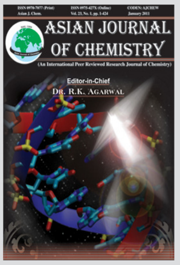
Asian Journal of Chemistry; Vol. 23, No. 9 (2011), 3898-3904

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Experimental and Predicted Viscosities of Binary Mixtures of Styrene with *o*-, *m*- or *p*-Xylene and Toluene at Different Temperatures

FIRDOSA NABI[1,*], MAQSOOD AHMAD MALIK[2] and CHRISTOPHER G. JESUDASON[1]

[1]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia
[2]Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author: Tel: +6 0105444912; E-mail: firdosachem@gmail.com

(*Received*: 14 September 2010; *Accepted*: 11 May 2011) AJC-9929

The viscosities (η) of pure styrene, toluene, *o*-xylene, *m*-xylene or *p*-xylene and those of their binary mixtures with styrene as common component, covering the whole composition range at the temperatures 298.15, 303.15, 308.15 and 313.15 K have been measured. From the experimental data the deviations in viscosity (Δη), deviations in Gibbs free energy of activation (ΔG), deviations in entropies, (ΔS*) and deviations in enthalpies (ΔH*) of activation of viscous flow have been determined. The sign and magnitude of these parameters were found to be sensitive towards interactions prevailing in the studied systems. Further, the excess molar volumes, V^E, were calculated using the viscosity data for the binary mixtures. Moreover, theoretical values of viscosities of the binary mixtures were calculated using different empirical relations and theories.

Key Words: Viscosities, Deviation functions, Theoretical predictions, Binary mixtures.

INTRODUCTION

Thermodynamic and physical properties data have a well recognized importance in design calculations involving separations, fluid flow and heat transfer. The viscosity data presents a valuable insight into the structure and interactions in mixed solvents[1,2]. These considerations led us to undertake the present study in continuation to our research programme on the thermodynamic behaviour of binary liquid mixtures[3-5]. The mixing of different components gives rise to solutions that generally do not behave ideally. The deviation from ideality is expressed by many thermodynamic variables particularly by excess and deviation properties. The concentration and temperature dependence of these properties are required for the use in technological, biological and industrial applications as they provide wide choice of solvents with desired compositions and properties[6-8]. Here, we extend our study to the binary mixtures of styrene with *o*-, *m*- or *p*-xylene and toluene. These mixtures are interesting from the experimental as well as theoretical point of view because styrene is mixed with components having the similar functional groups (CH_3) but at different locations on the benzene ring. Styrene is a rigid plate like molecule with oriented structure, whereas *o*-, *m*- or *p*-xylene has a large quadrupole moment[9] that leads to the molecular order in the pure state. It would be interesting to examine the mixing of styrene with *o*-, *m*- or *p*-xylene and toluene in order to observe the effect of different location of methyl groups (CH_3) on the molecular interaction in these binary mixtures. A complete knowledge of thermodynamic and transport properties of these industrially important mixture are especially important because they are widely used as solvents for dyes, colouring raw materials in plastic industry used to make synthetic fibers and for air crafts and vehicles and large scale preparation of various polymers[10,11].

The experimental data have been used to evaluate the deviations in viscosity (Δη), deviations in Gibbs free energy of activation (ΔG), deviations in entropies (ΔS*) and deviations in enthalpies (ΔH*) of activation of viscous flow. An attempt has also been made to calculate excess molar volumes, V^E, using Δη data. Moreover, viscosities of the binary mixtures were calculated theoretically from the pure component data by using various empirical and semi-empirical relations and the results were compared with the experimental findings. Such studies offer a convenient, model free approach, for the study of the thermodynamic properties of the liquid mixtures[12].

EXPERIMENTAL

All the chemicals used for the present study were obtained from S.D. Fine-Chem Ltd., India, with purity greater than 99 %. The water content from the pure components, if any, was removed by storing them over 0.4 nm molecular sieves. The binary mixtures were prepared by mass at room temperature and kept in special air tight bottles. The weighings were done on a Precisa XB-120 (Swiss make) electronic balance with precision of ± 0.1 mg.

The viscosities of pure liquids and their binary mixtures were measured by using Ubbelhode type suspended level viscometer. The precision in viscosity measurement was within $\pm 1 \times 10^{-6}$ mPa.s. The temperature of the test liquids was maintained to an accuracy of ± 0.02 K using JULABO (Germany, Model: MD) in an electronically controlled thermostatic water bath. The uncertainties in the measured viscosities were not more than $\pm 2 \times 10^{-3}$ mPa.s. The observed viscosities of pure styrene, *o*-, *m*-, *p*-xylene at 298.15 K are 0.695, 0.755, 0.581, 0.611 and toluene at 303.15 K 0.554 mPa.s, respectively, which compare well with the literature values 0.695[4], 0.754[13], 0.581[14], 0.603[13] and 0.527[15] mPa.s, respectively.

RESULTS AND DISCUSSION

The experimental values of η for the mixtures of styrene with *o*-, *m*- or *p*-xylene and toluene including those of their pure liquids, were measured over the entire composition range at 298.15, 303.15, 308.15 and 313.15 K are presented in Table-1. The density data in the present work were taken from earlier work[16,17]. Using the experimental values of viscosity together with the values of density, the derived properties such as deviations in viscosity ($\Delta\eta$), deviations in Gibbs free energy of activation (ΔG), deviations in entropies (ΔS^*) and deviations in enthalpies (ΔH^*), of activation of viscous flow were calculated. These properties correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and new arrangements after mixing. The values of deviation functions $\Delta\eta$ and ΔG, were calculated by using the following standard relations:

