

Physico-Chemical and FTIR Studies on Tri-ethylene Glycol Monomethyl Ether in Water Using Density Functional Theory

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Abstract: The impact of simultaneous presence of ethereal oxygen (–O–) and alcoholic (OH) groups on the excess thermodynamic properties and the corresponding behaviour of alkoxy alkanol in binary mixtures has great relevance in understanding the nature of interactions patterns among molecules. Density functional theory (DFT) has progressively developed as a foremost method for modelling and simulation of chemical systems. The objective of the present work is to investigate how the methods based on density functional theory (DFT) can predict structural and spectroscopic properties. The quantum chemical calculations have been performed to study the Geometry optimization, bond length, bond angles and hydrogen bond interactions between Tri-ethylene glycol monomethyl ether (TEGMME) & water using Density Functional Theory (DFT) at B3LYP/6-311G, g(d,p). The exothermic formation energy (ΔE) for binary mixture of TEGMME) & water calculated is $-0.012632 \text{ kcal.mol}^{-1}$. The IR spectra calculated using SCF, GIAO approach under DFT calculations predict that stretching vibrational band of hydroxyl inside the TEGMME shifts to higher frequency and bending vibrational band of water shifts to lower frequency in the binary mixtures. The result shows a strong molecular interaction between tri-ethylene glycol monomethyl ether and water molecule, which is influenced not only by the principle hydrogen bond of the. O---H with the proton acceptor, but also by additional hydrogen bonds of C---H moiety with alcoholic oxygen as a proton acceptor. Toward that end, DFT provides only a useful methodology.

Keywords: Alkoxyalkanol, Excess Molar Volume, Bond Length, Bond Angle, FTIR Spectra, Density Functional Theory

1. Introduction

In continuation of our research work on thermodynamic, spectroscopic, acoustic and transport properties of liquid mixtures containing straight chain or branched chain alkoxyethanols/polyethers with organic solvents [1–6], in the present study we have focused our attention on optimized geometry using DFT with hybrid B3LYP programme at basis sets 6-311G+ g(d,p). Glycol ethers are non-ionic amphiphiles behave as surfactants being used in industrial applications. Moreover, glycol ethers in combination with alcohol & amides provides versatile solvency characteristics behaviour with both polar and non-polar molecules [7]. The solvent–

solvent, solute-solute, solute-solvent molecular interactions are significant properties which pave the way to understand structural changes and type of patterns of molecular interaction behavior [8, 9]. Density Functional Theory (DFT) has progressively been emerged as a reliable tool for modelling and simulation of liquid mixtures systems and joining hands with experimental chemists [10-13]. The Density Functional Theory (DFT) calculations are being used to study pharmaceutical molecules, protein folding kinetics, complexation equilibria, binding constant etc. [14-16].

In Density Functional Theory (DFT) approach the electronic structure is evaluated based on potential acting on electron which is considered as sum of external potentials

determined exclusively by structure of the system and effective potential resulting from inter-electronic interactions of valence electrons [17]. In quantum chemistry computations basis sets, such as, plane-wave has great relevance in calculations involving periodic boundary conditions that leads to converge in a smooth, monotonic manner to the targeted wavefunction [18]. Chelikowsky et.al [19] has quantified that quantum-based forces are particularly important as they directly contain the chemical nature of the forces present without the use of any adjustable parameters and further cited that the real-space mesh approach allows the use of state-of-the-art algorithms, which utilize sparse-matrix linear algebra for massively parallelized solutions of large systems

The Density Functional Theory (DFT) computational methods have paved the way to overcome the errors arises due to electron correlation and anharmonicity of the vibrations in interpreting the experimental conclusions [20-22].

The Density Functional Theory (DFT) applications based on Kohn–Sham theory is formally considered exact one, but it involves a functional parameter called exchange–correlation functional (χ_c). Unfortunately, this exact exchange–correlation functional is unknown, making it essential to pursue the quest of finding more accurate and reliable functionals [23-24]. One traditional approach to solving the Kohn–Sham equation is to expand the wave functions in a basis, e.g., plane waves, or linear combinations of atomic-like orbitals, e.g. Gaussians. The combination of a plane-waves basis and pseudopotentials is one of the most popular methods for determining the electronic and structural properties of materials owing to its ease of implementation and the simplicity of the method. Another approach to the problem is to use real-space methods [25–28]. A real-space mesh approach to this problem is frequently the one of choice.

