RJC

RASĀYAN J. Chem.
Vol. 13 | No. 1 |707 – 722| January - March | 2020
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

THERMO-PHYSICAL, SPECTRAL EVALUATION OF MOLECULAR INTERACTIONS IN LIQUID BINARIES OF DIETHYL MALONATE AND AMIDES AT TEMPERATURES (303.15, 308.15, 313.15, 318.15) K

Ch. Udayalakshmi[1], Shaik Beebi[2], P.B. Sandhya Sri[3],V.N.S.R. Venkateswararao,[4] G. Lakshmana Rao,[5] and C. Rambabu[6]
[1]Y.V.N.R.Govt. Degree College, Kaikaluru, Krishna Dt.A.P.India.
[2]Y.V.N.R.Govt. Degree College, Kaikaluru, Krishna Dt.A.P.India.
[3]K.B.N.College, Vijayawada, Krishna Dt. A.P. India.
[4]Institute of Aeronautical Engineering (IARE), Dundigal, Hyderabad.
[5]Govt. Degree College, Salur. A.P. India.
[6]Acharya Nagarjuna University, A.P. India.
*E-mail:lakshmi.chtn@gmail.com

ABSTRACT

The velocity and density of binary mixtures of diethyl malonate with formamide, dimethylformamide and dimethylacetamide were experimentally measured at temperatures (303.15, 308.15, 313.15, 318.15)K. Various acoustic and thermodynamic parameters were evaluated using experimental data, the results have been discussed based on molecular interactions and geometric effects of the components in the mixture. FT-IR spectral analysis gives evidence of molecular association.

Keywords: Diethyl Malonate, Ultrasonic Velocity, Density, Acoustical, Molecular Interactions.

INTRODUCTION

Ultrasonic velocity measurement is highly sensitive due to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interactions in binary liquid mixtures. The analysis of excess thermodynamic properties of liquid mixtures can be used to obtain the information about the energetic and structural effects and packing phenomena in the mixtures.[1, 2] The variation of the properties with temperature and composition of mixtures is complex due to the presence of hydrogen-bonded interactions between the component molecules.[3]

Diethyl malonate (DEM) is a colorless fragrant liquid used in the synthesis of vitamin B_1 and vitamin B_6, barbiturates, pharmaceutical, agrochemical industrial products, flavors, fragrance compounds. It is also used for the synthesis of drugs such as chloroquine and in paint and spice industries.

Amides are key molecules because of containing the carbonyl and amino functional groups in the same molecular unit (peptide bond), which is of pivotal relevance for biochemical purposes as models for describing intermolecular interactions in proteins or nucleic acids.

Formamide (FA) is the simplest amide molecule, which is used as a model to study the behavior of amides in the liquid phase. The inclusion of alkyl chains in the $-NH_2$ group leads to remarkable changes in the hydrogen bonding ability of amides and thus, the substituted amide molecules such as N, N-dimethylformamide(DMF), N, N-dimethylacetamide(DMA) have also been the subject of research interest. DMF is primarily used as a solvent in the production of polyurethane products and acrylic fibers, pharmaceutical industry, formulation of pesticides, manufacture of fine chemicals, synthetic leathers, fibers, films, surface coatings and more importantly its mixture with supercritical CO_2 is of major interest

Rasayan J. Chem., 13(1), 707-722(2020)
http://dx.doi.org/10.31788/RJC.2020.1315595

in supercritical fluid extraction in separation processes. DMA is a dipolar aprotic solvent. It is used as a solvent in the production of acrylic, pharmaceuticals, antibiotics and polyimide resins.

The hydrogen-bonded network in pure FA is characterized by the formation of two H-bonds per molecule on average, whereas the structure of DMF is characterized by intermolecular interactions through dipole‒dipole mechanisms.[4-7] Knowledge of excess mixing properties of a binary mixture is used in the design process in the chemical and petrochemical industries.[8] Because of the fascinating nature of these compounds, the author has been worked on these amides.

EXPERIMENTAL

In the present investigation, the author made use of a pulse-echo interferometer (MODEL M-81) for the measurement of ultrasonic velocities of pure liquids and liquid mixtures supplied by the Mittal Enterprises, New Delhi for velocity measurements. Densities (ρ) of pure liquids and all liquid mixtures are measured by employing a 10^{-5} m^3 double-arm pycnometer at (303.15, 308.15, 313.15 and 318.15) K as described by Nikam *et al.*[9] It is calibrated using conductivity water with 995.61 kg m^{-3} as its density at 303.15 K. Thermostat is employed to maintain the constancy in temperature and with an accuracy of ±0.01K. The weighings are carried using METTLER TOLEDO (Switzerland make) ABB5-S/F ACT digital balance with an accuracy of ±0.01mg. The experimental samples, Diethyl malonate, amide such as Formamide, N,N–dimethylformamide, N,N– dimethylacetamide used in the present study are of high-quality samples, obtained from S.D. Fine chemicals, India with purity > 99%. Comparison of experimental values with literature values at all temperatures are shown in Table-1.[10-13] It is evident from Table-1, that there is good agreement between the experimental and reported values.

From the experimental data, various acoustical parameters were evaluated using the following standard equations**:**

- Mean molar volume (V) evaluated by the equation$V = M / \rho$
- Excess volume (V^E):$V^E = V - (V_1X_1+V_2X_2)$
- Adiabatic compressibility (β_{ad}):$\beta_{ad} = 1/ \rho U^2$
- Deviation in adiabatic compressibility ($\Delta\beta_{ad}$): $= \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2)$
- Intermolecular free length (L_f^E):$L_f = K (\beta_{ad})^{½}$
- Excess intermolecular free length (L_f^E):$L_f^E = L_f - (L_{f1}X_1+ L_{f2}X_2)$

Where, L_{f1} and L_{f2} are the individual intermolecular free length values of pure liquids in the binary mixtures.

Redlich-Kisterequation: $Y^E=Y^M_{real}-Y^M_{ideal}$

The standard deviations $\sigma (Y^E)$ were calculated by using the relation

$$\sigma (Y^E) = \Sigma[(Y_{exp}^E - Y_{cal}^E)^2/m-n]^{1/2}$$

Where, m is the number of experimental data points and n is the number of coefficients considered and (n=3 in the present calculation). Y_{cal}^E has been obtained from the above equation using the best - fit values of A_i.

Table-1: Comparison of Experimental Values with Literatures Data [10-13] at 308.15K

Liquid	Density (Kg cm^{-3})		Velocity (ms^{-1})	
	Expt.	Lit.	Expt.	Lit.
Diethylmalonate (DEM)	1038.2	1038.7 [a] 1038.8 [b]	1267.2	1267.2 [a]
Formamide	1119.9	1119.9 [c]	1576.0	1578.0 [d]
N,N-dimethyl formamide	934.10	934.7 [c]	1424.0	1420.0 [c]
N,N-dimethyl acetamide	927.6	927.1 [c]	1426.0	1423.0 [c]

[a] Reference 10; [b] Reference 11; [c] Reference 12; [d] Reference [13].

RESULTS AND DISCUSSION

Experimental values of densities and velocities of pure liquids with literature values are reported in Table-1. There is a good agreement between the experimental values with the literature values. The values of density (ρ) and ultrasonic velocity (U) along with the excess properties for diethyl malonate with formamide, N, N-dimethylformamide and N, N-dimethylacetamide from temperatures (303.15 to 318.15) K are summarized in Tables-2,4 and 6. The values of coefficients and standard deviations are incorporated in Tables-3, 5 and 7. The non-rectilinear behavior of ultrasonic velocity, compressibility and other thermo dynamical parameters of liquid mixtures with changing mole fractions are attributed to the difference in the size of the molecules and strength of interactions.

The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components, reported by Eyring and Kincaid[14]. The intermolecular free length and ultrasonic velocity are interdependent. The ultrasonic velocity decreases if the intermolecular free length increases or vice versa as a result of the mixing of components. This is observed in the present investigation for DEM + FA, DEM + DMF, and DEM + DMA systems. It is also observed that velocity decreases with an increase in temperature at any concentration. The ultrasonic velocity values decrease with the increase of temperature due to the breaking of hetero and homo molecular clusters at high temperatures.

