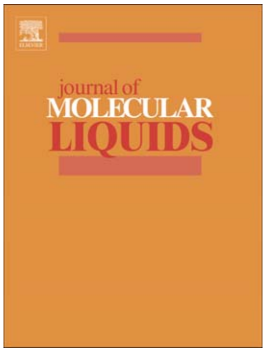

Mesomeric effect on thermodynamic parameters of binary liquid mixtures of *N*-methyl formamide and o-substituted anilines

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Mesomeric effect on Thermodynamic parameters of binary liquid mixtures of N-methyl formamide and o- substituted anilines

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Abstract

In the present investigation, the densities (ρ) and viscosities (η) are reported for binary mixtures N-methylformamide with o-substituted aniline (2-chloroaniline, 2-methylaniline and 2-methoxyaniline) over the entire composition range from 303.15 K to 318.15 K and at atmospheric pressure 0.1 MPa. The experimental data is used to calculate excess volume (V^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}). The excess partial molar volumes, $\bar{V}^{\mathrm{E}}_{\mathrm{m},1}$ and $\bar{V}^{\mathrm{E}}_{\mathrm{m},2}$ and excess partial molar volumes $\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$ and $\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ at infinite dilution have also been calculated. The variations in these properties with composition for all the binary mixtures suggest loss of dipolar association, difference in size and shape of the component molecules, dipole-dipole interaction and hydrogen bonding between N-methylformamide with o-substituted aniline. Furthermore, the FTIR spectra have been recorded at 298.15 K and found to be useful for understanding the presence of hydrogen bonding between nitrogen atom of amino group of o-substituted aniline and hydrogen atom of the amide group of N-methylformamide in the liquid mixtures. A good agreement is obtained between excess quantities and spectroscopic data.

Keywords: partial molar volume; hydrogen bonding; o-substituted aniline; FTIR spectra

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1. Introduction

Many of the liquid mixtures are non ideal and are endowed with specific characteristics. Of the three states of matter, the nature of liquids is complicated because diverse interactions between the constituent molecules influence the solution behavior. The thermophysical properties of solutions including density, viscosity and their corresponding volumetric and viscosity properties such as excess molar volume and deviation in viscosity are useful in the study of molecular dynamic and molecular interaction [1]. These solution properties not only dependent on size of the molecules but also on solute-solute, solvent-solvent and solute-solvent interactions between components present in the solution. Moreover, investigation on the thermophysical properties is essential for designing, testing and extending of the theoretical models for fluid mixtures [2]. From the industrial view point, many processes require accurate thermodynamics and transport values of liquids which are indispensable for many practical problems concerning heat transport, mass transport, fluid flow and pipeline systems.

The present paper continues our investigation of the thermodynamic properties of binary liquid acid-base mixtures [3,4]. Densities and viscosities at different mole fraction have been measured at various temperatures for the following systems: N-methylformamide+2-chloroaniline, N-methylformamide+2-methylaniline and N-methylformamide+2-methoxyaniline, where all species are polar and show hydrogen bonds in the pure state. With the classification of Barker and Smith [5], our systems can be classified as ‘associated solutions’. The following thermodynamic functions have been calculated from the experimental results: V^E (excess molar volume), $\Delta\eta$ (deviation in viscosity), G^{*E} (excess Gibbs free energy of activation of viscous flow) and $\overline{V}_{m,1}^{\circ E}$, and $\overline{V}_{m,2}^{\circ E}$ (excess partial molar volumes at infinite dilution).

The liquid components selected as binary liquid mixtures are used in various fields of chemistry in addition to being used in industries and routine analytical work. N-methylformamide is used in various organic syntheses for some applications as a highly polar solvent. Ortho-substituted anilines are chosen as polar solvents in view of their self association nature through hydrogen bonding via amine group. The amine group imparts electron donor as well as proton-acceptor nature to the molecules.

The endeavor of the present work is to find the basic strength of the ortho substituted group in the aniline molecule which can affect both the sign and magnitude of various thermodynamic functions when mixed with N-methylformamide. The present study is undertaken to determine experimentally, the density and viscosity of pure liquids of 2-chloroaniline, 2-methylaniline and 2-methoxyaniline and their binary mixtures with N-methylformamide at temperature (T) 303.15 - 318.15 K. A review of the literature has shown that the thermodynamic properties of a binary mixture containing N-methylformamide and aromatic hydrocarbons [6], o-toluidine and tetrahydropyran have been reported earlier [7]. However, no systematic study is reported on excess volume, excess entropic compressibility, deviation in viscosity and excess Gibbs free energy of activation of viscous flow of o-substituted anilines in N-methylformamide over the entire composition range at temperature (T) of 303.15 - 318.15 K.

.2 Experimental

2.1 Materials

All the compounds were used without further purification. Table 1 contains information regarding their source and purity and Table 2 shows their physical properties, density (ρ) and viscosity (η). The values listed in Table 2 are in good agreement with the data available in the literature [8-15].

2.2 Apparatus and Procedure

All the binary liquid mixtures were prepared by weighing required amounts of pure liquids in an electric balance (ER-120A, Afoset, India) with a precision of ± 0.1 mg by syringing each component into air-tight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1 \times 10^{-4}$. After mixing the sample, the bubble free homogenous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with ±0.03 K accuracy of temperature. The uncertainty density measurement liquid mixtures were $+2\times10^{-5}$ $g.cm^{-3}$ and the uncertainty of temperature + 0.01K. Proper calibrations at each temperature were achieved with doubly distilled deionized water and with dry air as standards. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure at T = (303.15 - 318.15) K by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile, and doubly distilled water. The kinetic energy corrections were calculated from these values and they were found to be negligible. The Ubbelohde viscometer bulb capacity was 15 ml and the capillary tube had a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried, filled with the sample liquid by fitting the viscometer to about 30^{o} from the vertical and its limbs were closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ±0.1 K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ±

0.01 s was used for flow time measurements. The experimental uncertainty of viscosity estimated as ± 0.03 mPa·s and the uncertainty of temperature ± 0.1K.

