Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2014, Vol. 30, No. (3):
Pg. 953-967

Derived Thermodynamic Properties of Binary Mixtures of *m*-Xylene, *o*-Xylene, and *p*-Xylene, with *N,N*-Dimethylformamide at *T* = (293.15, 303.15, 313.15 and 323.15) K

EZEKIEL DIXON DIKIO*

Applied Chemistry and Nanoscience Laboratory, Department of Chemistry,
Vaal University of Technology, P. O. Box X021, Vanderbijlpark1911, Republic of South Africa.
*Corresponding author E-mail: ezekield@vut.ac.za

http://dx.doi.org/10.13005/ojc/300306

(Received: June 30, 2014; Accepted: August 08, 2014)

ABSTRACT

Experimental data on dynamic viscosities and densities of binary mixtures of *N,N*-dimethylformamide (DMF) and *o*-xylene, *m*-xylene and *p*-xylene were measured at 293.15, 303.15, 313.15, and 323.15 K. Computed data from experiment for deviations in viscosity, excess molar volume and excess Gibbs energy of activation of viscous flow were correlated with Redlish-Kister polynomial equation. Grundberg-Nissan interaction constant (*d'*), Hind, Frenkel and a modified Kendall-Monroe equation ($E\eta_m$) were determined quantitatively. Deviation in viscosity were both negative and positive while excess molar volume and excess Gibbs energy of activation of viscous flow were all positive. These results have been interpreted on the basis of intermolecular interactions between unlike molecules.

Key words: Density, Viscosity, Thermodynamic parameters, Binary mixtures, Xylenes, *N,N*-dimethylformamide.

INTRODUCTION

Intermolecular interactions have continued to capture the interest of chemists because of its important role in many chemical and biological systems.[1]Solvent systems are frequently used as media for many chemical, industrial and biological processes in that they provide a wide range of desired properties.[2] Properties such as density and viscosity at several temperatures both for pure chemicals and their binary liquid mixtures over a whole composition range are useful for a full understanding of their thermodynamic and chemical engineering purposes.[3]Experimental data and excess thermodynamic properties of liquid mixtures are necessary in drawing information on the structure and interactions of liquid mixtures.[4]*N,N*-dimethylformamide (DMF) is a polar aprotic solvent with a high boiling point,[5] a large dipole moment and high dielectric constant facilitate reactions that

provide a good donor acceptor property.[1-7]In the pure state, *N,N*-dimethylformamide show association through dipole-dipole interaction.[7]It finds applications in polymer science and pharmaceutical Industries and serves as a model compound of peptides to obtain information on protein systems.[6]Formamides also find application in industrial processes that involve their use as synthetic intermediates in the preparation of fungicides and polymers such as polyacrylonitrile.[8]

Xylenes are frequently utilized as raw materials in many organic syntheses. High-purity xylenes are difficult to separate from common distillation operations, as it forms several binary azeotropes. *N,N*-dimethylformamide has been widely used as a selective extractant solvent for xylene separation from naphtha feed.[1]

Measurements of densities, viscosities, speeds of sound and other thermodynamic properties of binary mixtures of *o*-, *m*-, *p*-xylene and isopropyl benzene and 2-butanone,[9]pyridine,[10]1-decanol,[11]*N,N*-diethylformamide,[8] acetic acid,[12]methylformate[13]have been studied.

There are apparently no studies in the literature of thermodynamic studies of densities, viscosities and excess properties of the xylenes with *N,N*-dimethylformamide at the temperatures 293.15, 303.15, 313.15 and 323.15 K.[1,7]

We have studied *o*-, *m*-, *p*-xylene with pyridine at 293.15, 303.15, 313.15 and 323.15 K to determine inter- and intra-molecular interactions that exits in their binary mixtures[10]In this study, Experimental viscosities and densities are reported at four temperatures 293.15, 303.15, 313.15 and 323.15 K for binary mixtures of m-xylene, o-xylene and p-xylene with N,N-dimethylformamide. Deviation in viscosity ($\Delta\eta$), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the density (ρ), and viscosity (η), data. Modified Kendall-Monroe[10,14,15] equation with no parameters has been used in correlating viscosity data of the binary mixtures. Calculated deviation in viscosity and excess functions were fitted to the Redlich-Kister[16] polynomial equation and the results analyzed in terms of molecular interactions.

EXPERIMENTAL

Materials

Reagent grade *m*-xylene, *o*-xylene, *p*-xylene and *N,N*-dimethylformamide were purchased from Sigma-Aldrich South Africa and used without further purification. The purity of the liquids was ascertained by comparing their measured densities (ρ), and viscosities (η), with those reported in the literature.[8-17]

Mixture preparation

Binary mixtures were prepared by weighing appropriate amounts of *N,N*-dimethylformamide and xylene on an electronic balance. An AE Adam balance (Adam Equipment Inc. USA) model PW124 with a maximum capacity of 120 g, a readability range 0.0001 g and repeatability (S.D.) of 0.00015 g, linearity 0.0002 g, operating temperature +10°C to 40°C was used in all measurements.

Density measurement

Density measurements were carried out with an Anton Paar DMA-4500 M digital densitometer thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers were provided for good precision in temperature control internally (T ± 0.01 K). The densitometer protocol includes an automatic correction for the viscosity of the sample. The calibration for temperature and pressure was made by the producer. The apparatus is precise to within $1.0x10^{-5}$ g/cm^3, and the uncertainty of the measurements was estimated to be better than ± $1.0x10^{-4}$ g/cm^3. Calibration of the densitometer was performed at atmospheric pressure using doubly distilled and degassed water.

Viscosity measurement

Viscosity measurements were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of 0.2 to 20 000 mPa.s, a kinematic viscosity range of 0.2 to 20 000 mm^2/s and a density range of 0.65 to 3 g/cm^3. The instrument is equipped with a maximum temperature range of +105°C and a minimum of 20°C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility of 0.0005g/cm^3.

RESULTS AND DISCUSSION

Table 1 presents a comparison of experimental densities and viscosities of all liquids at T = 293.15, 303.15, 313.15 and 323.15) K used in this work as well as accepted literature values.

Experimental density (ρ*)*, dynamic viscosity (η*)*, at temperatures of (293.15, 303.15, 313.15 and 323.15 K) are presented in table 2. The table also lists deviation in viscosity, (Δη*)*, excess molar volume, V^E and excess Gibbs free energy of activation of viscous flow ΔG^{*E}, for (*m*-xylene + *N,N*-dimethylformamide), (*o*-xylene + *N,N*-dimethylformamide), and (*p*-xylene + *N,N*-dimethylformamide) as a function of mole fraction.

To investigate the molecular interaction between *N,N*-dimethylformamide and m-xylene, o-xylene and p-xylene, viscosity deviation, Δ*h*, excess molar volumes V^E and excess Gibbs free energy of activation of viscous flow, ΔG^{*E}, have been evaluated from experimental density and viscosity using the equations 1 and 2 respectively.

