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Study of ultrasonic, volumetric and transport properties of Anisic aldehyde - acetate mixtures at different temperatures

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ABSTRACT

Densities, viscosities and ultrasonic velocities have been measured for the binary mixtures of anisic aldehyde with methyl acetate, ethyl acetate and n- butyl acetate over the entire composition range at 303.15,308.15,313.15 and 318.15K .The excess values were correlated using Redlich – Kister polynomial equation. The excess values were examined in order to have an insight into the inter molecular interactions among the components of the binary mixtures that lead to the possible dipole- dipole interactions or hydrogen bond formation between unlike molecules. Excess molar volumes, deviation in adiabatic compressibilities, deviation in viscosity and excess free length are negative in the whole composition range for all the systems at all temperatures.

Introduction

The excess thermodynamic properties of binary liquid mixtures are very important to understand the properties and interactions of different molecules. The interactions in terms of these parameters are of interest to a wide range of disciplines ranging from oceanography, geology, mechanical engineering and to fundamental chemistry and physics [1, 2]. Thermodynamic data of binary mixtures find extensive application in solution theory and molecular dynamics. [3]

Systematic studies of the thermodynamic behaviour of physical properties of aldehydes in their binary liquid mixtures have been performed [4]. Para anisic aldehyde is chemically known as 4- methoxy benzaldehyde and used in perfumery to create fruity and roast characteristics.

Anisic aldehyde is used in the synthesis of other organic compounds including pharmaceuticals especially antihistamines, agro chemical, dyes and plastic additives. It is an important intermediate for the processing of perfumes and flavoury compounds.

Acoustical and viscosity data of liquid mixtures of esters find extensive applications as they provide better insight into molecular environments. Having wide usage in flavouring perfumery, artificial essences and cosmetics esters become one of the industrially important classes of liquids. The volume of mixing data of binary mixtures consisting of esters is useful in the petrochemical industries. In the recent years, a few attempts have been made to study the various thermodynamic and transport properties for the binary mixtures of esters [5,6]. We are not aware of much data in the earlier literature on such mixtures of this study and hence we made an attempt to present the data on U, ρ,η to compute excess molar volume, V^E Deviation in adiabatic compressibility ,Δβad, Deviation in viscosity , Δη,Excess intermolecular free length, L_f^E of anisic aldehyde + methyl acetate, anisic aldehyde + ethyl acetate and anisic aldehyde + n-butyl acetate over the entire range of composition at the temperatures 303.15,308.15,313.15 and 318.15K.

Materials and methods

Anisic aldehyde, methyl acetate, ethyl acetate and n- butyl acetate from Merck were purified as described in the literature [7,8]. The purity of the samples were checked by comparing the measured densities with those reported in the literature [9,5] and these are given in Table 1.

The density was measured with a pycnometer having a bulb volume of about 25 cm^3 and an internal capillary diameter of about 1 mm. The density was then determined from the mass of the sample and the volume of pycnometer is used to determine the density. Uncertainties in density measurements were estimated to be within ± 0.0001 g cm^{-3}

The viscosity was measured using a commercial Ubbelohde capillary viscometer of 0.55 mm diameter calibrated with double distilled water at temperatures of 303.15, 308.15, 313.15 and 318.15K.

Table 1: Comparison of experimental densities (ρ), viscosities (η) and speeds of sound (u) of pure components with available literature at 303.15 K

Compound	Density		Viscosity		Velocity	
	Lit	Expt	Lit	Expt	Lit	Expt
Anisic Aldehyde	1.120[a]	1.1204	3.5783[a]	3.5783	1542[a]	1543.50
Methyl Acetate	0.9219[b]	0.9201	0.368[b]	0.3514	1106[b]	1106.50
Ethyl Acetate	0.8884[b]	0.8884	0.410[b]	0.3995	1122[b]	1122.80
n- butyl acetate	0.8712[b]	0.8695	0.624[b]	0.6407	1176[b]	1176.40

Ref a → [10]

Ref b → [11]

Theoretical considerations

Assuming that ultrasonic absorption is negligible, adiabatic compressibilities can be obtained from the densities and ultrasonic sound velocities using the relation

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$\beta_{ad} = (\rho u^2)^{-1}$ …….. (2)

The molar volumes of the binary mixtures were calculated using the equation

$V = (X_1M_1+X_2M_2) / \rho$ …….. (3)

Intermolecular free length (L_f) has been evaluated by Jacobson's formula [15]

$L_f = K/ u\rho^{1/2}$ …… (4)

where K is the temperature dependent Jacobson constant and T is the absolute temperature.

The strength of interaction between the component molecules of binary mixtures is well reflected in the deviation of the excess functions from ideality. Thermodynamic excess functions are found to be very sensitive towards mutual interactions between component molecules of liquid mixtures. The sign and extent of deviation of these functions from ideality depends on the strength of interaction between unlike molecules.

The excess properties such as $\Delta\beta_{ad}$,, V^E , $\Delta\eta$ and L_f^E have been calculated using the equation

$Y^E = Y_{mix} - (X_1Y_1+X_2Y_2)$ ……. (5)

where Y^E is $\Delta\beta_{ad}$ or V^E or $\Delta\eta$ or L_f^E, and X represent mole fraction of the component and subscripts 1 and 2 stand for the components1and 2. These excess functions were fitted to Redlich - Kister type polynomial equation [12].

$Y_{cal}^E = X_1 X_2 \Sigma a_{j-1} (X_2-X_1)^{j-1}$ ….. (6)

The values of coefficient a_{j-1} evaluated by the method of least squares with all points weighed equally with the standard deviations are listed in Table 3 and are calculated as

$\sigma (Y^E) = (Y_{ob}^E - Y_{cal}^E)/ (m-n))$ ½ ….. (7)

where m is the number of experimental data points and n is the number of coefficients considered (n = 5 in the present calculation.)

Results and Discussion

The values of density (ρ), ultrasonic velocity (u) and viscosity (η) along with the excess properties for anisic aldehyde with methyl acetate, ethyl acetate and n- butyl acetate from temperatures 303.15 to 318.15K are summarized in Table 2, 3 and 4. The values of the parameters a_0, a_1, a_2, a_3, a_4 obtained following the least square analysis, are included in Table 5 along with standard deviation.

