

CHAPTER VIII

**Excess Properties of Binary Mixtures of
N – Methylacetamide + 2-Methoxyethanol,
and N – Methylacetamide and Water at 308.15, 313.15 and 318.15 K**

In recent years, there has been a considerable upsurge in the theoretical and experimental investigations of the excess thermodynamic properties of binary liquid mixtures.¹⁻³ The main reason for this is the fact that the composition dependence of thermodynamic properties of binary liquid mixtures has proved to be a useful indicator of the existence of significant effects resulting from intermolecular interactions between the various species present in the liquid mixture. Besides this, dependence of these properties on temperature and pressure is of great importance to a chemical engineer in the design of industrial separation processes especially in petrochemical industries, on-line quality control, and underwater research,⁴ and to a chemist for arriving at theories of liquid mixtures. The interaction between the molecules can be established from a study of the characteristic departure from ideal behaviour of some physical properties like molar volume, compressibility, viscosity, etc.

The importance of N– methylacetamide (NMA) as a strongly hydrogen-bonded, highly structured, protic and basic solvent inspired us to investigate its excess properties by combining it with the familiar solvents 2-methoxyethanol and water. The amide group in NMA is a good model of a peptide bond. We believe that a systematic study of the structural and energetic consequences of the interaction between NMA and water will enable us to understand how water exercises thermodynamic and kinetic control over the

chemical activities of polypeptides in aqueous media. It will also serve us to compare these properties with the results obtained with the binary mixtures of N,N-dimethylacetamide + 2-methoxyethanol and N,N-dimethylacetamide + water given in the next chapter. Although some work has been done in amides + water mixtures,⁵⁻⁷ relatively fewer studies have been made in the binary mixtures of amides and organic solvents.

Viscosities of liquid mixtures offer knowledge that is indispensable in solving many practical problems concerning heat transport, mass transport, and fluid flow. For liquid mixtures, viscosity data have yielded valuable information regarding the nature of interaction forces operating within and between the molecules and the existence of complex if any. Attempts have been made to interpret viscosity data theoretically and empirically.⁸

Ultrasonic sound velocity measurements of solutions have been mostly attempted in water and binary mixtures containing water as a component.⁹ Such studies in organic solvents and in mixed organic solvents are rather few in literature.^{10,11} However, ultrasonic velocity measurements coupled with density and viscosity measurements offer very fruitful information regarding the solvation behaviour of electrolytes in pure and mixed solvents. Using the ultrasonic velocity (u) data, isentropic compressibility (κ_s) can be easily calculated using the relation $\kappa_s = 1/(u^2\rho)$. In a binary mixture, these parameters provide significant information on the behaviour of the component solvents and the solvent – solvent interactions.¹²

We have measured densities, viscosities and ultrasonic velocities for the liquid mixtures of NMA + ME and NMA + water over the entire range of their compositions at 308.15, 313.15, and 318.15 K. The excess molar volumes (V^E), viscosity deviations ($\Delta\eta$) and isentropic compressibility changes ($\Delta\kappa_s$) of these systems have been calculated at these temperatures.

Very recently, Gill and co-workers¹³ have shown that another parameter called shear relaxation time (τ) can be derived from viscosity and isentropic compressibility (κ_s) data. Starting from the equations of Kinsler and Frey,¹⁴ Gill and his colleagues derived a simple relation,

$$\tau = 4. \eta \kappa_s / 3. \quad (1)$$

(the symbols have the usual meanings) which is very useful for predicting the solvent structural effect in binary solvent mixtures. A rigorous examination of the validity of this equation has been done by them.¹³ If ion-solvent or solvent-solvent interactions are present in solutions or mixtures, the τ values should increase with the increase of salt concentration or with the change of solvent composition or with the change of temperature. We have calculated the κ_s and τ values for NMA + ME and NMA + water mixtures at the three temperatures mentioned above.

8.1 EXPERIMENTAL SECTION

The purification of the chemicals used and the experimental procedure for the measurement of the above properties have been described in Chapter 3. The measurements of densities, viscosities and ultrasonic velocities have also been described in Chapter 3. In all cases, the experiments were performed at least in five replicates for each composition and the results were averaged.

8.2 RESULTS

8.2.1 Solvent Parameters of the Mixtures

The densities, viscosities and ultrasonic velocities of NMA + ME mixture, and NMA + water mixture as a function of mole fractions of NMA, at 308.15, 313.15 and 318.15 K, have been presented in Tables 1-2. The corresponding values have been represented in Figures 1-3.

Two derived parameters, namely κ_s and τ , have been evaluated and these have been reported in Table 3-4. The variations of κ_s and τ values with the composition of the mixtures (mole fraction of NMA) have been shown in Figures 4 and 5.

8.2.2 Excess Properties of the Mixtures

The excess functions have been evaluated using the following equations:

$$V^E = V - (V_1x_1 + V_2x_2) \quad (2)$$

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \quad (3)$$

$$\Delta\kappa_s = \kappa_s - (\kappa_{s1}x_1 + \kappa_{s2}x_2) \quad (4)$$

where x_1 and x_2 are the mole fractions of NMA and ME / water respectively. V , η and κ_s are the respective solution properties, V_1 and V_2 , η_1 and η_2 and κ_{s1} and κ_{s2} are the molar volumes, the coefficients of viscosities and, the isentropic compressibilities of NMA and ME / water in the mixture respectively.

The molar volume V is defined by the relation, $V = (M_1x_1 + M_2x_2)/\rho$, where, M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture.

The excess functions at 308.15, 313.15 and 318.15 K have been presented in Tables 5-6.

Graphical representations of V^E , $\Delta\eta$ and $\Delta\kappa_s$ as functions of mole fractions of NMA are given in Figures 6-8.

The excess properties Y^E were fitted to the Redlich-Kister¹⁵ equation:

$$Y^E = x_1 (1 - x_1) \sum A_j (1 - 2x_1)^j, \quad (5)$$

where Y^E is $V^E / (\text{cm}^3 \text{mol}^{-1})$ or $\Delta\eta / (\text{mPa}\cdot\text{s})$ or $\Delta\kappa_s / (\text{bar}^{-1})$, and A_0, A_1, A_2, \dots etc., are adjustable parameters. These parameters were evaluated by fitting $Y^E / x_1 (1 - x_1)$ to equation (5) by the method of least squares. The values of these parameters along with the standard deviation $\sigma (Y^E)$ of Y^E as defined by the equation,

$$\sigma (Y^E) = [\sum (Y^E_{\text{observed}} - Y^E_{\text{calculated}})^2 / (N-M)]^{0.5} \quad (6)$$

are recorded in Tables 7-8; for NMA + ME and NMA + water systems respectively. In equation (6), N is the total number of experimental points and M is the number of parameters.

8.3 DISCUSSION

8.3.1 Solvent Properties of NMA + ME and NMA + Water Systems

The plots of densities, viscosities, and ultrasonic velocities of NMA + ME and NMA + water mixtures at various compositions and at different temperatures offer some information about the nature of these systems. For both the systems, the variation of density, viscosity, and ultrasonic velocity as a function of mole fraction of NMA is non-linear (Figures 1-3) at all three temperatures investigated. However, in the case of NMA + ME, only the density curves show broad maxima (around mole fraction 0.40 in NMA) at the given temperatures. The viscosity values gradually increase with the concentration

of NMA up to a mole fraction of 0.30 in NMA and increase more steeply thereafter. The ultrasonic velocity curves show a gradual rise in ultrasonic velocity as the mole fraction of NMA increases up to 0.60 but after that the curves flatten off and run almost parallel to the concentration axis. With further addition of NMA, there is only a slight increase in ultrasonic velocity values. In terms of temperatures, all the three parameters (ρ , η and 'u') decrease with increase in temperature for the NMA + ME system.

For the NMA + water system, however, the non-linear behaviour of all these parameters is very well pronounced. The curves obtained are distinct and characteristic of each parameter. All three curves (ρ , η and 'u') show clear maxima (Figures 1-3). The variations of density and ultrasonic velocity with concentration of NMA are very similar. Both show slight increase initially but after the maxima (around mole fraction 0.15 in NMA), the values fall off uniformly. The viscosity curves show broad maxima around mole fraction 0.55 in NMA at all three temperatures and thereafter they decline slightly. All these three parameters decrease with rise in temperature.

The plots of the two derived parameters, κ_s and τ , for NMA + ME also exhibit non-linear character (Figures 4-5). κ_s , like ultrasonic velocity, is very much affected by the addition of NMA up to its mole fraction about 0.60 but remains almost unaffected by it after that composition. No maxima or minima are observed here.

