Green synthesis, characterization and optical properties of eutectics and 1:1 intermolecular compounds: *N,N*-dimethylaminobenzaldehyde–anthranilic acid and 2-(4-(dimethylamino)benzylideneamino)benzoic acid–*p*-nitroaniline systems

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Abstract. Phase diagrams of *N,N*-dimethylaminobenzaldehyde (DMAB)–anthranilic acid (AA) and 2-(4-(dimethylamino)benzylideneamino)benzoic acid (DMABAB)–*p*-nitroaniline (PNA) systems, determined by the thaw-melt method, give two eutectics and a 1:1 intermolecular compound (IMC) in each case. Appropriate amounts (10 g) of each of the eutectics and the IMCs were prepared by a green synthetic method involving a solid state reaction without any solvent. These materials were characterized by X-ray diffraction, thermal and spectral methods and the optical properties of the pure components and the IMCs were studied. While negative values of heat of mixing in the case of a DMAB–AA system suggest clustering of molecules in both eutectic melts, those of positive value in E_1 and negative value in E_2 of the DMABAB–PNA system indicate the formation of a quasi-eutectic structure in E_1 melt and clustering of molecules in E_2 melt. The IMC of DMAB–AA system shows strong dual emission with two $\lambda_{\max}$ one at 380 nm and the second at 450 nm with a total quantum efficiency of 0.49. The IMC of DMABAB–PNA system also shows a similar observation with two $\lambda_{\max}$ one at 390 nm and second at 435 nm with a total quantum efficiency of 0.31.

Keywords. Phase-diagram; inter-molecular compound; heat of fusion; powder XRD; optical properties.

1. Introduction

It is well known that the increasing demand for materials to cater to the needs of modern civilization is a global challenge for chemists, physicists, metallurgists and materials scientists. It is of immense importance to develop more and more materials with specific properties at low cost. Metallic poly-phase alloys, namely, metal eutectics, monotectics and inter-metallic compounds offer an interesting area of investigation [1–3] in metallurgy and materials science to develop new materials of commercial and technical importance. But due to high transition temperature, difficulties involved in their purification, opacity, large density difference and limited choice of materials, the metallic systems are not suitable for detailed investigations. Organic materials which offer additional advantages in terms of cost, ease of processing and great degree of freedom in properties due to attachment of different functional groups at different position in the compounds are used for different electronic applications including conductors, semiconductors, dielectric, non-linear optics and lasers [4–6]. Horiuchi *et al* [7,8] have discovered a novel class of binary organic

intermolecular compounds (IMCs) in which bonds form a supra-molecular structure where arrangement of molecules in three dimension and crystal structure decides the properties of materials. The IMCs formed by the non-covalent bonding such as hydrogen bonding, polar–polar, polar-induced polar interactions and dispersion forces between the parent components require further exploration to synthesize novel materials [9]. The parent components with acidic or phenol groups are found to be potential candidates for the O–H...O, O–H...N or N–H...O interactions through hydrogen bonds in solid phases [10]. During the last two decades, the potential use of organic compounds for non-linear optical (NLO) materials and for other electronic applications has prompted the researchers to undertake various physicochemical investigations in detail [11–13]. In addition, they have ability to produce as well as modify, the NLO and white light emitting diode materials [14,15].

With a view to develop novel materials and also throw light on physicochemical interactions among the components, *N,N*-dimethylaminobenzaldehyde (DMAB)–anthranilic acid (AA) and 2-(4-(dimethylamino)benzylideneamino)benzoic

acid (DMABAB)–*p*-nitroaniline (PNA) systems were chosen and their phase diagrams, X-ray diffraction (XRD) and spectral and thermal behaviour were studied. The optical emissions and fluorescence properties were also studied in a suitable solvent.

2. Experimental

2.1 Materials and their purification

All compounds, namely, AA (99%), DMAB (99%) and PNA (99%) obtained from Aldrich (Germany), were further purified by repeated crystallization from ethyl acetate. The purity of each of the materials was ascertained by comparing their melting temperatures provided in the literature [16]. The experimental melting temperatures of AA, DMAB and PNA were found to be 148, 74 and 149°C, respectively. DMABAB was synthesized by green synthesis by taking a 1:1 molar ratio of AA and DMAB in a test tube, homogenized them properly by heating at 185°C in a silicone oil bath and after the reaction was complete the solution was cooled in an ice bath and then purified by repeated crystallization from methanol.