The variation of excess volume (V^E) with the mole fraction of anisic aldehyde for all three systems studied at all the temperatures are graphically shown in the Figures 2,6, and 10. The factors that are mainly responsible for the volume expansion i.e., positive values V^E are:

i) Chemical interaction between constituent molecules such as hetero-molecular association through the formation of H-bond, often termed as strong specific interaction.

(ii) Association through weaker physical forces such as dipolar force or any other forces of this kind.

(iii) Accommodation of molecules of one component into the interstitial positions of the structural network of molecules of the other component.

The strength of unlike molecular interactions in the solution is better estimated by the sign and magnitude of V^E. The values of V^E are negative for all the three systems. However, it is observed that the methyl acetate shows considerable larger negative V^E values compared to other esters. This observation supports the interstitial accommodation of methyl acetate molecules due to the smaller size in dipolar network of the anisic aldehyde . The fact that V^E values become more negative with the temperature further supports the interstitial accommodation of methyl acetate molecules [13].

The algebraic values of V^E of anisic aldehyde with aliphatic esters fall in the order at 303.15K.

methyl acetate > ethyl Acetate > butyl acetate

The factors which contribute for the expansion in volume include the dissociation of molecular aggregates or dipolar molecules due to the addition of second type of molecule and dispersion forces between unlike molecules.

However the sign of V^E of a system depends upon the relative magnitude of expansion and contraction of the two liquids due to mixing. Same results were observed by earlier workers [14].

The closure packing of molecules due to the hydrogen bond formation and / dipole – dipole interactions between hetero molecules is found to have greater influence on over all compressibility of the system. The deviation in adiabatic compressibility can be explained by taking into consideration the following factors.

a) Loss of dipolar association and difference in size and shape of component molecules which lead to decrease in velocity and increase in compressibility.

b) Dipole-Dipole interaction or hydrogen bonded complex formation between unlike molecules which lead to increase in sound velocity and decrease of compressibility.

The actual deviation depends on the resultant effect. From the Figs, 1, 5 and 9 deviation in adiabatic compressibilities are found to be negative over the mole fraction of anisic aldehyde for three studied systems

Fig. 1. Plots of deviation in adiabatic compressbility against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+MA) systems

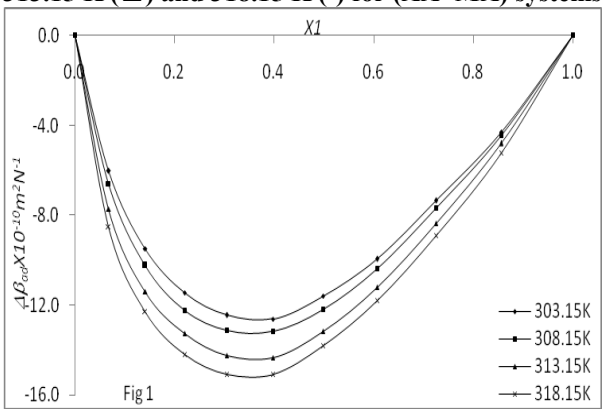


Fig. 2. Plots of excess molar volume against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+MA) systems

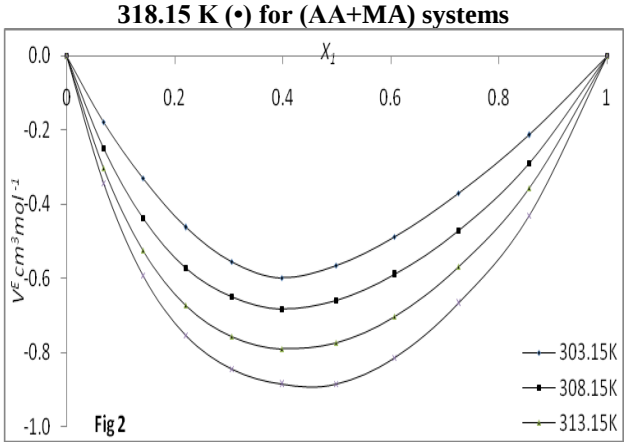


Fig. 3. Plots of deviation in deviation in viscosity gainst mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+MA) systems

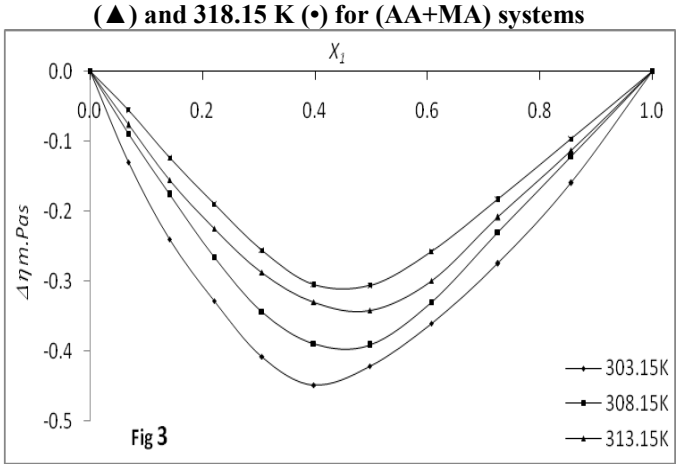


Fig. 4. Plots excess intermolecular free length against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+MA) systems