3. Results and discussion:

The experimental results for pure liquids are reported in Table 2 along with the values from the literature for comparison. The experimental densities and viscosities for all the systems at various temperatures have been used to calculate the excess thermodynamic functions with following equations:

$$V^E / cm^3.mol^{-1} = [x_1M_1 + x_2M_2] / \rho - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

$$\Delta\eta / mPa\cdot s = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

$$G^{*E} / J\cdot mol^{-1} = RT [\ln\eta V - (x_1 \ln\eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (3)$$

where ρ , η and V are density, viscosity and molar volume of the binary mixture. x_1, M_1, ρ_1, η_1,V_1 and x_2, M_2, ρ_2, η_2,V_2 are the mole fraction, molar mass, density, viscosity and molar volume of pure components 1 and 2 respectively. *R* is the gas constant and T is the absolute temperature.

The variation of V^E and $\Delta\eta$ with mole fraction was fitted to the Redlich - Kister polynomial equation [16]

$$Y^E = x_1x_2[a_0 + a_1(x_1-x_2) + a_2(x_1-x_2)^2] \quad (4)$$

where Y^E is the V^E or $\Delta\eta$. The values of a_0, a_1 and a_2 are the coefficients of the polynomial equation and the corresponding standard deviations (σ) obtained by the method of least - squares with equal weights assigned to each point are calculated. The standard deviations (σ) are calculated as:

$$\sigma (Y^E) = [\sum(Y^E{}_{obs} - Y^E{}_{cal})^2/(n-m)]^{1/2} \quad (5)$$

where n is the total number of experimental points and m is the number of coefficients. The values of $a_{0,}$ a_1 and a_2 which are the coefficients determined by multiple-regression analysis on the least square method and summarized along with the standard deviations between the experimental and fitted values of V^E and $\Delta\eta$ are presented in Table 4.

The density and viscosity for mixtures of various mole fractions of N-methylformamide are presented in Table 3 along with excess molar volumes and deviation in viscosity at various temperatures. Figs. 1, 2 and 3 show experimental values of V^E, $\Delta\eta$ and G^{*E} as a function of the molar fraction of N-methylformamide, respectively

As shown in Table 3, the mixture volumes of all the measured binary systems show negative deviations from ideality over the whole composition range and at all experimental temperatures. The volume contraction of the binary mixtures is a result of the existence of specific interactions (mostly heteroassociations through hydrogen bonding) and association interactions between the mixture components. Accordingly, the negative values for V^E obtained in this study can be explained mainly by the hydrogen bonded complex formation between the components of the mixtures. Spectroscopic data which confirm the N-H·····N hydrogen bonded complex formation of N-methylformamide with o-substituted aniline are presented in Figs from 4 to 6.

The negative values of V^E in Fig. 1 for the three systems are explained by Prigogine [17] in terms of the different sizes of the molecules or dipole-dipole or hydrogen bonding interactions between them. The intermolecular association complex also contributes to these negative values. In our case, all the chemical species are cyclic, so that little differences of size in the molecules are not important in the excess molar volume.

The magnitude of V^E shows the following sequence:

2-methoxyaniline > 2-methylaniline > 2-chloroaniline

The minimum value of V^E for the system N-methylformamide + 2-methoxyaniline is explained by the great basic strength of 2-methoxyaniline [18] and stability of the association complex. Hence above order is justified.

An examination of curves in Fig. 1 show that the values of negative excess volumes increases with the rise of temperature, which means that the temperature coefficients of the excess volume are negative, for the systems under study. When the temperature rises, the self-association of o-substituted aniline / N-methylformamide molecules decreases owing to thermal agitation and increases association between unlike molecules, resulting in further increase in the negative V^E values. The same has been described in literature for 1-alkanol+hexane systems [19], alcohol + triethlene glycol systems [20] and 1-hexanol + ether systems [21].

According to Kaufman and Eyring [22], the viscosity of a mixture strongly depends on the entropy of mixture, which is related with the structure of the liquid, the enthalpy (and consequently with molecular interactions between the components of the mixture).

So, the viscosity deviations are functions of molecular interactions as well as of size and shape of the molecules. Vogel and Weiss [23] affirm that mixtures with strong interactions between different molecules and negative deviations from Raoult's law present positive viscosity deviations; whereas, for mixtures with positive deviations of Raoult's law and without specific interactions the viscosity deviations are negative. Thus, positive values of $\Delta\eta$ signify strong intermolecular interaction and negative $\Delta\eta$ values are indicative of weak intermolecular interaction.

As shown in Fig.2, the values of $\Delta\eta$ are positive over the entire composition range of the binary mixtures at temperature (T) of 303.15 - 318.15 K. Positive values of deviation in viscosity show that hetero association in the mixtures is more prominent than the self association of pure components. The effect of temperature increase is to disrupt hetero and homo association of the molecules resulting in an increase in fluidity of the liquids giving higher $\Delta\eta$ values at higher temperatures. The viscosity deviation values are found to be opposite to the sign of excess molar volumes for all binary mixtures, which is in agreement with the view proposed by Brocos et al. [24, 25].

The excess Gibbs free energy of activation of viscous flow, like viscosity deviations, can be used to detect molecular interactions [26].The positive excess Gibbs free energy of activation of viscous flow values are indicative of specific interactions between the molecules of binary liquid mixtures while negative values are indicative of dispersive forces [27-29]. From Fig.3, G^{*E} values on mixing are positive for the whole composition range of N-methylformamide with o-substituted aniline. It suggests that there is a heterogeneous interaction between the o-substituted aniline with N-methylformamide. Thus, the values of deviation in viscosity and excess Gibbs free energy of activation of viscous flow are dependent on the basic nature of o-substituted aniline, indicating a different extent of molecular interactions in o-substituted aniline.

