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Physicochemical analysis on molecular interactions in 2-methoxyaniline with aliphatic alcohols (propan-1-ol, 2-propen-1-ol, 2-propyn-1-ol) at various temperatures and 0.1 MPa

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The density (ρ), viscosity (η), and sound speed (u) are presented for binary combinations of 2-methoxyaniline with aliphatic primary alcohols (propan-1-ol, 2-propen-1-ol, 2-propyn-1-ol) at temperatures ranging from 303.15 K to 313.15 K at a pressure of 0.1 MPa. Some other parameters (V^E, κ_s^E) and viscosity deviation were calculated from the density, sound speed and viscosity with experiment temperature values. The difference among these properties with the mixture composition proposes hydrogen bond and charge-transfer compound formation between 2-methoxyaniline and primary alcohols. A theory named Prigogine Flory Patterson theory was utilized for the analysis of results V^E. All mixtures generate negative values for free volume effect.

Keywords: 2-Methoxyaniline, Density, Sound speeds, PFP theory, Primary alcohol.

INTRODUCTION

In industry point of view binary liquid mixtures play a key role as they generate huge varieties of mixtures with desired functionalities which can be utilized as a solvent in various chemical industries and biological process. Additionally, viscosity is utilized in hydraulic calculation, fluid transportation, energy and mass within industry [1]. Density, viscosity and sound speed values of binary liquid mixture help in understanding thermo physical properties. These values are a successfull source helpful in assumption of inter molecular interaction and characterization of structure alignment among liquid molecule components and also for enhancement of molecular models [2, 3].

In this research work, the molecular interactions are understood about the liquid components 2-methoxyaniline and primary alcohols (propan-1-ol, 2-propen-1-ol, 2-propyn-1-ol). Various fields of chemistry widely make use of these solvents as they are conventional organic liquids widely applied and used in chemical industries. The current examination is a continuation of previous studies conducted on binary liquid mixtures and their thermodynamic properties [4]. The current analysis is made for discovering the consequences of multiple bonds between carbon- carbon atoms in aliphatic primary alcohol molecules that can show impact on both magnitude and sign of different functionalities of thermodynamic when they are combined with 2-methoxyaniline. Data are not accessible representing enumerated material properties such as density, viscosity and sound speed for the binary mixture of 2-methoxyaniline with primary alcohols. Therefore, a study is conducted on the binary mixtures. In this study, densities (ρ), viscosities (η), sound speed (u) of pure 2-methoxyaniline, primary alcohols and the binary mixtures at temperatures ranging from T = 303.15 K to 313.15 K were determined. From the observations of experiment, the surplus values of these experimental data, the values of isentropic flexibility variations in viscosity and surplus Gibbs free energy in actuation of viscous flow are calculated in view of hydrogen bond formation and complex charge transfers.

EXPERIMENTAL

Materials

The sources required for experiment including resultant purity and analysis procedure are presented in Table 1. Table 2 presents density, viscosity and sound speed values. The available data in the literature [5-19] are compatible with the tabular values.

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Table 1. Source details of chemicals, CAS number, water content and purity.

Name of the chemical	CAS Number	Source	**Water content (%)	Mass fraction purity
2-methoxyaniline	90-04-0	Sigma Aldrich, India	0.045	0.995
Propan-1-ol	71-23-8	S.D. Fine chemicals	0.042	0.995
2-propen-1-ol	107-18-6	Sigma Aldrich, India	0.042	0.995
2-propyn-1-ol	107-19-7	Sigma Aldrich, India	0.042	0.997

** Karl Fischer method.

Table 2. Density, viscosity and sound speed data of pure elements at various temperatures and pressures.

Component	Density (ρ /g·cm^{-3})		Sound speed (u / m·s^{-1})		C_P (J· K^{-1} · mol^{-1})	Viscosity (η / mPa·s)	
(in K)	Exp.	Lit.	Exp.	Lit.	Lit.	Exp.	Lit.
2-methoxy aniline							
303.15	1.09157	1.0917[5]	1597.4		190.52[6]	4.923	4.924[5]
308.15	1.08799		1583.2		192.05[6]	4.571	
313.15	1.08432		1569.9		193.62[6]	4.217	-
2-propen-1-ol							
303.15	0.84460	0.8446[8]	1307		141.5[6]	1.122	1.122[9]
308.15	0.84041	0.8404[8]	1287		143.2[6]	1.019	1.016[9]
313.15	0.83591	0.8359[8]	1266		145.6[6]	0.921	0.921[9]
2-propyn-1-ol							
303.15	0.94201	0.9420[8]	1404		146.5[6]	1.345	1.3447[9]
308.15	0.93701	0.9370[8]	1384		148.1[6]	1.221	1.2143[9]
313.15	0.93270	0.9327[8]	1364		151.1[6]	1.104	1.103[9]
1-propanol							
303.15	0.79577[7]	0.7958[8]	1194.8[4]	1189.26[19]	147.36[6]	1.735[4]	1.735[9]
		0.79597[19]		1192[17]			1.7309[14]
		0.7961[15]		1189[11]			1.705[16]
		0.79540[16]		1189[12]			1.720[10]
		0.79559[17]					
		0.7953[14]					
		0.7956[10]					
		0.7955[11]					
308.15	0.79181	0.7918[8]	1174.6	1172.37[19]	150.62[6]	1.547	1.548[9]
		0.79189[19]		1175.2[18]			1.546[15]
		0.7911[15]		1171.41[13]			1.526[16]
		0.79130[16]					1.5440[14]
		0.7912[14]					
313.15	0.78771	0.7877[08]	1155.3	1155.53[19]	153.20[6]	1.385	1.386[9]
		0.78777[19]		1158[17]			1.372[16]
		0.78720[17]					1.390[10]
		0.7873[10]					1.376[15]
		0.7871[14]					1.380[14]
		0.78710[16]					

