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Solid−Liquid Equilibria for *p*-Dichlorobenzene + *p*-Dibromobenzene and *p*-Dibromobenzene + Resorcinol

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Phase-diagram studies have shown the formation of eutectics in the *p*-dichlorobenzene + *p*-dibromobenzene and resorcinol + *p*-dibromobenzene systems. The linear velocity of crystallization measurements in the molten materials has shown that there is some sort of molecular association in the eutectic mixtures. Microstructural studies have revealed that the microstructures of the eutectics are dependent on the microstructures of the components.

Introduction

Organic materials in many cases may act as analogues to metallic systems. Because they have low melting temperatures, it is easy to study the solidification behavior of organic compounds. Organic eutectics may also act as composite materials. The solidification behavior of a number of organic eutectic systems has been studied (Singh and Dwivedi, 1982; Rastogi, 1971). In this communication, the solidification behavior and microstructures of *p*-dichlorobenzene + *p*-dibromobenzene and resorcinol + *p*-dibromobenzene eutectic systems are discussed.

Experimental Section

Materials. *p*-Dichlorobenzene (BDH) and resorcinol (BDH) were purified by successive crystallizations from hot water, and the melting points were found to be 52.5 and 110.0 °C, respectively. *p*-Dibromobenzene (BDH) was purified by distillation under reduced pressure, and the purified sample melted at 88.8 °C.

Methods. Phase Diagram Studies. The phase diagrams were studied by the thaw melt method (Rastogi and Verma, 1956). The components were weighed in different proportions in glass test tubes which were sealed. Homogeneous mixtures were made by heating above the melting points and chilling the test tubes. Ultimately the mixtures were taken out from the test tubes and crushed into fine powders. The thaw and melting points of the mixtures were determined.

Undercooling Measurements. Undercooling studies were performed in a similar way as described elsewhere (Rastogi and Verma, 1956). Mixtures (5 g) were placed in clean glass test tubes which were then sealed. The tubes were kept in an oil bath at a temperature 2 °C higher than the melting points of the mixtures. The bath was allowed to cool slowly. The temperature at which the first observable nuclei formed was noted, and the difference between this temperature and the melting point gave the undercooling value for a particular mixture.

Linear Velocity of Crystallization. The linear velocity of crystallization values were determined by the method described earlier (Rastogi and Bassi, 1964). The molten mixtures were placed in Pyrex glass tubes kept horizontally and vertically in an oil thermostat maintained at temperatures slightly lower, 0.5 °C, than the melting temperatures (in the range of undercooling temperature). The seed crystals of the same mixture or of different compounds were introduced from one side of the tube in both the cases. The time for the crystallization of a definite length in the tube was noted with a stopwatch.

Microscopic and Microphotographic Studies. A small amount of the pure component or the eutectic was placed on a glass slide and placed at a temperature higher than the melting temperature of the pure components or eutectics, 1 °C higher, so as to ensure melting. The cover slip was glided over the melt and allowed to undercool between about 8 and 2 °C. Nucleation started from one side, and care was taken to have unidirectional freezing. The microphotographs were taken with the help of a camera with the microscope at a suitable magnification.

Results and Discussion

The phase diagrams of the *p*-dichlorobenzene + *p*-dibromobenzene and resorcinol + *p*-dibromobenzene systems were recorded, and the representative phase diagram is shown in Figure 1 and the solid−liquid equilibrium data are given in Table 1. The undercooling data are also given in the same table. Thermodynamic analysis shows that the systems are nonideal at the eutectic points.

To study the process of crystallization, experiments were performed in U-shaped (in horizontal portions only) and vertical tubes using seed crystals of any compound or the same eutectic mixture. When seed crystals of the same material (eutectic mixtures) were introduced into the U tubes, the time required for the start of crystallization was lower at each undercooling as compared to that when picric acid was used as a seed crystal (Table 2). The results indicate that seed crystals having identical crystal structures to that of the crystallizing material accelerate the process of crystallization. It was also observed that the time required for crystallization was lower in vertical tubes, which might be due to the gravitational effect (Table 3).

