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Fourier Transform Infrared Spectroscopic Studies on the Binary Solutions of 1-Propanol with Xylene Isomers

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ABSTRACT

Fourier Transform infrared spectroscopic study is performed in 4000-400 cm^{-1} wavenumber rangeon pure Propanol (PRO), pure o-xylene (OXY), pure m-xylene(MXY), pure p-xylene (PXY) and their binary solutions (SS1 = 0.2 PRO + 0.8 OXY/MXY/PXY, SS2 = 0.4 + 0.6, SS3 = 0.6 + 0.4 and SS4 = 0.8 + 0.2) at various mole fractions. It was observed that neat propanol liquid appears to have multimer especially as cyclic tetramer and involve in classical and non-classical hydrogen bond interactions with the three xylene isomers in all the binary solutions.

Keywords: FTIR, Classical and non classical H-bond, Propanol, Xylene isomers.

INTRODUCTION

Hydrogen bond is a strong form of intermolecular interaction which is a very important intermolecular force in chemical, physical and biological processes that is being an active research area[1-8]. The H-bond is a bond between electron–deficient hydrogen and a region of high electron density. The H-bond is of the X-H…Y type, where X and Y are electronegative elements and Y possesses one or two electron pairs. Based on the shift observed in the X-H stretching frequency, it is broadly classified as classical (red shifting) and the non-classical(red and blue shift in mostly the C-H stretching frequency) H-bonds. The relatively weaker non-conventional H-bondsalso play a key role in stabilization of biological systems[9-13].

1-Propanol (PRO) is a well known common solvent used in chemical, pharmaceutical, cosmetic industry and biochemical research[14-18]. Fang *et al.,*[19] studied the overtone absorption spectrum of PRO by intracavity photoacoustic and FTIR-spectroscopy in gas phase. The associative nature of PRO with water has been investigated by Max *et al.,*[20]. Its electrical conductivity has been reported at different temperature[21].The degree of associative properties of n-alcohols, including PRO, in carbon tetrachloride solutions by hydrogen bond formation has been examined by Wilson[22]. The experimental and theoretical study on liquid PRO in the MIR region has been carried out by Michniewicz *et al.,*[23] to probe the self-association through a detailed numerical analysis of the vibrational spectra. They have confirmed that the cyclic polymeric structures of PRO are more stable.

Xylene is an aromatic compound that has many industrial applications which exist as three different isomers namely o-xylene, m-xylene and p-xylene. They are used as materials for polyester fibers or films, materials for thermally stable aramid fibers or alkyd resins and plasticizers[24-26]. Hobza *et al.,*[27] have studied the various complexes of benzene, hydrogen cyanide, chloroform and given the initiation to study the possibility of C-H…π bond. The viscosity, ultrasonic velocity and refractive indices of PRO and xylene isomers at two different temperatures has been reported by Gahlyan *et al.,*[28] and they studied the intermolecular interaction between PRO and xylene binary solutions. The objective of this work is to pay attention on the study of FTIR-spectroscopic behaviour and heteromolecular interactions in the solutions of these important molecules.

MATERIALS AND METHODS

Propanol (PRO) of anhydrous grade and 99.7% purity is purchased from Sigma Aldrich, USA. o-xylene (OXY), m-xylene (MXY) and p-xylene (PXY) of HPLC grade were obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. These chemicals were used without any further purification.

The FTIR-spectra of pure OXY/MXY/PXY, Pure PRO and their binary solutions (SS1 = 0.2 PRO + 0.8 OXY/MXY/PXY, SS2 = 0.4+0.6, SS3 = 0.6 + 0.4 and SS4 = 0.8 + 0.2) were recorded using Perkin Elmer FTIR spectrophotometer of resolution 1 cm^{-1} in the 4000 to 400 cm^{-1} region at room temperature.