This approach allows the use of state-of-the-art algorithms, which utilize sparse-matrix linear algebra for massively parallelized solutions of large systems which are accurate and well suited for modern, massively parallel computing resources [29-30]. In the present study we have used Density Functional Theory B3LYP programme as basis sets 6-311G+g (d, p) on binary mixtures of Tri-ethylene Glycol monomethyl ether with water to generate their optimized geometry and IR spectral parameters to confirm the existence of hydrogen bonding or electron donor/ acceptor type interactions.

2. Results and Discussion

2.1. Physico-Chemical Properties

The excess molar volumes V^E of the binary liquid mixtures of Triethylene glycol monomethyl ether with water at corresponding mole fraction are calculated from our measured densities at 298.15, 308.15, and 318.15 K reported in our earlier study [31] following the equation:

$$\rho = (x_1 M_1 + x_2 M_2) / (V^E + x_1 V^{\circ}_1 + x_2 V^{\circ}_2) \quad (1)$$

And deviation in viscosity $\Delta \ln \eta$ have been determined from viscosities data measured at 298.15, 308.15, and 318.15 K reported in our earlier study [31]. Moreover, the fitting parameters a_i of The Redlich Kister polynomial [32] have

$$Y(x) = x_1 x_2 \sum_{i=1}^n a_i (x_1 - x_2)^{i-1} \quad (2)$$

been calculated for V^E , $\Delta \ln \eta$, R-Square values and ANOVA test have been calculated using the OriginPro-2023b software for Graphing and Analysis [33]. The calculated values of the parameters are reported in Table 1.

Table 1. Values of Fitting Parameters, Standard Deviation σ , Adj. R-Square and ANOVA Test (Prob>F) for the Various Mixtures.

System	Prop.	Temp. K	Fitting Parameters						Adj. R-Square	ANOVA Test
			a_0	a_1	a_2	a_3	a_4	σ	R-Square	Prob>F*
TEGMME + H ₂ O	V_m^E (cm ³ . mole ⁻¹)	298.15	-4.0755	2.6786	-3.0324	2.6582	-1.5866	0.015	0.9991	2.268E-13
		308.15	-3.8794	2.6317	-3.5750	2.2030		0.014	0.9987	2.220E-16
		318.15	-3.7720	2.7016	-3.3452	1.5833		0.016	0.9982	9.992E-16
	$\Delta \ln \eta$ (mPa.s)	298.15	17.2600	-17.9174	19.0471	-9.1705	12.3640	0.065	0.9993	8.770E-15
		308.15	12.1875	-13.7247	9.6969			0.072	0.9984	0
		318.15	8.6138	-9.3890	6.5767			0.052	0.9985	0

*Confidence Level 95%

2.2. Calculation Using Density Function Theory

The density functional theory calculations have been worked out at B3LYP using basic set 6-311 G(d,p) to generate the optimized geometry of Tri-ethylene glycol mono methyl ether as monomer, dimer (under self-association) and in binary mixture of Tri-ethylene glycol mono methyl ether with water. The optimized geometry of monomeric form of TEGMME consisting of 27 atoms has been presented in Figure 1 that of dimeric form with 54 atoms in Figure 2 while

Figure 3 shows the optimized geometry of binary mixture of TEGMME + water. The total energy calculated at single point of potential surface, RMS Gradient, polarizability, and heat capacity are reported in Table 2. The total energies for one H₂O and a H₂O dimer are -76.447448 and -152.896075 Hartree, respectively. The takeaway message is that in the following reactions,



$\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_2$ (ΔE) -577.380906 Hartree

$\text{H}_2\text{O} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} \cdots$
 $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (ΔE) - 0.001179 Hartree

