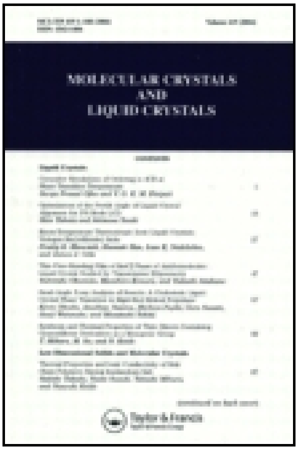

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Vanillin–*p*-Anisidine System: Solid-State Reaction and Density Functional Theory Studies

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Vanillin reacts with p-anisidine in 1:1 molar ratio in the solid and molten states, in microwave oven and in solution. In all the cases, reaction occurred with the formation of N-(4-methoxy phenyl)–4-hydroxy-3-methoxy phenyl methanimine (NHM) and water. Single crystal X-ray analysis shows that NHM crystallizes in the chiral orthorhombic space group $P2_12_12_1$. *An optimized geometry of NHM was computed by using density functional theory. In the case of solid-state reaction, it is proposed that a thin layer of water molecules is formed at the junction of vanillin and p-anisidine which moves progressively towards vanillin as the reaction proceeds. The overall mechanism of solid-state reaction has been proposed by a model.*

Keywords: excess thermodynamic function; microcrystallites; orthorhombic crystal system; solid-state reaction

INTRODUCTION

Organic solid-state reactions have now emerged as a new area of chemical research because of its tremendous applications in variety of disciplines and in industries [1–6]. Solid-state reactions are eco-friendly, and in many cases they occur faster than those in the presence of a solvent. Recently, it has been reported [2,7] that in many organic solid-state reactions liquid phase also appears as a result of the formation of low melting eutectic mixtures or one of the reaction

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products is a liquid. Attempts have been made to understand the mechanism of reactions occurring between solids but it is not fully understood.

In this article we report the study of solid-state reaction between vanillin and *p*-anisidine. The reactions were also performed in solution, in molten state, and in a microwave oven. The products obtained via different reaction routes were characterized. An attempt has been made to discuss the mechanism of the reaction in the solid state. The optimized geometry of the reaction product was also obtained with the help of density functional theory.

EXPERIMENTAL

Materials and Purification

Vanillin (HI MEDIA) and *p*-anisidine (S. D. Fine Chemicals) were purified by repeated crystallizations from ethanol-chloroform and water-ethanol mixtures, respectively. The purity of the compounds was checked from the thin layer chromatographic technique and melting temperatures.

Preparation of N-(4-methoxy phenyl)–4-hydroxy-3-methoxy Phenyl Methanimine (NHM)

(a) By the Reaction of Vanillin and p-Anisidine in Solid State

Solid powders of vanillin (0.1522 g) and *p*-anisidine (0.1232 g) were mixed thoroughly in 1:1 molar ratio in an agate mortar. As soon as the two solids were ground together, formation of a yellow colored sticky viscous paste took place which rapidly solidifies to yield the desired reaction product. The yellow colored reaction product (solid) was kept in an incubator at 35°C for 7 days with crushing and mixing everyday to ensure 100% yield of the product. The reaction product melted sharply at 132.9°C, which indicates the formation of single-phase pure crystalline compound.

(b) By the Reaction of Vanillin and p-Anisidine in Molten State

Vanillin and *p*-anisidine were mixed together in 1:1 molar ratio in a glass tube and melted in an oil bath at 135°C. The melt was cooled in an ice bath. The solidified mass was crushed into a fine powder. The process of melting, cooling, and crushing was repeated 2 or 3 times to ensure 100% yield of the product. The yellow colored reaction product melted sharply at 133.8°C.

(c) By the Reaction of Vanillin and p-Anisidine in a Microwave Oven

Solid vanillin and *p*-anisidine were mixed together in an equimolar ratio in a glass tube which was then sealed. The tube was kept in a microwave oven for a minute, where the mixture melted. Since both reactants are polar, the reaction is accelerated by selective absorption of microwave energy. The molten mass obtained was chilled in an ice cold water. A yellow colored solidified mass thus obtained was crushed into a fine powder. The process of melting of the reaction product in the microwave oven and the chilling was repeated 2 or 3 times in order to get 100% yield. A sharp melting point at 131.2°C of the reaction product was observed.

(d) By the Reaction of Vanillin and p-Anisidine in Solution

Vanillin (0.1522 g) and *p*-anisidine (0.1232 g) were dissolved in 15 mL of ethanol and acetone separately. Both solutions were mixed. After 48 hours, prismatic shaped yellow colored crystals were obtained (m. p. 128.5°C).

(e) By Reaction of Vanillin and p-Anisidine solids in a Glass Capillary

Reaction between solid vanillin and solid *p*-anisidine was allowed to occur in a glass capillary (6.0 cm in length) which was sealed at one end. The half portion of the capillary was filled with fine powder of vanillin (particle size <200 mesh) and its other half with p-anisidine (particle size <200 mesh). The capillary was then sealed with a sealing wax. Within two minutes a yellow colored highly viscous liquidus boundary was formed at the junction of the two components. This liquidus boundary got solidified within 5 minutes, and the thickness increased with time towards vanillin.

