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THERMODYNAMIC EVALUATIONOF MOLECULAR INTERACTIONS OF BINARY LIQUID MIXTURES OF DIETHYL MALONATE WITH ALKOXYETHANOLS

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ABSTRACT:
At temperatures (303.15, 308.15, 313.15, 318.15) K, the velocity and density of binary mixtures of diethyl malonate with methoxyethanol, ethoxyethanol, and butoxy ethanol were experimentally measured. Through the use of experimental data, several thermodynamic and acoustic characteristics were assessed. Based on the geometric consequences of the mixture's components and dipole-dipole interactions, the results have been addressed.

KEY WORDS: Acoustic Parameters, Dipole-Dipole Interactions.

INTRODUCTION:

Numerous applications of thermodynamic studies exist for comprehend the chemical and physical behavior of liquid mixtures. Study of ultrasonics has long been a topic of considerable interest. This area of the physical sciences has been very important in determining how molecules interact with one another. It may also be used to assess the energy exchange between different degrees of freedom and nonlinear features in binary liquid mixtures.

Diethyl malonate (DEM) is a colourless, aromatic liquid that finds applications in the paint and spice industries, gas chromatography, pharmaceuticals, agrochemical industrial products, fragrance compounds, and the synthesis of vitamin B_1 and B_6 barbiturates.

Alkoxyethanols were thought to be composed of four distinct functional subgroups: the methyl group ($-CH_3$), the methylene groups ($-CH_2$), the ether subgroup ($-CH_2O$), which consists of an oxygen atom and a methylene group, and the 1^0 alcohol subgroup (-OH). Numerous sectors, including the petroleum, cosmetics, textile, dyes, gums, pharmaceutical, and others, have found extensive uses for these solvents [i-iii].

The systems chosen for present study are:
Diethyl malonate (DEM) + 2-methoxyethanol (MOE)
Diethyl malonate (DEM) + 2-ethoxyethanol (EOE)
Diethyl malonate (DEM) + 2-butoxyethanol (BOE)
By comparing the actual data (velocity and density) at 308.15K with those published in the literature, the purity of the selected solvents was determined (Table.1) [iv,v]. The experimental values match published values in the literature quite well.
Thermodynamic and spectral studies of binary liquid mixtures of 2-butoxy ethanol with alcohols in temperature ranges of (293.15–313.15) K were conducted by Gyan Prakash Dubey et al.[vi]. Densities were measured by K. K. Hossein A. Zarei et al. [vii] and thermodynamic characteristics of 2-methoxyethanol plus 1-propanol, 2-propanol, or 1, 2-propandiol) at T = (293.15 to 343.15) at different temperatures Theoretical work on ultrasonic velocities and their use in binary liquid mixes of ethyl benzoate with 2-alkoxyethanols at varying temperatures was done by K. G. Lakshmana Rao et al.[viii]. Theoretical, spectrophotometric, and ultrasonic characteristics of binary liquid mixtures of phenol and alkoxyethanol at various temperatures were assessed by G.R. Satyanarayana et al.[ix,x]. At varying temperatures, Sk. Beebi et al. evaluated molecular interactions in mixes of dimethyl carbonate and n-alkoxyethanol (2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, and 2-butoxyethanol)[xi]. A survey of literature indicates that extensive work has been reported on alkoxyethanols with various organic liquids. Still there is a scope to further extend the study on compounds with combination of other industrially important solvents. Hence, an attempt has been made to study the molecular interactions between DEM and alkoxyethanols.
By measuring the thermodynamic and volumetric properties of the constituents of binary liquid mixtures, such as excess molar volumes, deviations in adiabatic compressibility, excess intermolecular free length, etc., it is possible to predict the relative strength of molecular interactions operating among them.

MATERIALS AND METHODS:
The author used an ultrasonic pulse echo interferometer (MODEL M-81) from Mittal Enterprises in New Delhi to detect velocity during the current experiment. According to Nikamet.al's description[xii], a 10^{-5} m^3 double-arm pycnometer at (303.15, 308.15, 313.15, and 318.15) K is used to measure the density (ρ) of pure liquids and all liquid combinations. For calibration, water with a density of 995.61 kg m^{-3} and conductivity of 303.15 K is utilized. All measurements were made at all temperatures with an accuracy of ±0.01K using a thermostat.With an accuracy of ±0.01 mg, the METTLER TOLEDO (Switzerland make) ABB5-S/F ACT digital balance is used for the task of weighing. Diethyl malonate and alkoxyethanols, including butoxyethanol, ethoxyethanol, and methoxyethanol, which were employed in the current investigation are high-quality experimental materials whose purity was greater than 99%. They were acquired from S.D. Fine Chemicals in India. Table 1 displays the comparison of experimental values with those from the literature at 308.15K.
Table 1 makes clear that there is a high degree of consistency between the reported and experimental values.

RESULTS:
Based on measurements of ultrasonic velocity (U) and density (ρ), the author presents the findings of a study on a binary mixture of diethyl malonate (DEM) with 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE), and 2-butoxyethanol (BOE), in order to analyze the molecular interactions and mixing behavior among the components of mixture by taking into

consideration the effect of composition and temperature. Together with excess molar volumes, deviation in adiabatic compressibility, and excess intermolecular free length, thermodynamic properties such as molar volume, adiabatic compressibility, and intermolecular free length are computed. In order to get the binary coefficients that would be used to assess the standard deviation between the estimated and experimental data, the values were fitted to the Redlich-Kister equation, which is a multi-parametric non-linear regression analysis technique.

Negative trends may be seen in the excess molar volume fluctuation displayed in Figures 1(a), 2(a), and 3 (a). As the mole fraction of DEM increases, the negative value drops until it reaches its lowest value at 0.34 mole fraction, after which it climbs once more. It makes the mixture's volume contraction quite evident. Figures 1(b), 2(b), and 3(b) show the deviation in adiabatic compressibility; at any given concentration, it increases with temperature and reduces with an increase in the mole fraction of DEM. At roughly 0.34 mole fraction of DEM, the negative deviation in adiabatic compressibility reaches its maximum value. According to Figures 1(c), 2(c), and 3(c), the values of L_f^E rise with increasing temperature and decrease with the mole fraction of DEM.