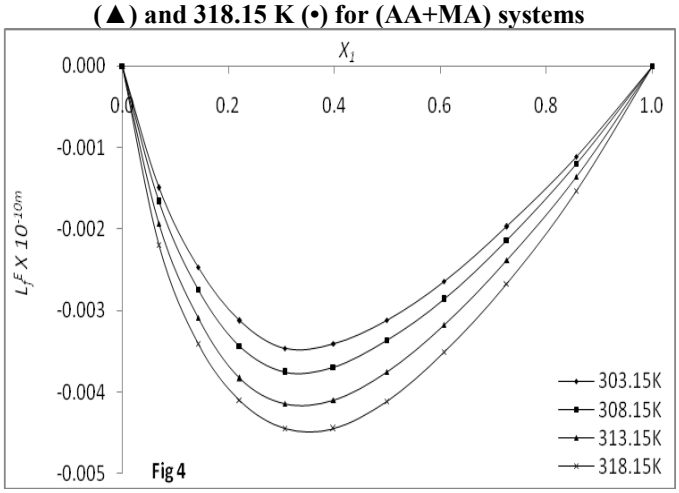
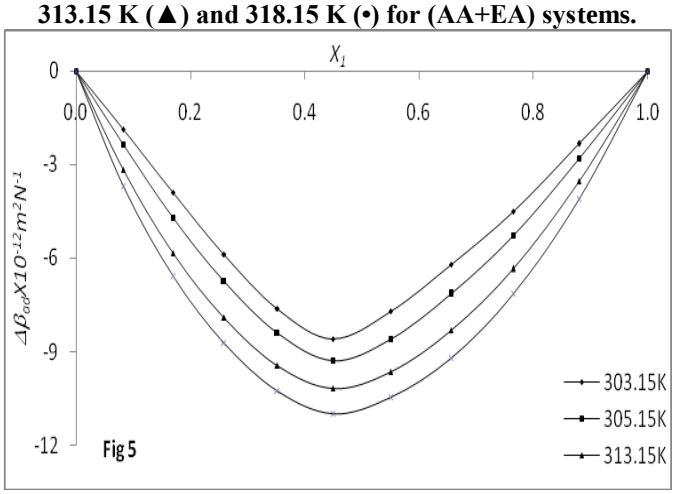


Fig. 5. Plots of deviation in adiabatic compressbility, against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+EA) systems.



The $\Delta\beta_{ad}$ values are negative over the whole composition range for all mixtures and become more negative at higher temperatures. It can be pointed out that the influence of the structure of the homologous series of esters on the adiabatic compressibility behaviour is very marked. An inspection of Figs. 1,5 and 9 reveals that the $\Delta\beta_{ad}$ values become more negative with decreasing chain length of the ester.

In the present study, the behaviour of V^E and $\Delta\beta_{ad}$ are similar in nature. The sign of $\Delta\beta_{ad}$ supports the postulates used to interpret the sign of excess molar volume. The negative V^E and $\Delta\beta_{ad}$ values may result from dipole – dipole and dipole – induced dipole interactions. [15-18] that enhance the solvent structure in the mixture, in turn making negative contributions to V^E and $\Delta\beta_{ad}$.

Fig. 6. Plots of excess molar volume, against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+EA) systems

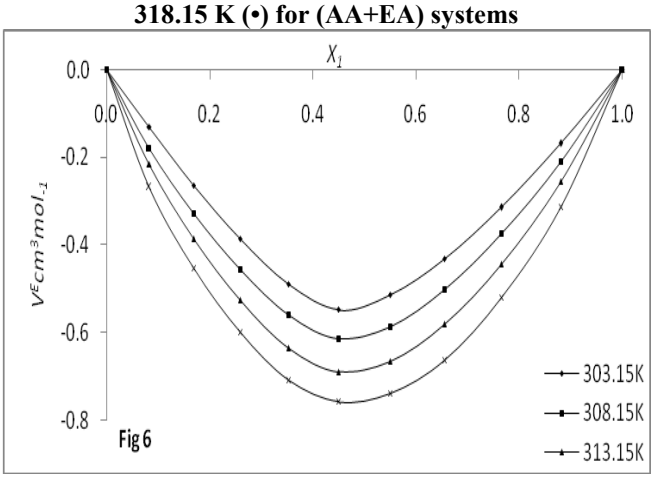


Fig. 7. Plots of deviation in viscosity and against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+EA) systems

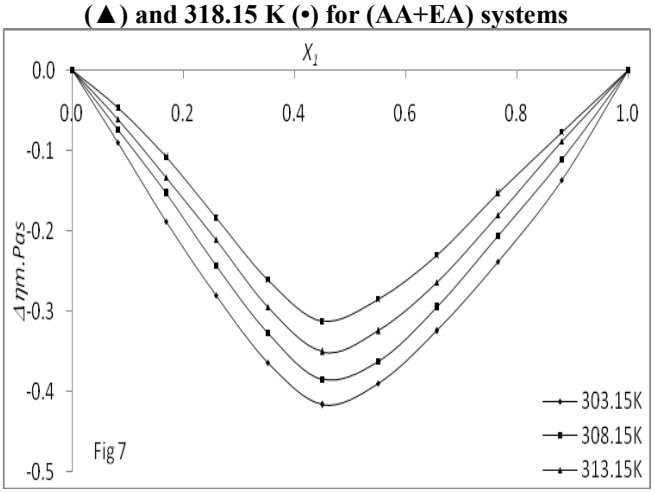


Fig. 8. Plots of excess intermolecular free length against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+EA) systems

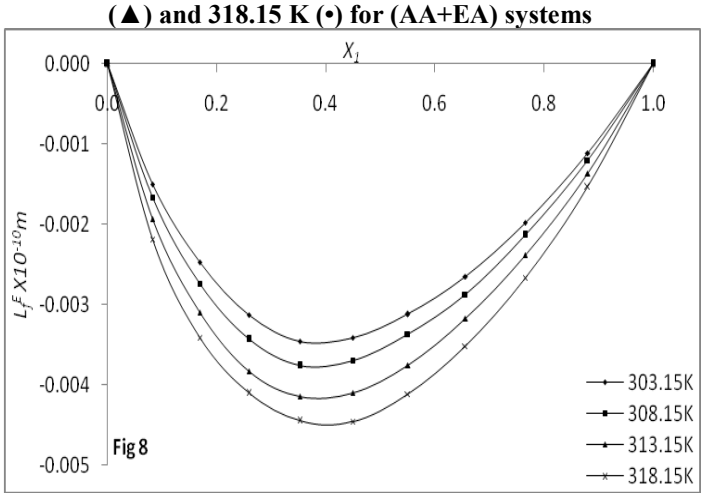


Table 2. Values of ultrasonic velocity (U), density(ρ), viscosity (η), related thermo dynamic parameters and their excess values for anisic aldehyde+ methyl acetate system at different temperatures

