

Excess Viscosity and Compressibility of Binary Mixtures of Methanol with Acetonitrile and Dimethyl Formamide at Different Temperatures

¹Neeta Sharma, ¹Seema Rana, ¹Anunidhi Sharma and ²Kawaljit Arora

¹Department of Chemical Engineering and Technology, Panjab University, Chandigarh, India 160014

²University Institute of Engineering and Technology, Panjab University, Chandigarh, India 160014

Abstract: The densities, viscosities and ultrasonic velocities of binary mixtures of methanol with acetonitrile and dimethyl formamide have been determined at 298.15, 303.15, 308.15 and 313.15 K over the whole composition range. From the experimental data the values of compressibility (K_s), excess compressibility ($K_{s,e}$) and excess viscosity (η_e) have been calculated. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding. The data at various temperatures also provide an opportunity to study the effect of temperature on the sign and magnitude of the deviation in viscosity and compressibility. Results show that excess properties are found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

Key words:

INTRODUCTION

The study of molecular interactions in binary liquid mixtures has attracted the attention of scientific community for more than a century. The study finds direct applications in chemical and biological industry [1]. Mixed solvents rather than single pure liquids are of utmost practical importance in most of chemical and industrial processes as they provide a wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustment of desired properties of the medium [2-5].

In recent years the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components. The composition dependence of ultrasonic properties of binary liquid mixtures has proved to be a useful tool to investigate the interaction between the components of binary liquid mixtures. The ultrasonic

speed and thermodynamic data derived from it has been widely used for this purpose [6-10].

In the present study, densities (ρ), viscosities (η) and ultrasonic velocities (u) of binary mixtures of methanol (MeOH) with acetonitrile (AN) and dimethylformamide (DMF) covering the entire composition range (expressed by the mole fraction of MeOH) at 298.15, 303.15, 308.15 and 313.15 K are reported. From the experimental value of ρ , η and u , the excess viscosity (η_e), compressibility (K_s) and excess compressibility ($K_{s,e}$) have been calculated. The present study is expected to reveal the nature and extent of interaction between the component molecules in these binary mixtures. The dependence of these thermodynamic parameters on composition and temperature has also been discussed.

MATERIALS AND METHODS

The spectral grade acetonitrile (E.Merck, 99.5%) and dimethylformamide (E.Merck, 99.5%) were used as such without further purification. Methanol (E.Merck) was refluxed over calcium oxide (CaO) and distilled at atmospheric pressure. Methanol obtained is then stored over 4 Å type molecular sieve [11,12]. The purity of the purified chemicals was checked by comparing their

measured densities (ρ), viscosities (η) and ultrasonic velocities (u) with those reported in the literature [13,14]. All the mixtures were prepared by mixing known masses of pure liquids. The weighing was done on electronic balance (Afcoset ER-120A) with a precision of $\pm 1 \times 10^{-4}$ g. The probable error in mole fraction was estimated to be less than ± 0.0001 .

The densities of pure liquids and their binary mixtures were measured by using bicapillary pycnometer. The accuracy in density measurements was found to be 0.0001 g cc^{-1} . The viscosities of pure liquids and their binary mixtures were measured by using a modified Ubbelohde capillary type viscometer. The viscometer was calibrated with pure water. The viscometer containing the test liquid was allowed to stand for about 30 min in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The accuracy in viscosity data was $\pm 0.002 \text{ mPa.s}$.

The ultrasonic velocity of pure liquids and their binary mixtures was measured using ultrasonic time intervalometer model UTI-101 purchased from Innovative Instrument (Hyderabad).

The temperature of the test liquids during the measurement was maintained at an accuracy of $\pm 0.02 \text{ K}$ in an electronically controlled thermostatic water bath.

The reliability of the experimental measurements of ρ , η and u was checked by comparing the observed values of these properties of pure liquids (Table 1) with the corresponding literature values [1-8].

RESULTS AND DISCUSSION

The experimental values of densities (ρ), viscosities (η) and ultrasonic velocities (u) of pure MeOH, AN, DMF and binary mixtures of methanol (MeOH) with acetonitrile (AN) and dimethyl formamide (DMF) covering the entire composition range (expressed by the mole fraction of MeOH) at 298.15, 303.15, 308.15 and 313.15 K are reported in Table 2 and 3.

