



Intermolecular Interactions in Acetonitrile + Acetone Binary Mixtures: FTIR Spectroscopic Studies

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Received: 10 April 2021;

Accepted: 7 May 2021;

Published online: 5 June 2021;

AJC-20383

FTIR spectra of neat acetone (ACT), neat acetonitrile (AN) and their binary solutions at various molar ratios 1:2, 1:3, 2:1 and 3:1 (AN:ACT) have been recorded in 4000–400 cm⁻¹ region at room temperature. The acetone is a self-associated molecule and existed as a mixture of monomers, dimers and trimers. The acetonitrile is also a mixture of monomer and weakly bonded dimers. The acetone is associated through the H-bond interaction (ACT)C-H...O=C(ACT) and the acetone and acetonitrile molecules are interacted through the non-classical H-bonds (ACT) C-H...N≡C (AN) and (AN) C-H...O=C (ACT).

Keywords: FTIR, Acetone, Acetonitrile, Self association, Hydrogen bonding.

INTRODUCTION

Acetonitrile is a multipurpose solvent generally used in batteries, rubber, chemicals and catalytic industries. It is a simple structured polar compound, an important solvent used as a model solvent for many theoretical and simulation studies of liquid structures [1-7]. Acetone is also a well known and widely used polar solvent commonly used in pharmaceuticals. Many of the spectroscopic studies have focused on the acetonitrile as well as acetone [8-18]. Acetone has been chosen as a solvent in the present work because of the high polar and self-associative nature. Hydrogen bonding play a vital role in the investigation of the intermolecular interactions between any two molecules. The magnitude as well as the sign of the shifts in the frequencies of vibrational modes are closely related to the H-bond formation which is an important diagnostic tool to find out the stability and properties of molecular structures. The non-classical H-bonds has an important role in the stabilization of biological systems [19-23]. Hobza & Havlas [24], on their study of various complexes especially on benzene have explained the nature of non-classical H-bond. The non-conventional H-bonds are stronger in some suitable circumstances as reported by Scheiner [25]. Musso *et al.* [26] have studied the associative

behaviour of acetone by Raman spectroscopic study of acetone + methanol solution. The polymeric structure of acetone has been reported by Guan *et al.* [27] from their size-selective infrared plus vacuum ultraviolet (IR + VUV) studies on gas phase acetone. Beuckeleer & Herrebout [28] studied the infrared spectrum of acetone + krypton at various concentrations and resolved the monomer and dimer bands of acetone.

Different analyses have been carried out on acetonitrile, *e.g.* (i) the FTIR and theoretical calculations were performed for DMSO + acetonitrile to study the associative nature of DMSO and acetonitrile [29]; (ii) the FTIR studies of acetonitrile + ethanol [30]; and (iii) the FTIR and ¹³C NMR studies have been carried out on acetonitrile + ethylene glycol binary solutions in order to analyze the intermolecular interactions of acetonitrile [31]. Takamuku *et al.* [32] discussed the dipole-dipole interaction between acetonitrile + water binary solution by X-ray diffraction and infrared spectroscopy. In this work, the spectroscopic studies of acetonitrile, acetone and their binary solutions have been carried out and the self associative nature of acetone, the weak dimeric structures of acetonitrile and interaction between acetonitrile (AN) and acetone (ACT) through the non-classical H-bonds were analyzed.

EXPERIMENTAL

Acetonitrile of HPLC grade with >99.9% purity was procured from Sigma-Aldrich, USA. Acetone for HPLC 99.9% was purchased from Sigma-Aldrich, USA. FTIR spectrum of pure compounds and their binary solutions at different molar ratios (1:2, 1:3, 2:1, 3:1) were recorded using Perkin-Elmer spectrophotometer in 4000 to 400 cm^{-1} wavenumber range at room temperature with 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

The FTIR spectra of pure acetonitrile (AN), pure acetone (ACT) and their binary mixtures at various molar ratios 1:2, 1:3, 2:1 and 3:1 (AN:ACT) are presented in Fig. 1. The vibrational frequencies of pure ACT are compared with the literatures [33-35] and the values are shown in Table-1 along with the pure AN and their binary solutions. The bands (Fig. 1a) at 3006.3 and 2971.3 cm^{-1} are assigned as $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{s}}(\text{CH}_3)$, respectively. Since C=O peak of pure acetone showed asymmetry, the region in its pure form as well as in their solutions has been deconvoluted into four peaks to get an insight of the structure. It was observed that the four C=O peaks appear at 1754.6, 1749.1, 1739.2 and 1726.2 cm^{-1} (Fig. 2a). It can be seen that three consequent bands appeared in the $\nu(\text{C}-\text{C})$ stretching