RESULTS AND DISCUSSION

Figures 1-3 present the FTIR spectra of pure 1-propanol(PRO), three isomers of xylene and their binary solutions. The two O-H stretching frequencies can be observed (Fig. 1 and Table 1), one is the sharp bandat 3671.7 cm^{-1} and the other is a broad absorption centering around 3352.1 cm^{-1}. The former is assigned to free of monomer and the latter is assigned to the bonded/self-associated stretching vibration of multimeric PRO units. The appearance of bonded at 3352.1 cm^{-1}, is close to the value of cyclic tetramer[23] and it could be interpreted as the dominatio of the cyclic tetramer structures in the pure PRO. This conclusion is also supported by the finding ofSum *et al.,*[29] who studied clusters of various alcohols including PRO theoretically and Isao Akiyama *et al.,*[30] who have done large angle X-ray studies on liquid propanol.The band due to the asymmetric and symmetric stretching vibrations of PRO occurred at 2972.8 cm^{-1} and 2874.3 cm^{-1} respectively. The symmetric vibration is observed at 2941.1 cm^{-1}.The assignment of the infrared spectra of 1-propanol in the liquid state is on the basis of comparison of the spectra given in the earlier work[23].In the spectrum of (Fig. 1) pure o-xylene(OXY), 2940.6, 2881.8 and 3109.8 cm^{-1} are assigned the asymmetric, symmetric and symmetric stretching bands, respectively. The observed doublet of 3067.5 cm^{-1} and 3020.6 cm^{-1} are assigned to asymmetric vibration.

The frequency of bonded PRO O-H band is red shifted to 3347.7 cm^{-1} in sample SS1 and the trend continues in SS3 (3344.8 cm^{-1}) and SS4 (3345.3 cm^{-1}) solutions, whereas in SS2, the band is blue shifted to 3353.2 cm^{-1}. The red/blue shifting of bonded O-H band may be reported as the breaking of multimers/dissociation of self-associated PRO molecules through the classical H-bond interaction, in to monomers/open multimers (blue shift) and the interaction of freed O-H with the π electrons(red shift) in the OXY. The interaction by with higher energy will be the prominent. The free O-H red shifted in all the binary solutions from the corresponding value in its pure form. This by reveals the formation of PRO+MXY by complexes that are H-bonded through the hetero interaction. The v(C-O) and v(C-C-O) red shift trend is observed also in CH_2 asymmetric and symmetric vibrational mode, and this confirms' the intermolecular H-bond between PRO and OXY through the non-classical H-bonding interaction. The and of PRO have been observed at 1066.0 cm^{-1} and 1056.9 cm^{-1} in its pure form. Very feeble red shiftsin SS1, SS2, SS4 and null shift in SS3 have been observed in. A significant red shift has also been noticed in v(C-O) of all the solutions.

Table 1: Vibrational v(C-C-O) bands of PRO, OXY and their binary solutions

Vibrational bands$_a$	PRO	Solutions (PRO + OXY)			
		0.2+0.8 SS	1 0.4+0.62 SS	0.6+ 0.4 SS3	0.8+0.2 SS4
v(O-H)	3671.7	3671.7	3671.4	3671.6	3671.5
bonded v(O-H)	3352.1	3344.7	3353.2	3344.8	3345.3
vas(CH_3)	2972.0	2972.8	2972.1	2972.1	2971.0
vas(CH_2)	2941.5	2941.1	2941.3	2941.1	2940.7
vs(CH_2)	2881.4	2874.3	2880.5	2880.5	2880.5
v(C-O)	1066.0	1065.0	1065.8	1066.0	1066.0
ν(C-C-O)	1056.9	1053.0	1052.6	1053.6	1056.1