A separate experiment was also performed in which an air gap (0.6 cm) was kept between the two components in a glass capillary. In this case, a yellow colored solid boundary was formed at the surface of vanillin, thickness of which increased with time. It was noticed that the air gap increases with time due to diffusion of p-anisidine molecule towards vanillin.

Phase Diagram Studies

The phase diagram of vanillin–*p*-anisidine system was studied by thaw melt method [8]. In this method different amounts of vanillin and *p*-anisidine were weighed in glass tubes in order to prepare mixtures of different compositions. The tubes were sealed and the mixtures were then melted in an oil bath at a temperature slightly higher than the melting temperatures of the components. The melts were shaken well and chilled in ice cold water. The process of melting and cooling was repeated several times and finally the tubes were broken. The solidified mass from each tube was crushed into a fine powder to have a homogenous mixture. Thaw and true melting temperatures were determined with the help of a precision thermometer. Phase diagram was drawn by plotting melting temperatures against compositions.

Microscopic Studies

(a) Reaction of p-Anisidine Vapors at the Surface of a Crystal of Vanillin

A crystal of vanillin ($7 \times 2 \times 0.5\,mm^3$) was grown from ethanol–chloroform mixture and fixed at the surface of a glass slide with the help of an adhesive (quick fix). It was exposed with the vapors of *p*-anisidine for different time intervals, and the microphotographs were recorded.

(b) Reaction of p-Anisidine Vapours at the Surface of Vanillin Microcrystallites Obtained by Anisotropic Crystallization

Vanillin was crystallized on a glass slide and exposed with the vapours of *p*-anisidine for 45 minutes. It was observed that fine particles of reaction product were formed.

(c) Microstructures of Eutectic Mixtures

Separate glass slides of the two eutectic mixtures formed in the vanillin and *p*-anisidine system were prepared placing small amounts of fine powders on the glass slide. These were then placed in an oven maintained at temperature slightly above their melting temperatures. When the substance melted on the glass slide, the melts were crystallized by moving separate glass cover slips over them in one direction. The photographs of microstructures were recorded with the help of the digital camera attached to an optical microscope (Olympus Chi20) at a magnification of 100×.

FT-IR Studies

The FT-IR spectra of components and the reaction products prepared by different methods were recorded on Bruker Vertex 70 spectrometer in KBr phase in the frequency range of 4000–500 cm^{-1}.

NMR Studies

NMR spectra of reaction product prepared by different methods were recorded on BRUKER 300 MHz DPX NMR spectrometer by using $CDCl_3$ as a solvent.

Powder X-Ray Diffraction Studies

Powder X-ray diffraction pattern of the reaction products prepared by different routes were recorded with a powder X-ray diffractrometer using CuK_α radiation.

Single Crystal Structure Analysis of NHM by X-Ray Diffraction Technique

Formula $C_{15}H_{15}NO_3$, M 257.28, light yellow crystal $0.60 \times 0.40 \times 0.30\,cm^3$, a 5.8385(1), b 8.6945(2), c 25.1404(6) Å, $\alpha = \beta = \gamma = 90°$, v 1276.20(5) $Å^{-3}$, ρ_{calc} 1.339 g cm^{-3}, μ0.94 cm^{-1}, Z 4, orthorhombic, space group $P2_12_12_1$(No.19), λ 0.71073 Å, T 223(2) k, 8927 reflection collected ($\pm$ h, $\pm$ k, $\pm$ 1) $[(\sin\,\theta/\lambda)]_{max}0.67Å^{-1}$, 3088 independent ($R_{int}$0.037) and 2797 observed reflection [I $> 2\sigma$ (I)], 175 refined parameters, R 0.036, Rw^2 0.094, largest diffraction peak and hole 0.17 ($-$ 0.14)e $Å^{-3}$.

Data set was collected with a Nonius Kappa CCD diffractrometer, equipped with a rotating anode generator. COLLECT [9] was used for data collection, Denzo-SMN [10] for data reduction, SHELXS-97 [11] for structure solution, SHELXTL-97 [12] for structure refinement, XP [13a] and SCHAKAL [13b] is used for graphics.

Differential Scanning Calorimetric (DSC) Studies

Heats of fusion values of pure components, eutectic mixtures, and products obtained from different methods were determined with the help of differential scanning calorimeter (METTLER STAR W 900) in a nitrogen atmosphere at a heating rate of 5°C/min.

Computational Studies

The ground state geometry of NHM in gaseous phase was optimized by DFT method using B3LYP function. The geometry optimization was done using Gaussian 03 package [14] employing Becke's three-parameter exchange function (B3) [15] in combination with LYP correlation function of Lee et al. [16], polarized and diffuse functions 6–31 + G (d). The initial structures as an input file were made through Gauss View [17].