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \quad ...(1)$$

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad ...(2)$$

Where x_1 and x_2 are the mole fractions calculated from mass fractions. M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, η_1 and η_2 are viscosities of pure components 1 and 2 respectively. ρ_m and η_m are the density and viscosity of the mixture. The excess Gibbs free energy of activation of viscous flow were obtained from equation 3.

$$\Delta G^{*E} = RT\left[ln\eta_m V_m - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)\right] \quad ...(3)$$

where *R* is the universal constant of gases, T is the absolute temperature, V_1 and V_2 are the molar volumes of component 1 and 2, x_1 and x_2 represents the mole fraction of component 1 and 2. V_m is obtained from equation 4. η_1, η_2 and h_m are the viscosity of component 1 and 2 and mixture respectively.

$$V_m = \frac{x_1M_1 + x_2M_2}{\rho_m} \quad ...(4)$$

The values of V^E, Δη and ΔG^{*E} were correlated by a Redlich-Kister[16] type polynomial, equation 5.

$$\Delta Y = x_1x_2\sum_{k=1}^{n} A_k(2x_1 - 1)^{k-1} \quad ...(5)$$

The values of the parameters A_k, are obtained by fitting the equation to the experimental values with the least-squares method. The correlated results for excess molar volume, viscosity deviation and excess Gibbs free energy of activation of viscous flow are presented in Table 3. The standard deviation s(ΔY) is calculated from equation 6.

$$\sigma(\Delta Y) = \left[\frac{\sum\left(Y_{expt} - Y_{calc}\right)^2}{N - n}\right]^{1/2} \quad ...(6)$$

where Δ*Y* is the excess volume, V^E, deviation in viscosity Δη, and excess Gibbs free energy of activation of viscous flow, ΔG^{*E}. The subscript *expt* and *calc* represents the experimental and calculated values respectively. *N* and *n* are the number of experimental data points and the number of coefficients in the Redlich-Kister polynomial equation.

Kendall and Monroe[14] derived equation 7 for analyzing the viscosity of binary mixtures based on zero adjustable parameter.

$$\eta_m = \left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \quad ...(7)$$

$$E\eta_m = x_1x_2\left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \quad ...(8)$$

where $E\eta_m$ is a modified Kendall-Monroe[10,15] equation, 8.

The predictive ability of some selected viscosity models such as the one parameter model of Frenkel[20] equation 9 and Hind[21] equation 10, apply to the studied binary mixtures.

$$\ln\eta = x_1^2 ln\eta_1 + x_2^2 ln\eta_2 + 2x_1x_2 ln\eta_{12} \quad ...(9)$$

Table 1: Comparison of experimental densities (ρ) and viscosities (η) with literature values

Component		T = 293.15		T = 303.15		T = 313.15		T = 323.15	
		ρ(g/cm³)	η(mPa.s)	ρ(g/cm³)	η(mPa.s)	ρ(g/cm³)	η(mPa.s)	ρ(g/cm³)	η(mPa.s)
m-xylene	Experiment	0.8640	0.5522	0.8550	0.5009	0.8460	0.4463	0.8380	0.3949
	Literature	0.8643[8] 0.8638[17]	0.5580[13] 0.719[17]	0.8556[8] 0.8558[13] 0.8559[17]	0.5580[13] 0.650[17]	0.8469[8]		0.8380[8]	
o-xylene	Experiment	0.8794	0.76036	0.8711	0.6725	0.8626	0.58924	0.8541	0.51766
	Literature	0.8798[8] 0.8794[17]	0.920[17]	0.8714[8] 0.8716[13] 0.8714[17] 0.8707[18]	0.6930[13] 0.814[17]	0.8630[8]		0.8545[8]	
p-Xylene	Experiment	0.8605	0.57562	0.8518	0.52028	0.8430	0.45918	0.8342	0.4046
	Literature	0.8609[8] 0.8607[17]	0.566[13] 0.752[17]	0.8523[8] 0.8523[13] 0.8524[17]	0.5660[13] 0.676[17]	0.8435[8]		0.8347[8]	
DMF	Experiment	0.9478	0.8370	0.9382	0.7470	0.9286	0.6652	0.9189	0.5901
	Literature	0.9436[7] 0.9487[19]		0.9336[7]		0.9261[7]		0.9149[7]	

Table 2: Experimental values of density ρ (g/cm³), viscosity η(mPa.s), deviation in viscosity Δη(mPa.s), excess molar volumes V^E(cm³/mol), molar volume of mixture V_m(cm³/mol), excess Gibbs free energy of activation of viscous flow ΔG^{*E}(J/mol), Grunberg-Nissan parameter (d') and modified Kendall and Monroe viscosity correlation $E\eta_m$ (mPa.s) with xylene (x_1) and *N,N*-dimethylformamide (x_2) at 293.15, 303.15, 313.15 and 323.15 K

o-Xylene x_1	ρ (g/cm³)	η (mPa.s)	Δh (mPa.s)	V^E (cm³/mol)	V_m (cm³/mol)	ΔG^{*E} (J/mol)	d'	$E\eta_m$ (mPa.s)
				293.15K				
0.0000	0.9478	0.8370	0.0000	0.0000	77.1154	0.000	0.0000	0.0000
0.1003	0.9404	0.8459	0.0166	-0.4046	81.3571	2.929	0.2239	0.0748
0.1970	0.9322	0.8510	0.0291	-0.6332	85.6080	4.519	0.2244	0.1300
0.2951	0.9237	0.8497	0.0353	-0.7704	90.0152	5.536	0.2086	0.1693
0.3935	0.9160	0.8465	0.0397	-0.9110	94.4328	6.126	0.2055	0.1924
0.5010	0.9092	0.8390	0.0404	-1.1551	99.1686	6.314	0.2019	0.1995
0.5879	0.9026	0.8279	0.0359	-1.1744	103.1749	6.133	0.1878	0.1917
0.6875	0.8973	0.8171	0.0328	-1.3959	107.5671	5.590	0.1951	0.1684
0.7872	0.8906	0.8000	0.0233	-1.3900	112.1915	4.594	0.1811	0.1300
0.8994	0.8863	0.7841	0.0160	-1.7290	117.0502	2.840	0.2325	0.0695
1.0000	0.8682	0.7604	0.0000	0.0000	123.4393	0.000	0.0000	0.0000
				303.15K				
0.0000	0.9382	0.7470	0.0000	0.0000	77.9045	0.000	0.0000	0.0000
0.1003	0.9309	0.7527	0.0132	-0.2430	82.1874	2.923	0.2013	0.0667
0.197	0.9228	0.7514	0.0191	-0.3139	86.4800	4.467	0.1683	0.1158
0.2951	0.9145	0.7488	0.0238	-0.2998	90.9207	5.485	0.1604	0.1507
0.3935	0.9068	0.7439	0.0263	-0.2698	95.3909	6.071	0.1560	0.1711
0.501	0.9001	0.7361	0.0264	-0.3404	100.1712	6.265	0.1519	0.1773
0.5879	0.8936	0.7281	0.0249	-0.2188	104.2140	6.120	0.1492	0.1702
0.6875	0.8884	0.7170	0.0212	-0.2824	108.6448	5.577	0.1454	0.1494
0.7872	0.8819	0.7033	0.0150	-0.1277	113.2983	4.614	0.1340	0.1152
0.8994	0.8777	0.6929	0.0129	-0.2918	118.1971	2.923	0.2133	0.0615
1.0000	0.8711	0.6725	0.0000	0.0000	123.0284	0.000	0.0000	0.0000
				313.15 K				
0.0000	0.9286	0.6652	0.0000	0.0000	78.7099	0.000	0.0000	0.0000
0.1003	0.9214	0.6709	0.0133	-0.2419	83.0348	2.945	0.2297	0.0593
0.197	0.9133	0.6672	0.0170	-0.2999	87.3796	4.470	0.1702	0.1028
0.2951	0.9052	0.6627	0.0200	-0.2912	91.8549	5.475	0.1543	0.1336
0.3935	0.8976	0.6566	0.0213	-0.2576	96.3686	6.051	0.1453	0.1514
0.501	0.891	0.6485	0.0214	-0.3266	101.1943	6.245	0.1416	0.1566
0.5879	0.8846	0.6390	0.0185	-0.2031	105.2743	6.080	0.1287	0.1502
0.6875	0.8795	0.6306	0.0176	-0.2681	109.7442	5.567	0.1395	0.1316
0.7872	0.8732	0.6168	0.0114	-0.1246	114.4271	4.593	0.1194	0.1013
0.8994	0.869	0.6067	0.0100	-0.2799	119.3804	2.908	0.1915	0.0540
1.0000	0.8626	0.5892	0.0000	0.0000	124.2407	0.000	0.0000	0.0000
				323.15 K				
0.0000	0.9189	0.5901	0.0000	0.0000	79.5408	0.000	0.0000	0.0000
0.1003	0.9118	0.5960	0.0078	-0.2392	83.9090	2.882	0.2563	0.0526
0.197	0.9039	0.5910	0.0045	-0.3020	88.2883	4.311	0.1725	0.0910
0.2951	0.8959	0.5854	0.0007	-0.2882	92.8084	5.219	0.1474	0.1182
0.3935	0.8884	0.5785	-0.0044	-0.2501	97.3666	5.701	0.1328	0.1339
0.501	0.8819	0.5708	-0.0101	-0.3164	102.2384	5.806	0.1291	0.1383