DISCUSSION:

The nature and relative strength of molecular interactions among the constituents of liquid mixtures have been successfully predicted by analyzing their thermodynamic and volumetric properties, such as excess molar volumes, deviation in adiabatic compressibility, excess intermolecular free length etc. Strong interactions between component molecules are indicated by negative deviations in excess molar volumes, excess adiabatic compressibility, and excess intermolecular free length in the systems under investigation.

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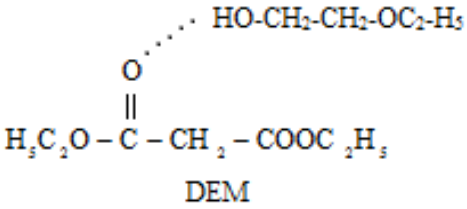
EXCESS MOLAR VOLUME:

In the present investigation for DEM and 2- alkoxyethanols, the results obtained from the experimental methods are depicted in Fig.1(a) (DEM+MOE) Fig.2(a) (DEM+EOE) and in Fig.3(a) (DEM+BOE). The V^E show negative deviations in the entire composition range for all the three systems at all the temperatures



DEM

Hydrogen bonding of DEM and alkoxyethanols

The geometry of the molecules which may favour fitting of small methoxyethanol, ethoxyethanol, butoxyethanol molecules into the voids created by three dimensional hydrogen bonded net work of DEM molecules contributes to the negative V^E values[xiii].

1. The observed negative values of V^Eindicate the specific interaction [xiv] between alkoxyethanol and DEM molecules.
2. The decreasing V^Evalues in all studied mixtures suggest that with increase in carbon chain length of the 2-alkoxyethanol, the effect of formation of hydrogen bonding decreases between unlike molecules [xv,xvi]

DEM +MOE > DEM + EOE > DEM + BOE

DEVIATION IN ADIABATIC COMPRESSIBILITY:

The variations of the deviation in adiabatic compressibilities for the systems (DEM + 2-methoxy ethanol, DEM + 2-ethoxyethanol, DEM + 2-butoxyethanol) are shown in Fig. Fig.1 (b), Fig.2 (b) and in Fig.3 (b) as a function of mole fraction of DEM at (303.15, 308.15, 313.15 and 318.15) K respectively. The deviation in adiabatic compressibility is the difference between the adiabatic compressibility and the total of the fractional contributions of the two liquids. Liquids with varying molecular sizes typically mix with a drop in volume, producing negative $\Delta\beta_{ad}$values, according to Fort and Moore [xvii]. Heavy heteromolecular interaction in the liquid mixes is indicated by a negative excess adiabatic compressibility. For every system examined in this work, the extra adiabatic compressibility is negative. This observation, together with the findings of Fort and Moore, points to the presence of intermolecular interactions in all of the aforementioned systems. It's also probable that these mixes between the OH group of alkoxyethanols and the (-C=O) of DEM contain dipole-dipole interactions.

The creation of a complex by hydrogen bonding between diethyl malonate and alkoxy ethanol molecules can account for the negative $\Delta\beta_{ad}$ observed in the mixtures under investigation. It is evident that for all of the combinations under study, the divergence in adiabatic compressibility is negative over the whole diethyl malonate content range. Previous researchers observed similar results [xviii,xix]. As the alkoxyethanols' chain length increases, the magnitude of the negative value diminishes. In comparison to 2-MOE molecules in any associated structure, molecules in this case encounter more steric hindrance because of the increased number of attached alkoxy groups. Steric hindrance weakens the bond between mixture components at any given temperature. In all three of the binary systems under study, it is evident that the negative value rises as temperature rises. It is commonly recognized that when temperature rises, heat energy breaks down the associated molecules of the pure components of DEM and 2-alkoxyethanols, allowing DEM and 2-alkoxyethanol molecules to form hetero associates through hydrogen bonding[xx].

The strength of interaction is in the order of

DEM + MOE > DEM + EOE > DEM + BOE

EXCESS INTERMOLECULAR FREE LENGTH:

The excess intermolecular free length in the systems under investigation is shown in Figs. 1(c), 2(c), and 3(c) for DEM+MOE, DEM+ EOE, and DEM+BOE, respectively, at all four temperatures. For each of the three systems in our analysis, the L^{E}_{f} values are negative. According to Fort [xxi], hydrogen bonds between the solute and solvent are what cause the negative values of excess intermolecular free length, whereas the dispersive forces are responsible for the positive values. Spence, Jeffrey, and Robert [xxii] have found similar results, concluding that the negative L_f^E values indicate a strong molecular interaction between the components in all systems. As the temperature increases from (303.15 to 318.15) K, the L_f^E values decrease for all three systems.

This could be explained by the kinetic energy of the molecules and the breaking of ring-like formations between alkoxyaethanol molecules. Alkoxyalkanol molecules' ring-like shapes break apart when temperature rises and as a result, kinetic energy of the molecules increases along with temperature, increasing the likelihood of molecules coming into contact with one another. The distance between the unlike molecules decreases as a result of this. The intermolecular distance increases as a function of temperature. As a result, the liquid becomes less densely packed, which causes the density and ultrasonic velocity of binary mixtures to drop and the compressibility to rise.

FT-IR SPECTRAL ANALYSIS:

The FT-IR spectra of the pure components and that of various binary liquid mixtures at equimolar compositions at room temperatures are recorded to study the strength of molecular association. The information provided by the IR spectra is evident for the existence of hydrogen bonding, dipole-dipole interactions, among components of binary liquids.