Table-2: System-1: Diethyl Malonate (X_1) + Formamide (X_2) Ultrasonic Velocities, Densities, Excess Molar Volume, Deviation in Adiabatic Compressibility, and Excess Free Length

Mole fraction X_1	Velocity (U) ms^{-1}	Density (ρ) Kgm^{-3}	Ad. Comp. βad $\times 10^{-10}\ m^2N^{-1}$	Mol.Vol. V $10^{-6}m^3\ mol^{-1}$	Int Mol. Free Length L_f $10^{-10}m$	V^E $10^{-6}m^3\ mol^{-1}$	$\Delta\beta_{ad}$ $\times 10^{-10}\ m^2N^{-1}$	L_f^E $10^{-10}m$
303.15K								
0.0000	1584.0	1124.4	22.315	40.057	0.938	0.000	0.000	0.000
0.0282	1576.5	1144.1	21.723	42.205	0.925	-1.048	-0.402	-0.008
0.0613	1566.9	1148.7	21.374	45.354	0.918	-1.649	-0.528	-0.011
0.1007	1555.5	1154.6	20.957	49.048	0.909	-2.417	-0.681	-0.013
0.1483	1541.6	1159.7	20.493	53.561	0.898	-3.302	-0.824	-0.016
0.2071	1524.3	1164.3	19.956	59.160	0.887	-4.366	-0.967	-0.019
0.2815	1502.3	1163.0	19.407	66.597	0.874	-5.361	-1.016	-0.020
0.3786	1472.9	1154.3	18.795	76.789	0.860	-6.182	-0.974	-0.019
0.5109	1431.2	1135.0	18.047	91.509	0.843	-6.453	-0.833	-0.016
0.7015	1370.0	1102.4	17.026	114.127	0.819	-5.438	-0.573	-0.011
1.0000	1276.0	1044.2	15.593	153.390	0.784	0.000	0.000	0.000
308.15K								
0.0000	1576.0	1119.9	22.179	40.218	0.935	0.000	0.000	0.000
0.0282	1568.4	1140.2	21.573	42.348	0.922	-1.086	-0.416	-0.008
0.0613	1558.7	1144.9	21.221	45.505	0.914	-1.704	-0.546	-0.011
0.1007	1547.3	1151.3	20.796	49.189	0.905	-2.510	-0.707	-0.014
0.1483	1533.2	1156.4	20.328	53.714	0.895	-3.418	-0.855	-0.017
0.2071	1515.8	1161.9	19.776	59.286	0.883	-4.552	-1.013	-0.020
0.2815	1493.6	1159.6	19.237	66.788	0.870	-5.535	-1.052	-0.021
0.3786	1464.3	1150.2	18.641	77.057	0.857	-6.349	-0.996	-0.019
0.5109	1422.6	1130.9	17.896	91.844	0.840	-6.649	-0.853	-0.016
0.7015	1361.1	1097.5	16.881	114.636	0.815	-5.599	-0.589	-0.011
1.0000	1267.2	1038.2	15.467	154.277	0.781	0.000	0.000	0.000
313.15K								

0.0000	1564.0	1115.5	21.928	40.377	0.929	0.000	0.000	0.000
0.0282	1556.4	1136.6	21.313	42.485	0.916	-1.123	-0.416	-0.009
0.0613	1546.4	1141.3	20.953	45.646	0.908	-1.754	-0.546	-0.011
0.1007	1535.3	1147.6	20.540	49.346	0.899	-2.565	-0.707	-0.014
0.1483	1521.3	1153.0	20.073	53.871	0.889	-3.498	-0.855	-0.017
0.2071	1503.8	1158.7	19.518	59.449	0.877	-4.656	-1.013	-0.021
0.2815	1481.5	1156.3	18.981	66.979	0.865	-5.651	-1.052	-0.021
0.3786	1452.2	1147.6	18.377	77.236	0.851	-6.528	-0.996	-0.020
0.5109	1410.6	1127.9	17.642	92.089	0.834	-6.833	-0.853	-0.017
0.7015	1349.5	1094.2	16.643	114.973	0.810	-5.790	-0.589	-0.012
1.0000	1256.0	1033.6	15.263	154.963	0.775	0.000	0.000	0.000
318.15K								
0.0000	1555.0	1110.9	21.766	40.544	0.926	0.000	0.000	0.000
0.0282	1547.2	1132.3	21.142	42.647	0.913	-1.134	-0.427	-0.008
0.0613	1537.1	1137.5	20.772	45.801	0.905	-1.778	-0.567	-0.011
0.1007	1525.4	1144.2	20.335	49.491	0.895	-2.607	-0.717	-0.014
0.1483	1511.2	1149.9	19.860	54.016	0.884	-3.549	-0.867	-0.017
0.2071	1493.7	1155.6	19.308	59.609	0.872	-4.704	-1.030	-0.020
0.2815	1471.3	1153.2	18.771	67.160	0.860	-5.692	-1.071	-0.021
0.3786	1441.8	1144.7	18.159	77.426	0.846	-6.578	-1.027	-0.019
0.5109	1399.8	1124.3	17.429	92.383	0.829	-6.804	-0.880	-0.016
0.7015	1338.1	1092.3	16.392	115.175	0.804	-5.892	-0.609	-0.011
1.0000	1244.0	1031.2	15.007	155.324	0.769	0.000	0.000	0.000

Table-3: System-1: Diethyl Malonate (X_1) + Formamide (X_2) Values of Coefficients and Standard Deviations (σ)

Temp K	A_0	A_1	A_2	A_3	A_4	σ
Excess Volume						
303.15K	-50.3966	-50.3966	-35.8056	289.8139	-235.9330	1.2020
308.15K	-54.3572	-54.3572	-40.8851	311.7159	-250.8513	1.3217
313.15K	-57.1002	-57.1002	-42.7438	329.2229	-265.5036	1.3862
318.15K	-55.7029	-55.7029	-42.5581	322.9679	-260.6330	1.3221
Deviation in Adiabatic Compressibility						
303.15K	-27.0202	-27.0202	-19.6702	141.8961	-117.0868	0.6056
308.15K	-28.7257	-28.7257	-21.6897	151.0658	-123.5680	0.6519
313.15K	-29.8700	-29.8700	-22.2449	157.5288	-129.0791	0.6765
318.15K	-28.2361	-28.2361	-21.1765	148.0792	-121.9610	0.6300
Excess Inter Molecular Free Length						
303.15K	-0.5726	-0.5726	-0.4180	3.0135	-2.4804	0.0129
308.15K	-0.6118	-0.6118	-0.4642	3.2248	-2.6299	0.0139
313.15K	-0.6397	-0.6397	-0.4784	3.3814	-2.7630	0.0145
318.15K	-0.6063	-0.6063	-0.4575	3.1887	-2.6179	0.0135

Excess Molar Volume (V^E)

In the present systems DEM+FA, DEM+DMF, DEM+DMA, the variation in excess molar volumes are represented in Fig.-1.The excess molar volumes are negative over the entire composition range at all experimental temperatures and atmospheric pressure.

The sign of V^E of a system depends upon the relative magnitude of expansion and contraction of the two liquids due to mixing. The factors that are mainly responsible for the volume expansion i.e., positive values of V^E are:

1. The geometry of molecular structure if it does not favor fitting of the molecules with each other.

2. Disruption of one or both components in a system.
3. The rupture of H-bonding of one compound by the other, or breaking up of associates held together by weaker physical forces such as dipole or dipole-induced dipole interactions or by any other Van der Waal forces.
4. Due to the steric hindrance of the compounds which opposes the proximity of the constituent molecules.

The negative V^E arises due to the dominance of the following factors:

1. Hetero-molecular association through the formation of H-bond often termed as strong specific interaction
2. Association through weaker physical forces such as dipolar force or any other forces.
3. Accommodation of molecules of one component into the interstitial spaces of the structural network other component molecules.