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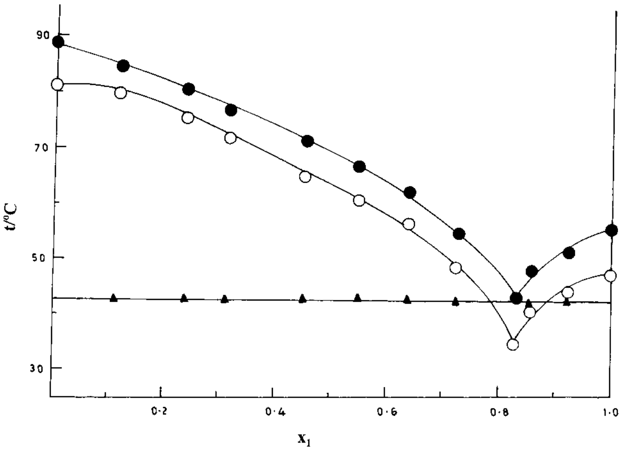

Figure 1. Phase diagram and undercooling for the *p*-dichlorobenzene + *p*-dibromobenze eutectic: (●) melting point; (▲) thaw point; (○) undercooling.

Table 1. Phase Equilibrium for the Eutectic Systems

x_1	thaw temp/°C	t_f/°C	undercooling/°C
p-Dichlorobenzene (1) + *p*-Dibromobenzene (2)			
1.0		54.0	8.8
0.9275	42.5	51.0	8.3
0.8640	42.0	47.5	6.0
0.8325		42.5	8.5
0.8247	42.5	44.2	5.0
0.7335	42.2	54.2	5.9
0.6472	42.6	61.8	6.0
0.5560	43.0	66.1	6.1
0.4525	42.2	70.1	5.2
0.3158	42.5	76.0	4.8
0.2455	42.8	80.5	5.5
0.1250	42.8	84.0	4.5
0.000		89.0	8.1
Resorcinol (1) + *p*-Dibromobenzene (2)			
1.0000		110.0	8.5
0.9435	73.0	108.6	8.2
0.8322	73.0	107.5	9.0
0.7385	72.8	104.0	7.3
0.6645	73.0	100.5	5.8
0.5374	73.0	93.0	8.0
0.4081	72.8	79.8	9.5
0.3780		72.8	9.5
0.3475	72.0	74.1	8.2
0.2825	72.5	78.2	8.0
0.2130	72.2	82.5	8.9
0.1225	72.5	85.0	5.3
0.0000		89.0	8.1

Table 2. Time Interval after which Crystallization Starts in a U Tube for Eutectic Melts on the Addition of Seed Crystals

undercooling (ΔT/°C)	time interval when seed crystal is from	
	(a) same mixture (*t*/s)	(b) picric acid (*t*/s)
p-Dichlorobenzene + *p*-Dibromobenzene		
8.0	11.0	16.0
6.0	19.0	24.0
4.0	27.0	37.0
2.0	31.0	52.0
Resorcinol + *p*-Dibromobenzene		
8.0	43.0	57.0
6.0	52.0	63.0
4.0	61.0	77.0
2.0	76.0	89.0

Table 3. Time Interval after which Crystallization Starts in a Vertical Tube for Eutectic Melts on the Addition of Seed Crystals of the Respective Eutectic Mixtures

undercooling (ΔT/°C)	time interval (*t*/s)	
	p-dicholorobenzene + *p*-dibromobenzene	resorcinol + *p*-dibromobenzene
8.0	9.0	27.0
6.0	17.0	36.0
4.0	21.0	43.0
2.0	23.0	52.0