FTIR analysis of the binary liquid mixtures of DEM+ alkoxyethanols:

The systems that are studied are

DEM + 2-methoxyethanol (MOE)
DEM + 2-ethoxyethanol (EOE)
DEM + 2-butoxyethanol (BOE)

The FT-IR spectra were examined in the current study at equimolar doses and room temperature. The IR frequencies observed for the systems (DEM+MOE/EOE/BOE) are presented in the Table 6 and spectra of pure components is shown in Figs. 4.1, 4.2, 4.4 and 4.6 respectively. The mixtures of equimolar concentrations for the systems (DEM+MOE/EOE/BOE) are shown in Figs. 4.3, 4.5 and 4.7respectively. Generally the O-H stretching band appears around 3200-3600 cm^{-1} in pure state. The OH stretching frequencies of MOE, EOE, BOE are (3417.48, 3404.88, 3397.41) cm^{-1} respectively. The resultant absorption bands OH stretching frequencies in (DEM+MOE), (DEM+EOE) and (DEM+BOE) are (3407.24, 3398.25, 3394.12) cm^{-1} respectively and for all the systems, broad bands are observed. It is commonly known that the peak broadens and moves to a lower frequency due to an intermolecular hydrogen bonding. It can be seen that from the above data there is a reasonable shift in the wave numbers for hydroxyl and carbonyl groups in the binary mixtures under investigation. Intermolecular hydrogen bonds are present between the C=O of DEM and hydroxyl group of alkoxyethanol. On mixing DEM with ethers, the intra molecular hydrogen bonds in the ethers seems to broken and new intermolecular hydrogen bonds are formed between DEM and ethers, which could be the reason for broadening of the band. The C=O (str.) frequency observed for pure component of DEM is 1730.30 cm^{-1} and for the mixtures (DEM+MOE), (DEM+EOE) and (DEM+BOE) the absorptions bands appear at (1720.12, 1724.56 and 1726.53) cm^{-1} respectively i.e., the absorption band shifted to lower frequency. This indicates the strong intermolecular interaction between the component molecules. As the chain length of alkoxyethanols increases the absorption band shifted towards lower frequency. The $\Delta\upsilon$ value is highest for MOE, then for EOE and lower values are observed for BOE binary. The strength of interaction decreases with increase of chain length. The thermo-physical properties from the excess parameters also proved the strength of the specific interactions are in the order of **MOE > EOE > BOE**.

The degree of contact is diminished by the longer alkyl chain in BOE, which offers a greater +I impact than in EOE and MOE. Similar outcomes are seen when alkoxyethanols are dissolved in polar solvents like 2-butanone and N-methyl pyrrolidone [xxiii,xxiv].

Strong evidence of intermolecular hydrogen bonding between ether and DEM may be found in the IR spectra. Mehta et al. [xxv] have documented a similar shift in the stretching frequency values of the C-O band for mixes containing NMP and butanediol. Whereas intramolecular hydrogen bonding produces a sharper peak, intermolecular hydrogen bonding broadens the peak and causes it to move to a lower frequency [xxvi]. Comparable outcomes noted by Gyan Prakash Dubey[xxvii].

CONCLUSION:

The three binary systems studied viz., DEM + 2-methoxyethanol (DEM+MOE), DEM + 2-ethoxyethanol (DEM+EOE) and DEM+ 2-butoxyethanols (DEM+BOE) at (303.15, 308.15, 313.15 and 318.15) K are computed over the entire composition range and at atmospheric pressure. This work presents experimental data on ultrasonic velocity (U), density (ρ) and their excess parameters. Among various excess properties, excess molar volumes (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and excess inter molecular free length (L_f^E) are observed in negative trends. From all the observations it is obvious that there are strong interactions between molecules of diethylmalonate (DEM) and alkoxyethanols (AOE) when they are mixed with each other than in the pure components and strength of interactions increases with composition. The Redlich-Kister equation is fitted with all of the excess parameters. These findings are qualitatively consistent with previous researchers' findings. Thus, an analysis of these factors suggests that components of the binary mixtures may interact with one another to establish hydrogen bonds (of the type O-H-O) between dissimilar molecules.

Table-1

Comparison of experimental results at 308.15 K with data from the literature

Solvent	Density (gm cm^{-3})		Velocity (ms^{-1})	
	Experimental	Literature	Experimental	Literature
Diethylmalonate (DEM)	1038.200	1038.7 [iv] 1038.8[iv]	1267.2	1267.2 [iv]
2 – Methoxy ethanol	950.600	950.3[v]	1346.0	1344.0
2 – Ethoxy ethanol	917.200	916.0[v]	1290.4	1298.0 [v]
2 – Butoxy ethanol	887.400	887.0[v]	1274.5	1274.0

Table-2: Ultrasonic velocity (U), density (ρ), excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and excess intermolecular free length (L_f^E) of Diethyl Malonate + 2-methoxyethanol (MOE)

