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PHYSICAL CHEMISTRY OF ORGANIC EUTECTICS

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Abstract

Phase diagrams of urea–α-naphthol and urea benzoic acid systems, determined by the thaw-melt method, show the formation of simple eutectic in each case. The growth velocity data, determined at different undercooling (ΔT) by observing the rate of movement of interface in a capillary, obey the Hillig-Turnbull equation, $v=u(\Delta T)^n$, where u and n are constants depending on the nature of the materials. Using enthalpy of fusion, undercooling (ΔT) and melting point data, entropy of fusion, interfacial energy, enthalpy of mixing, critical radius size and excess thermodynamic functions were calculated. The microstructural investigations give characteristic features of the eutectics.

Keywords: growth kinetics, microstructure, organic eutectics, phase diagram, thermochemistry

Introduction

Chemists, metallurgists and materials scientists are actively involved in the study of chemistry of eutectic alloys. The fundamental interest lies in the study of the crystallization mechanism, microstructure, thermochemistry and thermodynamics of eutectics with a view to develop new materials of technological and commercial importance. Because of their potential use in the modern civilization, the metal eutectics and the intermetallic compounds constitute an interesting area of investigation in metallurgy and materials science [1]. The direct observation on solidification of transparent organic systems [2–4] has been the most useful technique to unfold the mysteries of solidification, which in turn, control the properties of materials. The low transformations temperature, transparency, ease in purification and experimentation, minimised convection effects and wider choice of materials are the special features which have prompted a number of research workers [5–10] to choose organic systems as model systems for detailed investigation of the parameters which control the mechanism of solidification.

With a view to explain the mechanism of formation of eutectic alloys, various [11] theories have been put forward from time to time. According to one [12] the eutectics are chemical compounds in the form of clusters existing at higher tem-

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perature and in the liquid state. During solidification the clusters decompose with the formation of initial compounds. On the other hand, according to the other theory [13] the eutectics are mechanical mixture of the two components. However, none of the theories explains all the properties of eutectics. In the present article, phase diagram, crystallization behaviour, thermochemistry and microstructure of binary organic systems of urea (U) with each of α-naphthol (AN) and benzoic acid (BA) have been reported.

Experimental

Materials and purification

Urea was recrystallized from conductivity water below 60°C. While α-naphthol was purified by repeated distillation under reduced pressure, benzoic acid was recrystallized from boiling water. The purity of each compound was checked by comparing its melting point from those reported in the literature.

Phase diagram

Phase diagrams of U–AN and U–BA systems were determined by the thaw melt method [14 and 15]. In this method mixtures of two components covering the entire range of composition are prepared in long necked test tubes, they are homogenized and their melting and thawing temperatures are determined. A graph between melting temperature and composition gives the phase diagram of a system.

Growth velocity

The values of linear velocity of crystallization of pure components and eutectics were determined at different undercoolings by observing the rate of movement of the solid-liquid interface in a capillary [16 and 17].

Enthalpy of fusion

The enthalpy of fusion values of pure components and eutectics were determined [18] using a Mettler DSC-4000 system. The maximum percentage error in the experimental values is 1.5. Indium was used as standard sample to calibrate the apparatus.

Microstructure

Microstructures of pure components and eutectics were determined [19] by placing small amount of the sample on a glass slide maintained at a temperature slightly higher than the melting point of the compound. The sample was unidirectionally solidified and then it was placed on the platform of an optical microscope (Leitz, laborlux D) to record its microstructure in different regions.

Results and discussion

Phase diagram

The phase diagrams of U–AN and U–BA systems are given in Figs 1 and 2, respectively. In both the diagrams the melting point of urea decreases with addition of the second components and it reaches the minimum value at the eutectic point of the system. At this point the system is invariant. Above this temperature the system has single phase only and below this temperature the system has two

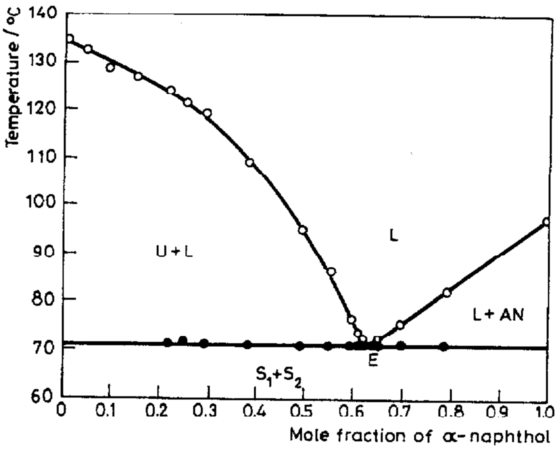

Fig. 1 Phase diagram of urea–α-naphthol; • – thaw temperature; o – melting temperature