Table 4. Linear Velocity of Crystallization

undercooling (ΔT/°C)	linear velocity of crystallization (V mm/s)		
	p-dichlorobenzene	*p*-dibromobenzene	eutectic
8.0	1.005	0.283	0.683
6.0	0.660	0.265	0.413
4.0	0.457	0.240	0.335
2.0	0.387	0.230	0.287

undercooling (ΔT/°C)	linear velocity of crystallization (V mm/s)		
	resorcinol	*p*-dibromobenzene	eutectic
8.0	0.277	0.283	0.204
6.0	0.159	0.265	0.109
4.0	0.139	0.240	0.074
2.0	0.094	0.230	0.056

The variations of the linear velocity of crystallization with undercooling are given in Table 4. If one assumes that the eutectics are simply a mechanical mixture of two components, the data on the linear velocity of crystallization should obey the mixture law (eq 1).

$$v = x_1v_1 + x_2v_2 \qquad (1)$$

where x_1 and x_2 are the mole fractions and v_1 and v_2 are the linear velocity of crystallization of components 1 and 2, respectively. The variation of the velocity of crystallization (v) with undercooling for experimental data and those calculated from eq 1 is also shown in Figure 2. From the figure the undercooling increases as the linear velocity of crystallization increases and the calculated values are higher than the experimental values. Winegard et al. (1957) and others (Rastogi and Rastogi, 1969) proposed that eutectic solidification begins with the formation of the nucleus of one of the phases. This will grow until the surrounding liquid becomes richer in the other component and reaches a stage when the second component starts nucleating. Two possibilities exist. First, the two initial crystals may grow side by side. This is the case in which the rate of solidification of eutectics is not lower than that of the parent components. The second possibility is that there may be alternate nucleation of the two components. This explains the phenomenon in which the linear velocity of crystallization of the eutectic is lower than that of either component. The crystallization rate in the resorcinol + *p*-dibromobenzene eutectic system is lower than that in the *p*-dichlorobenzene + *p*-dibromobenzene eutectic system. In the first system, there are hydroxyl groups in the resorcinol and hence molecular association will be more, resulting in lower crystallization rate values.

The microstructural properties of the components and eutectics have been studied by unidirectional solidification on glass slides and by taking microphotographs. The microstructure of *p*-dichlorobenzene shows rectangular-shaped crystals whereas the microstructure of *p*-dibromobenzene is irregular with regularity in a particular line. The microstructure of the eutectic between the two components shows rectangular-shaped crystals converging around a central point. It appears that in the eutectic the crystals of *p*-dibromobenzene lose their identity and influence the shape of the rectangular crystals of *p*-dichloroben-

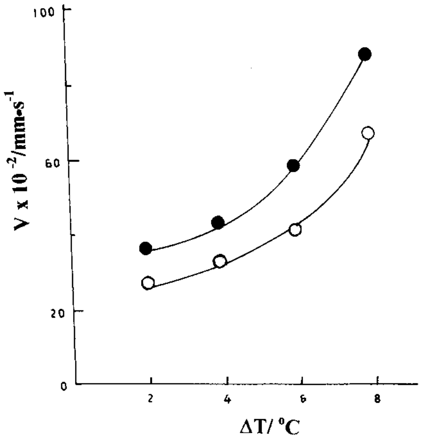

Figure 2. Experimental (○) and mixture law (●) values of the linear velocity of crystallization for the *p*-dihlorobenzene + *p*-dibromobenzene eutectic.

zene in such a manner that they seem to orient around a central point. Thus, it can be said that both the components influence the crystallization pattern of each other in the eutectic. The microstructure of resorcinol is lamellar type, and that of the resorcinol + *p*-dibromobenzene eutectic appears to be lamellar with irregular spacing. Again, the two components influence the crystallization process and the microstructure of the eutectic.

The overall results show that the eutectics are not a mechanical mixture of the two components but that there is some sort of weak molecular association between them. The microstructures of the eutectics are controlled by the microstructures and crystallization behavior of the components.

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