SOLID–LIQUID EQUILIBRIA, PHYSICOCHEMICAL AND MICROSTRUCTURAL STUDIES OF BINARY ORGANIC EUTECTIC ALLOY: UREA + 2-AMINOBENZOTHIAZOLE SYSTEM

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Abstract: Phase diagram of binary organic system of urea (U) with 2-aminobenzothiazole (ABT) shows the formation of a eutectic at 0.350 mole fraction of urea. Growth kinetics of the eutectic and pure components studied by measuring the rate of movement of solid-liquid interface in a thin glass U-tube at different undercoolings ($\ddot{A}T$) suggests the applicability of Hillig-Turnbull's equation: $v = u\ (\ddot{A}T)^n$. The thermodynamic functions such as heat of mixing, entropy of fusion, roughness parameter, interfacial energy and excess thermodynamic functions were calculated from the enthalpy of fusion values, obtained from DSC data. The optical microphotographs of pure and eutectic alloy show their characteristic features.

Keywords: Phase equilibria; Thermochemistry; Microstructure; Eutectic; Interfacial energy.

INTRODUCTION

Metal eutectic and intermetallic compounds constitute an interesting area of investigation in metallurgy and materials science.[1-5] Due to high transformation temperature, difficulty in purification, optical opacity, large difference in density and a limited choice of materials, they are not appropriate for detailed investigations. Binary organic materials in many cases may act as analogues to metallic systems. Because of low transformation temperature, ease in purification, transparency, wider choice of materials and simplicity in experimentation, organic systems are being used as model systems for detailed physicochemical investigations.[6-8] Mechanism of solidification controls the various properties of materials, which in organic systems can be visually observed. Physical and chemical properties of the eutectic alloys can be understood to a great extent in terms of thermodynamic properties like excess free energy, enthalpy of mixing, roughness parameters and interfacial energy. In this communication, studies on phase diagram, linear velocity of crystallization, heat of fusion, Jackson's roughness parameter, excess thermodynamic functions and microstructural analysis of urea (U) – 2-aminobenzothiazole (ABT) system are studied. It is of interest to note that the system is an organic analogue of nonmetal-nonmetal system.[9,10]

EXPERIMENTAL

Materials and purification

2-aminobenzothiazole (Aldrich, Germany) was purified by recrystallization from ethanol while urea (CDH, India) was purified by recrystallization from conductivity water.

Melting points of the purified U and ABT were found to be 133.0 ^{0}C and 129.0 ^{0}C respectively, which are in accord to their respective literature values.[11,12]

Phase diagram

The phase diagram of U-ABT system was established by plotting the melting temperatures of various compositions against composition.[13] In this method mixtures of the two components covering entire range of compositions were taken in long necked test tubes. The test tubes were sealed and the mixtures were then homogenized by repeating the process of melting followed by chilling in ice cooled water for 4-5 times. The test tubes were broken; the solidified mass from each tube was taken out and crushed into fine powder. The melting points were determined using Toshniwal melting point apparatus attached with a precision thermometer of accuracy ± 0.5 ^{0}C. The melting temperatures were plotted against respective molar compositions to get phase diagram.

Enthalpy of fusion

The values of heat of fusion of the eutectic and the pure components were determined by differential scanning calorimeter (Mettler DSC-4000 system). Indium sample was used to calibrate the system and the amount of test sample and heating rate were about 7 mg and 10 ^{0}C min^{-1}, respectively. The values of enthalpy of fusion are reproducible with in ± 1.0 %.

Growth kinetics

The linear velocity of crystallization of pure components and the eutectic were determined at different undercoolings by measuring the rate of movement of the solid–liquid

Table 1: Value of u and n for pure and eutectic:

Material	n	u(mm sec^{-1}deg^{-1})
Urea	5.196	1.731 X 10^{-6}
ABT	2.081	7.198 X 10^{-3}
U-ABT(Eu)	1.886	1.068 X 10^{-4}

interface in a U-shaped thin glass tube with about 150 mm horizontal portion and 5 mm internal diameter.[13] Molten samples were separately taken in U-tube and placed in a silicone oil bath. The temperature of oil bath was maintained using microprocessor temperature controller of accuracy ±0.1 ^{0}C. At different undercoolings, a seed crystal of the same composition was added to start nucleation, and the rate of movement of the solid–liquid interface was measured using a traveling microscope and a stop watch.