Table -4: System-2 : Diethyl Malonate (X_1) + N, N Dimethylformamide (X_2) Ultrasonic Velocities, Densities, Excess Molar Volume, Deviation in Adiabatic Compressibility, and Excess Free Length

Mole fraction X_1	Velocity (U) ms^{-1}	Density (ρ) kgm^{-3}	Ad. Comp. βad $\times 10^{-10}$ m^2N^{-1}	Mol.Vol. V 10^{-6} m^3 mol^{-1}	Int Mol. Free Length L_f $10^{-10}m$	V^E $10^{-6}m^3$ mol^{-1}	$\Delta\beta_{ad}$ $\times 10^{-10}$ m^2N^{-1}	L_f^E $10^{-10}m$
303.15K								
0.0000	1436.0	939.3	21.954	77.813	0.930	0.000	0.000	0.000
0.0534	1428.5	955.1	21.365	81.390	0.917	-0.456	-0.249	-0.005
0.1125	1419.6	971.6	20.742	85.317	0.904	-1.002	-0.495	-0.010
0.1786	1409.8	985.2	20.173	89.969	0.891	-1.341	-0.644	-0.012
0.2527	1398.8	997.5	19.616	95.340	0.879	-1.573	-0.730	-0.014
0.3366	1386.2	1009.6	19.032	101.421	0.866	-1.829	-0.781	-0.015
0.4321	1371.8	1020.3	18.445	108.521	0.852	-1.951	-0.760	-0.014
0.5421	1354.1	1029.6	17.808	116.830	0.838	-1.950	-0.697	-0.013
0.6699	1332.3	1036.3	17.128	126.816	0.821	-1.624	-0.564	-0.011
0.8203	1306.6	1041.3	16.395	138.788	0.804	-1.022	-0.341	-0.006
1.0000	1276.0	1044.2	15.593	153.390	0.784	0.000	0.000	0.000
308.15K								
0.0000	1424.0	934.1	21.708	78.246	0.925	0.000	0.000	0.000
0.0534	1416.6	951.2	21.096	81.721	0.912	-0.582	-0.279	-0.005
0.1125	1407.6	966.9	20.493	85.732	0.898	-1.071	-0.513	-0.010
0.1786	1398.1	980.3	19.941	90.427	0.886	-1.398	-0.653	-0.013
0.2527	1387.3	992.3	19.395	95.833	0.874	-1.628	-0.736	-0.014
0.3366	1374.9	1004.3	18.823	101.964	0.861	-1.871	-0.784	-0.015
0.4321	1360.7	1014.9	18.244	109.096	0.848	-2.004	-0.768	-0.015
0.5421	1343.5	1024.2	17.623	117.446	0.833	-2.013	-0.702	-0.013
0.6699	1322.3	1031.2	16.955	127.442	0.817	-1.735	-0.572	-0.011
0.8203	1297.0	1035.8	16.240	139.523	0.800	-1.093	-0.349	-0.007
1.0000	1267.2	1038.2	15.467	154.277	0.781	0.000	0.000	0.000
313.15K								
0.0000	1396.0	930.2	20.951	78.575	0.908	0.000	0.000	0.000
0.0534	1389.4	947.3	20.379	82.065	0.896	-0.586	-0.279	-0.005
0.1125	1381.4	963.3	19.809	86.047	0.883	-1.126	-0.513	-0.010
0.1786	1373.0	976.4	19.306	90.781	0.872	-1.435	-0.653	-0.013
0.2527	1363.5	988.5	18.808	96.208	0.861	-1.672	-0.736	-0.014
0.3366	1352.4	1000.5	18.280	102.342	0.849	-1.942	-0.784	-0.015
0.4321	1339.6	1011.1	17.747	109.499	0.836	-2.085	-0.768	-0.015
0.5421	1324.5	1020.2	17.195	117.906	0.823	-2.075	-0.702	-0.013
0.6699	1305.3	1027.5	16.583	127.911	0.808	-1.835	-0.572	-0.011
0.8203	1282.4	1031.7	15.941	140.090	0.792	-1.148	-0.349	-0.007
1.0000	1256.0	1033.6	15.263	154.963	0.775	0.000	0.000	0.000

318.15K								
0.0000	1392.0	925.8	20.930	78.948	0.908	0.000	0.000	0.000
0.0534	1384.7	944.5	20.300	82.300	0.894	-0.723	-0.268	-0.005
0.1125	1376.4	959.6	19.742	86.378	0.882	-1.166	-0.501	-0.010
0.1786	1367.2	973.2	19.206	91.079	0.870	-1.509	-0.628	-0.013
0.2527	1356.9	985.4	18.685	96.510	0.858	-1.740	-0.705	-0.014
0.3366	1345.2	997.5	18.142	102.659	0.845	-1.994	-0.756	-0.015
0.4321	1331.8	1008.2	17.592	109.815	0.832	-2.137	-0.745	-0.015
0.5421	1315.8	1017.5	17.016	118.229	0.819	-2.119	-0.672	-0.013
0.6699	1295.6	1025.3	16.372	128.186	0.803	-1.925	-0.557	-0.011
0.8203	1271.6	1029.6	15.704	140.365	0.786	-1.236	-0.344	-0.007
1.0000	1244.0	1031.2	15.007	155.324	0.769	0.000	0.000	0.000

In the present investigation, the negative V^E values indicate the specific interactions such as intermolecular hydrogen bonding and also interstitial accommodation of the mixing components because of the difference in molar volumes[15]. The negative V^E values are also due to the difference in the dielectric constants of the liquid components of the binary mixtures. The negative V^E values for all the studied systems may be attributed to dipole-dipole interactions between the component liquids of the mixtures resulting in the formation of electron donor-acceptor complexes.[16-17]

Table -5: System-2: Diethyl Malonate (X_1) + N, N Dimethylformamide (X_2) Values of Coefficients and Standard Deviations (σ)

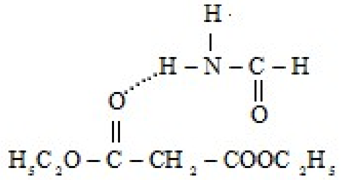
Temp K	A_0	A_1	A_2	A_3	A_4	□
Excess Volume						
303.15K	0.3340	0.3340	-3.8649	-4.9934	8.0390	0.0779
308.15K	-0.1375	-0.1375	-0.8580	-3.6545	0.0168	0.0260
313.15K	-0.3361	-0.3361	-0.9217	-2.9464	-0.1134	0.0351
318.15K	-1.1197	-1.1197	1.9894	-0.8378	-8.8901	0.0548
Deviation in Adiabatic Compressibility						
303.15K	-1.1291	-1.1291	-2.0648	-1.1916	2.3042	0.0159
308.15K	-1.3046	-1.3046	-1.2159	-0.7766	0.1512	0.0081
313.15K	-1.3220	-1.3220	-1.1810	-0.4762	-0.0429	0.0123
318.15K	-1.6579	-1.6579	-0.2006	0.1657	-2.7077	0.0181
Excess Inter Molecular Free Length						
303.15K	-0.0220	-0.0220	-0.0438	-0.0246	0.0513	0.0003
308.15K	-0.0258	-0.0258	-0.0260	-0.0158	0.0054	0.0002
313.15K	-0.0269	-0.0269	-0.0258	-0.0090	0.0007	0.0003
318.15K	-0.0342	-0.0342	-0.0045	0.0055	-0.0578	0.0004

Due to the presence of acid-base interactions between DEM and FA, DMF and DMA molecules, V^E values are negative. The importance of acid-base interactions between t-butyl alcohol and N,N-dimethylformamide and N,N-dimethylacetamide were predicted by Nam-Tran[18] to assess the interactions of lewis acid-base system. To explain the nature of intermolecular interaction among amides chosen for study i.e (FA, DMF and DMA) assumed as lewis bases and diethyl malonate as lewis acid. Since FA has high dielectric constant values (ε = 109 at 25℃)[19], it can act as excellent electron donor and can easily form complexes with another component of liquid binaries, when compared with the DMF (ε = 36.7 at 25℃) and DMA (ε =37.80 at 25℃). Hence due to the high dielectric constant value of FA, the strength of the interaction is more in case of (DEM+FA), when compared with (DEM+DMF) and (DEM+ DMA) systems.