Vibrational bands^a	OXY	Solutions (PRO + OXY)			
		0.2+0.8	0.4+0.6	0.6+0.4	0.8+0.2
vs(C-H)	3109.8	3095.0	3108.2	3108.9	3109.1
vas(C-H)	3067.5	3020.6	3066.8	3020.9	3066.1
	3018.2	3067.3	3018.6	3069.6	3018.7
vas(CH_3)	2940.6	2924.4	2926.9	2927.0	
vs(CH_3)	2881.8	2894.5	2891.8	2891.6	2899.4

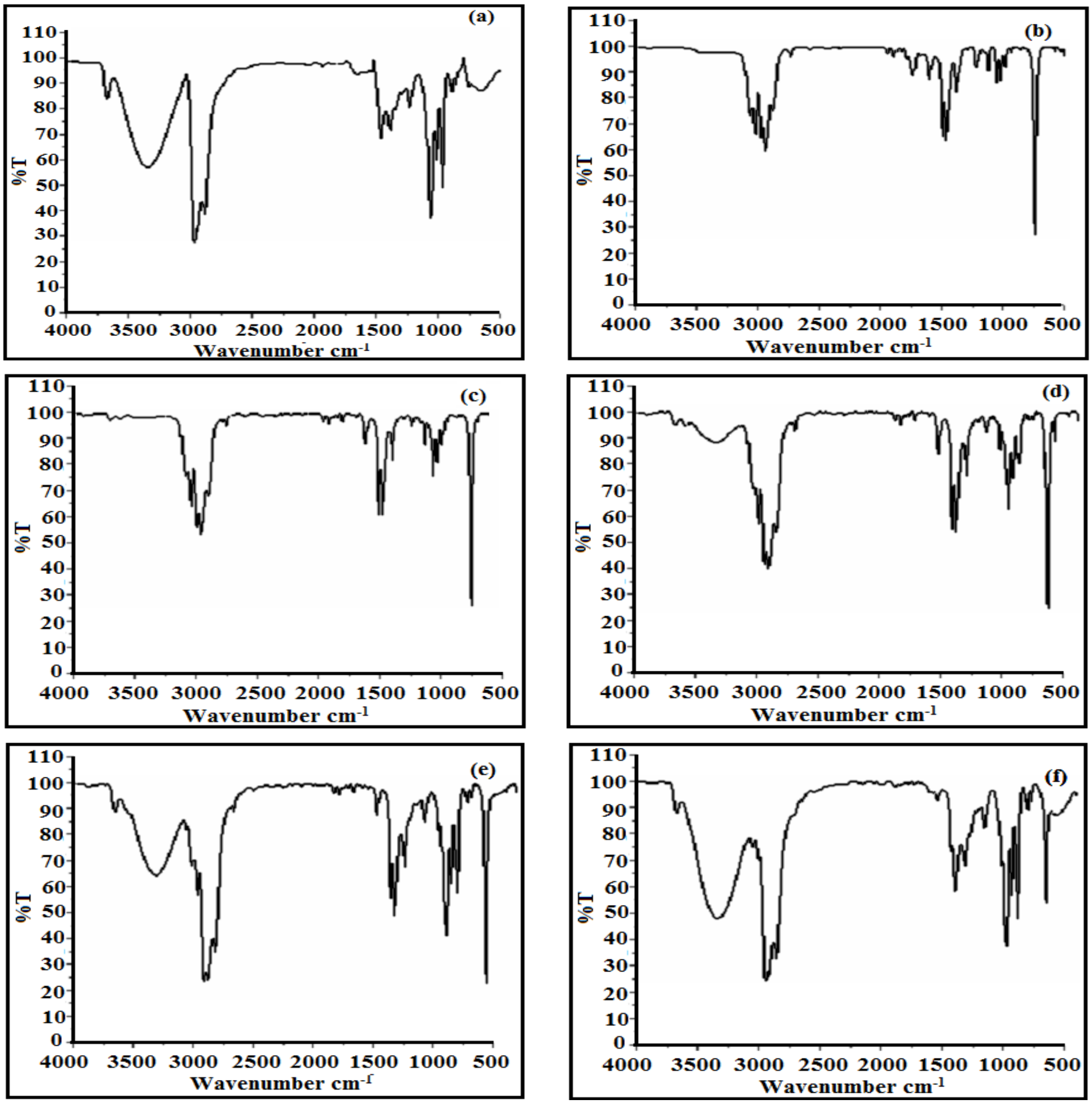

Fig. 1. FTIR-spectrum of (a) Pure PRO, (b) Pure OXY, (c) PRO 0.2 + OXY 0.8, (d) PRO 0.4 + OXY 0.6, (e) PRO 0.6 + OXY 0.4 and (f) PRO 0.8 + OXY 0.2 binary solutions

In the PRO+MXY system the band (Fig. 2 and Table 2) of self-associated bond v(O-H) absorbed at 3352.1 cm^{-1} in pure propanol has O-H suffered appreciable blue shifts in all the sample solutions except in SS4. The blue shift of band of homoassociated propanol structures is an v(O-H) indication(PRO) O-H...O-C(PRO)of breaking/dissociation in the classical O-H...O-C bond[31] which holds the alcohol molecules together. Moreover, the magnitude of this blue shift is very strongin SS1 which has m-xylene in high proportion whereas in the other two solutions SS2 and SS3 the magnitude of blue shift is only about 9 cm^{-1} approximately. Thus, with the increasing concentration of alcohol from SS1 to SS2, the degree of dissociation is reduced and (MXY)aromatic/methyl C-H...O-H(PRO) the band experiences no shift in SS4. The formation of and H-bonds can also influence the shift of band but (PRO)O-H...pi(MXY) the overruling effect of classical hydrogen v(O-H) bond has resulted in the blue shift. In the O-H...O-C alcohol concentrated SS4 solution with the more numbers of MXY molecules, the dissociation of PRO multimer structures would have not happened and thus the O-H stretching vibration has been by observed at the same position observed in pure PRO. On the other hand, the band of free of PRO monomer has been shifted from v(O-H) 3671.7 cm^{-1} (pure PRO) to 3671.9, 3671.3, 3671.8 and 3671.7 cm^{-1}, respectively in SS1, SS2, SS3 and