Microstructure

Microstructures of the pure components and the eutectics of both systems were recorded by placing a drop of molten compound on a hot glass slide. A cover slip was glided over the melt and it was allowed to solidify unidirectionally.[13] The slide was placed on the platform of a polarizing binocular microscope (LOMO, USA), different regions were viewed and interesting regions were photographed with suitable magnification of a digital camera (Nikon coolpix 4500)] attached with the microscope.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram of the U-ABT (urea-aminobenzothiazole) system is shown in Figure 1. The phase diagram curve suggests the formation of a eutectic mixture at 0.35 mol fraction of urea with melting point 111.5 ^{0}C. At the eutectic temperature, three phases, namely a binary liquid phase L and two solid phases S_1 and S_2, are in equilibrium and the system is invariant. When a solution of the eutectic composition is cooled below eutectic temperature, it dissociates into two solid phases as:

$$L \leftrightarrow S_1 + S_2$$

Growth kinetics

In order to study the crystallization and solidification behavior of the pure components and the eutectic

Table 2: Heat of fusion, heat of mixing, entropy of fusion, roughness parameter and Interfacial energy.

Material	Heat of fusion (kJ mol^{-1})	Heat of mixing (kJ mol^{-1})	Entropy of fusion (Jmol^{-1}K^{-1})	Roughness Parameter (kJmol^{-1}K^{-1})	Interfacial Energy (ergs cm^{-2})
Urea	14.60		35.96	4.33	47.87
ABT	19.63		48.84	5.87	35.75
U-ABT (Eu) Exp.	16.09	-1.76	41.85	5.03	39.99
Cal.	17.87				

Table 3: Excess thermodynamic Functions for eutectics

Material	g^E (kJ mol^{-1})	h^E (kJ mol^{-1})	s^E (kJ mol^{-1}K^{-1})
U-ABT(Eutectic)	1.244	-5.301	-0.011

composition the linear velocities of crystallization (v) were determined at different undercoolings (ÄT) by measuring the rate of movement of solid-liquid interface in a thin glass U-tube. The plots between log ÄT and log v are given in Figure 2. The linear dependence of these plots is in accordance with the Hillig-Turnbull's equation[14]

$$v = u\,(Ä T)^n \qquad \ldots (1)$$

where u and n are constants and depend on the solidification behavior of the materials involved. The experimental values of these constants are given in Table 1. These values suggest that the growth velocity of eutectic composition is in between its parent components. The results may be explained on the basis of the mechanism proposed by Winegard *et al.*[15] According to this, the eutectic crystallization begins with the formation of a nucleus of one of the phases. The phase with higher melting point will start nucleating first and this phase grows until the surrounding liquid becomes rich in the other phase and a stage is reached when the second component also start nucleating. Now there are two possibilities, either the two initial crystals may grow side-by-side or there may be alternate nucleation of the two phases. The alternate nucleation process explains the lower crystallization velocity of a binary melt compared to the pure components. It is evident from the Table 1 that the value of u for the eutectic mixture is in between to its pure components which suggests the two phases of eutectic solidify and grow with side-by side mechanism.

Thermochemistry

Enthalpy of fusion

The values of enthalpy of fusion of the pure components and the eutectic determined by the DSC method are reported in Table 2. For comparison, the value of enthalpy of fusion of eutectic calculated by the mixture law[8] is also

Table 4: Critical radius of Pure and eutectic composition

Undercooling [ÄT (^{0}C)]	Critical radius (X 10^{-8} m)		
	Urea	ABT	U-ABT(Eu)
5.0		3.09	
7.0	3.80	2.21	
8.0	3.33		2.39
9.0	2.96	1.17	
10.0	2.66		
11.0	2.42	1.41	1.74
13.0	2.05		
14.0			1.37
17.0			1.12
20.0			0.96

included in the same table. The enthalpy of mixing which is the difference of experimental and the calculated values, for eutectic of U-ABT system is found to be -1.76kJmol^{-1}. As such, three types of structures are suggested;[16] quasi-eutectic for $D_{mix}H > 0$, clustering of molecules for $D_{mix}H < 0$ and molecular solution for $D_{mix}H = 0$. The negative value of $D_{mix}H$ for the eutectic suggests the clustered structure in the binary melt. The entropy of fusion ($D_{fus}S$) values, for different materials has been calculated by dividing the enthalpy of fusion by their corresponding absolute melting temperatures (Table 2). The positive values in all components suggest that the entropy factor favors the melting process.