Mole fraction X	(U) m/s	ρ x 10^{-3} kg/m^3	η Cp	V_m cm^{-3} mol^{-1}	β_{ad} 10^{12} m^2 N^{-1}	L_f 10^{-10} m	V_m^E cm^{-3} mol^{-1}	β_{ad}^E 10^{12} m^2 N^{-1}	η^E Cp	L_f^E 10^{-10} m
T=303.15K										
0.0000	1106.5	0.9207	0.3514	80.4605	88.7113	0.0591	0.0000	0.0000	0.0000	0.0000
0.0685	1157.0	0.9437	0.4616	83.2742	85.1995	0.0576	-0.2639	-6.0373	-0.1110	-0.0019
0.1420	1200.0	0.9651	0.5799	86.2917	81.4331	0.0561	-0.3988	-9.4774	-0.2300	-0.0029
0.2210	1240.5	0.9858	0.7290	89.5362	77.3835	0.0545	-0.4687	-11.4614	-0.3360	-0.0036
0.3062	1281.0	1.0061	0.9292	93.0342	73.0175	0.0527	-0.5137	-12.4492	-0.4100	-0.0039
0.3984	1322.7	1.0263	1.1963	96.8166	68.2964	0.0508	-0.5424	-12.6031	-0.4400	-0.0040
0.4983	1361.5	1.0461	1.5365	100.9196	63.1753	0.0488	-0.5388	-11.6100	-0.4230	-0.0037
0.6071	1403.6	1.0653	1.9457	105.3858	57.6008	0.0465	-0.4798	-9.9550	-0.3640	-0.0032
0.7259	1445.4	1.0840	2.4150	110.2655	51.5101	0.0440	-0.3622	-7.3545	-0.2780	-0.0024
0.8563	1496.1	1.1025	2.9550	115.6191	44.8280	0.0413	-0.2153	-4.3035	-0.1590	-0.0014
1.0000	1543.5	1.1204	3.5777	121.5191	37.4640	0.0384	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	1099.6	0.9165	0.3504	80.8292	90.2398	0.0600	0.0000	0.0000	0.0000	0.0000
0.0685	1152.5	0.9396	0.4495	83.6662	86.7294	0.0586	-0.2944	-6.6004	-0.0850	-0.0021
0.1420	1195.9	0.9615	0.5542	86.7088	82.9646	0.0571	-0.4978	-10.2465	-0.1770	-0.0032
0.2210	1235.2	0.9826	0.6842	89.9802	78.9168	0.0554	-0.6215	-12.2147	-0.2600	-0.0039
0.3062	1274.0	1.0028	0.8447	93.5071	74.5526	0.0537	-0.6779	-13.1126	-0.3280	-0.0042
0.3984	1313.5	1.0224	1.0649	97.3209	69.8336	0.0518	-0.6828	-13.1439	-0.3550	-0.0043
0.4983	1352.0	1.0417	1.3442	101.4579	64.7146	0.0498	-0.6493	-12.2000	-0.3440	-0.0040
0.6071	1390.6	1.0605	1.6887	105.9611	59.1425	0.0475	-0.5787	-10.3777	-0.2910	-0.0034
0.7259	1429.0	1.0789	2.1000	110.8813	53.0544	0.0451	-0.4546	-7.6643	-0.1990	-0.0025
0.8563	1475.2	1.0965	2.5489	116.2793	46.3751	0.0424	-0.2493	-4.4691	-0.1000	-0.0015
1.0000	1516.9	1.1139	3.0347	122.2282	39.0142	0.0394	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	1090.5	0.9090	0.3351	81.4961	92.5092	0.0612	0.0000	0.0000	0.0000	0.0000
0.0685	1149.7	0.9322	0.4270	84.3419	88.8880	0.0597	-0.3111	-7.7318	-0.0670	-0.0024
0.1420	1193.2	0.9543	0.5220	87.3939	85.0044	0.0582	-0.5289	-11.4087	-0.1420	-0.0036
0.2210	1231.5	0.9756	0.6350	90.6754	80.8287	0.0565	-0.6794	-13.2423	-0.2120	-0.0042
0.3062	1271.4	0.9961	0.7712	94.2133	76.3268	0.0547	-0.7607	-14.2200	-0.2720	-0.0046
0.3984	1312.4	1.0161	0.9433	98.0389	71.4588	0.0528	-0.7983	-14.3200	-0.3140	-0.0047
0.4983	1349.8	1.0356	1.1712	102.1888	66.1782	0.0506	-0.7897	-13.1791	-0.3170	-0.0043
0.6071	1388.3	1.0544	1.4650	106.7059	60.4303	0.0484	-0.7084	-11.2182	-0.2750	-0.0037
0.7259	1426.8	1.0727	1.8310	111.6414	54.1500	0.0458	-0.5782	-8.3574	-0.1840	-0.0028
0.8563	1470.0	1.0902	2.2204	117.0561	47.2599	0.0431	-0.3520	-4.8117	-0.0960	-0.0017
1.0000	1509.3	1.1067	2.6489	123.0234	39.6666	0.0401	0.0000	0.0000	0.0000	0.0000
318.15K										
0.0000	1084.6	0.8979	0.3165	82.5036	94.6745	0.0623	0.0000	0.0000	0.0000	0.0000
0.0685	1147.0	0.9215	0.3971	85.3356	90.9863	0.0609	-0.3327	-8.5043	-0.0580	-0.0027
0.1420	1190.2	0.9444	0.4865	88.3727	87.0308	0.0593	-0.5971	-12.2820	-0.1170	-0.0039
0.2210	1228.3	0.9661	0.5835	91.6383	82.7778	0.0576	-0.7573	-14.1707	-0.1800	-0.0045
0.3062	1266.9	0.9871	0.7030	95.1590	78.1926	0.0558	-0.8543	-15.0744	-0.2330	-0.0049
0.3984	1306.5	1.0075	0.8515	98.9660	73.2345	0.0538	-0.8953	-15.0863	-0.2710	-0.0050
0.4983	1342.0	1.0274	1.0434	103.0957	67.8561	0.0517	-0.8873	-13.8112	-0.2810	-0.0046
0.6071	1379.6	1.0467	1.2860	107.5908	62.0018	0.0493	-0.8166	-11.8080	-0.2590	-0.0040
0.7259	1417.5	1.0654	1.5916	112.5023	55.6053	0.0468	-0.6781	-8.8919	-0.1940	-0.0030
0.8563	1459.0	1.0831	1.9626	117.8907	48.5876	0.0440	-0.4262	-5.2179	-0.0870	-0.0018
1.0000	1492.1	1.0995	2.3402	123.8290	40.8538	0.0409	0.0000	0.0000	0.0000	0.0000