For the NMA + water system, the plot of κ_s versus mole fraction of NMA gives a distinct minimum at around mole fraction 0.15 in NMA at each temperature studied. The

initial decrease in κ_s values up to the minimum (around mole fraction 0.15 in NMA) may be due to water whose ultrasonic velocity value increases with temperature leading to a decrease in κ_s up to the minimum. Thereafter, the decrease in ρ_{mixture} more than compensates for the increase in 'u' giving rise to a steep hike in κ_s values.

The variation of shear relaxation time (τ) with the concentration of NMA is similar in both the systems, the only difference being the steeper slopes obtained for NMA + water. The τ values decrease with temperature for both the systems.

The non-linear variation of any of the solvent parameters with solvent composition is due to solvent structural effects. The solvent structural effects become very strong when a solvent parameter passes through a maximum or minimum.¹⁶ From these considerations it appears that there is a well-pronounced and strong solvent structural effect in the binary mixtures of NMA + water but a weak solvent structural effect in NMA + ME mixtures.

8.3.2 Excess Properties of NMA + ME and NMA + Water Systems

8.3.2.1 Excess Molar Volume:

NMA + ME System

It is well known that the sign and magnitude of V^E give a good estimate of the strength of the unlike interactions in the binary mixtures.¹⁷ Large positive V^E values are taken as indicative of weak intermolecular interactions whereas large negative values of

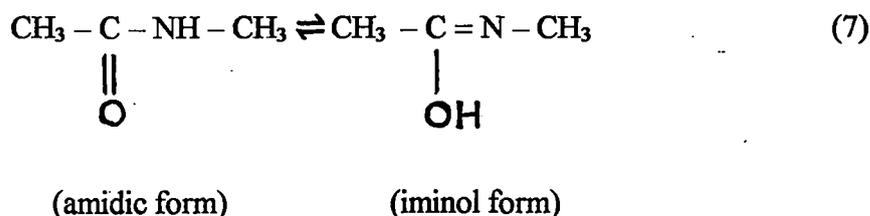
V^E are usually found when these interactions are strong and intermolecular association "complexes" are believed to be present.

The systems NMA + ME and NMA + water show negative V^E values over the entire range of mole fraction and over the entire range of temperatures studied (Figures 6-9). Both the systems show clear minima at a mole fraction of about 0.40 of NMA.

In general, V^E may be due to several effects, which may be conveniently divided into (1) physical, (2) chemical and (3) geometrical contributions. The physical interactions involve mainly dispersive forces making V^E positive. The chemical effects may arise from specific interactions accompanied by a decrease in volume and make V^E negative. They also may be due to the disruption of: (i) hydrogen bonds present in one of the components, and (ii) the intermolecular dipolar interactions. Finally, a negative V^E may arise due to the existence of hydrogen-bond interactions between unlike molecules. The geometrical effect is due to the fitting of one component into the other, due to the difference in molecular sizes between the two components and the availability of free volume, leading to a negative contribution to V^E .

NMA is a dipolar protic solvent with a very high dielectric constant ($\epsilon = 191.3$ at 305.15 K), which is attributed to the liquid being highly structured with polymeric chains linked by hydrogen bonding.¹⁸

NMA may exist in two forms as shown below:



The iminol form, with its phenolic - OH group and the availability of a lone pair of electrons from the nitrogen atom, is capable of making extensive bonds - both intramolecular as well as intermolecular.

On the other hand, the molecules of n-alkoxyethanols, in general, are self-associated and form intermolecular as well as intramolecular hydrogen bonds. IR studies on ME indicate that intermolecular hydrogen bonding exists in ME molecules in the liquid state.¹⁹ Moreover, the values of the Kirkwood correlation factors, g_k , for pure ME in the temperature range studied are not much greater than unity (the g_k values of ME are: 1.483, 1.478, and 1.463 at 298.15, 308.15 and 318.15 K respectively). This indicates that 2-methoxyethanol is a relatively unstructured liquid and that there are strong but not specific dipole-dipole forces. It is also a quasi-aprotic solvent.

Thus, the interaction between a highly structured NMA, with many hydrogen bonding sites, and a relatively unstructured ME, results in a negative V^E . This may be due to the disruption of (i) intermolecular hydrogen bonds in the ME molecules, and (ii) intermolecular dipolar interactions in NMA. Secondly, the existence of hydrogen bonds between the unlike molecules is likely to offer a negative contribution to V^E .

Considering the molar volumes of NMA and ME (77.25 and 80.38 cm³ mol⁻¹ respectively, at 308.15 K), the interstitial accommodation of one component into the other may be ruled out.

NMA + Water System

In the NMA + water mixture the excess molar volumes at the three temperatures investigated are negative over the whole range of compositions (Figure 6). However, the V^E values are three times bigger than those of NMA + ME mixture. Again the minima in the curve have V^E values in the range of -1.10 to -1.13 cm³ mol⁻¹ (around mole fraction 0.40 in NMA), which is in conformity with an earlier work of Böje and Hvidt²⁰ done at 298.15 K, whereas in NMA + ME, the minima have V^E values in the range of -0.35 to -0.39 cm³ mol⁻¹. The mixing of NMA with water is a slightly exothermic process. Thus the magnitude of V^E decreases with temperature to a very, very minute extent so that there is hardly any change in V^E even when the temperature is hiked by ten degrees.

One of the possible effects that may contribute to this negative V^E is the disruption of (i) the hydrogen bonding present in self-associated water molecules, and (ii) the intramolecular hydrogen bonding and intermolecular dipolar interactions in NMA. Secondly, the difference in the molecular sizes between the two components of the mixture may play a vital role in reducing the excess molar volume. The molar volumes of NMA and water at 308.15 K are 77.25 and 18.13 cm³ mol⁻¹ respectively. Due to the extensive polymeric chains linked by hydrogen bonding, NMA is likely to have a much bigger effective molar volume than what is given above from strictly theoretical

considerations. On the other hand, the negative V^E values may also indicate strong solvation by hydrogen bonding accompanied by a minor destruction of water structure, besides interstitial accommodation of NMA molecules inside the water cavities. Hence, the molar volume of the mixture is reduced to a large extent. This also accounts for the fact that the excess molar volume is practically unaffected by small changes in temperature even to the extent of ten degrees.

The negative V^E values at the three temperatures studied for this mixture and the clear minima in the curves indicate strong association through multiple hydrogen bonding between the polar group of NMA and water, although the pure liquids are presumed to be highly structured. The observation that the V^E values here are three times bigger than that for the NMA + ME system is a sign of strong solvation by hydrogen bonding probably accompanied by a minor disruption of the water and/or NMA structure, besides the interstitial accommodation of NMA molecules inside the water cavities. Although both are protic, NMA is less protic than water. Hence, there is interaction among them reducing the molar volume of the mixture considerably.

All this suggests that the hydrogen bonding between water and NMA is stronger and more compact than that between water molecules themselves.

The actual V^E would depend upon the balance between the two opposing contributions. The experimental data indicate that the negative contributions predominate in these binaries.

8.3.2.2 Viscosity Deviations

NMA + ME System

The NMA + ME system displays a sharp negative deviation of $\Delta\eta$ from ideality over the entire mole fraction range and over the whole range of studied temperatures. The minima correspond to the mole fraction of about 0.60 in NMA (Figure 7). As the temperature increases the $\Delta\eta$ values become less and less negative and tend to approach ideality.

This unique behaviour of negative deviation can be explained in the light of the behaviour of water when mixed with certain non-aqueous solvents. When small amounts of certain non-aqueous solvents are added to water, the water structure is reinforced; the viscosity, Walden's products and heats of solution give maxima. But additional quantities of the organic compounds cause progressive disruption of water structure until a minimum is reached around the equimolar region of the two components. Presumably this corresponds to a maximum breakdown or depolymerization of the water structure by the non-aqueous component.²¹ A similar structure-breaking effect is observed when N,N-dimethylformamide (DMF) is added to the hydrogen bonded NMA. Such effects are not observed when none of the components is highly associated in the pure state.²¹

The highly associated NMA seems to undergo a structure-breaking effect when mixed with ME, similar to NMA's behaviour with DMF. The change in the variation of

density, viscosity and ultrasonic velocity between mole fraction of 0.3 and 0.6 in NMA supports this. Earlier studies indicate that in NMA, tetraalkylammonium ions exert a structure-breaking effect.²² Apart from this, dispersion and dipolar forces between these two weakly protic and unlike solvents may also give rise to negative $\Delta\eta$ values. Such negative deviation from ideality are also observed in propylene carbonate (PC) + ME, PC + DME, PC + methanol and PC + tetrahydrofuran mixtures.²³ As the temperature increases these forces decrease and the system approaches ideality.