Vibrational bands ^a	ACT	Solutions (AN + ACT)			
		1:2	1:3	2:1	3:1
$\nu_{\text{as}}(\text{CH}_3)$	3006.3	3010.1	3006.7	3009.6	3011.7
$\nu_{\text{s}}(\text{CH}_3)$	2971.3	2963.3	2971.7	2969.6	2963.2
$\nu(\text{C}=\text{O})$	1749.1	1742.7	1743.6	1745.8	1744.8
	1739.2	1732.5	1732.5	1735.2	1733.9
	1726.8	1725.4	1725.0	1726.3	1725.9
	1206.6				
$\nu(\text{C}-\text{C})$	1217.2	1221.0	1212.2	1224.0	1221.6
	1229.2		1223.5		
Vibrational bands ^a	AN	Solutions (AN + ACT)			
		1:2	1:3	2:1	3:1
$\nu_{\text{as}}(\text{CH}_3)$	3003.0	2999.1	2994.6	2998.5	3002.0
$\nu_{\text{s}}(\text{CH}_3)$	2947.5	2944.3	2947.8	2945.0	2943.9
$\nu(\text{C}=\text{N})$	2254.3	2254.3	2253.7	2254.2	2254.3

^a ν : stretching, s: symmetric, as: asymmetric

region of pure ACT at 1206, 1217.2 and 1229.2 cm^{-1} . In contrary to the above given literatures, the C=O stretch and the C-C bend of ACT both in its pure form as well as in their solution with acetonitrile, have multiple frequencies, which have revealed