3.1 Partial molar properties

The partial molar properties (partial molar volume and partial molar compressibility), $\overline{Y}_{\mathrm{m},1}$ of component 1 (N-methylformamide) and $\overline{Y}_{\mathrm{m},2}$ of component 2 (o-substituted aniline) in these mixtures over entire composition range were calculated by using the following relations [30, 31]

$$\overline{Y}_{\mathrm{m},1} = Y^{\mathrm{E}} + Y^{*}_{\mathrm{m},1} + x_2 \left(\partial Y^{\mathrm{E}} / \partial x_1\right)_{\mathrm{T,\,p}} \quad (6)$$

$$\overline{Y}_{\mathrm{m},2} = Y^{\mathrm{E}} + Y^{*}_{\mathrm{m},2} - x_1 \left(\partial Y^{\mathrm{E}} / \partial x_1\right)_{\mathrm{T,\,p}} \quad (7)$$

where$Y$ is V; $Y^{*}_{\mathrm{m},1}$ and $Y^{*}_{\mathrm{m},2}$ are the molar properties for pure components, N-methylformamide and o-substituted aniline, respectively. The derivative, $(\partial Y^{\mathrm{E}} / \partial x_1)_{\mathrm{T,p}}$ in equations (6) and (7) was obtained by differentiation of the Eq. (4), which leads to the following equations for $\overline{Y}_{\mathrm{m},1}$ and $\overline{Y}_{\mathrm{m},2}$

$$\overline{Y}_{\mathrm{m},1} = Y^{*}_{\mathrm{m},1} + x_2^2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i - 2x_1 x_2^2 \sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \qquad (8)$$

$$\overline{Y}_{\mathrm{m},2} = Y^{*}_{\mathrm{m},2} - x_1^2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i + 2x_1^2 x_2 \sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \qquad (9)$$

The excess partial molar properties, $\overline{Y}^{\mathrm{E}}_{\mathrm{m},1}$ and $\overline{Y}^{\mathrm{E}}_{\mathrm{m},2}$ over the whole composition range were calculated by using the following relations [30, 31]

$$\overline{Y}^{\mathrm{E}}_{\mathrm{m},1} = \overline{Y}_{\mathrm{m},1} - Y^{*}_{\mathrm{m},1} \qquad (10)$$

$$\overline{Y}^{\mathrm{E}}_{\mathrm{m},2} = \overline{Y}_{\mathrm{m},2} - Y^{*}_{\mathrm{m},2} \qquad (11)$$

The variations of $\overline{V}^{\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{\mathrm{E}}_{\mathrm{m},2}$ with composition and temperature were presented in Table 6.

The values of partial molar properties, $\overline{Y}^{\circ}_{\mathrm{m},1}$ and $\overline{Y}^{\circ}_{\mathrm{m},2}$, of N-methylformamide and o-substituted aniline at infinite dilution were calculated by using the Eqs. (6) –(9) and the excess partial molar properties, $\overline{Y}^{\circ\mathrm{E}}_{\mathrm{m},1}$ and $\overline{Y}^{\circ\mathrm{E}}_{\mathrm{m},2}$ at infinite dilution were calculated using the Eqs. (10) and (11) by substituting $\overline{Y}^{\circ\mathrm{E}}_{\mathrm{m},i}$ and $\overline{Y}^{\circ}_{\mathrm{m},i}$ in place of $\overline{Y}^{\mathrm{E}}_{\mathrm{m},i}$ and $\overline{Y}_{\mathrm{m},i}$, respectively. The values of $\overline{V}^{\circ}_{\mathrm{m},1}$, $V^{*}_{\mathrm{m},1}$, $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$, $\overline{V}^{\circ}_{\mathrm{m},2}$, $V^{*}_{\mathrm{m},2}$ and $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ for the binary mixtures at each investigated temperature are listed in Table 6.

In general, the negative of excess partial molar volume component 1 and excess partial molar volume component 2 ($\overline{V}^{E}_{m,1}$ and $\overline{V}^{E}_{m,2}$) values indicate the presence of significant solute-solvent interactions between unlike molecules, whereas the positive excess partial molar volume component 1 and excess partial molar volume component 2 data indicate presence of solute-solute / solvent-solvent interactions between like molecules in the mixtures [32,33].

A close perusal of Table 5 indicates that the values of $\overline{V}^{\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{\mathrm{E}}_{\mathrm{m},2}$ are negative for all the binary mixtures over the whole composition range. This suggests that the interactions between unlike molecules exceed the structure breaking effect between like molecules. These interactions are relatively strong between N-methylformamide and o-substituted aniline.

A close perusal of Table 6 indicates that the values of $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ are negative for these binary systems at each investigated temperature. The observed negative $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ values indicate that N-methylformamide + o-substituted aniline interactions are stronger than interactions between like molecules. The decrease in the values of $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$ and $\overline{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ with increase in temperature further supports the trends observed in V^{E} values.

FT-IR spectroscopy has been extensively used to study an intermolecular hydrogen bonding interactions between component molecules. Generally, intermolecular hydrogen bonds give rise to broad band. The o-substituted aniline namely 2-chloroaniline, 2-methylaniline, 2-methoxyaniline and N-methylformamide exhibit some characteristic absorption peaks at 3373 cm^{-1} (N-H, str), 3361cm^{-1} (N-H, str), 3288 cm^{-1} (N-H, str) and 3288 cm^{-1} (N-H str) respectively. In the present investigation, FT-IR spectrum was measured at room temperature and at equimolar concentration of the components of the binary blends. The absorption bands (N-H str) of N-methylformamide +2-chloroaniline, N-methylformamide +2-methylaniline and N-methylformamide + 2-methoxyaniline at 3315 cm^{-1}, 3316 cm^{-1} and 3317 cm^{-1} respectively, indicate the weak intermolecular interactions between component molecules and further, it is inferred that with increase in the size of the o-substituted aniline molecules, the absorption band is shifted towards lower frequency [34, 35]**.** These frequency shifts are caused by the strong intermolecular interactions like hydrogen bonding between the hydrogen atom of the amide group of N-methylformamide and nitrogen atom of amino group of o-substituted aniline, as is shown in Figs. 4-6.