The exothermic formation energy (ΔE) calculated for dimer of $(\text{H}_2\text{O})_2$ & $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})_2$ is -0.001179 Hartree and -577.380906 Hartree respectively. while for the binary mixture of TEGMME & water it is -0.012632 Hartree. The frequency calculation reveals 75 active fundamental modes of vibration in monomeric, 156 active fundamental modes of vibration in dimeric state of TEGMME. However, 84 active fundamental modes of vibration are observed in binary mixture of TEGMME + water which agrees with the reported formula $(3N-6)$ for numbers of modes of vibrations in a non-linear molecule containing N atoms [34]. The calculated bond length and bond angles have been reported in Table 3. The observed average divergence in bond lengths is 0.001 Å to 0.003 Å while the average change in bond angle is 0.5 degree. These deviations may be attributed due to intramolecular hydrogen bonding interactions and interstitial accommodation resulting due to breaking of self-association

in the Tri-ethylene glycol monomethyl ether in presence of water molecule.

2.3. FTIR Spectral Properties

The calculation of the vibrational frequencies in IR-spectrum of monomer and dimeric forms of Tri-ethylene glycol monomethyl ether, water and their mixtures have been worked out using DFT under B3LYP function with 6-311+G(d,p) basis set. Absorption of IR frequency can occur only if the dipole moment of the molecule is different in two vibration levels. The calculated values of frequency for C – H, O – H, C – C and O – C stretching and wagging of alkyl chain in the monomer and binary mixture of Tri-ethylene glycol monomethyl ether and water are reported Table 4. It has been reported in literature [35] that wagging of alkyl chain generally contributes to the intermolecular interactions of a binary mixture rather than the translational motion of the molecules. The stretching frequency of chemical bond depend upon the bond strength and reduced masses of the atom forming bond. The factors increasing the bond strength will enhance the stretching frequency. Moreover, the increase in reduced mass will decrease the stretching frequency.

Table 2. The parameters calculated using DFT B3LYP/6-311 G(d,p).

System	Energy (Hartree)	RMS Gradient (Hartree Bohr)	Polarizability (a u.)	Heat Capacity (C_v) Cal/mol /K
TEGMME (1)	-577.37941	6.0728E-5	99.858	47.6
H_2O (2)	-76.447448	1.2813E-4	5.9153333	6.008
TEGMME (Dimer)	-1154.760316	1.0E-6		
Water dimer	-152.896075	0.000004		15.908
TEGMME(1)+ H_2O (2)	-653.83949	1.24707E-6	107.0308	57.707

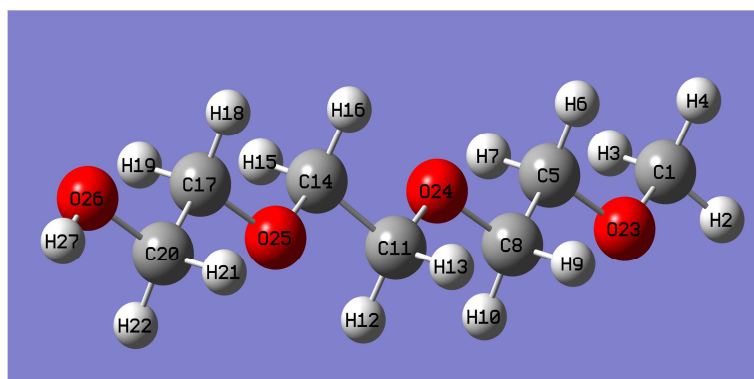


Figure 1. Optimized geometry of TEGMME calculated using DFT, B3LYP/6-311 G(d,p).

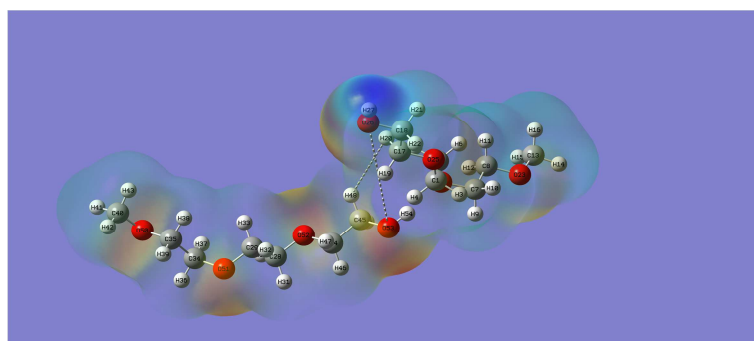


Figure 2. Optimized geometry of Dimer of TEGMME calculated using DFT, B3LYP/6-311 G(d,p).