Excess viscosities were obtained by using the relation:

$$\eta_e = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (1)$$

where, x_1 , x_2 are the mole fraction of components 1 and 2, respectively and η_1 , η_2 the viscosities of pure components 1 and 2 and η is the viscosity of the mixture.

Compressibilities (K_s) were calculated from the values of density (ρ) and ultrasonic velocity (u) from the equation given as:

Table 1: Experimental measurement of the physical properties

	Observed values	Literature values
Density (g cc^{-1})		
Methanol	0.77664	0.7866
Acetonitrile	0.7765	0.7762
Dimethyl formamide	0.9487	0.9444
Viscosity (cP)		
Methanol	0.553	0.545
Acetonitrile	0.341	0.342
Dimethyl formamide	0.86	0.825
Ultrasonic Velocity (m s^{-1})		
Methanol	1266.00	Not available
Acetonitrile	1250.00	1280.80
Dimethyl formamide	1431.00	1456.70

$$K_s = 1/u^2 \rho \quad (2)$$

Excess compressibilities ($K_{s,e}$) were obtained by using the relation:

$$K_{s,e} = K_s - (x_1 K_{s,1} + x_2 K_{s,2}) \quad (3)$$

where, K_s is the compressibility of the mixture and $K_{s,1}$ and $K_{s,2}$ the compressibilities of pure component 1 and 2. The calculated values of η_e , $K_{s,e}$ using equation 1, 2 and 3 are given in Table 1 and 2.

For both AN+MeOH and DMF+MeOH solvent systems the values of ultrasonic velocity at different temperature were plotted as a function of mixture composition (Fig. 1a and 1b). All the curves show a decrease in ultrasonic velocity with increase in mole fraction of MeOH. Increasing the temperature for a particular mole fraction causes an increase in velocity. It is significant here to compare density and ultrasonic velocity as density decreases the ultrasonic velocity increases [15] (Table 1 and 2).

The variation of compressibility with mole fraction for AN+MeOH and DMF+MeOH is shown in Fig. 2a and 2b. It has been observed that the value of compressibility increases with increase in mole fraction of MeOH at a constant temperature this indicates that as the mole fraction of MeOH increases the intermolecular interactions between the molecules increases [7, 8] because of formation of hydrogen bonds in MeOH.

The excess viscosity η_e are negative for AN+MeOH system under study over the whole composition range at all investigated temperatures as derived from Fig. 3a. The negative η_e values indicate that the dispersion forces are dominant in these systems. It has been reported [7,8,16,17] that dispersion forces are dominant in the systems where the component molecules have different molecular size as in the present case. However in case of DMF+MeOH system (Fig. 3b) it shows positive deviation