Table 3. Values of ultrasonic velocity (U), density(ρ), viscosity (η), related thermo dynamic parameters and their excess values for anisic aldehyde+ Ethyl acetate system at different temperatures

Mole fraction X	(U) m/s	ρ x 10^{-3} kg/m^3	η Cp	V_m cm^{-3} mol^{-1}	β_{ad} 10^{12} m^2 N^{-1}	L_f 10^{-10} m	V_m^E cm^{-3} mol^{-1}	β_{ad}^E 10^{12} m^2 N^{-1}	η^E Cp	L_f^E 10^{-10} m
T=303.15K										
0.0000	1122.0	0.8884	0.3995	99.178	89.4140	0.0593	0.0000	0.0000	0.0000	0.0000
0.0832	1170.2	0.9136	0.5600	100.810	79.9287	0.0561	-0.2258	-5.1656	-0.1040	-0.0015
0.1695	1215.1	0.9381	0.7350	102.603	72.1983	0.0533	-0.3617	-8.4116	-0.2030	-0.0025
0.2592	1259.7	0.9622	0.8131	104.516	65.4971	0.0507	-0.4524	-10.4538	-0.4100	-0.0031
0.3524	1303.0	0.9859	1.0410	106.536	59.7388	0.0485	-0.5149	-11.3683	-0.4790	-0.0035
0.4494	1342.5	1.0095	1.3397	108.671	54.9642	0.0465	-0.5474	-11.1032	-0.4880	-0.0034
0.5504	1381.6	1.0326	1.7180	110.936	50.7326	0.0447	-0.5391	-10.0868	-0.4310	-0.0031
0.6557	1421.7	1.0553	2.1192	113.347	46.8841	0.0429	-0.4802	-8.4661	-0.3650	-0.0026
0.7655	1462.3	1.0774	2.5607	115.911	43.4076	0.0413	-0.3702	-6.2377	-0.2720	-0.0020
0.8802	1503.5	1.0992	3.0345	118.628	40.2445	0.0398	-0.2147	-3.4447	-0.1630	-0.0011
1.0000	1543.5	1.1204	3.5783	121.519	37.4649	0.0384	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	1101.5	0.8826	0.3803	99.830	93.3828	0.0610	0.0000	0.0000	0.0000	0.0000
0.0832	1151.5	0.9078	0.4782	101.463	83.0807	0.0576	-0.2281	-5.7800	-0.1230	-0.0017
0.1695	1197.2	0.9323	0.6039	103.238	74.8341	0.0546	-0.3857	-9.3320	-0.2260	-0.0027
0.2592	1241.8	0.9565	0.7714	105.137	67.7996	0.0520	-0.4948	-11.4893	-0.2970	-0.0034
0.3524	1284.5	0.9802	0.8926	107.157	61.8323	0.0497	-0.5619	-12.3860	-0.4230	-0.0038
0.4494	1323.5	1.0036	1.1924	109.306	56.8842	0.0476	-0.5847	-12.0582	-0.3810	-0.0037
0.5504	1361.5	1.0265	1.4817	111.593	52.5528	0.0458	-0.5596	-10.8958	-0.3600	-0.0034
0.6557	1401.2	1.0490	1.8274	114.023	48.5536	0.0440	-0.4871	-9.1695	-0.2930	-0.0029
0.7655	1440.3	1.0711	2.2081	116.594	45.0047	0.0424	-0.3737	-6.7462	-0.2040	-0.0021
0.8802	1479.7	1.0929	2.6056	119.313	41.7908	0.0408	-0.2223	-3.7250	-0.1110	-0.0012
1.0000	1517.1	1.1140	3.0347	122.217	38.9999	0.0394	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	1082.5	0.8759	0.3623	100.594	97.4293	0.0628	0.0000	0.0000	0.0000	0.0000
0.0832	1136.5	0.9011	0.4946	102.213	85.9179	0.0590	-0.2462	-6.7078	-0.0580	-0.0019
0.1695	1184.0	0.9256	0.6187	103.992	77.0706	0.0558	-0.4029	-10.5682	-0.1310	-0.0031
0.2592	1230.1	0.9496	0.7454	105.893	69.5924	0.0531	-0.5133	-12.8656	-0.2090	-0.0038
0.3524	1273.2	0.9734	0.8753	107.909	63.3740	0.0506	-0.5893	-13.6977	-0.2930	-0.0041
0.4494	1314.2	0.9968	1.0408	110.051	58.0852	0.0485	-0.6228	-13.3821	-0.3490	-0.0041
0.5504	1353.9	1.0197	1.2974	112.339	53.4998	0.0465	-0.6006	-12.1318	-0.3230	-0.0037
0.6557	1393.8	1.0421	1.5987	114.783	49.4001	0.0447	-0.5184	-10.1495	-0.2630	-0.0032
0.7655	1434.0	1.0640	1.9334	117.377	45.7056	0.0430	-0.3876	-7.5000	-0.1790	-0.0024
0.8802	1473.8	1.0856	2.2861	120.111	42.4082	0.0414	-0.2245	-4.1742	-0.0890	-0.0014
1.0000	1509.4	1.1067	2.6487	123.023	39.6608	0.0401	0.0000	0.0000	0.0000	0.0000
318.15K										
0.0000	1055.9	0.8663	0.3454	101.708	103.5347	0.0652	0.0000	0.0000	0.0000	0.0000
0.0832	1112.5	0.8918	0.4505	103.279	90.6009	0.0610	-0.2683	-7.7220	-0.0610	-0.0022
0.1695	1160.0	0.9170	0.5620	104.961	81.0405	0.0577	-0.4968	-11.8718	-0.1210	-0.0034
0.2592	1205.3	0.9407	0.6673	106.899	73.1743	0.0548	-0.5420	-14.1169	-0.1950	-0.0041
0.3524	1249.5	0.9648	0.7777	108.869	66.3864	0.0522	-0.6350	-15.0608	-0.2710	-0.0044
0.4494	1293.0	0.9882	0.9206	111.006	60.5262	0.0498	-0.6437	-14.8403	-0.3210	-0.0045
0.5504	1334.5	1.0114	1.1517	113.262	55.5191	0.0477	-0.6220	-13.5157	-0.2920	-0.0041
0.6557	1376.0	1.0343	1.4182	115.648	51.0659	0.0458	-0.5653	-11.3701	-0.2350	-0.0035
0.7655	1417.5	1.0567	1.7149	118.180	47.0958	0.0440	-0.4628	-8.4572	-0.1580	-0.0027
0.8802	1458.0	1.0782	2.0224	120.937	43.6300	0.0423	-0.2418	-4.7367	-0.0790	-0.0015
1.0000	1492.0	1.0995	2.3402	123.829	40.8571	0.0409	0.0000	0.0000	0.0000	0.0000