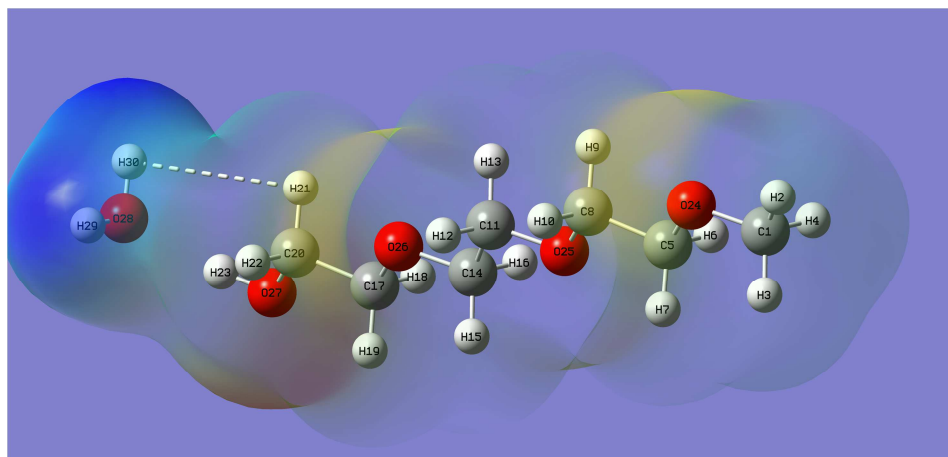


Figure 3. Optimized geometry of Binary Mixture of TEGMME + water. Dotted lines showing intermolecular hydrogen bonding.

Table 3. Bond length(\AA) and bond angle calculated using DFT Gauss view at B3LYP/6-311 G(d,p).