RESULTS AND DISCUSSION

The phase diagram of vanillin–*p*-anisidine system is shown in Fig. 1. It shows the formation of 1:1 addition compound melting at 133.8°C. The two eutectic mixtures are formed at 0.1493 and 0.9080 mole fractions of *p*-anisidine which melted at 73.8°C and 53.8°C, respectively. The reaction between vanillin and *p*-anisidine were studied (i) in the solid state, (ii) in the molten state, (iii) in a microwave oven, and (iv) in the solution. The reaction products obtained by different methods were characterized by FT-IR and NMR spectroscopic techniques, XRD, and DSC technique. The FT-IR spectra of the reaction products obtained via different methods were found almost identical. The peak appearing at 1588 cm^{-1} is attributed to the presence of C=N bond in the reaction product. The peak appearing at ~3400 cm^{-1} indicates the presence of water. The NMR spectra of the reaction products show peaks in the range 6.5–7.5, 8.0–9.0, and at 3.8 ppm. These peaks are assigned to aromatic protons, the aldehydic protons and methoxy protons, respectively. No peak for $-NH_2$ protons was observed in the all NMR spectra indicating that the protons of $-NH_2$ group are involved in the reaction. DSC studies gave melting points of the reaction product obtained by using different methods of preparation [132.9°C (solid

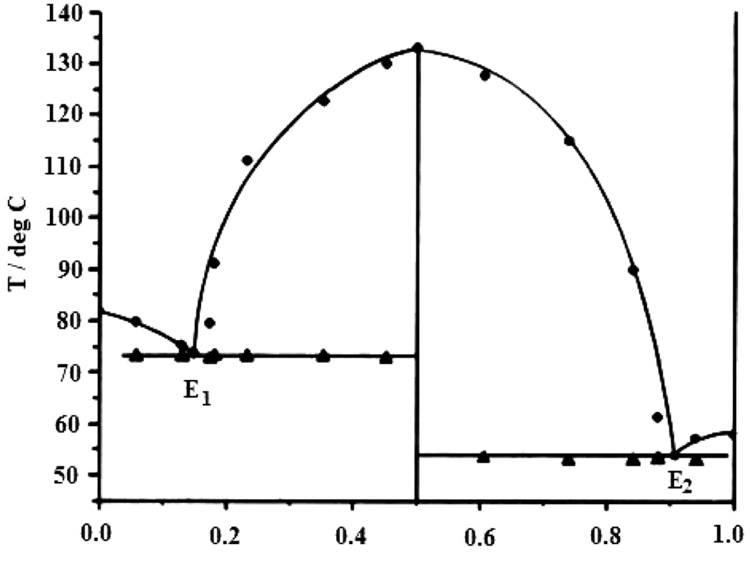
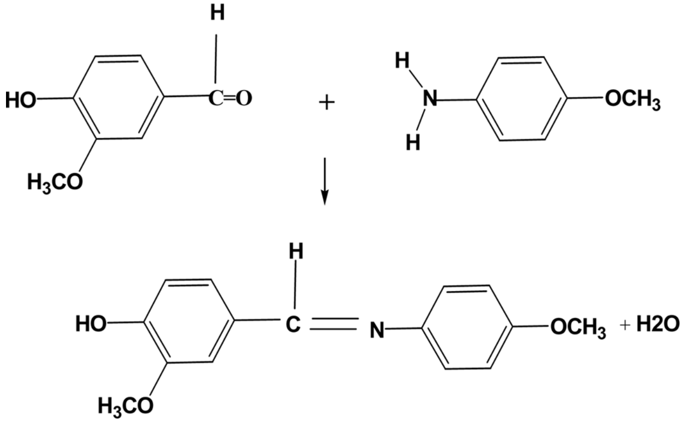


FIGURE 1 Phase diagram of vanillin–*p*-anisidine system.

state), 133.8℃ (molten state), 127.7℃ (in microwave oven), 128.5℃ (solution), respectively]. Their heat of fusion values are 128.25 Jg^{-1}, 150.88 Jg^{-1}, 93.46 Jg^{-1}, and 117.32 Jg^{-1}, respectively. Powder X-ray diffraction studies of the reaction product yielded almost similar XRD pattern. Powder XRD and DSC studies have shown that the products obtained from different methods are almost identical but there are differences in the size of crystallites and their distributions. During the solid state grinding, one of the reaction products obtained was liquid. The reaction taking place between vanillin and *p*-anisidine can be represented by Scheme 1.

Single crystals of NHM the compound were grown from solution, and the structure was determined by XRD technique (Fig. 2). The crystal structure determined by XRD technique belongs to orthorhombic system with space group $P2_12_12_1$. All the bond lengths and angles were found in the expected region. The predominant structural feature is the formation of the C=N bond between one carbon atom of vanillin C2 with the nitrogen atom of *p*-anisidine N1[N (1)-C (2): 1.281(2) Å and C (2)-N (1)-C (11):117.7(1)°]. An intermolecular hydrogen bond is formed between H29 and N1* (O29-H29 0.83 Å, H29 ··· N1* 1.99 Å, O29-H29 ··· N1* 167°). The crystal packing is shown in Fig. 3.

The ground state optimized geometry of NHM as obtained by density functional theory (DFT) is shown in Fig. 4. It is found that the calculated bond length and bond angles (Table 1) match reasonably well with the experimental values obtained from the X-ray crystal structure data. The dipole moment of NHM has been computed 2.55 D,



SCHEME 1 Reaction between vanillin and *p*-anisidine showing the formation of NHM and water.