Table 4. Values of ultrasonic velocity (U), density(ρ), viscosity (η), related thermo dynamic parameters and their excess values for anisic aldehyde+ n- butyl acetate system at different temperatures

Mole fraction X	(U) m/s	ρ x 10^{-3} kg/m^3	η Cp	V_m cm^{-3} mol^{-1}	β_{ad} 10^{12} m^2 N^{-1}	L_f 10^{-10} m	V_m^E cm^{-3} mol^{-1}	$\beta_{ad}^E 10^{12}$ m^2 N^{-1}	η^E Cp	L_f^E 10^{-10} m
T=303.15K										
0.0000	1176.1	0.8695	0.6407	133.5940	83.1461	0.0572	0.0000	0.0000	0.0000	0.0000
0.1086	1227.4	0.8958	0.8657	132.0906	74.1029	0.0540	-0.1918	-4.0811	-0.0940	-0.0012
0.2152	1274.5	0.9220	1.1104	130.6553	66.7728	0.0512	-0.3404	-6.5433	-0.1620	-0.0019
0.3197	1319.0	0.9479	1.3780	129.2878	60.6386	0.0488	-0.4454	-7.9010	-0.2020	-0.0023
0.4223	1359.9	0.9736	1.6650	127.9832	55.5410	0.0467	-0.5110	-8.3111	-0.2160	-0.0025
0.5231	1397.5	0.9990	1.9600	126.7411	51.2537	0.0449	-0.5369	-7.9975	-0.2170	-0.0025
0.6219	1430.0	1.0241	2.2674	125.5662	47.7512	0.0433	-0.5180	-6.9830	-0.2000	-0.0022
0.7190	1461.5	1.0488	2.5829	124.4641	44.6412	0.0419	-0.4477	-5.6580	-0.1700	-0.0018
0.8144	1490.8	1.0729	2.9117	123.4351	41.9357	0.0406	-0.3255	-4.0081	-0.1210	-0.0013
0.9080	1519.2	1.0967	3.2501	122.4648	39.5066	0.0394	-0.1651	-2.1593	-0.0580	-0.0007
1.0000	1543.5	1.1204	3.5783	121.5191	37.4635	0.0384	0.0000	0.0000	0.0000	0.0000
308.15K										
0.0000	1154.8	0.8655	0.5968	134.2114	86.6402	0.0588	0.0000	0.0000	0.0000	0.0000
0.1086	1207.3	0.8919	0.7929	132.6733	76.9225	0.0554	-0.2353	-4.5437	-0.0690	-0.0013
0.2152	1255.6	0.9178	0.9993	131.2500	69.1079	0.0525	-0.3805	-7.2825	-0.1220	-0.0021
0.3197	1300.2	0.9434	1.2265	129.8980	62.7024	0.0500	-0.4784	-8.7077	-0.1500	-0.0026
0.4223	1340.0	0.9690	1.4643	128.5864	57.4707	0.0479	-0.5593	-9.0517	-0.1620	-0.0027
0.5231	1377.4	0.9942	1.7170	127.3547	53.0159	0.0460	-0.5830	-8.7091	-0.1550	-0.0027
0.6219	1408.7	1.0191	1.9694	126.1887	49.4488	0.0444	-0.5631	-7.5665	-0.1440	-0.0023
0.7190	1439.1	1.0434	2.2294	125.1052	46.2777	0.0430	-0.4822	-6.1132	-0.1200	-0.0019
0.8144	1467.7	1.0671	2.4920	124.1118	43.5060	0.0417	-0.3320	-4.3435	-0.0900	-0.0014
0.9080	1493.7	1.0907	2.7703	123.1422	41.0909	0.0405	-0.1784	-2.2981	-0.0400	-0.0007
1.0000	1517.0	1.1140	3.0347	122.2172	39.0071	0.0394	0.0000	0.0000	0.0000	0.0000
313.15K										
0.0000	1137.0	0.8609	0.5577	134.9286	89.8517	0.0603	0.0000	0.0000	0.0000	0.0000
0.1086	1192.9	0.8872	0.7288	133.3762	79.2082	0.0566	-0.2592	-5.1917	-0.0560	-0.0015
0.2152	1242.2	0.9128	0.9115	131.9692	70.9972	0.0536	-0.3976	-8.0544	-0.0960	-0.0023
0.3197	1287.8	0.9382	1.1060	130.6181	64.2665	0.0510	-0.5039	-9.5373	-0.1200	-0.0028
0.4223	1328.9	0.9635	1.3095	129.3264	58.7746	0.0488	-0.5741	-9.8791	-0.1310	-0.0030
0.5231	1367.5	0.9885	1.5286	128.0904	54.0995	0.0468	-0.6110	-9.4992	-0.1230	-0.0029
0.6219	1399.6	1.0131	1.7369	126.9246	50.3874	0.0451	-0.5996	-8.2486	-0.1210	-0.0026
0.7190	1430.1	1.0372	1.9492	125.8496	47.1410	0.0437	-0.5189	-6.6223	-0.1120	-0.0021
0.8144	1460.0	1.0607	2.1806	124.8601	44.2284	0.0423	-0.3733	-4.7496	-0.0800	-0.0015
0.9080	1486.6	1.0841	2.4204	123.8953	41.7431	0.0411	-0.2233	-2.5349	-0.0360	-0.0008
1.0000	1509.4	1.1067	2.6487	123.0234	39.6608	0.0401	0.0000	0.0000	0.0000	0.0000
318.15K										
0.0000	1106.2	0.8543	0.5228	135.9710	95.6582	0.0626	0.0000	0.0000	0.0000	0.0000
0.1086	1166.0	0.8805	0.6722	134.3839	83.5315	0.0585	-0.2682	-6.1741	-0.0480	-0.0017
0.2152	1216.7	0.9062	0.8372	132.9271	74.5415	0.0553	-0.4311	-9.3245	-0.0770	-0.0027
0.3197	1263.8	0.9316	1.0032	131.5496	67.2040	0.0525	-0.5392	-10.9322	-0.1010	-0.0032
0.4223	1305.9	0.9567	1.1843	130.2381	61.2902	0.0501	-0.6047	-11.2229	-0.1060	-0.0033
0.5231	1345.7	0.9817	1.3751	128.9763	56.2508	0.0480	-0.6436	-10.7429	-0.0980	-0.0033
0.6219	1380.1	1.0062	1.5530	127.7977	52.1772	0.0463	-0.6218	-9.3980	-0.1000	-0.0029
0.7190	1412.6	1.0303	1.7399	126.6993	48.6405	0.0447	-0.5413	-7.6145	-0.0900	-0.0024
0.8144	1442.3	1.0539	1.9345	125.6677	45.6122	0.0433	-0.4154	-5.4179	-0.0680	-0.0017
0.9080	1469.3	1.0770	2.1442	124.7048	43.0110	0.0420	-0.2412	-2.8873	-0.0290	-0.0009
1.0000	1492.0	1.0995	2.3402	123.8290	40.8571	0.0409	0.0000	0.0000	0.0000	0.0000