4. Conclusions:

Densities and viscosities of binary mixtures of N-methylformamide with o-substituted aniline (2-chloroaniline, 2-methylaniline and 2-methoxyaniline) have been measured at different temperatures and derived parameters along with their excess values $\overline{V}^{E}_{m,1}$,$\overline{V}^{E}_{m,2}$, $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$ were calculated. The results were analyzed in terms of the molecular interactions through the hydrogen bonding between nitrogen atom of amino group of o-substituted aniline and hydrogen atom of the amide group of N-methylformamide in the binary liquid mixtures. The presence of hydrogen-bonding between o-substituted aniline and N-methylformamide molecules is strongly supported by the FTIR spectra of these binary mixtures

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Figure captions:

Fig.1: Variation of excess volume (V^E) of the binary liquid mixture of N-methylfromamide with 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼) at 303.15 K.

Fig. 2 Variation of deviation in viscosity (Δη) of the binary mixture of N-methylfromamide with 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼) at 303.15 K.

Fig. 3 Excess Gibbs energy of activation of viscous flow (G^{*E}) of the binary liquid mixture of N-methylfromamide with 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼) at 303.15 K

Fig 4 Experimental Fourier Transform Infrared spectra of pure N-methylformamide (black), 2- chloroaniline (green) and N-methylformamide + 2-chloroaniline (red) in the ratio 1:1

Fig 5 Experimental Fourier Transform Infrared spectra of pure N-methylformamide (black), 2-methyl aniline (blue) and N-methylformamide + 2-methylaniline (red) in the ratio 1:1

Fig 6 Experimental Fourier Transform Infrared spectra of pure N-methylformamide (black), 2-methoxyaniline (green) and N-methylformamide + 2-methoxyaniline (red) in the ratio 1:1

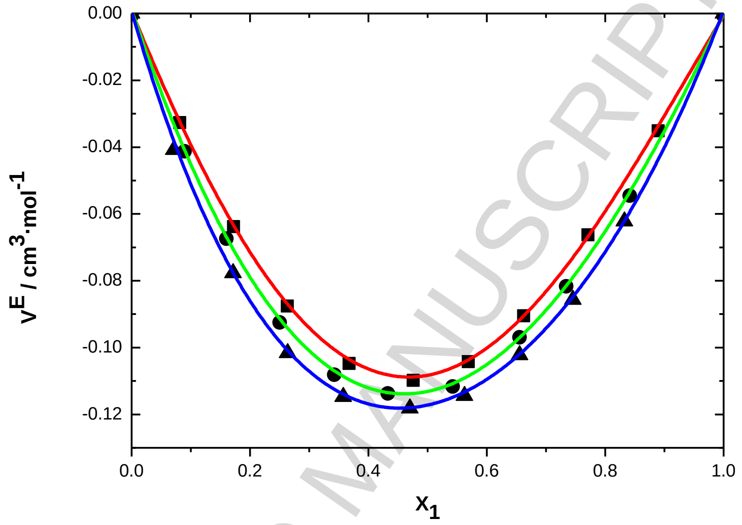


Figure-1

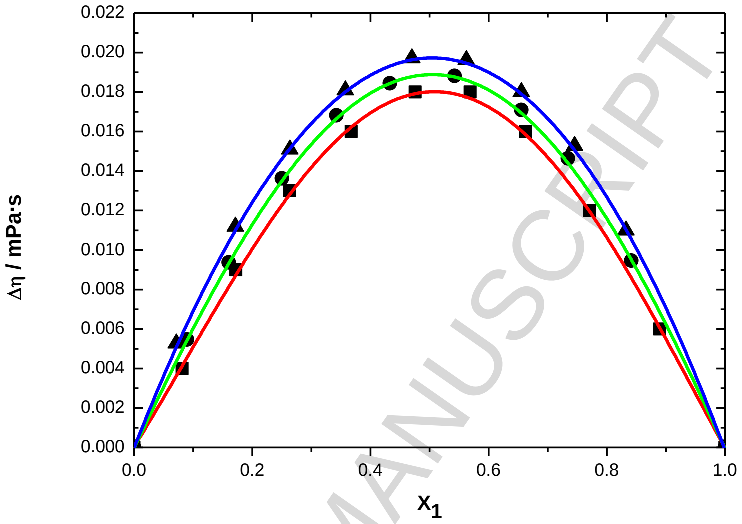

0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
Δη / mPa·s
0.0
0.2
0.4
0.6
0.8
1.0
x_1

Figure-2

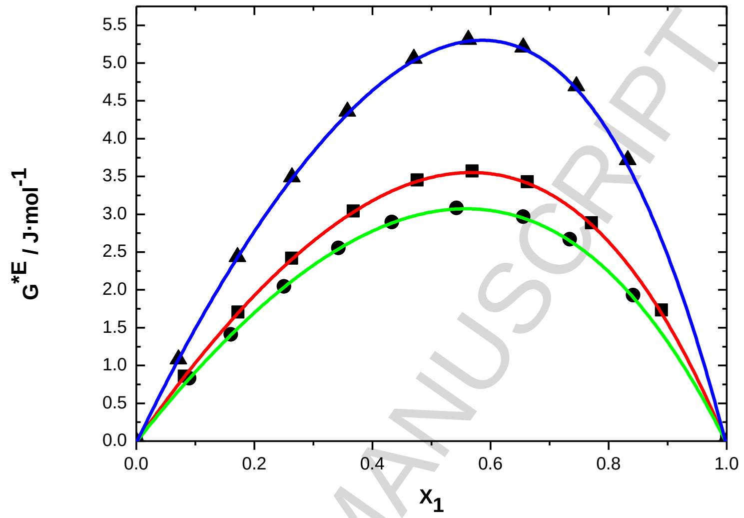
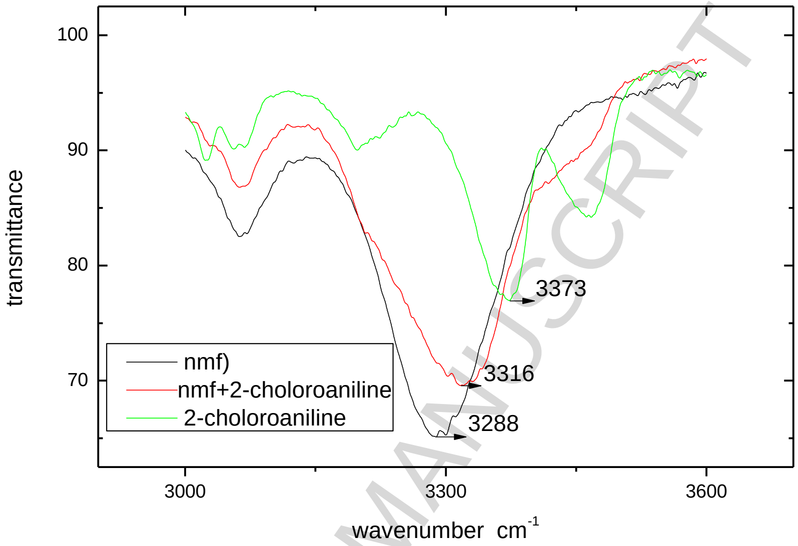