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{1}$$

$$\Delta G = G - (x_1G_1 + x_2G_2) \tag{2}$$

The sign and magnitude of these deviations depend on the strength of interaction between the unlike molecules in the mixtures. The values of $\Delta\eta$ and ΔG and for each mixture and at each investigated temperature were fitted to Redlick and Kister[18] polynomial equation:

$$\Delta Y = x_1 x_2 \sum_{i=1}^{4} A_i (1 - 2x_1)^{i-1} \tag{3}$$

where ΔY stands for $\Delta\eta$ or ΔG. The coefficients A_i of the fitting eqn. 3, evaluated using least-squares method and the standard deviations σ (ΔY), calculated as:

$$\sigma(\Delta Y) = (\sum[(Y_{expt} - Y_{cal})^2] / (m-k))^{1/2} \tag{4}$$

where m is the number of experimental data points and k is the number of A_i coefficients considered, have been listed in Table-2. The variations of $\Delta\eta$ or ΔG with mole fraction, x_1 of styrene are graphically shown in Figs. 1 and 2 at 298.15 K only, to avoid over crowding of data points at remaining temperatures.

From Fig. 1, it is clear that $\Delta\eta$ shows positive deviations for the mixtures of styrene with toluene and *m*-xylene, turn negative for *o*-xylene, become more so for *p*-xylene and follow the sequence: toluene < *m*-xylene < *o*-xylene < *p*-xylene. An explanation for the behaviour of negative $\Delta\eta$ values may be observed due to the difference in the molecular size of the component molecule[19]. $\Delta\eta$ are considering order in the pure liquids and in the solution and also by considering the interactions between the component molecules in the mixtures. The observed small positive $\Delta\eta$ values for styrene + toluene and *m*-xylene mixtures suggest that destruction in order takes place. On the other hand, negative $\Delta\eta$ values for styrene + *o*-xylene or *m*-xylene indicate that accommodation of the component molecules into each other's structure and because of the dispersion or weak dipole-dipole forces which are primarily responsible for the interaction between component molecules. This sequence is same as in the molar volume of styrene with *o*-, *m*- and *p*-xylenes[16].

The variations of ΔG with mole fraction x_1 of styrene for all the binary mixtures are presented in Fig. 2. The values of ΔG for the system styrene + toluene and *m*-xylene are entirely positive and turn negative for styrene + *o*-xylene and *p*-xylene. In general, the positive contribution to ΔG values may be attributed to the presence of specific interactions whereas negative contribution may be ascribed to the dispersion forces[20,21]. Thus, the observed positive ΔG values for the mixtures of styrene + toluene and *m*-xylene suggest that the specific interactions of the donor-acceptor type are prevailing in the system, whereas negative ΔG values for the other indicates the dominance of dispersion forces between the component molecules.

Further, by using the temperature dependence of viscosity data the activation parameters for viscous flow have been investigated. The Eyring's viscosity equation[22,23] is given as:

$$\eta = \left(\frac{h \cdot N}{V}\right) \exp\left(\frac{\Delta G^*}{R \cdot T}\right) \tag{5}$$

where h is Planck's constant, N is Avogadro's number and ΔG^* is the Gibbs energy of activation of viscous flow. Combining eqn. 5 with $\Delta G^* = \Delta H^* - T\Delta S^*$ gives the equation:

$$R \cdot \ln\left(\frac{\eta \cdot V}{h \cdot N}\right) = \left(\frac{\Delta H^*}{T}\right) - \Delta S^* \tag{6}$$

where ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow, respectively. The plots of the left hand side of eqn. 6, *i.e.*, $R \cdot \ln\left(\frac{\eta \cdot V}{h \cdot N}\right)$ against $\frac{1}{T}$ for all the binary mixtures at different compositions were found to show linear trend for each composition of the system under study. This indicates that ΔH^* values are almost constant in the investigated temperature range, *i.e.*, ΔH^* is independent of temperature. Thus, the values of ΔH^* and ΔS^* were obtained as the slopes and intercepts of the above plots by using a linear regression procedure.

The values of ΔH^* and ΔS^* along with the linear correlation factor, r of eqn. 6 are given in Table-3. A close perusal of Table-3 indicates that for all the binary mixtures the values of ΔH^* are positive and an opposite negative trend in ΔS^* values with mole fraction x_1 of styrene were observed. It has been suggested[24] that the enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between

TABLE-1
THEORETICALLY EVALUATED VISCOSITIES BY USING VARIOUS CO-RELATIONS ALONG WITH EXPERIMENTAL VALUES AND AVERAGE DEVIATIONS FOR THE BINARY MIXTURES AT DIFFERENT TEMPERATURES