Table 5. Values of coefficients of Eq.6 and standard deviation (σ□□for anisic aldehyde + di methyl acetate, anisic aldehyde + ethyl acetate and anisic aldehyde + n- butyl acetate at different temperatures

Temp(K)	A0	A1	A2	A3	A4	σ
AA+MA						
V_m^E						
303.15	-2.1525	-0.5585	0.3531	-0.9766	-2.0472	0.0004
308.15	-2.5948	-0.9859	-1.1362	-0.8964	0.4609	0.0005
313.15	-3.1191	-0.8576	-0.8150	-0.3796	-0.2953	0.0051
318.15	-3.5236	-0.7469	-1.3981	-0.3617	0.4141	0.0058
$\Delta\beta_{ad}$						
303.15	-47.2168	-25.6548	-0.5052	-8.7378	-34.6866	0.1026
308.15	-49.0971	-26.6409	-3.7314	-13.5586	-35.7504	0.0587
313.15	-53.8772	-29.6786	10.2404	-17.1531	-68.9633	0.2363
318.15	-56.6777	-31.2901	9.6206	-20.3768	-78.6613	0.2863
η^E						
303.15	-1.6894	-0.7712	0.1011	0.6889	0.1766	0.0017
308.15	-1.3764	-0.6369	0.5218	0.3797	-0.0689	0.0024
313.15	-1.2656	-0.3794	0.7524	0.2410	-0.3097	0.0044
318.15	-1.1326	-0.0931	0.5414	-0.1971	0.0501	0.0019
L_f^E						
303.15	-0.0152	-0.0078	0.0007	-0.0018	-0.0117	0.0000
308.15	-0.0160	-0.0081	-0.0007	-0.0035	-0.0115	0.0000
313.15	-0.0178	-0.0091	0.0045	-0.0045	-0.0233	0.0001
318.15	-0.0188	-0.0096	0.0040	-0.0053	-0.0264	0.0001
AA+MA						
V_m^E						
303.15	-2.1961	-0.1626	0.0928	-0.5516	-0.7764	0.0001
308.15	-2.3125	-0.5026	0.0414	0.0016	-0.6006	0.0001
313.15	-2.4766	-0.4416	0.4645	-0.2771	-1.1318	0.0000
318.15	-2.5776	-0.2137	-0.1302	-0.7891	-0.4466	0.0299
$\Delta\beta_{ad}$						
303.15	-42.8319	-19.3587	-7.6662	-2.7034	-3.9126	0.0670
308.15	-46.4454	-21.5359	-10.0101	-4.3071	-4.0613	0.0708
313.15	-51.5205	-24.1136	-11.0895	-7.1416	-9.3459	0.0685
318.15	-57.4207	-24.3485	-7.3346	-13.1014	-22.5181	0.0760
η^E						
303.15	-1.8744	-0.9757	-0.0827	1.5716	0.9738	0.0276
308.15	-1.5041	-0.4397	0.8556	0.1713	-0.9038	0.0274
313.15	-1.4075	-0.2396	2.0533	0.4806	-1.7784	0.0093
318.15	-1.2897	-0.2784	1.9884	0.4328	-1.8860	0.0090
L_f^E						
303.15	-0.0132	-0.0054	-0.0018	-0.0002	-0.0013	0.0000
308.15	-0.0143	-0.0059	-0.0025	-0.0006	-0.0011	0.0000
313.15	-0.0158	-0.0066	-0.0028	-0.0013	-0.0028	0.0000
318.15	-0.0174	-0.0061	-0.0014	-0.0031	-0.0073	0.0000
AA+BA						
V_m^E						
303.15	-2.1388	0.2913	0.0016	-0.4351	0.3664	0.0002
308.15	-2.3194	0.3920	0.1987	-0.9085	-0.2762	0.0078
313.15	-2.4302	0.4167	0.0657	-0.7007	-0.7386	0.0093
318.15	-2.5661	0.3041	0.0743	-0.4081	-0.7773	0.0046
$\Delta\beta_{ad}$						
303.15	-32.5452	-10.5263	0.6895	0.2184	-5.0418	0.0272
308.15	-35.4811	-12.3731	-0.1410	0.0496	-4.5263	0.0457
313.15	-38.7135	-13.7517	0.5502	-1.8649	-9.5514	0.0543
318.15	-43.7657	-15.4201	-4.3872	-5.1635	-7.3699	0.0513
η^E						
303.15	-0.8739	-0.0959	-0.1615	-0.1062	0.3410	0.0011
308.15	-0.6265	-0.1212	-0.1872	-0.0248	0.3607	0.0026
313.15	-0.4918	0.0023	-0.5236	-0.1234	0.7768	0.0042
318.15	-0.3933	-0.0343	-0.5227	-0.0696	0.7406	0.0050
L_f^E						
303.15	-0.0100	-0.0025	0.0011	0.0004	-0.0023	0.0000
308.15	-0.0109	-0.0031	0.0009	0.0003	-0.0020	0.0000
313.15	-0.0119	-0.0034	0.0014	-0.0002	-0.0040	0.0000
318.15	-0.0132	-0.0036	-0.0006	-0.0013	-0.0027	0.0000