Table -6: System-3 : Diethyl Malonate (X_1) + N, N Dimethylacetamide (X_2) Ultrasonic Velocities, Densities, Excess Molar Volume, Deviation in Adiabatic Compressibility, and Excess Free Length

Mole fraction X_1	Velocity (U) ms^{-1}	Density (ρ) Kgm^{-3}	Ad. Comp. βad ×10^{-10} m^2N^{-1}	Mol.Vol. V $10^{-6}m^3$ mol^{-1}	Int Mol. Free Length L_f 10^{-10}m	V^E $10^{-6}m^3$ mol^{-1}	$\Delta\beta_{ad}$ ×10^{-10} m^2N^{-1}	L_f^E 10^{-10}m
303.15K								
0.0000	1438.0	931.8	22.192	93.496	0.935	0.000	0.000	0.000
0.0634	1428.6	944.6	21.605	97.130	0.922	-0.165	-0.168	-0.003
0.1322	1418.1	958.1	20.989	101.009	0.909	-0.407	-0.330	-0.006
0.2071	1406.9	972.6	20.352	105.135	0.895	-0.767	-0.473	-0.008
0.2889	1394.4	986.4	19.712	109.723	0.881	-1.079	-0.573	-0.010
0.3787	1380.4	999.0	19.075	114.903	0.867	-1.275	-0.618	-0.011
0.4776	1364.8	1009.9	18.443	120.808	0.852	-1.295	-0.597	-0.010
0.5872	1346.9	1019.9	17.788	127.479	0.837	-1.185	-0.529	-0.009
0.7091	1326.5	1028.6	17.107	135.065	0.821	-0.905	-0.405	-0.007
0.8458	1302.8	1036.5	16.374	143.657	0.803	-0.499	-0.236	-0.004
1.0000	1276.0	1044.2	15.593	153.390	0.784	0.000	0.000	0.000
308.15K								
0.0000	1426.0	927.6	21.922	93.920	0.929	0.000	0.000	0.000
0.0634	1416.4	940.9	21.323	97.521	0.916	-0.227	-0.189	-0.003
0.1322	1406.1	954.6	20.712	101.386	0.903	-0.515	-0.356	-0.006
0.2071	1394.9	968.8	20.083	105.538	0.889	-0.883	-0.502	-0.009
0.2889	1382.7	982.5	19.458	110.150	0.875	-1.210	-0.599	-0.011
0.3787	1369.2	994.7	18.846	115.391	0.862	-1.386	-0.631	-0.011
0.4776	1353.8	1005.8	18.222	121.308	0.847	-1.440	-0.617	-0.011
0.5872	1336.3	1015.3	17.587	128.050	0.832	-1.309	-0.544	-0.010
0.7091	1316.3	1023.8	16.924	135.700	0.816	-1.022	-0.420	-0.007
0.8458	1293.2	1031.6	16.212	144.350	0.799	-0.620	-0.250	-0.004
1.0000	1267.2	1038.2	15.467	154.277	0.781	0.000	0.000	0.000
313.15K								
0.0000	1404.0	923.2	21.352	94.367	0.917	0.000	0.000	0.000
0.0634	1395.0	937.3	20.761	97.889	0.904	-0.322	-0.189	-0.004
0.1322	1385.3	951.2	20.174	101.741	0.891	-0.639	-0.356	-0.007
0.2071	1374.8	965.1	19.584	105.948	0.878	-0.971	-0.502	-0.009
0.2889	1363.4	978.9	18.990	110.565	0.865	-1.311	-0.599	-0.011
0.3787	1350.7	991.3	18.404	115.789	0.851	-1.526	-0.631	-0.012
0.4776	1336.5	1002.2	17.823	121.738	0.838	-1.571	-0.617	-0.012
0.5872	1320.2	1011.7	17.227	128.503	0.824	-1.444	-0.544	-0.010
0.7091	1301.5	1020.0	16.607	136.201	0.809	-1.138	-0.420	-0.008
0.8458	1280.0	1027.5	15.945	144.918	0.792	-0.702	-0.250	-0.005
1.0000	1256.0	1033.6	15.263	154.963	0.775	0.000	0.000	0.000
318.15K								
0.0000	1384.0	918.6	20.852	94.840	0.906	0.000	0.000	0.000
0.0634	1375.4	933.4	20.268	98.305	0.893	-0.372	-0.204	-0.003
0.1322	1366.1	947.6	19.695	102.135	0.881	-0.703	-0.372	-0.006
0.2071	1356.1	962.4	19.109	106.250	0.868	-1.118	-0.507	-0.009
0.2889	1345.2	976.0	18.541	110.889	0.855	-1.427	-0.602	-0.011
0.3787	1333.3	988.3	17.987	116.141	0.842	-1.605	-0.642	-0.011
0.4776	1319.9	999.5	17.430	122.071	0.829	-1.657	-0.621	-0.011
0.5872	1304.5	1009.5	16.858	128.795	0.815	-1.559	-0.550	-0.010
0.7091	1286.7	1017.9	16.266	136.486	0.800	-1.246	-0.427	-0.007
0.8458	1266.5	1025.3	15.644	145.229	0.785	-0.769	-0.256	-0.004
1.0000	1244.0	1031.2	15.007	155.324	0.769	0.000	0.000	0.000

It is also possible that addition of DEM to the FA may induce the mutual dissociation of hydrogen-bonded structures among the FA molecules and subsequent formation of new hydrogen bonds (>C=O:········HN<) between lone pair of electrons of proton acceptor oxygen atom of >C=O group of DEM and proton of >N−H group of FA. Thus, the formation of the hydrogen bonding phenomenon is more pronounced which is substantiated by the considerable contraction in volume producing negative values of V^E in the studied liquid binaries[20]. Diagram underneath shows the existence of H-bond formation between DEM and FA molecule.



Hydrogen bonding in DEM+FA mixture

The obtained values of molar volumes for DEM, FA, DMF, DMA are 153.390, 40.057, 77.813, and 93.496,10^{-6} $m^3·mol^{-1}$ respectively at 303.15 K. From these values we can assume that fitting of smaller molecules into the voids created by the bigger molecules is most favorable in (DEM+FA) rather than (DEM+DMF) and (DEM+DMA) liquid binaries.

From the Tables-2, 4 and 6 the minima of excess molar volumes for the binary mixtures at 303.15 K is as follows: For DEM + FA (V^E= -6.453 x10^{-6} m^3 mol^{-1} at X_1=0.5109), for DEM + DMF (V^E= -1.951 x 10^{-6} m^3 mol^{-1} at X_1=0.4321) and for DEM + DMA it is found to be(V^E = -1.295 x 10^{-6} m^3 mol^{-1} at X_1= 0.4776). The same type of trend can be observed for all other temperatures also. It is to be noted that the interaction between DEM and amide molecules in the mixtures decreases when more CH_3 groups are present in the amide molecule as evident from a comparison of V^E values.

Thus, hydrogen bonding, the higher dielectric constant and small size of the FA molecules make (DEM+FA) mixture to exhibit stronger interactions when compared with (DEM+DMF) and (DEM+DMA) binaries. Among the DMF and DMA binaries, the less negative values of V^E in the case of (DEM+DMA) mixture may be ascribed due to the bulkiness of three methyl groups in DMA make it less available for interstitial accommodation. The order of magnitude of V^E of DEM+FA, DMF, DMA at minima is as follows:

(DEM + FA) > (DEM + DMF) > (DEM + DMA)

Table -7: System-3 : Diethyl Malonate (X_1) + N, N Dimethylacetamide (X_2) Values of Coefficients and Standard Deviations (σ)

Temp K	A_0	A_1	A_2	A_3	A_4	□
Excess Volume						
303.15K	-1.5982	-1.5982	2.8258	2.8863	-0.3867	0.0202
308.15K	-1.4235	-1.4235	1.7988	2.6948	-0.0900	0.0151
313.15K	-1.6446	-1.6446	3.8072	3.0083	-4.3952	0.0208
318.15K	-1.0135	-1.0135	0.4862	0.9430	0.4266	0.0255
Deviation in Adiabatic Compressibility						
303.15K	-1.0888	-1.0888	-0.0741	0.6230	0.2151	0.0027
308.15K	-1.0350	-1.0350	-0.4512	0.3268	0.4343	0.0044
313.15K	-1.1317	-1.1317	0.0276	0.4981	-0.5864	0.0037
318.15K	-1.0459	-1.0459	-0.6015	0.1410	0.2954	0.0045
Excess Inter Molecular Free Length						
303.15K	-0.0216	-0.0216	0.0006	0.0144	0.0033	0.0001
308.15K	-0.0204	-0.0204	-0.0081	0.0082	0.0087	0.0001
313.15K	-0.0228	-0.0228	0.0024	0.0123	-0.0138	0.0001
318.15K	-0.0210	-0.0210	-0.0121	0.0044	0.0064	0.0001