X_1	U / $m{\cdot}s^{-1}$	ρ / $kg{\cdot}m^{-3}$	$V^E/10^6$ $m^3{\cdot}mol^{-1}$	$\Delta\beta_{ad}/10^{-10}$ $m^2{\cdot}N^{-1}$	$L_f^E/10^{-11}$m	U / $m{\cdot}s^{-1}$	ρ / $kg{\cdot}m^{-3}$	V^E /10^6 $m^3{\cdot}mol^{-1}$	$\Delta\beta_{ad}/10^{-10}$ $m^2{\cdot}N^{-1}$	$L_f^E/10^{-11}$m
		303.15K						**308.15K**		
0.0000	1357.0	952.0	0.0000	0.0000	0.0000	1346.0	950.6	0.0000	0.0000	0.0000
0.0547	1353.5	966.6	-0.4630	-0.1840	-0.0040	1342.3	965.2	-0.5090	-0.1950	-0.0040
0.1153	1349.3	978.6	-0.7380	-0.3070	-0.0070	1338.1	977.2	-0.8150	-0.3210	-0.0070
0.1825	1344.5	989.6	-0.9390	-0.3920	-0.0080	1333.4	987.8	-1.0240	-0.4030	-0.0090
0.2578	1338.8	1000.0	-1.0980	-0.4520	-0.0100	1328.0	997.7	-1.1950	-0.4570	-0.0100
0.3426	1332.2	1009.4	-1.1720	-0.4750	-0.0100	1321.6	1006.9	-1.2950	-0.4810	-0.0100
0.4387	1324.6	1017.7	-1.1490	-0.4580	-0.0100	1314.2	1014.7	-1.2650	-0.4610	-0.0100
0.5487	1315.5	1025.5	-1.0450	-0.4090	-0.0090	1305.3	1021.9	-1.1670	-0.4150	-0.0090
0.6758	1304.7	1032.5	-0.8490	-0.3220	-0.0070	1294.8	1028.5	-0.9820	-0.3310	-0.0070
0.8242	1291.8	1038.7	-0.5090	-0.1870	-0.0040	1282.3	1033.9	-0.5980	-0.1940	-0.0040
1.0000	1276.0	1044.2	0.0000	0.0000	0.0000	1267.2	1038.2	0.0000	0.0000	0.0000
		313.15K						**318.15K**		
0.0000	1336.0	945.6	0.0000	0.0000	0.0000	1313.0	942.7	0.0000	0.0000	0.0000
0.0547	1332.1	961.1	-0.5860	-0.1950	-0.0050	1309.6	959.3	-0.6850	-0.2150	-0.0040
0.1153	1327.7	972.9	-0.8790	-0.3210	-0.0070	1305.7	970.9	-0.9650	-0.3400	-0.0070
0.1825	1322.8	983.7	-1.1110	-0.4030	-0.0090	1301.6	982.0	-1.2160	-0.4280	-0.0090
0.2578	1317.2	993.7	-1.2820	-0.4570	-0.0110	1296.7	991.9	-1.3840	-0.4830	-0.0100
0.3426	1310.8	1002.7	-1.3720	-0.4810	-0.0110	1291.2	1001.0	-1.4810	-0.5020	-0.0100
0.4387	1303.3	1010.8	-1.3800	-0.4610	-0.0110	1284.7	1009.0	-1.4770	-0.4860	-0.0100
0.5487	1294.3	1017.8	-1.2610	-0.4150	-0.0090	1277.0	1016.3	-1.3920	-0.4350	-0.0090
0.6758	1283.6	1024.3	-1.0570	-0.3310	-0.0080	1267.8	1022.5	-1.1520	-0.3490	-0.0070

0.8242	1270.9	1029.8	-0.6830	-0.1940	-0.0050	1256.7	1027.8	-0.7560	-0.2130	-0.0040
1.0000	1256.0	1033.6	0.0000	0.0000	0.0000	1244.0	1031.2	0.0000	0.0000	0.0000

Table-3: Ultrasonic velocity (U), density (ρ), Excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and Excess intermolecular free length (L_f^E) of Diethyl Malonate + 2-ethoxyethanol (EOE)

X_1	U / $m\cdot s^{-1}$	ρ / $kg\cdot m^{-3}$	V^E /10^6 $m^3\cdot mol^{-1}$	$\Delta\beta_{ad}$/ 10^{-10} $m^2\cdot N^{-1}$	L_f^E/ 10^{-11}m	U / $m\cdot s^{-1}$	ρ / $kg\cdot m^{-3}$	V^E /10^6 $m^3\cdot mol^{-1}$	$\Delta\beta_{ad}$/ 10^{-10} $m^2\cdot N^{-1}$	L_f^E/ 10^{-11}m
		303.15K						**308.15K**		
0.0000	1306.1	919.6	0.0000	0.0000	0.0000	1290.4	917.2	0.0000	0.0000	0.0000
0.0664	1304.8	933.8	-0.1930	-0.1230	-0.0030	1289.1	931.7	-0.2530	-0.1390	-0.0030
0.1379	1303.2	946.9	-0.2650	-0.2070	-0.0040	1288.0	944.6	-0.3450	-0.2210	-0.0050
0.2152	1301.6	959.5	-0.2880	-0.2580	-0.0060	1286.8	957.1	-0.4040	-0.2760	-0.0060
0.2990	1299.6	972.2	-0.3230	-0.2940	-0.0060	1285.6	969.5	-0.4420	-0.3030	-0.0070
0.3901	1297.2	984.7	-0.3310	-0.3070	-0.0070	1283.9	981.6	-0.4640	-0.3140	-0.0070
0.4897	1294.4	996.9	-0.3140	-0.2950	-0.0060	1281.7	993.5	-0.4570	-0.3040	-0.0070
0.5988	1290.9	1009.1	-0.2960	-0.2660	-0.0060	1279.1	1005.2	-0.4180	-0.2690	-0.0060
0.7190	1286.7	1020.9	-0.2150	-0.2070	-0.0040	1275.7	1016.7	-0.3500	-0.2150	-0.0050
0.8520	1281.8	1032.6	-0.1180	-0.1190	-0.0030	1271.8	1027.6	-0.2110	-0.1250	-0.0030
1.0000	1276.0	1044.2	0.0000	0.0000	0.0000	1267.2	1038.2	0.0000	0.0000	0.0000
		313.15K						**318.15K**		
0.0000	1277.6	911.8	0.0000	0.0000	0.0000	1258.4	908.2	0.0000	0.0000	0.0000
0.0664	1276.4	927.0	-0.3310	-0.1390	-0.0030	1257.6	924.4	-0.4280	-0.1520	-0.0030
0.1379	1275.2	940.0	-0.4300	-0.2210	-0.0050	1256.8	937.1	-0.4920	-0.2380	-0.0050
0.2152	1274.0	952.5	-0.4710	-0.2760	-0.0070	1256.0	950.0	-0.5650	-0.2930	-0.0060
0.2990	1272.7	965.0	-0.5210	-0.3030	-0.0070	1255.3	962.4	-0.6010	-0.3270	-0.0070
0.3901	1271.1	977.3	-0.5520	-0.3140	-0.0080	1254.4	974.8	-0.6350	-0.3390	-0.0070
0.4897	1269.2	989.2	-0.5350	-0.3040	-0.0070	1253.2	986.9	-0.6190	-0.3240	-0.0070
0.5988	1266.5	1000.8	-0.4850	-0.2690	-0.0070	1251.2	998.8	-0.5920	-0.2940	-0.0060
0.7190	1263.4	1012.3	-0.4070	-0.2150	-0.0050	1249.0	1010.3	-0.5010	-0.2360	-0.0050
0.8520	1259.9	1023.3	-0.2590	-0.1250	-0.0030	1246.6	1021.3	-0.3370	-0.1400	-0.0030
1.0000	1256.0	1033.6	0.0000	0.0000	0.0000	1244.0	1031.2	0.0000	0.0000	0.0000

