

Solid–liquid equilibrium, thermal and physicochemical studies of organic eutectics

R. S. B. Reddi · V. S. A. Kumar Satuluri ·
R. N. Rai

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Abstract The solid–liquid phase equilibrium data of two binary organic systems, namely, urea (U)–3-aminophenol (AP) and 3-hydroxybenzaldehyde (HB)– β -naphthol (BN) show formation of a eutectic in each case. The enthalpies of fusion of the pure components and binary eutectics have been determined using differential scanning calorimeter (Mettler DSC-4000) system. The thermal properties of the materials such as heat of mixing, entropy of fusion, roughness parameter, interfacial energy and excess thermodynamic functions were computed using the enthalpy of fusion values. The microstructures of eutectics were developed using unidirectional thermal gradient and interested region were photographed.

Keywords Phase diagram · Thermal properties · Organic eutectic · Microstructure

Introduction

Organic systems are found suitable than metallic systems due to low transformation temperature, transparency, wider choice of materials, and minimized convection effects. These are the special features which have prompted a number of research groups to study binary organic materials in detail [1–4] rather considering the metallic systems [5]. To begin with, organic systems are used as model systems for detailed investigation of several parameters

which control the mechanism of solidification and decide the properties of materials. Thus, the understanding of controlling parameters could be applied for metallic systems in which experimentation is difficult. During last two decades, the potential use of organic materials for nonlinear optical (NLO) and for different other electronic applications [6, 7] have prompted for their various physicochemical investigations in detail. Furthermore, syntheses of binary organic materials have shown potential to produce, as well as to modify, the NLO and white light emitting diode (WLED) materials [8, 9].

3-Aminophenol belongs to orthorhombic system with lattice parameters ($a = 6.14$, $b = 11.1$, and $c = 8.38$ Å) and it is good candidate for nonlinear optical (NLO) applications [10]. The urea is also an attractive material for frequency conversion of IR lasers to UV but the frequent use of urea crystal at normal atmosphere is troublesome due to its hygroscopic nature. The efforts made to resolve the problem associated with urea, the technique of binary preparation is imperative [11, 12]. β -Naphthol crystal belongs to monoclinic system with space group C_c , lattice parameters, $a = 32.141$, $b = 5.931$, and $c = 32.141$ and it is known organic material for second harmonic generation [13]. The 3-hydroxybenzaldehyde crystal belongs to orthorhombic unit cell, space group P_{na21} with lattice parameters, $a = 18.858$, $b = 3.864$ and $c = 8.190$ Å [14]. The significance of knowledge of phase diagram study for crystal growth as well as in synthesis of binary materials is known. With a view of synthesizing new materials, we selected two binary organic systems, namely, urea (U)–3-aminophenol (AP) and 3-hydroxybenzaldehyde (HB)– β -naphthol (BN) for the study in detail. In this article, we report the phase diagram study, thermal study of the pure compounds and the eutectics such as heat of fusion, Jackson's roughness parameter, excess thermodynamic functions, and

R. S. B. Reddi · V. S. A. Kumar Satuluri · R. N. Rai (✉)
Department of Chemistry, Centre of Advanced Study, Faculty
of Science, Banaras Hindu University, Varanasi 221 005, India
e-mail: rn_rai@yahoo.co.in

microstructural study. However, the others materials properties and crystal growth of interested binary are in progress.

Experimental procedure

Materials and purification

The starting materials urea (CAS: 57-13-6, 99%), 3-aminophenol (CAS: 591-27-5, 98%), 3-hydroxybenzaldehyde (CAS: 100-83-4, 97%), and β -naphthol (CAS: 135-19-3, 98%) were obtained from Sigma-Aldrich, Germany. The melting points of the received compounds of urea, 3-aminophenol, 3-hydroxybenzaldehyde, and β -naphthol are found to be 133.5, 122.5, 103.0, and 122.0 °C, respectively. Urea was purified by recrystallization from conductivity water below 60 °C. 3-Hydroxybenzaldehyde, 3-aminophenol, and β -naphthol were purified by recrystallization from ethanol. The melting points of urea, 3-aminophenol, 3-hydroxybenzaldehyde, and β -naphthol after purification were found 134.0, 123.0, 103.0, and 122.0 °C, respectively. The purity of each compound was assessed more than 99% by comparing their melting temperature with the standard values [15] and NMR study.