NMA + Water System

On the other hand, NMA + water system exhibits a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Fig 7). Very symmetric curves with clear maxima corresponding to a mole fraction of about 0.40 in NMA are obtained for the three temperatures. As the temperature increases the $\Delta\eta$ values become less and less positive. These positive $\Delta\eta$ values clearly indicate very strong and specific hydrogen bond interactions between NMA and water with the possibility of the formation of a 'complex' species, probably between the peptido group in NMA and water. This is also supported by the excess molar volume studies as reported above. With the rise in temperature, these interactions decrease and the system approaches ideal behaviour.

8.3.2.3 Isentropic Compressibility Changes:

The results of deviations in isentropic compressibility versus mole fraction of NMA are given in Figures (8) for NMA + ME and NMA + water systems respectively. For both the systems, the values of $\Delta\kappa_s$ are negative over the entire composition range and at all the three temperatures studied. In NMA + ME, V-shaped curves are obtained with minima around a mole fraction of about 0.40 in NMA at all the three temperatures. These $\Delta\kappa_s$ values are less than the values recorded for the NMA + water system. As the temperature increases the $\Delta\kappa_s$ values become more and more negative. For the NMA + water system, the minima occur at a mole fraction of about 0.25 in NMA at all the three temperatures. The $\Delta\kappa_s$ values here are five times more than those obtained for the NMA + ME system. However, the $\Delta\kappa_s$ values decrease with the increase of temperature.

Negative $\Delta\kappa_s$ values for both the systems indicate that the mixtures are more compressible than the corresponding ideal mixture suggesting the predominance of interactions between NMA and ME, and NMA and water. Due to these interactions, the ultrasonic velocity increases and the compressibility of these solutions decreases until the minima are reached and then these parameters follow the reverse trend.

In the case of NMA + ME, the negative $\Delta\kappa_s$ values and these values becoming more negative as temperature increases point to the maximum deviation from ideality around the mole fraction of 0.40 in NMA. Similarly, V^E too becomes more negative with

the rise in temperature of this system. Along with the negative $\Delta\eta$ values, this behaviour of the NMA + ME system indicates a possible structural effect in this system.

The observation that $\Delta\kappa_s$ values in the NMA + water system are five times more than those obtained for the NMA + ME system can be explained as follows. The decrease in κ_s values up to the minima is due to the interstitial accommodation of the two components into one another. This process may be followed by the formation of the hydrophobic NMA aggregates and a possible rupture of water structure. Thus it is apparent that the interstitial accommodation effect is more effective and the positive contribution from the breaking of hydrogen bonds becomes less predominant, giving negative $\Delta\kappa_s$ values over the entire mole fraction range for this mixture. The increase of temperature slows down this process and hence $\Delta\kappa_s$ values are less at higher temperatures.

However, for a quantitative description of such effects more work should be done in future based on the extended real associated solution (ERAS) model.²⁴

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TABLE 1. Density (ρ), Viscosity (η) and Ultrasonic Velocity (u) of N-Methylacetamide + 2-Methoxyethanol mixtures at different mole fractions (x) of NMA, at 308.15, 313.15 and 318.15 K.

x (NMA)	ρ (g cm ⁻³)			η (mPa s)			u (m s ⁻¹)		
	308.15	313.15	318.15	308.15	313.15	318.15	308.15	313.15	318.15 (K)
0.0000	0.946802	0.942336	0.937624	1.3152	1.2004	1.0982	1309.67	1294.26	1276.94
0.0301	0.947281	0.942959	0.938379	1.3621	1.2422	1.1355	1314.35	1298.93	1281.53
0.0501	0.947608	0.943373	0.938880	1.3928	1.2698	1.1601	1316.87	1301.33	1283.92
0.0752	0.948004	0.943876	0.939491	1.4312	1.3038	1.1909	1319.66	1304.17	1286.93
0.1036	0.948494	0.944363	0.940126	1.4761	1.3433	1.2266	1322.33	1307.00	1289.90
0.1301	0.948900	0.944852	0.940668	1.5150	1.3783	1.2587	1324.68	1309.35	1292.39
0.1700	0.949475	0.945419	0.941248	1.5744	1.4324	1.3069	1327.85	1312.65	1296.00
0.2032	0.949834	0.945773	0.941611	1.6243	1.4771	1.3476	1330.39	1315.22	1298.92
0.2501	0.950242	0.946202	0.942051	1.6955	1.5414	1.4042	1333.86	1318.55	1302.77
0.3020	0.950573	0.946534	0.942354	1.7760	1.6130	1.4677	1337.09	1322.03	1306.24
0.4032	0.950827	0.946793	0.942628	1.9403	1.7576	1.5959	1342.25	1327.13	1311.81
0.5037	0.950725	0.946687	0.942653	2.1140	1.9096	1.7299	1346.32	1331.45	1316.26
0.6033	0.950254	0.946231	0.942333	2.3081	2.0742	1.8759	1349.49	1334.34	1319.46
0.6500	0.949900	0.945901	0.942073	2.4085	2.1597	1.9495	1350.66	1335.46	1320.39
0.7021	0.949465	0.945472	0.941700	2.5258	2.2588	2.0381	1351.61	1336.55	1321.41
0.7503	0.949063	0.945071	0.941326	2.6410	2.3573	2.1239	1352.27	1337.41	1322.31
0.8032	0.948566	0.944581	0.940890	2.7746	2.4772	2.2273	1352.78	1338.15	1323.11
0.8524	0.948007	0.944050	0.940411	2.9077	2.5941	2.3283	1353.36	1338.77	1323.70
0.9035	0.947430	0.943442	0.939850	3.0613	2.7235	2.4390	1353.94	1339.41	1324.31
0.9301	0.947094	0.943107	0.939544	3.1451	2.7953	2.5003	1354.06	1339.43	1324.46
0.9702	0.946604	0.942617	0.939079	3.2771	2.9130	2.5969	1354.35	1339.51	1324.75
1.0000	0.946244	0.942235	0.938715	3.3796	3.0038	2.6734	1354.28	1339.48	1324.80

TABLE 2. Density (ρ), Viscosity (η) and Ultrasonic Velocity (u) of N-Methylacetamide + Water mixtures at different mole fractions (x) of NMA, at 308.15, 313.15 and 318.15 K.

x (NMA)	ρ (g cm ⁻³)			η (mPa s)			u (m s ⁻¹)		
	308.15	313.15	318.15	308.15	313.15	318.15	308.15	313.15	318.15(K)
0.0000	0.994108	0.992206	0.990268	0.7211	0.6562	0.6001	1519.36	1528.58	1535.48
0.0301	0.995317	0.992952	0.990740	0.9967	0.8931	0.8115	1575.71	1563.16	1564.53
0.0600	0.996618	0.993851	0.991131	1.2926	1.1367	1.0256	1609.87	1602.90	1598.87
0.1002	0.997153	0.994028	0.991302	1.6931	1.4647	1.3008	1645.22	1639.95	1633.16
0.1500	0.997620	0.994361	0.991086	2.2399	1.9016	1.6510	1658.71	1652.29	1645.58
0.1999	0.997540	0.993698	0.989917	2.7656	2.3255	2.0013	1654.34	1645.42	1636.10
0.2450	0.995953	0.992088	0.988304	3.1081	2.6261	2.2571	1644.46	1632.75	1621.49
0.3006	0.992735	0.988956	0.985087	3.4015	2.8819	2.4833	1626.26	1611.60	1599.04
0.3502	0.989098	0.985176	0.981625	3.5974	3.0633	2.6462	1604.04	1588.82	1575.75
0.4012	0.985263	0.981583	0.977803	3.7477	3.1981	2.7685	1576.24	1561.27	1548.32
0.4501	0.981501	0.977790	0.974075	3.8520	3.2996	2.8589	1548.65	1533.78	1520.12
0.5000	0.977749	0.974076	0.970337	3.9214	3.3699	2.9142	1521.75	1506.54	1492.51
0.5502	0.974070	0.970296	0.966666	3.9421	3.3983	2.9375	1497.54	1481.64	1467.37
0.6018	0.970282	0.966394	0.962825	3.9056	3.3822	2.9278	1475.24	1459.56	1444.48
0.6550	0.966477	0.962560	0.958945	3.8252	3.3269	2.8938	1454.41	1438.53	1423.55
0.7019	0.963345	0.959398	0.955777	3.7651	3.2806	2.8686	1436.93	1421.58	1406.30
0.7551	0.959874	0.955861	0.952282	3.6881	3.2262	2.8321	1419.04	1403.08	1388.62
0.8070	0.956692	0.952666	0.949110	3.6064	3.1673	2.7966	1403.33	1387.46	1372.97
0.8450	0.954387	0.950402	0.946767	3.5541	3.1299	2.7680	1392.64	1376.62	1362.60
0.9015	0.951169	0.947179	0.943609	3.4953	3.0772	2.7325	1378.36	1362.50	1348.20
0.9500	0.948615	0.944616	0.941069	3.4399	3.0437	2.7030	1366.24	1350.74	1336.34
1.0000	0.946244	0.942235	0.938715	3.3796	3.0038	2.6734	1354.28	1339.48	1324.80