0.5879	0.8716	0.5874	0.0081	0.2977	106.8445	5.975	0.2988	0.1325
0.6875	0.8706	0.5534	-0.0241	-0.2559	110.8661	4.965	0.1200	0.1159
0.7872	0.8643	0.5412	-0.0345	-0.0964	115.6054	3.916	0.0986	0.0892
0.8994	0.8603	0.5332	-0.0405	-0.2683	120.5876	2.157	0.1795	0.0475
1.0000	0.8541	0.51771	-0.0541	0.0000	125.4771	-0.826	0.0000	0.0000
				293.15 K				
0.0000	0.9461	0.8357	0.0000	0.0000	77.2329	0.0000	0.0000	0.0000
0.0894	0.938	0.7818	-0.0286	-0.2727	81.1498	2.3162	-0.3639	0.0657
0.1962	0.9317	0.8246	0.0445	-0.8202	85.6074	4.7632	0.4307	0.1220
0.2943	0.9182	0.7826	0.0303	-0.5156	90.5093	5.6645	0.2711	0.1545
0.3922	0.9116	0.7974	0.0729	-0.7862	94.8267	6.6890	0.4849	0.1705
0.4904	0.9006	0.7228	0.0261	-0.5118	99.7031	6.4337	0.2323	0.1717
0.5885	0.886	0.6687	-0.0002	0.3094	105.1217	6.0486	0.0864	0.1597
0.687	0.8805	0.6406	-0.0003	0.1647	109.5931	5.5241	0.0874	0.1360
0.7785	0.8732	0.6122	-0.0028	0.3661	114.0825	4.6647	0.0659	0.1049
0.8818	0.8711	0.5855	-0.0002	-0.1562	118.4013	3.1757	0.0919	0.0606
1.0000	0.8636	0.5522	0.0000	0.0000	124.0968	0.0000	0.0000	0.0000
				303.15 K				
0.0000	0.9365	0.7676	0.0000	0.0000	78.0246	-0.0005	0.0000	0.0000
0.0894	0.9284	0.6903	-0.0534	-0.2674	81.9889	1.9985	-0.8345	0.0603
0.1962	0.9223	0.7180	0.0027	-0.8318	86.4799	4.3388	0.1073	0.1119
0.2943	0.9089	0.6915	0.0024	-0.5199	91.4354	5.3725	0.1020	0.1415
0.3922	0.9023	0.6984	0.0354	-0.7853	95.8041	6.3346	0.3057	0.1559
0.4904	0.8914	0.6400	0.0032	-0.5056	100.7322	6.1806	0.1101	0.1568
0.5885	0.8769	0.5961	-0.0145	0.3313	106.2126	5.8628	-0.0066	0.1457
0.687	0.8715	0.5718	-0.0125	0.1810	110.7248	5.3591	-0.0055	0.1239
0.7785	0.8643	0.5482	-0.0118	0.3823	115.2573	4.5354	-0.0249	0.0955
0.8818	0.8624	0.5284	-0.0040	-0.1689	119.5958	3.1202	0.0287	0.0551
1.0000	0.8549	0.5009	0.0000	0.0000	125.3597	0.0000	0.0000	0.0000
				313.15 K				
0.0000	0.8269	0.6823	0.0000	0.0000	88.3662	0.0000	0.0000	0.0000
0.0894	0.9189	0.6097	-0.0515	-8.9520	82.8366	1.0791	-0.9158	0.0536
0.1962	0.9128	0.6250	-0.0110	-8.4972	87.3800	3.3985	-0.0284	0.0995
0.2943	0.8995	0.6128	0.0000	-7.2418	92.3909	4.6730	0.0842	0.1258
0.3922	0.893	0.6118	0.0221	-6.5787	96.8018	5.6304	0.2411	0.1387
0.4904	0.8822	0.5667	0.0002	-5.3572	101.7826	5.6568	0.0904	0.1395
0.5885	0.8678	0.5274	-0.0160	-3.5690	107.3264	5.4234	-0.0316	0.1297
0.687	0.8625	0.5062	-0.0139	-2.7859	111.8802	5.0157	-0.0319	0.1103
0.7785	0.8554	0.4849	-0.0137	-1.7126	116.4565	4.2700	-0.0640	0.0850
0.8818	0.8535	0.4689	-0.0053	-1.2807	120.8429	2.9783	-0.0068	0.0491
1.0000	0.8462	0.4463	0.0000	0.0000	126.6485	0.0000	0.0000	0.0000
				323.15 K				
0.0000	0.9172	0.6057	0.0000	0.0000	79.6664	-0.0003	0.0000	0.0000
0.0894	0.9093	0.5380	-0.0488	-0.2621	83.7111	1.8975	-0.9847	0.0476
0.1962	0.9032	0.5598	-0.0044	-0.8097	88.3087	4.2462	0.0345	0.0882
0.2943	0.8901	0.5419	-0.0015	-0.4779	93.3666	5.3261	0.0730	0.1116
0.3922	0.8836	0.5355	0.0128	-0.7293	97.8316	6.1104	0.1901	0.1229
0.4904	0.873	0.4998	-0.0021	-0.4365	102.8553	6.1117	0.0745	0.1236
0.5885	0.8587	0.4650	-0.0162	0.4460	108.4638	5.7880	-0.0473	0.1148
0.687	0.8534	0.4467	-0.0137	0.3102	113.0732	5.2994	-0.0435	0.0976
0.7785	0.8464	0.4275	-0.0134	0.5236	117.6948	4.4651	-0.0800	0.0752

