H-Bond Interactions in Triethylene Glycol-Acetonitrile Binary Solutions: FTIR Spectral Studies

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FTIR spectral signature of neat acetonitrile (AN), triethylene glycol (TEG) and their binary solutions at various mole fractions of acetonitrile/ triethylene glycol have been obtained. The spectral features endorse that multimers of various orders coexist in liquid phase of triethylene glycol. When triethylene glycol was dissolved in acetonitrile, the combination of multimers present in neat triethylene glycol seems to be not disturbed much but C≡N···H(CH$_2$/H-O) and (AN methyl)H···O(TEG C-O-C) heteromolecular H-bonds have been formed between the triethylene glycol multimers and acetonitrile in all the solutions. The strength of these interactions were found to be acetonitrile/triethylene glycol concentration dependent.

Keywords: FTIR, H-bond Interactions, Acetonitrile, Triethylene glycol, Multimers.

INTRODUCTION

Glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, *etc.* which have two O-H groups are the important precursor for the syntheses of plastics, pharmaceutical and cosmetic compounds [1]. Due to its antimicrobial properties, triethylene glycol (TEG) have applications in lubricants and disinfectants [2-4] and also capable of absorbing some hydrocarbons like methane, ethane, *etc.* from the gas stream [5]. Triethylene glycol (TEG) may also be used in its binary solution with amines to capture CO$_2$ which is the major greenhouse gas which increases the global warming [6-9].

The knowledge on the behaviour of such compound under different chemical environment is essential so that its applications can be explored to some other research areas. Its behaviour can be studied by spectroscopic as well as non-spectroscopic methods. FTIR spectroscopy is the most effective tool that is providing precise information at the structural and interaction forces points of view. FTIR studies has been carried out on the binary solutions with TEG as one of the solution partners by many researchers [6,10-12]. Unfortunately, none of them provided some clear information on the fundamental vibrational bands of TEG in neat as well as in binary solutions. In present work, the FTIR spectral behaviour of the major fundamental

vibrational bands of TEG has been reported. Also its behaviour in the presence of acetonitrile, which is a polar solvent with simple structure and high symmetry and used as a model solvent for theoretical studies on liquid structure [13-16], at various mole fractions has been investigated.

EXPERIMENTAL

Acetonitrile (AN) and triethylene glycol (TEG) of HPLC grade were procured from Sigma-Aldrich, USA, each of with purity 99%. They were used without any further purification. FTIR spectra of neat AN, TEG and their binary solutions (SS1 (0.2 AN + 0.8 TEG), SS2 (0.4 AN + 0.6 TEG), SS3 (0.6 AN + 0.4 TEG) and SS4 (0.8 AN + 0.2 TEG)) at various mole fractions of AN/TEG have been recorded using an FTIR spectrometer (Spectrum RXI) supplied by Perkin-Elmer, USA.

RESULTS AND DISCUSSION

The infrared absorption appearing at 3004.7, 2945.1, 2254.0 and 919.0 cm^{-1} (Fig. 1) are assigned to the ν_{as}(CH$_3$), ν_s(CH$_3$), ν(C≡N) and ν(C−C) bands, respectively, of pure AN. These values slightly deviate from the literature values [17-20] and this may be due to the difference in resolution used in this work in which it is 1 cm^{-1}. The broadening of the band centering
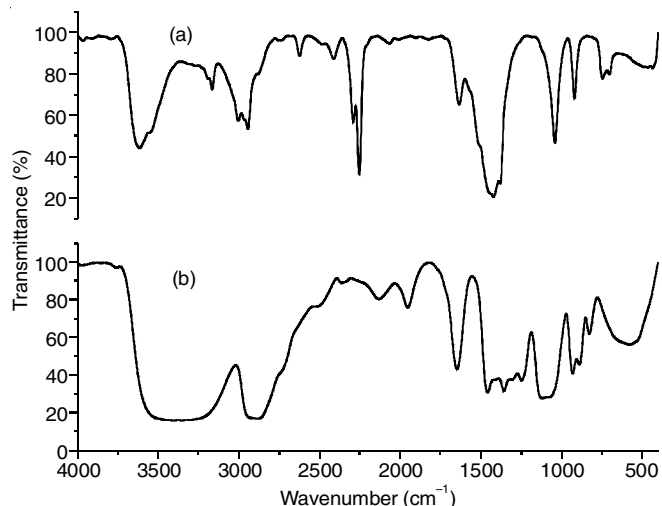
Fig. 1. Experimental FTIR spectrum of (a) neat acetonitrile (AN) and (b) neat triethylene glycol (TEG)

