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RESEARCH ARTICLE

MOLECULAR SPECTROSCOPY CHARACTERIZATION OF BINARY LIQUID MIXTURES USING ATTENUATED TOTAL REFLECTANCE-FOURIER TRANSFORMS INFRARED APPROACH.

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Abstract

The spectrometry properties are important in understanding the molecular interaction between unlike molecules in binary liquid mixtures. The spectrometry characterizations of individual components and binary mixtures of MTBE, methanol, DIPE and NMA were succinctly investigated in this study. The interaction between MTBE and other components such as DIPE, methanol and NMA can be observed mainly through interaction between the C-O-C groups of MTBE and the functional groups of the other components. These interactions can either be through the hydrogen bonding or the formation of complexes. As such, some of the functional groups of interest in the components studied herein include C-O-C, -OH, C-H, C-O and N-H groups. All these indicate that intermolecular interaction between MTBE and methanol is more evident in the binary mixture containing 70 % MTBE and 30 % methanol, compared to the binary mixture containing 30 % MTBE + 70 % methanol. Moreover, the results of the interaction between MTBE and DIPE indicated that there is no intermolecular interaction between them. However, the interaction between MTBE and NMA showed that most of these peaks are slightly shifted in the spectrum of the binary mixture containing 70 % MTBE and 30 % which indicated a more effective molecular interaction between MTBE and NMA are more effective at higher MTBE content rather than lower MTBE content.

Introduction:-

The thermo-physical and spectroscopic properties are the major source of information in the for the characterization of interactions between the binary liquid mixtures. The properties are important attributes of the inherent observed changes to the appearance of the hydrogen bond network. The use of organic solvents together with other hydrocarbon chain structures helps in the provision of dual characteristics comprising of polar and non-polar properties. This is partly due to the presence of the –O– and –OH groups in the same molecule. Take, for instance, the structure of NMA is of great interest as it is related to many structural problems in molecular biology. It is used as a latent and coupling solvent and is also used as an intermediate for dyes, agrochemicals and other organic products manufacturing. NMA is a principal component of monomethylaniline, an antiknock agent, used to increase the octane number [1]. The tert-Butyl methyl ether (MTBE) on the other hand is generally considered to

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be resistant to chemical transformation in aqueous solution. Blanco et al. [2] studied on branched ethers and lower alcohols which can be used to improve its performance. They were the first to produce a systematic spectrometry properties study for the mixtures of ether and alcohol to improve the performance of binary mixtures. They have reported on excess volumes of binary mixtures formed by methanol, ethanol, propan-2- ol, diisopropyl ether (DIPE), methyl tert-butyl ether (MTBE) and 2, 2, 4-trimethylpentane.

Therefore, the measurement of spectrometry property is very important in the fundamental understanding of the nature of interactions between unlike molecules. It has been a qualitative and quantitative way to predict the deviation from ideal behaviour of liquid binary mixtures compared to experimental data. From a more fundamental point of view, this study succinctly elucidated the complex molecular interactions and mechanisms of the solution in a binary mixture of MTBE, methanol, DIPE and NMA using attenuated total reflectance-Fourier transform Infrared (ATR-FTIR) spectroscopy characterization technique.

Materials and methods:-

Characterization Technique

The total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was carried to study the functional group's characteristics in the binary mixtures using a Thermo Scientific Nicolet Spectrometer (iS5 iD7 ATR, Germany) (Figure 1). The instrument is equipped with OMNIC software was employed in the spectrometry analysis [3]. The peak intensity and wavelength for the binary mixtures and their respective pure components were studied to validate for any presence of molecular interaction. The analysis was executed using the conventional KBr standard procedure with wavenumber ranging from 4000-500 cm^{-1}. Under this study, the spectrum of the observed bond and associated group frequencies were compared with the table of expected absorption bands [4].

Figure 1:-Thermo Scientific Nicolet iS50 FTIR Spectrometer

Results and discussion:-

Molecular Spectroscopy of the Binary Liquid Mixture

The ATR-FTIR spectra of ATR-FTIR spectra of MTBE, methanol, DIPE and NMA pure components elucidated and provided useful information about the sites for potential chemical bonding between two or more of the components (Figure 2- Figure 5). It is pertinent to note that the interaction of hydrogen (H) bond is of paramount importance in the structural understanding of the intermolecular interactions within the binary mixtures. However, each bond within a molecule has its own peculiar frequency at which it vibrates as a result of changes in dipole moment as reported by Silverstein and Bassler, [5]. Hence, the interaction between binary mixtures of MTBE/NMA can be identified from the shifting of bond attributes which could be either an appearance of new bonds or disappearance. This provides a good justification for molecular interactions between the components of mixtures as reported in the literature [6].