x_1	η (mPa s)	Average deviations (η_{expt}-η_{theo})				x_1	η (mPa s)	Average deviations (η_{expt}-η_{theo})			
		Wilke	Wvis/RT	Hind	Grunberg-Nissan			Wilke	Wvis/RT	Hind	Grunberg-Nissan
Styrene + *o*-Xylene											
Temperature = 298.15 K						Temperature = 303.15 K					
0.1077	0.7430	0.7484	0.7436	0.7438	0.7347	0.1077	0.6736	0.6774	0.7048	0.7070	0.6737
		(-0.0054)	(-0.0006)	(-0.0008)	(-0.0006)			(-0.0038)	(-0.0312)	(-0.0334)	(-0.0001)
0.2009	0.7336	0.7426	0.7347	0.7349	0.7254	0.2009	0.6675	0.6749	0.7212	0.7243	0.6687
		(-0.0090)	(-0.0011)	(-0.0013)	(-0.0011)			(-0.0074)	(-0.0537)	(-0.0568)	(-0.0012)
0.3110	0.7245	0.7359	0.7254	0.7256	0.7183	0.3110	0.6625	0.6719	0.7342	0.7379	0.6638
		(-0.0114)	(-0.0009)	(-0.0011)	(-0.0009)			(-0.0094)	(-0.0717)	(-0.0754)	(-0.0013)
0.4090	0.7178	0.7299	0.7182	0.7183	0.7125	0.4090	0.6591	0.6693	0.7397	0.7437	0.6602
		(-0.0121)	(-0.0005)	(-0.0005)	(-0.0005)			(-0.0102)	(-0.0806)	(-0.0846)	(-0.0011)
0.4991	0.7125	0.7245	0.7125	0.7125	0.7067	0.4991	0.6568	0.6670	0.7392	0.7439	0.6575
		(-0.0120)	(0.0000)	(0.0000)	(0.0000)			(-0.0102)	(-0.0829)	(-0.0871)	(-0.0007)
0.6071	0.7069	0.7181	0.7067	0.7066	0.7025	0.6071	0.6552	0.6642	0.7331	0.7376	0.6552
		(-0.0112)	(0.0002)	(0.0003)	(0.0002)			(-0.0090)	(-0.0779)	(-0.0824)	(0.0000)
0.7060	0.7029	0.7122	0.7024	0.7022	0.6992	0.7060	0.6545	0.6616	0.7210	0.7255	0.6538
		(-0.0093)	(0.0005)	(0.0007)	(0.0005)			(-0.0071)	(-0.0665)	(-0.0710)	(0.0007)
0.7988	0.7001	0.7067	0.6992	0.6990	0.6966	0.7988	0.6544	0.6593	0.7047	0.7087	0.6532
		(-0.0066)	(0.0009)	(0.0011)	(0.0009)			(-0.0049)	(-0.0503)	(-0.0543)	(0.0012)
0.9022	0.6974	0.7007	0.6966	0.6964	0.6950	0.9022	0.6543	(-0.0023)	(-0.0268)	(-0.0295)	(0.0009)
		(-0.0033)	(0.0008)	(0.0010)	(0.0008)						
Temperature = 308.15 K						Temperature = 313.15 K					
0.1077	0.6360	0.6395	0.6865	0.6913	0.6363	0.1077	0.5909	0.5934	0.6644	0.6725	0.5908
		(-0.0035)	(-0.0505)	(-0.0553)	(-0.0003)			(-0.0025)	(-0.0735)	(-0.0735)	(0.0001)
0.2009	0.6311	0.6371	0.7173	0.7237	0.6318	0.2009	0.5861	0.5912	0.7141	0.7233	0.5868
		(-0.0060)	(-0.0862)	(-0.0926)	(-0.0007)			(-0.0051)	(-0.1280)	(-0.1280)	(-0.0007)
0.3110	0.6263	0.6344	0.7432	0.7499	0.6274	0.3110	0.5815	0.5885	0.7574	0.7649	0.5828
		(-0.0081)	(-0.1169)	(-0.1236)	(-0.0011)			(-0.0070)	(-0.1759)	(-0.1759)	(-0.0013)
0.4090	0.6232	0.6320	0.7555	0.7623	0.6241	0.4090	0.5787	0.5862	0.7792	0.7852	0.5797
		(-0.0088)	(-0.1323)	(-0.1391)	(-0.0009)			(-0.0075)	(-0.2005)	(-0.2005)	(-0.0010)
0.4991	0.6211	0.6298	0.7576	0.7645	0.6217	0.4991	0.5766	0.5841	0.7840	0.7899	0.5774
		(-0.0087)	(-0.1365)	(-0.1434)	(-0.0006)			(-0.0075)	(-0.2074)	(-0.2074)	(-0.0008)
0.6071	0.6194	0.6272	0.7481	0.7558	0.6195	0.6071	0.5750	0.5817	0.7702	0.7780	0.5753
		(-0.0078)	(-0.1287)	(-0.1364)	(-0.0001)			(-0.0067)	(-0.1952)	(-0.1952)	(-0.0003)
0.7060	0.6187	0.6249	0.7285	0.7367	0.6181	0.7060	0.5743	0.5794	0.7398	0.7502	0.5739
		(-0.0062)	(-0.1098)	(-0.1180)	(0.0006)			(-0.0051)	(-0.1655)	(-0.1655)	(0.0004)
0.7988	0.6186	0.6227	0.7012	0.7093	0.6175	0.7988	0.5739	0.5773	0.6976	0.7096	0.5730
		(-0.0041)	(-0.0826)	(-0.0907)	(0.0011)			(-0.0034)	(-0.1237)	(-0.1237)	(0.0009)
0.9022	0.6182	0.6203	0.6621	0.6678	0.6174	0.9022	0.5735	0.5750	0.6380	0.6476	0.5726
		(-0.0021)	(-0.0439)	(-0.0496)	(0.0008)			(-0.0015)	(-0.0645)	(-0.0645)	(0.0009)
Styrene + *m*-Xylene											
Temperature = 298.15 K						Temperature = 303.15 K					
0.1004	0.5933	0.5912	0.5933	0.5934	0.5933	0.1004	0.5591	0.5566	0.5761	0.5796	0.5590
		(0.0021)	(0.0000)	(-0.0001)	(0.0000)			(0.0025)	(-0.0170)	(-0.0205)	(0.0001)
0.2049	0.6061	0.6021	0.6060	0.6062	0.6060	0.2049	0.5714	0.5669	0.6032	0.6084	0.5713
		(0.0040)	(0.0001)	(-0.0001)	(0.0001)			(0.0045)	(-0.0318)	(-0.0370)	(0.0001)
0.3120	0.6191	0.6136	0.6188	0.6189	0.6188	0.3120	0.5838	0.5777	0.6269	0.6324	0.5836
		(0.0055)	(0.0003)	(0.0002)	(0.0003)			(0.0061)	(-00431)	(-0.0486)	(0.0002)
0.4097	0.6308	0.6243	0.6303	0.6304	0.6303	0.4097	0.5947	0.5877	0.6445	0.6494	0.5945
		(0.0065)	(0.0005)	(0.0004)	(0.0005)			(0.0070)	(-0.0498)	(-0.0547)	(0.0002)
0.5032	0.6417	0.6348	0.6411	0.6411	0.6411	0.5032	0.6050	0.5976	0.6573	0.6614	0.6048
		(0.0069)	(0.0006)	(0.0006)	(0.0006)			(0.0074)	(-0.0523)	(-0.0564)	(0.0002)
0.6075	0.6533	0.6468	0.6530	0.6529	0.6530	0.6075	0.6160	0.6089	0.6668	0.6698	0.6159
		(0.0064)	(0.0003)	(0.0003)	(0.0003)			(0.0071)	(-0.0508)	(-0.0538)	(0.0001)
0.7065	0.6639	0.6585	0.6640	0.6638	0.6640	0.7065	0.6260	0.6199	0.6709	0.6729	0.6261
		(0.0054)	(-0.0001)	(0.0001)	(-0.0001)			(0.0061)	(-0.0449)	(-0.0469)	(-0.0001)
0.7958	0.6733	0.6693	0.6737	0.6735	0.6737	0.7958	0.6347	0.6301	0.6704	0.6716	0.6350
		(0.0040)	(-0.0004)	(-0.0002)	(-0.0004)			(0.0046)	(-0.0357)	(-0.0369)	(-0.0003)
0.8924	0.6835	0.6813	0.6839	0.6838	0.6839	0.8924	0.6440	0.6413	0.6653	0.6659	0.6443
		(0.0022)	(-0.0004)	(-0.0003)	(-0.0004)			(0.0027)	(-0.0213)	(-0.0219)	(-0.0003)