Table-4: Ultrasonic velocity (U), density (ρ), Excess molar volume (V^E), deviation in adiabatic compressibility ($\Delta\beta_{ad}$) and Excess inter molecular free length (L_f^E) of Diethyl Malonate + 2-butoxyethanol (BOE)

X_1	U/ $m\cdot s^{-1}$	ρ / $kg\cdot m^{-3}$	V^E /10^6 $m^3\cdot mol^{-1}$	$\Delta\beta_{ad}$/ 10^{-10} $m^2\cdot N^{-1}$	L_f^E/ 10^{-11}m	U/ $m\cdot s^{-1}$	ρ / $kg\cdot m^{-3}$	V^E /10^6 $m^3\cdot mol^{-1}$	$\Delta\beta_{ad}$/ 10^{-10} $m^2\cdot N^{-1}$	L_f^E/ 10^{-11}m
		303.15K						**308.15K**		
0.0000	1325.0	892.1	0.0000	0.0000	0.0000	1274.5	887.4	0.0000	0.0000	0.0000
0.0876	1321.3	907.9	-0.0810	-0.0920	-0.0020	1274.2	904.0	-0.2270	-0.0960	-0.0020
0.1776	1317.4	923.4	-0.1230	-0.1580	-0.0030	1274.0	920.0	-0.3600	-0.1580	-0.0030
0.2701	1313.5	938.7	-0.1380	-0.1950	-0.0030	1273.7	935.3	-0.3980	-0.1930	-0.0040
0.3654	1309.3	953.9	-0.1360	-0.2150	-0.0040	1273.4	950.8	-0.4540	-0.2130	-0.0040
0.4634	1304.7	969.1	-0.1430	-0.2210	-0.0040	1272.9	965.9	-0.4550	-0.2150	-0.0040
0.5644	1299.6	984.3	-0.1430	-0.2150	-0.0040	1272.0	981.0	-0.4590	-0.2100	-0.0040
0.6683	1294.1	999.3	-0.1120	-0.1900	-0.0030	1270.9	995.8	-0.4170	-0.1880	-0.0040
0.7755	1288.3	1014.4	-0.0840	-0.1480	-0.0030	1269.7	1010.4	-0.3410	-0.1480	-0.0030
0.8860	1282.3	1029.4	-0.0620	-0.0850	-0.0020	1268.5	1024.5	-0.2070	-0.0850	-0.0020
1.0000	1276.0	1044.2	0.0000	0.0000	0.0000	1267.2	1038.2	0.0000	0.0000	0.0000
		313.15K						**318.15K**		
0.0000	1264.0	882.8	0.0000	0.0000	0.0000	1252.0	879.1	0.0000	0.0000	0.0000
0.0876	1263.5	900.0	-0.3220	-0.0960	-0.0020	1251.4	897.1	-0.4210	-0.1120	-0.0020
0.1776	1263.0	915.7	-0.4190	-0.1580	-0.0040	1250.8	912.7	-0.4870	-0.1750	-0.0030
0.2701	1262.7	931.2	-0.4680	-0.1930	-0.0040	1250.4	928.3	-0.5420	-0.2090	-0.0040
0.3654	1262.3	946.5	-0.5140	-0.2130	-0.0050	1250.0	943.7	-0.5830	-0.2280	-0.0040
0.4634	1261.7	961.7	-0.5310	-0.2150	-0.0050	1249.5	959.1	-0.6100	-0.2320	-0.0040
0.5644	1260.7	976.9	-0.5350	-0.2100	-0.0050	1248.5	974.3	-0.6070	-0.2280	-0.0040
0.6683	1259.5	991.6	-0.4910	-0.1880	-0.0040	1247.4	989.3	-0.5740	-0.2060	-0.0040
0.7755	1258.3	1006.1	-0.4020	-0.1480	-0.0040	1246.2	1004.1	-0.4990	-0.1620	-0.0030
0.8860	1257.2	1020.2	-0.2500	-0.0850	-0.0020	1245.1	1018.1	-0.3270	-0.0930	-0.0020
1.0000	1256.0	1033.6	0.0000	0.0000	0.0000	1244.0	1031.2	0.0000	0.0000	0.0000

Table-5

Values of Coefficients and Standard Deviations (σ) for the systems DEM + 2-methoxyethanol (MOE), DEM +2-ethoxyethanol (EOE) and DEM +2- butoxyethanol (BOE) systems at (303.15, 308.15, 313.15 and 318.15)K

