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RESEARCH ARTICLE

Solid-Liquid Equilibrium Study for Binary System Forming Intermolecular Compound: Phase Diagram, Thermal, Physicochemical and Powder XRD study.

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ABSTRACT

The phase diagram study of the binary organic system has been investigated by the thaw melt method using 4-hydroxy-3-methoxybenzaldehyde (HMB) and 4-nitroaniline (NA). The temperature-composition plot showed that the intermolecular compound (IMC) has formed at 1:1 molar ratio with two eutectics on either side of IMC. The melting points of eutectics and IMC along with parents are verified by the DSC method. The different phases of the systems which are in equilibrium and their physicochemical properties are estimated using the enthalpy of fusion values obtained from DSC. The higher melting temperature of IMC suggested the formation of the Schiff base during the homogenization process. The new and moderately sharp Bragg's peaks at specific 2θ values found in the diffractogram of IM Crevealed the novelty and crystalline nature of IMC while repeated peaks in the diffractogram of eutectics suggest the mechanical mixture of eutectics.

Keywords: *Phase diagram, Intermolecular compound, Eutectic, DSC, PXRD*

Introduction

The study of phase diagrams using solid-liquid equilibrium (SLE) data of an organic system is of great technical importance for the development, design, and operation of novel intermolecular compounds with promising properties [1-2]. The equilibrium data provides the details of phases that are in equilibrium from which various physicochemical properties could be investigated as well as their crystallization and separation processes [3-4]. The phase diagram also provides the thermodynamic aspects of different components like eutectic, peritectic, monotectic, etc, and could provide the physicochemical information about these components.

In this paper, we measured the solid-liquid equilibrium data of the binary organic system, 4-hydroxy-3-methoxybenzaldehyde (HMB)–4-nitroaniline (NA). The phase diagram was established to study the different equilibrium phases at particular temperatures and compositions. The melting temperature of compositions forming eutectics and intermolecular compound was confirmed by a differential scanning calorimetric study. The powder X-ray diffraction technique was employed for eutectic and IMC along with parent compounds to predict the crystallinity of the components and their mixing behavior.

Materials and Method

The parent compounds, HMB and NA were purchased from Sigma Aldrich, Germany. The melting points of starting materials are in agreementwith their literature value [5]. The phase diagram was established by the thaw melt method where binary mixtures covering the entire range of compositions were prepared by solid-state synthesis [6]. Toshniwal melting point apparatus, attached with a thermometer which could read up to ±0.5°C with accuracy was used for melting point determination. Differential Scanning Calorimetry (Mettler DSC-4000 system) was used

to obtain the enthalpy of fusion of IMC, eutectics, and parent compounds [7]. Indium metal was used to calibrate the DSC unit and samples were heated at a heating rate of 10 °C/min under the constant flow of liquid nitrogen at 20 $mLmin^{-1}$. Powder X-ray diffraction (PXRD) diffractograms of parent compounds, eutectics, and IMC were recorded using an 18kW rotating (Cu) anode-based Rigaku powder diffractometer fitted with a graphite monochromator in the diffracted beam [8]. The samples were scanned from 10° to 70° with a scanning rate of 4° min^{-1} using Cu-Kα radiation of wavelength 1.5406 Å

Result and Discussion

Phase diagram and thermal study

The solid-liquid equilibrium data of HMB-NA system showed the formation of an intermolecular compound at an equimolar ratio and two eutectics; E_1 and E_2 at 0.25 and 0.85 molar composition of HMB, respectively, as shown in Figure 1. The melting temperatures of IMC, E_1, and E_2 are found to be 179, 126, and 106 °C, respectively. The compositions with the lowest melting temperatures, E_1 and E_2, represent the equilibrium state between the homogeneous liquid phase (L) and two solid phases (S_1 and S_2) as given in equation 1. But, at the equimolar point there exist an equilibrium between the solid and liquid phases of IMC (equation 2). DSC study confirmed the single-phase transition of eutectics and IMC by showing a single and sharp exothermic peak for each component. The various thermodynamic quantities with the phase diagram are also evaluated by using the thermogram obtained from DSC technique. The DSC thermograms of E_1, E_2, and IMC along with parents are shown in Figure 2. The small humps observed at 86 °C in the case of eutectics and IMC is due to the phase transition during heating [9]. However, the energy absorbed is so small that it could not be estimated. The enthalpy of fusion values $\Delta_{fus}H$ for different components are calculated experimentally by DSC curve and theoretically by using mixture law. The difference between experimental and theoretical values gives the enthalpy of mixing ($\Delta_{mix}H$) which predicts the nature of interaction in the binary melt. As such, three types of structures are suggested: quasi-eutectic for $\Delta_{mix}H > 0$, clustering of molecules for $\Delta_{mix}H < 0$ and molecular solution for $\Delta_{mix}H = 0$ [10-12]. The system shows the negative and positive $\Delta_{mix}H$ values for E_1 and E_2 inferred clustering of molecules and quasi-eutectic, respectively, in the eutectic melt. The thermodynamics data obtained from different components using DSC thermograms are given in Table 1.

$$L \rightleftharpoons S_1 + S_2 \quad \ldots (1)$$

$$A + B \rightarrow AB_{(Liquid)} \rightleftharpoons AB_{(Solid)} \quad \ldots (2)$$

where A and B represent parent compounds and AB represents intermolecular compound.