Temperature = 308.15 K						Temperature = 313.15 K					
0.1004	0.5130	0.5100 (0.0030)	0.5484 (-0.0354)	0.5565 (-0.0435)	0.5127 (0.0003)	0.1004	0.4930	0.4897 (0.0033)	0.5418 (-0.0488)	0.5535 (-0.0605)	0.6927 (0.0003)
0.2049	0.5265	0.5214 (0.0051)	0.5943 (-0.0678)	0.6053 (-0.0788)	0.5264 (0.0001)	0.2049	0.5043	0.4984 (0.0058)	0.5981 (-0.0939)	0.6135 (-0.1093)	0.5040 (0.0003)
0.3120	0.5402	0.5333 (0.0069)	0.6337 (-0.0935)	0.6439 (-0.1037)	0.5402 (0.0000)	0.3120	0.5150	0.5076 (0.0073)	0.6455 (-0.1305)	0.6593 (-0.1444)	0.5151 (-0.0001)
0.4097	0.5523	0.5445 (0.0078)	0.6613 (-0.1090)	0.6692 (-0.1169)	0.5524 (-0.0001)	0.4097	0.5243	0.5162 (0.0081)	0.6767 (-0.1524)	0.6871 (-0.1628)	0.5248 (-0.0005)
0.5032	0.5635	0.5555 (0.0080)	0.6790 (-0.1155)	0.6843 (-0.1208)	0.5638 (-0.0003)	0.5032	0.5331	0.5246 (0.0085)	0.6940 (-0.1609)	0.7013 (-0.1682)	0.5336 (-0.0005)
0.6075	0.5758	0.5680 (0.0078)	0.6879 (-0.1121)	0.6909 (-0.1151)	0.5761 (-0.0003)	0.6075	0.5426	0.5342 (0.0084)	0.6977 (-0.1551)	0.7028 (-0.1602)	0.5430 (-0.0004)
0.7065	0.5872	0.5801 (0.0071)	0.6853 (-0.0981)	0.6871 (-0.0999)	0.5873 (-0.0001)	0.7065	0.5513	0.5436 (0.0077)	0.6857 (-0.1344)	0.6902 (-0.1389)	0.5513 (0.0000)
0.7958	0.5970	0.5914 (0.0056)	0.6739 (-0.0769)	0.6752 (-0.0782)	0.5971 (-0.0001)	0.7958	0.5585	0.5522 (0.0063)	0.6625 (-0.1040)	0.6672 (-0.1087)	0.5584 (0.0001)
0.8924	0.6072	0.6038 (0.0034)	0.6523 (-0.0451)	0.6534 (-0.0462)	0.6073 (-0.0001)	0.8924	0.5656	0.5618 (0.0038)	0.6256 (-0.0600)	0.6298 (-0.0642)	0.5655 (0.0001)
Styrene + *p*-Xylene											
Temperature = 298.15 K						Temperature = 303.15 K					
0.0994	0.6139	0.1682 (-0.0043)	0.6128 (0.0011)	0.6125 (0.0014)	0.6128 (0.0011)	0.0994	0.5590	0.5617 (-0.0027)	0.5805 (-0.0215)	0.5838 (-0.0248)	0.5577 (0.0013)
0.2029	0.6179	0.6264 (-0.0085)	0.6166 (0.0013)	0.6162 (0.0017)	0.6166 (0.0013)	0.2029	0.5660	0.5716 (-0.0056)	0.6067 (-0.0407)	0.6115 (-0.0455)	0.5643 (0.0017)
0.3383	0.6240	0.6374 (-0.0134)	0.6236 (0.0004)	0.6232 (0.0008)	0.6236 (0.0004)	0.3383	0.5745	0.5849 (-0.0104)	0.6351 (-0.0606)	0.6400 (-0.0655)	0.5745 (0.0000)
0.4032	0.6273	0.6427 (-0.0154)	0.6278 (-0.0005)	0.6275 (-0.0002)	0.6278 (-0.0005)	0.4032	0.5792	0.5913 (-0.0121)	0.6461 (-0.0669)	0.6506 (-0.0714)	0.5801 (-0.0009)
0.5047	0.6345	0.6512 (-0.0167)	0.6355 (-0.0010)	0.6354 (-0.0009)	0.6355 (-0.0010)	0.5047	0.5880	0.6015 (-0.0135)	0.6596 (-0.0716)	0.6632 (-0.0752)	0.5897 (-0.0017)
0.6038	0.6430	0.6596 (-0.0166)	0.6444 (-0.0014)	0.6445 (-0.0015)	0.6444 (-0.0014)	0.6038	0.5980	0.6117 (-0.0137)	0.6681 (-0.0701)	0.6707 (-0.0727)	0.6002 (-0.0022)
0.6933	0.6523	0.6674 (-0.0151)	0.6537 (-0.0014)	0.6540 (-0.0017)	0.6537 (-0.0014)	0.6933	0.6089	0.6210 (-0.0121)	0.6717 (-0.0628)	0.6735 (-0.0646)	0.6106 (-0.0017)
0.8005	0.6654	0.6769 (-0.0115)	0.6664 (-0.0010)	0.6668 (-0.0014)	0.6664 (-0.0010)	0.8005	0.6240	0.6324 (-0.0084)	0.6708 (-0.0468)	0.6718 (-0.0478)	0.6244 (-0.0004)
0.9003	0.6800	0.6858 (-0.0058)	0.6799 (0.0001)	0.6802 (-0.0002)	0.6799 (0.0001)	0.9003	0.6390	0.6432 (-0.0042)	0.6649 (-0.0259)	0.6654 (-0.0264)	0.6386 (0.0004)
Temperature = 308.15 K						Temperature = 313.15 K					
0.0994	0.5448	0.5465 (-0.0017)	0.5762 (-0.0314)	0.5822 (-0.0374)	0.5435 (0.0013)	0.0994	0.5590	0.4971 (-0.0011)	0.5484 (-0.0524)	0.5595 (-0.0635)	0.4948 (0.0012)
0.2029	0.5502	0.5541 (-0.0039)	0.6097 (-0.0595)	0.6187 (-0.0685)	0.5486 (0.0016)	0.2029	0.5660	0.5052 (-0.0028)	0.6033 (-0.1009)	0.6179 (-0.1155)	0.5010 (0.0014)
0.3383	0.5562	0.5643 (-0.0081)	0.6442 (-0.0880)	0.6538 (-0.0976)	0.5565 (-0.0003)	0.3383	0.5745	0.5160 (-0.0060)	0.6597 (-0.1497)	0.6720 (-0.1620)	0.5101 (-0.0001)
0.4032	0.5598	0.5693 (-0.0095)	0.6564 (-0.0966)	0.6654 (-0.1056)	0.5608 (-0.0010)	0.4032	0.5792	0.5213 (-0.0073)	0.6788 (-0.1648)	0.6889 (-0.1749)	0.5149 (-0.0009)
0.5047	0.5665	0.5772 (-0.0107)	0.6692 (-0.1027)	0.6771 (-0.1106)	0.5683 (-0.0018)	0.5047	0.5880	0.5297 (-0.0087)	0.6969 (-0.1759)	0.7038 (-0.1828)	0.5229 (-0.0019)
0.6038	0.5743	0.5851 (-0.0108)	0.6741 (-0.0998)	0.6807 (-0.1064)	0.5764 (-0.0021)	0.6038	0.5980	0.5380 (-0.0088)	0.6996 (-0.1704)	0.7047 (-0.1755)	0.5314 (-0.0022)
0.6933	0.5828	0.5923 (-0.0095)	0.6718 (-0.0890)	0.6773 (-0.0945)	0.5845 (-0.0017)	0.6933	0.6089	0.5456 (-0.0076)	0.6891 (-0.1511)	0.6938 (-0.1558)	0.5397 (-0.0017)
0.8005	0.5950	0.6011 (-0.0061)	0.6608 (-0.0658)	0.6650 (-0.0700)	0.5952 (-0.0002)	0.8005	0.6240	0.5550 (-0.0045)	0.6614 (-0.1109)	0.6662 (-0.1157)	0.5504 (0.0001)
0.9003	0.6065	0.6095 (-0.0030)	0.6428 (-0.0363)	0.6454 (-0.0389)	0.6061 (0.0004)	0.9003	0.6390	0.5638 (-0.0020)	0.6222 (-0.0604)	0.6264 (-0.0646)	0.5612 (0.0006)

