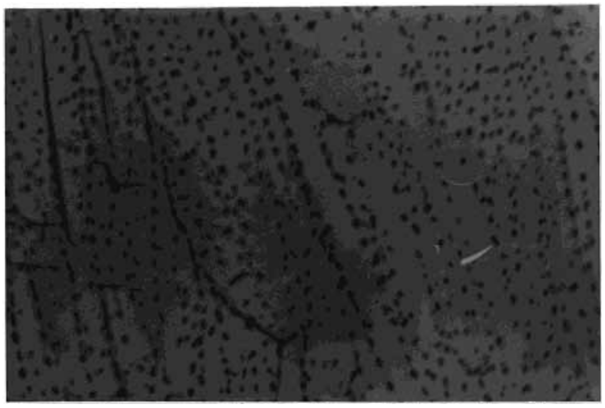

Figure 7. Microstructure of the 1:1 addition compound of 2,4-dinitrophenol (1) + naphthalene (2) × 150.

not simply a mechanical mixture of the components. There may be some sort of weak interaction or molecular association between the components. The linear velocities of crystallization determined experimentally and calculated from the mixture rule are given in Table 5. The values obtained from the mixture rule are much higher than the experimental values. The differences in the two values are also much higher for the addition compound than those values for the eutectics.

The flow times of the components, the eutectics, and the addition compound in the molten state were measured at 388.0 ± 0.1 K in an Ostwald viscometer, and the values are given in Table 6. The flow times were calculated from the mixture rule using eq 2 and are given in Table 6. The values for the eutectic and the addition compound are much higher than those obtained from the mixture rule.

$$t_f = x_1 t_{f1} + x_2 t_{f2} \qquad (2)$$

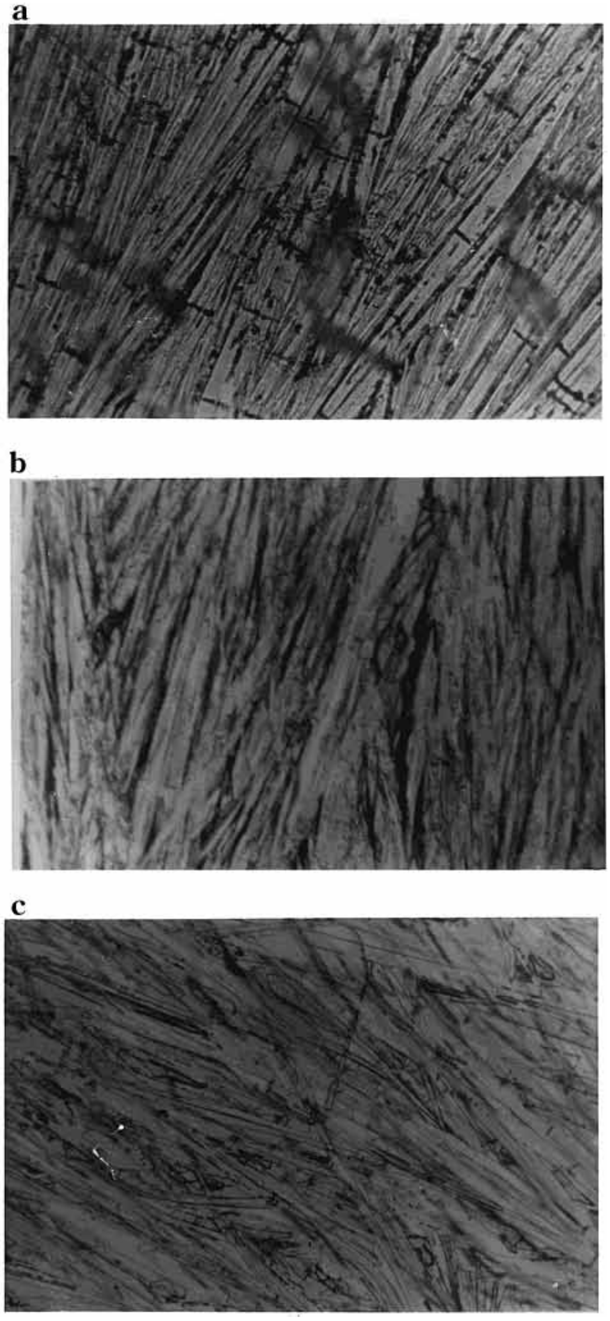

Figure 8. Microstructure of (a) the 1:1 addition compound of 2,4-dinitrophenol (1) + naphthalene (2) in the presence of 0.1 mass % *p*-nitrophenol as an impurity × 150, (b) the 1:1 addition compound of 2,4-dinitrophenol (1) + naphthalene (2) in the presence of 0.1 mass % 2,4-dinitrophenol as an impurity × 150, and (c) the 1:1 addition compound of 2,4-dinitrophenol (1) + naphthalene (2) in the presence of 0.1 mass % picric acid as an impurity × 150.

where t_f is the flow time of the addition compound and t_{f1} and t_{f2} are the times of flow for components 1 and 2, respectively. This again indicates some sort of weak molecular interaction.

Microstructure. The microstructures of the components, eutectics I and II, and the addition compound are given in Figures 4−8. The microstructure of 2,4-dinitrophenol is broken lamellar type (Figure 4a). When this was exposed to vapors of naphthalene at 333.0 ± 0.1 K for 10 min, the microstructure was changed (Figure 4b). It appears that naphthalene vapors react rapidly on the surface of 2,4-dinitrophenol, forming a very thin layer of reaction product which cracks. When the slide with 2,4-dinitrophenol is exposed to the vapors of naphthalene for 1 h, the microstructure is changed completely and the reaction product appears in the form of small particles having rod type morphology (Figure 4c). This indicates the possibility of structural change during the solid-state reaction.

The microstructures of eutectics I and II are shown in Figures 5 and 6. The microstructures of the two eutectics are almost similar with rectangular crystals crystallizing from some points and are intermingled. Eutectic II shows thinner rectangles with spots on them which are absent in the microstructure of eutectic I.

Since the mole fraction of naphthalene is higher in eutectic I than in eutectic II, it can be inferred that the presence of naphthalene modifies the broken lamellar structure of 2,4-dinitrophenol to a greater extent in the case of eutectic I than in the case of eutectic II.

The microstructure of the 1:1 addition compound (Figure 7) shows rod type crystals, and the broken lamellar structure of 2,4-dinitrophenol appears to be lost in the presence of an equal mole fraction of naphthalene.

The effects of different impurities (0.1 mass %) on the microstructures of the addition compound are shown in Figure 8. In the presence of the impurities, the microstructure of the addition compound is changed from rod to lamellar type. The lamellar width is maximum in the presence of 2,4-dinitrophenol and minimum in the presence of picric acid. Further, in the presence of picric acid the structure appears to be broken lamellar. The results very clearly show that the impurities modify the structure.

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Received for review June 12, 2000. Accepted September 7, 2000.

JE000179T