Bond length \AA			Bond Angle degree		
Atoms	Calculated at using DFT at B3LYP/6-311 G(d,p)		Bond Angles in between the Atoms	Calculated using DFT at B3LYP/6-311 G(d,p)	
	TEGMME (Monomer)	TEGMME+ Water		TEGMME (Monomer)	TEGMME+ Water
C ₁ – H ₂	1.09039	1.09042	H ₂ -C ₁ -H ₃	108.95	108.94
C ₁ – H ₃	1.09970	1.09968	H ₂ -C ₁ -H ₄	108.95	108.94
C ₁ – H ₄	1.09970	1.09968	H ₃ -C ₁ -H ₄	108.44	108.44
C ₁ – O ₂₄	1.41248	1.41237	H ₂ -C ₁ -O ₂₄	107.23	107.25
C ₅ – O ₂₄	1.41391	1.41412	H ₃ -C ₁ -O ₂₄	111.59	111.60
C ₅ – H ₅	1.10017	1.10004	H ₄ -C ₁ -O ₂₄	111.59	111.60
C ₅ – H ₇	1.10017	1.10003	O ₂₄ -C ₅ -H ₆	111.12	111.11
C ₅ – H ₈	1.51806	1.51841	O ₂₄ -C ₅ -H ₇	111.12	111.11
C ₅ – H ₉	1.09930	1.09933	H ₆ -C ₅ -C ₈	109.64	109.63
C ₅ – H ₁₀	1.09930	1.09933	H ₇ -C ₅ -C ₈	109.64	109.63
C ₅ – O ₂₅	1.41574	1.41511	H ₉ -C ₈ -C ₅	109.67	109.64
C ₁₁ – O ₂₅	1.41530	1.41563	H ₁₀ -C ₈ -C ₅	109.67	109.64
C ₁₁ – H ₁₂	1.09943	1.09942	C ₁ -O ₂₄ -C ₅	112.96	112.96
C ₁₁ – H ₁₃	1.09943	1.09942	C ₅ -C ₈ -O ₂₅	107.62	107.63
C ₁₁ – H ₁₄	1.51822	1.51855	H ₉ -C ₈ -O ₂₅	110.10	111.02
C ₁₄ – H ₁₅	1.09942	1.09960	H ₁₀ -C ₈ -O ₂₅	110.10	111.02
C ₁₄ – H ₁₆	1.09942	1.09960	C ₈ -O ₂₅ -C ₁₁	113.42	113.42
C ₁₄ – O ₂₆	1.41511	1.41358	O ₂₅ -C ₁₁ -H ₁₂	111.00	110.96
C ₁₇ – O ₂₆	1.41586	1.41800	O ₂₅ -C ₁₁ -H ₁₃	111.00	110.96
C ₁₇ – H ₁₈	1.09942	1.09926	O ₂₅ -C ₁₁ -C ₁₄	107.58	107.71
C ₁₇ – H ₁₉	1.09942	1.09926	H ₁₂ -C ₁₁ -C ₁₄	109.69	109.66
C ₁₇ – C ₂₀	1.51740	1.51787	H ₁₃ -C ₁₁ -C ₁₄	109.69	109.66
C ₂₀ – H ₂₁	1.10007	1.10055	C ₁₁ -C ₁₄ -H ₁₅	109.69	109.66
C ₂₀ – H ₂₂	1.10007	1.10055	C ₁₁ -C ₁₄ -H ₁₆	109.69	109.66
C ₂₀ – O ₂₇	1.42397	1.41380	H ₁₅ -C ₁₄ -O ₂₆	111.02	111.10
O ₂₇ – H ₂₃	0.96066	0.96951	H ₁₆ -C ₁₄ -O ₂₆	111.02	111.10
O ₂₈ – H ₂₉	0.95720	0.96253	O ₂₆ -C ₁₇ -H ₁₈	110.99	110.88
O ₂₈ – H ₃₀	0.95720	0.96253	O ₂₆ -C ₁₇ -H ₁₉	110.99	110.88
			O ₂₆ -C ₁₇ -C ₂₀	107.75	108.11
			C ₁₇ -C ₂₀ -H ₂₁	108.99	108.59
			C ₁₇ -C ₂₀ -H ₂₂	108.99	108.59
			C ₁₇ -C ₂₀ -O ₂₇	106.82	107.40
			H ₂₁ -C ₂₀ -O ₂₇	111.89	112.29
			H ₂₂ -C ₂₀ -O ₂₇	111.89	112.29
			C ₂₀ -O ₂₇ -H ₂₃	108.12	107.67
			H ₂₉ -O ₂₈ -H ₃₀	104.50	105.19
			C ₁₁ -C ₁₄ -O ₂₆	107.56	107.52
			C ₁₄ -O ₂₆ -C ₁₇	113.45	113.45

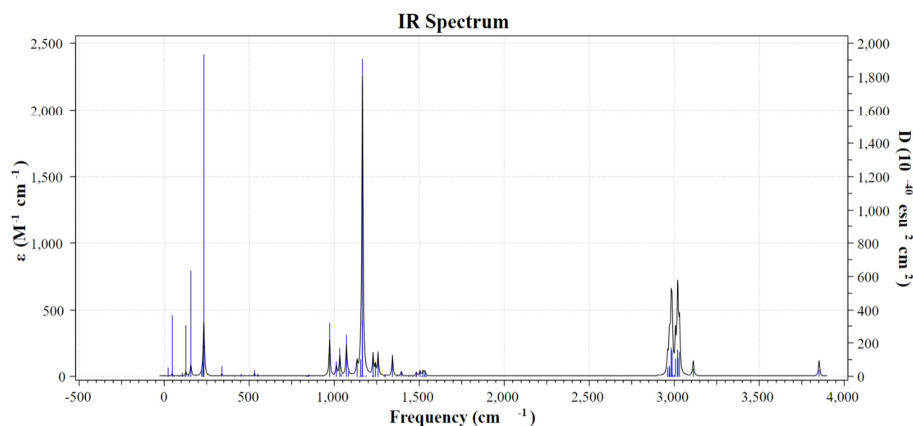


Figure 4. IR spectra of TEGMME in monomeric state using DFT B3LYP/6-311 G(d,p).