at 3616 cm^{-1} may be due to the trace of some water molecules. The TEG has (i) two C-O-C equivalent oxygens, (ii) two sets of equivalent CH$_2$ groups, one is the methylene groups adjacent to the O-H groups and the other is that exists between the two C-O-C oxygens; and (iii) two equivalent O-H groups. The C-O-C oxygens, CH$_2$ hydrogens and the O-H oxygen and hydrogen are capable of involving in H-bond interactions. So, neat liquid TEG is expected to have a complicated self-associated structure of different orders. This can be ascertained from the FTIR spectrum of TEG (Fig. 1b) which exhibits the broad O-H stretching absorption that spreads over a frequency range of 3700-3100 cm^{-1} with no single minimum and a band around 1100

cm^{-1}, which has multiple peaks. It is difficult to assign precisely each one of the deconvoluted peaks of the 3700-3100 cm^{-1} band to a specific multimer and therefore, the band around 1100 cm^{-1} has been deconvoluted (Fig. 2). The best fit has been obtained for a group of six Gaussian peaks which are at 1154.9, 1141.2, 1119.8, 1079.0, 1042.3 and 1021.8 cm^{-1}. Of these six peaks, the first three have been assigned to the C-O-C stretching bands and the remaining three are the bands due to the C-C-O(H) vibrations [21]. Because of the presence of two different equivalent CH$_2$ groups, the FTIR spectrum of TEG displays (Figs. 1b and 3) two ν_{as}(CH$_2$) bands (2966.6 and 2930.4 cm^{-1}) and two ν_s(CH$_2$) bands (2863.8 and 2801.6 cm^{-1}) (Table-1). Even though the presence of many different multimers is signaled by the spectral feature of O-H stretching band, only three bands are noticed for C-O-C and C-C-O(H) stretching vibrations each and two different sets of asymmetric and symmetric CH$_2$ stretching bands appear. This shows that the multimerization mainly involves the O-H groups.

Significant changes in the shape of the ν(O-H) absorption occurs in the spectra of the solutions of AN with TEG (Fig. 4). It is clear that from Fig. 4a to 4d, the flattening of the ν(O-H) band is found to be more and more pronounced. This confirms that structural changes either through the dissociation of TEG-TEG associated multimers or formation of AN-TEG hetero-associated networks have taken place. Of course, the formation of AN-TEG heterostructures is always associated with the dissociation of TEG-TEG multimers. Density functional theory (DFT) calculations on AN monomers and dimers from our research group show that when the CH$_3$ and C≡N of AN involve in H-bond interactions to form dimers, ν_{as}(CH$_3$) undergoes blue shift while the ν_s(CH$_3$) as well as the ν(C≡N) bands suffer red shifts [19].
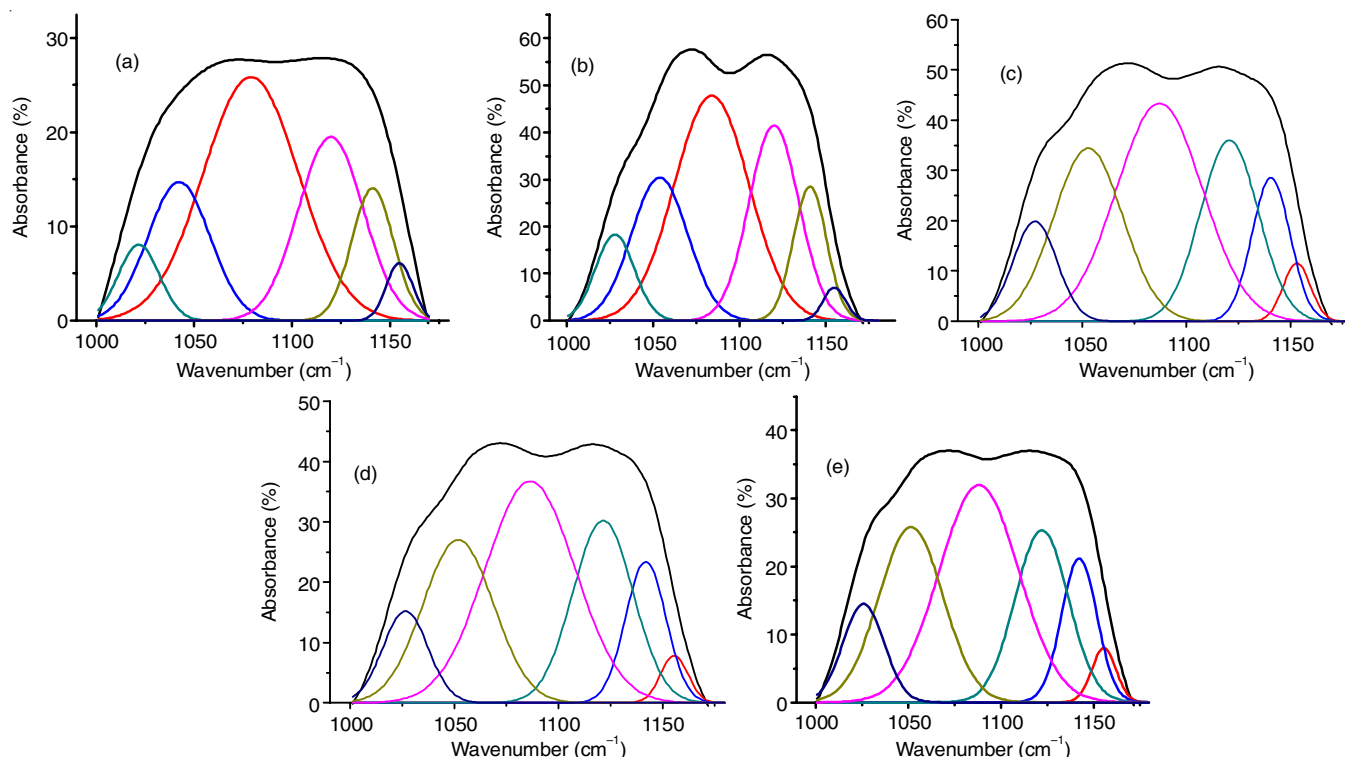