2.2 Phase diagram

The phase diagrams of DMAB–AA and DMABAB–PNA systems were determined by the thaw-melt method [17] in the form of a temperature–composition curve. In this method, mixtures of two components, covering the entire range of compositions, were prepared and they were homogenized by repeating the process of their melting followed by chilling in ice cold water five times. The melting temperature of each of compositions was recorded using a melting point apparatus (Toshniwal) attached with a precision thermometer with an accuracy of $\pm 0.5^\circ\text{C}$.

2.3 Spectroscopic studies

Infrared spectra of the pure components and the IMCs were recorded at 300 K in the region $4000\text{--}400\text{ cm}^{-1}$ using a PerkinElmer FT-IR Spectrum 1000 infrared spectrometer. The NMR spectra were recorded in CDCl_3 using a JOEL 300 MHz spectrometer.

2.4 Enthalpy of fusion

The values of heat of fusion of the pure components, the eutectics and the IMCs were determined [18] by the differential scanning calorimetry (DSC) method using (Mettler DSC-4000 System). Indium and zinc samples were used to calibrate the DSC unit. The amount of test sample and heating rate were about 7 mg and 5°C min^{-1} , respectively.

2.5 X-ray diffraction

Powder XRD patterns of the pure components, the eutectics and the IMCs were recorded using an 18 kW rotating (Cu) anode-based Rigaku powder Diffractometer fit with a graphite monochromator in the diffracted beam. The samples were scanned from 10 to 70° with a scanning rate of 4° min^{-1} .

2.6 Optical characterization

The absorption spectra of all starting compounds and the IMCs were studied using a UV/Vis/NIR (JASCO model V-670) spectrometer from 190 to 700 nm at room temperature in methanol solution ($1.0 \times 10^{-5}\text{ M}$). Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer using pyrene as a reference at room temperature in the same solvent and concentration.

3. Results and discussion

3.1 Phase diagram

3.1a DMAB–AA system: The phase diagram of the DMAB–AA system shows the formation of a 1:1 IMC (DMABAB) with congruent melting point and two eutectics E_1 and E_2 containing 0.10 and 0.95, mole fractions of AA, respectively. The IMC shows a higher melting point compared to both parent materials because there is new covalent bond formation between both parents. The melting points of E_1 , E_2 and the IMC are 68, 143 and 187°C , respectively (figure 1). It is obvious from figure 1 that the melting point of DMAB decreases with the addition of the second component AA and it attains the minimum value at the first eutectic point E_1 because up to this eutectic composition AA behaves just like impurity in DMAB and is completely miscible in DMAB. The eutectic composition also behaves just like a single moiety in which both parents are held together *via* weak interactions stable in the solid state and dissociate in the liquid state. However, in some cases it also remains stable in the liquid state, especially in deep eutectic solvents [19,20]. Further addition of second component causes the melting point to rise till it attains the maximum at C where the compositions of liquid and solid phases are identical. This maximum temperature is the congruent melting point of the DMABAB. Further increase in mole fraction of the second component causes the melting point of the mixture to decrease and it attains the minimum at the second eutectic point E_2 . In the phase diagram, DMABAB behaves just like a parent component for both individual starting parent molecules. The existence of the maximum along with eutectic points on either side of the maximum point imparts stability [21] to the DMABAB. The reaction between the two components can be represented by equation:

Figure 1. Phase diagram of AA and DMAB system.

In the liquid phase, the addition compound AB must remain as a single moiety and phase diagram would show a sharp maximum. However, when dissociation occurs in the molten state, the products of dissociation lower the effective mole fraction of the solute, and the curve would be flattened. For each eutectic, DMABAB behaves as one of the components. The observed maximum in the system under investigation is sharp indicating thereby that DMABAB is capable of existing in the solid form in equilibrium with a liquid of the same composition.