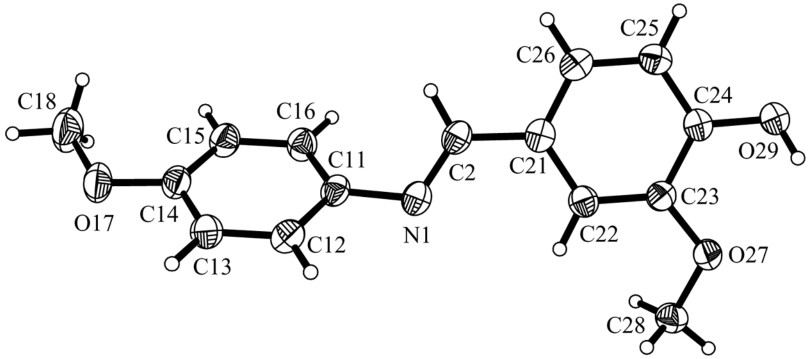


FIGURE 2 Single crystal structure of compound NHM (50% probability level).

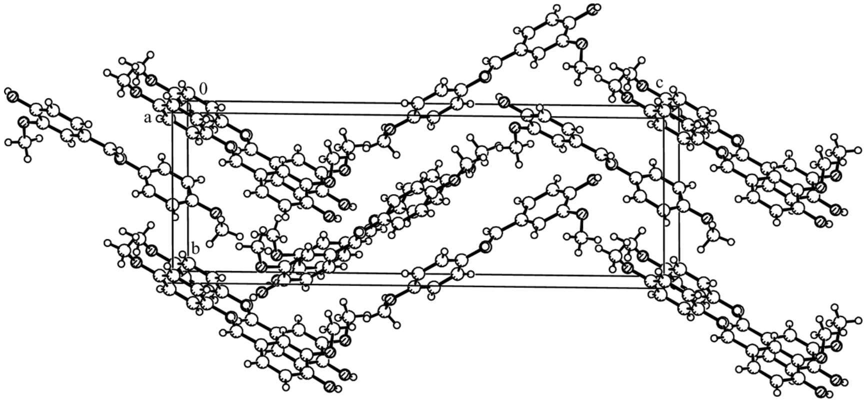


FIGURE 3 Crystal packing in NHM.

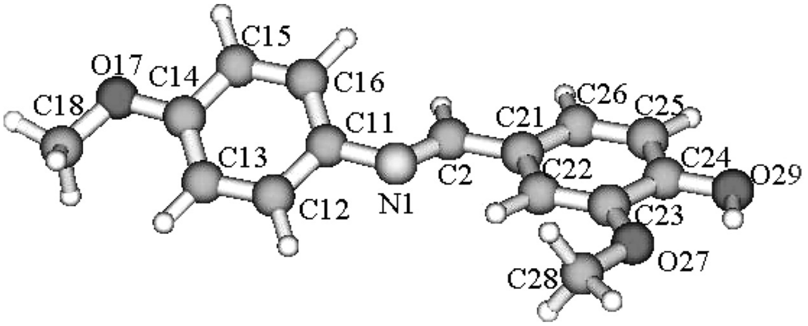


FIGURE 4 Optimized geometry of NHM as obtained with the DFT method.

whereas dipole moments of *p*-anisidine and vanillin were computed 1.78 D and 2.81 D, respectively. The reaction between *p*-anisidine and vanillin is a nucleophlic addition with the elimination of the water molecule. The net result is the formation of an imine bond between the two components. In order to study the mechanism of approach of *p*-anisidine towards vanillin molecule and its subsequent imine bond formation, a potential energy profile (Fig. 5) was drawn by varying the energy with C=N bond length (between 1.0 Å–1.8 Å). It could be observed that the potential energy of NHM is minimum at the C=N bond length of 1.28 Å.

Solid state reactions may be carried out by two different methods. In one method, the two reactants are ground together, where the reaction product is continuously removed and fresh surfaces of reactants come in contact. In this process, the reaction is fast and generally goes to completion. In the second method, the two reactants are kept side by side, and the diffusion of one of the components or both the components may take place. These reactions are slow and take either longer time to complete or sometimes do not reach completion.

TABLE 1(a) Bonds Length (Å) of the NHM Molecule

Bonds	*Bond length* (Å) determined from X-ray crystal data	*Bond length* (Å) calculated from DFT theory
N(1)-C(2)	1.281(2)	1.2840
N(1)-C(11)	1.428(2)	1.4062
C(11)-C(16)	1.387(2)	1.4113
C(11)-C(12)	1.397(2)	1.4019
C(12)-C(13)	1.382(2)	1.3971
C(13)-C(14)	1.392(2)	1.4011
C(14)-O(17)	1.372(2)	1.3688
C(14)-C(15)	1.391(2)	1.4036
C(15)-C(16)	1.397(2)	1.3894
O(17)-C(18)	1.421(2)	1.4026
C(2)-C(21)	1.463(2)	1.4633
C(21)-C(26)	1.394(2)	1.4019
C(21)-C(22)	1.405(2)	1.4121
C(22)-C(23)	1.384(2)	1.3853
C(23)-O(27)	1.368(2)	1.3744
C(23)-C(24)	1.409(2)	1.4152
C(24)-O(29)	1.358(2)	1.3613
C(24)-C(25)	1.387(2)	1.3908
C(25)-C(26)	1.387(2)	1.3969
O(27)-C(28)	1.426(2)	1.4250