Phase diagram

The phase diagram of U–AP and HB–BN were studied, using the method reported earlier [16, 17], in the form of temperature–composition curve. In order to craft mixtures of different compositions covering entire range, the pure components were weighed using four digit electronic balance (Denver SI-234, Germany) of accuracy ± 0.0002 g. The mixtures of different compositions were taken in different glass test tubes, and the mouth of each test tube was sealed. The mixtures were homogenized by melting and mixing in oil bath followed by chilling in ice cooled water, and the process was repeated three times. During homogenization, the temperature of oil bath was maintained 5.0 °C above than the melting temperature of parent component of higher melting temperature. The melting temperatures of all the mixtures were determined with the help of a melting point apparatus (Toshniwal melting point) attached with thermometer which could read up to ± 0.5 °C, and the rate of rise of temperature, during melting point determination, was 0.5 °C per minute around the melting. The graphs were plotted between melting temperatures and their respective compositions.

Enthalpy of fusion

The values of heat of fusion of the pure components and the eutectics were determined [17, 18] by differential scanning

calorimeter (Mettler DSC-4000 system). Indium and Zinc samples were used to calibrate the DSC unit. The DSC experiments were performed under nitrogen gas environment and the gas flow rate was maintained to be 35 mL per minute. The amount of test sample and heating rate were about 5–7 mg and 5 °C/min, respectively. The values of enthalpy of fusion are reproducible within ± 0.01 kJ/mol.

Microstructure

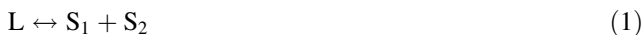
Microstructures of the pure components and the eutectics were recorded [18] by placing a drop of molten compound on a hot glass slide. To avoid the inclusion of the impurities from the atmosphere, a cover slip was glided over the melt and it was allowed to cool to get a super cooled liquid. The melt was nucleated with a seed crystal of the same composition at one end and the care was taken to have unidirectional freezing. The directionally solidified crystal system on the glass slide was then placed on the platform of an optical microscope (Leitz Labourlux D). The different regions of the slide were viewed with suitable magnification and photographs of interesting region were recorded using a camera attached with the microscope.

Results and discussions

Phase diagram

The phase diagrams of U–AP and HB–BN systems, reported in terms of melting temperature–composition curves, show the formation of simple eutectics (Figs. 1, 2). However, the concern data have been given in Table 1. The melting point of U is 134.0 °C and it decreases with the addition of AP and reaches to the minimum melting temperature, i.e., the eutectic temperature (85.5 °C) of U–AP system. Further addition of AP increases the melting point and reaches to 123.0 °C, which is the melting point of AP. The eutectic temperature and composition of U–AP system are 85.5 °C and 0.56 mol fraction of AP, respectively. Similarly, in case of HB–BN, the melting temperature of HB (103.0 °C) is decreases with the addition of BN and reaches to the minimum melting temperature and further addition of BN increases the melting point and reaches to the melting point of BN (122.0 °C). The eutectic temperature and composition of HB–BN system are 80.0 °C and 0.40 mol fraction of β -naphthol, respectively. It should be noted that composition other than eutectic composition, in both cases, does not melt at a particular temperature rather they melt in a range of temperatures. The reported temperatures in figures are the temperature where melting process completes. When a solution of the eutectic

composition is cooled below eutectic temperature, it dissociates into two solid phases as:



Three phases, namely, a binary liquid phase L and two solid phases S_1 and S_2 are in equilibrium at the eutectic point which is invariant point of the system.

Thermochemistry

It is well known that values of heat of fusion of the pure components and the eutectics are important in understanding the mechanism of solidification, structure of eutectic melt and the nature of interaction between two components forming the eutectics. The values of enthalpy of fusion of the pure components and the eutectics were determined by DSC and reported in Table 2. For comparison, the value of enthalpy of fusion of eutectic is also calculated by the mixture law [19] and included in the same table. The enthalpy of mixing, which is the difference of experimentally determined and the calculated values of the enthalpy of fusion, was found -7.0 and 0.9 kJ mol^{-1} for the eutectics of U-AP and HB-BN systems, respectively. As such, three types of structures are suggested [20]: quasi-eutectic for $\Delta_{\text{mix}}H > 0$, clustering of molecules for $\Delta_{\text{mix}}H < 0$ and molecular solution for $\Delta_{\text{mix}}H = 0$. The highly negative value of enthalpy of mixing in case of U-AP system suggests that there is associative interaction in the molecules of eutectic melt, and the positive value of