0.8818	0.8447	0.4142	-0.0049	-0.0459	122.1018	3.0951	-0.0097	0.0434
1.0000	0.8383	0.3941	0.0000	0.0000	127.8421	-0.0002	0.0000	0.0000
				293.15 K				
0.0000	0.9478	0.8370	0.0000	0.0000	77.0943	0.0000	0.0000	0.0000
0.0896	0.9455	0.9666	0.1530	-0.8325	80.5133	3.9870	0.1908	0.0661
0.1961	0.9338	0.9375	0.1517	-0.9879	85.4112	5.7378	0.2777	0.1231
0.2942	0.9181	0.7689	0.0088	-0.5385	90.5154	5.4089	-0.4828	0.1564
0.3923	0.9116	0.8533	0.1188	-0.8783	94.8304	7.1070	0.2435	0.1732
0.4904	0.9017	0.8315	0.1227	-0.7821	99.5815	7.4054	0.3456	0.1751
0.5885	0.8856	0.6851	0.0019	0.1508	105.1692	6.0339	-0.2194	0.1635
0.6866	0.8788	0.7203	0.0628	0.1164	109.7896	6.2598	0.2377	0.1400
0.7847	0.8715	0.6254	-0.0065	0.2197	114.5476	4.5132	-0.2128	0.1058
0.8828	0.8642	0.6073	0.0010	0.4033	119.3861	3.1999	-0.1082	0.0624
1.0000	0.8605	0.5756	0.0000	0.0000	124.5439	0.0000	0.0000	0.0000
				303.15 K				
0.0000	0.9382	0.7470	0.0000	0.0000	77.8832	0.0001	0.0000	0.0000
0.0896	0.9361	0.8311	0.1044	-0.7538	81.3218	3.6728	-1.5502	0.0591
0.1961	0.9243	0.8047	0.1021	-0.7698	86.2891	5.4079	-0.5659	0.1101
0.2942	0.9087	0.6743	-0.0060	-0.1974	91.4518	5.2546	-0.9724	0.1401
0.3923	0.9023	0.7412	0.0831	-0.4315	95.8079	6.8702	-0.1814	0.1553
0.4904	0.8924	0.7189	0.0831	-0.2103	100.6193	7.1287	-0.0383	0.1572
0.5885	0.8765	0.6082	-0.0054	0.8414	106.2611	5.9729	-0.4659	0.1470
0.6866	0.8698	0.6307	0.0394	0.9156	110.9256	6.0819	-0.0571	0.1260
0.7847	0.8626	0.5569	-0.0122	1.1294	115.7295	4.4712	-0.4307	0.0954
0.8828	0.8553	0.5429	-0.0040	1.4381	120.6284	3.1889	-0.3295	0.0563
1.0000	0.8596	0.5203	0.0000	0.0000	124.6743	0.0005	0.0000	0.0000
				313.15 K				
0.0000	0.9286	0.6652	0.0000	0.0000	78.6884	0.0005	0.0000	0.0000
0.0896	0.9265	0.7202	0.0735	-0.8642	82.1645	3.4465	-3.1684	0.0526
0.1961	0.9148	0.6949	0.0701	-1.0024	87.1852	5.1533	-1.3404	0.0979
0.2942	0.8993	0.5910	-0.0136	-0.5320	92.4077	5.1232	-1.4302	0.1244
0.3923	0.8929	0.6478	0.0634	-0.8753	96.8165	6.7160	-0.5404	0.1379
0.4904	0.8831	0.6246	0.0604	-0.7649	101.6789	6.9234	-0.3563	0.1394
0.5885	0.8674	0.5365	-0.0075	0.1800	107.3759	5.8942	-0.6802	0.1303
0.6866	0.8608	0.5486	0.0248	0.1374	112.0853	5.8859	-0.3068	0.1115
0.7847	0.8536	0.4910	-0.0126	0.2497	116.9497	4.3880	-0.5961	0.0844
0.8828	0.8464	0.4777	-0.0056	0.4448	121.8968	3.0899	-0.4990	0.0497
1.0000	0.843	0.4592	0.0000	0.0000	127.1293	0.0000	0.0000	0.0000
				323.15 K				
0.0000	0.9189	0.5901	0.0000	0.0000	79.5190	-0.0001	0.0000	0.0000
0.0896	0.9617	0.6240	0.0505	-4.7471	79.1579	2.8573	-4.7885	0.0466
0.1961	0.9052	0.5986	0.0448	-1.0085	88.1098	4.9196	-2.1299	0.0867
0.2942	0.8899	0.5502	0.0147	-0.5367	93.3838	5.5413	-1.5952	0.1102
0.3923	0.8834	0.5648	0.0474	-0.8650	97.8576	6.5951	-0.9076	0.1220
0.4904	0.8737	0.5425	0.0434	-0.7519	102.7729	6.7778	-0.6715	0.1233
0.5885	0.8582	0.4719	-0.0091	0.2001	108.5270	5.8583	-0.9024	0.1151
0.6866	0.8517	0.4737	0.0109	0.1539	113.2829	5.7004	-0.5855	0.0985
0.7847	0.8446	0.4317	-0.0129	0.2648	118.1959	4.3591	-0.7699	0.0745
0.8828	0.8374	0.4100	-0.0164	0.4736	123.2069	2.8658	-0.8971	0.0439
1.0000	0.8342	0.4046	0.0000	0.0000	128.4704	0.0000	0.0000	0.0000

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12} \quad ...(10)$$

where η_{12} is a constant attributed to unlike pair interactions. Its value is obtained from equation

11.

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \quad ...(11)$$

Grunberg and Nissan[22] formulated equation

Table 3: Adjustable parameters A_i, with standard deviations (ΔY), for deviation in viscosity ($\Delta\eta$), Excess volume (V^E), and Excess Gibbs free energy (ΔG^{*E}), for binary mixtures at various temperatures

Parameter/Function	T/K	A_o	A_1	A_2	A_3	A_4	s
Δh (mPa.s)	o-Xylene (1) +N,N-dimethylformamide(2)						
	293.15	0.0026	-0.003	3.0×10^{-18}			0.09
	303.15	0.0176	-0.0021	1.0×10^{-16}			0.05
	313.15	0.0155	-0.0036	1.0×10^{-16}			0.04
	323.15	0.0148	-0.0057	1.0×10^{-16}			0.06
V^E(cm^3/mol)	293.15	0.4639	-0.8186				3.90
	303.15	-0.2378	0.0418	2.00×10^{-15}			0.68
	313.15	-0.2303	0.044	-4.0×10^{-15}			0.65
	323.15	-0.2053	0.099	-2.0×10^{-15}			0.43
ΔG^{*E} (kJ/mol)	293.15	4.0857	-0.0665				12.56
	303.15	4.042	-0.003	3.0×10^{-14}			13.34
	313.15	4.0425	-0.0246	6.0×10^{-14}			13.29
	323.15	4.0612	-0.8382				10.65
m-Xylene (1) + N,N-dimethylformamide (2)							
$\Delta\eta$ (mPa.s)	293.15	0.02	-0.0146	9.00×10^{-16}	-1.00×10^{-15}		0.032
	303.15	0.0083	0.0073	7.00×10^{-15}	-4.00×10^{-15}		0.021
	313.15	-0.0133	0.0106	-1.00×10^{-15}	9.00×10^{-16}		0.019
	323.15	-0.0129	0.009	2.00×10^{-15}	1.00×10^{-15}		0.021
V^E (cm^3/mol)	293.15	-0.4914	0.5896	-4.00×10^{-14}	2.00×10^{-14}		0.16
	303.15	-0.4911	0.5961	-6.00×10^{-14}	3.00×10^{-14}		0.14
	313.15	-7.0323	5.8139	-5.00×10^{-13}	3.00×10^{-13}		9.26
	323.15	-0.4740	0.6914	-6.00×10^{-14}	3.00×10^{-14}		0.18
ΔG^{*E} (kJ/mol)	293.15	4.0471	0.1411	5.00×10^{-13}	-5.00×10^{-13}		14.65
	303.15	3.742	0.3593	5.00×10^{-13}	-7.00×10^{-13}		14.16
	313.15	3.0122	0.9246	-2.00×10^{-13}			12.25
	323.15	3.650	0.4054	-5.00×10^{-13}			13.06
p-Xylene (1) + N,N-dimethylformamide (2)							
$\Delta\eta$ (mPa.s)	293.15	0.1052	-0.1005	-4.00×10^{-15}			0.096
	303.15	0.0699	-0.0712	-4.00×10^{-15}	4.00×10^{-15}		0.056
	313.15	0.0482	-0.0513	-9.00×10^{-16}	9.00×10^{-16}		0.033
	323.15	0.0385	-0.0462	-5.00×10^{-15}	3.00×10^{-15}		0.012
V^E (cm^3/mol)	293.15	-0.7738	0.9959	9.00×10^{-14}	-5.00×10^{-14}		0.067
	303.15	-0.6223	1.6294	2.00×10^{-13}	-1.00×10^{-13}		2.16
	313.15	-0.7860	1.0396	5.00×10^{-14}	-4.00×10^{-14}		0.007
	323.15	-1.8478	2.4993	2.00×10^{-13}	-1.00×10^{-13}		0.165
ΔG^{*E} (kJ/mol)	293.15	4.8265	-0.6362	-9.00×10^{-13}	5.00×10^{-13}		15.33
	303.15	4.5807	-0.4326	2.00×10^{-11}	-1.00×10^{-11}		15.01
	313.15	4.4064	-0.3423	5.00×10^{-13}	-2.00×10^{-13}		14.63
	323.15	4.2570	-0.2502	-2.00×10^{-13}			13.42