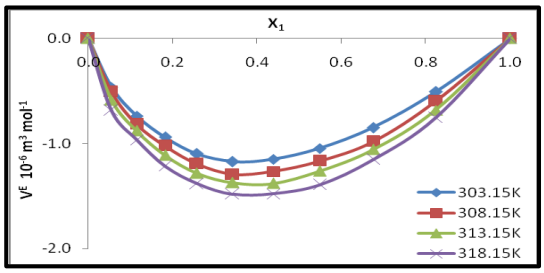
Temp K	A_0	A_1	A_2	A_3	A_4	∞
DEM+MOE						
Excess Molar Volume						
303.15	-2.7219	-2.7219	1.8793	1.2289	-6.9723	0.0400
308.15	-2.9783	-2.9783	2.3861	1.9101	-8.5858	0.0569
313.15	-2.8895	-2.8895	2.6774	1.6514	-10.5594	0.0529
318.15	-2.9471	-2.9471	3.9083	1.3616	-13.9004	0.0644
Deviation in Adiabatic Compressibility						
303.15	-1.1341	-1.1341	0.2459	0.1850	-1.7643	0.0101
308.15	-1.1358	-1.1358	0.2505	0.1309	-2.0192	0.0117
313.15	-1.1477	-1.1477	0.2473	0.0843	-2.4063	0.0118
318.15	-1.2066	-1.2066	0.6101	0.1837	-3.3228	0.0147
Excess Inter Molecular Free Length						
303.15	-0.0251	-0.0251	0.0062	0.0048	-0.0397	0.0002
308.15	-0.0252	-0.0252	0.0061	0.0036	-0.0457	0.0003
313.15	-0.0255	-0.0255	0.0058	0.0026	-0.0545	0.0003
318.15	-0.0273	-0.0273	0.0143	0.0049	-0.0768	0.0003
DEM+EOE						
Excess Molar Volume						
303.15	-0.3526	-0.3526	0.9397	-1.0066	-2.6744	0.0118
308.15	-0.4767	-0.4767	0.7250	-0.8174	-3.2114	0.0159
313.15	-0.7227	-0.7227	1.9508	-0.6647	-6.2097	0.0278
318.15	-0.4429	-0.4429	1.9470	-1.5901	-7.6316	0.0374
Deviation in Adiabatic Compressibility						
303.15	-0.4328	-0.4328	0.0183	-0.1968	-0.5340	0.0031
308.15	-0.4570	-0.4570	-0.1441	-0.3135	-0.5923	0.0034
313.15	-0.4688	-0.4688	0.0173	-0.2917	-0.9623	0.0051
318.15	-0.4040	-0.4040	-0.1096	-0.5061	-0.9656	0.0065
Excess Inter Molecular Free Length						
303.15	-0.0094	-0.0094	0.0007	-0.0044	-0.0122	0.0001
308.15	-0.0101	-0.0101	-0.0033	-0.0071	-0.0135	0.0001
313.15	-0.0104	-0.0104	0.0005	-0.0066	-0.0225	0.0001
318.15	-0.0089	-0.0089	-0.0027	-0.0119	-0.0226	0.0002
DEM+BOE						
Excess Molar Volume						
303.15	-0.2078	-0.2078	-0.1067	-0.0103	-0.4369	0.0067
308.15	0.0408	0.0408	-0.5023	-0.7353	-0.6353	0.0119
313.15	0.1905	0.1905	-0.3476	-1.5906	-1.9795	0.0070
318.15	0.3377	0.3377	-0.3001	-2.1092	-3.6426	0.0185
Deviation in Adiabatic Compressibility						
303.15	-0.1282	-0.1282	-0.2409	-0.0856	0.1073	0.0015

308.15	-0.0992	-0.0992	-0.3175	-0.1892	0.1151	0.0014
313.15	-0.0670	-0.0670	-0.3356	-0.3373	-0.0041	0.0009
318.15	-0.0946	-0.0946	-0.3774	-0.3601	-0.1526	0.0022
Excess Inter Molecular Free Length						
303.15	-0.0021	-0.0021	-0.0055	-0.0018	0.0026	0.0000
308.15	-0.0016	-0.0016	-0.0076	-0.0043	0.0030	0.0000
313.15	-0.0008	-0.0008	-0.0081	-0.0079	0.0003	0.0000
318.15	-0.0014	-0.0014	-0.0092	-0.0083	-0.0033	0.0001

Table-6

Stretching frequencies in FT-IR for the DEM + AOE binary mixtures

O-H(st)	pure	mix	Δυ	DEM pure C=O(st)	C=O(st)	Δυ
MOE	3417.48	3407.24	10.24	1730.3	1720.12	10.18
EOE	3404.88	3398.25	6.63	1730.3	1724.56	5.74
BOE	3397.41	3394.12	3.29	1730.3	1726.53	3.77



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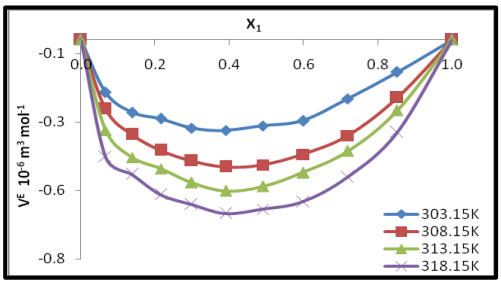
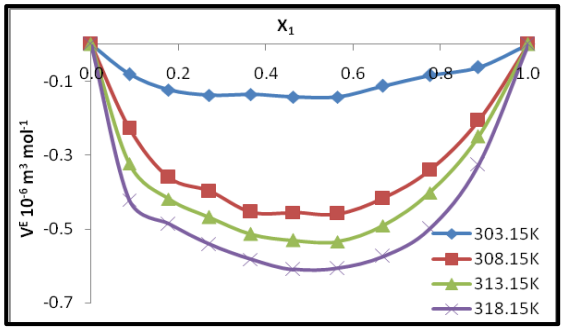
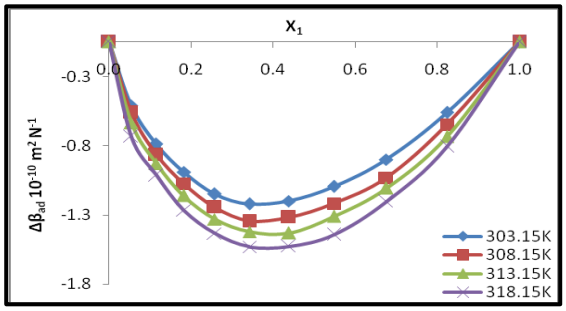


[b]



[c]

FIG-1: Variation of Excess molar volume with X_1 of DEM for the systems a. DEM+MOE, b. DEM+EOE & c. DEM+BOE