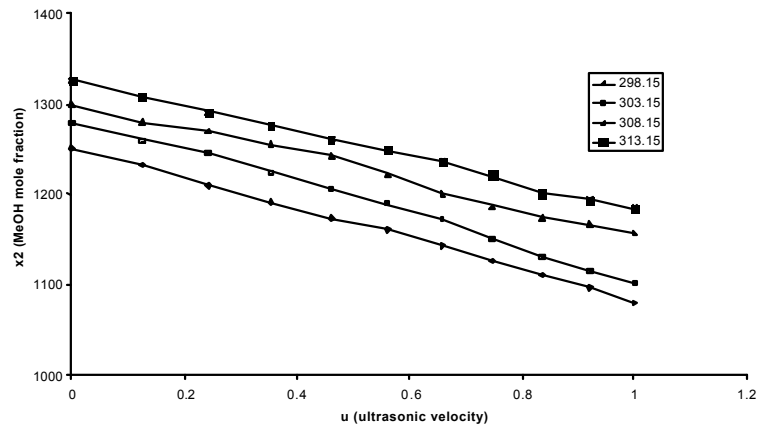


Fig. 1a: Ultrasonic velocity versus mole fraction of MeOH in AN-MeOH system

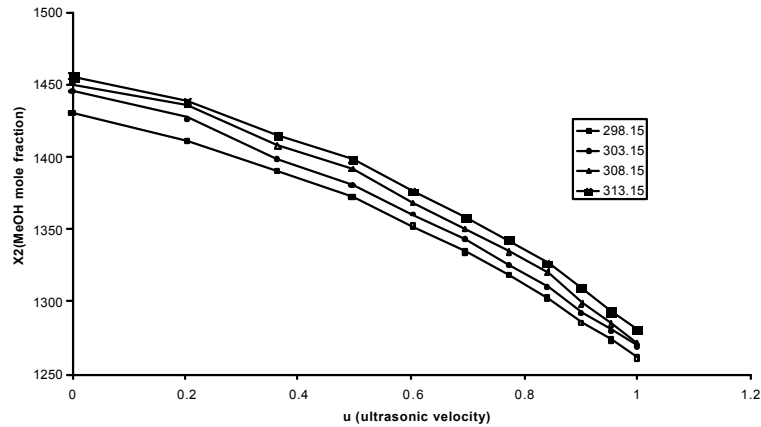


Fig 1b: Ultrasonic velocity versus mole fraction of MeOH in DMF-MeOH system

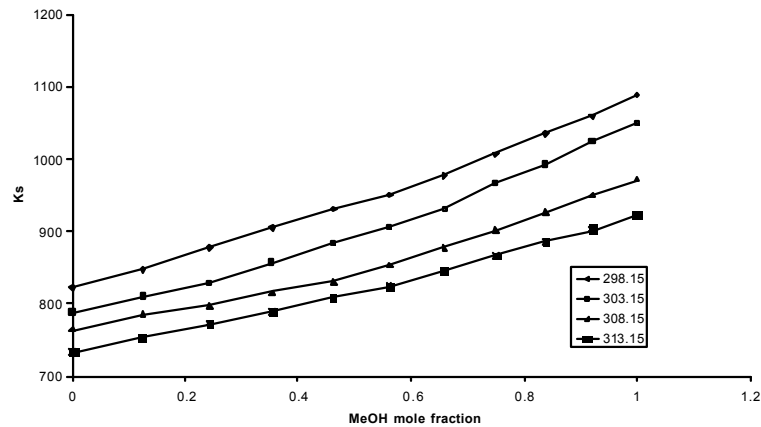


Fig 2a: Compressibility versus mole fraction of MeOH in AN-MeOH system

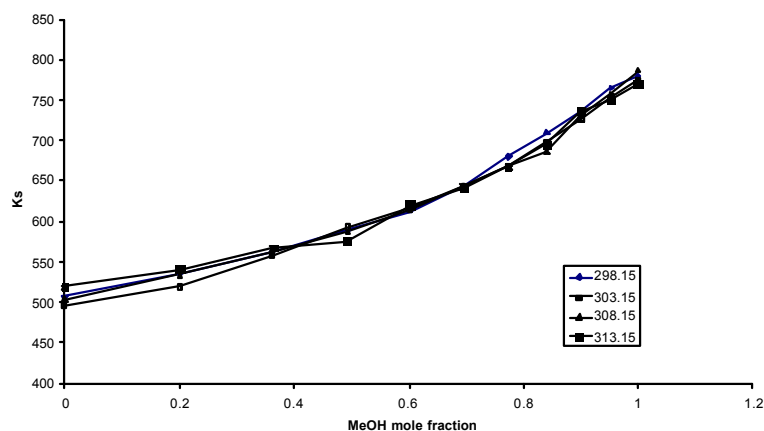


Fig 2b: Compressibility versus mole fraction of MeOH in DMF-MeOH system

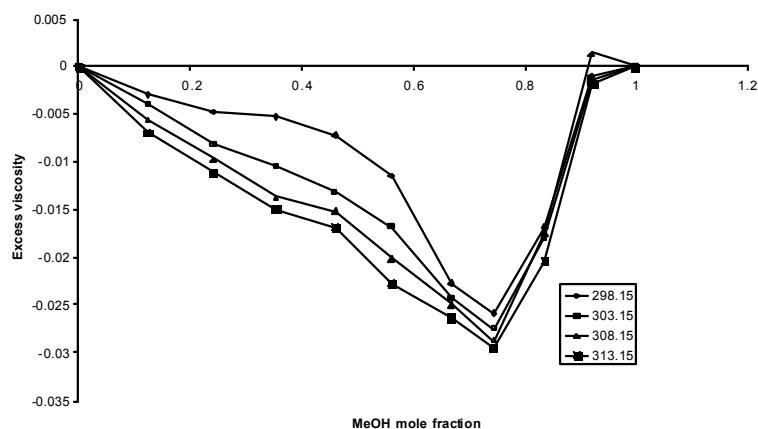


Fig 3a: Excess viscosity versus MeOH mole fraction for AN-MeOH system

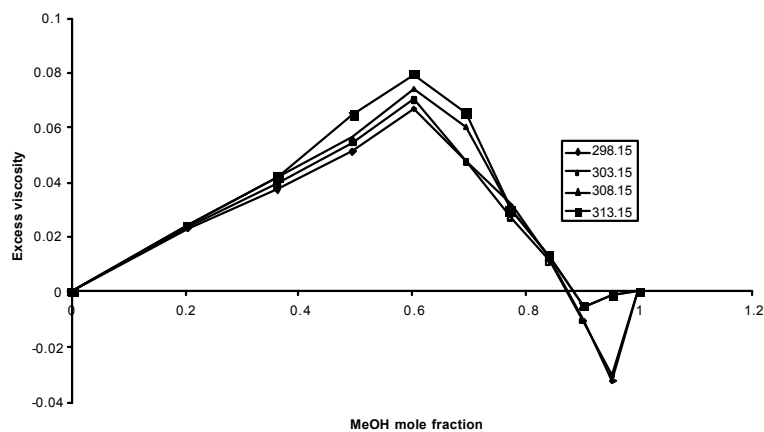


Fig 3b: Excess viscosity versus MeOH mole fraction for DMF-MeOH system

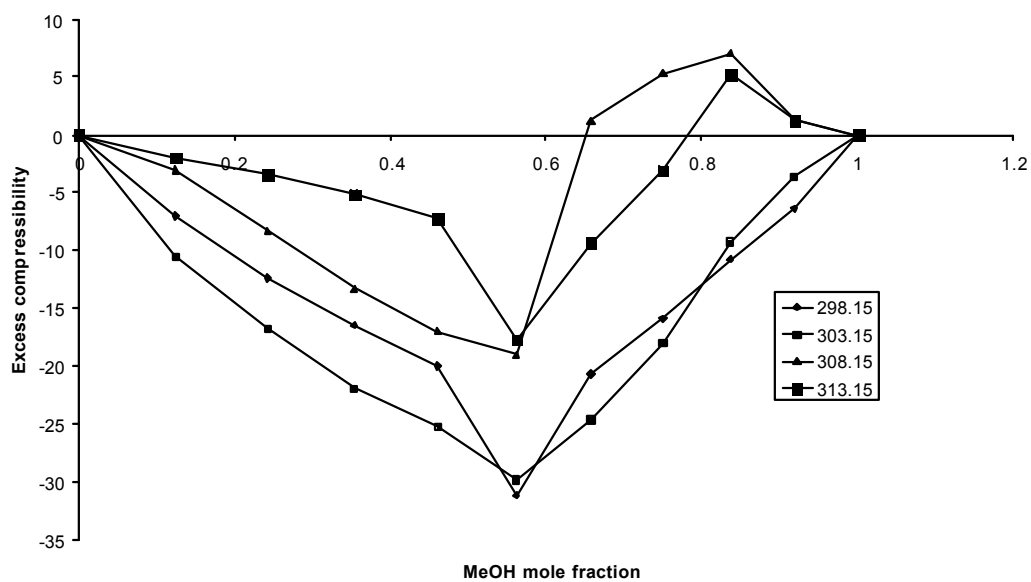


Fig 4a: Excess compressibility versus MeOH mole fraction in AN-MeOH system

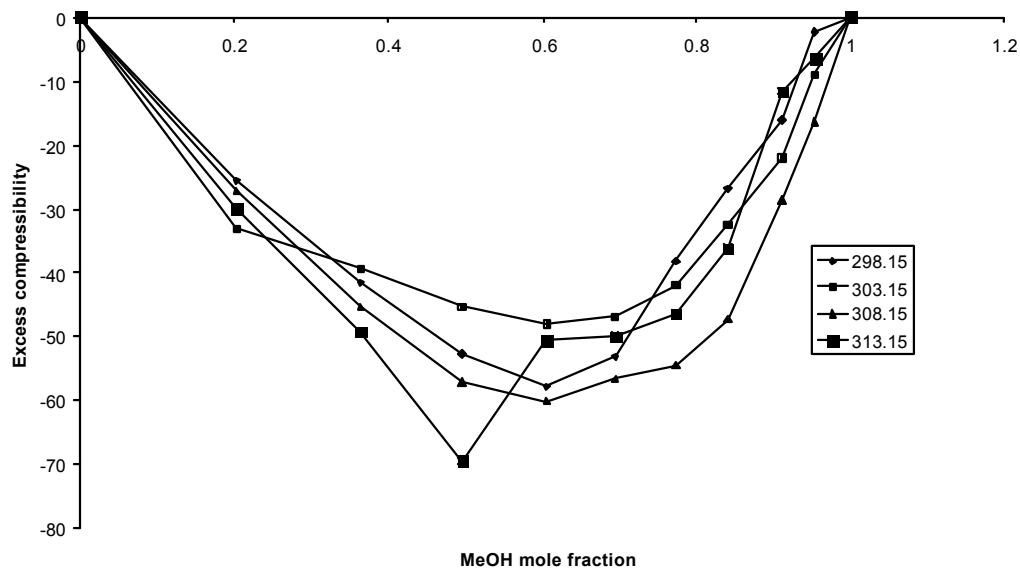


Fig 4b: Excess compressibility versus MeOH mole fraction in DMF-MeOH system

Table 2: Densities, viscosities, ultrasonic velocities, compressibilities, excess viscosities, excess compressibilities for AN + MeOH(X_2) system at 298.15, 303.15, 308.15 and 313.15 K

T(K)	X_2	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa.s})$	$u (\text{m s}^{-1})$	$K_s \times 10^{-12} (\text{m}^2 \text{N}^{-1})$	$\eta_e (\text{mPa.s})$	$K_{e,s} \times 10^{-12} (\text{m}^2 \text{N}^{-1})$