TABLE 3. Isentropic Compressibility (κ_s) and Shear Relaxation Time (τ) of the mixtures of N-Methylacetamide + 2-Methoxyethanol, at different mole fractions, at three temperatures.

x (NMA)	$\kappa_s \times 10^5$ (bar ⁻¹)			$\tau \times 10^{13}$ (s)		
	308.15K	313.15 K	318.15 K	308.15K	313.15 K	318.15 K
0.0000	6.1577	6.3351	6.5408	10.80	10.14	9.58
0.0301	6.1108	6.2854	6.4888	11.10	10.41	9.82
0.0501	6.0854	6.2595	6.4612	11.30	10.60	9.99
0.0752	6.0571	6.2290	6.4269	11.56	10.83	10.21
0.1036	6.0296	6.1989	6.3930	11.87	11.10	10.46
0.1301	6.0056	6.1734	6.3647	12.13	11.35	10.68
0.1700	5.9733	6.1387	6.3254	12.54	11.72	11.02
0.2032	5.9483	6.1124	6.2946	12.88	12.04	11.31
0.2501	5.9148	6.0789	6.2545	13.37	12.49	11.71
0.3020	5.8843	6.0448	6.2193	13.93	13.00	12.17
0.4032	5.8376	5.9968	6.1647	15.10	14.05	13.12
0.5037	5.8029	5.9586	6.1230	16.36	15.17	14.12
0.6033	5.7786	5.9357	6.0954	17.78	16.42	15.25
0.6500	5.7707	5.9277	6.0885	18.53	17.07	15.83
0.7021	5.7652	5.9208	6.0815	19.42	17.83	16.53
0.7503	5.7621	5.9157	6.0756	20.29	18.59	17.21
0.8032	5.7607	5.9122	6.0711	21.31	19.53	18.03
0.8524	5.7592	5.9101	6.0688	22.33	20.44	18.84
0.9035	5.7578	5.9082	6.0668	23.50	21.45	19.73
0.9301	5.7588	5.9102	6.0674	24.15	22.03	20.23
0.9702	5.7593	5.9125	6.0678	25.16	22.96	21.01
1.0000	5.7621	5.9152	6.0697	25.96	23.69	21.64

TABLE 4. Isentropic Compressibility (κ_s) and Shear Relaxation Time (τ) of the mixtures of N-Methylacetamide + Water, at different mole fractions, at three temperatures.

x (NMA)	$\kappa_s \times 10^5$ (bar ⁻¹)			$\tau \times 10^{13}$ (s)		
	308.15K	313.15 K	318.15 K	308.15K	313.15 K	318.15 K
0.0000	4.3576	4.3134	4.2831	4.19	3.77	3.43
0.0301	4.0466	4.1216	4.1236	5.38	4.91	4.46
0.0600	3.8716	3.9162	3.9468	6.67	5.94	5.40
0.1002	3.7050	3.7406	3.7821	8.36	7.31	6.56
0.1500	3.6433	3.6837	3.7261	10.88	9.34	8.20
0.1999	3.6629	3.7170	3.7738	13.51	11.53	10.07
0.2450	3.7129	3.7810	3.8484	15.39	13.24	11.58
0.3006	3.8088	3.8932	3.9702	17.27	14.96	13.15
0.3502	3.9295	4.0211	4.1028	18.85	16.42	14.48
0.4012	4.0851	4.1794	4.2661	20.41	17.82	15.75
0.4501	4.2482	4.3474	4.4427	21.82	19.13	16.94
0.5000	4.4166	4.5232	4.6264	23.09	20.32	17.98
0.5502	4.5778	4.6947	4.8045	24.06	21.27	18.82
0.6018	4.7356	4.8574	4.9777	24.66	21.90	19.43
0.6550	4.8914	5.0204	5.1459	24.95	22.27	19.86
0.7019	5.0274	5.1577	5.2904	25.24	22.56	20.24
0.7551	5.1736	5.3142	5.4459	25.44	22.86	20.56
0.8070	5.3077	5.4528	5.5894	25.52	23.03	20.84
0.8450	5.4025	5.5522	5.6888	25.60	23.17	21.00
0.9015	5.5338	5.6871	5.8304	25.79	23.33	21.24
0.9500	5.6475	5.8023	5.9504	25.90	23.55	21.45
1.0000	5.7621	5.9152	6.0697	25.96	23.69	21.64

TABLE 7. Coefficients of Least-Square Fit by equation (5) for Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility Changes of N-Methylacetamide + 2-Methoxyethanol mixtures at 308.15, 313.15 and 318.15 K.

Property	Temp. (K)	A ₀	A ₁	A ₂	A ₃	A ₄	σ (Y ^E)
V ^E	308.15	-1.3817	0.5037	-0.1594	-0.2859	0.4126	0.002
	313.15	-1.4621	0.5591	-0.2733	-0.1552	0.3112	0.002
	318.15	-1.4928	0.6443	-0.6279	-0.0717	0.5042	0.006
$\Delta\eta$	308.15	-0.9521	-0.4792	-0.0435	-0.0037	0.0211	0.001
	313.15	-0.7940	-0.4502	-0.0791	-0.0123	0.0031	0.001
	318.15	-0.6482	-0.3582	0.0294	0.0048	-0.0773	0.001
$\Delta\kappa_s$	308.15	-0.6378	0.1729	0.1128	0.2058	-0.3862	0.002
	313.15	-0.6631	0.1852	0.0324	0.2014	-0.3215	0.002
	318.15	-0.7296	0.2455	0.0440	0.1434	-0.2766	0.002

TABLE 8. Coefficients of Least-Square Fit by equation (5) for Excess Molar Volumes, Viscosity Deviations and Isentropic Compressibility Changes of N-Methylacetamide + Water mixtures at 308.15, 313.15 and 318.15 K.

Property	Temp. (K)	A ₀	A ₁	A ₂	A ₃	A ₄	σ (Y ^E)
V ^E	308.15	-4.3872	1.7434	-0.3593	-0.8871	1.2388	0.007
	313.15	-4.3929	1.6890	-0.1248	-0.9063	1.0421	0.006
	318.15	-4.3396	1.5804	0.0160	-0.7844	0.8828	0.004
$\Delta\eta$	308.15	7.4524	-4.9177	-0.4478	3.9205	-2.3466	0.032
	313.15	6.1492	-3.6705	-0.9434	2.7013	-1.2185	0.022
	318.15	5.1063	-2.9198	-0.9254	1.9479	-0.5084	0.012
$\Delta\kappa_s$	308.15	-2.6676	3.2055	-1.5566	2.7700	-3.1008	0.022
	313.15	-2.2988	3.7868	-3.8487	0.7347	1.3313	0.024
	318.15	-2.1215	3.7966	-3.9381	0.1937	1.8652	0.027