TABLE 1(b) Bonds angles in the NHM molecule

Bond angle	*Bond angle* (°) from X-ray crystal data	*Bond angle* (°) from DFT method
C(2)-N(1)-C(11)	117.7(1)	120.59
C(16)-C(11)-C(12)	119.1(1)	117.99
C(16)-C(11)-N(1)	122.2(1)	124.09
C(12)-C(11)-N(1)	118.6(1)	117.87
C(12)-C(13)-C(11)	120.4(1)	121.53
C(12)-C(13)-C(14)	120.4(1)	119.67
O(17)-C(14)-C(15)	124.4(1)	115.82
O(17)-C(14)-C(13)	115.8(1)	124.70
C(15)-C(14)-C(13)	119.9(1)	119.47
C(14)-C(15)-C(16)	119.4(1)	120.38
C(11)-C(16)-C(15)	120.9(1)	120.90
C(14)-O(17)-C(18)	117.4(1)	118.50
N(1)-C(2)-C(21)	124.9(1)	123.08
C(26)-C(21)-C(22)	119.3(1)	119.26
C(26)-C(21)-C(2)	118.1(1)	119.74
C(22)-C(21)-C(2)	122.6(1)	121.00
C(23)-C(22)-C(21)	120.0(1)	119.88
O(27)-C(23)-C(22)	125.4(1)	126.04
O(27)-C(23)-C(24)	114.4(1)	113.54
C(22)-C(23)-C(24)	120.2(1)	120.42
O(29)-C(24)-C(25)	119.4(1)	120.07
O(29)-C(24)-C(23)	121.0(1)	120.08
C(25)-C(24)-C(23)	119.6(1)	119.85
C(26)-C(25)-C(24)	120.1(1)	119.70
C(25)-C(26)-C(21)	120.7(1)	120.88
C(23)-O(27)-C(28)	116.9(1)	118.25

To understand the mechanisms of diffusion during the solid-state reaction between vanillin and *p*-anisidine, the two reactants were placed side by side in a glass capillary. Formation of the products in the form of a yellow colored liquidus boundary at the junction of the two reactants takes place immediately. This liquidus boundary solidifies within 5 minutes and the thickness increases with time. As the time proceeds, this product interface moves towards vanillin. In this process, eutectic mixtures and the reaction products are formed. During the course of the reaction, a small amount of water is formed as one of the reaction products which gets adsorbed at the surface of vanillin as a very thin layer (may be of nanosize). *p*-Anisidine molecules now migrate towards vanillin through this thin layer of water, eutectic mixtures and reaction product. As the diffusion is occurring through multilayer, it may be asymmetric at the interfaces. The asymmetry

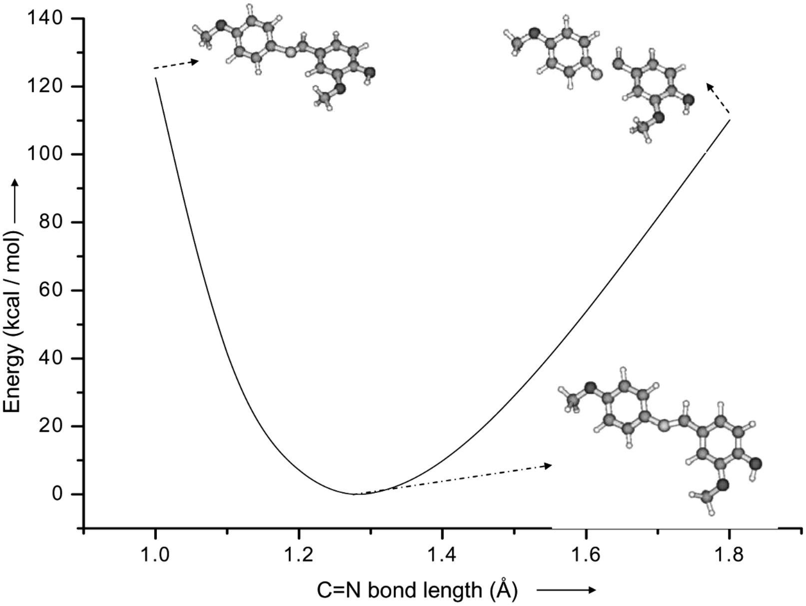


FIGURE 5 Potential energy profile of NHM with change in the C=N bond length.

in diffusion may be related with the asymmetry in the structure of the interfaces. As the reaction progresses, the thin layer of water also moves towards vanillin and the distance between *p*-anisidine and the product layer increases. A very thin layer of water (nanosize) may play a vital role in controlling the progress of the reaction. A schematic model has been proposed which represents the various sequences involved in this solid-state reaction (Fig. 6).