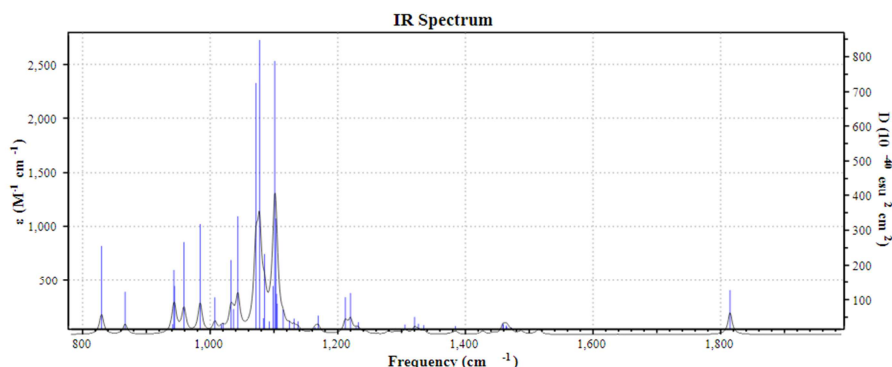


Figure 5. IR spectra of TEGMME in dimeric state using DFT B3LYP/6-311 G(d,p).

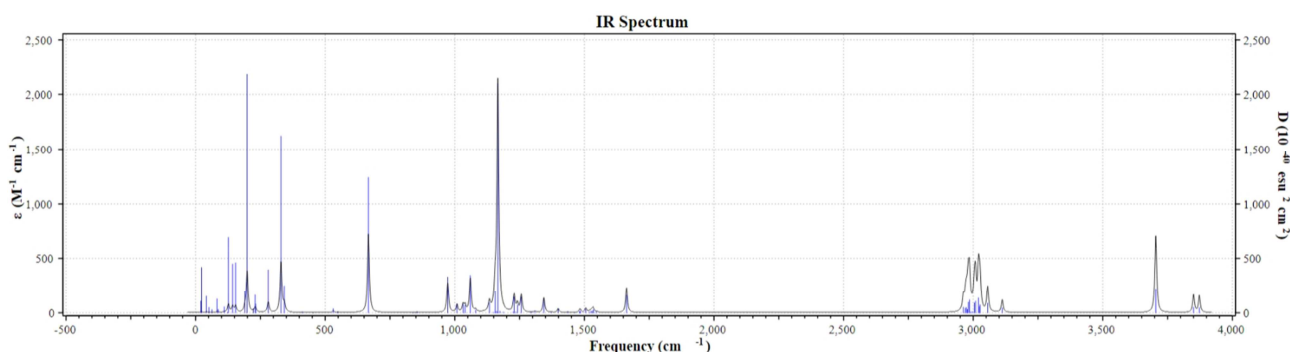


Figure 6. IR spectra of binary mixture of TEGMME + water using DFT B3LYP/6-311 G (d,p).

3. Discussion

The calculated IR spectrum reported in Figures 4-6 forecast that in binary mixture of TEGMME + H₂O stretching vibrational band of hydroxyl O–H is found to shift toward lower frequency by $\Delta\nu = -153.2 \text{ cm}^{-1}$. However, the O–H asymmetric stretching in binary mixture of TEGMME and water shifts toward higher frequency by $\Delta\nu = 237.7 \text{ cm}^{-1}$ which possibly may be due to electronic effects of simultaneous presence of ethereal -O- oxygen and alcoholic OH groups in the same molecule. The conformational behaviour around the C – C bond and C – O bonds in the oxyethylene chain in presence of water suggests the presence of several types of hydrogen bonds between the amphiphile molecule and water [7]. The H-O-H bending vibrational band