Figure-3



100
90
80
70
transmittance
3000
3300
3600
wavenumber cm^{-1}
nmf)
nmf+2-choloroaniline
2-choloroaniline
3373
3316
3288

Figure 4

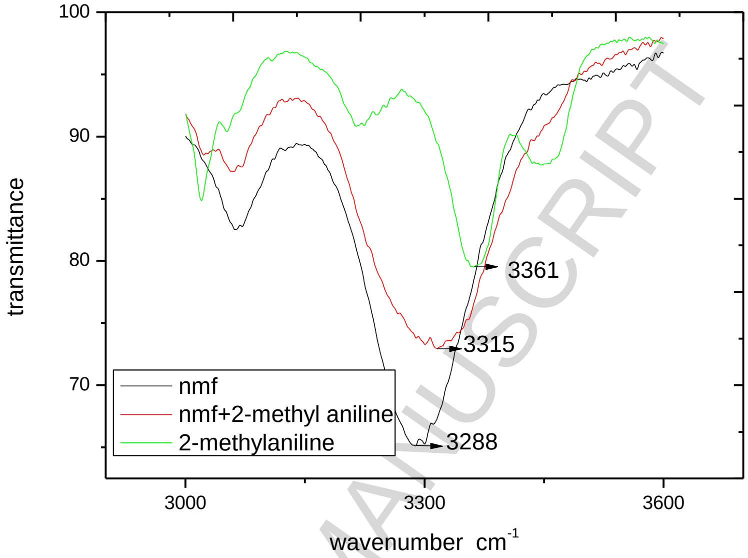

100
90
80
70
transmittance
3000
3300
3600
wavenumber cm^{-1}
3361
3315
3288
nmf
nmf+2-methyl aniline
2-methylaniline

Figure 5

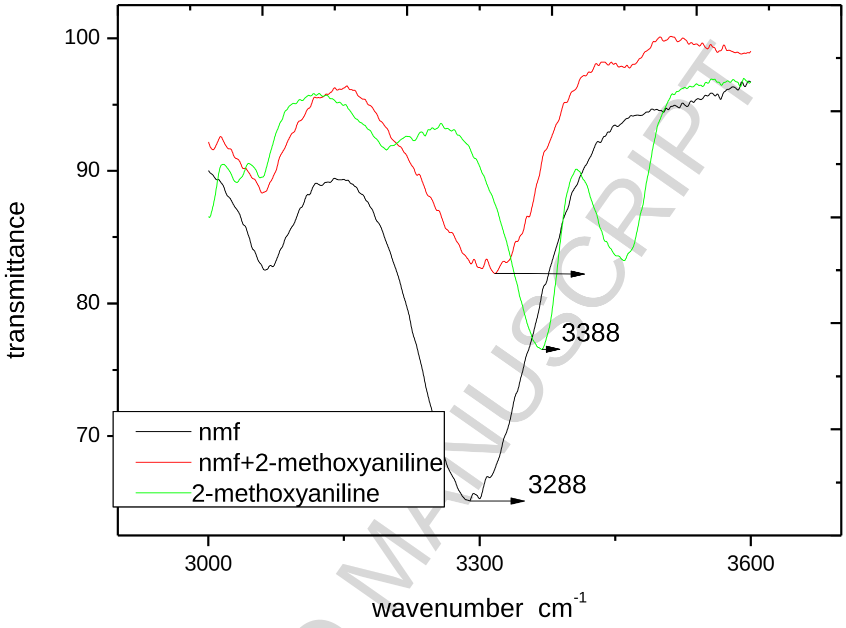

100
90
80
70
transmittance
3000
3300
3600
wavenumber cm^{-1}
3388
3288
nmf
nmf+2-methoxyaniline
2-methoxyaniline

Figure 6

Table 1:-Provenance and purity of the materials used

Chemicals	CAS Number	Source	water content in mass fraction	purity in mass fraction
N-methylformamide	123-39-7	Sigma Aldrich, India	0.049	0.997
2-chloroaniline	95-51-2	Sigma Aldrich, India	0.042	0.996
2-methylaniline	95-53-4	Sigma Aldrich, India	0.042	0.995
2-methoxyaniline	90-04-0	Sigma Aldrich, India	0.042	0.995

Table 2**:-** Densities, speed of sounds and viscosities data of pure components at different temperatures and p= 0.1MPa