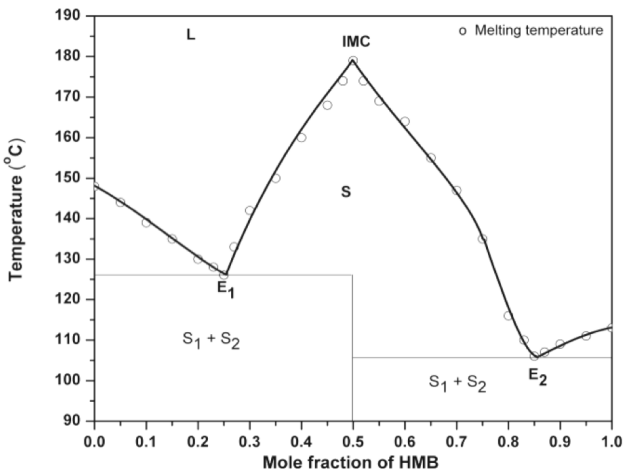

Figure 1. Phase diagram of HMB-NS system.

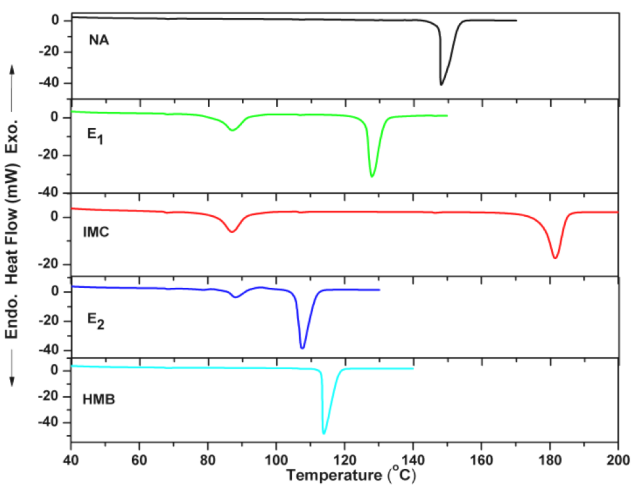

Figure 2. DSC thermograms of IMC, eutectics, and their parents

Table 1: Melting temperature (T_M), enthalpy of fusion ($\Delta_{fus}H$), enthalpy of mixing ($\Delta_{mix}H$) and the entropy of fusion ($\Delta_{fus}S$) of parent compounds eutectics, and intermolecular compounds.

Component	T_M (K)	$\Delta_{fus}H$ (kJ mol^{-1})	$\Delta_{mix}H$ (kJ mol^{-1})	$\Delta_{fus}S$ (kJ mol^{-1} K^{-1})
HMB	382.0	19.39		0.050
NA	421.0	21.48		0.051
IMC	452.0	Exp. 32.64 Cal. 29.77	4.97	0.072
E_1	399.0	Exp.24.06 Cal. 27.74	-3.68	0.062
E_2	379.0	Exp. 25.98 Cal.22.31	3.67	0.068

Powder XRD Study

Powder X-ray diffraction (PXRD) patterns of parent compounds, eutectics, and intermolecular compounds (IMC) are given in Figure-3.The appearance of weak intense peaks of IMC and eutectics revealed the poor crystalline nature of the components [13-14]. However, some new peaks in diffractogram of IMC which are not found in the parent notified its novel nature. The diffractograms of eutectics mostly retain the peaks of IMC and their parents of respective sites signify the binary nature of the mixture.

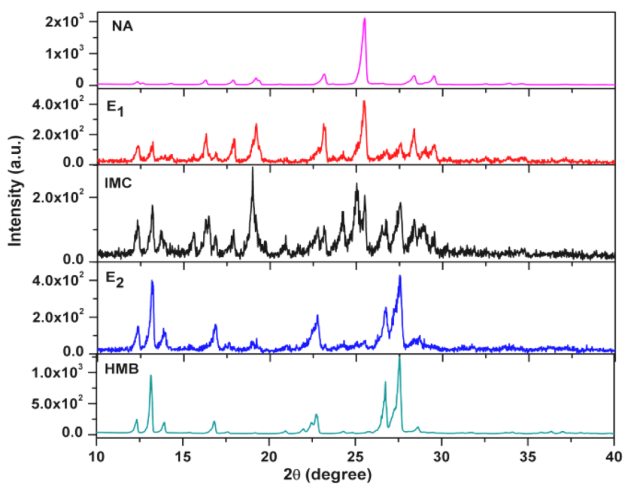

Figure 3. P-XRD patterns of IMC, eutectics and parents

Conclusion

The binary phase diagram was established between two organic compounds; 4-hydroxy-3-methoxybenzaldehyde and 4-nitroaniline using the thaw melt method. The samples are prepared by solid-state synthesis method. The temperature-composition curve results an intermolecular compound with two eutectics on either side of IMC. DSC study has been done to confirm the melting temperature of synthesized components and also to evaluate the thermodynamic parameters of the components. The single and sharp exothermic peak of the intermolecular compound revealed the stability and purity of the novel compound. Powder XRD study of IMC and eutectics showed the novelty, crystallinity, and mechanical mixing behaviors.

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