

CHAPTER VIII

SECTION A

EXCESS MOLAR VOLUMES AND VISCOSITY DEVIATIONS IN BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE WITH FORMAMIDE AND N,N-DIMETHYL FORMAMIDE AT (298.15, 308.15 AND 318.15)K.

Amides are very interesting compounds and they possess the very common in nature donor-acceptor – CO-NH-peptide bond and display the property of self association by the H-bond¹. Further, tertiary amides offer great interest because they are related to structural problems in molecular biology. This lead us to investigate the excess properties of the mixtures of N,N-dimethylacetamide (DMA) with familiar solvents formamide (FA) and N,N-dimethylformamide (DMF). DMA is a dipolar aprotic solvent and due to the moderate dielectric constant ($\epsilon = 37.8$ at 298.15K) it is likely to be moderately structured.² On the other hand, formamide mainly consists of the chain like hydrogen bonded structure by combining through –NH₂.....O = CH – interactions³ and its dielectric constant and dipole moment ($\epsilon = 109.5$ and $\mu = 3.86\text{D}$ at 298.15K)⁴ are very high. DMF manifests no significant intermolecular H-bonding ability⁵ and has moderate dielectric constant and high dipole moment ($\epsilon = 36.71$ and $\mu = 3.86\text{ D}$ at 298.15K)⁶. Thus a systematic study of the structural and energetic consequence of the interactions between DMA and FA and between DMA and DMF will enable us to understand how primary and tertiary

amide exercises thermodynamic and kinetic control over the chemical activities of peptide bonds in another tertiary amide i.e. N,N-dimethylacetamide. In the present study, we have tried to explore the sensitivity of the composition dependence of the excess molar volume (V^E) plus viscosity deviations ($\Delta\eta$) of liquid mixtures containing the amide functional group which constitute an important tool in the interpretation of complex molecules of biological interest.

Experimental

The purification of solvents and the experimental technique has been described earlier in chapter III. In all cases, the experiments were performed at least in five replicates for each composition and at each temperature and the results averaged.

Results and Discussion

The densities, viscosities, excess molar volumes and viscosity deviations of N,N-dimethylacetamide + formamide mixture and N,N-dimethylacetamide + N,N-dimethyl formamide mixture as a function of mole fraction of N,N-dimethylacetamide at (298.15, 308.15 and 318.15)K are presented in Tables 1 and 2 respectively. The excess functions have been calculated using the following equations

$$V^E = V - (v_1x_1 + v_2x_2) \quad (1)$$

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \quad (2)$$

where V and η are the respective solution properties and v_1 and v_2 and η_1 and η_2 are the molar volumes and the viscosities of the pure components. The molar volume V is defined by the relation

$$V = \frac{M_1x_1 + M_2x_2}{\rho} \quad (3)$$

where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture.

Graphical representations of Y^E and $\Delta\eta$ as functions of mole fraction of DMA are given in Figs. 1 and 2 respectively.

The excess properties Y^E were fitted to the Redlich-Kister equations.⁷

$$Y^E = x_1(1 - x_1) \sum A_j(1 - 2x_1)^j \quad (4)$$

where A_0, A_1, A_2 are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1 - x_1)$ to equation 4 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.

$$\sigma(Y^E) = [\sum (Y_{\text{obs}}^E - Y_{\text{cal}}^E)^2 / (N - M)]^{0.5} \quad (5)$$

are recorded in Table 3. In equation 5, N is the total no. of points and M is the number of parameters.

Excess Molar Volume

The systems DMA + FA and DMA + DMF show negative V^E values over the entire range of mole fraction and over the range of temperatures studied (Fig. 1). Such trends in V^E values have been observed in other systems also. Though both the systems show minima at a mole fraction of about 0.55 of DMA but the substitution of H by CH_3 at the N site in N,N-dimethylformamide caused a noticeable effect on the V^E values which may be explained qualitatively by postulating the two opposing set of contributions : (i) expansion due to dipole-dipole interactions of the unlike components of amide mixtures and size differences; (ii) contraction due to multiple hydrogen bonding between unlike molecules of the mixture or self association of the components. The actual value would be the balance between the two opposing effects. However, the experimental results suggest that the latter effect is more prominent than the former. The value of V^E in case of formamide mixture is much more -ve than in DMF mixture. This indicates that primary amide has a greater H-bonding ability than tertiary amide in amide-amide mixtures. The steric hindrance of the two methyl groups of DMF⁸ makes DMF weaker in hydrogen bonding ability than formamide which has a capability of three hydrogen bond donors and three acceptors.¹ From Fig.1 we see that as the temperature increases, the V^E values become more -ve in formamide system but in DMF system the result becomes reversed. The decrease of V^E with the increase in temperature is explained by considering the difference in the molar volumes of the two liquids at different temperatures. The difference in the

molar volumes of DMA and FA is $52.94 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15K while its value at 318.15K is $54.08 \text{ cm}^3 \text{ mol}^{-1}$. This shows that as the temperature of the mixture increases, the difference in the molar volumes of the two liquids also increases, but the smaller size molecules of FA easily fit⁹ into the voids created by larger molecules of DMA resulting in less increase in the volume of the mixture with increase of temperature. In case of DMF mixtures, the difference in the molar volumes of DMA and DMF is very low i.e. $15.56 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15K, so the interstitial accommodation of one component into the other is ruled out. A rise in temperature leads to the breaking of hydrogen bonded structures between unlike molecules and thus the dipole-dipole interactions of the unlike components make the V^E values less -ve compared to lower temperature.

Viscosity

The experimental viscosities as a function of mole fraction of DMA for both the systems are given in the Tables 1 and 2. The broad maxima observed in case of FA + DMA mixture at about 0.25 mole fraction of DMA suggest high association or complex formation between formamide and DMA. On the other hand, the viscosities of DMF + DMA system increase almost linearly without any maxima or minima with an increase in the DMA content in the mixture. The absence of any maxima in the intermediate composition gives an indication of the possible absence of specific interaction between DMF and DMA.

Viscosity Deviations

The DMA + FA system exhibits a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Fig. 2) with maxima corresponding to a mole fraction of about 0.3 in DMA. Such trends are also observed in DMA + ME and DMA + H₂O system. These $\Delta\eta$ values indicate specific hydrogen bonding interactions between DMA and formamide molecules. This is also supported by the excess molar volume studies as reported above. As the temperature increases, the magnitude of the viscosity deviation sharply decreases due to the rapid breaking up of the hydrogen bonds in the system and ultimately tend to approach ideality.