Styrene + Toluene											
Temperature = 298.15 K						Temperature = 303.15 K					
0.1148	0.5952	0.5851 (0.0101)	0.5962 (-0.0010)	0.5972 (-0.0020)	0.5962 (-0.0010)	0.1148	0.5786	0.5654 (0.0132)	0.5917 (-0.0131)	0.5963 -0.0177)	0.5781 (0.0005)
0.2116	0.6170	0.5968 (0.0202)	0.6154 (0.0016)	0.6166 (0.0004)	0.6154 (0.0016)	0.2116	0.5982	0.5748 (0.0234)	0.6194 (-0.0212)	0.6255 (-0.0273)	0.5962 (0.0020)
0.3030	0.6362	0.6079 (0.0283)	0.6320 (0.0042)	0.6329 (0.0033)	0.6320 (0.0042)	0.3030	0.6142	0.5838 (0.0304)	0.6417 (-0.0275)	0.6480 -0.0338)	0.6114 (0.0028)
0.3999	0.6520	0.6197 (0.0323)	0.6478 (0.0042)	0.6482 (0.0038)	0.6478 (0.0042)	0.3999	0.6274	0.5933 (0.0341)	0.6607 (-0.0333)	0.6663 (-0.0389)	0.6254 (0.0020)
0.5156	0.6658	0.6339 (0.0319)	0.6639 (0.0019)	0.6636 (0.0022)	0.6639 (0.0019)	0.5156	0.6390	0.6048 (0.0342)	0.6765 (-0.0375)	0.6808 (-0.0418)	0.6389 (0.0001)
0.5976	0.6740	0.6441 (0.0299)	0.6735 (0.0005)	0.6727 (0.0013)	0.6734 (0.0006)	0.5976	0.6452	0.6131 (0.0321)	0.6829 (-0.0377)	0.6862 (-0.0410)	0.6463 (-0.0011)
0.7070	0.6812	0.6578 (0.0234)	0.6835 (-0.0023)	0.6824 (-0.0012)	0.6835 (-0.0023)	0.7070	0.6510	0.6241 (0.0269)	0.6849 (-0.0339)	0.6871 (-0.0361)	0.6531 (-0.0021)
0.8028	0.6868	0.6699 (0.0169)	0.6898 (-0.0030)	0.6887 (-0.0019)	0.6898 (-0.0030)	0.8028	0.6534	0.6339 (0.0195)	0.6805 (-0.0271)	0.6821 (-0.0287)	0.6563 (-0.0029)
0.9124	0.6924	0.6838 (0.0086)	0.6940 (-0.0016)	0.6933 (-0.0009)	0.6940 (-0.0016)	0.9124	0.6558	0.6451 (0.0107)	0.6687 (-0.0129)	0.6694 (-0.0136)	0.6566 (-0.0008)
Temperature = 308.15 K						Temperature = 313.15 K					
0.1148	0.5538	0.5374 (0.0164)	0.5801 (-0.0263)	0.5886 (-0.0348)	0.5518 (0.0020)	0.1148	0.5230	0.5038 (0.0192)	0.5668 (-0.0438)	0.5799 (-0.0569)	0.5196 (0.0034)
0.2116	0.5722	0.5460 (0.0262)	0.6189 (-0.0467)	0.6300 (-0.0578)	0.5702 (0.0020)	0.2116	0.5392	0.5111 (0.0281)	0.6203 (-0.0811)	0.6361 (-0.0969)	0.5378 (0.0014)
0.3030	0.5870	0.5541 (0.0329)	0.6495 (-0.0625)	0.6605 (-0.0735)	0.5854 (0.0016)	0.3030	0.5522	0.5181 (0.0341)	0.6619 (-0.1097)	0.6763 (-0.1241)	0.5525 (-0.0003)
0.3999	0.5990	0.5628 (0.0362)	0.6741 (-0.0751)	0.6837 (-0.0847)	0.5990 (0.0000)	0.3999	0.5632	0.5255 (0.0377)	0.6942 (-0.1310)	0.7052 (-0.1420)	0.5654 (-0.0022)
0.5156	0.6089	0.5732 (0.0357)	0.6917 (-0.0828)	0.6991 (-0.0902)	0.6117 (-0.0028)	0.5156	0.5718	0.5344 (0.0374)	0.7141 (-0.1423)	0.7215 (-0.1497)	0.5767 (-0.0049)
0.5976	0.6148	0.5807 (0.0341)	0.6958 (-0.0810)	0.7019 (-0.0871)	0.6182 (-0.0034)	0.5976	0.5766	0.5408 (0.0358)	0.7149 (-0.1383)	0.7046 (-0.1280)	0.5820 (-0.0054)
0.7070	0.6202	0.5907 (0.0295)	0.6904 (-0.0702)	0.6951 (-0.0749)	0.6234 (-0.0032)	0.7070	0.5816	0.5494 (0.0322)	0.6988 (-0.1172)	0.6756 (-0.0940)	0.5852 (-0.0036)
0.8028	0.6226	0.5996 (0.0230)	0.6755 (-0.0529)	0.6794 (-0.0568)	0.6248 (-0.0022)	0.8028	0.5834	0.5570 (0.0264)	0.6695 (-0.0861)	0.6256 (-0.0422)	0.5845 (-0.0011)
0.9124	0.6236	0.6098 (0.0138)	0.6476 (-0.0240)	0.6500 (-0.0264)	0.6226 (0.0010)	0.9124	0.5822	0.5658 (0.0164)	0.6208 (-0.0386)	0.5728 (0.0094)	0.5797 (0.0025)