The standard unpredictability is u(x_1) = 1×10^{-4}, u (ρ) ±2×10^{-5}g.cm^{-3}, u (u) = ±0.4%., u (η) = ±0.08mPa·s, u (T) = 0.01 K for density, sound speed and viscosity, and u (P) = 1 kPa.

Apparatus and procedure

Electric balance is used to weigh the amount of pure liquids which is used in preparation of binary liquid mixtures (ER-120A, Afoset, India) with an accuracy of ± 0.1 mg by syringing each element in to an air-tight container to avoid loss occurred due to evaporation. The molar fraction uncertainty is ± 1×10^{-4}. The particulars of procedure and

measurement techniques have been described elsewhere [20]. The unpredictability of liquid mixtures density value is $\pm 2\times10^{-5}$g.cm^{-3}. The sound speed unpredictability is ±0.4%. The viscosity unpredictability value is ±0.08 mPa.s. The stable temperature is maintained in the range of ±0.01 K. Circular pump is to circulate thermostatic water bath within the cell.

RESULTS

The following equations are useful to calculate surplus parameters and deviating functions are as follows:

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (1)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_1\eta_1) \quad (2)$$

$$\Delta G^{*E} = RT\,[\ln\eta V - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2 \quad (3)$$

where η, η_1, η_2, *and* V, V_1, V_2 are viscosity and molecular values of mixture and pure components correspondingly.

From the relation [21] the isentropic flexibilities are calculated:

$$\kappa_s = (u^2\rho)^{-1} \quad (4)$$

In a mixture ρ is used to present density and u is used to present sound speed. Later, surplus isentropic flexibilities (k_s^E) are assessed with the help of relations below as suggested by Benson and Kiyohara [22]:

$$k_s^E = k_s - k_s^{id} \quad (5)$$

$$k_s^{id} = \sum_{i=1}^{2}\varphi_i\left[\kappa_{s,i} + \frac{TV_i\left(\alpha_i^2\right)}{C_{p,i}}\right] - \left\{\frac{T\left(\sum_{i=1}^{2}x_iV_i\right)\left(\sum_{i=1}^{2}\varphi_i\alpha_i\right)^2}{\sum_{i=1}^{2}x_iC_{p,i}}\right\} \quad (6)$$

where φ_i, $C_{p,i}$, V_i, $\kappa_{s,i}$ and α_i are volume fractions, heat capacity of molar, volume of molars, isentropic flexibility and isobaric thermal expansion coefficient of pure elements correspondingly.

The density, viscosity and sound speed for binary mixture of different molar fractions of 2-methoxyaniline are represented in Table.3 including surplus or deviation in parameters such as (V^E, κ_s^E, $\Delta\eta$ and ΔG^{*E}) at different temperatures. The values of V^E, κ_s^E $\Delta\eta$ and ΔG^{*E} are represented as a function in the form of molar fraction of 2-methoxyaniline in Figures 1, 2, 3 and 4, respectively.

Surplus / deviation in parameters such as V^E, κ_s^E, $\Delta\eta$ and ΔG^{*E} depends on different factors as follows:

(a) Degree of unsaturation in hydrocarbon chains of alcohols;

(b) Hybridization of carbon;

(c) Boiling point of aliphatic primary alcohols.