3.1b DMABAB-PNA system: In this system, we select IMC (DMABAB) as one parent component and the second component is PNA molecule and as such this system also shows the formation of a 1:1 IMC having congruent melting point and two eutectics E_1 and E_2 containing 0.25 and 0.60 mole fractions of DMABAB, respectively. There is hydrogen bonding and in the present case it is more convenient to say IMC [22] instead of addition compound. The melting points of E_1 , E_2 and the IMC are 127, 144 and 149°C, respectively (figure 2). It is evident from the figure that the melting point of PNA decreases with the addition of the second component DMABAB and it attains the minimum value at the first eutectic point, just like the AA-DMAB

system but in the present case E_1 composition is 1:1 of PNA and IMC (DMABAB-PNA) while in the above mentioned (AA-DMAB) case the ratio of E_1 composition is 5:1 of AA and DMABAB, respectively. The eutectic composition may depend upon size of parent molecules, IMC molecules as well as interstitial space available in all these molecules, and in the case of crystalline compound it is also dependent on the crystal system and space group. Some authors also believe that the eutectic point is a transition state of IMC in the case of hydrogen bonding.

3.2 Spectroscopic studies on AA, DMAB, PNA, DMABAB and their IMCs

AA: The peaks observed at 3325, 3240, 1677 and 1662 cm^{-1} in the spectrum of AA is indicative of N-H, O-H, $>\text{C}=\text{O}$ stretching frequency of amine (NH_2), hydroxyl and carbonyl of carboxylic groups, respectively. In ^1H NMR (300 MHz, CDCl_3 , ppm) spectrum of AA the peaks appear at δ 6.67 (4H, d), 7.32 (2H, t) and 7.94 (1H, d).

DMAB: The peaks observed at 2795, 2713 and 1662 cm^{-1} in the spectrum of DMAB is due to $>\text{C}=\text{O}$ stretching frequency of aldehyde group. In ^1H NMR (300 MHz, CDCl_3 ,

Figure 2. Phase diagram of DMABAB and PNA system.

ppm) spectrum of DMAB peaks appear at δ 9.87 (1H, s), δ 7.63 (2H, d), δ 6.78 (2H, d) and δ 2.85 (2H, d).

PNA: The peaks observed at 3432, 3343 and 1681 cm^{-1} in spectrum of PNA is indicative of amine (NH_2), $>\text{C}=\text{O}$ stretching frequency and carbonyl groups, respectively. In ^1H NMR (300 MHz, CDCl_3 , ppm) spectrum of PNA the peaks appear at δ 7.97 (2H, d), δ 6.97 (2H, d) and δ 3.41 (2H, s).

DMABAB: The peaks observed at 3434, 2922, 1677 and 1587 cm^{-1} in its spectrum is indicative of O–H, N–H, $>\text{C}=\text{O}$ stretching frequency of hydroxyl, imine ($-\text{C}=\text{N}-$) and carboxyl groups, respectively. In the ^1H NMR (300 MHz, CDCl_3 , ppm) spectrum of DMABAB peaks appear at δ 3.11 (6H, s), δ 8.52 (1H, s), δ 8.33 (1H, d), δ 7.77 (1H, t), δ 7.55 (1H, t), δ 7.44 (1H, d), δ 7.33 (2H, d), δ 6.77 (2H, d) and δ 9.67 (1H, s).

DMABAB–PNA (IMC): The shifts observed in O–H and $>\text{C}=\text{O}$ stretching frequency of carbonyl and amine groups (3183, 1633 and 1588 cm^{-1}) in the spectrum is due to hydrogen bonding and other peaks centred at 3481 and 3362 cm^{-1} are ascribed to the hydrogen bonded amine group of the PNA molecules. The ^1H NMR (300 MHz, CDCl_3 , ppm) spectrum of IMC shows peaks at δ 9.73 (1H, s), δ 3.08 (6H, s), δ 3.11 (2H, s), δ 6.70 (2H, d), δ 7.40 (2H, d), 8.33 (1H, d),

δ 8.11 (2H, d), 8.52 (1H, s), δ 7.50 (1H, d), δ 7.77 (1H, t), δ 7.36 (1H, t) and δ 6.66 (2H, d).