298.15	0	0.964	0.796	1430.8	506.7166	0	0
	0.2022	0.9362	0.77	1411.2	536.3573	0.023135	-25.49867508
	0.3632	0.9143	0.745	1392.3	564.2163	0.037258	-41.54398873
	0.4944	0.9	0.727	1373.8	588.7223	0.051139	-52.81592185
	0.603306	0.8852	0.716	1357.2	613.2971	0.066603	-57.93950347
	0.69524	0.8677	0.6745	1338.6	643.1744	0.047443	-53.13232383
	0.7739	0.8415	0.6391	1322.3	679.6509	0.031158	-38.10623745
	0.84185	0.824	0.6037	1307.8	709.5616	0.01227	-26.72527694
	0.90124	0.82715	0.5668	1282.7	734.7939	-0.0102	-17.68851467
	0.95356	0.805	0.532	1274	765.3591	-0.03228	-1.390809176
	1	0.8	0.553	1266.4	779.414	0	0
	0	0.965	0.79	1445.2	496.1543	0	0
303.15	0.2022	0.943	0.765	1428.8	519.452	0.02373	-33.03586532
	0.3632	0.9186	0.742	1396.6	558.1224	0.039531	-39.22054314
	0.4944	0.8842	0.725	1380.9	593.096	0.05415	-40.79967406
	0.6033	0.8773	0.7	1360.2	616.0931	0.055397	-48.14420384
	0.69524	0.8621	0.67	1343.3	642.8303	0.047553	-47.02010915
	0.7739	0.8565	0.63	1322	668.0512	0.02651	-43.71415654
	0.84185	0.8498	0.598	1298	698.4477	0.010886	-32.24870912
	0.90124	0.8252	0.562	1292.6	725.2913	-0.0108	-21.95133215
	0.95356	0.81	0.53	1280.5	752.9321	-0.03019	-8.887062956