The DMA + DMF system displays very slight negative deviation of $\Delta\eta$ from ideality over the entire mole fraction range at the studied temperatures. The minima correspond to the mole fraction of about 0.5 of DMA (Fig.2). Further, with the increase of temperature $\Delta\eta$ values become more and more negative. The moderately structured DMA seems to undergo a structure-breaking effect when mixed with DMF, similar to N-methylacetamide's behaviour with DMF.¹⁰ Apart from this, dispersion and dipolar forces between these two aprotic and unlike solvents may also give rise to negative $\Delta\eta$ values. Such negative deviations from ideality are also observed in propylene carbonate (PC) + methanol and PC + tetrahydrofuran mixtures.¹¹

So far the results discussed reveal that in the DMA + FA system strong heteroassociation is present through multiple hydrogen bonding between the polar groups of the unlike molecules. Also large negative V^E and large positive $\Delta\eta$ values of this system are indicators for this phenomenon. On the other hand, there is a weak dipole-dipole interaction and a slight structure breaking effect in the DMA + DMF mixture as observed from the experimental data.

SECTION B

MOLECULAR INTERACTION STUDY IN BINARY MIXTURES OF N,N-DIMETHYLACETAMIDE WITH 2-ETHOXYETHANOL AT THREE DIFFERENT TEMPERATURES.

Thermodynamic excess properties of the binary liquid mixtures have been very useful to obtain information on the intermolecular interactions and geometrical effects in the systems.^{1,12} Solvents like 2-ethoxyethanol (EE) commercially known as 'cellosolves', are widely used as components of solvents, co-emulsifiers and stabilisers of emulsions, dyes and lacquers.¹³ They can be considered to be ethylene glycol derivatives obtained by the replacement of one of the hydroxy groups by an alkoxy group. Their molecules contain both hydroxylic and ether groups (as well as an alkyl group). The cellosolves in their pure state are self-associated and form cyclic dimers in which the hydroxy proton of one cellosolve molecule is bound to the ether oxygen atom of the other.¹⁴⁻¹⁷ They can also form intramolecularly hydrogen bonded five membered ring monomers.^{14,15,18-20} In view of their properties and structure the 2-ethoxyethanol is often regarded as 'quasi-aprotic' solvent²¹ On the other hand N,N-dimethylacetamide (DMA) is a dipolar aprotic solvent and due to the moderate dielectric constant ($\epsilon = 37.8$ at 298.15K), it is likely to be moderately structured. In this work, we made an attempt to study the behaviour of a dipolar aprotic solvent in a binary mixture with a 'quasi-aprotic' solvent over the entire range of their compositions at 298.15, 308.15 and 318.15K by measurement of their densities, viscosities and ultrasonic velocities. From these

experimental data excess volume (v^E), excess viscosity ($\Delta\eta$), excess intermolecular free length (L_f^E) and isentropic compressibility changes (β^E) were calculated.

Experimental

The purification of solvents and the experimental technique has already been discussed in chapter III

Results and Discussion

The experimental values of density ρ , viscosity η , and ultrasonic velocity u , of pure liquids and their binary mixtures at three different temperatures have been used to calculate the values of isentropic compressibility β , intermolecular free length L_f , relative association R_A , acoustic impedance Z and molar sound speed R_m using the following standard relations :

$$\beta = 1/u^2\rho, \quad (6)$$

$$L_f = K/u\rho^{1/2}, \quad (7)$$

$$R_A = (\rho/\rho_0)(u_0/u)^{1/3}, \quad (8)$$

$$Z = u\rho, \quad (9)$$

$$R_m = Vu^{1/3}, \quad (10)$$

where K is a temperature dependent constant $[= (93.875 + 0.375 T) \times 10^{-8}]^{22}$, T is the absolute temperature; ρ_0 , ρ and u_0 , u are the densities and ultrasonic speeds

of the solvent (2-ethoxyethanol) and solution, respectively. The molar volume (V) of the binary mixtures was calculated using the equation

$$V = \frac{M_1X_1 + M_2X_2}{\rho} \quad (11)$$

where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture. The values of ρ , η , u , β , L_f , R_A , Z and R_m as a function of mole fraction X_1 of DMA at 298.15, 308.15 and 318.15K are listed in Table 4. The non-linear increase/decrease in ρ , η , u , β , L_f , R_A , Z and R_m values (Table 4) with composition indicates significant interactions between the component molecules.

The excess functions are found to be more sensitive towards intermolecular interactions in liquid mixtures. The excess volume V^E , excess intermolecular free length L_f^E , viscosity deviations $\Delta\eta$ and excess isentropic compressibility β^E have been calculated using the following relation :

$$Y^E = Y - [x_1Y_1 + x_2Y_2] \quad (12)$$

Where Y^E is V^E or L_f^E or $\Delta\eta$ or β^E ; x is mole fraction of pure solvent in the mixture and subscripts 1 and 2 stand for DMA and 2-ethoxyethanol respectively.

Graphical representations of V^E , L_f^E , $\Delta\eta$ and $\Delta\beta$ as function of mole fraction of N,N-dimethylacetamide are given in Figures 3-6, respectively.

The excess properties Y^E were fitted to the Redlich – Kister equation.⁷

$$Y^E = x_1 (1 - x_1) \sum A_j (1 - 2x_1)^j \quad (13)$$

where A_0, A_1, A_2 are adjustable parameters. These parameters were evaluated by fitting $Y^E/x_1(1 - x_1)$ to eq. (13) by the method of least squares. The values of these parameters along with standard deviation $\sigma(Y^E)$ of Y^E as defined by the equation

$$\sigma(Y^E) = [\sum (Y_{obs}^E - Y_{calc}^E)^2 / (N - M)]^{0.5} \quad (14)$$

are recorded in Table 5. In eq. (14), N is the total number of experimental points and M is the number of parameters.

It is observed from Table 4. that u and Z increases while β, L_f, R_A and R_m decreases as mole fraction (x_1) of DMA increases in the mixture. The decrease in β and L_f with x_1 in the present investigation indicates significant interaction between DMA and EE molecules. The addition of DMA to alkoxy alkanol tends to cause breaking of self associated alkanol molecules with a consequent increase in u and L_f . However, because of simultaneous formation of strong hydrogen bonds between the unlike molecules, there is a compensating effect resulting in an overall decrease in β and L_f or increase in u with x_1 . The rise in temperature makes the intermolecular free length to increase, as expected due to the thermal expansion of the liquid medium. In the present investigation, relative association R_A is found to decrease with mole fraction of DMA at all the three temperatures. The result signifies that unlike interactions are relatively weak compared to like interactions

in the studied mixture. A slight increase in Z with x_1 also supports weak interaction between DMA and EE molecules.