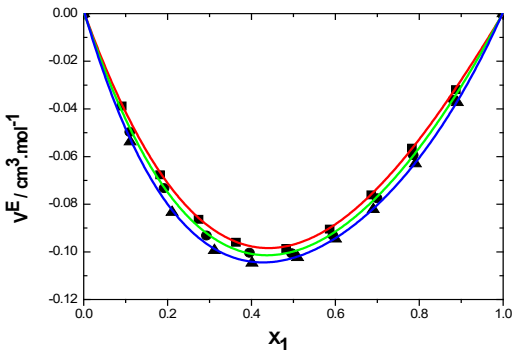

Fig 1. Surplus molar volume (V^E) curves with molar fraction for the binary mixtures of 2-methoxyaniline with 2-propyn-1-ol (**!**); 2-propen-1-ol (,) and propan-1-ol (▲) at 303.15 K

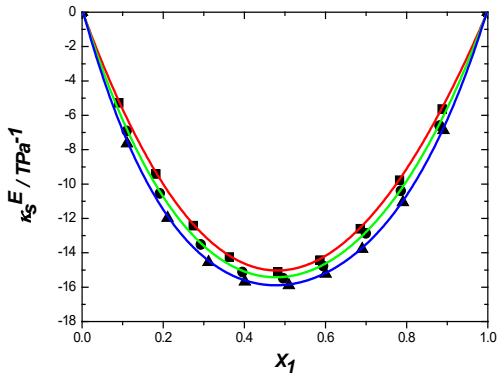

Fig. 2. Surplus isentropic flexibility curves with mole fraction for the binary mixtures of 2-methoxyaniline with 2-propyn-1-ol (**!**); 2-propen-1-ol (,) and propan-1-ol (▲) at 303.15 K

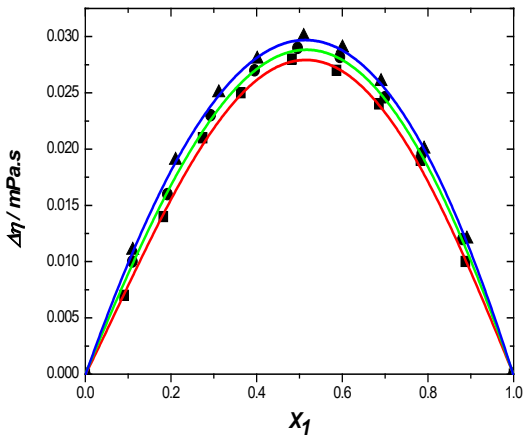

Fig. 3. Deviation in viscosity (Δη) curves with mole fraction for the binary mixtures of 2-methoxyaniline with 2-propyn-1-ol (**!**); 2-propen-1-ol (,) and propanol-1 (▲) at 303.15 K

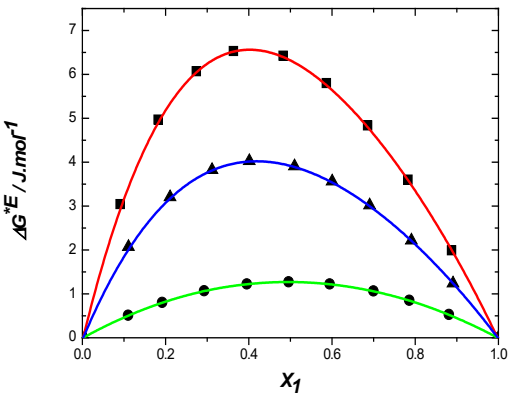

Fig. 4. Surplus Gibbs energy curves for actuation of viscous flow (ΔG^{*E}) with mole fraction for the binary mixtures of 2-methoxyaniline with 2-propyn-1-ol **(!);** 2-prpen-1-ol (,) and propan-1-ol (▲) at 303.15 K.

Negative deviations in V^E and κ_s^E and positive deviation in 8η and $8G^{*E}$ are recorded. The observations are from the entire system with complete range of composition at each temperature value of the experiment.

Negative deviations arise due to:

(a) Attractive forces between unlike polar molecules

(b) Dipole-dipole forces between unlike molecules.

(c) Hydrogen bonding interaction among opposite molecules.

From Table 3, the negative V^E and κ_s^E values suggest that attractive forces among unlike molecules are more powerful than the repulsive forces when compared with like molecules of binary liquid mixtures.

In the investigation, due to compression of free volume negative values arise which convert the ideal mixture to a more compressible one which in turn leads to negative values that are represented as V^E and κ_s^E in binary liquid mixtures. The identical pattern is followed by Jayalakshmi and Reddy [23] for the surplus amounts of ketone and nitrobenzene mixture Yang *et al*. [24], Kiyohara and Benson [22] explained the reasons for occurrence of such deviation.

V^E and κ_s^E values of 2-methoxyaniline with three primary alcohols decrease in the order:

propan-1-ol >2-propen-1-ol >2-propyn-1-ol

This order suggests that attractive forces decrease from propan-1-ol to 2-propyn-1-ol with 2-methoxyaniline as increases number of pi bonds between carbon-carbon atoms in primary alcohols. This may be because of the fact that the increase in temperature ultimately leads to increase in thermal energy which disrupts the self-associated primary alcohols molecules releasing more and more primary alcohols molecules for the formation of hetero-association molecules with 2-methoxyaniline molecules. Syal *et al.* [25] explain about dimethylsulfoxide/acetone in a binary mixture which is identical and supported by ultrasonic studies. Palani *et al.* [26] also explain ultrasonic studies dealing with monohydric alcohols and dimethylsulfoxide system.