Further, before *p*-anisidine reaches to a fresh surface of vanillin, it has also to diffuse through the layers of eutectic mixtures. The nature and microstructural features of the eutectic mixtures may also affect the process of diffusion. The phase diagram shown in Fig. 1 consists of two parts. The first part is the phase diagram of the vanillin – NHM system, and the second part is the phase diagram of the NHM – *p*-anisidine system. Both the eutectic mixtures show nonideal behavior since they possess definite excess thermodynamic functions. The excess Gibb's free energy (G^E), excess entropy (S^E), and excess enthalpy (H^E) values have been calculated by using the following equations [18]:

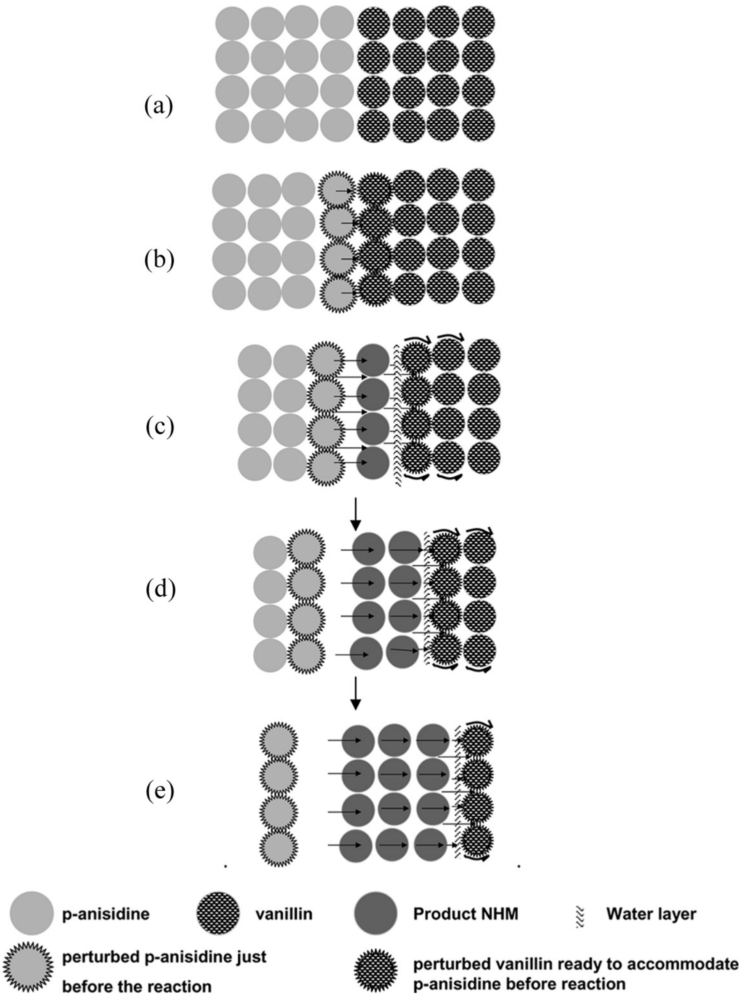


FIGURE 6 Reaction model: (a) Particles of the two reactants are in initial contact; (b) particles of the two reactants at the interface are in a state of perturbation and molecules of *p*-anisidine are intending to diffuse towards vanillin; (c) a layer of the reaction product NHM along a thin layer of water molecules is formed towards vanillin surface and the air gap between *p*-anisidine and vanillin increased; simultaneously surface and diffusion occurs; (d), (e) formation of reaction product (NHM) increased and water layer shifts towards vanillin surface. Surface migration and diffusion through the grain proceeds increasing the air gap between *p*-anisidine and vanillin till the whole vanillin reacts to *p*-anisidine.

$$G^E = RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2)$$

$$S^E = -R[X_1 \ln \gamma_1 + X_2 \ln \gamma_2 + X_1 T(\partial \ln \gamma_1/\partial T) + X_2 T(\partial \ln \gamma_1/\partial T)]$$

$$H^E = -RT^2[X_1(\partial \ln \gamma_1/\partial T) + X_2(\partial \ln \gamma_2/\partial T)],$$

where γ_1 and γ_2 are the activity coefficients of components 1 and 2, respectively.

The value of G^E, S^E, H^E (Table 2) is negative, which indicates that the eutectic mixtures are more ordered than the individual components. The microstructure of eutectic E_1 is irregular (disordered), whereas that of eutectic E_2 is lamellar type (ordered) (Fig. 7). Therefore, it will be easy for *p*-anisidine molecule to pass through a system which is more disordered as compared to the ordered one. Thus, *p*-anisidine molecule will easily pass through eutectic E_1 as compared to the eutectic E_2.

Further for the completion of this reaction in the solid state, the molecules of *p*-anisidine must enter into the crystal lattice of vanillin. This may be considered as a host–guest interaction, in which vanillin acts as a host and *p*-anisidine as a guest. Vanillin crystal is a monoclinic [19] with unit cell volume 1660.74 Å^3. On the completion of this reaction, NHM is formed, and crystal symmetry changes into orthorhombic with a unit cell volume 1276.20 Å^3. Thus during the reaction, crystal lattice of vanillin gets completely broken, and a new lattice is formed. In this process, two N-H and one C=O bonds are broken, and a new C=N bond is formed. The enthalpy change for this process has been calculated to be -874.5 kcals mol^{-1}, which suggests that the reaction between vanillin and *p*-anisidine is exothermic in nature. The unit cell volume of NHM is lower than that of vanillin. This indicates that there is contraction in the system, and hence the product layer will be more compact. Due to the compactness of the product layer, the process of diffusion is hindered and becomes slow. Diffusion may occur through grain boundaries, vapor phase, and surface migration. Grain boundary diffusion generally requires higher activation energy and is very slow [20]. For studying the diffusion via vapor phase, the vapors of *p*-anisidine were allowed to react with solid