3.3 Enthalpy of fusion

The idea about the structure of eutectic melt and the nature of interaction between the two components forming the eutectics and the addition compounds could be obtained from the knowledge of their enthalpy of fusion data. The DSC plots are shown in figures 3 and 4 for AA–DMAB and DMABAB–PNA systems, respectively. In the case of AA–DMAB system, AA has one more peak at 107°C in addition to their melting points which is due to the intra-molecular hydrogen bonding and the eutectic (E_2) also shows an additional peak at 101°C which is also due to the intra-molecular hydrogen bonding of AA. The DMABAB shows an additional peak at 70°C which may be due to the intra-molecular hydrogen bonding. The experimental values of enthalpy of fusion and the values that are computed using the mixture law [23] in the case of binary materials are included in table 1. The values of enthalpy of mixing, which is the difference between the experimental and the calculated values of heat of fusion, is negative in the case of the AA–DMAB system, suggesting thereby a clustering of molecules for both binary eutectic melts [24] and in the

Figure 3. DSC plots of AA, DMAB, their eutectics and IMC (DMABAB).

case of the DMABAB–PNA system the value of enthalpy of mixing is positive for E_1 and negative for E_2 , i.e., there is the formation of a quasi-eutectic structure in E_1 melt [25] and clustering of molecules in E_2 melt. The entropy of fusion ($\Delta_{\text{fus}}S$) of the pure components, the eutectic and the addition compound as well as IMC can be calculated using the equation:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} \quad (2)$$

where T is the melting temperature of the compound. The values of the entropy of fusion (table 1) being positive suggest that there is increase in randomness of the system during melting as expected. The enthalpy of fusion value also influences the critical radius and interfacial energy. When a melt is cooled below its equilibrium melting temperature, the liquid phase does not solidify spontaneously because, under equilibrium conditions, it contains a cluster of molecules. As long as the clusters are all below the critical size [26], they cannot grow to form crystals and, therefore, no solid would result. The interfacial energy (σ) is related to the

critical size (r^*) of the nucleus according to the following equation:

$$r^* = \frac{2\sigma T_{\text{fus}}}{\Delta_{\text{fus}}H \cdot \Delta T} \quad (3)$$

where T_{fus} , $\Delta_{\text{fus}}H$ and ΔT are melting temperature of eutectic, heat of fusion and degree of undercooling, respectively. The interfacial energy is given by the expression:

$$\sigma = \frac{C \cdot \Delta_{\text{fus}}H}{(N_A)^{1/3} (V_m)^{2/3}} \quad (4)$$

where N_A is the Avogadro number, V_m is the molar volume and parameter C lies between 0.30 and 0.35. The interfacial energies of pure components and eutectics were calculated by making use of enthalpy of fusion data and are reported in table 1. It is evident from the table that the value of interfacial energy is the maximum in the case of AA and it is the minimum in the IMC in the DMAB–AA system. On the other hand, in the case of the DMABAB–PNA system the value of

Figure 4. DSC plots of DMABAB, PNA, their eutectics and IMC.

interfacial energy is the maximum in the case of DMABAB and it is minimum in the case of the IMC. It is well known that the interfacial energy is a measure of instability of formation of critical nucleus. Evidently, the role of interfacial energy is more important in the case of AA and DMABAB than those of IMCs in destabilization of the formation of critical nucleus.

3.4 Excess thermodynamic functions

A measure of deviation from ideal behaviour can be best 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 (Y^E) is defined as the difference between the thermodynamic functions of mixing for a real system and the corresponding values for an ideal system at the same temperature and pressure. Thus,

$$Y^E = \Delta Y_{\text{mix}}(\text{real}) - \Delta Y_{\text{mix}}(\text{ideal}) \quad (5)$$

where Y is any of the excess thermodynamic function. The excess thermodynamic functions can be calculated using the

equations reported earlier [27,28] and the values are given in table 2.