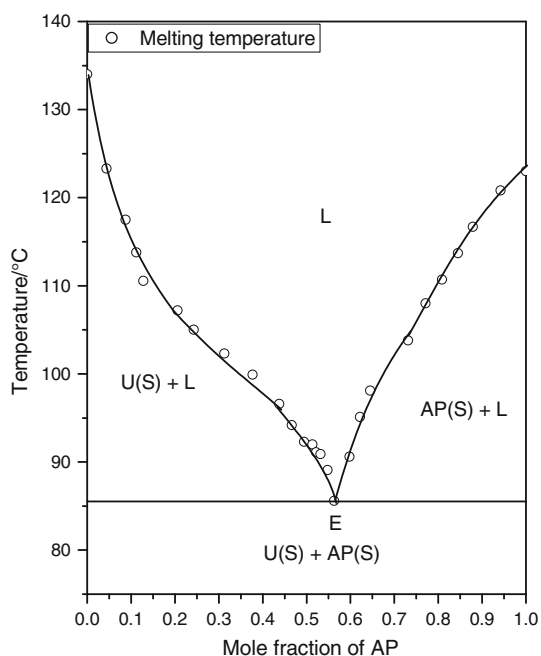


Fig. 1 Phase diagram of urea-3-aminophenol system

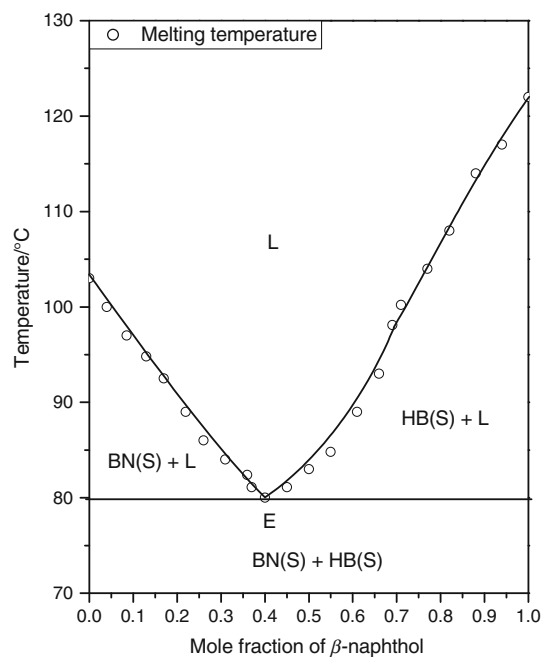


Fig. 2 Phase diagram of 3-hydroxybenzaldehyde- β -naphthol system

$\Delta_{\text{mix}}H$ for the eutectic suggests the formation of quasi-eutectic structure in the binary melt of the eutectic of HB-BN system [21]. The entropy of fusion ($\Delta_{\text{fus}}S$) values, for different materials has been calculated by dividing the enthalpy of fusion by their corresponding absolute melting temperatures (Table 2).

The deviation from the ideal behavior can best be 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 functions could be calculated by using equation [18, 22] reported earlier, and the calculated values are given in Table 3.

$$g^E = RT[x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l] \quad (2)$$

$$h^E = -RT^2 \left[x_1 \frac{\partial \ln \gamma_1^l}{\partial T} + x_2 \frac{\partial \ln \gamma_2^l}{\partial T} \right] \quad (3)$$

$$s^E = -R \left[x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l + x_1 T \frac{\partial \ln \gamma_1^l}{\partial T} + x_2 T \frac{\partial \ln \gamma_2^l}{\partial T} \right] \quad (4)$$

where $\ln \gamma_i^l$, x_i and $\frac{\partial \ln \gamma_i^l}{\partial T}$ are activity coefficient in the liquid state, the mole fraction and the variation of log of activity coefficient in liquid state as a function of temperature of the component i .