of water changes from 1637.92 to 1625.36 cm^{-1} *i. e.* shifts towards lower frequency demonstrate that the interactions result from the variational perty of hydrogen atom in H₂O. Meanwhile, the stretching vibrational band of C-O-C in TEG is found to shift toward lower frequency from $1165.11 - 1157.65 \text{ cm}^{-1}$. The fact that the stretching vibrational band of chain at C₂₀ in TEGMME shifts toward lower frequency (1257.7 cm^{-1} to 1223.84 cm^{-1}) predict that interactions can be related to the oxygen in C-O-C. The calculated optimized geometry and IR data shows that existing interactions between TEGMME and water may be possibly due to (1) hydrogen bonding and interaction of hydrogen atom in H₂O with hydroxyl oxygen atom in TEGMME by cross-linking as the formations of $\text{CH}_2\text{CH}_2\text{OH}\cdots\text{HOH}\cdot$ and $\text{CH}_2\text{CH}_2\text{OH}\cdots(\text{H})\text{OH}\cdot$ and (2) weak hydrogen bonding and interaction of hydrogen atom in water with ether oxygen

atom in TEGMME as the formation of $-\text{CH}_2-\text{CH}_2-\text{O}(\text{CH}_2-\text{CH}_2)\cdots\text{HOH}$.

Table 4. Calculated vibrational frequencies (cm^{-1}) for TEGMME and Binary mixture of TEGMME + Water at B3LYP/6-311+G(d,p).

At Atoms /Group	Bond	Frequency of vibrations of Molecules $\nu \text{ cm}^{-1}$		Change in frequency $\Delta\nu \text{ cm}^{-1}$
		TEGMME	TEGMME + Water	
O – H	$\text{V}_{\text{O-H}}$	3851.9	3698.6	-153.23
		1257.7	1495.4	+237.7
C_1	$\text{V}_{\text{C-H}}$	3111.77	3007.1	-104.67
		3030.79	3017.42	-13.37
$\text{C}_{17}-\text{C}_{20}$	$\text{V}_{\text{C-H}}$	2999.85	2978.2	-21.65
		3021.78	2968.0	-53.78
$\text{C}_{11}-\text{C}_{14}$	$\text{V}_{\text{C-H}}$	2994.19	2991.92	-2.27
		3019.26	2990.45	-28.81
C_5-C_8	$\text{V}_{\text{C-H}}$	2989.62	2961.0	-28.62
		3007.64	3111.34	+ 103.7
C_1 (CH ₃ Group)	$\text{V}_{\text{C-H}}$	2960.7	3007.68	+46.98
		2987.13	2978.20	-8.93
C_{20}	$\text{V}_{\text{C-H}}$	1257.7	1223.84	-33.86
		2960.4	2961.1	+0.7
C_1, C_5	$\text{V}_{\text{C-H}}$	972.95	973.25	+0.30
		1012.15	1013.09	+ 0.94
Chain	$\text{V}_{\text{C-O}}$	1032.58	1048.48	+15.9
		550.52	552.92	+2.4
$\text{C}_{17}-\text{C}_{20}$	$\text{V}_{\text{C-C}}$	3812.75 (sym)	3911.56 (sym)	+98.81
		3909.90 (asym.)	3811.96 (asym)	-97.94
$\text{H}-\text{O}-\text{H}$	$\text{V}_{\text{O-H}}$	1637.92 (bend)	1625.36 (bend)	-12.56

4. Conclusion

In this work, we have critically analysed the experimentally and theoretically calculated results of some thermodynamic properties. Excess molar volume V_m^E is negative and deviation in viscosity $\Delta\ln\eta$ is positive over the whole mole fraction range at all three temperatures indicating existence specific interactions. The observed negative value of V_m^E may be considered as a result of (i) contraction due to specific interactions between TEGMME and the water molecules, and (ii) contraction due to the breakdown of self-association of the components. The calculated FTIR spectra of TEGMME, water and their binary solutions shows blue and red shifts in various bond stretching vibrations. The density functional theory at DFT-B3LYP/6-311+ G(d,p) level is compatible for geometry optimization and spectral characteristics. In conclusions, it is fair to ask whether we are closer to any understanding regarding the proper elucidation of different types of interactions pattern that occur in the molecules of tri-ethylene glycol mono methyl ether.

Conflicts of Interest

The authors declare no conflicts of interest.

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