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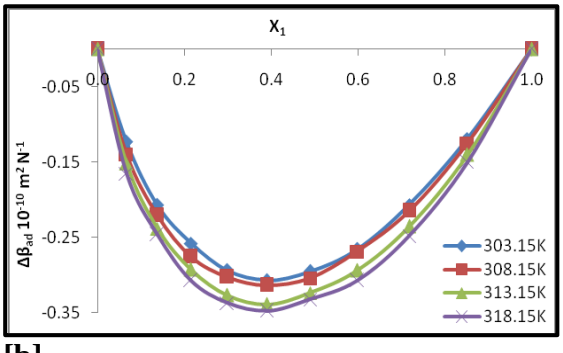
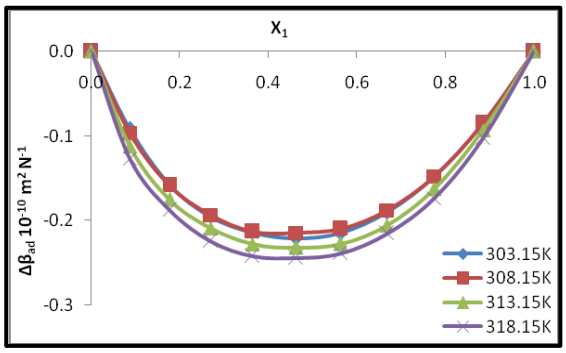
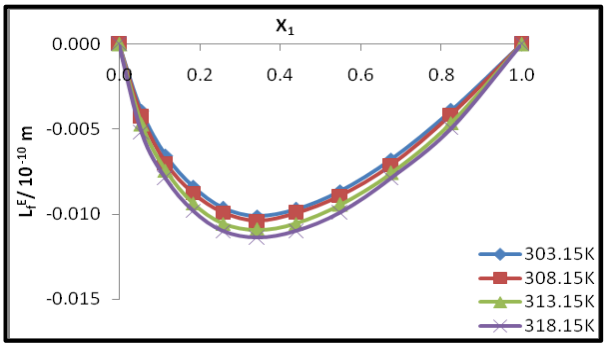


[b]



[c]

FIG-2: Variation of Deviation in adiabatic compressibility with X_1 of DEM for the systems a. DEM+MOE, b. DEM+EOE & c. DEM+BOE



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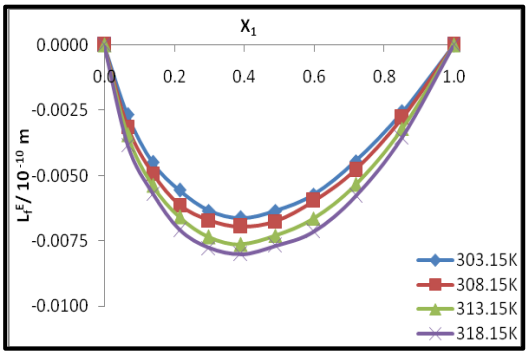

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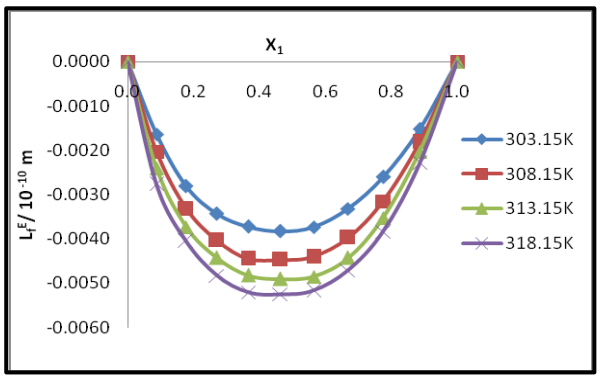

[c]

FIG-3: Variation of Excess intermolecular free length with X_1 of DEM for the systems a. DEM+MOE, b. DEM+EOE & c. DEM+BOE