	1	0.8	0.549	1270.2	774.7575	0	0
	0	0.944	0.785	1450.3	503.6308	0	0
	0.2022	0.9089	0.76	1435.5	533.9216	0.024539	-26.94181418
308.15	0.3632	0.8992	0.738	1408	560.9684	0.041984	-45.46602179
	0.4944	0.8804	0.72	1391.7	586.4469	0.056128	-57.12359965
	0.603306	0.8698	0.694	1368.2	614.1599	0.05681	-60.23646778
	0.69524	0.8522	0.685	1350.1	643.7639	0.070334	-56.65433908
	0.7739	0.842	0.625	1335	666.3853	0.029606	-56.29763327
	0.84185	0.8264	0.592	1328.2	685.9346	0.013253	-55.98145911
	0.90124	0.8152	0.559	1296	730.3412	-0.0052	-28.38517915
	0.95356	0.7994	0.55	1285.3	757.2283	-0.00138	-16.30726882
	1	0.7854	0.54	1272.2	786.6804	0	0
	0	0.9094	0.785	1455.2	519.2777	0	0
	0.2022	0.8952	0.76	1438.1	540.1343	0.024539	-29.86739699
	0.3632	0.8864	0.738	1410.3	567.2144	0.041984	-43.1758428
313.15	0.4944	0.8779	0.733	1409	573.7636	0.069128	-69.53956826
	0.603306	0.8586	0.694	1370.7	619.9038	0.05681	-50.71955662
	0.69524	0.84716	0.685	1356.3	641.6867	0.070334	-51.99925862
	0.7739	0.8323	0.625	1342.2	666.9383	0.029606	-46.4803744
	0.84185	0.8136	0.592	1330.3	694.5282	0.013253	-35.93642186
	0.90124	0.8024	0.559	1302.2	734.9431	-0.0052	-10.42014905
	0.95356	0.8	0.55	1290.5	750.5748	-0.00138	-7.913410648
	1	0.7849	0.54	1286.2	770.1382	0	0