SS4 solutions. Since the blue shift of monomer band cannot be considered as the effect of dissociation, the feeble blue shift noticed in SS1 and SS3 solutions can be ascribed as the result of H-bond formation only. The development of hydrogen bond at the H-bonding site of PRO (PRO)O-H...pi(MXY) monomer could not be discussed in these SS1 and SS3 solutions since this classical bond formation would have resulted in a appreciable red shift whereas in SS2 the feeble red shift can be understood as the combined effect of both this classical and non-classical H-bonds and in SS4 solution the band absorbs at the same frequency as in pure PRO similar to behavior of bonded) band. Thus, in SS4 solution, the influence of MXY at bonded v(O-H) position is nearly negligible. The formation (O-H) of H-bonds (MXY)aromatic/methyl C-H...O-H(PRO) is again confirmed from the appreciable blue/red shifts of bands of MXY and these shifts of bands can v_s(C-H), v_{as}(C-H), v_{as}(CH_3), v_s(CH_3) also result from the dissociation of v_s(C-H), v_{as}(C-H) dimers interacting with homoassociating H-bonds[32] in the presence of polar PRO (MXY)C-H...pi(MXY) molecules. The occurrence of other possible non-classical hydrogen bonds in this system can (PRO)C-H...pi(MXY) be confirmed from both the red/blue shifts of methyl and methylene groups of PRO. A significant red shift has been observed in all the solutions of v(C-O) and v(C-C-O) and except in band of SS3 of, and band SS4, of stretching bands. The values in both the bands v(C-O) in the alcohol rich solution SS4 approach theoriginal values in their pure form indicate the occurrence of the dominant O-H...O interaction.