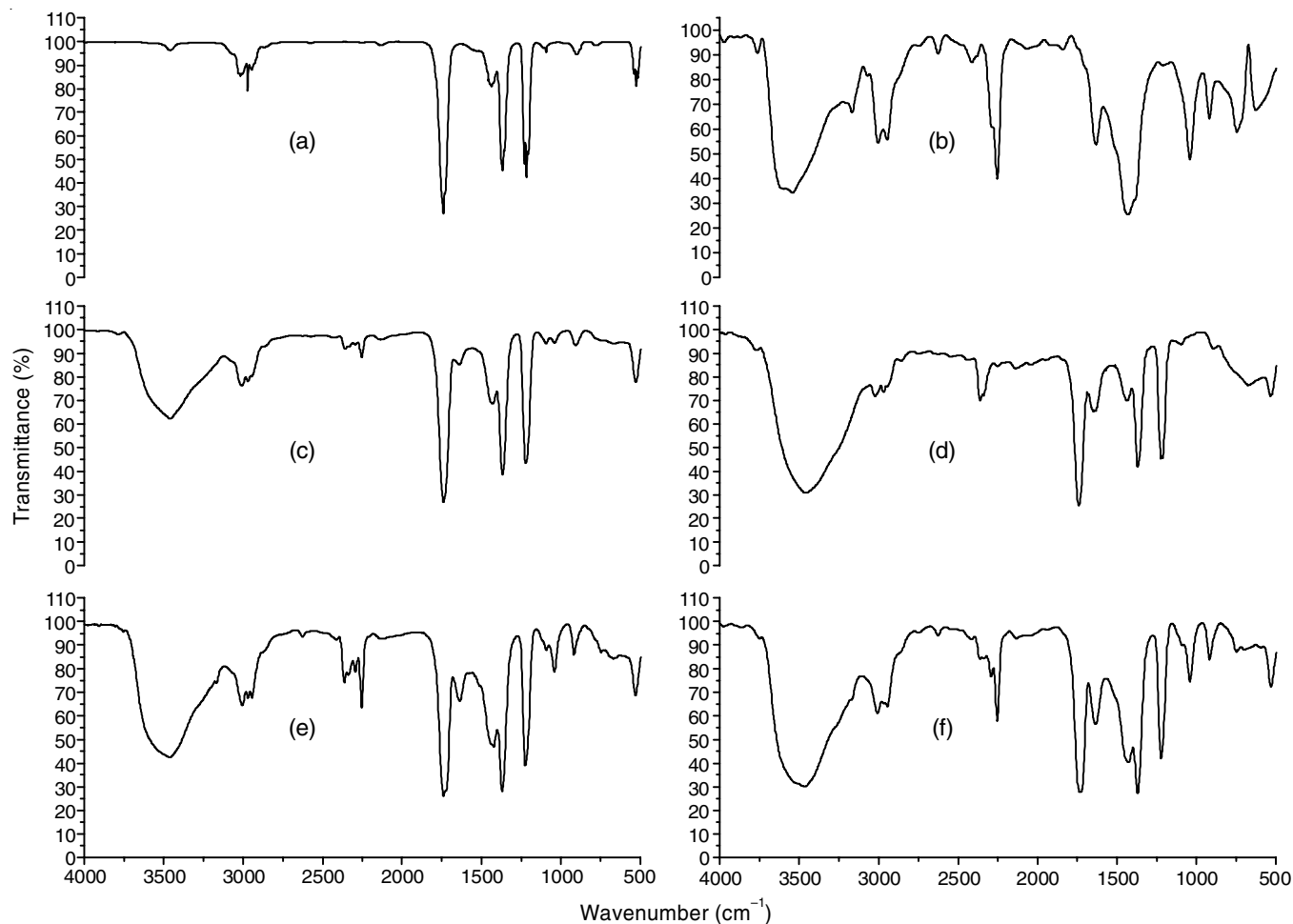


Fig. 1. FTIR spectrum of (a) pure ACT, (b) pure AN, (c) 1:2 (ACT:AN), (d) 1:3 (ACT:AN), (e) 2:1 (ACT:AN), and (f) 3:1 (ACT:AN) binary solutions