TABLE 2 Excess Thermodynamic Functions

Systems	$G^E \times 10^2$ (J mol^{-1})	S^E (J mol^{-1} K^{-1})	H^E (kJ mol^{-1})
Eutectic-1	−0.73	−27.23	−9.47
Eutectic-2	−3.74	−29.27	−9.94

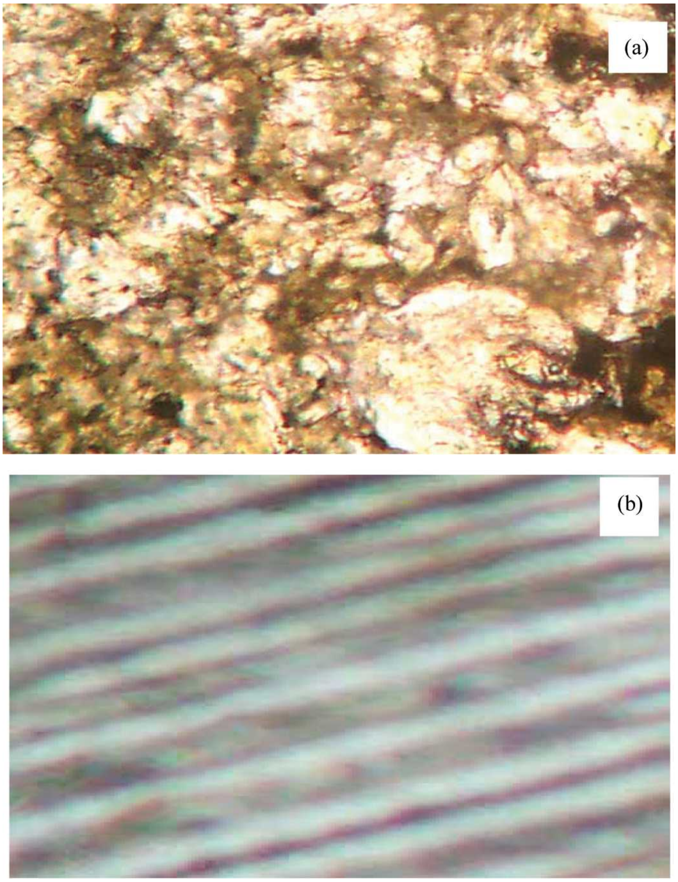


FIGURE 7 Microstructure of (a) Eutectic E_1 and (b) Eutectic E_2.

vanillin. It was found that even after one month of reaction at 35°C, a very little change in the weight of vanillin (5.75%) was observed. Thus, it could be inferred that vapor phase diffusion is also a slow process. Diffusion through surface migration requires low activation energy [20], hence it will be faster than vapor phase and grain boundary diffusions. Thus it could be inferred that in this system, diffusion through surface migration seems to be more effective.

Vapors of *p*-anisidine were allowed to react at the surface of a vanillin crystal, and the microphotographs (Fig. 8) were recorded after 5, 10, 15, 20, and 25 minutes of reaction. These microphotographs showed that the reaction occurred only at certain points (Fig. 8b) with