Table. 3 represents the attributes to the association of 2-methoxyaniline and primary alcohols which gives out the positive value for viscosity deviation due to intermolecular hydrogen bonds among –OH groups within primary alcohols and the 2-methoxyaniline.

Table 3. Surplus molar volume (V^E), density (ρ), sound speed (u), viscosity (η), surplus isentropic flexibility (κ_s^E), viscosity deviation ($\Delta\eta$) and surplus Gibbs energy for operation of viscous flow (G^{*E}) as a function of mole fraction, x_1 of 2-methoxyaniline of binary liquid mixture at T= (303.15 to 313.15) K and 0.1MPa pressure.

x_1	Density (ρ) g·cm^{-3}	V^E cm^3·mol^{-1}	u m.s^{-1}	κ_s^E /TPa^{-1}	Viscosity (η / mPa·s)	$\Delta\eta$ / mPa·s	ΔG^{*E} / J·mol^{-1}
2-Methoxyaniline (1)+ 2-propyn-1-ol (2)							
303.15 K							
0.0000	0.94201	0.0000	1404.0	0.000	1.345	0.000	0.000
0.0908	0.96640	-0.0388	1431.9	-5.280	1.677	0.007	3.046
0.1822	0.98739	-0.0677	1458.9	-9.418	2.011	0.014	4.970
0.2742	1.00560	-0.0864	1484.6	-12.42	2.347	0.021	6.073
0.3631	1.02094	-0.0960	1507.4	-14.25	2.669	0.025	6.530
0.4825	1.03873	-0.0986	1534.6	-15.11	3.099	0.028	6.426
0.5865	1.05208	-0.0905	1554.7	-14.43	3.471	0.027	5.802

0.6856	1.06328	-0.0761	1570.4	-12.61	3.822	0.024	4.837
0.7825	1.07304	-0.0565	1582.4	-9.783	4.163	0.019	3.602
0.8873	1.08250	-0.0319	1591.6	-5.634	4.530	0.010	1.992
1.0000	1.09157	0.0000	1597.4	0.000	4.923	0.000	0.000
308.15 K							
0.0000	0.93701	0.0000	1384.0	0.000	1.221	0.000	0.000
0.0908	0.96164	-0.0425	1412.7	-5.855	1.533	0.008	3.216
0.1822	0.98279	-0.0714	1440.2	-10.12	1.847	0.016	5.232
0.2742	1.00114	-0.0892	1466.0	-13.02	2.161	0.022	6.373
0.3631	1.01664	-0.1002	1489.0	-14.69	2.463	0.026	6.838
0.4825	1.03460	-0.1023	1516.7	-15.43	2.866	0.029	6.715
0.5865	1.04807	-0.0933	1537.5	-14.80	3.214	0.028	6.058
0.6856	1.05940	-0.0789	1554.3	-13.13	3.543	0.025	5.045
0.7825	1.06928	-0.0602	1567.5	-10.46	3.862	0.020	3.756
0.8873	1.07885	-0.0351	1577.6	-6.267	4.205	0.011	2.079
1.0000	1.08799	0.0000	1583.2	0.000	4.571	0.000	0.000
313.15 K							
0.0000	0.93270	0.0000	1364.0	0.000	1.104	0.000	0.000
0.0908	0.95745	-0.0462	1393.6	-6.430	1.395	0.009	3.387
0.1822	0.97867	-0.0751	1421.6	-10.82	1.688	0.017	5.495
0.2742	0.99708	-0.0919	1447.8	-13.61	1.980	0.023	6.671
0.3631	1.01266	-0.1043	1471.0	-15.13	2.261	0.027	7.142
0.4825	1.03069	-0.1060	1499.3	-15.74	2.635	0.029	7.002
0.5865	1.04422	-0.0960	1521.0	-15.16	2.959	0.029	6.311
0.6856	1.05560	-0.0816	1538.9	-13.65	3.264	0.026	5.252
0.7825	1.06554	-0.0639	1553.3	-11.13	3.561	0.021	3.909
0.8873	1.07515	-0.0384	1564.4	-6.901	3.879	0.013	2.167
1.0000	1.08432	0.0000	1569.9	0.000	4.217	0.000	0.000
2-Methoxyaniline (1) + 2-propen-1-ol (2)							
303.15 K							
0.0000	0.84460	0.0000	1307.0	0.000	7.146	0.000	0.000
0.1099	0.88680	-0.0497	1338.0	-6.918	6.912	0.010	0.512
0.1918	0.91468	-0.0733	1362.5	-10.55	6.736	0.016	0.804
0.2927	0.94555	-0.0932	1393.7	-13.52	6.518	0.023	1.069
0.3952	0.97351	-0.1004	1426.0	-15.12	6.294	0.027	1.226
0.4957	0.99815	-0.1006	1457.8	-15.48	6.073	0.029	1.276
0.5942	1.01998	-0.0932	1488.6	-14.77	5.853	0.028	1.226
0.6995	1.04113	-0.0775	1520.5	-12.87	5.616	0.025	1.066
0.7856	1.05695	-0.0594	1545.2	-10.40	5.419	0.020	0.853
0.8808	1.07311	-0.0362	1570.4	-6.604	5.200	0.012	0.531