Fourier Transforms Infrared Spectroscopy (ATR-FTIR) of MTBE - Methanol Binary Mixture

Moreover, binary mixtures can lead to the manifestation of self-induced interactive behaviour in some of the molecules of the components which make up the mixture. For example, if MTBE and methanol are mixed, this can induce self-association behaviour in the methanol molecules and this can facilitate interactions between dissimilar molecules. The ATR-FTIR spectra of the pure MTBE and methanol are included in Figure 2 (a) and (b) for ease of comparison. The ATR-FTIR spectra of the binary mixtures containing MTBE and methanol in the ratio 3:7 and 7:3 for MTBE and methanol respectively are illustrated in Figure 2 (c) and (d). Notably, the –OH peak which appears at 3318 cm^{-1} in the spectrum of pure methanol, was shifted to a higher wavelength 3320 cm^{-1} in the binary mixture containing 30 % MTBE and 70 % methanol. This was further shifted to a higher wavelength of 3356 cm^{-1} in the binary mixture containing 70 % MTBE and 30 % methanol.

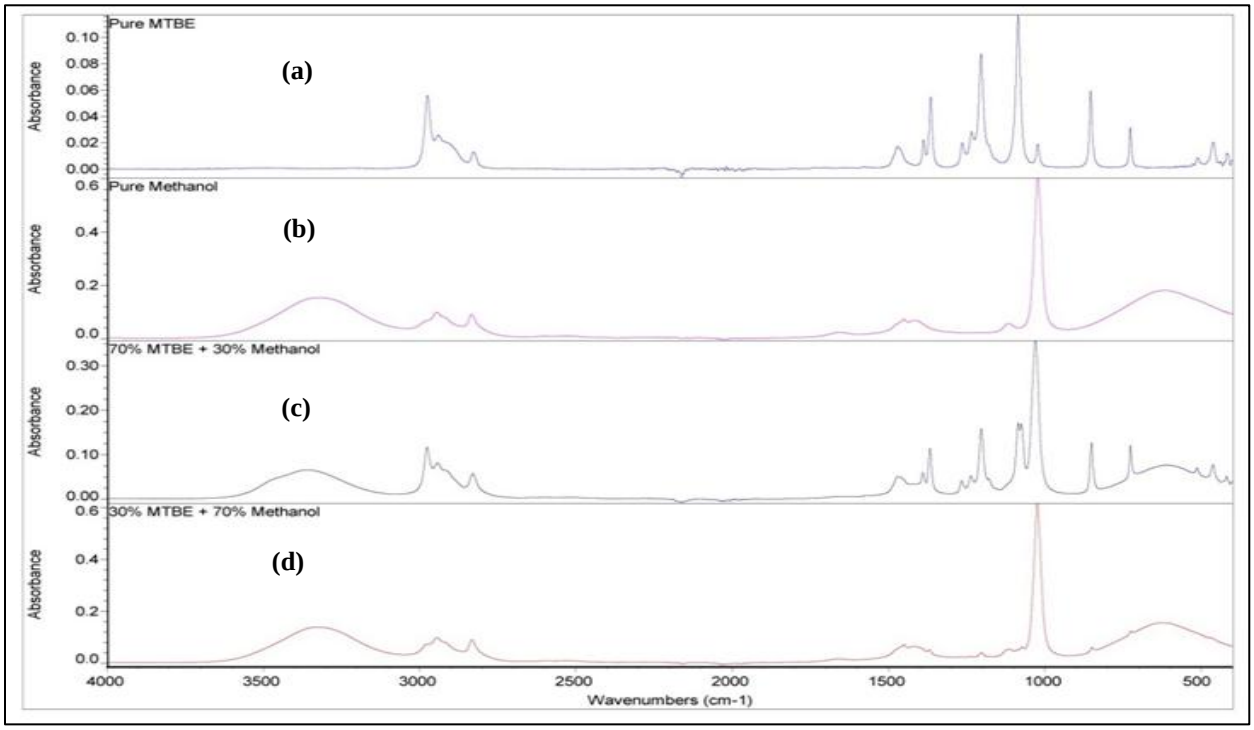

Figure 2:-FTIR spectrum (a) Pure MTBE (b) Pure methanol (c) 70 % MTBE with 30 % Methanol (d) 30 % MTBE with 70 % Methanol