Fig. 2. The deconvoluted Gaussian peaks of C–O stretching and C–OH stretching bands for (a) pure TEG, (b) SS1 (AN0.8 + TEG0.2), (c) SS2 (AN0.6 + TEG0.4), (d) SS3 (AN0.4 + TEG0.6) and (e) SS4 (AN0.2 + TEG0.8). Here, SS1,…,SS4 stands for the binary solutions
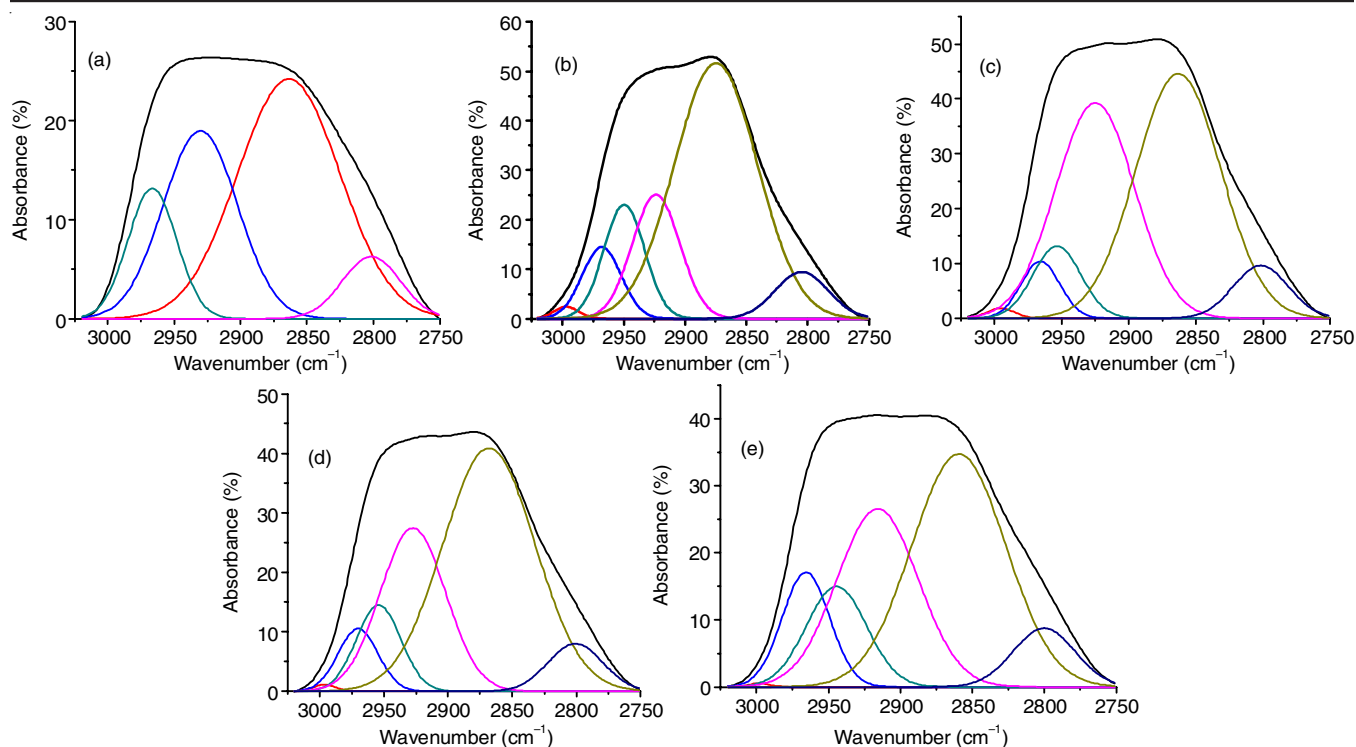
Fig. 3. The deconvoluted Gaussian peaks of CH₂ stretching bands for (a) pure TEG, (b) SS1 (AN0.8 + TEG0.2), (c) SS2 (AN0.6 + TEG0.4), (d) SS3 (AN0.4 + TEG0.6) and (e) SS4 (AN0.2 + TEG0.8). Here, SS1,…,SS4 stands for the binary solutions