1.0000	1.09157	0.0000	1597.4	0.000	4.923	0.000	0.000
308.15K							
0.0000	0.84041	0.0000	1287.0	0.000	6.012	0.000	0.000
0.1099	0.88270	-0.0539	1318.4	-7.500	5.864	0.011	0.457
0.1918	0.91062	-0.0774	1343.1	-11.20	5.753	0.017	0.716
0.2927	0.94153	-0.0960	1374.4	-14.04	5.614	0.024	0.945
0.3952	0.96956	-0.1036	1407.1	-15.63	5.471	0.028	1.076
0.4957	0.99426	-0.1038	1439.4	-15.99	5.328	0.030	1.114
0.5942	1.01616	-0.0964	1470.8	-15.27	5.185	0.029	1.063
0.6995	1.03739	-0.0812	1503.6	-13.38	5.030	0.026	0.918
0.7856	1.05329	-0.0649	1529.3	-10.99	4.901	0.021	0.730
0.8808	1.06949	-0.0399	1555.8	-7.259	4.756	0.013	0.452
1.0000	1.08799	0.0000	1583.2	0.000	4.571	0.000	0.000
313.15K							
0.0000	0.83591	0.0000	1266.0	0.000	4.774	0.000	0.000
0.1099	0.87831	-0.0580	1298.0	-8.082	4.724	0.012	0.407
0.1918	0.90629	-0.0815	1322.9	-11.85	4.686	0.019	0.635
0.2927	0.93727	-0.0987	1354.3	-14.55	4.636	0.025	0.831
0.3952	0.96539	-0.1069	1387.5	-16.14	4.583	0.029	0.939
0.4957	0.99018	-0.1070	1420.5	-16.49	4.529	0.031	0.965
0.5942	1.01217	-0.0997	1452.8	-15.78	4.473	0.030	0.914
0.6995	1.03350	-0.0848	1486.7	-13.89	4.411	0.027	0.784
0.7856	1.04949	-0.0705	1513.7	-11.57	4.358	0.022	0.620
0.8808	1.06575	-0.0435	1541.8	-7.914	4.297	0.014	0.383
1.0000	1.08432	0.0000	1569.9	0.000	4.217	0.000	0.000
2-Methoxyaniline (1) + propan-1-ol (2)							
303.15K							
0.0000	0.79577	0.0000	1194.8	0.000	1.735	0.000	0.000
0.1109	0.84280	-0.0538	1224.9	-7.648	2.100	0.011	2.072
0.2108	0.88102	-0.0834	1255.9	-11.98	2.426	0.019	3.205
0.3116	0.91615	-0.0994	1290.5	-14.55	2.753	0.025	3.824
0.4015	0.94493	-0.1047	1324.0	-15.68	3.043	0.028	4.028
0.5099	0.97682	-0.1024	1367.8	-15.90	3.391	0.030	3.909
0.6004	1.00137	-0.0946	1407.0	-15.23	3.678	0.029	3.560
0.6906	1.02416	-0.0822	1448.3	-13.78	3.963	0.026	3.018
0.7908	1.04770	-0.0630	1496.2	-11.07	4.276	0.020	2.217
0.8908	1.06951	-0.0373	1545.1	-6.874	4.587	0.012	1.240
1.0000	1.09157	0.0000	1597.4	0.000	4.923	0.000	0.000
308.15K							
0.0000	0.79181	0.0000	1174.6	0.000	1.547	0.000	0.000