Further, as the temperature increases from 303.15 K to 308.15 K, the magnitude of V^E values also increases, this tendency can be explained as with the increase of temperature, the strength of interaction among the liquid components also increases. Rastogi *et al.*[21] reported that, as temperature increases, thermal energy activates the molecule, this would increase the rate of association of unlike molecules[22]. A similar interpretation is observed by G.V. Ramarao[23].V^E values decreases (become more negative) with increase in temperature of the mixture, specify that the expansion in volume due to increase in temperature of the system seems to be dominated by more favorable fitting of smaller molecules into the voids of bigger aggregating molecules at higher temperatures leading to a contraction in volume, hence resulting in more negative values of V^E with rising in temperature[24,25].
The strength of strong interaction with temperature is in the order:

318.15>315.15>308.15>303.15) K

Deviations in Adiabatic Compressibility
In the present system DEM + FA, DEM + DMF, DEM + DMA, the deviations in adiabatic compressibility are represented in Fig.-2. The deviations in excess adiabatic compressibility are negative over the entire composition range at all the experimental temperatures and atmospheric pressure. The deviation in adiabatic compressibility can be explained by taking into consideration of the following factors.[26]

a. Loss of dipolar association
b. the difference in size and shape of component molecules which lead to a decrease in velocity and increase incompressibility
c. Breaking up of hydrogen bonding
d. Dipole-dipole interaction or
e. Hydrogen bonded association
f. Complex formation between unlike molecules

Table-8: FTIR Stretching Frequencies for the Binary Mixtures of DEM + Amides

DEM + FA

X_1	C=O(st)	$\Delta\upsilon$	N-H(st)
0.0	-		3342.7
0.5	1715.45	14.86	3300.5
1.0	1730.31		-

Table-9; FTIR Stretching Frequencies for the Binary Mixtures of DEM + Amides

DEM+DMF

X_1	C=O (st)	$\Delta\upsilon$	
0.0	-	-	
0.5	1723.25	7.06	
1.0	1730.31	-	

DEM+DMA

X_1	C=O (st)	$\Delta\upsilon$	
0.0	-	-	
0.5	1727.35	2.96	
1.0	1730.31	-	

The first three factors influence the increase in free length hence increase in the interspace between the molecules consequently sound waves travel longer distances in mixtures than in pure components resulting in the positive deviations in adiabatic compressibility and the other three factors constitute the decrease in free length, hence decrease in interspace between the molecules in mixtures; consequently, sound waves travel smaller distances in mixture than in pure components, this would result in the negative deviations in the adiabatic compressibility.
In general sign and magnitude of ($\Delta\beta_{ad}$) depends on two factors (i) increase in free length, due to loss of dipolar association, breaking up of hydrogen bonding[27] and difference in size and shapes of the molecules

and (ii) decrease in free length as a result of dipole-dipole interactions, hydrogen bonding association and complex formation between the component molecules. According to Fort and Moore[28], negative excess compressibility is an indication of strong hetero molecular interaction in the liquid mixture, while a positive sign indicates weak interaction and is attributed to dispersion forces (London forces).

Figure-2 illustrates that $\Delta\beta_{ad}$ values are negative over the entire mole fraction of DEM at all temperatures and the absolute value of $\Delta\beta_{ad}$ increases linearly with the increase of temperature. The negative sign in deviation of adiabatic compressibility values of mixture indicates that the mixture is less compressible than that of pure liquids. Interstitial accommodation of FA into the voids of DEM is most favorable in (DEM+FA), rather than (DEM+DMF) and (DEM+DMA), which leads to the molecular aggregation and thus the more compact structure in binary mixtures. Dipole-dipole interactions, the formation of acid-base complexes and H-bonding (in DEM+FA) among the components of DEM and FA/DMF/DMA in the binary mixture lead to an increase in sound velocity and negative deviation incompressibility is observed. Thus, based on the magnitude of negative values in $\Delta\beta_{ad}$, the order of the interaction in the amides under investigation with DEM is as follows:

(DEM+FA) > (DEM+DMF) > (DEM+DMA)

At any particular concentration, negative values of adiabatic compressibility increase with the increase in temperature. The negative $\Delta\beta_{ad}$ values indicate a closer approach of unlike molecules and hence stronger interaction between components of mixtures at all temperatures.

Thus $\Delta\beta_{ad}$ also supports the occurrence of strong specific interaction in the binary mixtures of DEM+FA, DMF and DMA and the negative values of Δβad increases with temperature, which suggests the increase of specific interactions with enhanced thermal energy of molecules.[29] Hence, values of $\Delta\beta_{ad}$ are observed to follow the trend: (318.15 > 313.15 > 308.15 > 303.15) K. This supports the inference drawn from V^E.

Excess Intermolecular Free Length (L_f^E)

The deviations in intermolecular free length for the systems DEM+FA, DEM+DMF and DEM+DMA are presented in Fig.-3. The L_f^E values are found to be negative in all compositions at all temperatures. The intermolecular free length is the distance between the surfaces of the neighboring molecules. The sign and magnitude of the observed values of L_f^E are found to depend on several physical and chemical contributions. The physical contributions comprise the dispersion forces and non-specific physical weak interactions that lead to positive values in L_f^E. Chemical contributions involve breaking up of hydrogen-bonded structures if any, resulting in positive L_f^E values and specific interactions such as the formation of new hydrogen bonds, charge transfer complex formation and strong dipole-dipole interaction between component molecules result in negative L_f^E values, making the system more ordered due to increased-intermolecular interaction.[30] The positive deviations of L_f^E are predominant when the breaking of hydrogen-bonded structures occurs. The negative L_f^E values are predominant when charge transfer complex formation and strong dipole-dipole interaction occur. The negative L_f^E values indicate that the sound wave has to travel a longer distance. This may be attributed to the dominant nature of interactions between unlike molecules.

In the present study, the excess intermolecular free length is negative and has the same sign as that of deviation in adiabatic compressibility ($\Delta\beta_{ad}$). The negative L_f^E values for all the systems indicate the existence of strong molecular interaction between the components. The molecular interactions are in the order of:

DEM + FA > DEM + DMF > DEM + DMA

For each of the three systems, the L_f^E values decrease with the increase of temperature from (303.15 to 318.15) K. This may be explained in terms of breaking of complexes with the increase kinetic energy of the molecules, and hence the association between, unlike molecules increases. This causes the lowering of the distance between the unlike molecules.

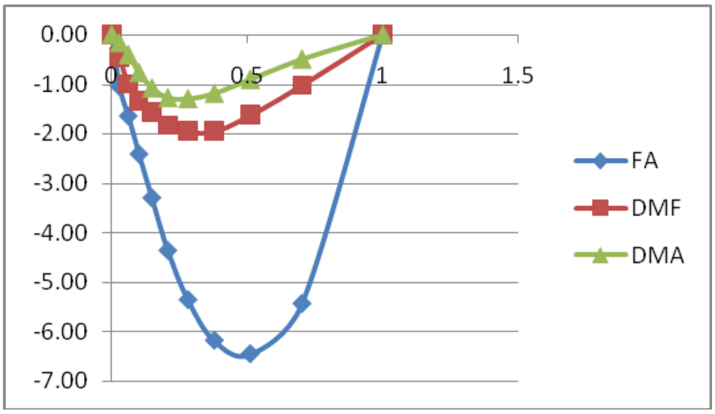


Fig.-1: Variation of Excess Molar Volume with the Mole Fraction of DEM for the System DEM+ FA, DMF and DMA

FT- IR SPECTRAL ANALYSIS

FT-IR Spectroscopy is useful to study the inter and intra molecular hydrogen bonding between the components. We can assess molecular interactions by analyzing band shifts and band shapes.