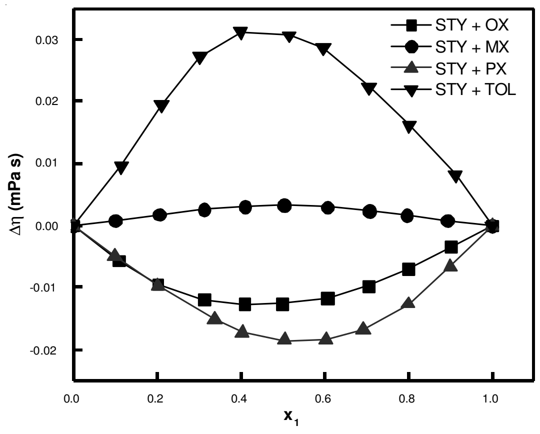


Fig. 1. Deviations of viscosity, Δη of binary mixtures of styrene (STY) with, *m*-xylene (MX), *o*-xylene (OX), *p*-xylene (PX) and toluene (TOL) at 298.15 K

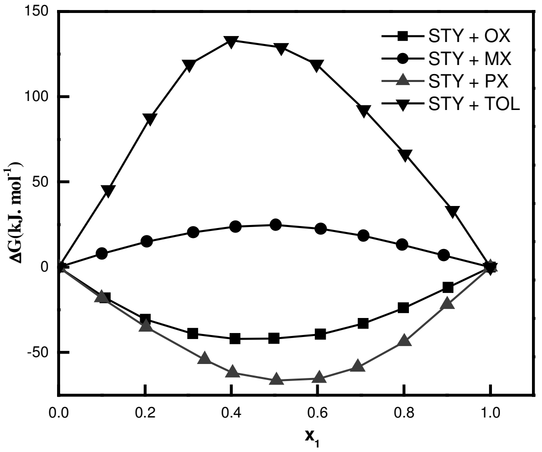


Fig. 2. Deviations of Gibbs free energy of activation, ΔG of binary mixtures of styrene (STY) with *m*-xylene (MX), *o*-xylene (OX), *p*-xylene (PX) and toluene (TOL) at 298.15 K

the species taking part in viscous flow. In a highly structured liquid there will be considerable degree of order and, hence, for cooperative movement of entities, a large heat of activation, is needed for the flow process. Therefore, a perusal of Table-3 indicates that the formation of activated species necessary for viscous flow seems to be easy in toluene and *m*-xylene rich region, owing to the low values of ΔH* and become difficult in the *p*-xylene rich region and relatively more difficult in *o*-xylene rich region owing to the high values of ΔH*, as the mole fraction of styrene in the mixture increases. This is supported by the decreasing value of ΔS* as the amount of styrene in the mixture increases.