0.1109	0.83887	-0.0579	1204.9	-8.227	1.895	0.012	2.292
0.2108	0.87710	-0.0871	1235.9	-12.70	2.205	0.020	3.519
0.3116	0.91225	-0.1029	1270.6	-15.23	2.515	0.026	4.176
0.4015	0.94105	-0.1077	1304.3	-16.29	2.790	0.029	4.383
0.5099	0.97301	-0.1069	1348.4	-16.46	3.120	0.031	4.244
0.6004	0.99761	-0.0991	1388.2	-15.81	3.393	0.030	3.855
0.6906	1.02044	-0.0870	1430.3	-14.40	3.663	0.027	3.262
0.7908	1.04403	-0.0672	1479.4	-11.72	3.960	0.022	2.396
0.8908	1.06590	-0.0413	1529.6	-7.397	4.254	0.013	1.341
1.0000	1.08799	0.0000	1583.2	0.000	4.571	0.000	0.000
313.15K							
0.0000	0.78771	0.0000	1155.3	0.000	1.385	0.000	0.000
0.1109	0.83481	-0.0620	1185.7	-8.805	1.712	0.013	2.479
0.2108	0.87304	-0.0909	1216.8	-13.41	2.003	0.021	3.788
0.3116	0.90822	-0.1064	1251.5	-15.91	2.294	0.027	4.484
0.4015	0.93705	-0.1107	1285.3	-16.90	2.552	0.030	4.688
0.5099	0.96908	-0.1113	1329.8	-17.02	2.861	0.032	4.530
0.6004	0.99373	-0.1036	1370.1	-16.39	3.116	0.031	4.108
0.6906	1.01662	-0.0917	1413.1	-15.03	3.369	0.028	3.472
0.7908	1.04027	-0.0714	1463.4	-12.37	3.648	0.023	2.552
0.8908	1.06219	-0.0452	1515.0	-7.920	3.922	0.014	1.428
1.0000	1.08432	0.0000	1569.9	0.000	4.217	0.000	0.000

Table 4. Redlich – Kister equation coefficients and standard deviation (σ) values for liquid mixtures of 2-methoxyaniline with 2-propyn-1-ol, 2-propen-1-ol and propan-1-ol at T= (303.15 - 313.15) K

T/K	A_0	A_1	A_2	σ
2-Methoxyaniline + 2-propyn-1-ol				
V^E/ cm^3·mol^{-1}				
303.15	-0.389	0.097	-0.004	0.001
308.15	-0.400	0.104	-0.044	0.001
313.15	-0.410	0.104	-0.086	0.002
κ_s^E/ TPa^{-1}				
303.15	-60.35	4.80	0.485	0.001
308.15	-61.60	4.83	-8.014	0.001
313.15	-62.85	4.85	-16.53	0.002
$\Delta\eta$/ mPa· s				
303.15	0.113	0.009	-0.031	0.001
308.15	0.117	0.007	-0.018	0.001
313.15	0.118	0.011	0.003	0.001
2-Methoxyaniline + 2-propen-1-ol				
V^E/ cm^3·mol^{-1}				
303.15	-0.401	0.102	-0.039	0.001
308.15	-0.412	0.101	-0.086	0.001
313.15	-0.423	0.099	-0.132	0.002
κ_s^E/ TPa^{-1}				
303.15	-61.87	4.919	-8.229	0.003
308.15	-63.52	4.832	-15.30	0.075

313.15	-65.15	4.745	-22.37	0.153
$\Delta\eta$/ mPa· s				
303.15	0.117	0.009	-0.015	0.001
308.15	0.119	0.013	0.003	0.001
313.15	0.123	0.008	0.009	0.001
2-Methoxyaniline + propan-1-ol				
V^E/ $cm^3 \cdot mol^{-1}$				
303.15	-0.412	0.104	-0.087	0.001
308.15	-0.426	0.102	-0.129	0.001
313.15	-0.439	0.101	-0.169	0.001
κ_s^E/ TPa^{-1}				
303.15	-63.70	4.473	-17.13	0.002
308.15	-65.95	4.827	-22.68	0.002
313.15	-68.21	5.144	-28.21	0.003
$\Delta\eta$/ mPa· s				
303.15	0.119	0.007	-0.033	0.001
308.15	0.123	0.009	0.008	0.001
313.15	0.127	0.009	0.018	0.001

Table 5. The values of $\overline{V}^{\circ}_{m,1}$, $V^{*}_{m,1}$, $\overline{V}^{\circ E}_{m,1}$, $\overline{V}^{\circ}_{m,2}$, $V^{*}_{m,2}$ and $\overline{V}^{\circ E}_{m,2}$ of elements for 2-methoxyaniline with 2-propyn-1-ol, 2-propen-1-ol and propan-1-ol of binary mixtures at T= (303.15 - 313.15) K

T/K	$\overline{V}^{\circ}_{m,1}$	$V^{*}_{m,1}$	$\cdot\overline{V}^{\circ E}_{m,1}$	$\overline{V}^{\circ}_{m,2}$	$V^{*}_{m,2}$	$\overline{V}^{\circ E}_{m,2}$
($cm^3 \cdot mol^{-1}$)						
2-Methoxyaniline (1) + 2-propyn-1-ol (2)						
303.15	112.52	112.82	-0.296	59.02	59.51	-0.490
308.15	112.85	113.19	-0.340	59.28	59.83	-0.548
313.15	113.18	113.57	-0.392	59.51	60.11	-0.600
2-Methoxyaniline (1) + 2-propen-1-ol (2)						
303.15	112.48	112.82	-0.338	68.22	68.77	-0.542
308.15	112.79	113.19	-0.397	68.51	69.11	-0.599
313.15	113.12	113.57	-0.456	68.83	69.48	-0.654
2-Methoxyaniline (1) + propan-1-ol (2)						
303.15	112.42	112.82	-0.395	74.92	75.52	-0.603
308.15	112.74	113.19	-0.453	75.24	75.90	-0.657
313.15	113.07	113.57	-0.507	75.58	76.29	-0.709