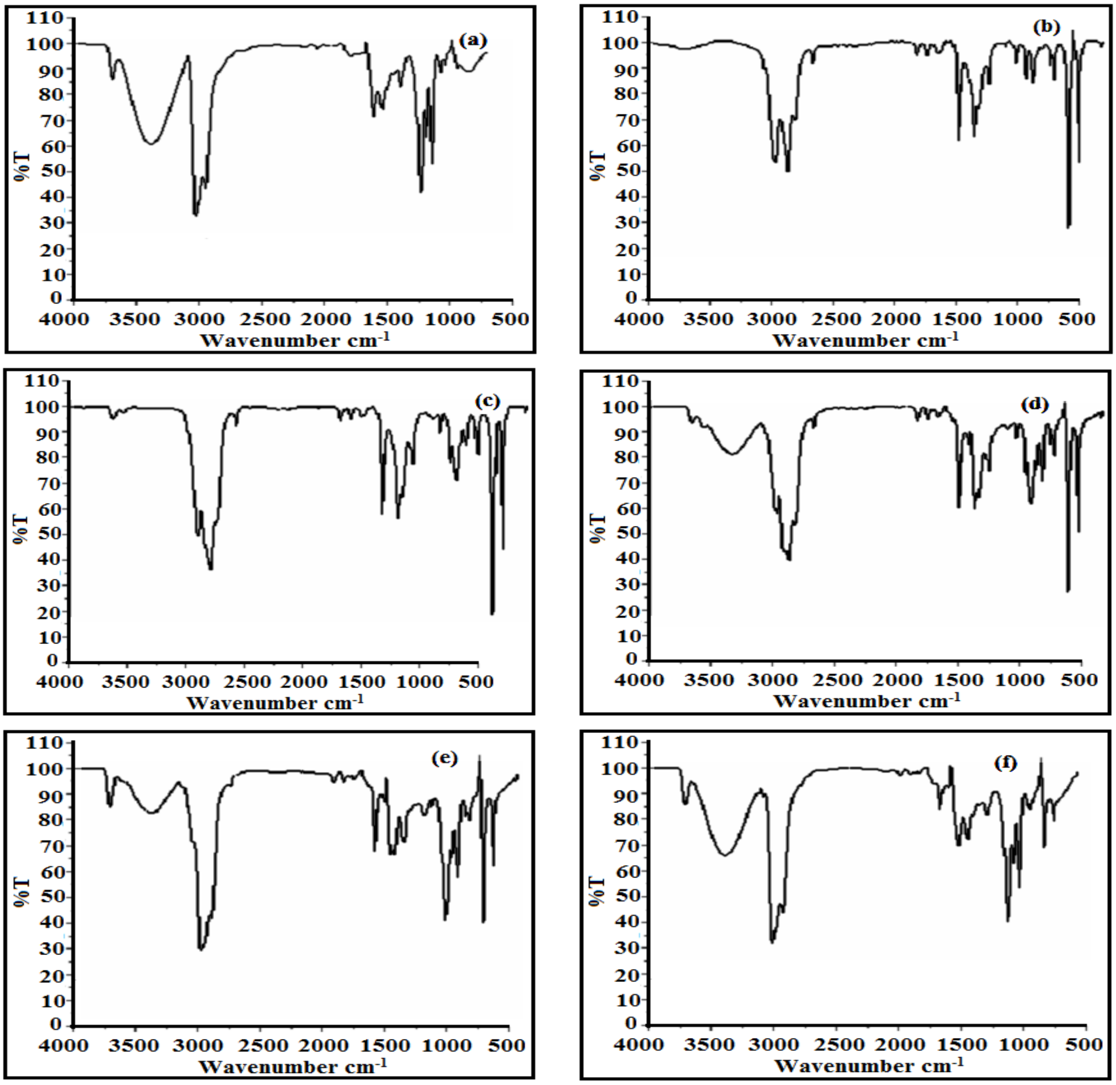

Fig. 2. FTIR-spectrum of (a) Pure PRO, (b) Pure MXY, (c) PRO 0.2 + MXY 0.8, (d) PRO 0.4 + MXY 0.6, (e) PRO 0.6 + MXY 0.4 and (f) PRO 0.8 + MXY 0.2 binary solutions