The system *N,N*-dimethylacetamide + 2-ethoxyethanol shows negative V^E and L_f^E values over the entire range of mole fraction and over the range of temperatures studied as given in Figures 3-4. The system shows broad minima of V^E and L_f^E at a mole fraction of about 0.5 and 0.4 of DMA respectively. The observed V^E and L_f^E values may be explained from several effects which can be divided into physical, chemical and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution to V^E and L_f^E . The chemical or specific interactions result due to forming and/or breaking of hydrogen bonds and other complex-forming interactions. It is well known that alkoxy ethanols exist as associated structures like the alcohols^{7,23} in the liquid state; the association may be due to the intramolecular hydrogen bond formation between the ether oxygen atom and the -OH group. The interaction between a moderately structured DMA and 2-ethoxyethanol may disrupt the hydrogen bonds in 2-ethoxyethanol molecules, accompanied by weak hydrogen bond formation between the unlike molecules and thus offer a negative contribution to V^E ²⁴ and L_f^E .

The *N,N*-dimethylacetamide + 2-ethoxyethanol system displays a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Fig.5). The positive deviation from a rectilinear dependence on mole fraction of DMA indicates the predominance of hydrogen

bonding interactions between the unlike molecules (DMA and EE) over the dissociation effects in the system. With the rise in temperature, the $\Delta\eta$ values become less and less positive indicating a tendency of the decrease of these interactions thereby the system approaches ideal behaviour. The results of deviations in isentropic compressibility versus mole fraction of DMA has been represented in Figure 6. The figure shows that the values of $\Delta\beta$ are negative over the entire composition range and at all the three studied temperatures, suggesting a predominant hydrogen bond interaction between DMA and 2-ethoxyethanol and thereby causing an increase in the ultrasonic velocity and a decrease in the compressibility of this solution. The process continues until the minima is reached and then these parameters follow the reverse trend.

Thus from the present investigation it may be concluded that due to the presence of highly polar ether group in 2-ethoxyethanol molecule, the hydrogen bonding interaction playing a predominate role over dispersion and other forces that are likely to be operative in non-aqueous solvent mixtures. This interaction accompanied by a minor disruption of 2-ethoxyethanol structure is responsible for the negative contribution of excess values in the experimental data.

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Table 1 Experimental density (ρ), absolute viscosity (η), excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) for the binary mixtures of N, N-dimethylacetamide with formamide at 298.15, 308.15 and 318.15K.

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethylacetamide (1) + formamide (2)				
T = 298.15K				
0.0000	1.1254	2.953	0.000	0.000
0.0350	1.1120	3.217	-0.044	0.335
0.0700	1.0997	3.457	-0.091	0.646
0.1110	1.0866	3.656	-0.149	0.928
0.1500	1.0752	3.822	-0.204	1.172
0.2053	1.0606	3.966	-0.272	1.428
0.2414	1.0518	3.971	-0.323	1.506
0.3009	1.0387	3.932	-0.402	1.587
0.3563	1.0275	3.789	-0.463	1.556
0.4177	1.0162	3.537	-0.517	1.428
0.4580	1.0092	3.338	-0.544	1.310
0.5011	1.0021	3.094	-0.564	1.153
0.5474	0.9948	2.826	-0.575	0.979
0.5972	0.9873	2.530	-0.569	0.783
0.6500	0.9797	2.251	-0.548	0.611
0.7092	0.9717	1.916	-0.505	0.395
0.7500	0.9663	1.720	-0.462	0.282
0.7948	0.9607	1.540	-0.404	0.192
0.8910	0.9492	1.210	-0.242	0.057
1.0000	0.9371	0.933	0.000	0.000

Contd.....

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethyl acetamide (1) + formamide (2)				
T = 308.15 K				
0.0000	1.1118	2.384	0.000	0.000
0.0350	1.1045	2.532	-0.051	0.203
0.0700	1.0923	2.677	-0.104	0.403
0.1110	1.0791	2.847	-0.164	0.637
0.1500	1.0677	2.950	-0.224	0.800
0.2053	1.0522	3.037	-0.304	0.974
0.2414	1.0442	3.057	-0.354	1.050
0.3009	1.0307	3.027	-0.424	1.113
0.3563	1.0195	2.920	-0.484	1.093
0.4177	1.0080	2.741	-0.544	1.010
0.4580	1.0011	2.594	-0.575	0.926
0.5011	0.9940	2.430	-0.600	0.830
0.5474	0.9867	2.235	-0.615	0.707
0.5972	0.9791	2.028	-0.609	0.578
0.6500	0.9715	1.812	-0.584	0.445
0.7092	0.9632	1.579	-0.532	0.305
0.7500	0.9578	1.441	-0.482	0.231
0.7948	0.9522	1.289	-0.429	0.148
0.8910	0.9406	1.035	-0.268	0.046
1.0000	0.9283	0.819	0.000	0.000
T = 318.15K				
0.0000	1.1072	1.951	0.000	0.000
0.0350	1.0944	2.077	-0.070	0.169
0.0700	1.0826	2.180	-0.140	0.315
0.1110	1.0700	2.286	-0.221	0.471
0.1500	1.0590	2.357	-0.299	0.590
0.2053	1.0446	2.416	-0.397	0.716
0.2414	1.0361	2.420	-0.459	0.764
0.3009	1.0228	2.389	-0.541	0.806
0.3563	1.0117	2.310	-0.609	0.795
0.4177	1.0001	2.160	-0.660	0.720
0.4580	0.9930	2.076	-0.686	0.686
0.5011	0.9859	1.953	-0.707	0.616
0.5474	0.9785	1.810	-0.715	0.529
0.5972	0.9709	1.650	-0.706	0.430
0.6500	0.9632	1.505	-0.678	0.350
0.7092	0.9550	1.316	-0.623	0.233
0.7500	0.9795	1.205	-0.564	0.172
0.7948	0.9437	1.096	-0.492	0.118
0.8910	0.9318	0.901	-0.291	0.041
1.0000	0.9193	0.726	0.000	0.000

Table 2 Experimental density (ρ), absolute viscosity (η), excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) for the binary mixtures of N, N-dimethylacetamide with N,N-dimethylformamide at 298.15, 308.15 and 318.15K.