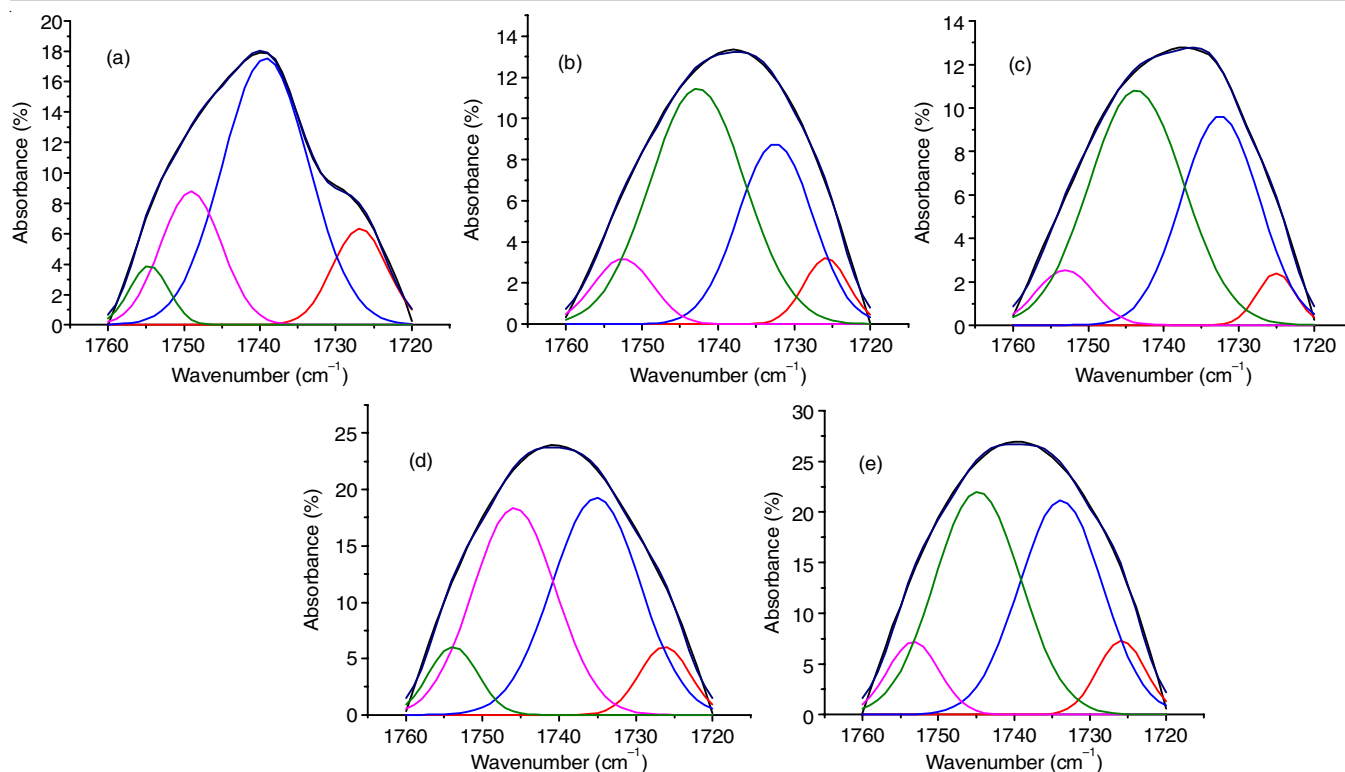


Fig. 2. Deconvoluted peaks in the $\nu(\text{C}=\text{O})$ region of (a) Pure ACT, (b) 1:2 (ACT:AN), (c) 1:3 (ACT:AN), (d) 2:1 (ACT:AN) and (e) 3:1 (ACT:AN)

the presence of self associated form of acetone molecules. Among the four peaks of C=O stretch, the weak band at 1754 cm^{-1} has been assigned as the combinational band which agreed well with the reported value 1752 cm^{-1} [26]. In the earlier work [27], the authors who have done both theoretical and experimental work in acetone arrived with four bands for C=O stretch, in which the highest value was assigned to monomer, next higher value to dimer and so on. In another work [28], the highest value amidst the two values has been assigned to the monomer. Based on these reports, in this work, the bands 1749.1 , 1739.2 and 1726.2 cm^{-1} are assigned to monomer, dimer and trimer, respectively. But the monomer value in this work deviates from the reported values 1738 cm^{-1} [36], 1721.4 cm^{-1} [37] and 1725.6 cm^{-1} [28]. It could be recognized as ACT is a combination of monomer, dimer and trimer structures. The ACT might have self associated through $(\text{ACT})\text{C}-\text{H}\dots\text{O}=\text{C}(\text{ACT})$ interaction. The multiple bands associated with $\nu(\text{C}-\text{C})$ also supported the self associated structures of ACT.

The $\nu_{\text{as}}(\text{CH}_3)$ is blue shifted to 3010.1 cm^{-1} in the 1:2 solution. This shift could be interpreted as either the formation non classical H-bond between the C-H of ACT and $\text{N}\equiv\text{C}$ of AN or the dissociation of self-associated ACT molecules into monomers. The trend of blue shift is continued in all the solutions irrespective of the increase/decrease of the number of ACT molecules. The $\nu_{\text{s}}(\text{CH}_3)$ band of pure ACT has red shifted in all the solutions (2969.3 cm^{-1} in 1:2, 2969.6 cm^{-1} in 2:1 and 2963.2 cm^{-1} in 3:1) except 1:3 (2971.7 cm^{-1}) in which it got blue shifted feebly. The monomer and dimer peaks of C=O stretch in ACT have showed appropriate red shifts in all the solutions from the corresponding value in its neat form and

the red shift of trimer band of $\nu(\text{C}=\text{O})$ in all the solutions also significant. The observed red shifts in all the bands of $\nu(\text{C}=\text{O})$ and $\nu_{\text{s}}(\text{CH}_3)$ bands could be interpreted the formation of $(\text{ACT})\text{C}-\text{H}\dots\text{N}\equiv\text{C}(\text{AN})$ and $(\text{AN})\text{C}-\text{H}\dots\text{O}=\text{C}(\text{ACT})$ non-classical hydrogen bonds. The free carbonyl oxygen of monomer of pure ACT could be interacted with the $\text{N}\equiv\text{C}$ nitrogen of AN or freed oxygen of dimers and trimers due to the dissociation of acetone molecules (blue shift of $\nu_{\text{as}}(\text{CH}_3)$) might have interacted with the $\text{N}\equiv\text{C}$ nitrogen of AN. Some of the $\nu(\text{C}-\text{C})$ peaks not observed in some solutions, but the observed peaks got red shifted in all the solutions which confirmed the formation of the non classical H-bonds.