Table 2: Vibrational bands of PRO, MXY and their binary solutions

Vibrational Bands^a	PRO	Solutions (PRO + MXY)			
		0.2 + 0.8	0.4 + 0.6	0.6 + 0.4	0.8 + 0.2
Free ν (O-H)	3671.1	3671.9	3671.3	3671.8	3671.7
Bonded ν (O-H)	3352.1	3461.2	3361.0	3361.7	3352.1
$\nu_{as}(CH_3)$	2972.0	2971.6	2975.2	2972.3	2972.8
$\nu_{as}(CH_2)$	2941.5	2945.6	2944.5	2943.6	2940.5
$\nu_s(CH_2)$	2881.4	2870.9	2879.8	2883.0	2882.8
ν(C-O)	1066.0	1064.3	1064.4	1068.7	1065.7
ν(C-C-O)	1056.9	1045.0	1054.3	1054.1	1057.2

Vibrational Bands^a	OXY	Solutions (PRO + MXY)			
		0.2+0.8	0.4+0.6	0.6+0.4	0.8+0.2
ν_s(C-H)	3106.8	3108.7	3107.9	3113.0	
ν_{as}(C-H)	3027.6	3020.7	3028.7	3033.8	3039.4
$\nu_{as}(CH_3)$	2923.4	2924.8	2926.8	2927.0	2928.9
$\nu_s(CH_3)$	2867.5	2880.9	2892.8	2893.2	2892.0

Figure 3 and Table 3 presentthe vibrational spectrum and band assignment of pure PRO, pure PXY and PRO-PXY binary solutions, respectively. The peaks observed at 3095.9 cm^{-1} in the pure PXY is assigned to symmetric mode whereas the asymmetric mode of stretching vibration appeared as a doublet at 3048.6 cm^{-1} and 3021.0 cm^{-1}. Furthermore, the C-H observed peaks at 2924.4 cm^{-1} and 2872.0 cm^{-1} are assigned to asymmetric and symmetric modes of stretching CH_3 vibration. The band assignment of xylene isomers are based on data given in[33-35].The monomer/free stretching band in the pure PRO is unaltered in SS1 O-H and has been shifted in all other solution. The bonded red shifted to 3344.7 cm^{-1} and 3344.0 cm^{-1} in SS1 O-H has been and SS4 respectively while blue shift has been observed in the other, two solutions. 'The shifting of lower frequencies in the monomer peak of O-H indicated that the interaction with the xylene molecule through H-bonding' may be repharesed as. The shifting of monomer O-H stretching peak to lower frequencies indicates that there is an interaction of PRO with the p-xylene molecule through H-bonding'. It appears more likely that the polymers might have broken in to lower orders and interacted with the xylene molecules. There are the possibilities of either one interactionto take place or both might have occurred simultaneously, hence the red and blue shifts in the solutions.The substitution order of CH_3 in the isomers of xylene didn't influence the position of C-H and CH_3 stretching bands. The asymmetric band of PRO has been blue shifted in SS1 CH_3 SS2 but red shifted in the remaining solutions. The mixed trend is also followed in followed by CH_2 asymmetric band, which has suffered blue shift in the first three sample solutions and red shifted in SS4. The band is downshifted in all the binary solutions vs(CH_2) from the corresponding value in its pure form. The red and blue shifts of and stretching bands might be the consequences CH_2 of the CH_3 hetero molecular interactions between propanol and xylene molecules which could be and The vibrational bands of asymmetric (PRO) O-H...pi(PXY) and CH_3 symmetric (PRO)C-H... pi(PXY) modes of PXY have suffered a strong blue shifts in all the binary solutions except in SS1 which is red shifted (2923.5 cm^{-1} $v_{as}(CH_3)$, 2892.0 cm^{-1} in SS1, 2926.9 cm^{-1}, 2892.7 cm^{-1} in SS2, 2928.6 cm^{-1} and 2893.4 cm^{-1} in SS3). The vs(CH_3) has been shifted to 2898.7 cm^{-1} and band is not observed in SS4. In the doublet of the higher wave number has suffered red shifts in all the vas(C-H), sample solution except SS4 while the lower wave number is blue shifted in all the solutions. Mixed shift is obtained in symmetric band. The magnitude of the blue shift in C-H is high and hence these shifts C-H suggest that the vs(CH_3) has also been formed in this solution. The (PXY aromatic/methyl) C-H...O-C(PRO) bond same trend of shifts in PRO-MXY in v(C-O) in v(C-O) and v(C-C-O) continues in PRO-PXY observed sample solutions, which indicates that the behavior of xylene isomers in the environment of PRO are the same.These shifts in the PRO and OXY/MXY/PXY binary solutions confirm the presence of (PRO) H-O... π (OXY/MXY/PXY), (PRO methyl) C-H...π (OXY/MXY/PXY) and (OXY/MXY/PXY aromatic/methyl)C-H...O-H (PRO) hetero interactionsbut with different strengths.