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethylacetamide (1) + N,N-dimethylformamide (2)				
T = 298.15K				
0.0000	0.9436	0.802	0.000	0.000
0.0500	0.9433	0.809	-0.009	-0.012
0.1062	0.9429	0.816	-0.016	-0.025
0.1500	0.9426	0.822	-0.021	-0.034
0.2171	0.9421	0.831	-0.025	-0.046
0.2600	0.9418	0.837	-0.027	-0.051
0.3094	0.9414	0.843	-0.029	-0.057
0.3500	0.9411	0.849	-0.031	-0.060
0.4050	0.9407	0.856	-0.032	-0.063
0.4550	0.9404	0.863	-0.033	-0.064
0.5042	0.9400	0.870	-0.034	-0.065
0.5500	0.9397	0.876	-0.034	-0.063
0.6071	0.9393	0.883	-0.033	-0.060
0.6550	0.9389	0.890	-0.032	-0.056
0.7140	0.9385	0.898	-0.030	-0.051
0.7500	0.9383	0.903	-0.028	-0.047
0.7968	0.9379	0.909	-0.025	-0.041
0.8500	0.9375	0.916	-0.020	-0.032
0.9112	0.9370	0.925	-0.013	-0.020
0.9500	0.9368	0.930	-0.007	-0.012
1.0000	0.9364	0.937	0.000	0.000

Contd.....

X_1	ρ gm cm ⁻³	η mPas	V^E cm ³ mol ⁻¹	$\Delta\eta$ mPas
N,N-dimethyl acetamide (1) + N,N-dimethylformamide (2)				
T= 308.15K				
0.0000	0.9348	0.713	0.000	0.000
0.0500	0.9345	0.718	-0.008	-0.017
0.1062	0.9341	0.724	-0.014	-0.034
0.1500	0.9338	0.729	-0.018	-0.045
0.2171	0.9332	0.737	-0.023	-0.059
0.2600	0.9330	0.742	-0.025	-0.065
0.3094	0.9326	0.747	-0.027	-0.072
0.3500	0.9323	0.752	-0.029	-0.077
0.4050	0.9319	0.758	-0.030	-0.081
0.4550	0.9316	0.763	-0.031	-0.083
0.5042	0.9313	0.769	-0.032	-0.084
0.5500	0.9309	0.774	-0.032	-0.081
0.6071	0.9305	0.781	-0.031	-0.079
0.6550	0.9302	0.786	-0.030	-0.074
0.7140	0.9298	0.793	-0.028	-0.069
0.7500	0.9295	0.797	-0.026	-0.064
0.7968	0.9292	0.803	-0.023	-0.056
0.8500	0.9288	0.809	-0.018	-0.043
0.9112	0.9284	0.816	-0.012	-0.028
0.9500	0.9281	0.820	-0.006	-0.017
1.0000	0.9277	0.826	0.000	0.000
T = 318.15K				
0.0000	0.9256	0.638	0.000	0.000
0.0500	0.9253	0.642	-0.006	-0.022
0.1062	0.9249	0.647	-0.012	-0.043
0.1500	0.9246	0.652	-0.016	-0.056
0.2171	0.9242	0.658	-0.021	-0.072
0.2600	0.9239	0.662	-0.023	-0.080
0.3094	0.9235	0.666	-0.026	-0.088
0.3500	0.9233	0.670	-0.027	-0.094
0.4050	0.9229	0.675	-0.028	-0.099
0.4550	0.9226	0.679	-0.029	-0.101
0.5042	0.9223	0.684	-0.030	-0.102
0.5500	0.9219	0.688	-0.030	-0.100
0.6071	0.9216	0.694	-0.029	-0.097
0.6550	0.9213	0.698	-0.028	-0.093
0.7140	0.9209	0.704	-0.026	-0.086
0.7500	0.9206	0.707	-0.024	-0.080
0.7968	0.9203	0.712	-0.021	-0.071
0.8500	0.9199	0.717	-0.017	-0.055
0.9112	0.9196	0.723	-0.011	-0.036
0.9500	0.9193	0.727	-0.006	-0.022
1.0000	0.9189	0.732	0.000	0.000

Table 3 Coefficients of equation 3 and the standard deviations

Function	T/ K	A ₀	A ₁	A ₂	A ₃	A ₄	σ (F)
N,N-dimethylacetamide + formamide							
V ^E /cm ³ mol ⁻¹	298.15K	-0.0025	-1.1334	-1.9690	4.8761	-1.7709	0.0005
	308.15K	-0.0041	-1.2927	-1.6146	4.4368	-1.5255	0.0011
	318.15K	0.0001	-2.0253	-0.1598	3.3254	-1.1380	0.0006
Δη/m Pas	298.15K	-0.0470	12.0894	-27.7521	18.0097	-2.2704	0.0066
	308.15K	-0.0488	8.2506	-18.0947	10.6810	-0.7675	0.0056
	318.15K	-0.0210	5.9409	-13.1388	8.0087	-0.7775	0.0029
N,N-dimethylacetamide +N,N-dimethylformamide							
V ^E /cm ³ mol ⁻¹	298.15K	-0.0010	-0.1771	0.3763	-0.4151	0.2179	0.0001
	308.15K	-0.0005	-0.1582	0.3019	-0.3017	0.1592	0.0001
	318.15K	-0.0001	-0.1383	0.2260	-0.1884	0.1010	0.0001
Δη/m Pas	298.15K	0.0000	-0.0028	0.0034	-0.0007	0.0002	0.0001
	308.15K	0.0000	-0.0037	0.0051	-0.0027	0.0013	0.0001
	318.15K	0.0000	-0.0047	0.0072	-0.0052	0.0026	0.0001

Table 4 : Values of experimental density (ρ) ; absolute viscosity(η), ultrasonic velocity (u), isentropic compressibility (β), intermolecular free length (L_f), relative association (R_A), acoustic impedance (Z) and molar sound speed (R_m) of binary mixtures of DMA and EE at 298.15, 308.15 and 318.15K.