Component	density (ρ /g·cm^{-3})		Viscosity (η / mPa·s)	
(in K)	Experimental	Literature	Experimental	Literature
N-methylformamide				
303.15	0.99464	0.9946[8]	1.5852	1.5859[8]
308.15	0.99033	0.9903[8]	1.4621	1.4627[8]
313.15	0.98614	0.9861[8]	1.3515	1.3520[8]
318.15	0.98204	0.9820[8]	1.2552	1.2557[8]
2-chloroaniline				
303.15	1.20269	1.20270[10]	3.8256	3.8256[9]
		1.2024[9]		3.7701[10]
308.15	1.19802		3.4122	
313.15	1.19302		3.0602	
318.15	1.18849		2.7621	
2-methylaniline				
303.15	0.99019	0.9902[12]	3.2580	3.31*[11]
308.15	0.98599	0.9860[13]	2.8240	
313.15	0.98169	0.9817[14]	2.4870	
318.15	0.97759	-	2.1530	
2-methoxyaniline				
303.15	1.09175	1.0917[15]	4.9225	4.9236[15]
308.15	1.08735	-	4.5124	
313.15	1.08378	-	4.1854	
318.15	1.08080	-	3.8825	

***298.15 K**

Table3**:** Density (ρ), excess molar volumes (V^E), viscosity (η), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E}) of binary liquid mixtures of N-methylformamide with ortho-substituted anilines (2-chloroaniline, 2-methylaniline and 2-methoxyaniline) at T= (303.15 to 318.15) K and 0.1MPa pressure

	density (ρ /g·cm^{-3})				V^E / cm^3·mol^{-1}			
x_1	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
N-methylformamide+ 2-chloroaniline								
0.0000	1.20269	1.19802	1.19302	1.18849	0.0000	0.0000	0.0000	0.0000
0.0815	1.19322	1.18861	1.18370	1.17924	-0.0327	-0.0365	-0.0414	-0.0467
0.1725	1.18172	1.17712	1.17227	1.16785	-0.0638	-0.0683	-0.0742	-0.0806
0.2634	1.16908	1.16450	1.15968	1.15527	-0.0876	-0.0921	-0.0963	-0.1017
0.3674	1.15300	1.14843	1.14367	1.13927	-0.1048	-0.1082	-0.1125	-0.1163
0.4756	1.13411	1.12958	1.12488	1.12051	-0.1098	-0.1138	-0.1170	-0.1202
0.5689	1.11575	1.11125	1.10663	1.10230	-0.1042	-0.1076	-0.1114	-0.1151
0.6623	1.09512	1.09068	1.08616	1.08188	-0.0905	-0.0958	-0.1006	-0.1043
0.7712	1.06771	1.06336	1.05896	1.05475	-0.0663	-0.0735	-0.0794	-0.0837
0.8895	1.03298	1.02866	1.02438	1.02027	-0.0351	-0.0398	-0.0435	-0.0489
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000
N-methylformamide+ 2-methylaniline								
0.0000	0.99019	0.98599	0.98169	0.97759	0.0000	0.0000	0.0000	0.0000
0.0896	0.99081	0.98664	0.98238	0.97835	-0.0413	-0.0451	-0.0494	-0.0567
0.1601	0.99128	0.98709	0.98288	0.97882	-0.0674	-0.0706	-0.0788	-0.0840
0.2501	0.99183	0.98764	0.98342	0.97936	-0.0925	-0.0951	-0.1022	-0.1076
0.3425	0.99235	0.98815	0.98393	0.97987	-0.1081	-0.1115	-0.1171	-0.1221
0.4328	0.99280	0.98859	0.98437	0.98031	-0.1138	-0.1170	-0.1216	-0.1263
0.5424	0.99330	0.98908	0.98487	0.98081	-0.1117	-0.1149	-0.1196	-0.1238
0.6554	0.99373	0.98953	0.98534	0.98129	-0.0969	-0.1023	-0.1075	-0.1126
0.7342	0.99399	0.98980	0.98565	0.98162	-0.0817	-0.0876	-0.0944	-0.1004
0.8414	0.99431	0.99012	0.98598	0.98195	-0.0545	-0.0611	-0.0669	-0.0726
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000
N-methylformamide+ 2-methoxyaniline								
0.0000	1.09157	1.08735	1.08378	1.08080	0.0000	0.0000	0.0000	0.0000
0.0714	1.08821	1.08399	1.08045	1.07745	-0.0408	-0.0422	-0.0484	-0.0517
0.1715	1.08286	1.07865	1.07511	1.07206	-0.0777	-0.0809	-0.0904	-0.0969
0.2636	1.07731	1.07309	1.06949	1.06637	-0.1016	-0.1040	-0.1123	-0.1187
0.3576	1.07092	1.06668	1.06303	1.05982	-0.1147	-0.1170	-0.1244	-0.1298
0.4701	1.06215	1.05791	1.05420	1.05087	-0.1182	-0.1212	-0.1281	-0.1321
0.5625	1.05391	1.04967	1.04589	1.04249	-0.1144	-0.1179	-0.1237	-0.1296
0.6556	1.04443	1.04022	1.03640	1.03289	-0.1022	-0.1081	-0.1150	-0.1208
0.7454	1.03400	1.02979	1.02593	1.02229	-0.0857	-0.0919	-0.1003	-0.1047
0.8325	1.02238	1.01819	1.01427	1.01051	-0.0622	-0.0699	-0.0786	-0.0831
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000