Table 3: Vibrational bands of PRO, PXY and their binary solutions

Vibrational bandsa	PRO	Solutions (PRO + PXY)			
		0.2 + 0.8	0.4 + 0.6	0.6 + 0.4	0.8 + 0.2
free v(O-H)	3671.7	3669.4	3671.0	3670.5	3671.3
bonded v(O-H)	3352.1	3344.7	3354.1	3352.0	3344.0
vas(CH_3)	2972.0	2977.0	2972.3	2971.8	2971.8
vas(CH_2)	2941.5	2946.0	2942.7	2944.2	2940.4
vs(CH_2)	2881.4	2873.1	2880.3	2881.2	2880.8
v(C-C)	1066.0	1064.0	1064.2	1066.6	1066.5
ν(C-C-O)	1056.9	1047.4	1053.0	1055.5	1056.4

Vibrational bandsa	OXY	Solutions (PRO + PXY)			
		0.2+0.8	0.4+0.6	0.6+0.4	0.8+0.2
vs(C-H)	3095.9	3094.6	3095.4	3098.5	3103.3
vas(C-H)	3048.6	3047.2	3047.6	3047.9	3050.2
	3021.0	3021.7	3023.2	3022.8	3021.2
vas(CH_3)	2924.4	2923.5	2926.9	2928.6	
vs(CH_3)	2872.0	2892.0	2892.7	2893.4	2898.7