x_1 (DMA)	ρ (kg m^{-3})	η ($10^{-3}\text{kg m}^{-1}\text{s}^{-1}$)	u (ms^{-1})	β ($10^{-10}\text{m}^2\text{N}^{-1}$)	L_f (10^{-11}m)	R_A	Z ($10^6\text{kg m}^{-2}\text{s}^{-1}$)	R_m [$10^4\text{m}^3\text{mol}^{-1}$ (ms^{-1}) $^{1/3}$]
T = 298.15K								
0.000	925.0	1.8243	1306.9	6.3290	5.1746	1.0000	1.2089	10.6518
0.0500	926.0	1.8031	1316.6	6.2300	5.1337	0.9986	1.2192	10.6489
0.1042	926.9	1.7780	1327.3	6.1235	5.0899	0.9969	1.2303	10.6480
0.1500	927.6	1.7517	1335.7	6.0420	5.0560	0.9955	1.2390	10.6461
0.2075	928.6	1.7147	1345.5	5.9485	5.0164	0.9942	1.2494	10.6400
0.2500	929.2	1.6834	1352.7	5.8808	4.9881	0.9931	1.2569	10.6369
0.3097	930.0	1.6350	1362.6	5.7910	4.9497	0.9915	1.2672	10.6323
0.3650	930.8	1.5868	1371.5	5.7113	4.9155	0.9902	1.2766	10.6264
0.4111	931.4	1.5449	1378.8	5.6480	4.8879	0.9891	1.2842	10.6219
0.4600	931.9	1.4986	1386.4	5.5824	4.8598	0.9878	1.2919	10.6181
0.5115	932.6	1.4473	1394.4	5.5151	4.8301	0.9866	1.3004	10.6119
0.5650	933.1	1.3916	1402.6	5.4474	4.8006	0.9853	1.3087	10.6078
0.6110	933.6	1.3433	1409.5	5.3910	4.7758	0.9842	1.3159	10.6029
0.6550	934.0	1.2968	1416.1	5.3385	4.7525	0.9831	1.3226	10.5990
0.7096	934.5	1.2391	1424.0	5.2770	4.7249	0.9818	1.3307	10.5933
0.7550	934.9	1.1912	1430.4	5.2282	4.7027	0.9807	1.3373	10.5881
0.8073	935.2	1.1359	1437.3	5.1756	4.6794	0.9795	1.3441	10.5828
0.8500	935.5	1.0907	1443.1	5.1326	4.6599	0.9785	1.3500	10.5782
0.9041	935.9	1.0339	1450.3	5.0795	4.6357	0.9773	1.3573	10.5716
1.000	936.4	0.9329	1463.5	4.9860	4.5927	0.9748	1.3704	10.5630

Contd....

x_I (DMA)	ρ (kg m^{-3})	η ($10^3 \text{kg m}^{-1} \text{s}^{-1}$)	u (ms^{-1})	β ($10^{10} \text{m}^2 \text{N}^{-1}$)	L_f (10^{11}m)	R_A	Z ($10^6 \text{kg m}^{-2} \text{s}^{-1}$)	R_m [$10^4 \text{m}^3 \text{mol}^{-1}$ ($\text{ms}^{-1})^{1/3}$]
T = 308.15K								
0.0000	916.4	1.4800	1274.4	6.7180	5.4304	1.0000	1.1678	10.6619
0.0500	917.4	1.4668	1284.5	6.6067	5.3830	0.9985	1.1784	10.6606
0.1042	918.4	1.4522	1295.3	6.4895	5.3352	0.9967	1.1896	10.6594
0.1500	919.1	1.4369	1303.8	6.4006	5.2984	0.9953	1.1983	10.6583
0.2075	920.1	1.4129	1313.5	6.2994	5.2565	0.9939	1.2085	10.6525
0.2500	920.7	1.3916	1320.5	6.2291	5.2269	0.9929	1.2158	10.6493
0.3097	921.5	1.3573	1329.9	6.1357	5.1877	0.9914	1.2255	10.6438
0.3650	922.3	1.3224	1338.3	6.0536	5.1529	0.9901	1.2343	10.6371
0.4111	922.9	1.2913	1345.2	5.9880	5.1248	0.9891	1.2415	10.6319
0.4600	923.5	1.2566	1352.4	5.9206	5.0958	0.9880	1.2489	10.6263
0.5115	924.1	1.2174	1359.8	5.8520	5.0665	0.9868	1.2566	10.6203
0.5650	924.7	1.1747	1367.4	5.7834	5.0367	0.9856	1.2644	10.6138
0.6110	925.2	1.1375	1373.9	5.7260	5.0115	0.9846	1.2711	10.6083
0.6550	925.6	1.1017	1380.1	5.6721	4.9879	0.9835	1.2774	10.6038
0.7096	926.1	1.0570	1387.6	5.6081	4.9596	0.9823	1.2850	10.5975
0.7550	926.5	1.0197	1393.7	5.5567	4.9368	0.9813	1.2913	10.5919
0.8073	926.9	0.9773	1400.6	5.4998	4.9115	0.9801	1.2982	10.5859
0.8500	927.2	0.9422	1406.3	5.4539	4.8908	0.9791	1.3039	10.5813
0.9041	927.5	0.8981	1413.5	5.3961	4.8650	0.9778	1.3110	10.5763
1.0000	927.9	0.8204	1426.3	5.2970	4.8204	0.9752	1.3234	10.5686

Contd.....

x_1 (DMA)	ρ (kg m^{-3})	η ($10^{-3}\text{kg m}^{-1}\text{s}^{-1}$)	u (ms^{-1})	β ($10^{-10}\text{m}^2\text{N}^{-1}$)	L_f (10^{-11}m)	R_A	Z ($10^6\text{kg m}^{-2}\text{s}^{-1}$)	R_m [$10^{-4}\text{m}^3\text{mol}^{-1}$ (ms^{-1}) ^{1/3}]
T = 318.15K								
0.000	907.9	1.2220	1242.2	7.1380	5.6956	1.000	1.1278	10.6714
0.0500	908.8	1.2135	1252.5	7.0134	5.6459	0.9982	1.1383	10.6708
0.1042	909.8	1.2060	1263.5	6.8850	5.5937	0.9964	1.1495	10.6706
0.1500	910.6	1.1986	1271.9	6.7878	5.5543	0.9951	1.1582	10.6693
0.2075	911.5	1.1840	1281.2	6.6780	5.5113	0.9937	1.1678	10.6641
0.2500	912.1	1.1697	1288.4	6.6043	5.4787	0.9925	1.1751	10.6618
0.3097	912.9	1.1456	1297.5	6.5067	5.4379	0.9910	1.1845	10.6561
0.3650	913.7	1.1204	1305.6	6.4210	5.4018	0.9898	1.1929	10.6490
0.4111	914.2	1.0974	1312.2	6.3524	5.3731	0.9887	1.1996	10.6456
0.4600	914.8	1.0708	1319.0	6.2823	5.3437	0.9876	1.2066	10.6383
0.5115	915.4	1.0402	1326.1	6.2120	5.3133	0.9865	1.2139	10.6319
0.5650	916.0	1.0070	1333.2	6.1413	5.2833	0.9854	1.2212	10.6246
0.6110	916.5	0.9779	1339.3	6.0823	5.2578	0.9844	1.2274	10.6183
0.6550	916.9	0.9499	1345.2	6.0263	5.2336	0.9834	1.2334	10.6134
0.7096	917.4	0.9146	1352.5	5.9589	5.2039	0.9822	1.2408	10.6070
0.7550	917.8	0.8850	1358.5	5.9041	5.1798	0.9812	1.2468	10.6016
0.8073	918.2	0.8519	1365.4	5.8420	5.1525	0.9799	1.2537	10.5959
0.8500	918.4	0.8242	1371.0	5.7927	5.1309	0.9788	1.2591	10.5926
0.9041	918.7	0.7893	1378.4	5.7292	5.1025	0.9774	1.2663	10.5885
1.0000	919.1	0.7285	1390.9	5.6230	5.0556	0.9749	1.2783	10.5808

Table 5 : Coefficients A_i of eq. (13) and standard deviations $\sigma(Y^E)$ for binary mixtures N,N-dimethylacetamide +2-ethoxy ethanol at 298.15, 308.15 and 318.15K.