Table 6. The values of $\overline{K}^{\circ}_{s,m,1}$, $K^{*}_{s,m,1}$, $\overline{K}^{\circ E}_{s,m,1}$, $\overline{K}^{\circ}_{s,m,2}$, $K^{*}_{s,m,2}$ and $\overline{K}^{\circ E}_{s,m,2}$ of elements for 2-methoxyaniline with propan-1-ol, 2-propen-1-ol and 2-propyn-1-ol of binary mixtures at T= (303.15 - 313.15) K

T/K	$\overline{K}^{\circ}_{s,m,1}$	$K^{*}_{s,m,1}$	$\overline{K}^{\circ E}_{s,m,1}$	$\cdot\overline{K}^{\circ}_{s,m,2}$	$K^{*}_{s,m,2}$	$\overline{K}^{\circ E}_{s,m,2}$
TPa^{-1}						
2-Methoxyaniline (1) + 2-propyn-1-ol (2)						
303.15	-59.32	4.050	-63.38	-37.83	3.205	-41.04
308.15	-69.26	4.151	-73.42	-45.20	3.333	-48.54
313.15	-79.36	4.250	-83.61	-52.63	3.464	-56.09
2-Methoxyaniline (1) +2-propen-1-ol(2)						
303.15	-69.75	4.050	-73.80	-51.47	4.766	-56.23
308.15	-79.26	4.151	-83.41	-58.86	4.965	-63.83
313.15	-88.90	4.250	-93.15	-66.38	5.186	-71.57
2-Methoxyaniline (1) + propan-1-ol (2)						
303.15	-82.02	4.050	-86.07	-64.70	6.648	-71.35
308.15	-90.31	4.151	-94.46	-72.11	6.947	-79.06
313.15	-98.86	4.250	-103.1	-79.64	7.256	-86.89

Positive deviation in viscosity of 2-methoxyaniline with primary alcohols is in the following order:

propan-1-ol > 2-propen-1-ol >2-propyn-1-ol

The experimental temperature of all binary mixture results in positive deviation is $8G^{*E}$ in overall composition of mixtures. Such functionality is promoted by the negative value of surplus molar volume and explains that association strength emerging due to the interaction of unlike molecules is higher when compared with the association strength of like molecules.

Surplus/ deviated functions (V^E, $\kappa_s{}^E$ and $\Delta\eta$) data are used in an equation called Redlich Kister polynomial equation [27]:

$$Y^E = x_1 x_2 \sum_{i=0}^{j=n-1} A_i (1-2x_1)^i \quad (7)$$

where Y^E is V^E, $\Delta\eta$ and κ_s^E. By using least squares method the coefficient values of A_i is determined and σ (Y^E) is the standard deviation, calculated by using the formula as given below:

$$\sigma(Y^E) = [\,\Sigma(Y^E_{exp} - Y^E_{cal})^2/(m\text{-}n)]^{1/2} \quad (8)$$

where m represents the total number of experiment points and the number of parameters is represented with n. The standard deviation value (σ) and coefficients A_i are shown in Table 4.

Partial molar properties

Surplus partial molar properties $\overline{V}^{E}_{m,1}$, $\overline{V}^{E}_{m,2}$, $\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$ and surplus partial molar property at infinite dilution $\overline{V}^{\circ E}_{m,1}$, $\overline{V}^{\circ E}_{m,2}$ $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ are determined for two components which is already explained [20].

Experimental temperature range of complete composition represents that $\overline{V}^{\circ E}_{m,1}$ and $\overline{V}^{\circ E}_{m,2}$ are negative values that are presented in Table 5. Negative values of the experimental observations explain that specific interactions predominated over non-specific interaction in binary mixtures [28].

Experimental temperature range of complete composition represents that $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ values are negative values that are presented in Table 6. Improved hydrogen bonding interaction is attributed to negative values among unlike molecular values [29].

Prigogine Flory Patterson Theory

A conventional theory named Prigogine Flory Patterson theory (PFP) can be used for quantitative prediction of various contributions to V^E. This PFP theory is explained clearly by Patterson and other researchers [30-34] and has been largely utilized for analysis of surplus properties with various types of mixtures which includes polar compounds explained by a number of authors. The three contributions used for estimated expression for V^E are given below as follows:

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}\Psi_1\theta_2\chi_{12}}{[\left(\frac{4}{3}\right)\tilde{V}^{\frac{1}{3}}-1]P_1^*}(\text{int.contribution})$$

$$+ \frac{-(\tilde{V}_1-\tilde{V}_2)[(14/9)\tilde{V}^{-1/3}-1]\Psi_1\Psi_2}{[\left(\frac{4}{3}\right)\tilde{V}^{\frac{1}{3}}-1]\tilde{V}}(\text{fv.contribution})$$

$$+ \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1+P_1^*\Psi_2}(P^*\text{contribution}) \quad (9)$$