Fig. 9. Plots of deviation in adiabatic compressbility against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+BA) systems

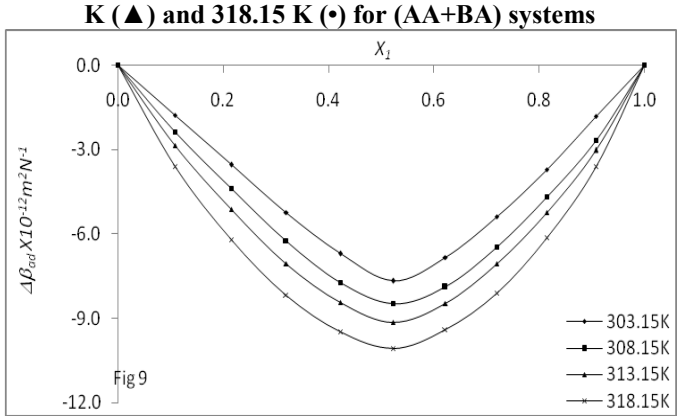


Fig. 10. Plots of excess molar volume, against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+BA) systems.

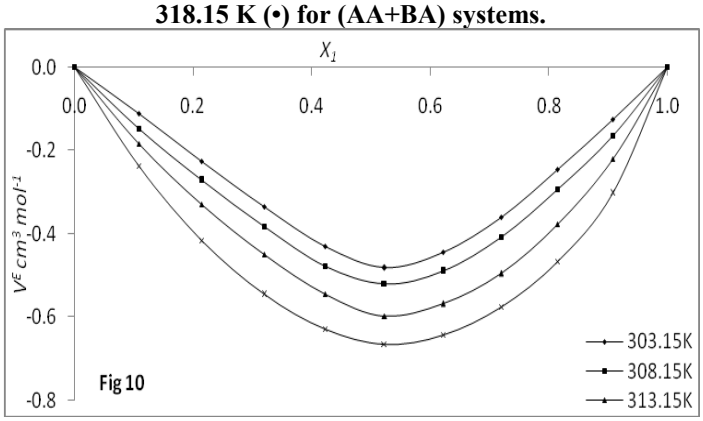


Fig. 11. Plots of deviation in viscosity and against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+BA) systems

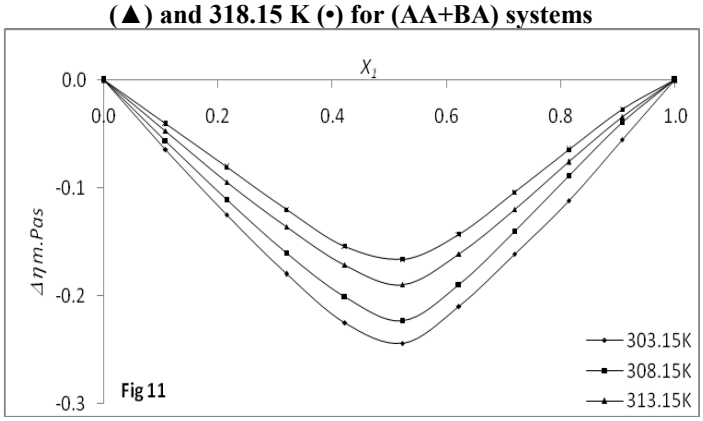
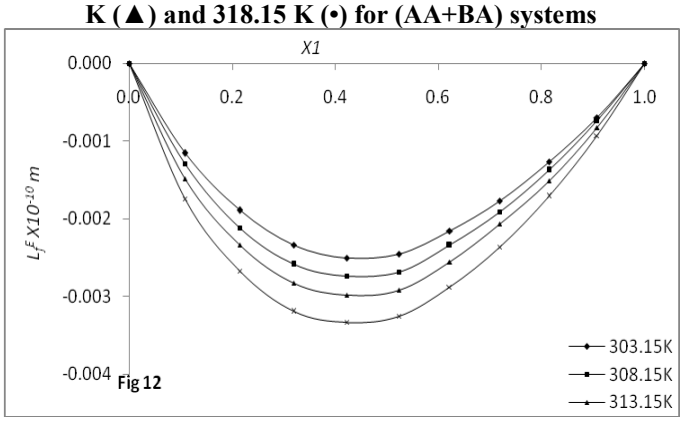


Fig. 12. Plots of excess intermolecular free length against mole fraction of AA (X_1) at 303.15 K, (♦) 318.15 K (■), 313.15 K (▲) and 318.15 K (•) for (AA+BA) systems



Figs 4, 8 and 12 indicate the variation of excess free length for the entire composition range of anisic aldehyde for the three systems under study. According to Ramamurthy and Sastry [19] the negative L_f^E values indicate that sound wave has to travel a longer distance. This may be attributed to dominant nature of interactions between unlike molecules. The $\Delta\beta_{ad}$ and L_f^E minima occur at the same concentrations further strengthens the occurrence of molecular associations.

It can be seen from Figs. 3,7 and 11 that the viscosity deviations are also negative for every binary system investigated over the entire mole fraction range and all the negative maximum values were located around 0.4 mole fractions. The viscosity deviations depend on strength of interactions between like and unlike molecules. The sign and magnitude of $\Delta\eta$ also varies with structural characteristics of liquid components arising from geometrical fitting of one component into the structure of other component due to difference in molecular size and shape of the components.

The negative deviations in viscosity may be attributed to the existence of dispersion or dipolar forces between unlike molecules to the difference in size and shape of the molecules.

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