Function	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
T = 298.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0014	-0.8416	1.0933	-0.4183	0.1686	0.0005
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0013	0.5766	-1.1516	0.7099	-0.1330	0.0001
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0045	-0.8271	2.8121	-4.0417	2.0783	0.0126
$L_f^E (10^{-11} \text{m})$	-0.0004	-0.2618	0.4654	-0.3143	0.1121	0.0001
T = 308.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0010	-0.9418	1.4826	-1.0197	0.4817	0.0004
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0021	0.5257	-0.9811	0.5069	-0.0484	0.0002
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0003	-0.9347	1.9575	-1.5724	0.5515	0.0003
$L_f^E (10^{-11} \text{m})$	-0.0007	-0.3639	0.8033	-0.6913	0.2534	0.0001
T = 318.15K						
$V^E (10^{-6} \text{m}^3 \text{mol}^{-1})$	-0.0008	-1.0313	1.8262	-1.5570	0.7655	0.0004
$\Delta\eta (10^{-3} \text{N m}^{-2} \text{S}^{-1})$	-0.0029	0.4746	-0.8098	0.3019	0.0374	0.0003
$\Delta\beta (10^{-10} \text{m}^2 \text{N}^{-1})$	-0.0014	-1.2952	3.3347	-3.3269	1.2921	0.0019
$L_f^E (10^{-11} \text{m})$	0.0001	-0.4213	0.9674	-0.8389	0.2929	0.0001

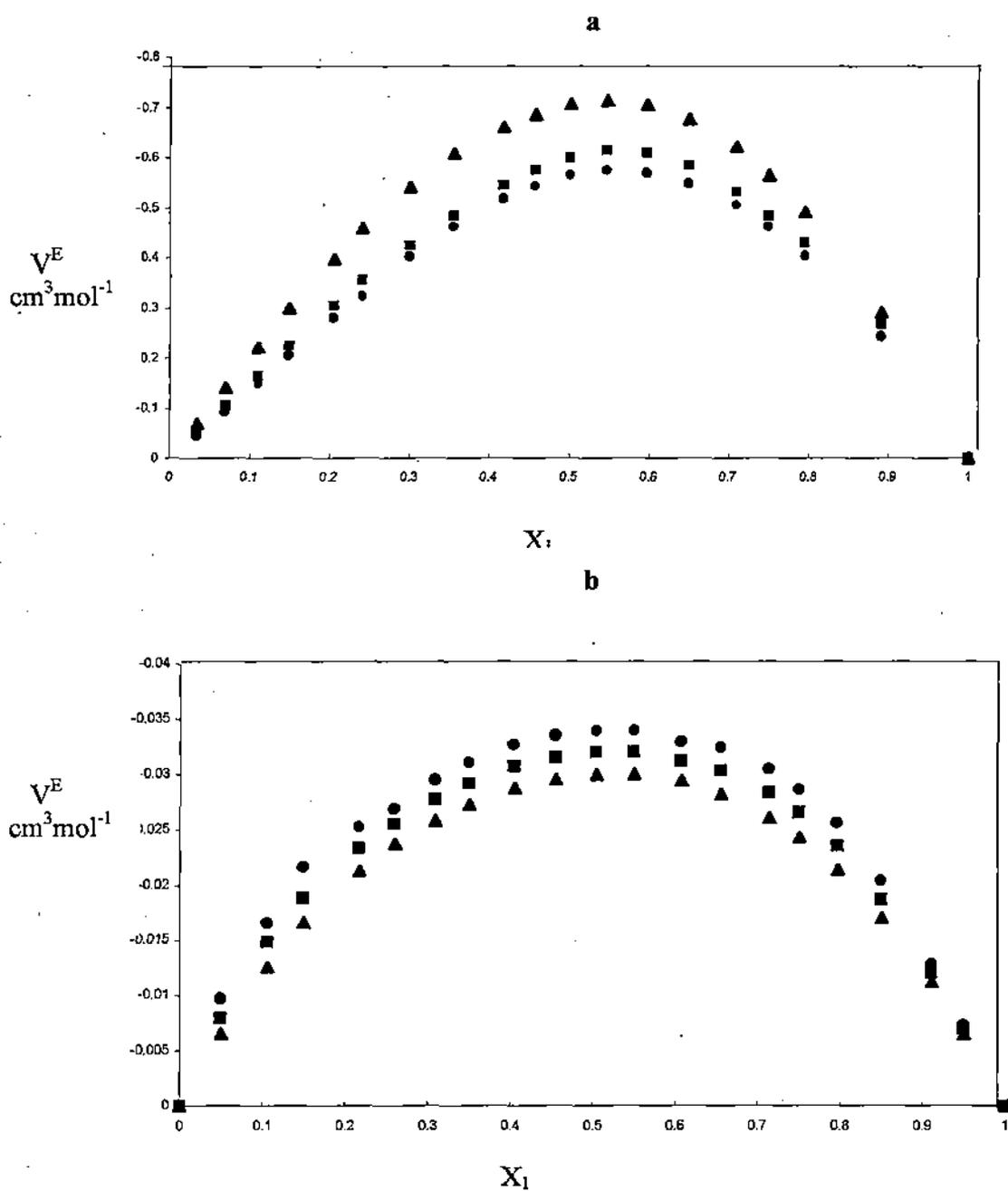
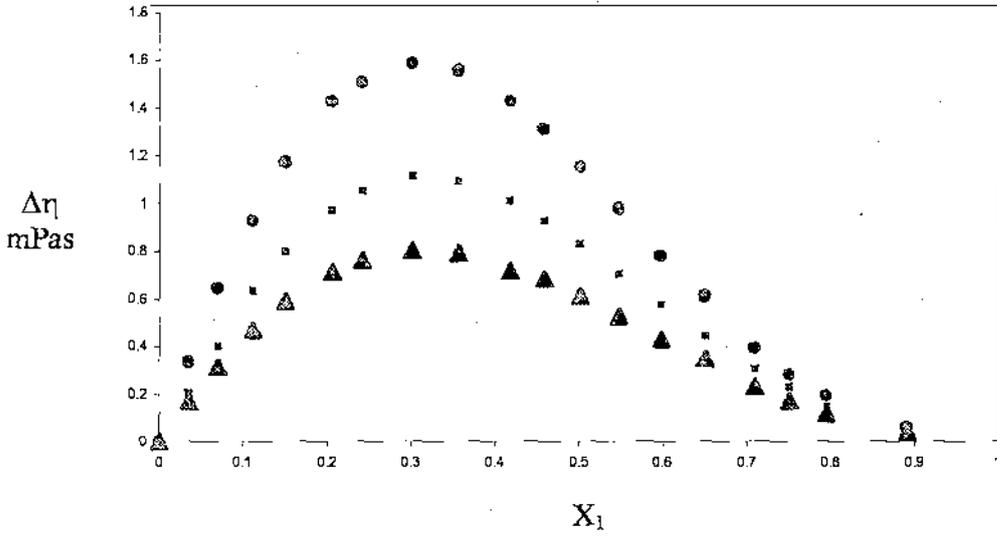