Table 3: Densities, viscosities, ultrasonic velocities, compressibilities, excess viscosities, excess compressibilities for DMF+MeOH (X_2) system at 298.15, 303.15, 308.15 and 313.15 K

T(K)	X_2	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa.s})$	$u (\text{m s}^{-1})$	$K_s \times 10^{-12} (\text{m}^2 \text{N}^{-1})$	$\eta_e (\text{mPa.s})$	$K_{e,s} \times 10^{-12} (\text{m}^2 \text{N}^{-1})$
298.15	0.1246	0.7765	0.3341	1250.8	846.83	0	0
	0.2426	0.7775	0.3584	1232.4	877.3455	-0.00297	-9.416348333
	0.3545	0.7785	0.3824	1210	905.9202	0.00481	-10.23725633
	0.4607	0.7795	0.4065	1190	931.1745	-0.0052	-11.37898313
	0.5617	0.7805	0.429	1173	941.6672	0.00595	-14.32749492
	0.6578	0.7815	0.447	1165.7	977.1638	0.01006	-30.65666532
	0.7497	0.7825	0.452	1143.6	1006.306	0.02609	-20.68063081
	0.8367	0.7835	0.476	1126.2	1034.573	0.02221	-15.94388361
	0.9202	0.7845	0.4931	1110	1059.048	0.02415	-10.78070344
	1	0.7855	0.5345	1096.4	1088.72	0.00103	-8.479814243
	0	0.7866	0.553	1080.6		0	0
	0	0.7758	0.338	1278.7	788.3388	0	0
303.15	0.1246	0.7767	0.36	1260	810.9715	0.00392	-9.885534071
	0.2426	0.7778	0.3793	1245	829.456	0.00916	-22.19682901
	0.3545	0.7787	0.402	1224.035	857.121	0.00974	-23.73560142