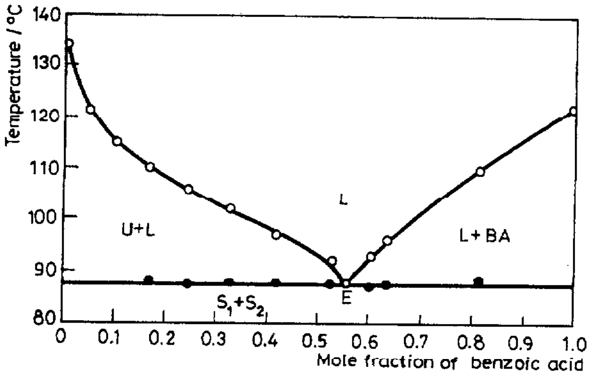

Fig. 2 Phase diagram of urea–benzoic acid; • – thaw temperature; o – melting temperature

phases. 0.360 and 0.442 are the mole fraction of urea in U–AN and U–BA systems, respectively. Beyond the eutectic point when the second component is added the melting point increases till the pure component is obtained. Melting points of eutectics of U–AN and U–BA systems are 71.0 and 87.5°C, respectively.

Growth velocity

According to Hillig-Turnbull [20], the growth velocity (v) is related to undercooling (ΔT) by the equation,

$$v = u(\Delta T)^{n} \tag{1}$$

where u and n are constants depending on the nature of solidification of the materials involved. Eq. (1) can be written as

$$\log v = \log u + n\log(\Delta T) \tag{2}$$

The linear plots of log$v$ against log(ΔT) are analysed by the least square fitting. Linear plots for U–AN and U–BA systems are given in Figs 3 and 4, respectively. The value of u and n, calculated by least squares fitting using a computer are given in table. In addition, the values of regression coefficient and confidence limit are also given in the Table 1. The data obey the parabolic law. The higher values of n of pure components than those of eutectics suggest that in these cases the solidification process is more effectively dependent on the undercooling in comparison to those of the eutectics.

It is well known that the value of u gives measure of rate of solidification. It can be inferred from Table 1 that the u values and hence rates of solidification of eutectics lies between those of the corresponding values of the pure components

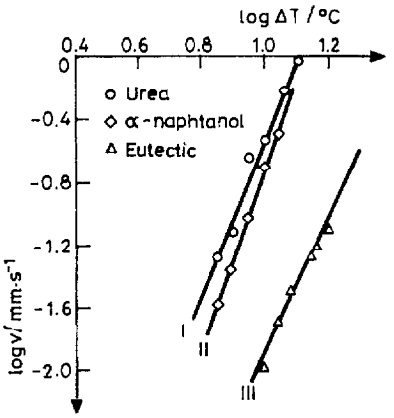

Fig. 3 Linear velocity of crystallization of urea, α-naphthol and their eutectic

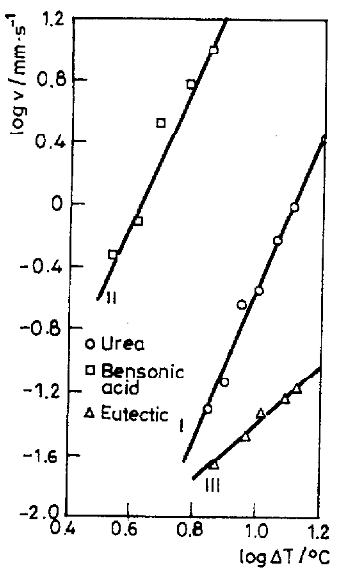

Fig. 4 Linear velocity of crystallization of urea, benzoic acid and their eutectic

of a system. These results can be explained by the mechanism proposed by Winegard *et al.* [21]. According to them the eutectic solidification begins with the formation of nucleus of one of the phases. This grows until the surrounding liquid becomes rich in the other component and a stage is reached when the second component starts nucleating. Now there are two possibilities. First, the two initial crystals may grow side by side. This explains the cases in which the rates of solidification of eutectics are not lower than those of the parent components. The second possibility is that there may be alternate nucleation of the two components. This explains the solidification phenomenon in cases where the crystallization velocity of the eutectic is lower than that of either component. In the present case first possibility is applicable in both the systems. In both cases, urea with

Table 1 Value of u and n of urea, α-naphthol, benzoic acid and their eutectics

Materials	u	n	Regression coefficient/ r^2	Confidence limit/ %
Urea	$3.04 \cdot 10^{-6}$	5.01	0.992	95
α-naphthol	$2.26 \cdot 10^{-7}$	5.91	0.989	95
Benzoic acid	$1.54 \cdot 10^{-3}$	4.59	0.989	95
Urea–α-naphthol eutectic	$1.93 \cdot 10^{-7}$	3.86	0.993	95
Urea–benzoic acid eutectic	$3.71 \cdot 10^{-4}$	2.01	0.991	95

high melting point nucleates first followed by the nucleation of the second components, namely, α-naphthol or benzoic acid. Now the two phases grow by side-by-side growth mechanism.