Size of critical nucleus and interfacial energy

When liquid is cooled below its melting temperature, it does not solidify spontaneously because under equilibrium condition, the melt contains number of clusters of molecules of different sizes. As long as the clusters are well below the critical size, they can not grow to form crystals and, therefore, no solid would result. The critical size ($r*$) of nucleus[10] is related to interfacial energy ( ) by the equation,

$$r* = \frac{2\sigma T_{fus}}{\Delta_{fus}H.\Delta T} \qquad \dots (2)$$

where, T_{fus}, $D_{fus}H$ and DT are melting temperature, heat of fusion, and degree of undercooling, respectively. An estimate of the interfacial energy is given by the expression

$$\sigma = \frac{C.\Delta_{fus}H}{(N_A)^{1/3}.(V_m)^{2/3}} \qquad \dots (3)$$

where, N_A is the Avogadro number, V_m is the molar volume, and parameter C lies between 0.30 and 0.35. The calculated values of critical nucleus of different materials at different undercoolings are reported in Table 4.

Excess thermodynamic functions

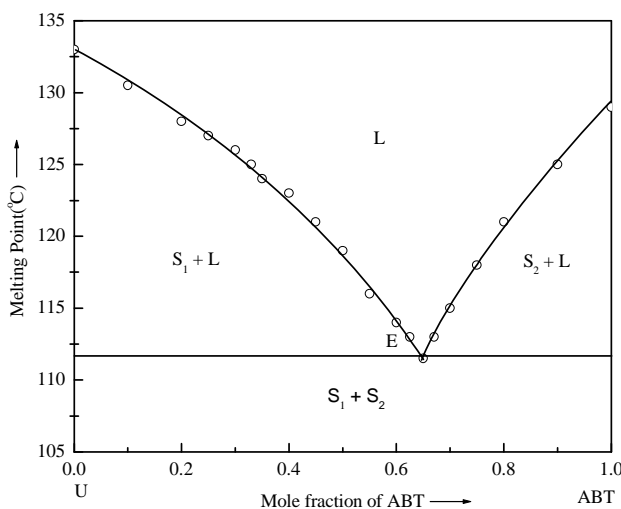The deviation from the ideal behavior can best be

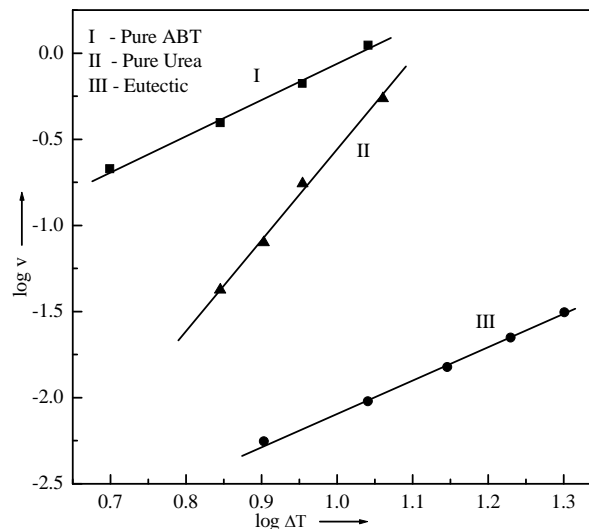Fig. 1: Phase diagram of U-ABT system Of Melting temperature.

expressed in terms of excess thermodynamic functions, namely, excess free energy (g^E), excess enthalpy (h^E), and excess entropy (s^E) which give a more quantitative idea about the nature of molecular interactions. The excess thermodynamic function[9] has been calculated by using the following equations and the values are given in Table 3.