TABLE-2
VALUES OF A_1 PARAMETERS OF EQUATION (3) AND STANDARD DEVIATIONS σ (Y^E) FOR THE BINARY MIXTURES AT DIFFERENT TEMPERATURES

Temp. (K)	A_1	A_2	A_3	A_4	σ (Y^E)
Styrene + *o*-Xylene					
$\Delta\eta$ (mPa s)					
298.15	-50.4953	-12.7674	-6.4423	12.3297	0.0232
303.15	-41.5759	-15.4058	5.7951	19.9920	0.0541
308.15	-36.1407	-10.7258	6.8613	6.3634	0.0329
313.15	-31.2402	-12.0407	9.7348	16.1430	0.0660
ΔG (kJ mol^{-1})					
298.15	-16.7705	-3.4281	-2.0601	4.0865	0.0079
303.15	-16.0089	-5.2744	3.1547	6.2754	0.0196
308.15	-15.0945	-3.9511	2.9986	2.6967	0.0127
313.15	-14.4420	-4.9681	4.2022	7.8219	0.0301
Styrene + *m*-Xylene					
$\Delta\eta$ (mPa s)					
298.15	13.2243	-0.6995	-10.4177	6.7910	0.0245
303.15	16.1446	-1.0832	-3.4816	3.3272	0.0307
308.15	17.8904	-1.4731	5.5038	-0.8656	0.0098
313.15	22.5207	-1.8035	10.8366	-4.2160	0.0238
ΔG (kJ mol^{-1})					
298.15	9.8695	0.4373	-3.9723	2.3377	0.0103
303.15	11.5587	0.3828	-1.4885	1.3131	0.0125
308.15	14.7557	0.5579	2.2294	0.1200	0.0071
313.15	15.7343	0.3579	5.2440	-1.8632	0.0117
Styrene + *p*-Xylene					
$\Delta\eta$ (mPa s)					
298.15	-74.8402	17.9281	15.2980	-10.0697	0.0913
303.15	-63.2413	18.9725	23.1068	-11.8049	0.0572
308.15	-50.0353	14.1762	21.4659	-1.9881	0.0351
313.15	-41.8872	16.7790	26.2796	-16.1571	0.0109
ΔG (kJ mol^{-1})					
298.15	-26.6713	5.3357	6.5930	-3.8192	0.0357
303.15	-23.2398	6.4175	10.7720	-5.1509	0.0263
308.15	-20.1728	5.3465	10.1862	-0.9457	0.0175
313.15	-17.8032	7.3013	13.5294	-7.6516	0.0057
Styrene + Toluene					
$\Delta\eta$ (mPa s)					
298.15	125.3651	34.5878	-41.0640	-73.5294	0.3131
303.15	133.6474	27.4522	-3.0375	-58.8513	0.0356
308.15	140.7858	23.4037	29.6321	-41.8684	0.1337
313.15	147.0969	9.9197	53.1088	-0.6225	0.1037
ΔG (kJ mol^{-1})					
298.15	52.6652	18.4705	-12.9783	-31.8255	0.1184
303.15	57.6360	15.2280	0.2769	-22.5832	0.0182
308.15	64.0861	14.9587	14.8743	-16.2929	0.0563
313.15	71.6212	9.4472	27.0228	3.6673	0.0485

TABLE-3
VALUES OF ENTHALPY, ΔH^* AND ENTROPY, ΔS^* OF ACTIVATION OF VISCOUS FLOW FOR THE BINARY LIQUID MIXTURES ALONG WITH THE LINEAR CORRELATION FACTOR, r

x_1	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	r
Styrene + *o*-Xylene			
0.0000	11.213	-1.149	0.993
0.1066	10.845	-1.139	0.994
0.1993	10.605	-1.132	0.995
0.3046	10.383	-1.126	0.996
0.3952	10.160	-1.120	0.997
0.5013	9.969	-1.114	0.997
0.6015	9.717	-1.107	0.998
0.7135	9.493	-1.100	0.998
0.8020	9.324	-1.095	0.997
0.9078	9.161	-1.090	0.997
1.0000	9.037	-1.086	0.996
Styrene + *m*-Xylene			
0.0000	9.381	-1.108	0.986
0.0702	9.172	-1.099	0.990
0.1162	9.044	-1.094	0.993
0.1687	8.981	-1.090	0.996
0.2383	8.952	-1.088	0.998
0.3091	8.923	-1.086	0.999
0.4032	8.868	-1.084	0.999
0.5043	8.820	-1.081	0.999
0.6492	8.821	-1.081	0.999
0.8251	8.888	-1.082	0.998
1.0000	9.037	-1.086	0.996
Styrene + *p*-Xylene			
0.0000	9.870	-1.120	0.973
0.0702	9.540	-1.109	0.976
0.1162	9.283	-1.100	0.979
0.1687	9.100	-1.094	0.984
0.2383	9.005	-1.091	0.985
0.3091	8.950	-1.089	0.988
0.4032	8.890	-1.086	0.990
0.5043	8.837	-1.083	0.992
0.6492	8.744	-1.079	0.994
0.8251	8.868	-1.082	0.995
1.0000	9.037	-1.086	0.996
Styrene + Toluene			
0.1148	6.611	-1.027	0.983
0.2116	5.888	-0.999	0.983
0.3030	6.155	-1.004	0.985
0.3999	6.487	-1.012	0.988
0.5156	6.725	-1.018	0.991
0.5976	7.022	-1.025	0.992
0.7070	7.202	-1.030	0.993
0.8028	7.297	-1.031	0.994
0.9124	7.531	-1.038	0.996
0.8251	8.024	-1.053	0.996
1.0000	9.037	-1.086	0.996