TABLE-1
FTIR SPECTRAL BAND ASSIGNMENT VALUES FOR NEAT AN, TEG AND THE BINARY SOLUTIONS OF
ANTEG AT VARIOUS MOLE FRACTIONS. HERE, THE FRACTIONAL NUMBERS ARE THE MOLE FRACTIONS

Vibrational modes	Wavenumber (cm⁻¹)				
	Neat AN	SS1 (AN0.8 + TEG0.2)	SS2 (AN0.6 + TEG0.4)	SS3 (AN0.4 + TEG 0.6)	SS4 (AN0.2 + TEG0.8)
$\nu_{as}(CH_3)$	3004.7	2996.7	2995.4	2996.2	2998.2
$\nu_s(CH_3)$	2945.1	2949.6	2953.6	2954.0	2944.4
$\nu(C\equiv N)$	2254.0	2252.5	2252.0	2252.1	2251.9
Vibrational modes	Neat TEG	SS1	SS2	SS3	SS4
$\nu(OH)$	3405.1	3396.1	3395.95	3394.8	3396.0
$\nu_{as}(CH_2)$	2966.6	2967.9	2965.9	2970.0	2965.6
$\nu_{as}(CH_2)$	2930.4	2923.6	2925.1	2927.3	2915.8
$\nu_s(CH_2)$	2863.8	2874.6	2863.2	2868.1	2859.4
$\nu_s(CH_2)$	2801.6	2804.7	2801.8	2800.8	2800.1
$\nu(C–O–C)$	1154.9	1154.9	1153.0	1155.7	1155.6
	1141.2	1140.8	1140.6	1142.0	1142.3
	1119.8	1120.0	1120.6	1121.4	1122.1
$\nu(C–C–O(H))$	1079.0	1084.0	1087.0	1086.4	1088.3
	1042.3	1053.9	1052.7	1051.9	1051.6
	1021.8	1028.0	1027.2	1026.5	1026.0

In present work, the $\nu(C\equiv N)$ got red shifted (Table-1) while the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ bands are found to be red and blue shifted, respectively, in the solution SS1. So, the red shift in the $\nu(C\equiv N)$ band position confirms the participation of the C≡N nitrogen in the heteromolecular interaction with either CH₂ or/and O-H hydrogen of TEG to form C≡N···H(CH₂/H-O) H-bonds. The formation of this H-bond has been endorsed by the positional shifts suffered by the asymmetric and symmetric stretching bands of CH₂ (Table-1) and also the bands shape of the O-H stretching band. The red and blue shifts in the frequency