The FT- IR spectra of pure and binary liquid mixtures of DEM and all solvents (FA, DMF and DMA) are measured over the entire range of composition and spectra are reported for 1:1 composition. The IR frequencies for the above system are shown in the Tables-8 and 9. N-H stretching for pure FA appears at 3314.27cm^{-1}. The N-H stretching for DEM+FA observed is 3300.15cm^{-1}.

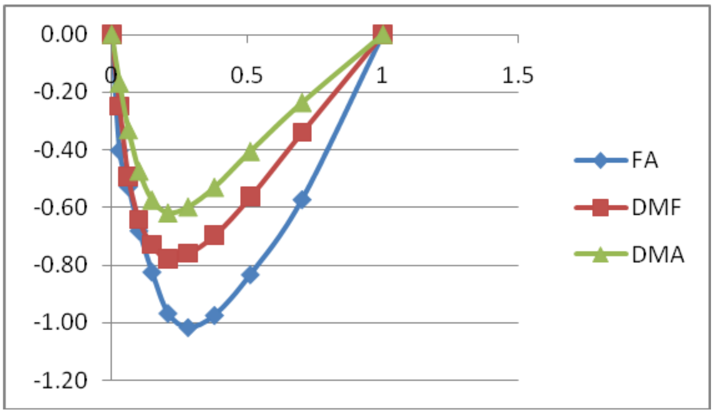


Fig.-2: Variation of Deviation in Adiabatic Compressibility with the Mole Fraction of DEM for the System DEM+FA, DMF and DMA

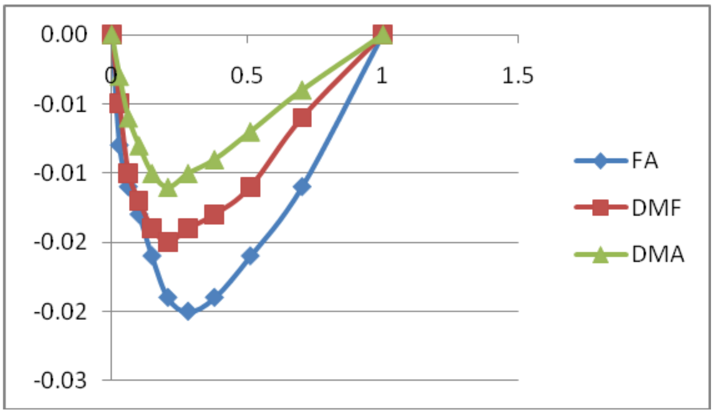


Fig.-3: Variation of Excess Intermolecular Free Length with the Mole Fraction of DEM for the System DEM+ FA, DMF and DMA

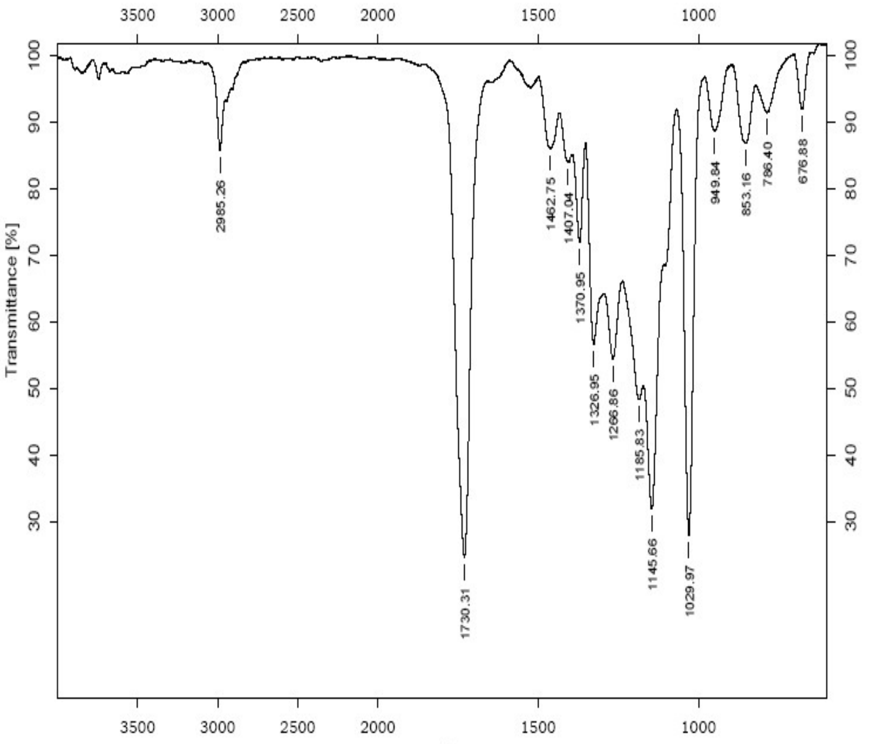


Fig.-4: FT-IR spectrum of DEM (pure)

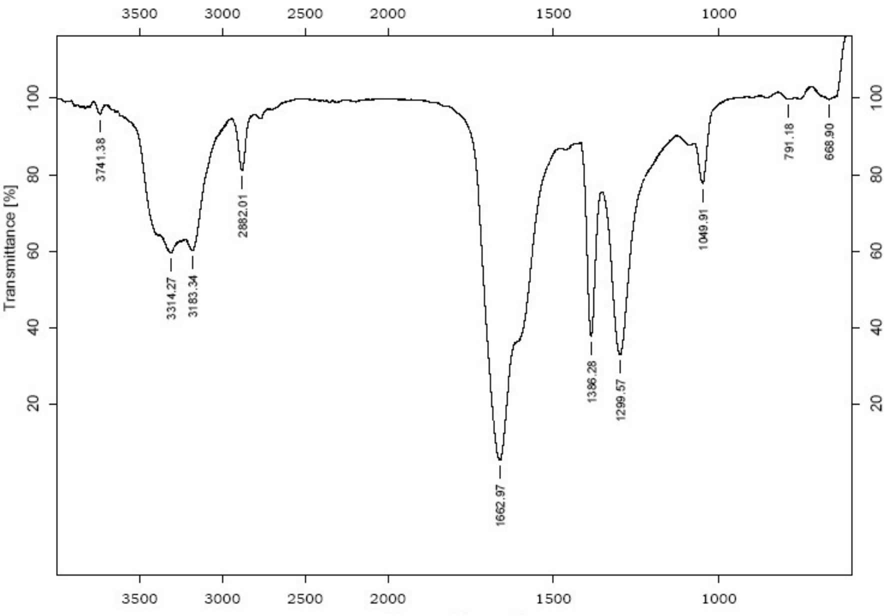


Fig.-5: FT-IR Spectrum of FA (Pure)

The variation in the wave number of these bands may be attributed to the formation of intermolecular hydrogen bonding of the N-H-O involving $-NH_2$ group of formamide and C=O group of DEM. Similar intermolecular hydrogen bonding in alkyl amines and a cyclic amide (NMP) with different solvents are reported by many researchers.[31] In the case of DEM+DMF and DEM+DMA systems, as there is no active hydrogen, the possibility of intermolecular hydrogen bonding may be ruled out. However, the complex formation between DEM + DMF and DEM+DMA is through dipole-dipole interaction. The IR spectrum of pure DEM exhibits a sharp intense band at 1730.3 cm^{-1}. The C=O stretching frequency observed for equimolar mixtures is (1715.45, 1723.25, 1727.35) cm^{-1} respectively. By comparing the experimental FT-IR spectra of the equimolar binary mixtures Figs.-6, 8, and10 with their respective pure compounds Figs.-4, 5, 7 and 9, we can observe significant shifts in the wave numbers. These shifts are caused by strong intermolecular interactions like hydrogen bonding between the oxygen in the C=O group of DEM and hydrogen in N-H group in case of FA, and strong dipole-dipole interactions in case of DEM+DMF and DEM+DMA. Thus, the FT-IR analysis proves intermolecular hydrogen bonding and dipole-dipole interactions in the equimolar binary mixtures in the above systems. From the above (Δυ) values we can substantiate that the strength of the interaction is in the order of:

DEM + FA > DEM + DMF > DEM + DMA

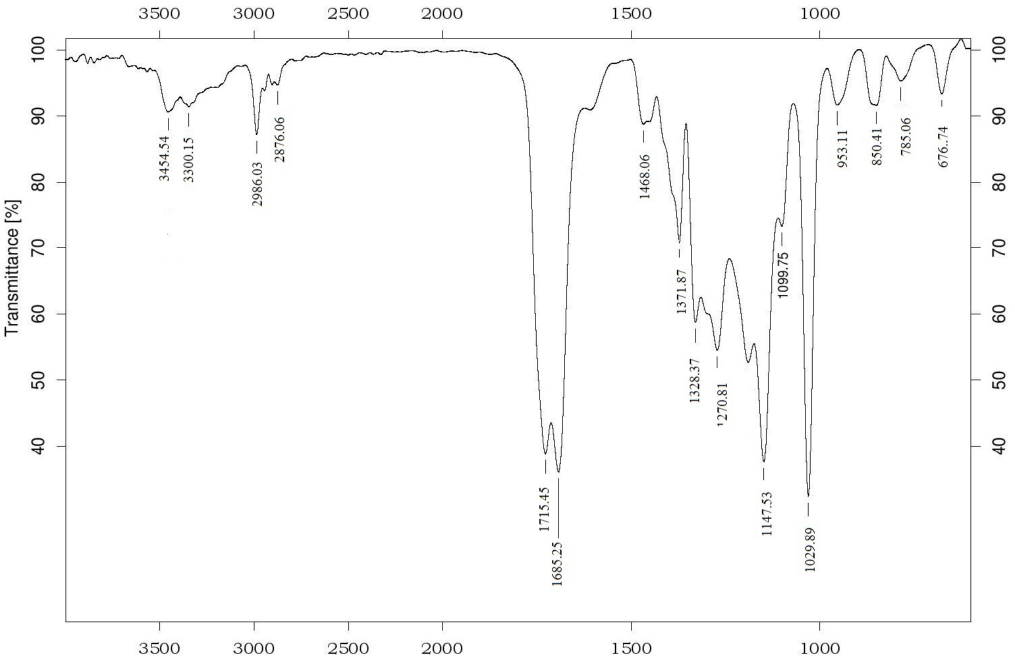


Fig.-6: FT-IR Spectrum of DEM 0.5+FA0.5

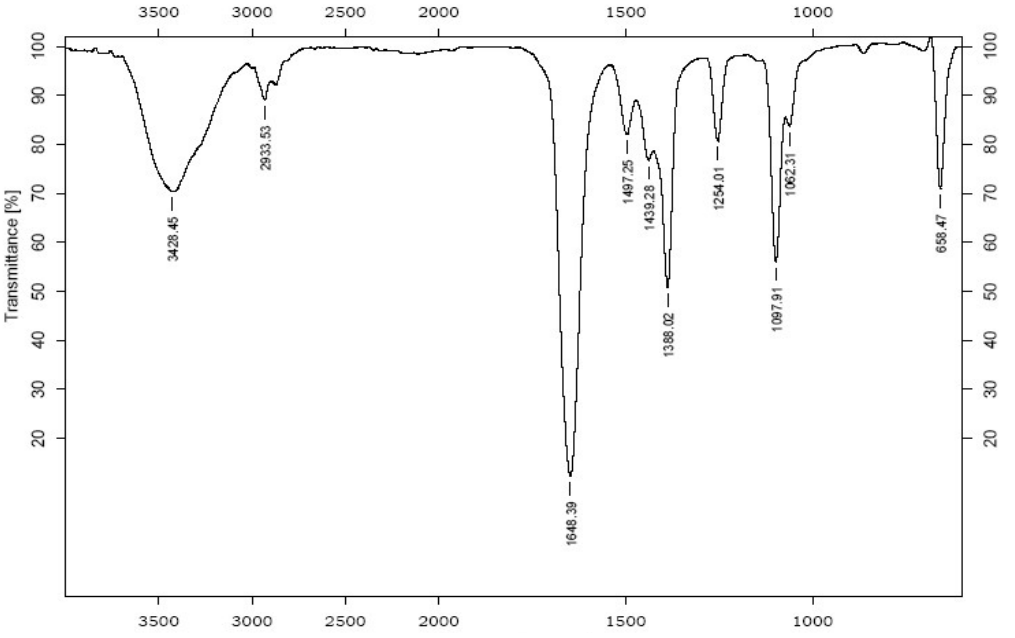


Fig.-7: FT-IR Spectrum of Pure DMF

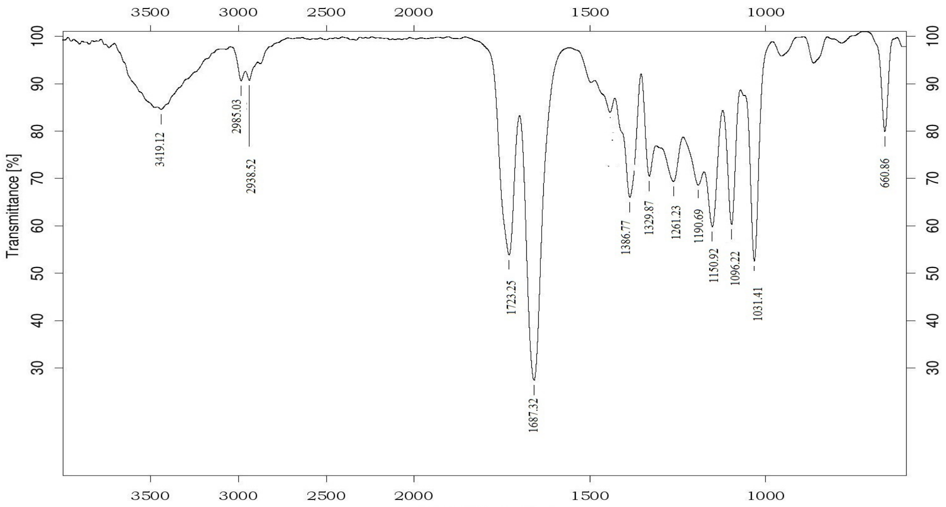


Fig.-8: FT-IR Spectrum of DEM 0.5 +DMF0.5

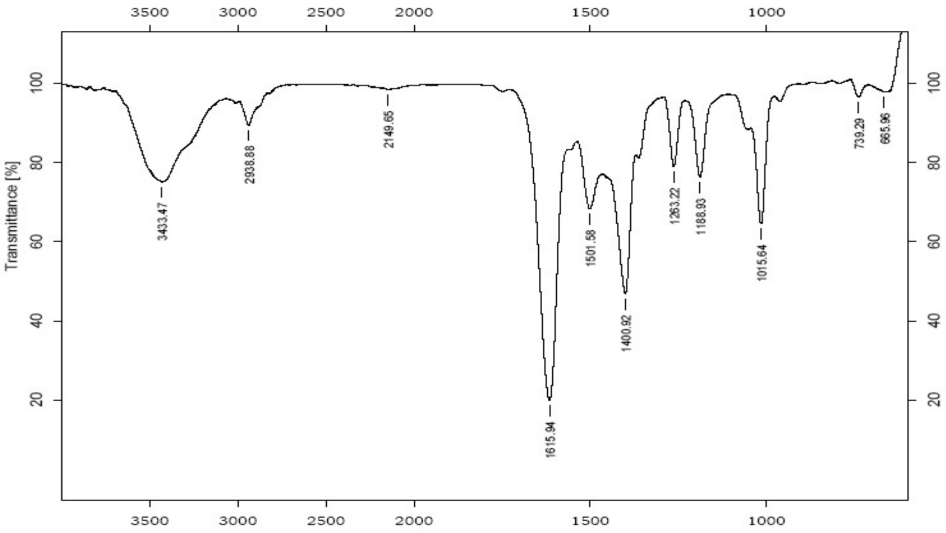


Fig.-9: FT-IR Spectrum of Pure DMA

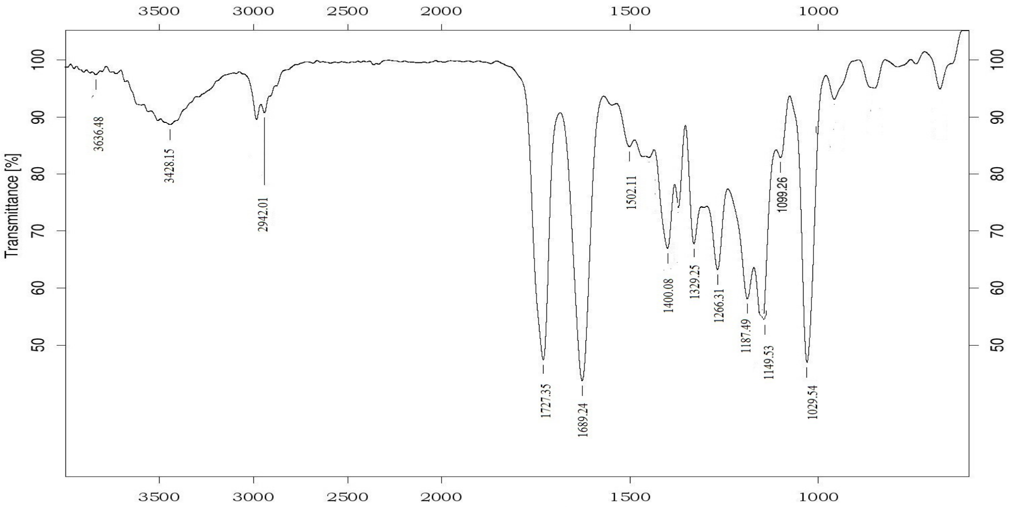


Fig.-10: FT-IR Spectrum of DEM0.5+DMA0.5

CONCLUSION

This paper reports experimental data of velocity and density for the binary mixtures of DEM+ FA/DMF/DMA measured at temperatures from 303.15K to 318.15K over the whole composition range. The excess molar volumes are negative for all the investigated systems, indicating strong intermolecular interactions. The DEM+FA are associated through H- bonding.

Due to the large difference in molar volume, this system shows more interaction. DEM+DMF and DEM+DMA are associated with dipole-dipole interactions due to the lack of hydrogen bonds. Because of the bulkiness of the methyl groups in DMA molecule the interaction in DMA binary is less than that of DMF binary. All the excess functions V^E, $\Delta\beta_{ad}$, L_f^E are negative. All the excess parameters are fitted to the Redlich-Kister polynomial equation. FT-IR spectral analysis gives strong evidence for the molecular association of amides. The specific interaction follows the order:

DEM + FA > DEM + DMF > DEM + DMA

REFERENCES

1. S. K. Mehta and R. K. Chauhan, *Journal of Solution Chemistry*, **26**, 295(1997), **DOI:** 10.1007/BF02768000
2. J. Antonio Gonzalez, Ismael Mozo, Marta Fernandez, Isaias Garcia de la Fuente and Jose Carlos Cobos, *Journal of Molecular Liquids*,**133**,77(2007) , **DOI:**10.1016/j.molliq.2006.07.004
3. E.Tsuchida, O.F.Nielsen, P.A.Lund and E.Praestgaard, *Journal of Chemical Physics,***121**, 4740(2004), **DOI:**10.1063/1.1781612.
4. S. Biswas and B. Mallik, *Journal of Chemical and Engineering Data,* **59(10)**, 3250(2014), **DOI:** 10.1021/je5002544
5. H.S. Byun, N.H. Kim and C. Kwak, *Fluid Phase Equilibria*, **208(1-2),** 53(2003), **DOI:**10.1016/S0378-3812(02)00324-2
6. C.J. Chang and C.Y. Chen, *Journal of Chemical and Engineering Data,* **40(4)**, 850(1995), **DOI:**10.1021/je00020a025
7. Gescher, *Chemical Research in Toxicology*, **6**, 245(1993), **DOI:** 10.1021/tx00033a001
8. W. Wang, H. Liu and Y. Wu, *The Journal of Chemical Thermodynamics,* **36**, 1079(2004) , **DOI:** 10.1016/j.jct.2004.07.010
9. P.S. Nikam, L.N. Shirsat and M. Hasan, *Journal of Indian Chemical Society*, **77**, 244(2000).
10. S. Baluja, Nirmal Pandaya, Nikunj Kachhadia , Asif Solanki and Pranav Inamdar, *Journal of Physics and Chemistry of Liquids,* **43(3),** 309(2005), **DOI:**10.1080/00319100500096940