Some of the notable peaks are summarized in Table 1. The broad peak at 3100-3400 cm^{-1} indicates characteristic stretching vibration of –OH groups (AbdErahman et al., 2018). The peaks around 2800-3000 cm^{-1} represent the vibrational stretching from C-H groups of methyl and methylene components [7]. The other important functional groups are summarized in Table 4.20. This includes the C-O symmetric and asymmetric. This is an indication of the molecular interaction between MTBE and methanol [8]. The higher wavelength of –OH group in the mixture containing 70 % MTBE suggests that intermolecular interaction is more pronounced at lower methanol content in the binary mixture compared to larger methanol content. Other notable evidence for intermolecular interaction includes the higher intensity of the C-H stretching vibration around 2900 cm^{-1}, the C-O symmetric and asymmetric stretching as well as the C-H and –OH bending peaks as illustrated in Table 1. All these indicate that intermolecular interaction between MTBE and methanol is more evident in the binary mixture containing 70 % MTBE and 30 % methanol, compared to the binary mixture containing 30 % MTBE + 70 % methanol.

Table 1:- Summary of ATR-FTIR functional groups of MTBE - methanol binary mixture

The position of the band (cm^{-1})		
30% MTBE + 70% Methanol	70% MTBE + 30% Methanol	Functional group attributes
3320	3356	-OH stretching
2943, 2831	2975, 2828	C-H stretching vibration
1448	1469, 1388, 1365	C-H bending

	1264, 1234, 1201	C-O-C asymmetric stretching
1022	1083, 1073, 1028	C-O-C symmetric stretching
	848, 723	C-H bending
624	609, 459	-OH bending

Fourier Transforms Infrared Spectroscopy (ATR-FTIR) of MTBE - DIPE Binary Mixture

The ATR-FTIR spectra of individual components and binary mixtures containing MTBE and DIPE in the ratio 3:7 and 7:3 are illustrated in Figure 3 (a), (b), (c) and (d). Most of the functional groups presented in individual components of the binary mixture are also evident in the spectrum of the binary mixture regardless of the percentage composition.