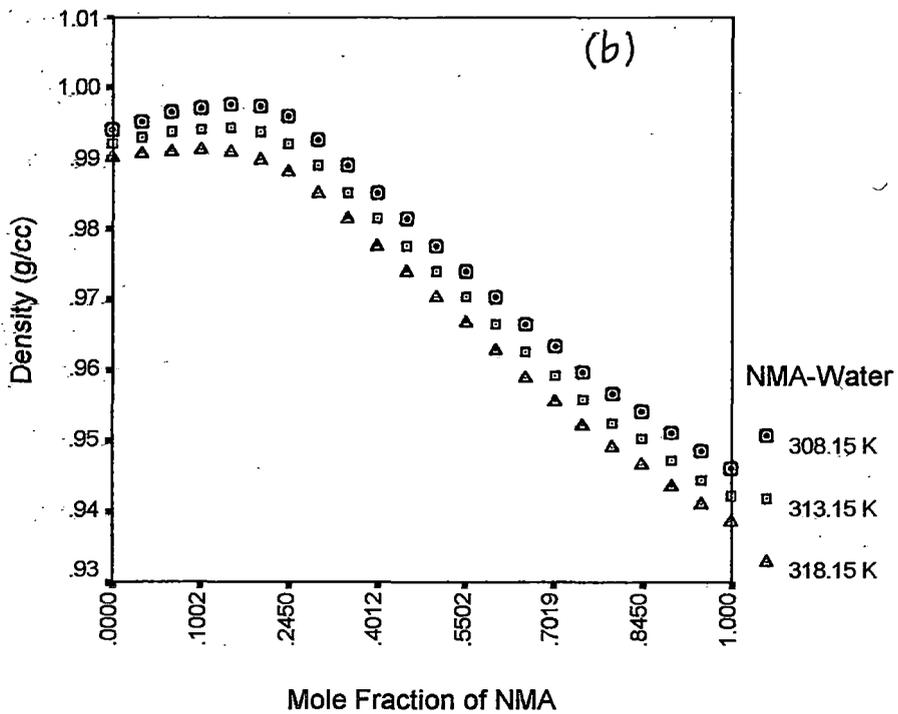
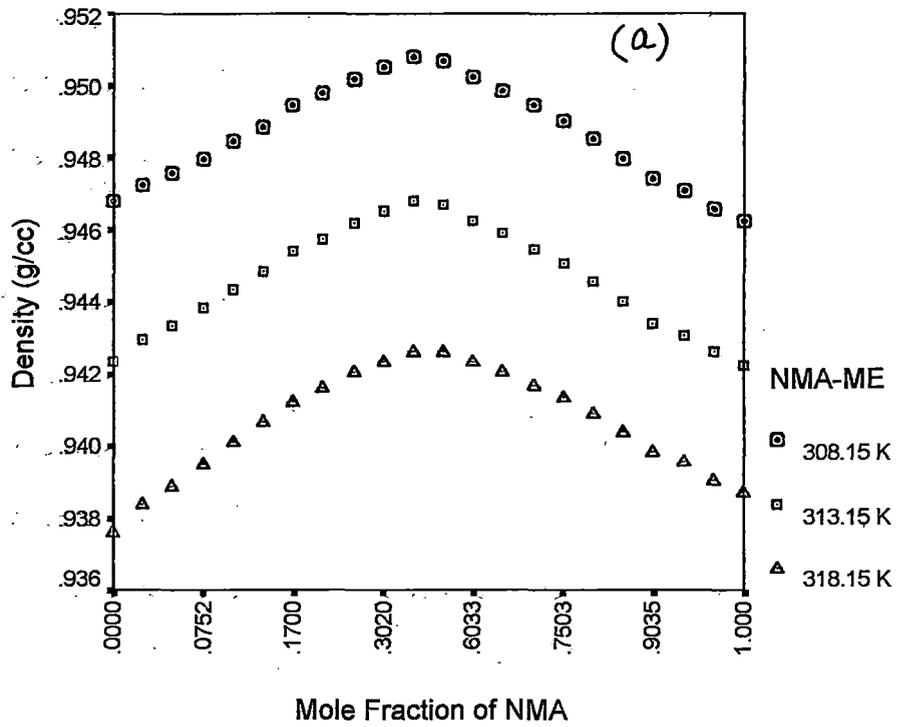


Figure 1. (a) Density (ρ) versus mole fraction of NMA in NMA + ME mixture at three temperatures.
(b) Density (ρ) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

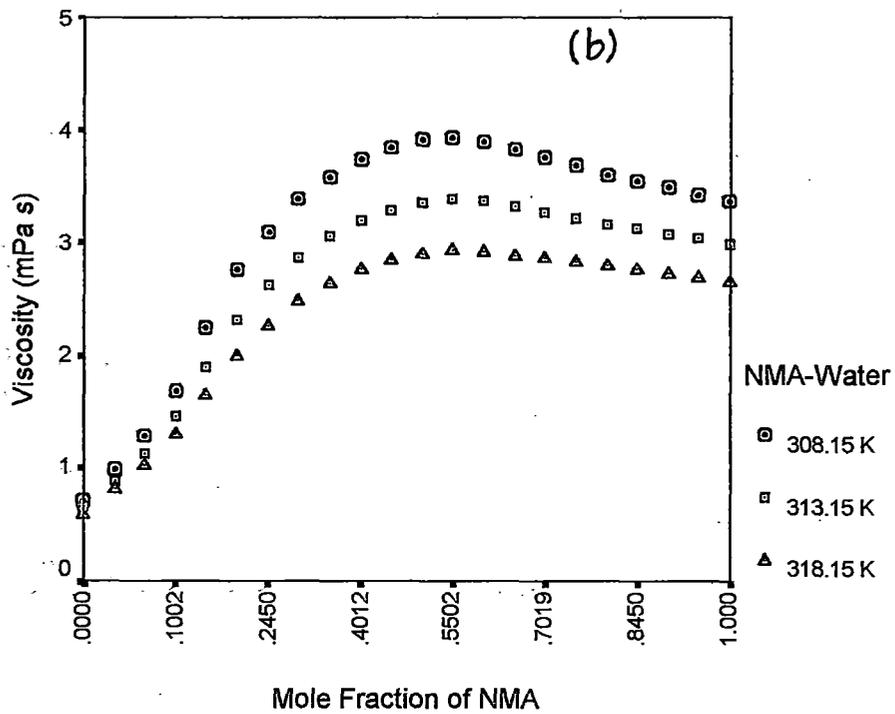
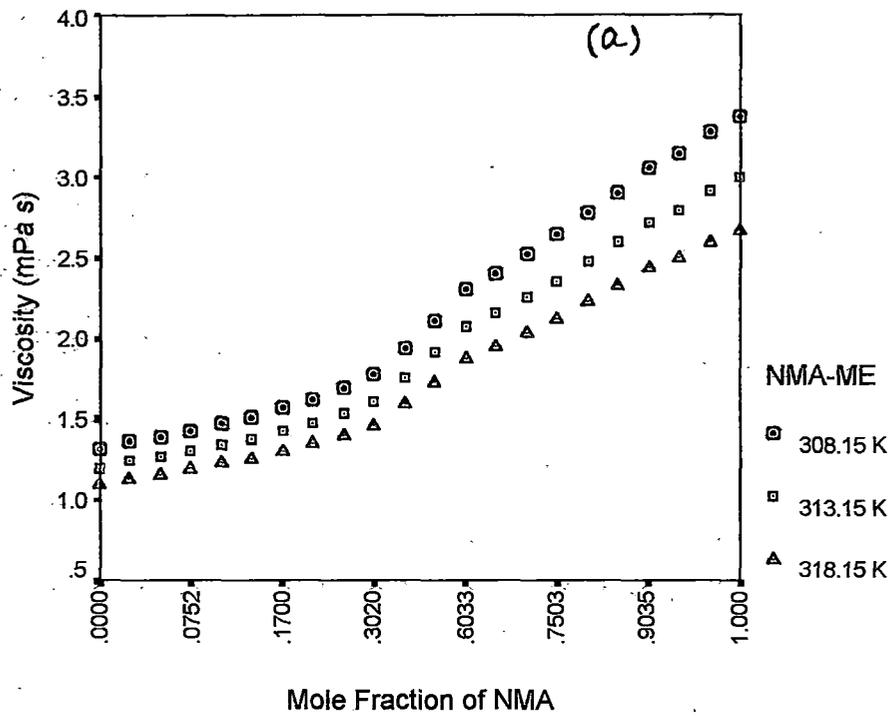


Figure 2. (a) Viscosity (η) versus mole fraction of NMA in NMA + ME mixture at three temperatures.
(b) Viscosity (η) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