12 to determine the molecular interactions leading to viscosity changes with one parameter to estimate the dynamic viscosity of binary liquid mixtures.

$$ln\eta_m = x_1 ln\eta_1 + x_2 ln\eta_2 + x_1 x_2 d' \quad ...(12)$$

where d^1 is an interaction parameter which is a function of the composition and temperature of binary liquid mixture.

The correlating ability of equations 8, 9, 10 and 12 were tested by calculating the average percentage deviations (*APD*) between the experimental and the calculated viscosity as shown in equation 14.

$$APD = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{(\eta_{expt} - \eta_{calc})}{\eta_{expt}}\right] \quad ...(13)$$

where η_{expt} and η_{calc} represent the viscosity of experimental and calculated data, N is the number of experimental data points.

Deviations in viscosity ($\Delta\eta$) for the binary system *N,N*-dimethylformamide (DMF) and *o*-xylene, *m*-xylene and *p*-xylene at 293.15, 303.15, 313.15 and 323.15 K, plotted against mole fraction with the curve calculated from Redlich-Kister equation are presented in figure 1(a-c). Viscosity deviations for *N,N*-dimethylformamide (DMF) with *o*-xylene and *p*-xylene are positive while that of *N,N*-dimethylformamide (DMF) and *m*-xylene were found to be both positive and negative. Deviation in viscosity are related to molecular interactions such as hydrogen bonding, charge transfer interactions and physical interactions of dispersion forces or weak dipole-dipole interactions between compounds in a mixture.[23] The reason why a positive V^E and a negative $\Delta\eta$ may result in a binary system is because of a disruption in associated molecules while a negative V^E and positive $\Delta\eta$ is caused by an association or compound formation between components.[24] In a system where positive values of Dh are observed, specific interactions cause complex formation. When negative values of $\Delta\eta$ are observed, dispersion forces are therefore dominant.[23] In our system, positive deviations in Dh show a complex formation between *N,N*-dimethylformamideand *o*-xylene, *m*-xylene and *p*-xylene while negative deviations in $\Delta\eta$, have resulted as a consequence of disruption in hydrogen bonding and increase in temperature as observed

Table 4: Fitting parameters with Average Percentage Deviations (APD) for binary mixtures at various temperatures

Temperature	Frenkel		Hind	
K	η_{12}	APD	η_{12}	APD
o-Xylene (1) + *N,N*-dimethylformamide (2)				
293.15	0.7987	11.58	0.7987	0.27
303.15	0.7098	13.39	0.7098	0.21
313.15	0.6272	15.71	0.6272	0.19
323.15	0.5539	18.57	0.5539	0.22
m-Xylene (1) + *N,N*-dimethylformamide (2)				
293.15	0.6940	13.91	0.6940	0.17
303.15	0.6343	15.81	0.6343	-0.07
313.15	0.5643	18.60	0.5643	-0.13
323.15	0.4999	22.09	0.4999	-0.16
p-Xylene (1) + *N,N*-dimethylformamide (2)				
293.15	0.7063	13.33	0.7063	0.66
303.15	0.6337	15.39	0.6337	0.47
313.15	0.5622	18.15	0.5622	0.36
323.15	0.4974	21.59	0.4974	0.29