Thermochemistry

It is well known that the phase transformation involves two steps: (i) nucleation and (ii) growth. The nucleation mechanism depends on the solid-liquid interfacial energy and the growth step depends on the manner in which particles from the liquid phase are added at the solid-liquid interface. While the former can be estimated from the heats of fusion data, the latter is determined by the structure of the interface which depends on the entropy of fusion of the material under investigation and the thermal environment in which the crystal is growing. Thus, the heats of fusion of pure components and eutectics are very important in understanding the mechanism of solidification. From the heat of fusion, undercooling (ΔT) and melting point data, the entropy of fusion, interfacial energy, radius of critical nucleus, enthalpy of mixing end excess thermodynamic functions can be calculated.

Enthalpy of mixing

The values of enthalpy of fusion of the pure components and the eutectic, determined experimentally, are reported in Table 2. If an eutectic is a simple mechanical mixture of two components, involving neither heat of mixing nor any type of association in the melt, the heat of fusion may simply be given by the mixture law [22],

$$(\Delta_f h)_e = x_1 \Delta_f h_1^o + x_2 \Delta_f h_2^o \tag{3}$$

where x and $\Delta_f h^o$ are the mole fraction and heat of fusion, respectively, of the component indicated by the subscript. For the purpose of comparison the calculated values are also given in the same table. When a solid eutectic melts, there is considerable possibility of association and heat of mixing, both causing violation of the mixture law. The heat of mixing [23] ($\Delta_{mix}H$) which is the difference between the experimental and the calculated values of heats of fusion are given in the table. Thermochemical studies [24] suggest that the structure of a binary eutetic melt depends on the sign and magnitude of the heat of mixing. As such, three types of structures are suggested: (i) quasi-eutectic for $\Delta_{mix}H>0$, (ii) clustering of molecules for $\Delta_{mix}H<0$, and (iii) molecular solutions for $\Delta_{mix}H=0$. The negative values of enthalpy of mixing suggest clustering of molecules in the binary eutectic melts.

Entropy of fusion and excess thermodynamic function

While the excess thermodynamic functions provide a quantitative measure of the deviation of the system from ideal behaviour, the entropy of fusion gives idea of role of this factor in melting of the eutectic. The entropy of fusion was calculated from the following equation:

$$\Delta_f S = \frac{\Delta_f H}{T} \tag{4}$$

where $\Delta_f H$ is the heat of fusion and T is the melting temperature. The values of entropy of fusion are given in Table 2.

Table 2 Heat of fusion, heat of mixing, entropy of fusion, roughness parameter and interfacial energy of urea–α-naphthol and urea benzoic acid system

Materials	Heat of fusion/ kJ mol^{-1}	Heat of mixing/ kJ mol^{-1}	Entropy of fusion/ J mol^{-1}K^{-1}	Roughness parameter $\alpha, \frac{\Delta_f S}{R}$	Interfacial energy/ erg cm^{-2}
Urea	14.6		35.9	4.3	54.7
α-naphthol	24.4		66.0	8.0	44.8
Benzoic acid	18.1		45.8	5.5	40.7
Urea–α-naphthol eutectic					
i) Experimental	12.8	–8.1	37.2	4.5	48.3
ii) Calculated (mixture law)	20.9				
Urea-benzoic acid eutectic					
i) Experimental	11.2	–5.3	31.1	3.8	46.9
ii) Calculated (mixture law)	16.5				

With a view to understanding the nature of interactions between the components forming the eutectic, some excess thermodynamic functions, such as free energy (g^E), enthalpy (h^E) and entropy s^E were calculated using the following equations [25]:

$$g^E = RT(x_1 \ln\gamma_1^l + x_2 \ln\gamma_2^l) \tag{5}$$

$$h^E = -RT^2\left(x_1\frac{\delta \ln\gamma_1^l}{\delta T} + x_2\frac{\delta \ln\gamma_2^l}{\delta T}\right) \tag{6}$$

$$s^E = -R\left(x_1 \ln\gamma_1^l + x_2 \ln\gamma_2^l + x_1 T\frac{\delta \ln\gamma_1^l}{\delta T} + x_2\frac{\delta \ln\gamma_2^l}{\delta T}\right) \tag{7}$$

The activity coefficient γ_i^l, of the component i in the eutectic melt was calculated using the relation,

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^o}{R}(T^{-1} - T_i^{o-1}) \qquad (8)$$

where x_i^l, $\Delta_f h_i^o$ and T_i^o are mole fraction, heat of fusion and melting temperature of component i, respectively; R is the gas constant and T is the melting temperature of the eutectic. The heat capacity difference (ΔC_p) between liquid and the solid is assumed to be zero. The values of excess thermodynamic functions are given in Table 3. The positive values of g^E predict [26] that molecular association between like molecules is stronger than between unlike molecules. On the other hand the negative values of g^E suggest that molecular association between unlike molecules is stronger than that between like molecules.