Table 3: Continued

T(K)	X ₂	$\rho \times 10^3 (\text{kg m}^{-3})$	$\eta (\text{mPa.s})$	$u (\text{m s}^{-1})$	$K_{x10-12} (\text{m}^2 \text{N}^{-1})$	$\eta_e (\text{mPa.s})$	$K_{ex10-12} (\text{m}^2 \text{N}^{-1})$
308.15	0.4607	0.7797	0.419	1205	883.2799	0.01483	-25.29288951
	0.5617	0.7803	0.438	1189.91	905.1283	0.01683	-29.80359731
	0.6578	0.7818	0.445	1171.77	931.5788	0.02982	-28.4334603
	0.7497	0.7828	0.465	1150	965.9475	0.02894	-18.04895125
	0.8367	0.7839	0.494	1130.038	998.9718	0.01803	-7.729944274
	0.9202	0.7843	0.5279	1115.378	1024.881	-0.0015	-3.612240429
	1	0.786	0.546	1101.12	1049.32	0	0
	0	0.7752	0.335	1298.5	765.072	0	0
	0.1246	0.7763	0.355	1279.4	786.9692	-0.00554	-1.081745033
	0.2426	0.7772	0.375	1269.8	797.9884	-0.00973	-11.82428467
	0.3545	0.7782	0.394	1255	815.8707	-0.01367	-14.57874972
	0.4607	0.7794	0.415	1242.2	831.4891	-0.01444	-18.54590745
	0.5617	0.7802	0.43	1228.25	849.6117	-0.02015	-19.04980967
	0.6578	0.7812	0.445	1200.3	888.5015	-0.02485	2.11701245
	0.7497	0.7822	0.46	1186.4	908.2803	-0.02869	4.947538286
	0.8367	0.7834	0.489	1173.8	926.4633	-0.01752	7.085835535
313.15	0.9202	0.7844	0.525	1167	936.0967	0.001359	1.320011292
	1	0.7854	0.54	1158	949.4935	0	0
	0	0.7745	0.33	1326.4	733.8876	0	0
	0.1246	0.7756	0.3488	1308	753.6101	-0.00687	-1.960539246
	0.2426	0.7766	0.37	1290.9	772.7116	-0.00998	-3.393578291
	0.3545	0.7777	0.388	1275.8	789.992	-0.01503	-5.586093451
	0.4607	0.7787	0.409	1260.8	807.8625	-0.0159	-6.196711785
	0.5617	0.7797	0.423	1255.5	813.6526	-0.02271	-17.98267969
	0.6578	0.7805	0.44	1235.8	838.9396	-0.02551	-9.419114061
	0.7497	0.7815	0.455	1220.05	859.6383	-0.02944	-4.712988744
	0.8367	0.7826	0.482	1201.8	884.6994	-0.02036	5.208311556
	0.9202	0.7838	0.5178	1193.8	895.2237	-0.00176	1.201834297
	1	0.7849	0.536	1184.6	907.9088	0	0

in viscosity which indicates the presence of significant interaction between the component molecules [7,8,18,19].

Variation of excess compressibility K_{se} plotted against the composition of MeOH in the binary system for different temperatures of study is shown in Fig. 4a,b. It can be seen that the excess compressibility is negative over the entire composition range. For AN+MeOH system the curve reaches negative maxima at 0.5617 mole fraction of MeOH at all the temperatures. The results show that the variation in excess compressibility exhibit inversion in sign with increasing mole fraction of MeOH at 308.15 and 313.15 K for AN+MeOH system. In case of DMF+MeOH system excess compressibility K_{se} is negative over the entire range and the negative maxima of all the curves are shifting towards right (higher mole fraction of MeOH) with increase in temperature from 298.15 to 313.15 K. Negative values of K_{se} are indicative of strong interaction between the component molecules due to hydrogen bonding as well as interstitial accommodation of molecules. Mixing of AN or DMF with MeOH will induce the dissociation of MeOH- MeOH associates with subsequent interstitial accommodation of AN or DMF molecules in alcohol aggregates. This leads to decrease in intermolecular free space and formation of closer molecular aggregates [17]. The effect of increase in the

temperature appears to increase the excess properties suggesting the presence of specific molecular interactions. As the temperature increases the values of K_{se} becomes more negative which may be due to thermal dissociation of hetero-aggregates in liquid mixtures and more interstitial accommodation of one component into another [20].

CONCLUSION

It is clear from all the curves and observations that close packed structure in the intermediate composition range of the binary system is formed. The temperature dependence of the different parameters suggests that the degree of deviation from ideality is strongly temperature sensitive and is influenced by the weakening of hydrogen bonds.

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