	Viscosity (η / mPa·s)				$\Delta\eta$ / mPa·s				G^{*E} / J·mol^{-1}			
x_1	303.15 K	308.15K	313.15K	318.15K	303.15 K	308.15K	313.15K	318.15K	303.15 K	308.15K	313.15K	318.15 K
N-methylformamide +2-chloroaniline												
0.0000	3.8256	3.4122	3.0602	2.7621	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0815	3.6470	3.2583	2.9269	2.6460	0.004	0.005	0.006	0.007	0.857	0.842	0.833	0.825
0.1725	3.4481	3.0860	2.7767	2.5147	0.009	0.010	0.011	0.013	1.706	1.672	1.647	1.631
0.2634	3.2485	2.9128	2.6252	2.3816	0.013	0.014	0.015	0.016	2.418	2.366	2.326	2.297
0.3674	3.0185	2.7131	2.4506	2.2278	0.016	0.017	0.018	0.019	3.043	2.974	2.919	2.876
0.4756	2.7781	2.5036	2.2675	2.0664	0.018	0.019	0.020	0.021	3.453	3.366	3.303	3.249
0.5689	2.5690	2.3216	2.1081	1.9258	0.018	0.019	0.020	0.021	3.571	3.476	3.409	3.351
0.6623	2.3578	2.1381	1.9472	1.7837	0.016	0.017	0.019	0.020	3.431	3.341	3.274	3.216
0.7712	2.1098	1.9219	1.7576	1.6163	0.012	0.014	0.015	0.016	2.888	2.811	2.757	2.711
0.8895	1.8388	1.6851	1.5491	1.4314	0.006	0.008	0.009	0.010	1.735	1.692	1.662	1.635
1.0000	1.5852	1.4621	1.3515	1.2552	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-methylformamide+ 2-methylaniline												
0.0000	3.2580	2.8240	2.4870	2.1530	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0896	3.1136	2.7085	2.3927	2.0808	0.005	0.007	0.007	0.008	0.832	0.796	0.776	0.743
0.1601	2.9996	2.6166	2.3167	2.0221	0.009	0.011	0.012	0.013	1.411	1.346	1.305	1.248
0.2501	2.8533	2.4982	2.2187	1.9456	0.014	0.015	0.016	0.017	2.044	1.943	1.878	1.789
0.3425	2.7019	2.3754	2.1167	1.8653	0.017	0.018	0.019	0.020	2.555	2.422	2.336	2.214
0.4328	2.5525	2.2541	2.0159	1.7861	0.018	0.020	0.020	0.022	2.898	2.743	2.644	2.502
0.5424	2.3695	2.1053	1.8921	1.6881	0.019	0.020	0.021	0.022	3.084	2.914	2.807	2.650
0.655	2.178	1.949	1.762	1.585	0.01	0.01	0.02	0.02	2.96	2.80	2.699	2.5

4	7	9	6	5	7	9	0	1	7	0		46
0.7342	2.0445	1.8404	1.6709	1.5126	0.015	0.016	0.018	0.019	2.670	2.520	2.428	2.292
0.8414	1.8600	1.6893	1.5445	1.4114	0.009	0.011	0.013	0.014	1.931	1.823	1.767	1.667
1.0000	1.5852	1.4621	1.3515	1.2552	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-methylformamide+ 2-methoxyaniline												
0.0000	4.9225	4.5124	4.1854	3.8825	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.0714	4.6895	4.3010	3.9902	3.7025	0.005	0.006	0.007	0.008	1.082	1.100	1.128	1.150
0.1715	4.3613	4.0015	3.7126	3.4464	0.011	0.012	0.013	0.015	2.436	2.471	2.529	2.579
0.2636	4.0579	3.7249	3.4558	3.2086	0.015	0.017	0.017	0.019	3.492	3.542	3.624	3.692
0.3576	3.7472	3.4405	3.1918	2.9640	0.018	0.019	0.020	0.021	4.358	4.412	4.516	4.598
0.4701	3.3734	3.0995	2.8747	2.6704	0.020	0.021	0.022	0.023	5.058	5.125	5.242	5.341
0.5625	3.0649	2.8174	2.6130	2.4278	0.020	0.021	0.022	0.023	5.310	5.378	5.507	5.612
0.6556	2.7526	2.5319	2.3479	2.1817	0.018	0.019	0.020	0.022	5.207	5.273	5.405	5.508
0.7454	2.4501	2.2558	2.0913	1.9436	0.015	0.017	0.018	0.020	4.696	4.763	4.887	4.985
0.8325	2.1552	1.9863	1.8407	1.7110	0.011	0.013	0.014	0.016	3.718	3.781	3.887	3.971
1.0000	1.5852	1.4621	1.3515	1.2552	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 4 -Coefficients of Redlich – Kister equation and standard deviation (σ) values

Binary mixtures	functions	A_1	A_2	A_3	σ
303.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.435	0.059	0.064	0.001
	Δη / mPa·s	0.073	0.003	-0.023	0.001
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.456	0.071	0.006	0.001
	Δη / mPa·s	0.076	0.001	-0.012	0.001
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.468	0.083	-0.088	0.001
	Δη / mPa·s	0.079	0.001	0.001	0.001
308.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.449	0.054	0.009	0.001
	Δη / mPa·s	0.077	0.005	-0.007	0.001
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.467	0.056	-0.055	0.001
	Δη / mPa·s	0.080	0.004	0.003	0.001
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.481	0.057	-0.135	0.001
	Δη / mPa·s	0.083	0.005	0.021	0.001
313.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.463	0.059	-0.049	0.001
	Δη / mPa·s	0.079	0.008	0.009	0.001
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.487	0.059	-0.113	0.001
	Δη / mPa·s	0.084	0.008	0.016	0.001
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.505	0.061	-0.226	0.001
	Δη / mPa·s	0.086	0.004	0.027	0.001
318.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.473	0.065	-0.126	0.001
	Δη / mPa·s	0.084	0.006	0.015	0.001
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.499	0.065	-0.196	0.001
	Δη / mPa·s	0.088	0.006	0.025	0.001
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.523	0.068	-0.264	0.001
	Δη / mPa·s	0.091	0.07	0.038	0.001

Table 5

The values $\overline{V}^{E}_{m,1}$, $\overline{V}^{E}_{m,2}$ of liquid mixtures of N-methylformamide with o-substituted aniline at T= (303.15 - 318.15) K