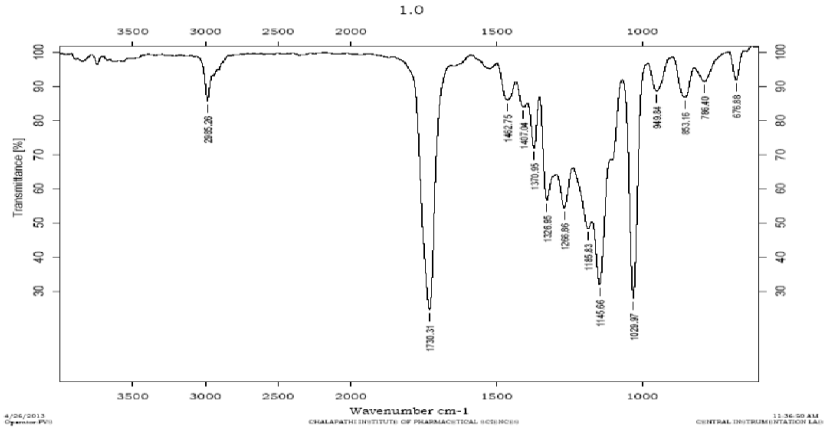

Fig 4.1: Pure Diethyl malonateFT-IR spectrum

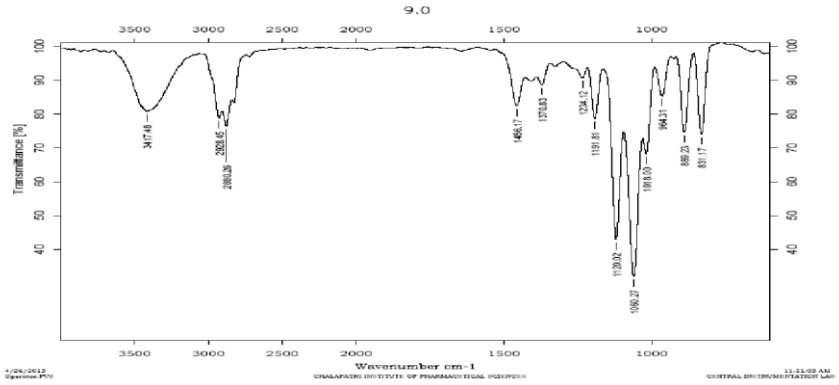

Fig 4.2: Pure MOE's FT-IR spectrum

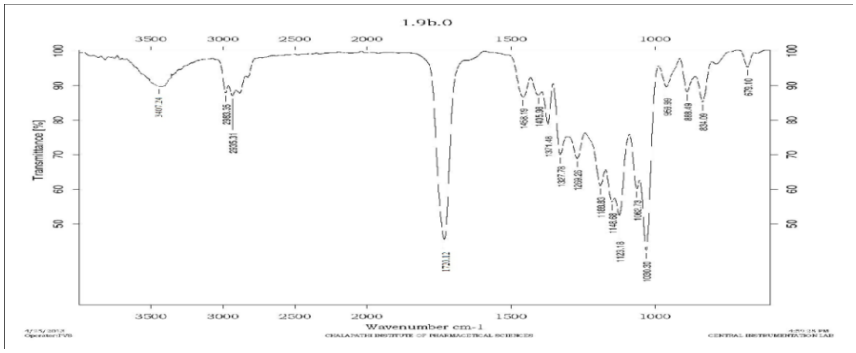

Fig 4.3: FT-IR spectrum of DEM 0.5 + MOE 0.5

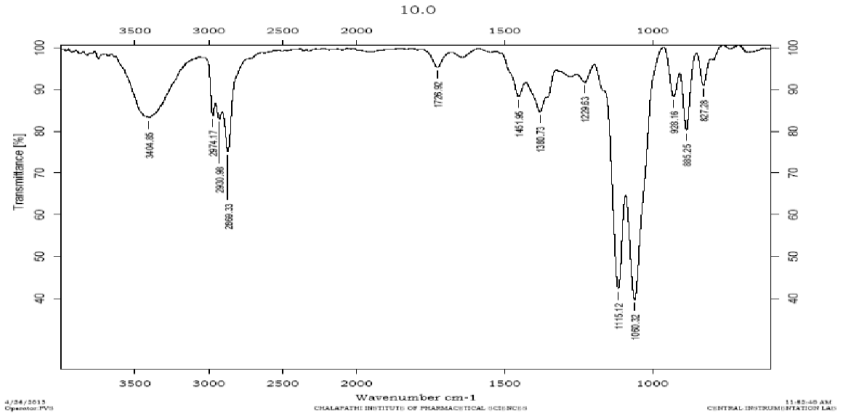

Fig 4.4: FT-IR spectrum of pure EOE

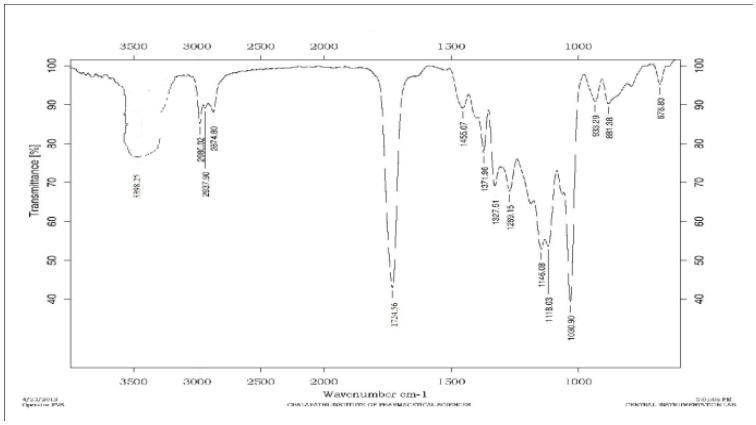

Fig 4.5: FT-IR spectrum of DEM 0.5 + EOE 0.5

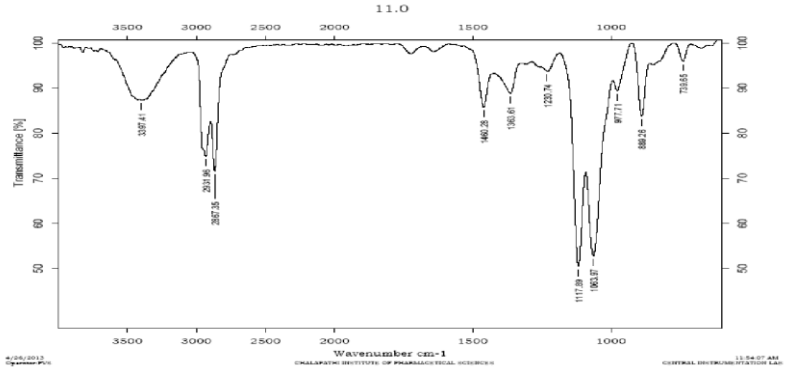

Fig 4.6: FT-IR spectrum of pure BOE

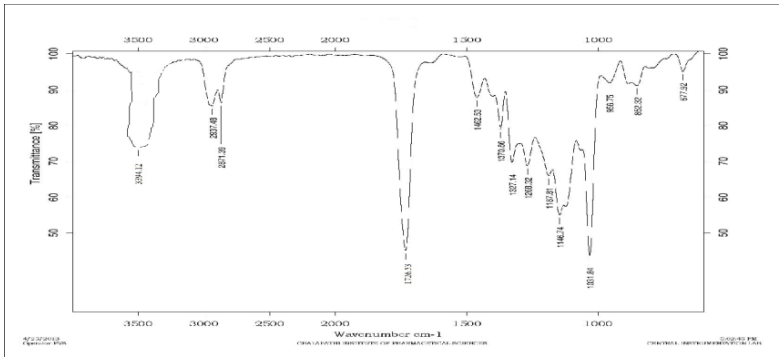

Fig 4.7: FT-IR spectrum of DEM 0.5 + BOE 0.5

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