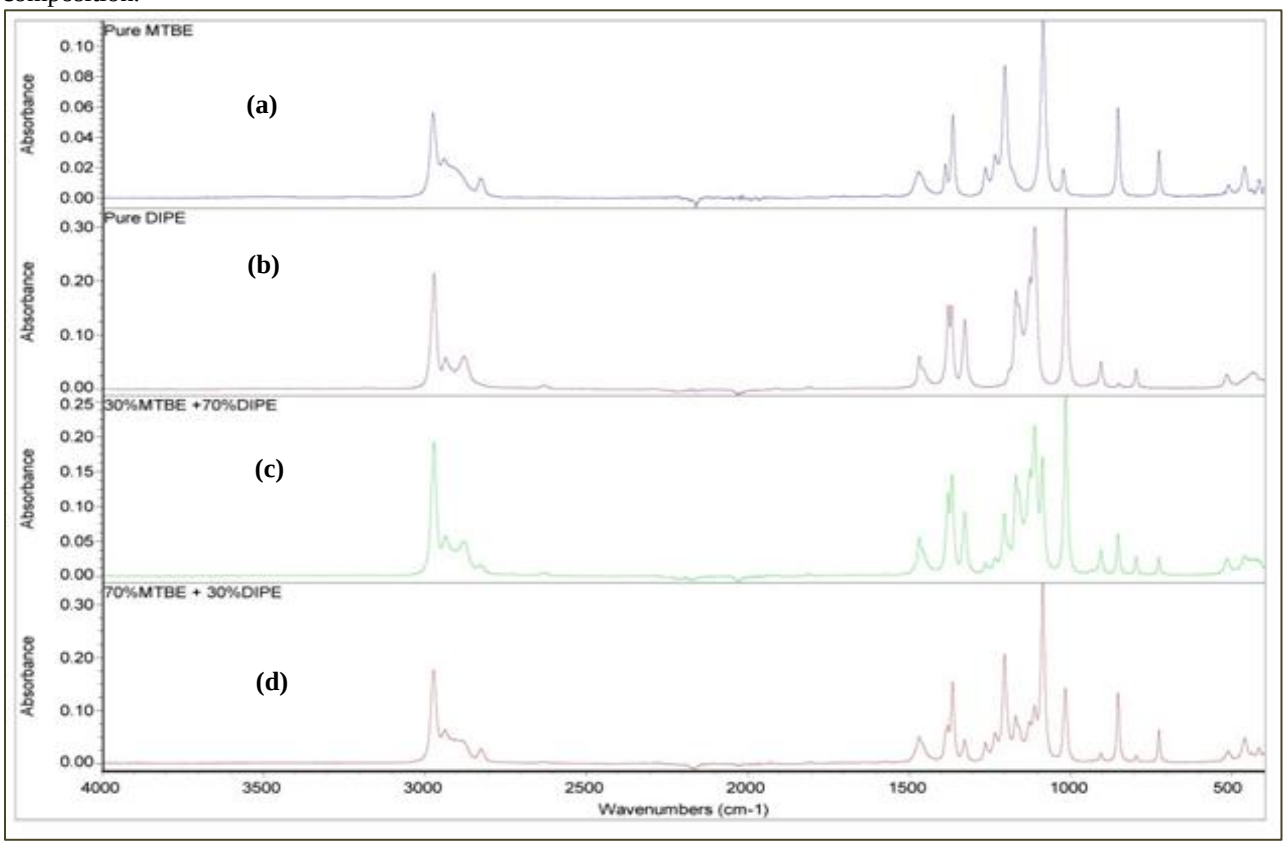

Figure 3:-FTIR spectrum (a) Pure MTBE (b) Pure DIPE (c) 30 % MTBE with 70 % DIPE (d) 70 % MTBE with 30 % DIPE

In Table 2, it can be inferred that intermolecular interaction did occur between MTBE and DIPE. However, the variation in the percentage composition of the individual components does not seem to significantly affect the spectrum of the binary mixture. Hence, this suggests that the intermolecular interaction between MTBE and DIPE is less dependent on the amount of DIPE present in the binary mixture.

Table 2:- Summary of ATR-FTIR functional groups of MTBE - DIPE binary mixture

The position of the band (cm^{-1})		
30% MTBE + 70% DIPE	70% MTBE + 30% DIPE	Functional group attributes
2971, 2936, 2879	2972, 2937, 2827	C-H stretching vibration
1467	1467	C-C asymmetric stretching
1373, 1366	1364	C-H symmetric deformation
1326	1327	C-H bending
1203, 1167, 1124, 1109, 1085, 1013, 904	1262, 1232, 1202, 1168, 1109, 1084, 1014, 904	C-O-C asymmetric stretching
851, 795, 724	851, 795, 724	C-H bending

512, 459	509, 459, 413	-OH bending

Fourier Transforms Infrared Spectroscopy (ATR-FTIR) of MTBE - NMA Binary Mixture

The ATR-FTIR spectra of the individual components (MTBE and NMA) are also illustrated in Figure 4 (a) and (b). Whereas the binary mixtures containing MTBE and NMA were in the ratio of 3:7 and 7:3, respectively are illustrated in Figure 4 (c) and (d).