	303.15 K		308.15 K		313.15 K		318.15 K	
x1	$\overline{V}^{E}_{m,1}$	$\overline{V}^{E}_{m,2}$	$\overline{V}^{E}_{m,1}$	$\overline{V}^{E}_{m,2}$	$\overline{V}^{E}_{m,1}$	$\overline{V}^{E}_{m,2}$	$\overline{V}^{E}_{m,1}$	$\overline{V}^{E}_{m,2}$
N-methylformamide+ 2-chloroaniline								
0.0000	-0.312	0.000	-0.381	0.000	-0.453	0.000	-0.534	0.000
0.0815	-0.303	-0.001	-0.340	-0.002	-0.380	-0.003	-0.422	-0.005
0.1725	-0.276	-0.004	-0.293	-0.009	-0.311	-0.013	-0.328	-0.019
0.2634	-0.239	-0.015	-0.244	-0.023	-0.252	-0.030	-0.257	-0.038
0.3674	-0.189	-0.040	-0.190	-0.049	-0.194	-0.055	-0.195	-0.063
0.4756	-0.135	-0.082	-0.137	-0.088	-0.142	-0.091	-0.145	-0.094
0.5689	-0.093	-0.131	-0.096	-0.134	-0.102	-0.132	-0.108	-0.129
0.6623	-0.057	-0.191	-0.061	-0.191	-0.067	-0.187	-0.074	-0.179
0.7712	-0.026	-0.269	-0.029	-0.273	-0.034	-0.273	-0.039	-0.270
0.8895	-0.006	-0.357	-0.007	-0.381	-0.009	-0.403	-0.011	-0.430
1.0000	0.000	-0.431	0.000	-0.500	0.000	-0.572	0.000	-0.665
N-methylformamide+ 2-methylaniline								
0.0000	-0.379	0.000	-0.451	0.000	-0.529	0.000	-0.631	0.000
0.0896	-0.337	-0.002	-0.371	-0.004	-0.413	-0.006	-0.465	-0.008
0.1601	-0.302	-0.007	-0.318	-0.012	-0.342	-0.017	-0.370	-0.023
0.2501	-0.256	-0.019	-0.258	-0.028	-0.271	-0.035	-0.281	-0.045
0.3425	-0.209	-0.039	-0.206	-0.050	-0.213	-0.058	-0.217	-0.068
0.4328	-0.163	-0.068	-0.161	-0.077	-0.167	-0.084	-0.170	-0.090
0.5424	-0.113	-0.117	-0.113	-0.122	-0.119	-0.124	-0.125	-0.123
0.6554	-0.067	-0.185	-0.070	-0.186	-0.076	-0.184	-0.084	-0.176
0.7342	-0.041	-0.244	-0.045	-0.245	-0.050	-0.244	-0.057	-0.238
0.8414	-0.015	-0.341	-0.018	-0.353	-0.021	-0.363	-0.024	-0.375
1.0000	0.000	-0.520	0.000	-0.593	0.000	-0.659	0.000	-0.761
N-methylformamide+ 2-methoxyaniline								
0.0000	-0.473	0.000	-0.569	0.000	-0.676	0.000	-0.742	0.000
0.0714	-0.398	-0.003	-0.455	-0.005	-0.516	-0.007	-0.559	-0.008
0.1715	-0.312	-0.015	-0.336	-0.022	-0.359	-0.029	-0.381	-0.033
0.2636	-0.249	-0.032	-0.258	-0.042	-0.265	-0.054	-0.276	-0.060
0.3576	-0.195	-0.055	-0.199	-0.065	-0.201	-0.077	-0.208	-0.084
0.4701	-0.142	-0.089	-0.146	-0.095	-0.148	-0.102	-0.154	-0.108
0.5625	-0.104	-0.127	-0.110	-0.127	-0.115	-0.128	-0.121	-0.131
0.6556	-0.070	-0.177	-0.077	-0.173	-0.083	-0.169	-0.089	-0.171
0.7454	-0.042	-0.243	-0.048	-0.242	-0.054	-0.239	-0.059	-0.244
0.8325	-0.020	-0.330	-0.024	-0.342	-0.028	-0.353	-0.031	-0.369

1.0000	0.000	-0.588	0.000	-0.684	0.000	-0.787	0.000	-0.857

Table 6: The values of $\bar{V}^{\circ}_{\mathrm{m},1}$, $V^{*}_{\mathrm{m},1}$, $\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$, $\bar{V}^{\circ}_{\mathrm{m},2}$, $V^{*}_{\mathrm{m},2}$ and $\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$ of the components for N-methylformamide + o-substituted aniline binary mixtures at T= (303.15 - 318.15) K

T/K	$\bar{V}^{\circ}_{\mathrm{m},1}$	$V^{*}_{\mathrm{m},1}$	$\cdot\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},1}$	$\bar{V}^{\circ}_{\mathrm{m},2}$	$V^{*}_{\mathrm{m},2}$	$\bar{V}^{\circ\mathrm{E}}_{\mathrm{m},2}$
			$(\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$			
			N-methylformamide+ 2-chloroaniline			
303.15	59.07	59.39	-0.312	105.64	106.07	-0.431
308.15	59.26	59.64	-0.387	105.99	106.48	-0.494
313.15	59.44	59.90	-0.453	106.36	106.93	-0.572
318.15	59.61	60.15	-0.534	106.67	107.34	-0.665
			N-methylformamide+ 2-methylaniline			
303.15	59.01	59.39	-0.379	107.70	108.22	-0.521
308.15	59.18	59.64	-0.466	108.10	108.68	-0.578
313.15	59.36	59.90	-0.540	108.50	109.16	-0.659
318.15	59.52	60.15	-0.631	108.86	109.62	-0.761
			N-methylformamide+ 2-methoxyaniline			
303.15	58.91	59.39	-0.473	112.24	112.83	-0.588
308.15	59.08	59.64	-0.568	112.58	113.27	-0.686
313.15	59.22	59.90	-0.679	112.85	113.64	-0.787
318.15	59.40	60.15	-0.742	113.10	113.95	-0.857

Research highlights:

- Thermophysical properties of N-methylformamide with O-substituted aniline were studied at various temperatures.
- Excess properties were correlated with Redlich-Kister equation.
- The effect of temperature on density and viscosity were discussed in term of intermolecular interactions.
- Hydrogen bonding interaction between N-methylformamide with O-substituted aniline is supported by the FTIR spectra.