The potential field controlling all the vibrations of methyl group will influence the vibrations of other deformation and bending vibrations [38]. During the dissociation of ACT molecules shortening the C-H bond occurs and it could be the reason of blue shift in the C-H stretching vibrations also tend to tie the hydrogen very loosely/unattached. The shift to lower frequencies of deformation and bending vibrations might be the consequences of lengthening of H-bond. Hence the red shifts in $\nu(\text{C}-\text{C})$ of this work.

The bands absorbed at 3003.0 , 2947.5 and 2254 cm^{-1} (Fig. 1b) in the spectrum of pure AN are assigned to $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_3)$ and $\nu(\text{C}\equiv\text{N})$, respectively. Since the $\nu_{\text{as}}(\text{CH}_3)$ bands of AN in the binary solutions overlaps significantly with $\nu_{\text{as}}(\text{CH}_3)$ of ACT, the C-H region have been deconvoluted (Fig. 3) in all the solutions and assigned to the corresponding bands. Of the peaks, in 1:3 binary solutions two frequencies have obtained for $\nu_{\text{s}}(\text{CH}_3)$ of ACT and one is reasoned out as a combinational band ($1222.3 + 1743.6\text{ cm}^{-1}$). Literatures reported that the AN

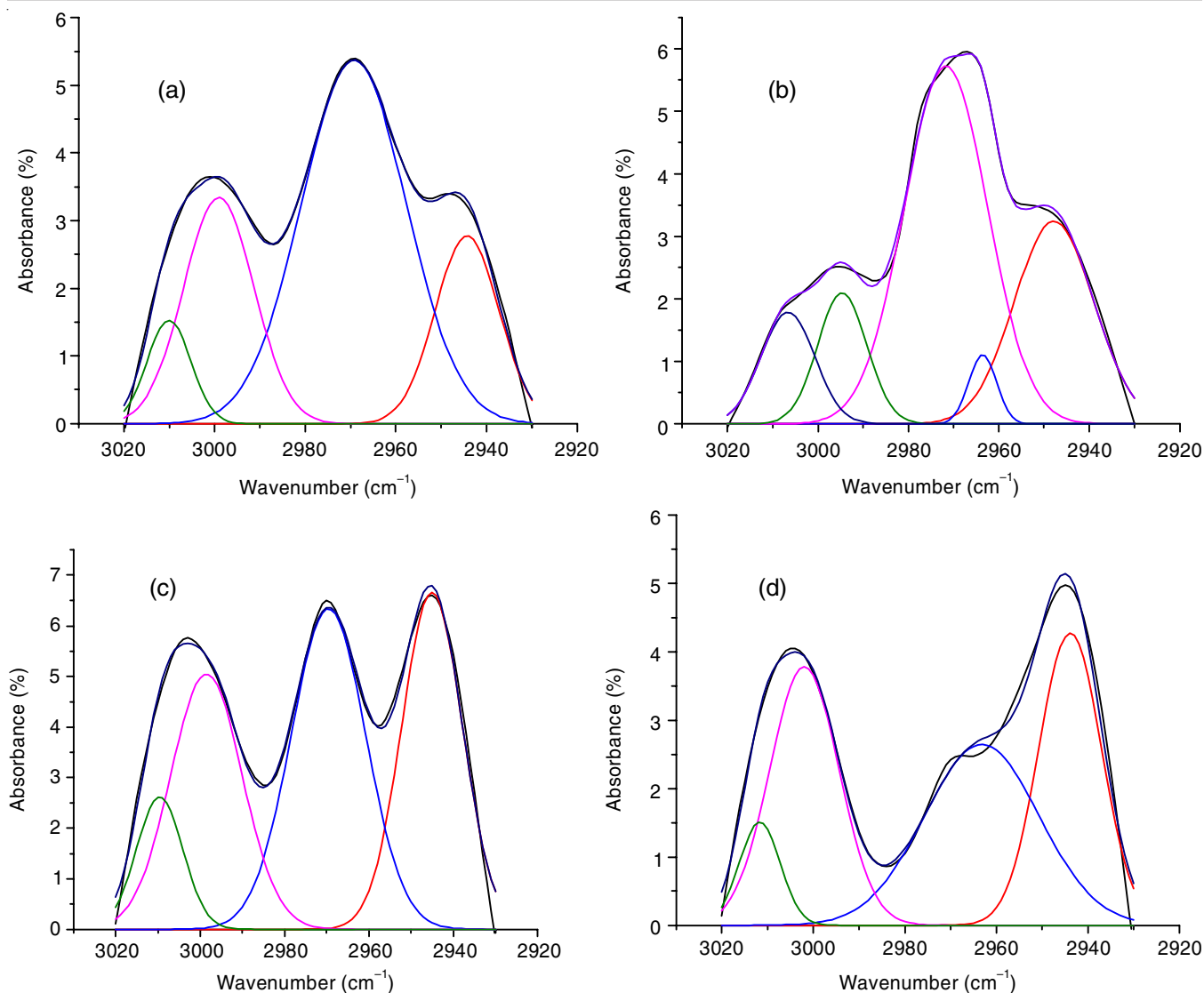


Fig. 3. Deconvoluted peaks in the (C–H) region of the binary solutions (a) 1:2 (ACT:AN), (b) 1:3 (ACT:AN), (c) 2:1 (ACT:AN) and (d) 3:1 (ACT:AN)

is weakly associated dimer and arrived the dimer peak for $\nu(\text{C}\equiv\text{N})$, whose magnitude is slightly greater than the monomer. But experimentally a single peak has been obtained for $\nu(\text{C}\equiv\text{N})$ band in this work. The peak assignments were made based on the earlier work [29–31] and all the wavenumbers are almost identical.

Jamroz *et al.* [39] reported two bands 2263 and 2267 cm^{-1} for $\nu(\text{C}\equiv\text{N})$ in the CD_3CN molecules and assigned to free and hydrogen-bonded ($\text{C}\equiv\text{N}$). According to Takamuku *et al.* [32] who have studied the acetonitrile-water binary mixtures by X-ray diffraction and IR spectroscopy, acquired two bands at 2254 and 2259 cm^{-1} for $\text{C}\equiv\text{N}$ and assigned the former one to monomer and later to dimer. In this work, it can be noticed that the observed value is 2254.3 cm^{-1} and could be interpreted as the free $\text{C}\equiv\text{N}$ peak. It could be revealed that the monomer molecules are dominant in AN in its pure form.