Table 3 Excess thermodynamic functions for eutectics of urea α naphthol and urea benzoic acid systems

Materials	g^E/J mol^{-1}	h^E/kJ mol^{-1}	S^E/J mol^{-1}K^{-1}
Urea–α-naphthol eutectic	–50.6	–3.2	–9.2
Urea–benzoic acid eutectic	433.1	6.0	15.3

Interfacial energy and radius of critical nucleus

The magnitude of the heat of fusion is affected by the interfacial tension. Also, the solid-liquid interfacial energy plays very important role in the kinetics of nucleation process during phase transfomation. The interfacial energy (σ) is given by the expression [27],

$$\sigma = \frac{C\Delta_f H}{N^{1/3}(V_m)^{2/3}} \qquad (9)$$

where N is the Avogadro number, V_m, is the molar volume and parameter C lies between 0.30 and 0.35. The calculated values of interfacial energy are given in Table 2.

It is well known that the melt contains a number of tiny particles, each containing a larger number of molecules. If the size of a particle is smaller than the size of the critical nucleus, it is called an embryo, and it does not provide a stable nucleus for subsequent growth to take place. When the particle size corresponds to the size of the critical nucleus, it gives a stable nucleus for growth of a crystal. The radius of the critical nucleus (r^*) depends on the interfacial energy, the melting temperature (T) and the undercooling (ΔT) according to the following equation [28],

$$r^* = \frac{2\sigma T}{\Delta_f H \Delta T} \qquad (10)$$

where $\Delta_f H$ is the enthalpy of fusion per unit volume. The radius of critical radius was calculated at different undercoolings and the results are given in Table 4. It is evident from the table that the radius of the critical nucleus decreases with increase in undercooling of the melt.

Table 4 Critical size of nucleus at different undercoolings

Undercoolings/ °C	Critical radius×10^8 cm				
	U	AN	BA	U–AN eutectic	U–BA eutectic
4.0			4.45		
5.0			3.56		
6.0			2.96		
7.0	4.35	1.94			
7.5					4.37
8.0	3.80	1.70	2.12	3.16	
9.0	3.38	1.51			
9.5					3.45
10.0	3.05	1.36		2.53	
10.5					3.13
11.0				2.30	
12.5					2.62
14.0				1.80	

Microstructure

The growth morphology [29] developed by a eutectic system is governed by the growth characteristics of the individual phases, on the basis of which phases solidify with either faced or non-faceted interfaces. This behaviour is related to the nature of solid-liquid interface and can be predicted from the value of entropy of fusion. According to Hunt and Jackson [30] the type of growth from an eutectic melt depends upon a factor α, defined as

$$\alpha = \xi \frac{\Delta_f H}{RT} = \frac{\Delta_f S}{R} \tag{11}$$

where ξ is crystallographic factor depending on the geometry of the molecules and has the value less than or equal to one. $\Delta_f S/R$ which is also known as the Jackson's roughness parameter, is the entropy of fusion in dimensionless unit and R is the gas constant. When α is less than two, it results in non-faceted growth. On the other hand when α is greater than two, the phases exhibit faceted growth. The values of α for pure components and the eutectics are given in Table 2. These val-

Fig. 5 Microstructure of eutectic of urea–α-naphthol×600

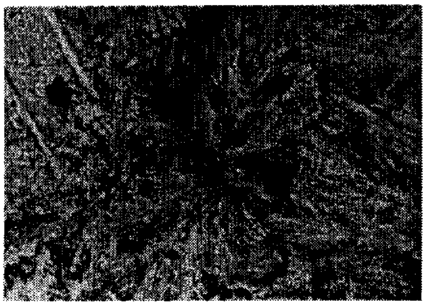

Fig. 6 Microstructure of eutectic of urea–benzoic acid×600

ues suggest faceted growth of these compounds. The typical microstructure of U–AN and U–BA systems are given in Figs 5 and 6, respectively. While Fig. 5 gives formation of eutectic colonies, Fig. 6 shows nucleation of a phase along with outward radiation of the other phase in all directions.

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