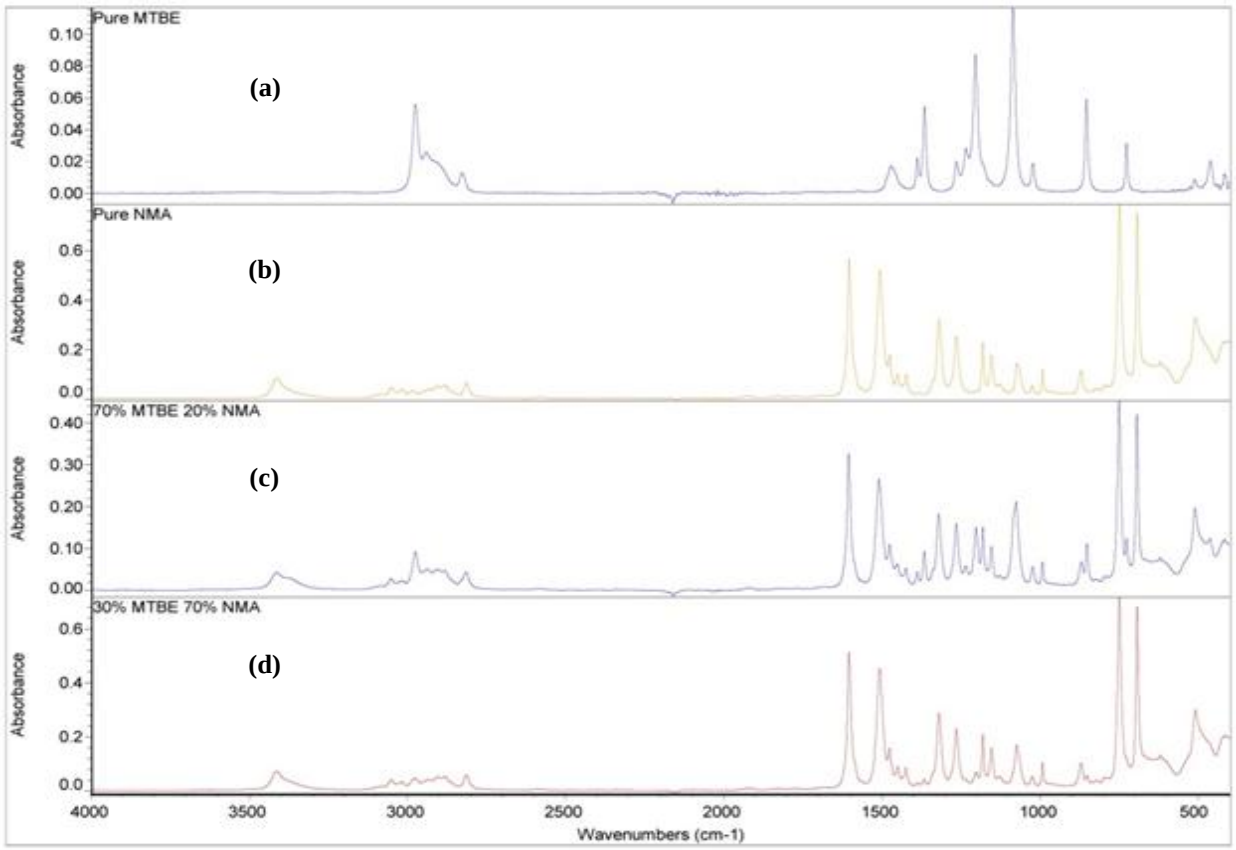

Figure 4:-FTIR spectrum of (a) Pure MTBE (b) Pure NMA (c) 70 % MTBE with 30 % NMA (d) 30 % MTBE with 70 % NMA

Based on the analysis of the spectra, the conspicuous peaks are presented in Table 3, with their representations. Some of the important peaks include the peak at 3412 cm^{-1} which is a characteristic N-H stretching vibration [1] and 1505 cm^{-1} which are an attribute of N-H bending vibration, 2879 cm^{-1}, and 2812 cm^{-1} which represents the vibrational stretching of C-H groups. Other important peaks include the C-O-C peaks emanating from MTBE among others. The result obtained showed that the addition of NMA to MTBE influences the C-H vibrations, N-H stretching, C-O-C asymmetric is stretching and N-H bending. These indicate possible molecular interaction in the binary mixture. However, it is worthy to note that at 30 % MTBE, there seems to be less interaction between MTBE and NMA. For instance, most of the peaks in the spectrum of pure NMA such as at 3411 cm^{-1}, 2897 cm^{-1}, 2812 cm^{-1}, 1602 cm^{-1} and 1505 cm^{-1} remained unchanged in the spectrum of the binary mixture containing 30 % MTBE and 70 % NMA. However, most of these peaks can be seen to be slightly shifted in the spectrum of the binary mixture containing 70 % MTBE and 30 % NMA. Hence, it can be inferred that molecular interaction between MTBE and NMA are more effective at higher MTBE content rather than lower MTBE content.

Table 3:- Summary of ATR-FTIR functional groups of MTBE - NMA binary mixture

The position of the band (cm^{-1})		
30% MTBE + 70% NMA	70% MTBE + 30% NMA	Functional group attributes
3412	3413	N-H stretching

2879, 2812	2974, 2814	C-H stretching
1602	1603	C-O stretching
1505	1507	N-H bending
1473, 1448, 1421	1422, 1363	C-H bending
1317, 1262	1318, 1263, 1200	C-O-C asymmetric stretching
1179, 1151, 1072, 1022, 990	1179, 1152, 1074, 1021, 990	C-O stretching
868, 747, 691	849, 747, 691	C-H bending

Conclusions:-

In this study, the attenuated total reflectance-Fourier transform Infrared (ATR-FTIR) spectroscopy characterization technique was employed to validate the presence of molecular interaction in the binary mixtures of MBTE and methanol, MTBE and DIPE. The ATR-FTIR of the binary mixtures containing MTBE with methanol, DIPE and NMA in the ratio 3:7 and 7:3. The observed that intermolecular interaction between MTBE with methanol and NMA is more evident in the binary mixture containing 70 % MTBE with 30 % methanol and 30% NMA, compared to the binary mixture containing 30 % MTBE + 70 % methanol and 30 % MTBE + 70 % NMA. Whereas the variation in percentage composition of MTBE with DIPE of the individual components does not seem to significantly affect the spectrum of the binary mixture. Hence, this suggests that the intermolecular interaction between MTBE and DIPE is less dependent on the amount of DIPE present in the binary mixture.

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