Theoretical analysis

Correlation of excess volumes with viscosity: The excess volumes were calculated using the deviation in viscosity data by a correlation proposed by Singh[25]. According to the relation, the deviations in viscosity ($\Delta\eta$) and excess molar volumes (V^E) are related to each other as:

$$\Delta\eta = KV^E \tag{7}$$

where K is a fitting parameter. The values of K for the presently investigated mixtures were evaluated by using the $\Delta\eta$ and experimentally reported V^E data[16,17] at $x_1 = 0.5$ (equimolar fraction). The values of K for styrene + *o*-, *m*-, *p*-xylene and toluene are found to be 144.31, 162.35, 191.80 and -329.37 mPa s m^{-3} at 298.15 K, respectively. From the experimental $\Delta\eta$ data, the V^E values at various mole fractions were calculated. The V^E values calculated from viscosity data using eqn. 7 were compared with reported V^E values[16,17], obtained experimentally for all the mixtures at 298.15 K and are presented in Fig. 3. A reasonable good agreement has been found between the experimentally calculated V^E and theoretically predicted $V^E\eta$ values. Thereby, it emphasizes the effectiveness of the present approach.

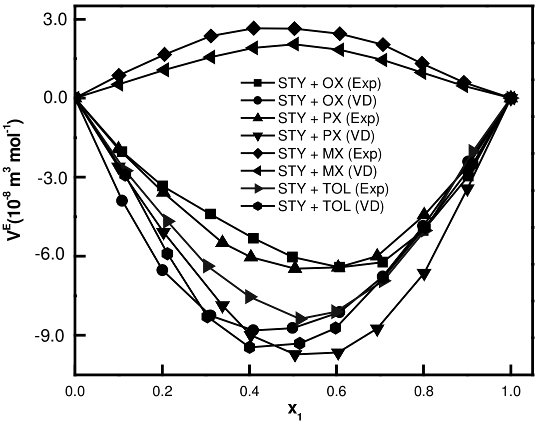


Fig. 3. Comparison of V^E between experimental value (Exp), and the $V^E\eta$ value calculated by viscosity data (VD) of binary mixtures of styrene (STY) with *m*-xylene (MX), *o*-xylene (OX), *p*-xylene (PX) and toluene (TOL) at 298.15 K

Correlation equations for viscosity: Various equations exist in literature to calculate the viscosities of the mixtures theoretically in terms of pure component data. Grunberg and Nissan[26] suggested the expression:

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2 + x_1x_2G_{12} \tag{8}$$

where G_{12} is a parameter proportional to interchange energy, which represents a measure of the strength of interaction between the component molecules in the mixture. It allows for the positive and negative deviations from the addivity rule. Katti and Chaudhary[27] derived the following equation:

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1x_2W_{vis}/RT \tag{9}$$

where W_{vis}/RT is an interaction term.

Hind *et al.*[28] proposed the following equation:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \tag{10}$$

where H_{12} is attributed to unlike pair interactions.

Wilke[29] proposed the viscosity equation:

$$\eta = \frac{x_1\eta_1}{x_1 + x_1\phi_{12}} + \frac{x_2\eta_2}{x_2 + x_1\phi_{21}} \tag{11}$$

where ϕ_{12} and ϕ_{21} are calculated by using the following equations:

$$\phi_{12} = \frac{\left[1+\left(\frac{\eta_1}{\eta_2}\right)^{1/2}\left({}^{M_2}\!/\!{}_{M_1}\right)^{1/4}\right]^2}{\left\{8+\left[1+\left({}^{M_1}\!/\!{}_{M_2}\right)\right]\right\}^{1/2}} \tag{12}$$

$$\phi_{21} = \phi_{12}\frac{\eta_2}{\eta_1}\frac{M_1}{M_2} \tag{13}$$

The predicted values of viscosities of the binary mixtures at 298.15, 303.15, 308.15 and 313.15 K were compared with the experimentally measured values and the results are presented in terms of average deviations in Table-1. A close perusal of Table-1 reveals that all the empirical equations tested show good agreements for all the binary mixtures investigated. The results show that Grunberg-Nissan provides the best results followed by Wilke relation in reproducing the experimental viscosity for the mixtures. However, Katti & Chaudhari[27] and Hind *et al.*[28] shows relatively large deviations for the binary mixtures.

Conclusion

The present study is based on the viscometric behaviour of binary mixtures of (styrene) with *o*-, *m*- or *p*-xylene and toluene at different temperatures. The values were calculated from viscosity data. A reasonable good agreement has been found between the experimentally calculated and theoretically predicted V^E values. It emphasizes the effectiveness of the present approach. $\Delta\eta$ and ΔG values are positive for the binary mixtures of styrene with toluene and *m*-xylene and the values turn negative for *o*-xylene, become more so for *p*-xylene, over the whole composition range and at all the investigated temperatures. This indicates that dispersion forces dominate in these mixtures. The positive contribution to ΔG attributed to the presence of specific interactions whereas negative contribution may be ascribed to the dispersion forces. The positive values of ΔH^* and ΔS^* along with the linear correlation factor, r were also deduced. The results indicates that the formation of activated species necessary for viscous flow seems to be easy in toluene and *m*-xylene rich region, resulting the lower values of ΔH^* and become difficult in the *p*-xylene rich region and relatively more difficult in *o*-xylene rich region owing to the high values of ΔH^*. This trend is supported by the decreasing value of ΔS^* as the amount of styrene in the mixture increases. It is found that experimental and predicted viscometric studies are in good agreement with each other.

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