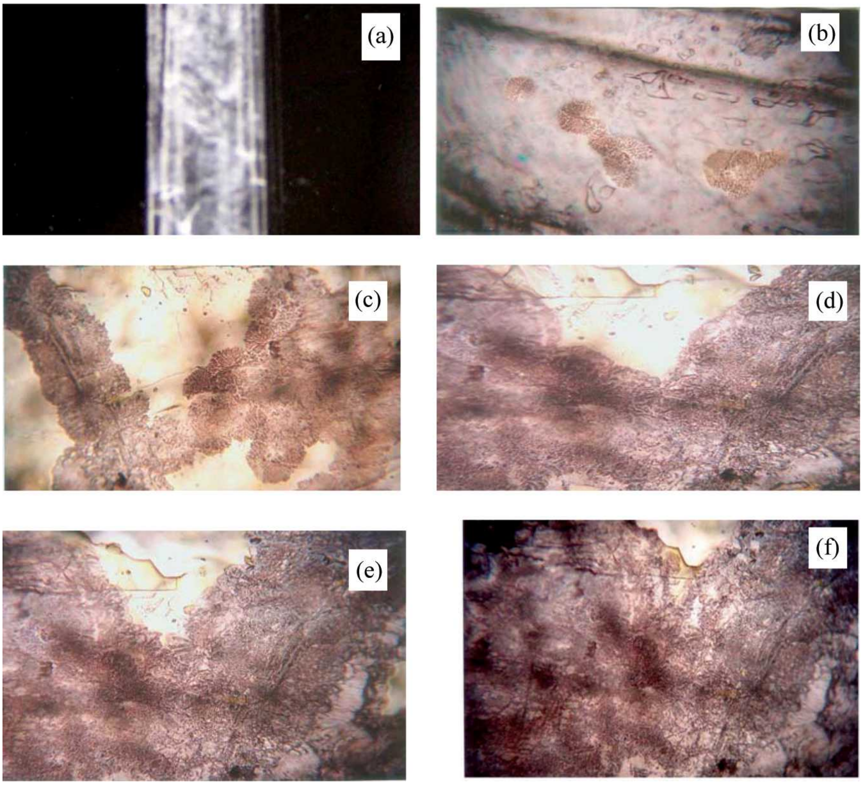


FIGURE 8 Photographs of (a) crystal of vanillin, (b) crystal of vanillin after reacting with the vapours of *p*-anisidine for 5 minutes, (c) crystal of vanillin after reacting with the vapours of *p*-anisidine for 10 minutes, (d) crystal of vanillin after reacting with the vapours of *p*-anisidine for 15 minutes, (e) crystal of vanillin after reacting with the vapours of *p*-anisidine for 20 minutes, (f) crystal of vanillin after reacting with the vapours of *p*-anisidine for 25 minutes.

the formation of spherulitic structure. When the time of exposure was increased, the spherulites grew in size and spread in different directions (Figs. 8c–e). Finally, after 25 minutes, they covered the whole surface of the crystal (Fig. 8f). This process starts with the formation of small nuclei of the reaction product at certain points on the surface of vanillin crystal. These points are the regions of defects. As the time increased, the nuclei grew in size showing spherulitic structure. From the surface morphology, it is seen that the vapors of *p*-anisidine reacts only at the surface. The inner penetration of *p*-anisidine molecule may depend on (i) size of the cavity present in the crystal lattice of vanillin, (ii) size of the *p*-anisidine molecules, (iii) type and concentration of the defects especially grain boundary, (iv) particle size of the reaction product, and (v) compactness of the reaction product. In case when the size of the reaction product is very small (nano size), it will hinder the process of diffusion, and the reaction will be slow.

The vapours of *p*-anisidine were also allowed to react at the surface of the thin layer of vanillin crystallized on the surface of a glass slide. After 45 minutes, the vanillin surface was found to be covered with fine particles of yellow colored reaction product (Fig. 9). The vanillin surface may possess defects. It is quite possible that the reaction starts at these defect sites simultaneously. As a result, a large number of

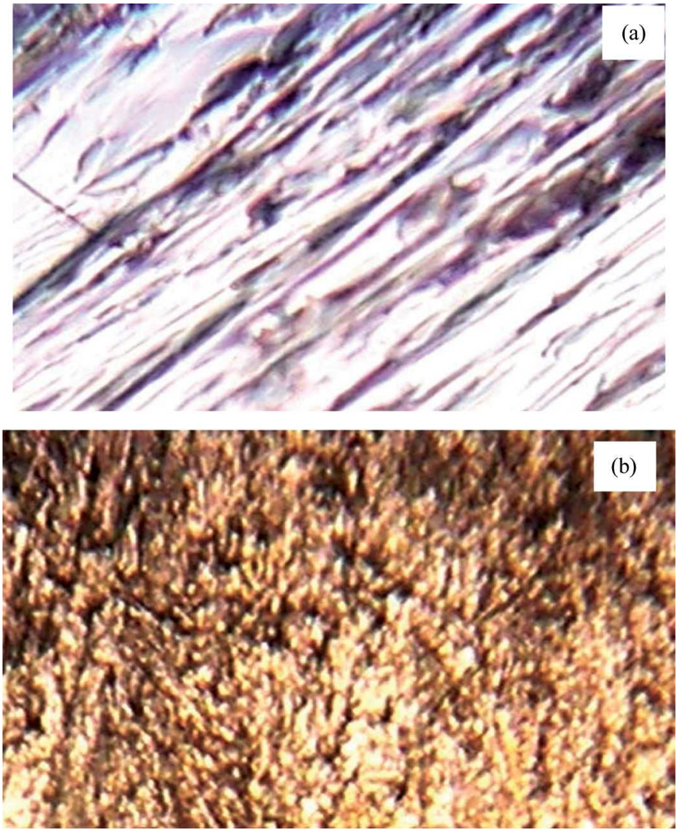


FIGURE 9 (a) microstructure of vanillin, (b) microstructure of vanillin after 45 minutes of reaction with *p*-anisidine vapour.

nuclei (of nanosize) of the reaction product is formed. These nuclei grow in size with time and cover the whole surface of vanillin. Therefore, at a microscopic level the entire surface of the vanillin (Fig. 9b) is seen to be covered with fine particles of the reaction product. However, in the case of vanillin crystal, the defect concentration is much lower which makes the situation different.

CONCLUSIONS

From the results, it is concluded that vanillin reacts with *p*-anisidine in 1:1 molar ratio forming NHM and water irrespective of the condition of the reaction. During solid state reaction, the *p*-anisidine diffuses towards vanillin through multilayer of eutectic mixtures, NHM, and the thin layer of water molecules. It is proposed that the water layer whose thickness may be of nano size will play a vital role in the diffusion during the solid state reaction. The crystal data of NHM are found to be in good agreement with the optimized geometry obtained from the density functional theory.

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