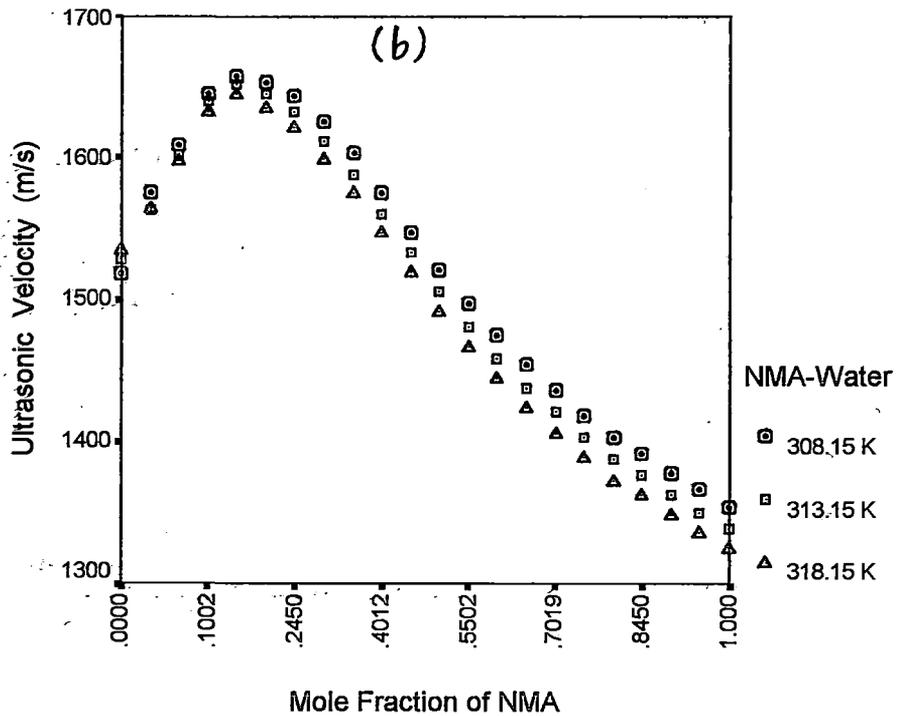
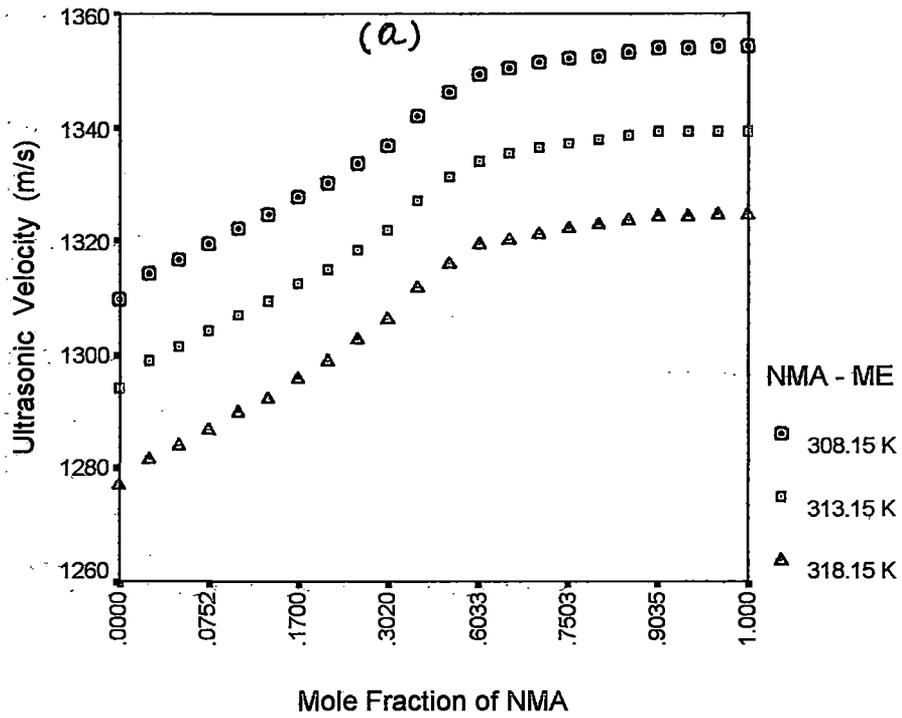


Figure 3. (a) Ultrasonic Velocity (u) versus mole fraction of NMA in NMA + ME mixture at three temperatures.

(b) Ultrasonic Velocity (u) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

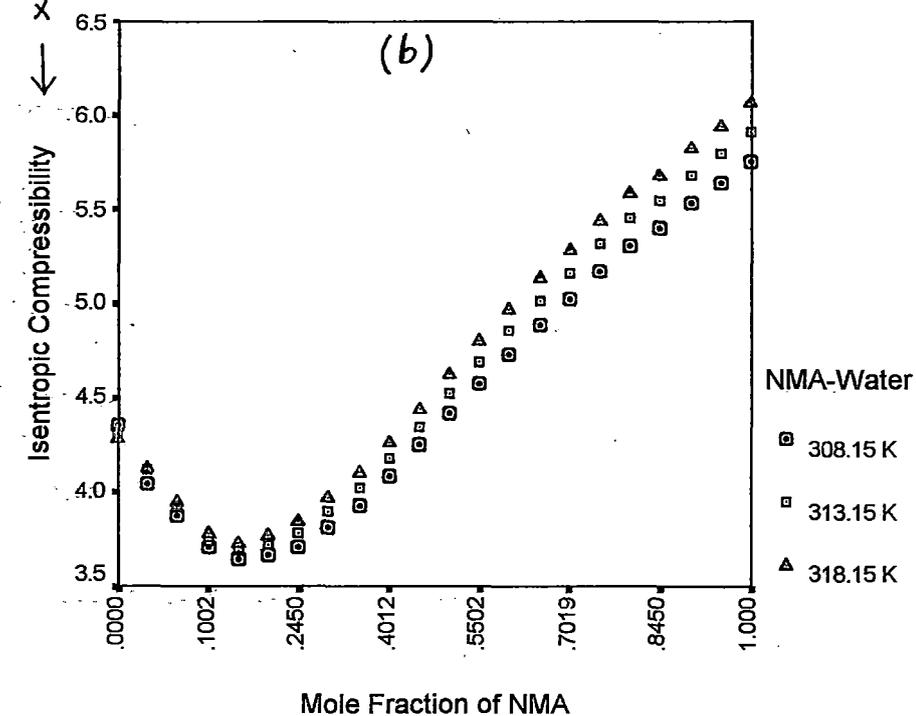
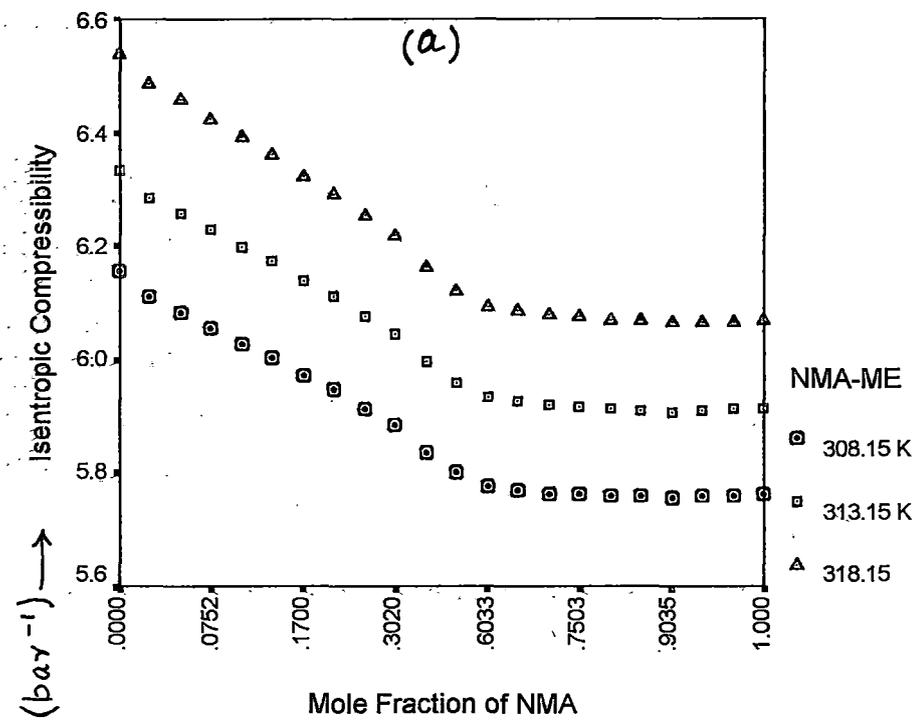


Figure 4. (a) Isentropic Compressibility (κ_s) versus mole fraction of NMA in NMA + ME mixture at three temperatures.
(b) Isentropic Compressibility (κ_s) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