Figure 1. Variation of excess molar volume of the binary mixtures N, N-dimethylacetamide (a) with formamide and (b) with N,N-dimethylformamide at 298.15K(●), 308.15K(■) and 318.15K(▲).

a



b

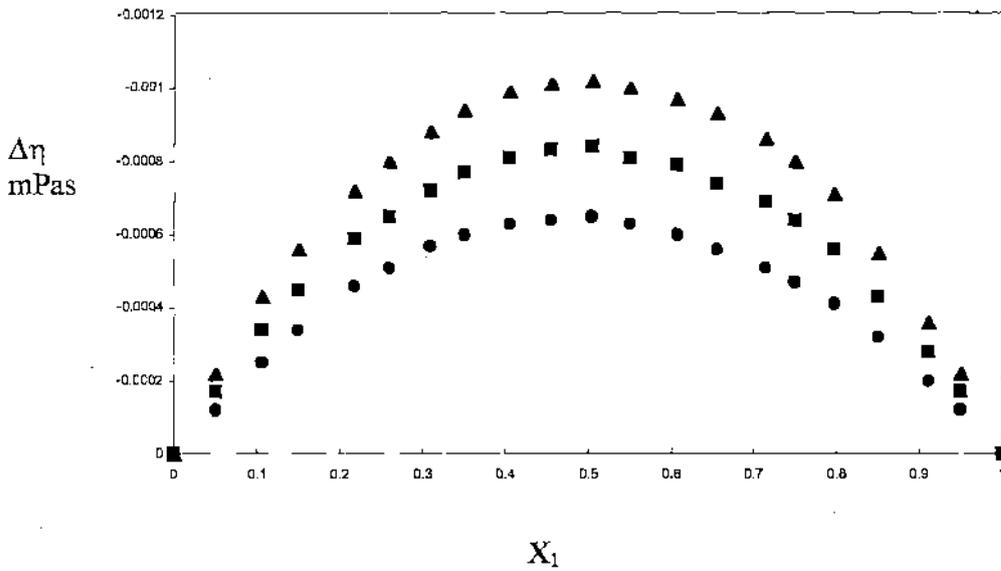


Figure 2. Variation of viscosity deviations of the binary mixtures of N, N-dimethylacetamide (a) with formamide and (b) with N, N-dimethylformamide at 298.15K(●), 308.15K(■) and 318.15K(▲).

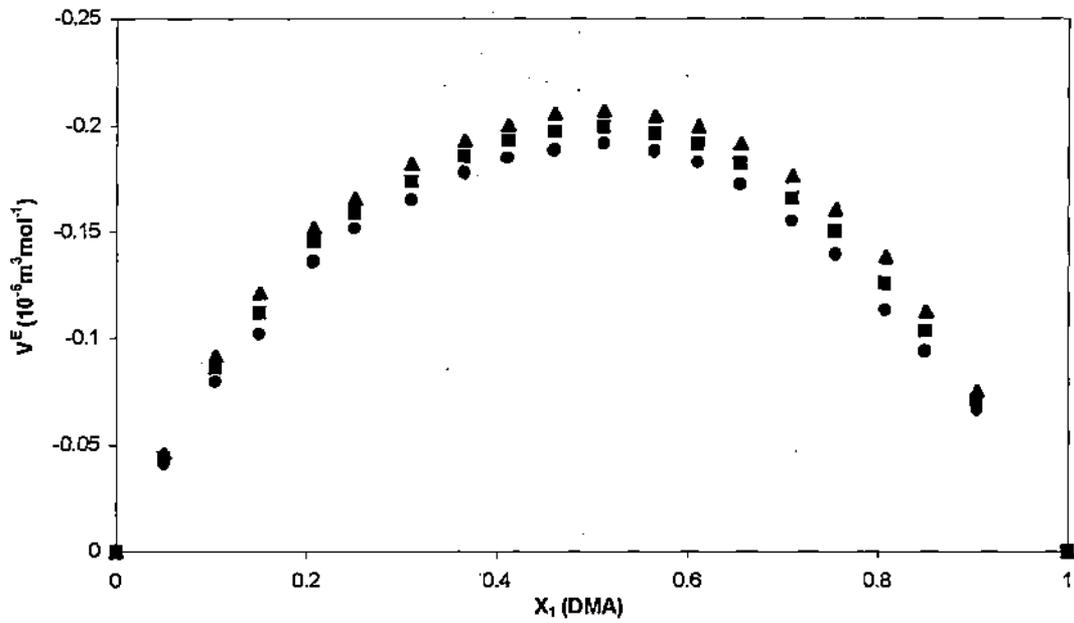


Figure 3. Variation of excess volume (V^E) versus mole fraction (x_1) of DMA at 298.15K (●); 308.15K (■) ; 318.15 K(▲)