It is evident from Eqs. 2–4, that activity coefficient and its variation with temperature is required to calculate the excess functions. Activity coefficient (γ_i^l) could be evaluated [18] using the equation,

Table 1 Solid–liquid equilibria data for U–AP and HB–BN systems

S. No.	Mole fraction of AP/U–AP system	Melting temperature/ °C	Mole fraction of BN/HB–BN system	Melting temperature/ °C
1	0.00	134.0	0.00	103.0
2	0.04	123.0	0.00	100.0
3	0.09	117.5	0.09	97.0
4	0.11	114.0	0.13	95.0
5	0.13	110.5	0.17	92.5
6	0.21	107.0	0.22	89.0
7	0.24	105.0	0.26	86.0
8	0.31	102.5	0.31	84.0
9	0.38	100.0	0.36	82.5
10	0.44	96.5	0.37	81.0
11	0.47	94.0	0.40	80.0
12	0.50	92.5	0.40	81.0
13	0.51	92.0	0.50	83.0
14	0.52	91.0	0.55	85.0
15	0.53	90.5	0.61	89.0
16	0.55	89.0	0.66	93.0
17	0.56	85.5	0.69	98.0
18	0.60	90.5	0.71	100.0
19	0.62	95.0	0.77	104.0
20	0.65	98.0	0.82	108.0
21	0.73	104.0	0.88	114.0
22	0.77	108.0	0.94	117.0
23	0.81	110.5	1.00	122.0
24	0.85	114.0	–	–
25	0.88	116.5	–	–
26	0.94	121.0	–	–
27	1.00	123.0	–	–

$$-\ln(x_i \gamma_i^l) = \frac{\Delta_{\text{fus}} H_i}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T_i} \right) \tag{5}$$

where x_i , $\Delta_{\text{fus}} H_i$, T_i , and T_{fus} are mole fraction, enthalpy of fusion, melting temperature of component i and melting

Table 2 Heat of fusion, heat of mixing, entropy of fusion, roughness parameter and interfacial energy of two systems

Material	Heat of fusion/ kJ mol ⁻¹	Heat of mixing/ kJ mol ⁻¹	Entropy of fusion/ J mol ⁻¹ K ⁻¹	Roughness parameter α	Interfacial energy $\times 10^{-3}$ / J m ⁻²
U	14.6		35.8	4.3	54.7
AP	27.6		69.7	8.4	56.4
Eutectic					
(Exp.)	14.9	-7.0	41.6	5.0	55.6
(Cal.)	21.9				
HB	24.6		65.4	7.9	51.3
BN	21.2		53.7	6.5	43.9
Eutectic					
(Exp.)	24.1	0.9	68.3	8.2	48.3
(Cal.)	23.2				

temperature of a eutectic, respectively. The variation of activity coefficient with temperature could be calculated by differentiating Eq. 5 with respect to temperature

$$\frac{\partial \ln \gamma_i^l}{\partial T} = \frac{\Delta_{\text{fus}} H_i}{RT^2} - \frac{\partial x_i}{x_i \partial T} \tag{6}$$

$\partial x_i / \partial T$ in this expression can be evaluated by considering two points around the eutectic. The negative values of excess free energy in case of U–AP indicate that there is an associative interaction between unlike molecules, whereas the positive value of excess free energy in case of HB–BN indicates that there is an association between like molecules [23].

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 [24], they cannot grow to form crystals and, therefore, no solid would result. During growth, the radius of critical nucleus is influenced by undercooling as well as the interfacial energy of the surface involved. The interfacial energy (σ) is related to the critical size (r^*) of the nucleus and enthalpy of fusion by the following equation:

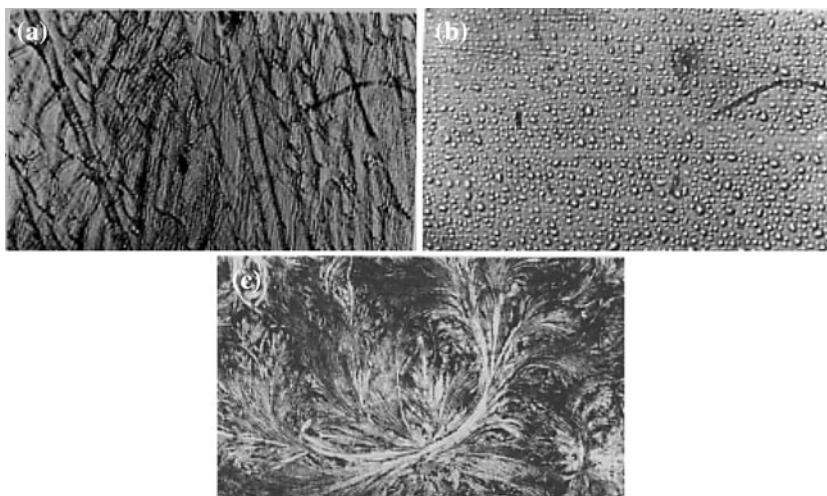
$$r^* = \frac{2 \sigma T_{\text{fus}}}{\Delta_{\text{fus}} H \cdot \Delta T} \tag{7}$$

where T_{fus} , $\Delta_{\text{fus}} H$ and ΔT are melting temperature, heat of fusion, and degree of undercooling, respectively. However, the interfacial energy (σ) is given by

Table 3 Excess thermodynamic functions for eutectics

Material	$g^E/\text{kJ mol}^{-1}$	$h^E/\text{kJ mol}^{-1}$	$s^E/\text{kJ mol}^{-1} \text{K}^{-1}$
Eutectic (U–AP)	-0.197	18.543	0.052
Eutectic (HB–BN)	0.171	52.111	0.147

Fig. 3 Microstructure of U–AP eutectic (a) and (b), and HB–BN eutectic (c)



$$\sigma = \frac{C \Delta_{\text{fus}} H}{(N_A)^{1/3} (V_m)^{2/3}} \quad (8)$$

where N_A is the Avogadro number, V_m is the molar volume, and parameter C lies between 0.30 and 0.35. The density used for the calculation of interfacial energy of U, AP, HB, and BN are 1.323, 1.27, 1.359, and 1.28 g/cm³, respectively. However, to compute the interfacial energy of the eutectic, the mixture law was used. The calculated values of interfacial energy are reported in Table 2.

Microstructure

It is well known that in polyphase materials the microstructure gives information about shape and size of the crystallites, which plays a very significant role in deciding mechanical, electrical, magnetic, and optical properties of materials. According to Hunt and Jackson [25] the type of growth from melts depends upon the interface roughness (α) defined by

$$\alpha = \xi \Delta_{\text{fus}} H / RT \quad (9)$$

where ξ is a crystallographic factor which is generally equal to or less than one, we have used one while calculating roughness. The values of α are reported in Table 2. If $\alpha > 2$ the interface is quite smooth and the crystal develops with a faceted morphology. On the other hand, if $\alpha < 2$, the interface is rough and many sites are continuously available and the crystal develops with a non-faceted morphology. In the present system, the values of α being greater than 2 in all the cases suggests that phases grow showing facets.

The unidirectional solidify microstructure of eutectic of U–AP and HB–BN systems are shown in Fig. 3. The microstructure of U–AP eutectic (Fig. 3a) shows the cellular morphology with variable width; however, the other view of microstructure of same eutectic shows droplet kinds of formation, which infact is vertical view of the

cellular lamella that has grown vertically (Fig. 3b). The observation of bifurcation of phases in microstructure infers the associative interaction between molecules of eutectic melts. The microstructure of eutectic HB–BN system shows the feather morphology (Fig. 3c) where the two phases of eutectic has grown almost together.

Conclusions

The phase diagram study of two binary organic systems, namely U–AP and HB–BN show the formation of simple eutectics with 0.56 mol fraction of AP and 0.40 mol fraction of BN, respectively. The highly negative value of enthalpy of mixing in case of U–AP system suggests that there is associative interaction in the molecules in the eutectic melt, and the positive value of $\Delta_{\text{mix}} H$ for the eutectic suggests the formation of quasi-eutectic structure in the binary melt of the eutectic of HB–BN system. The excess free energy ($-0.197 \text{ kJ mol}^{-1}$), in case of U–AP, indicates the associative interaction between unlike molecules. On the other hand, positive value of excess free energy for HB–BN is indicative of an association between like molecules. The Jackson's roughness parameters for binary eutectics suggest that phases grow with facets morphology. Microstructural studies of eutectics have shown the cellular and feather morphology.

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