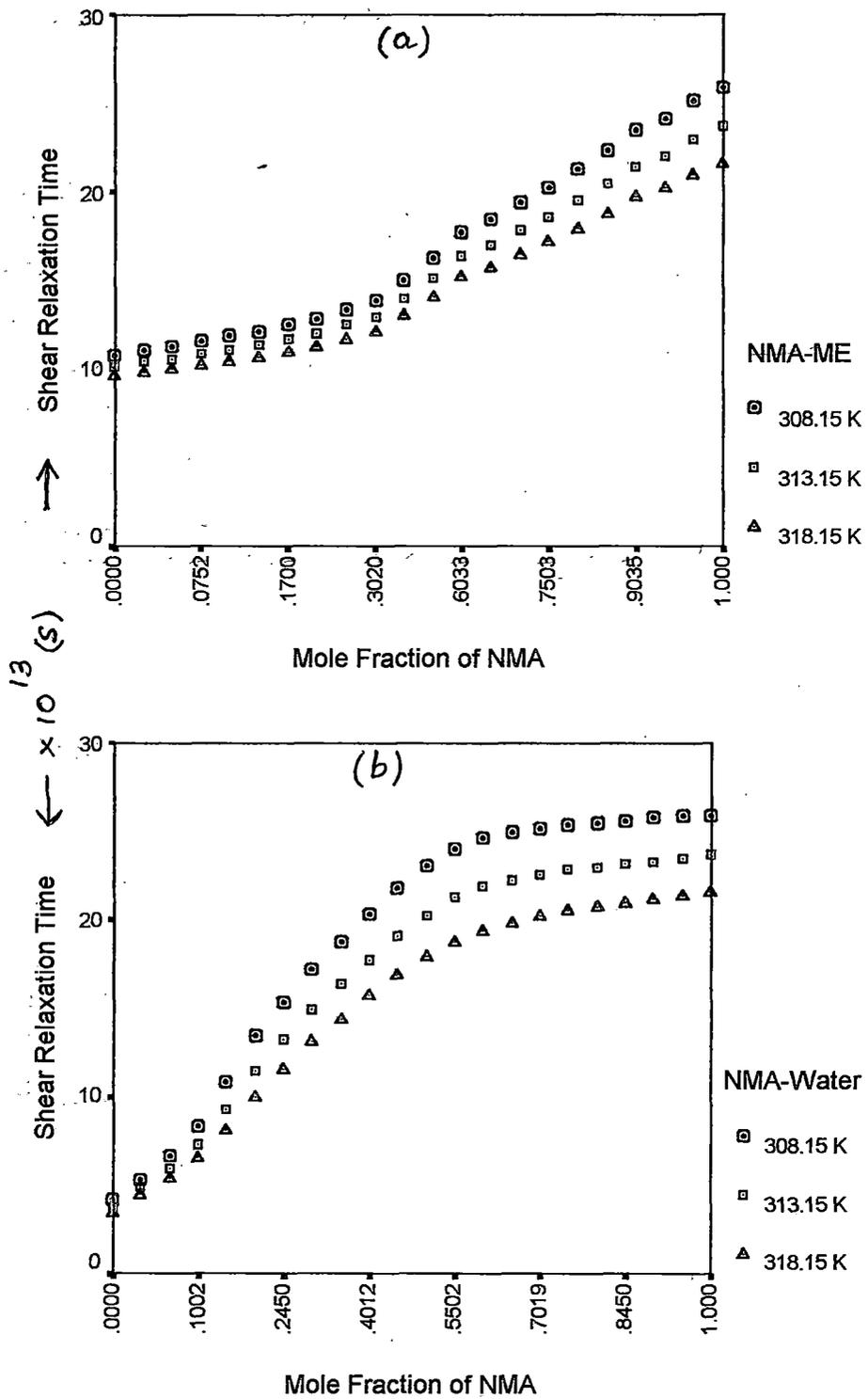


Figure 5. (a) Shear Relaxation Time (τ) versus mole fraction of NMA in NMA + ME mixture at three temperatures.

(b) Shear Relaxation Time (τ) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

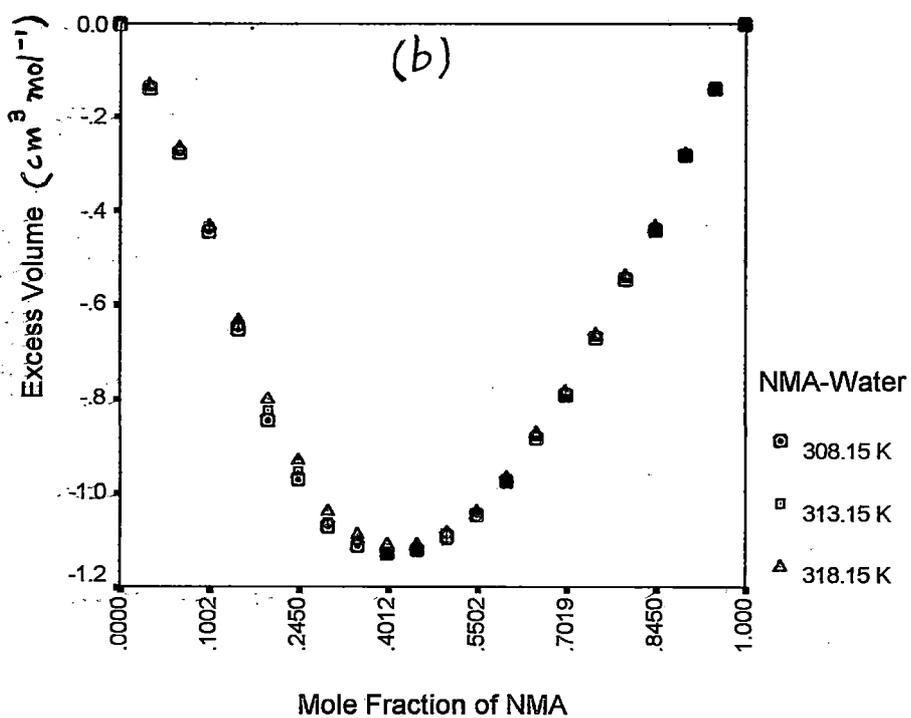
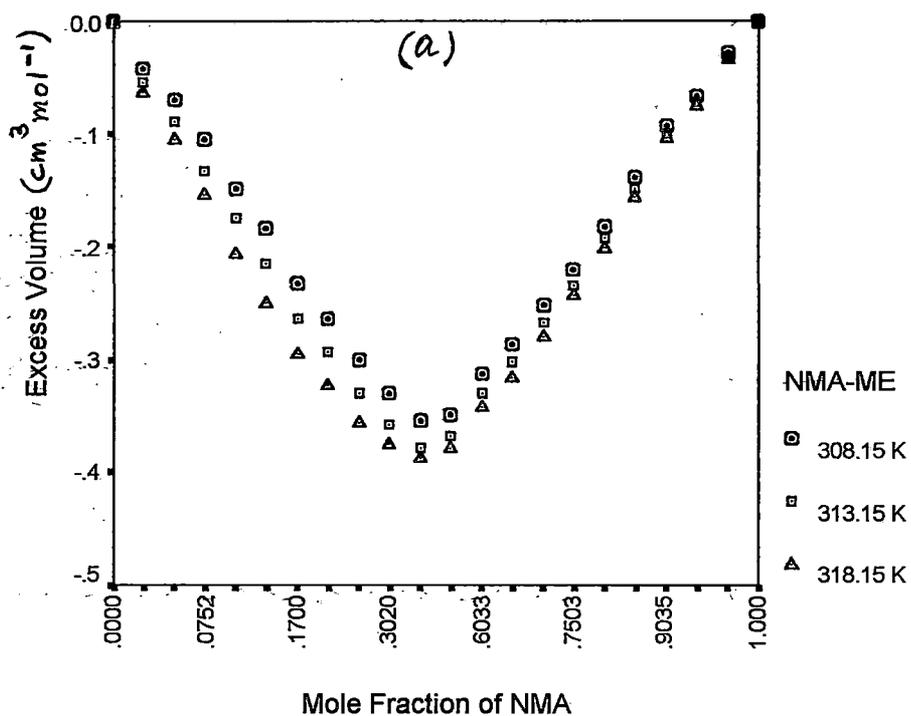


Figure 6. (a) Excess Molar Volume (V^E) versus mole fraction of NMA in NMA + ME mixtures at three temperatures. (b) Excess Molar Volume (V^E) versus mole fraction of NMA in NMA + Water mixtures at three temperatures.