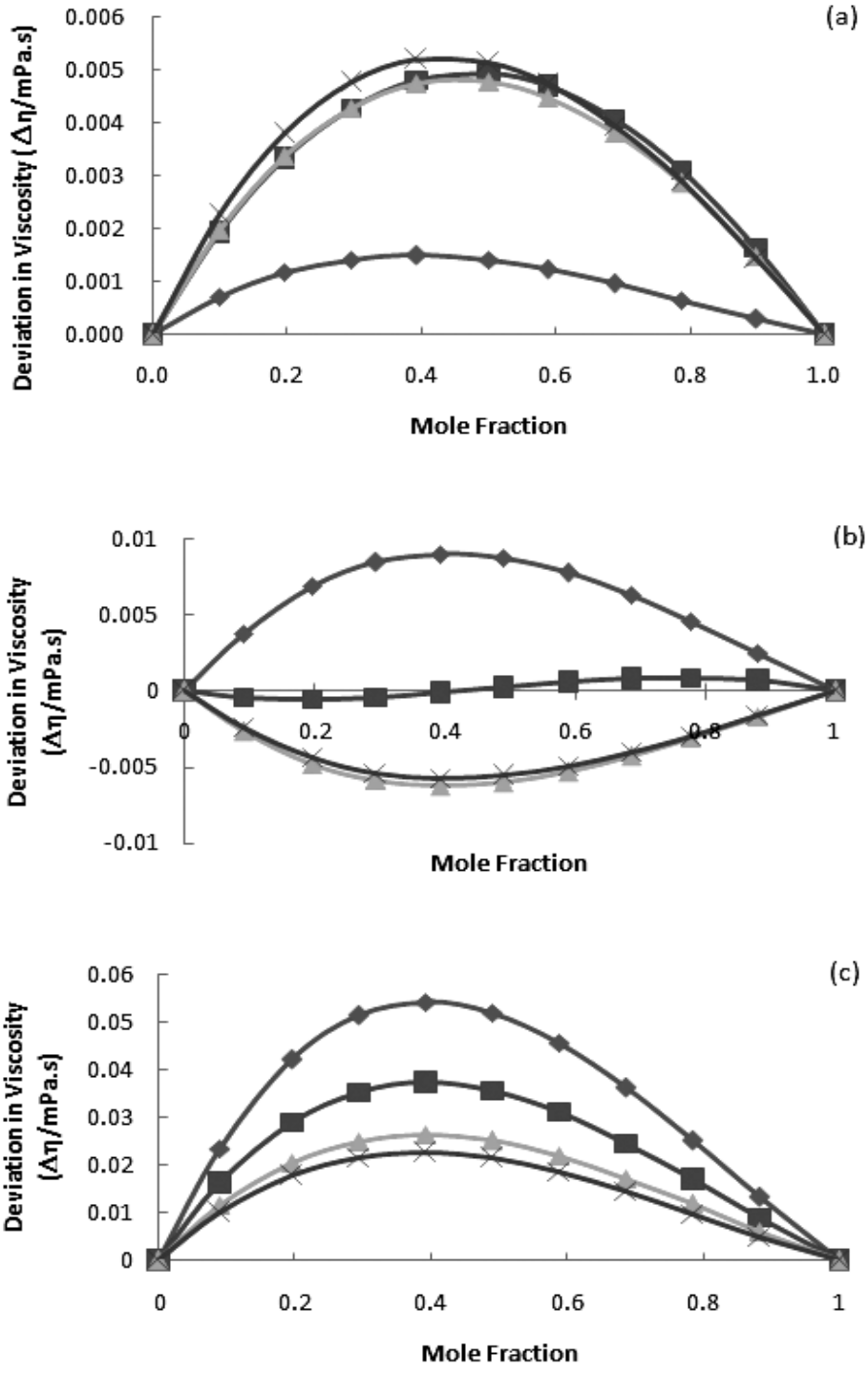

Fig. 1: Plots of deviation in viscosity (Δη) against mole fraction for the system (a) o-xylene (1) + N,N-dimethylformamide(2); (b) m-xylene (1) + N,N-dimethylformamide(2); (c) p-xylene (1) + N,N-dimethylformamide(2) at different temperatures: ♦, 293.15 K; ■, 303.15 K;▲, 313.15 K; x, 323.15 K. The solid line represents the corresponding correlation by the Redlich-Kister equation

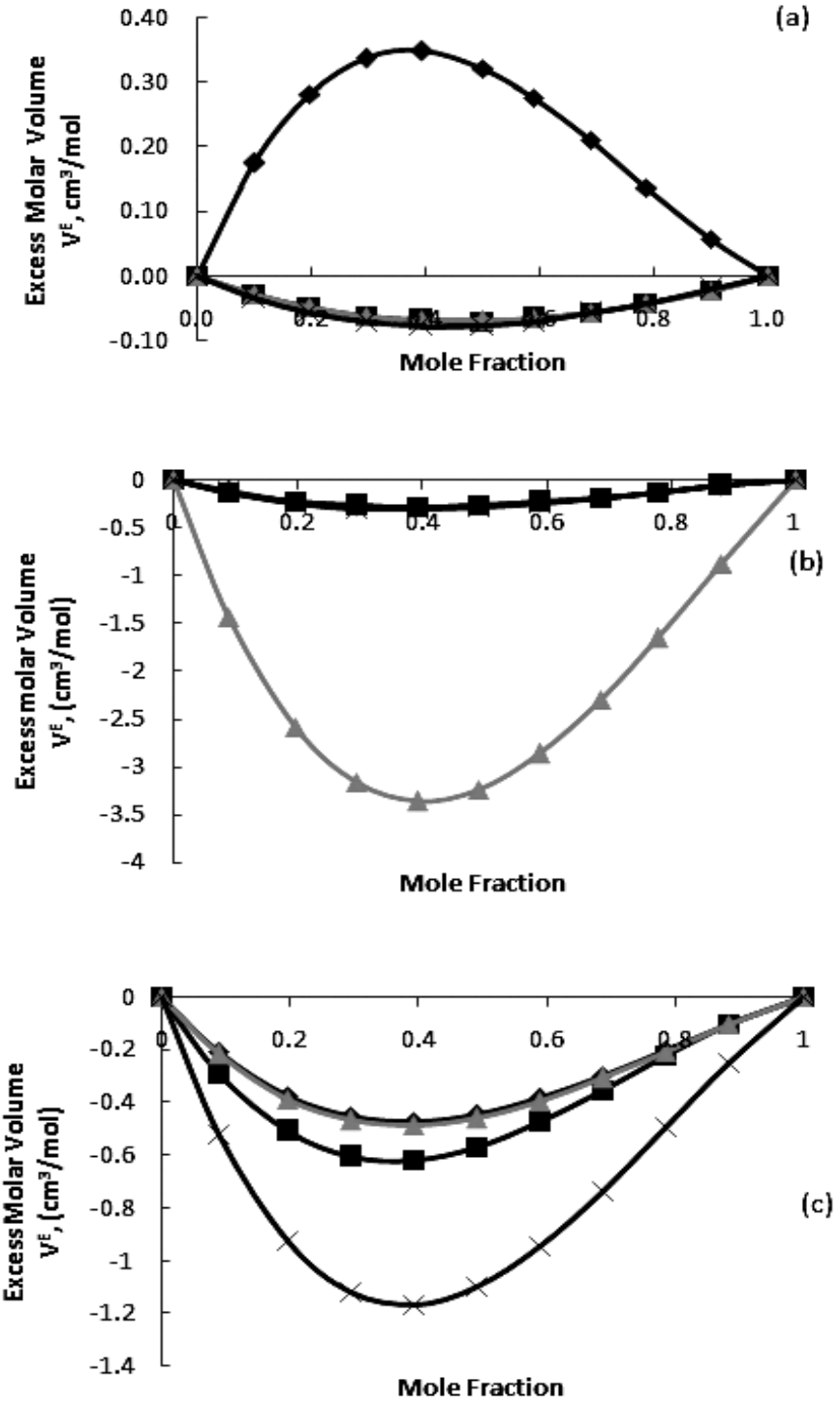

Fig. 2: Plots of Excess molar volume (V^E) against mole fraction for the system(a) *o*-xylene (1) + *N,N*-dimethylformamide(2); (b) *m*-xylene (1) + *N,N*-dimethylformamide (2); (c) *p*-xylene (1) + *N,N*-dimethylformamide (2) at different temperatures:◆, 293.15 K; ■, 303.15 K; ▲, 313.15 K; x, 323.15 K. The solid line represents the corresponding correlation by the Redlich-Kister equation