11. J.G. Baragi, M.I. Aralaguppi, T.M. Aminabhavi, Mahadevappa Y Kariduraganavar and Shrikant S Kulkarni, *Journal of Chemical & Engineering Data*, **50**, 917(2005), **DOI:**10.1021/je049609w.
12. A.K. Nain, *Journal of Molecular Liquids,* **140**,108(2008), **DOI:**10.1016/j.molliq.2008.01.016
13. M. Bhugian and M.H. Uddin, *Journal of Molecular Liquids,* **138**, 139(2008), **DOI:**10.1016/j.molliq.2008.12.003
14. H. Eyring and J.F. Kincaid, *Journal of Chemical Physics,* **6,** 620(1996), **DOI:**10.1063/1.1750078
15. R. Kumar Bhardwaj and Amalendu Pal, *Journal of Molecular Liquids,* **118**, 37(2005), **DOI:** 10.1016/j.molliq.2004.07.007
16. M.N. Roy, A. Sinha and B. Sinha, *Journal of Solution Chemistry*, **34**, 1311(2005), **DOI:** 10.1007/s10953-005-8022-0
17. K. Hsu-Chen and T. Chein-Hsiun, *Journal of Chemical and Engineering Data*, **50(2)**, 608(2005), **DOI:**10.1021/je049655w.
18. H. O. Nam-Tran, *Journal of Physical Chemistry*, **98**, 5362(1994) , **DOI:** 10.1021/j100071a029
19. F. Aroni, A. Kelarakis and V. Havredaki, *Journal of. Colloid and Interface Science*, **292**, 236(2005), **DOI:**10.1016/j.jcis.2005.06.020
20. S. Sharma, P. Patel and Bhalodia, *Journal of Physics and Chemistry of Liquids*, **54**, 42(2016), **DOI:** 10.1080/00319104.2015.1068661.

21. M. Rastogi, A. Awasthi, M. Gupta and J.P. Shukla, *Indian Journal of Pure and Applied Physics*, **40(4),** 256(2002).
22. J.G. Baragi, V.K. Mutalik and S.B. Mekali, *Intenational Journal of Pharmacy and Biological Science*, **3**, 185(2013).
23. G.V. Rama Rao, A. Viswanatha Sarma and C. Rambabu, *Indian Journal of Chemistry*, **43A**,752(2004)
24. M.N.M. Al – Hayanand M.A.M. Al –Bader, *Journal of Chemical Thermodynamics,* **38**, 1100(2006) , **DOI:** 10.1016/j.jct.2005.11.012
25. S.L.Oswal and N.B.Patel, *Journal of Chemical and Engineering Data*, **40(4),** 845(1995) , **DOI:** 10.1021/je00020a024
26. B.Nagarjun, A.V.Sarma,G.V.Ramarao and C.Rambabu, *Journal of Thermodynamics,* 2013 Art ID 285796, **DOI:**10.1155/2013/285796.
27. L.R.O. Storey, *Proceedings of the Physical Society, Section B,* **65B**, 943(1952) , **DOI:**10.1088/0370-1301/65/12/303
28. R.J. Fort and W.R. Moore, *Journal of Transactions of the Faraday Soc*iety, **61**, 2102(1965), **DOI:**10.1039/TF9656102102
29. F. Comelli, S. Ottani, R. Francesconi and C. Castellari., *Journal of Chemical Engineering Data,* **47 (1)**, 93(2002), **DOI:**10.1021/je010216w
30. A.Ali and A.K Nain, *Pramana- Journal of Physics*, **58(4)**, 695(2002), **DOI:**10.1007/s12043-002-0026-3
31. S.K. Mehta, G. Ram, C. Rajat, K.K. Bhasin, *The journal of Chemical Thermodynamics,* **41(12),** 1329 (2009), **DOI:**10.1016/j.jct.2009.06.006

[RJC-5595/2019]