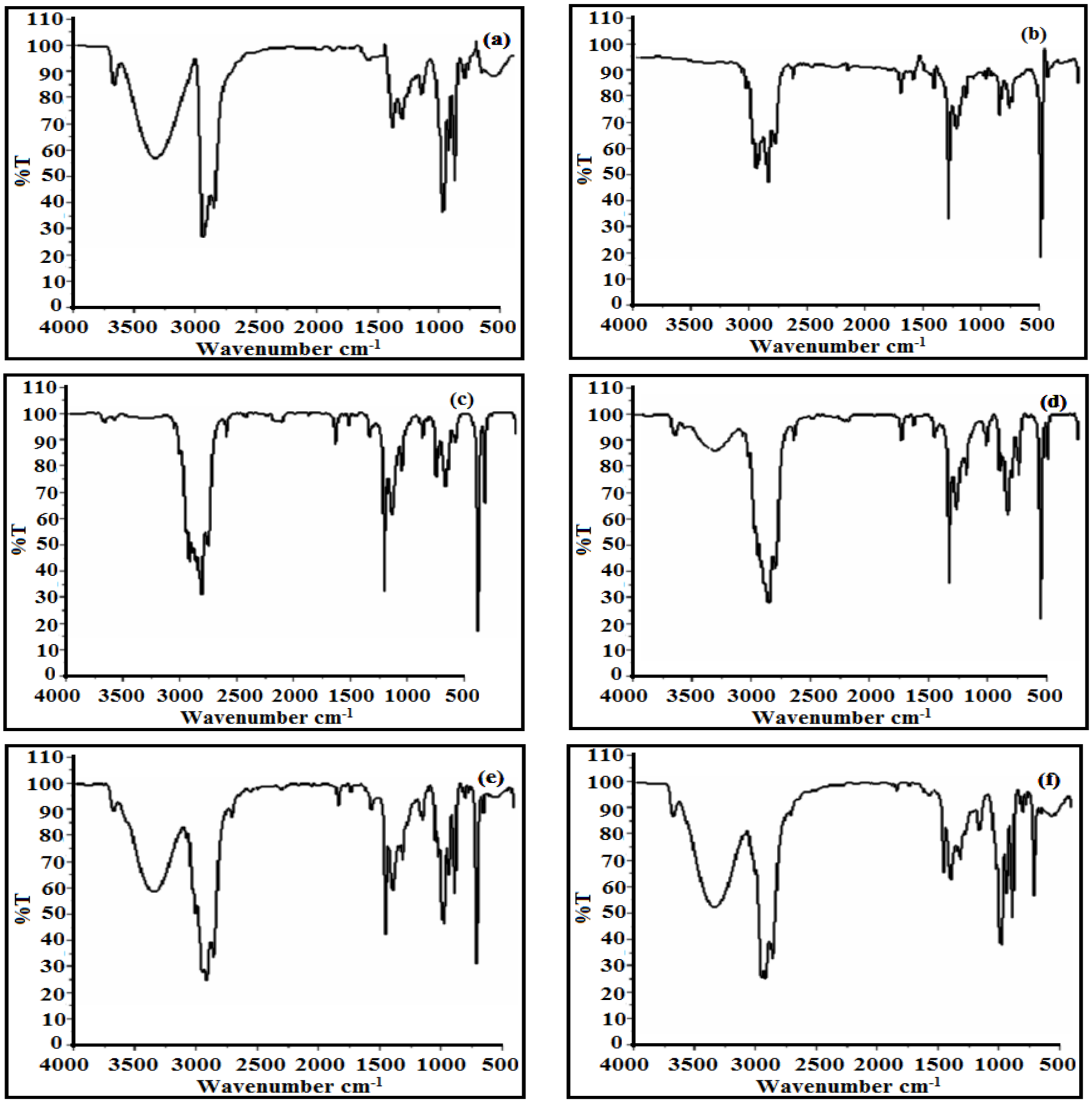

Fig. 3. FTIR spectrum of (a) Pure PRO, (b) Pure PXY, (c) PRO 0.2 + PXY 0.8, (d) PRO 0.4 + PXY 0.6, (e) PRO 0.6 + PXY 0.4 and (f) PRO 0.8 + PXY 0.2 binary solutions

CONCLUSION

The FITR spectroscopic studies carried out on neat PRO, xylene isomers and the binary solutions of isomers reveal the following.

- The pure PRO is a mixture of monomer, chain- or cyclic dimers, trimers, tetramers etc.
- The cyclic tetramer structures are dominant in the pure PRO.
- The MXY is a mixture of monomer and dimer but the dimer structures are unstable.
- (PRO) C-O...H (OXY/MXY/PXY aromatic C-H or methyl), (PRO methyl and/or methylene) H...π (OXY/MXY/PXY) and (PRO) O-H...π (OXY/MXY/PXY) H- bonds have been formed in all the solutions of PRO with each of the xylene isomers.

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Conflict of interest

The authors declare that we have no conflict of interest.

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