The pure component volume $\tilde{V}_i$ is reduced and calculated from isobaric thermal expression α_i by using the equation:

$$\tilde{V}_i = \left(\frac{1+\left(\frac{4}{3}\right)\alpha_i T}{1+\alpha_i T}\right) \quad (10)$$

The volume $\tilde{V}$ of the mixture is estimated by using an equation (18)

Divided by $\tilde{V} = \Psi_1\tilde{V}_1 + \Psi_2\tilde{V}_2$ (11)

The energy fraction of contact molecular elements Ψ_1 is calculated by:

$$\Psi_1 = 1 - \Psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \quad (12)$$

The typical volume is $V_i^* = V_i^*/\tilde{V}_i$ and the typical pressure is represented by:

$$P_i^* = \frac{T\tilde{V}_i^2\alpha_i}{\kappa_{Ti}} \quad (13)$$

where κ_{Ti} is the isothermal flexibility of pure component 'i'.

The hard core volume components of the elements 1 and 2($\phi_1$andϕ_2) are represented by

$$\phi_1\text{=}1\text{-}\phi_2 = \frac{x_1V_1^*}{x_1V_1^* + x_2V_2^*} \quad (14)$$

The κ_T value is calculated by using the expression below,

$$\kappa_T = \kappa_S + \frac{TV\alpha^2}{C_P} \quad (15)$$

By using Prigogine Flory Patterson theory the χ_{12} parameters needed for V^E expression calculation to the experiment, equimolar value of V^E for a system were examined. The three contributions for calculation of equimolar values having χ_{12} parameters for this system are shown in Table 7 and Fig. 5. The latter gives the graphical representation of comparative experimental values and calculated values of V^E from Prigogine Flory Patterson theory.

Table 7. Interaction parameter of PFP theory, χ_{12} and calculated value of the three contributions from the PFP theory with experiment surplus molar volumes at x_1= 0.5 at 303.15K

Binary mixtures	χ_{12} (10^{7})	Calculated contributions			V^E (x=0.5) $m^3.mol^{-1}$		
		Interactional (10^{-9})	Free volume	P* effect	EXP	PFP	δ / $m^3.mol^{-1}$
2-Methoxyaniline + 2-propyn-1-ol	-2.555	8.024	-0.2428	0.3505	-0.0973	-0.0974	0.0001
2-Methoxyaniline + 2-propen-1-ol	2.032	9.201	-0.0968	-0.1904	-0.1003	-0.1001	-0.0002
2-Methoxyaniline + propan-1-ol	4.261	10.40	-0.1123	-0.4338	-0.1030	-0.1032	0.0002

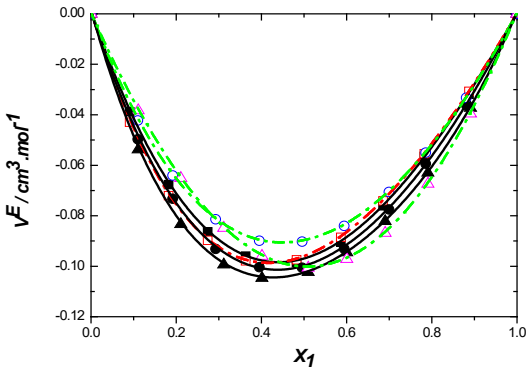

Figure 5. Surplus molar volumes with mole fraction (x_1) of 2-methoxyaniline binary liquid mixtures of 2-methoxyaniline with 2-propyn-1-ol (■); 2-propen-1-ol (●) and propan-1-ol (▲) at 303.15 K and (---) calculated with PFP theory using parameters

CONCLUSIONS

Current research presents experiment results of density, viscosities and sound speeds of 2-methoxyaniline with propan-1-ol, 2-propen-1-ol and 2-propyn-1-ol binary mixture above the entire configuration range of temperature is 303.15 K, 308.15 K and 313.15 K with a five-degree difference among the values. These experiment values are used for computation of surplus molar volume, surplus isentropic flexibility and viscosity deviation involving surplus Gibbs energy actuation of viscous flow at various temperatures 303.15 K, 308.15 K and 313.15 K. The surplus deviation parameters may be attribution to the attractive forces through the hetero-association interaction among the elements of mixtures that leads to associated complex formation through interactions of hydrogen bond. The analysis of result is performed in view of the molecular interaction through the hydrogen bond formed in the binary liquid mixtures by the unlike molecules.

Three contributions were examined to calculate V^E represents that interaction contribution is positive for entire system. All binary system values consisting of free volume contribution values are observed as negative. From Table 7, it is clearly seen that free volume effect is concerned element for magnitude and sign of surplus volumes for every binary mixture.

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