The $\nu(\text{C}\equiv\text{N})$ stretching mode was the base of the formation of hydrogen bond between AN and ACT molecules. The $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_3)$ bands of AN have red shifted in all the solutions

from their corresponding values in their pure form, except $\nu_{\text{as}}(\text{CH}_3)$ in the 1:3 solution in which very weak blue shift have occurred. The red shifts in the C–H region of AN could be inferred as the formation of intermolecular hydrogen bond between the ACT and AN molecules through $(\text{AN})\text{C}-\text{H}\dots\text{O}=\text{C}(\text{ACT})$ H-bond interaction. If the $\text{C}\equiv\text{N}$ band involved in the formation of H-bond between the ACT and AN molecules, the bond could have shifted to either blue or red. Instead, the $\nu(\text{C}\equiv\text{N})$ band is unaltered/not affected in 1:2, 2:1 and 3:1 solutions and very feeble blue shift has been observed in the 1:3 binary solution. Though the magnitude of blue shift is very less (0.3 cm^{-1}), it has some significance and insisted the presence of dimeric structures. The null shift of $\nu(\text{C}\equiv\text{N})$ could be reported as the resultant balanced effect of both dissociation/association process of AN molecules in the ACT environment.

Conclusion

FTIR spectroscopic studies have been carried out on the pure acetonitrile (AN), pure acetone (ACT) and the binary

solutions of (AN:ACT) at various mole ratios. Analysis of the results shows that (i) neat AN is a mixture of monomers and weakly bound dimers; (ii) neat ACT is a combination of monomer, dimer and trimer molecules; (iii) the ACT is self-associated through (ACT)C-H...O=C(ACT) homointeraction; and (iv) the H bonds are formed between the AN and ACT molecules through the non-classical H-bond interactions (ACT)C-H...N≡C(ACT) and (AN)C-H...O=C(ACT).

CONFLICT OF INTEREST

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

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