of the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ bands, respectively, suggest the disruption of H-bond in AN-AN dimer [19] and may be taken as the indication that the CH₃ of AN become free of H-bond interactions when it is dissolved in TEG. The feeble shift only in 1141.2 and 1119.8 cm⁻¹ $\nu(C-O-C)$ bands of pure TEG in the solutions SS1 may be due to the participation of CH₃ hydrogen of AN in (AN methyl)H···O(TEG C-O-C) H-bond formation. In such a case, the relatively weaker AN-TEG interaction in comparison with the AN-AN interaction could have resulted in red and blue shifts in the frequency of the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$
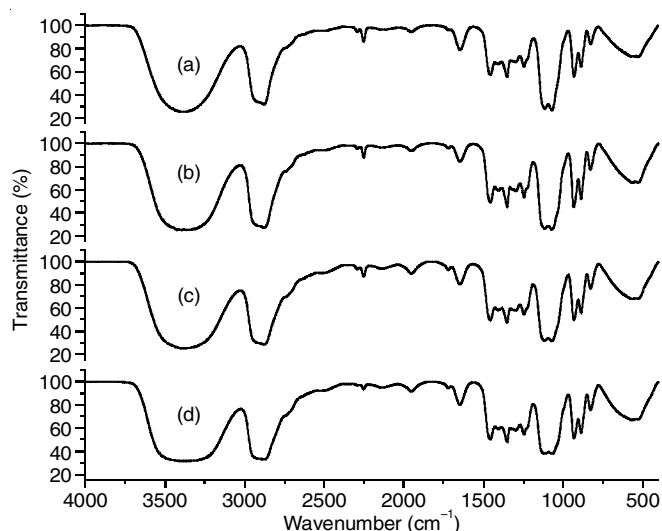
Fig. 4. Experimental FTIR spectrum of the binary solutions (a) SS1(0.8AN + 0.2TEG, (b) SS2 (0.6AN + 0.4TEG), (c) SS3 (0.4 AN + 0.6TEG) and (d) SS4 (0.2 AN + 0.8TEG)

bands of AN. The absorption position of all the three bands due to the C-C-O(H) stretching vibrations of pure TEG witness huge blue shifts in SS1 and this may be the consequence of the H-bond interaction of C≡N nitrogen at the O-H hydrogen.

The position of $\nu(C{\equiv}N)$, $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ bands are found to suffer red, blue and red shifts, respectively, from the that in pure AN in SS2 also as in SS1. The $\nu_{as}(CH_2)$ bands (2966.6 and 2930.4 cm^{-1}) and $\nu_s(CH_2)$ bands (2863.8 and 2801.6 cm^{-1}) of neat TEG appear now at (2965.9 and 2925.1 cm^{-1}) and (2863.2 and 2801.8 cm^{-1}), respectively, in SS2 in which the $\nu(C-O-C)$ bands are shifted to 1153.0, 1140.6 and 1120.6 cm^{-1} from 1154.9, 1141.2 and 1119.8 cm^{-1} (bands of pure TEG), respectively. Also, the bands due to the C-C-O(H) stretching vibrations have been shifted to 1087.0, 1052.7 and 1027.2 cm^{-1}. The nature of the shift in $\nu(C{\equiv}N)$, $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ bands observed in SS1 and SS2 continues in SS3 and SS4 also except $\nu_s(CH_3)$, which has suffered a slight red shift only in SS4. The methylene stretching vibrational bands undergo the same trend of shift in SS3, except the lower frequency band, as in SS1 but all these bands suffer red shifts in SS4. The $\nu_s(C-O-C)$ and C-C-O(H) stretching bands have been shifted to higher wavenumber in SS3 and SS4. All these shifts indicated that the C≡N···H(CH$_2$/ H-O) and (AN methyl)H···O(TEG C-O-C) H-bonds existed in SS1 continue to be present in SS2, SS3 and SS4 solutions also but with different interaction strengths as suggested by the slight deviation in the magnitude and nature of the shifts of the bands under consideration. It should be noted that the number of absorption bands remain conserved in all the solutions and only the positional shifts occur. This portray that the multimers existed in pure TEG are now being hetero-associated with AN in the solutions but not suffered severe dissociation so that lower order multimer are created.

Conclusion

FTIR spectra of neat acetonitrile, triethylene glycol and their binary solutions at various mole fractions of acetonitrile have been recorded and analyzed in order to probe the H-bond interactions present in the solutions. Pure triethylene glycol exist simultaneously as multimers of various orders in liquid phase. When mixed with acetonitrile, the combination of multimers present in neat triethylene glycol appears to be not disturbed much but C≡N···H(CH$_2$/H-O) and (AN methyl)H···O(TEG C-O-C) heteromolecular H-bonds have been formed in all the solutions. The strength of these interactions varies with the concentrations of acetonitrile/triethylene glycol.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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