In the case of AA–DMAB system, positive values of excess free energy for both eutectic (E_1 and E_2) indicate that the interaction between the like molecules (DMAB–DMAB, DMABAB–DMABAB and AA–AA) are stronger than the interaction between the unlike molecules (DMAB–DMABAB and DMABAB–AA) [27]. In the case of the DMABAB–PNA system both eutectic points have positive values of excess free energy i.e., at both eutectic point interactions between like molecules are stronger than unlike molecules (at E_1 interaction between PNA–PNA and IMC–IMC is stronger than PNA–IMC and at E_2 interaction between DMABAB–DMABAB and IMC–IMC is stronger than DMABAB–IMC).

3.5 XRD studies

Powder XRD patterns of parent compounds, their eutectics and addition compounds are recorded for AA–DMAB and DMABAB–PNA systems and the data are depicted in figures 5 and 6, respectively.

Table 1. Enthalpy of fusion, heat of mixing, entropy of fusion, roughness parameters and interfacial energy of pure components, their eutectics and addition compound as well as IMC.

Sl. no.	Materials	Enthalpy of fusion (kJ mol ⁻¹)	Heat of mixing (kJ mol ⁻¹)	Entropy of fusion (J mol ⁻¹ K ⁻¹)	Roughness parameter (α)	Interfacial energy (erg cm ⁻²)
<i>AA-DMAB system</i>						
1	AA	24.59		58.5	7.04	47.96
2	DMAB	20.03		57.7	6.94	31.45
3	Eutectic 1 (exp.) (cal.)	20.63	-0.36	60.0	7.22	30.84
4	Eutectic 2 (exp.) (cal.)	20.27	-4.17	57.9	6.96	46.00
5	DMABAB (solid) (exp.) (cal.)	24.09 24.26 21.24 22.31	-1.07	45.9	5.52	28.42
<i>DMABAB (solⁿ)-PNA system</i>						
6	DMABAB (sol ⁿ)	30.55		67.0	8.06	40.88
7	PNA	20.29		48.1	5.79	40.07
8	Eutectic 1 (exp.) (cal.)	32.06 24.01	8.06	80.2	9.65	32.93
9	Eutectic 2 (exp.) (cal.)	20.43 28.22	-7.79	49.5	5.95	28.44
10	IMC (exp.) (cal.)	27.73 25.42	2.31	66.3	7.97	25.80

Table 2. Excess thermodynamic functions of eutectics of all three systems.

Sl. no.	Systems	g^E (kJ mol ⁻¹)	h^E (kJ mol ⁻¹)	s^E (kJ mol ⁻¹ K ⁻¹)
<i>AA–DMAB system</i>				
1	Eutectic 1	0.2013	8.4020	0.0238
2	Eutectic 2	0.4624	−1.8704	0.0056
<i>DMABAB–PNA system</i>				
3	Eutectic 1	1.1793	4.9219	0.0094
4	Eutectic 2	0.8145	8.9341	0.0197

Figure 5. Powder XRD pattern of AA, DMAB, their eutectics and DMABAB.

In the case of the AA–DMAB system, it is evident from figure 5 that the XRD pattern of IMC (DMABAB) shows some new peaks which could not be assigned for either of parent components. In addition, a change in the intensity of some of the parent peaks was also observed. These observations confirm the formation of a new compound as DMABAB [21]. While the powder XRD pattern of the E_1 shows almost all the peaks of AA compound and some peaks of DMABAB the E_2 powder XRD pattern shows the peaks

of the DMABAB and DMAB which confirm that at the eutectic point E_1 , weak interactions exist between DMAB and DMABAB and at eutectic E_2 weak interactions exist between DMABAB and AA. For eutectic E_1 the peaks of AA could not be assigned and similarly for eutectic E_2 the peaks of DMAB could not be assigned and the peaks of DMABAB were present in both eutectics. From this observation it can be inferred that DMABAB behaves as a parent component for both eutectics.

Figure 6. Powder XRD pattern of DMABAB, PNA, their eutectics and IMC.

In the case of the DMABAB–PNA system, it is evident from figure 6 that the XRD pattern of IMC shows a completely different set of peaks which could not be assigned for either of parent components and this confirms the formation of a new IMC [21]. The powder XRD pattern of E_1 shows almost all the peaks of the PNA compound and IMC with different peak intensities, because the ratio of PNA and IMC at E_1 is 1:1 whereas at the E_2 , powder XRD peak shows almost the same pattern as IMC, because the ratio of IMC and DMABAB at E_2 is 4:1 and there is no signature of PNA. Similar to the AA–DMAB system, both eutectics of this system also give only IMC X-ray peaks and corresponding parent compound peaks from which it can be inferred that the IMC behaves as a parent component for both eutectics.