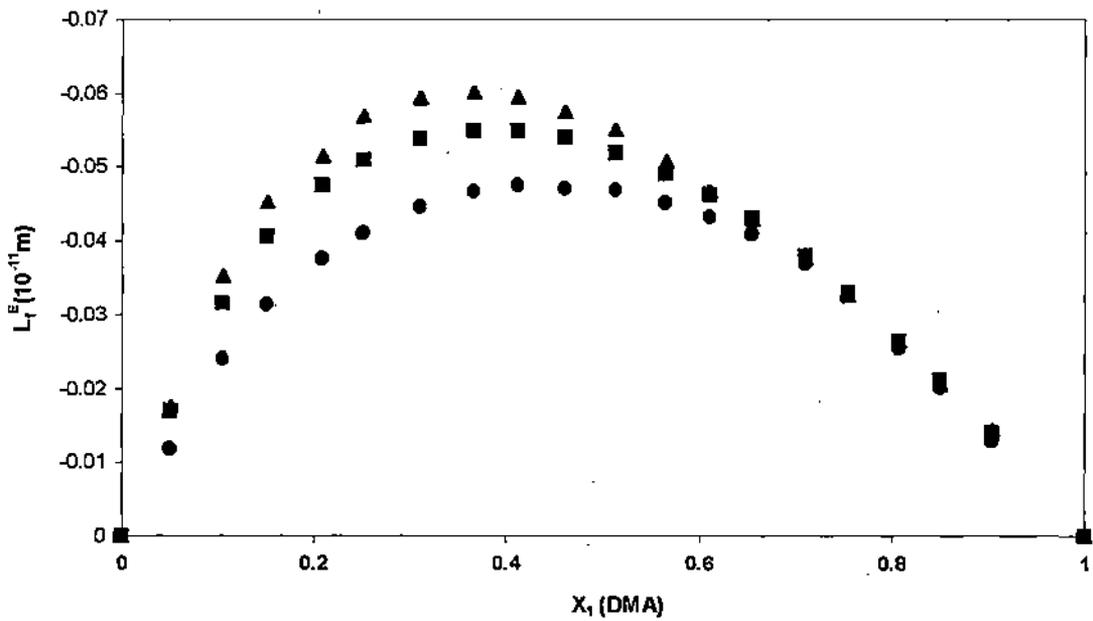


Figure 4 : Variation of intermolecular free length (L_f^E) versus mole fraction (x_1) of DMA at 298.15K (●) ; 308.15K (■) ; 318.15K (▲)

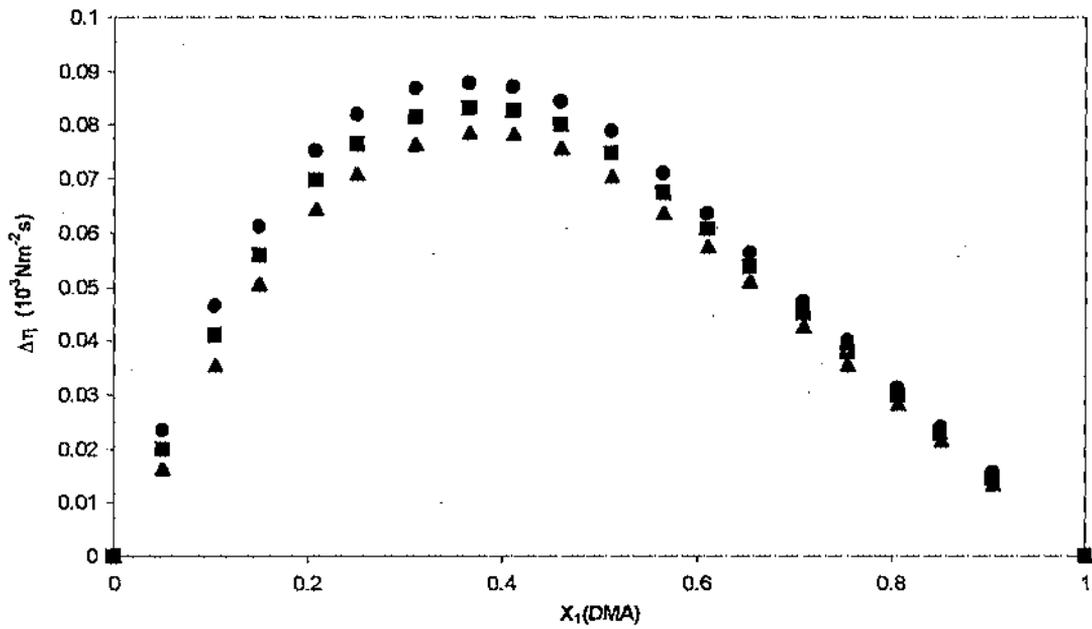


Figure 5. Variation of excess viscosity ($\Delta\eta$) versus mole fraction (x_1) of DMA at 298.15K (●); 308.15K (■); 318.15K (▲).

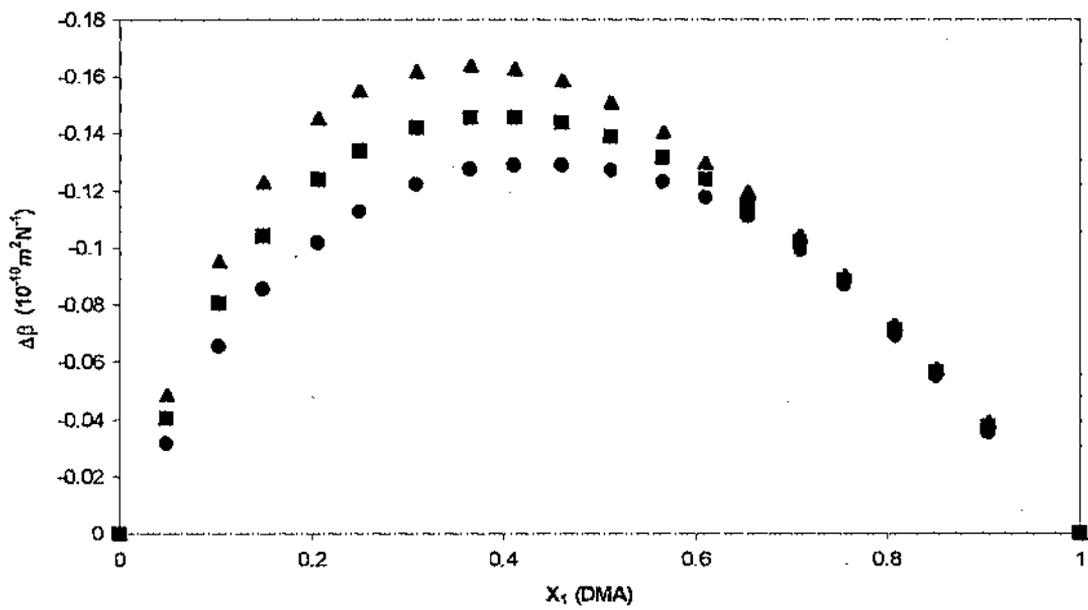


Figure 6. Variation of excess isentropic compressibility ($\Delta\beta$) versus mole fraction (x_1) of DMA at 298.15K (●); 308.15K (■); 318.15K (▲).