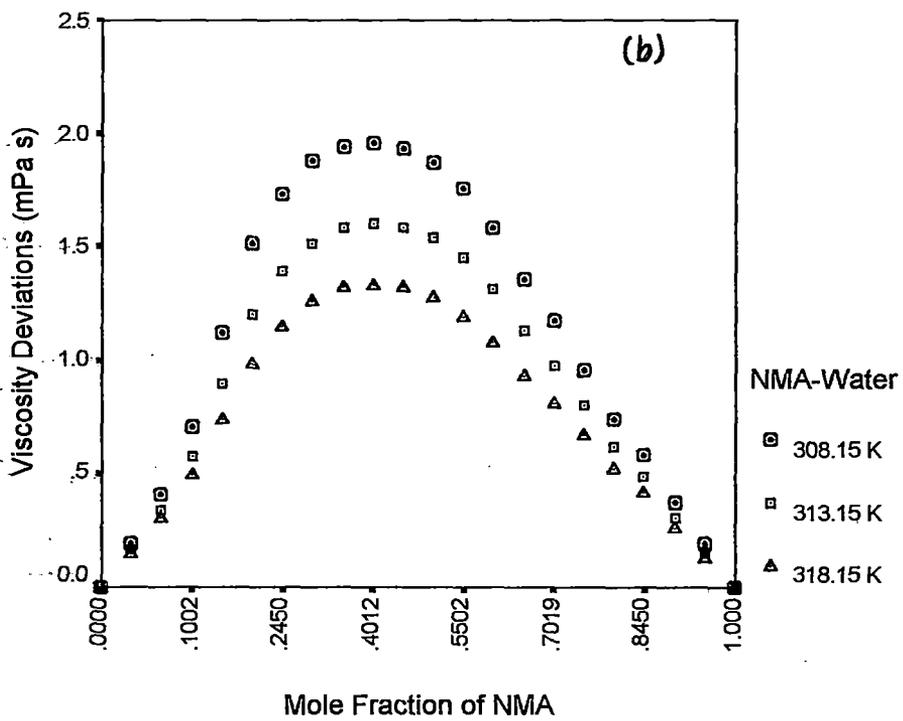
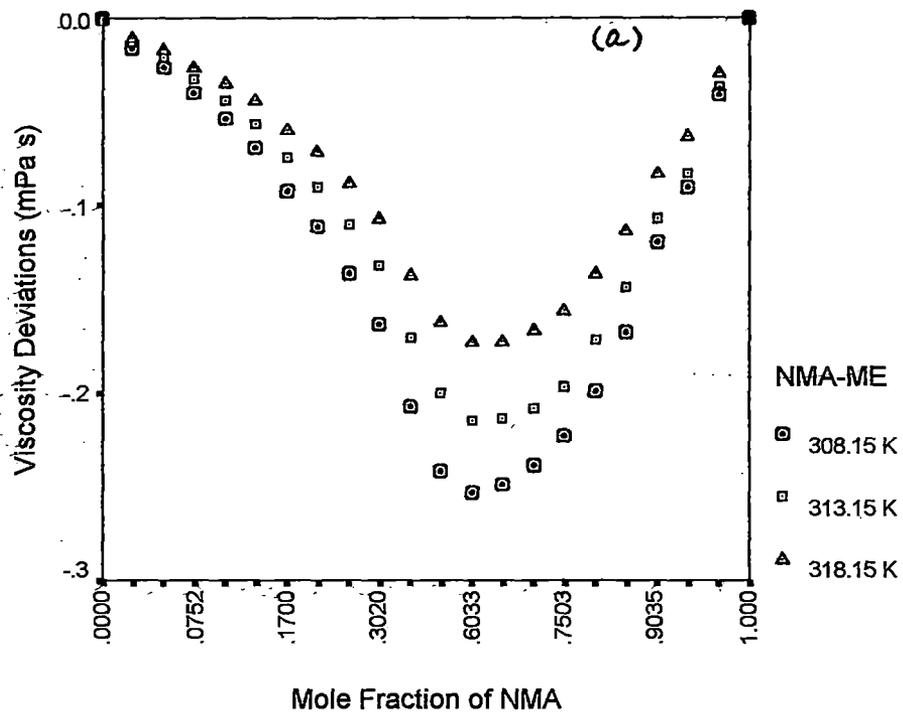


Figure 7. (a) Viscosity Deviations ($\Delta\eta$) versus mole fraction of NMA in NMA + ME mixture at three temperatures.

(b) Viscosity Deviations ($\Delta\eta$) versus mole fraction of NMA in NMA + Water mixture at three temperatures.

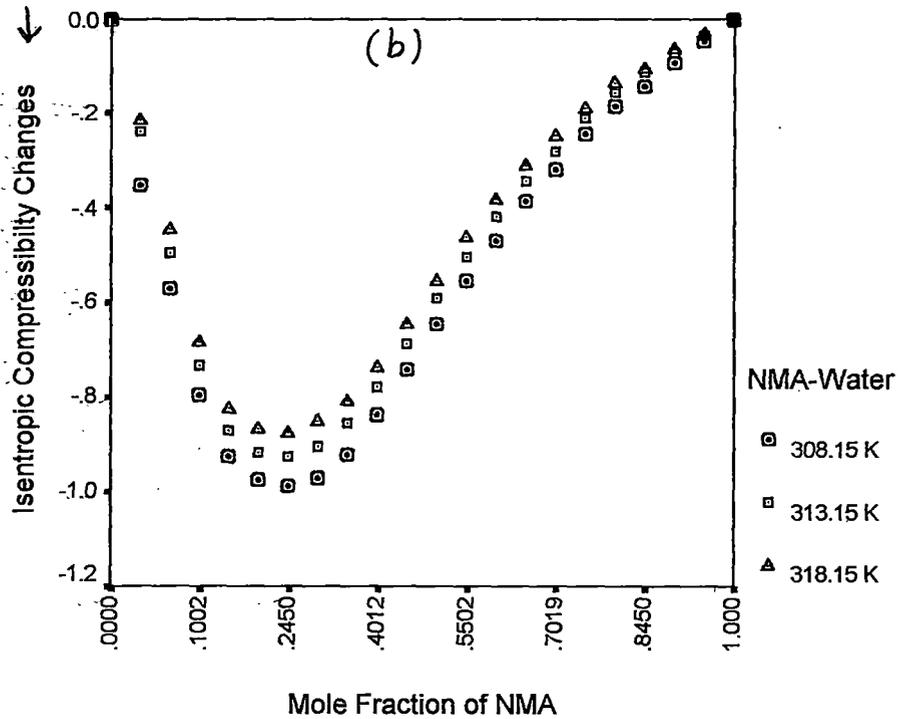
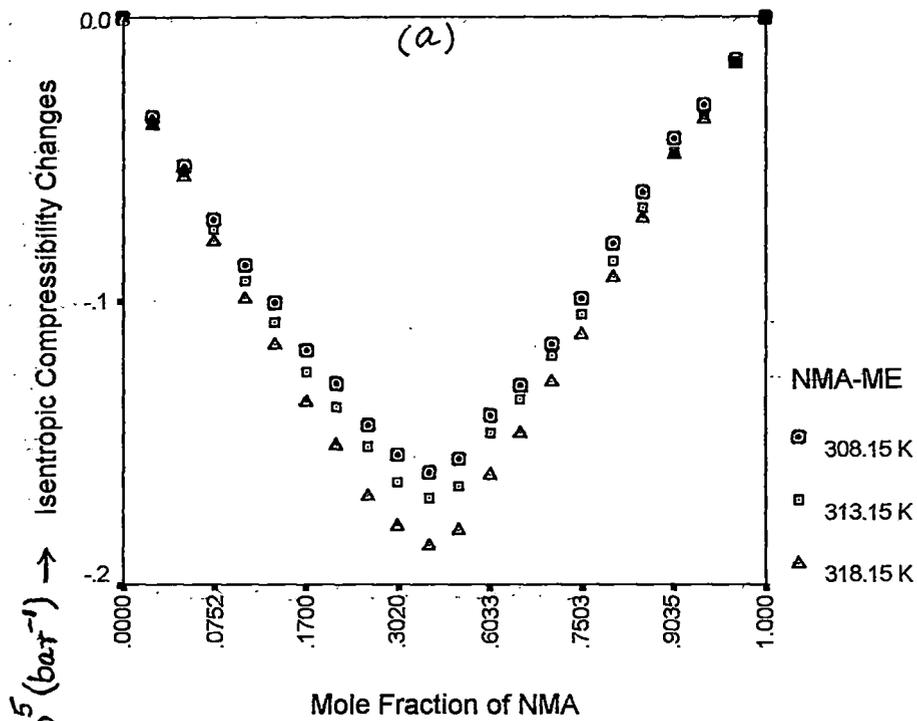


Figure 8. (a) Isentropic Compressibility Changes ($\Delta\kappa_s$) versus mole fraction of NMA in NMA + ME mixture at three temperatures.
(b) Isentropic Compressibility Changes ($\Delta\kappa_s$) versus mole fraction of NMA in NMA + Water mixture at three temperatures.