3.6 Optical characterization

3.6a Absorption spectra: AA–DMAB system: The absorption spectrum of AA shows three bands at 216, 249 and

335 nm ascribed to the $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, and DMAB also gives three bands at 204, 242 and 341 nm ascribed to the $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, figure 7a. The absorption spectrum of the IMC (DMABAB) shows three bands same as AA but with different intensities. The $\lambda_{\max}$ absorption shows hypochromic and hyperchromic shifts with respect to DMAB and AA, respectively.

DMABAB–PNA system: PNA shows $\lambda_{\max}$ at 370 nm due to the $n \rightarrow \pi^*$ transition and another band at 229 nm due to the $\pi \rightarrow \pi^*$ transition. DMABAB shows absorption maximum at 339 nm due to the $n \rightarrow \pi^*$ transition and another band at 250 nm due to the $\pi \rightarrow \pi^*$ transition as shown in figure 8a. Absorption spectra of DMABAB–PNA IMC do not show any significant change at $\pi \rightarrow \pi^*$ transition band at 249 nm. The $\lambda_{\max}$ at 370 nm has a broad range of absorption which shows red shift (9 nm) with respect to PNA with a hump at 380 nm. This red shift in IMC is due to the intermolecular hydrogen bonding between both parents [29].

Figure 7. (a) Absorption spectra and (b) emission spectra of AA, DMAB and their DMABAB.

3.6b Emission spectra: DMAB–AA system: DMAB and AA show very low emission with $\lambda_{\max}$ 380 nm and $\lambda_{\max}$ 405 nm upon their $\lambda_{\max}$ excitation, respectively. DMABAB IMC shows strong dual emission with two $\lambda_{\max}$: one at 380 nm and the second at 450 nm (Stokes' shift 39 and 112 nm) upon excitation at 339 nm, figure 7b. The total quantum efficiency of DMABAB was found to be 0.49.

DMABAB–PNA system: PNA shows very low emission with $\lambda_{\max}$ 418 nm upon excitation at 371 nm. DMABAB gives strong dual emission with two $\lambda_{\max}$ one at 380 nm and the other at 450 nm (Stokes' shift 39 and 112 nm) upon excitation at 339 nm as shown in figure 8b. DMABAB–PNA IMC also shows strong dual emission with two $\lambda_{\max}$: one at 390 nm and second at 435 nm (Stokes' shift 42 and 87 nm). First emission peak shows a red-shift of 12 nm and the second emission peak shows a blue-shift of 16 nm. Total quantum efficiency (0.31) of IMC is less than that of DMABAB quantum efficiency (0.49).

Figure 8. (a) Absorption spectra and (b) emission spectra of DMABAB, PNA and their IMC.

4. Conclusions

The phase diagram of two systems, namely, DMAB–AA and DMABAB–PNA shows the formation of 1:1 IMC with congruent melting point and two eutectics one on either side of the IMC. The spectroscopic studies suggest the formation of hydrogen bonding between both parents in DMABAB–PNA and AA–DMAB systems. The heat of mixing is negative in the case of the AA–DMAB system, suggesting thereby a clustering of molecules for both binary eutectic melt and in the case of the DMABAB–PNA system the enthalpy value of mixing is positive for E_1 and negative for E_2 i.e., there is the formation of quasi-eutectic structure in E_1 melt and clustering of molecules in E_2 melt. The powder XRD patterns confirm the formation of IMC that behaves as a pure component for both eutectics, which supports the phase diagram data. The DMABAB IMC shows strong dual emission with two $\lambda_{\max}$: one at 380 nm and second at 450 nm with a

total quantum efficiency of 0.49. DMABAB–PNA IMC also shows strong dual emission with two λ_{max} : one at 390 nm and second at 435 nm with a total quantum efficiency of 0.31.

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