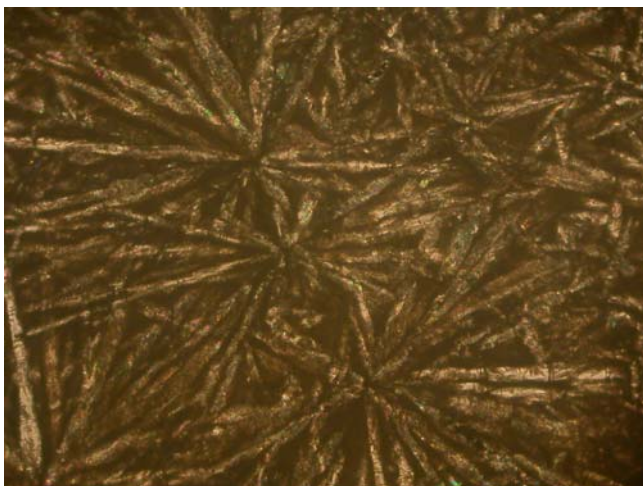$$g^E = RT\left[x_1\ln\gamma_1^1 + x_2\ln\gamma_2^1\right] \qquad \dots(4)$$

$$h^E = -RT^2\left[x_1\frac{\partial\ln\gamma_1^1}{\partial T} + x_2\frac{\partial\ln\gamma_2^1}{\partial T}\right] \qquad \dots(5)$$

$$s^E = -R\left[x_1\ln\gamma_1^1 + x_2\ln\gamma_2^1 + x_1T\frac{\partial\ln\gamma_1^1}{\partial T} + x_2T\frac{\partial\ln\gamma_2^1}{\partial T}\right] \dots(6)$$

Where $\ln\gamma_i^1$, x_i and $\dfrac{\partial\ln\gamma_i^1}{\partial T}$ are activity coefficient in liquid state, the mole fraction and variation of *log* of activity coefficient in liquid state as a function of temperature of component *i*. It is evident from equations (4) - (6) that activity coefficient and its variation with temperature are required to calculate the excess functions. Activity coefficient (γ_i^1) could be evaluated by using the equation

$$-\ln\left(x_i\gamma_i^1\right) = \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{fus}} - \frac{1}{T_i}\right) \qquad \dots (7)$$

Where x_i, $\Delta_{fus}H_i$, T_i and T_{fus} are mole fraction, enthalpy of fusion, melting temperature of component *i* and eutectic melting temperature, respectively. The variation of activity coefficient with temperature could be calculated by differentiating equation[7] with respect to temperature

Fig. 2: Linear velocity of crystallisation at various degrees of undercooling for U, ABT and their eutectic

Fig. 3: Directionally solidify optical microphotograph of U-ABT eutectic

$$\frac{\partial \ln \gamma_i^l}{\partial T} = \frac{\Delta_{fus} H_i}{RT^2} - \frac{\partial x_i}{x_i \partial T} \qquad \dots (8)$$

$\partial x_i / \partial T$, in this expression was evaluated by taking two points near the eutectic. The positive value of excess free energy, g^E in both the systems suggests that the interaction between like molecules is stronger than those between unlike molecules.[17] The negative values of h^E and s^E very much related to g^E, are measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

Microstructure

It is well known that in polyphase materials the microstructure gives the information about shape and size of the crystallites, which plays a significant role in deciding about mechanical, electrical, magnetic and optical properties of materials. The growth morphology of a eutectic system is controlled by the growth characteristics of the constituent phases. According to Hunt and Jackson[18] the type of growth from melts depends upon the interface roughness (a) defined by

$$a = x \, D_{fus} H / RT \qquad \dots (9),$$

where, x is a crystallographic factor which is generally equal to or less than one. The values of a are reported in Table 2. If a > 2 the interface is quite smooth and the crystal develops with a faceted morphology. On the other hand, if a < 2, the interface is rough and many sites are continuously available and the crystallization or solidification develops with a non-faceted morphology. In the present system, the values of a for each parent components and eutectic are more than 2 (Table 2), suggesting thereby their faceted growth. The optical microphotograph of eutectic (Fig. 3) shows cellular dendrite morphology. The eutectic solidification starts from various nucleation points and grows outwards in all directions from that point.

CONCLUSION

The phase diagram study shows that urea forms simple eutectic systems with 2-aminobenzothiazole. The growth kinetics of pure components and eutectic determined at different undercoolings suggest that crystallization takes place according to the Hillig-Turnbull equation. The enthalpies of fusion, entropy of fusion, enthalpy of mixing, excess thermodynamic functions and interfacial energy have been studied using the values of enthalpy of fusion as determined by the DSC method. The negative values of enthalpies of mixing of the system, suggests the cluster structure in the binary melt of the eutectic. The calculated (+ve) values of excess free energy of eutectic indicate that the interaction between like molecules is stronger than the unlike molecules. Microstructural investigation of the parents and eutectic of the system shows their characteristic features.

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