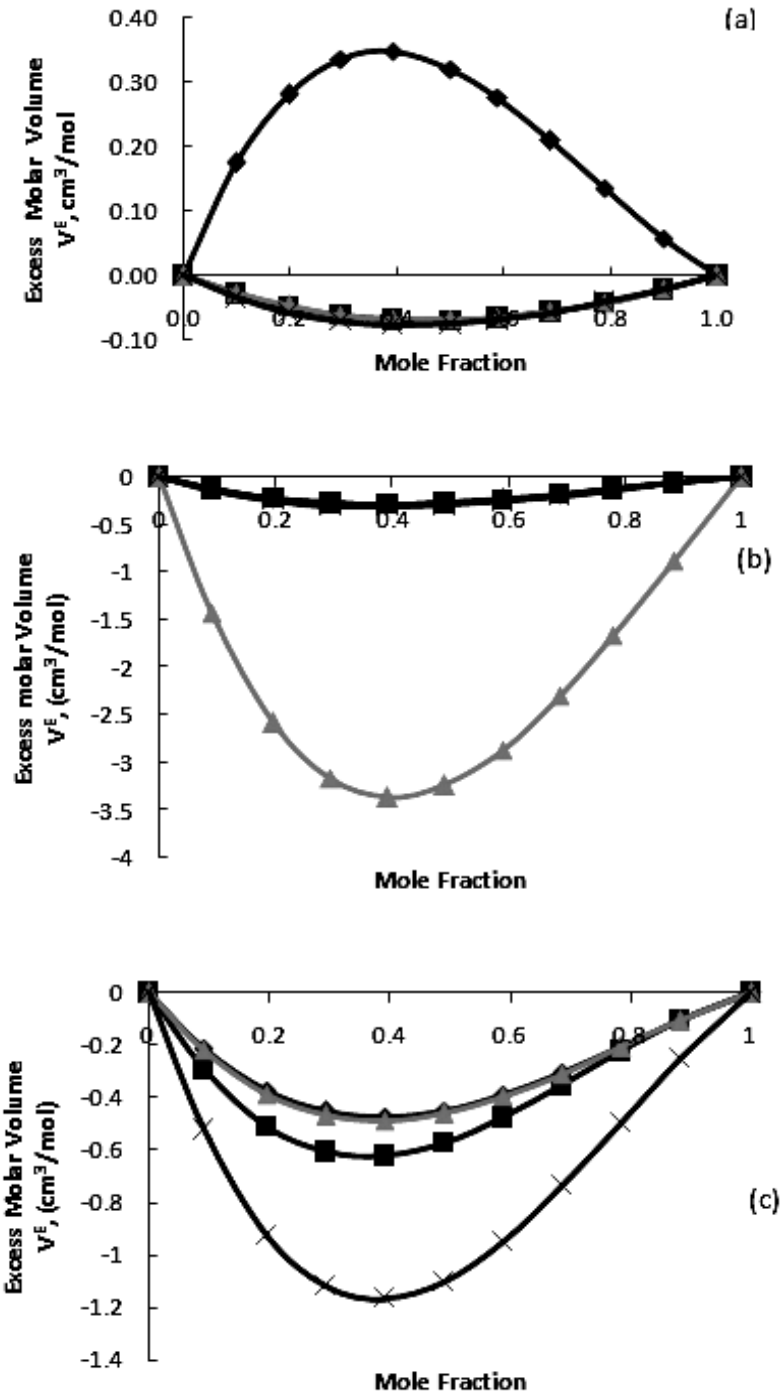

Fig. 3: Plots of Excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) against mole fraction for the system(a) *o*-xylene (1) + *N,N*-dimethylformamide(2); (b) *m*-xylene (1) + *N,N*-dimethylformamide (2); (c) *p*-xylene (1) + *N,N*-dimethylformamide (2) at different temperatures: ◆, 293.15 K; ■, 303.15 K; ▲, 313.15 K; x, 323.15 K. The solid line represents the corresponding correlation by the Redlich-Kister equation

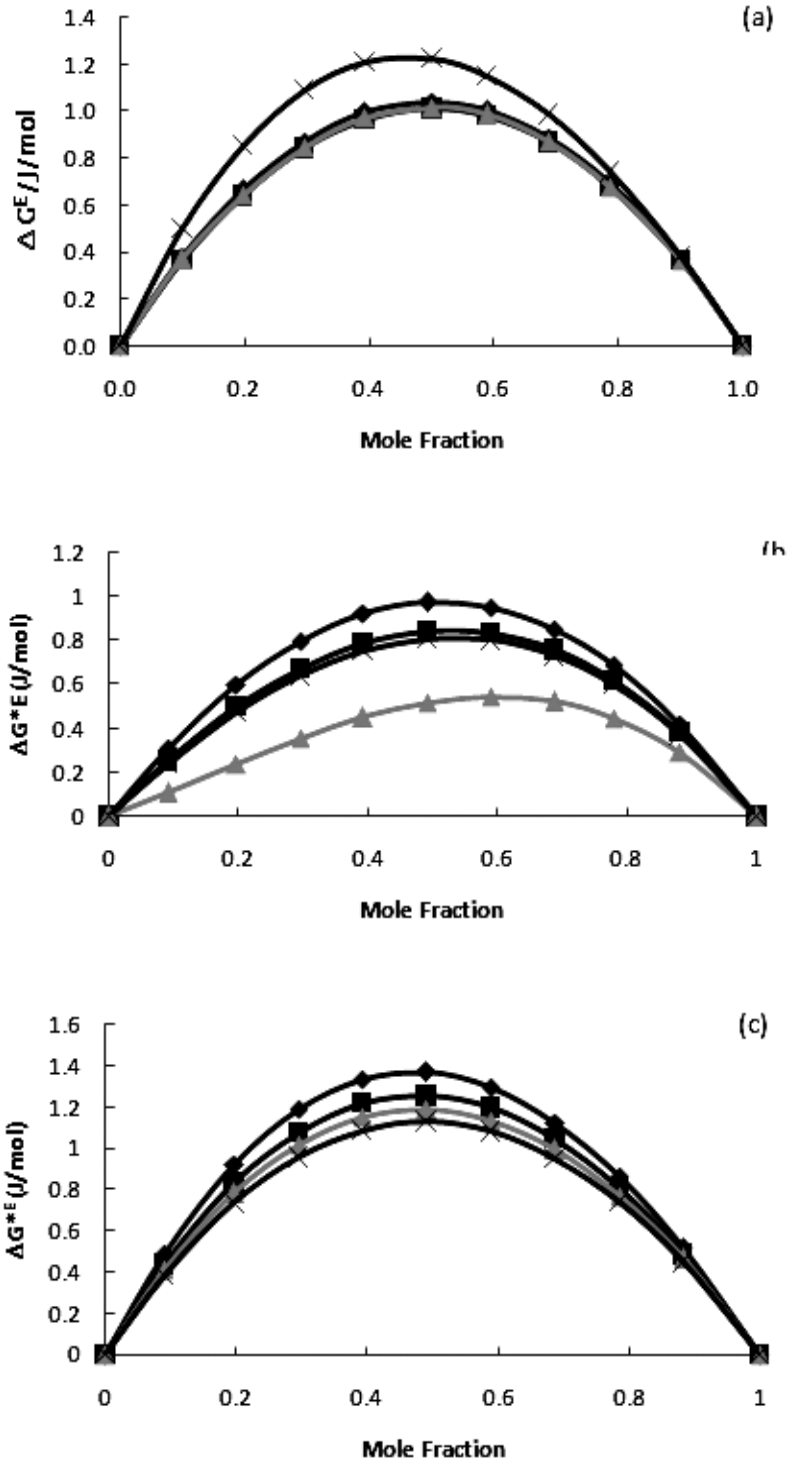

Fig. 4: Plots of modified Kendall and Monroe viscosity correlation Eh_m (mPa.s) against mole fraction for the system(a) *o*-xylene (1) + *N,N*-dimethylformamide(2); (b) *m*-xylene (1) + *N,N*-dimethylformamide (2); (c) *p*-xylene (1) + *N,N*-dimethylformamide (2) at different temperatures: ◆, 293.15 K; ■, 303.15 K;▲, 313.15 K; x, 323.15 K

by other researchers.[24] *N,N*-dimethylformamide has a lone pair of electron on the oxygen atom making it an electron donor while the xylenes on the other hand are electron acceptors. It is therefore possible for hydrogen bonding interactions between *N,N*-dimethylformamide and the xylenes to occur resulting in complex formation.[8]

The plots of excess molar volume (V^E) against mole fraction at 293.15, 303.15, 313.15 and 323.15 K for *N,N*-dimethylformamide (DMF) and *o*-xylene, *m*-xylene and *p*-xylene calculated from Redlich-Kister equation are presented in figure 2 (a-c). Excess parameters associated with a liquid mixture are a quantitative measure of deviation in the behavior of the liquid mixture from ideality.[10]These functions are found to be sensitive towards the intermolecular forces and also on the difference in size and shape of the molecules. Excess volumes of liquid mixtures reflect the result of different contributions arising from structural changes undergone by the pure cosolvent. Positive contributions arise from breakup interactions between molecules namely, the rupture of hydrogen bonded chains and the loosening of dipole interactions.[25] Excess molar volume were found to be both positive and negative for the binary system between *N,N*-dimethylformamide and *o*-xylene, figure 2(a). The binary system of *N,N*-dimethylformamide with *m*-xylene and *p*-xylene, figures 2(b-c), excess molar volumes are negative. For the binary systems, *N,N*-dimethylformamide with *m*-xylene and *p*-xylene, that form a negative deviation, the curves are not shifted in a regular manner with increase in temperature. For the binary system of *N,N*-dimethylformamide and *o*-xylene, positive deviation is observed at 293.15 K only. At the other temperatures, deviations are negative. Mixing *N,N*-dimethylformamide (DMF) with *o*-xylene, *m*-xylene and *p*-xylene may have resulted in complex formation leading to a volume contraction.

Excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) against mole fraction at 293.15, 303.15, 313.15 and 323.15 K for *N,N*-dimethylformamide (DMF) and *o*-xylene, *m*-xylene and *p*-xylene calculated from Redlich-Kister equation are presented in figure 3(a-c). Excess properties provide information about the molecular interactions and macroscopic behavior of fluid mixtures which can be used to test and improve thermodynamic models for calculating and predicting fluid phase equilibria.[10] The magnitude of ΔG^{*E} represents the strength of interaction between unlike molecules.[26] Excess Gibbs free energy of activation of viscous flow are positive at all experimental temperatures.

A comparison of experimental thermodynamic data of multicomponent mixtures with that calculated by means of various predictive methods is very useful from different points of view: (i) it suggests which model is more appropriate to the characteristics of the system, (ii) it may indicate which parameters should be improved when the model involves group contributions and (iii) it may allow the identification of some model as a convenient reference for the interpretation of the deviations observed.[10,27] The viscosity data have been correlated with semi-empirical equations of modified Kendall and Monroe, Frenkel, Hind, and Grunberg-Nissan. The values of the Grunberg and Nissan constant (d') and modified Kendall-Monroe (Eh_m) for all systems under study are presented in table 2. Grunberg-Nissan interaction parameters are both positive and negative while the modified Kendall-Monroe viscosity correlation data are all positive. Plots for the modified Kendall-Monroe viscosity correlation are presented in Figure 4(a-c). Plots of modified Kendall-Monroe viscosity correlation at different temperatures show a decrease in viscosity with increase in temperature. The value of Frenkel and Hind are presented in Table 4. Positive and negative Grunberg-Nissan parameters indicate the presence of both strong and weak interactions between unlike molecules.[28]

CONCLUSION

Density and viscosity for the binary mixtures of *N,N*-dimethylformamide with *o*-xylene, *m*-xylene and *p*-xylene are presented as a function of mixture composition at 293.15, 303.15, 313.15, and 323.15 K. These results have been employed to calculate deviations in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow. The study has shown that there are intermolecular interactions between the components of the system *N,N*-dimethylformamide (DMF) with *o*-xylene, *m*-xylene and *p*-xylene, leading to hydrogen bonds and complex formation. A comparison of experimental thermodynamic data

with calculated data by means of various predictive methods are presented resulting in positive and negative correlations.

ACKNOWLEDGEMENTS

This work was supported by a research grant from the Faculty of Applied and Computer Science Research and Publications Committee of Vaal University of Technology, Vanderbijlpark, Republic of South Africa.

REFERENCES

1. Xiao-Hui, R.;Hai-Jun, W.;Yan-Yan, S.;Wei-Bo, D.*Struct. Chem*. **2008**,*19*, 233 – 238.
2. Nain, A. K.;Sharma,R.*J. Chem. Thermodyn.* **2013**,*58*,36
3. Clara, R. A.;Marigliano, A. C. G.;Campos, V. V.;Solimo,H. N. *Fluid Phase Equilib*. **2010**, 293,151
4. Mohammad, A. A.;Alkhald, K. H. A. E.;AlTuwaim, M. S.;Al-Jimaz,A. S.*J. Chem. Thermodyn.***2013,***56*,106
5. Weissermel, K.;Arpe,H.-J. Industrial Organic Chemistry: Important raw materials and intermediates. Wiley-VCH Verlag GmbH. Weinheim, Germany, **1997**, p. 45
6. Hao, Y.;Zhang, S.;Yao,K. *J. Chem. Eng. Data.***2012**, *57*,1244
7. Chen, B.;Liu,W.*J. Chem. Thermodyn*. **2007**, 39,192
8. Gu, Y.;Wu,J.*J. Mol. Liq.***2008,***137*,165
9. Singh, S.;Sethi,B. P. S.;Katyal, R. C.;Rattan,V. K. *J. Chem. Eng. Data.***2005,***50*,125
10. Dikio, E. D.;Vilakazi, G.;Ngoy,P.*J. Mol. Liq.***2013**, *177*,190
11. Bhatia, S. C.;Rani, R.;Bhatia,R.*J. Mol. Liq*. **2011**, *159*,132
12. Yan, Q.;Zhiguo, D.I.;Youguang, M.A.; PeishengM.A.;Shuquian,X. *Chin. J. Chem. Eng.***2010,**183,446
13. Rathnam, M.V.;Mohite, S.;Kumar,M.S.S.*Ind. J. Chem. Tech.***2008,***157*, 409 – 412.
14. Kendall, J.;Monroe,K. P.*J. Am. Chem. Soc.***1917**, *39(9),* 1787 – 1802.
15. Dikio, E. D.;Nelana, S. M.;Isabirye, D. A.;Ebenso,E. E.*Int. J. Electrochem. Sci.***2012**, *7(6)*, 11101
16. Redlich, O.;Kister,A. T.*Ind. Eng. Chem.***1948**, *40(2),* 345
17. Serrano, L.;Silva, J. A.;Farelo,F.*J. Chem. Eng. Data*. **1990**, *35*, 288
18. Narendra, K.;Narayanamurthy, P.;Srinivasu,C.*E. J. Chem*. **2010**, *7(3),* 927
19. Lange's Handbook of Chemistry 10th edition, p. 1525
20. FrenkelYa. I. Theory of the Viscosity of liquid mixtures. Petroleum (London) 9, **1946**, p. 27
21. Hind, R. K.;McLaughlin, E.;Ubbelohde,A. R.*Trans Faraday Soc.***1960,***56*, 328
22. Grunberg, L.;Nissan,A. H.*Nature***1949**, 164, 799
23. Živkoviæ, E. M.;Kijevèanin, M. Lj.;Radoviæ, I. R.;Šerbanoviæ, S. P.;Djordjeviæ,B. D. *Fluid Phase Equilib.***2010**, *299*, 191
24. Chowdhury, M. A.;Majid, M. A.;Saleh,M. A.*J. Chem. Thermodyn*. **2001**, 33, 347
25. El-Banna,M. M.*Can. J. Chem.***1997,**75, 1890
26. Shafiq, M.;Asif, S. M.; Farooqui,*A. J. Biochem. Pharm. Res.***2011**, *1(2),* 419
27. Parveen, S.;Yasmin, M.;Gupta, M.;Shukla,J. P.*Int. J. Thermodyn.* **2010,***13(2),* 59
28. Sathyanarayana, B.;Ranjithkumar, B.; Jyostna, T. S.;Satyanarayana,N.*J. Chem. Thermodyn.***2007**, *39*, 16