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Orientation effect on sign and magnitude of excess thermodynamic functions of non electrolyte solutions at different temperatures (303.15 K, 308.15 K, and 313.15 K)

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Abstract−Experimental values of the density and viscosity have been measured for binary mixtures of N-ethylaniline with isomeric butanols (1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol) at 303.15, 308.15 and 313.15 K over the entire mole fraction range. These data, the excess molar volumes, and deviation viscosity for the binary systems at the above-mentioned temperatures were calculated and fitted to Redlich-Kister equation to determine the fitting parameters and the root-mean-square deviations. The excess molar volumes, deviation viscosity and excess Gibbs energy of activation of viscous flow have been analyzed in terms of acid-base interactions, hydrogen bond, and dipole-dipole interaction between unlike molecules. The results obtained for dynamic viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg-Nissan, Katti-Chaudhri, and Hind et al. equations.

Keywords: Viscosity, Excess Molar Volume, N-ethylaniline, Isomeric Butanols

INTRODUCTION

Information based on the viscosity of pure liquids and liquid mixtures is important in applications in chemical engineering, such as in the determination of flow of flow, mass-transfer, and heat-transfer operations. The present investigation is a continuation of our earlier research [1-5] on thermodynamic properties of binary liquid mixtures. The liquids were chosen in the present study on the basis of their industrial importance. N-ethyl aniline is chosen as polar solvent and self associated through hydrogen bonding of their amine group. The amino group in N-ethyl aniline is an electron-donor, and the hydrogen atom in the -NH_2 group can also play the role of electron-acceptor centers; alcohol molecules are polar and self-associated through hydrogen bonding of their hydroxyl groups. N-ethyl aniline is used as an intermediate to manufacture dyes, agrochemicals and in preparation of some organic compounds. Alcohols are used as hydraulic fluids in pharmaceutical and cosmetics, in medications for animals, in manufacturing perfumes, paint removers, flavors and dyestuffs, as defrosting and as an antiseptic agent. The present work was undertaken to determine the effect of the position of the -OH group in the alkyl chain in the alkanol molecule that may influence both the sign and magnitude of various thermodynamic functions when it is mixed with N-ethylaniline. Recently, substantial research work has been reported on the excess properties of methyl isobutyl ketone+alkanols [6], 1,3-Dioxolane+Monoalcohols [7], acetonitrile with alkanols-1 [8], 2-Butanone with Branched alcohols [9], Anisole with Alkanols [10], N-methylpiperazine with alcohols [11] while that on N-ethyl aniline with alkanols is relatively rare. This work reports viscosity and density values for binary mixtures of N-ethyl aniline with alcohols over the entire range of mole fraction at 303.15, 308.15, and 313.15 K and atmospheric pressure. The viscosity deviation and excess molar volume are calculated and are fitted to a Redlich-Kister type polynomial equation. The variations of the excess or deviation properties with composition are discussed from the strong association between the alcohol and N-ethyl aniline molecules through the hydrogen bond. The thermodynamic functions of activation have been estimated from the experimental data and the viscosity data have been correlated with several semi-empirical equations.

EXPERIMENTAL

1. Materials

The mass fraction purity of all the liquids from S.D Fine Chemicals, Ltd., India was as follows: N-ethyl aniline (99.5%), 1-butanol (99.8%), 2-butanol (99.8%), 2-methyl -1-propanol (99.5%), and tert2-methyl-2-propanol (99.5%). Prior to experimental measurements, all the liquids were purified as described in the literature [12, 13] and given in Table 1 along with their CAS number and water content. The purity samples were attained by fractional distillation and the purity of chemicals were checked by comparing the measured densities and viscosity, which were in good agreement with literature values [14-18] and these are given in Table 2. The purity of the sample was further confirmed by GLC single sharp peak. Before use, the chemicals were stored over 0.4 nm molecular sieves for about 72 hrs to remove water and were later degassed.

2. Apparatus and Procedure

The water content of solvents used in this work was measured by Analab (MicroAqua Cal 100) Karl Fischer Titrator and Karl Fischer reagent from Merck. It can detect water content from less than 10×10^{-6} to 100% by conductometric titration with dual platinum electrodes. All the binary liquid mixtures were prepared by weighing an amount of pure liquids in an electric balance (Afoset, ER-120A, and India) with a precision of ±0.1 mg by syringing each

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Table 1. Provenance and purity of the materials used

Name of the chemical	Supplier	CAS number	Purity (as received from supplier)	Purity (after purification)	Water content %
N-ethylaniline	S.D Fine Chemicals	103-69-5	99%	99.5%	0.037
1-Butanol	S.D Fine Chemicals	71-36-3	99.5%	99.8%	0.040
2-Butanol	S.D Fine Chemicals	78-92-2	99.5%	99.8%	0.038
2-Methyl-1-butanol	S.D Fine Chemicals	78-83-1	99%	99.5%	0.040
2-Methyl-2-butanol	S.D Fine Chemicals	75-65-0	99%	99.5%	0.038

Table 2. Comparison of experimental and literature values of density (ρ), and viscosity (η) data of pure components at T=308.15 K

	Density (ρ)/gm cm^{-3}		Viscosity (η)/mPa·s	
Pure components	Experimental	Literature	Experimental	Literature
N-ethylaniline	0.94843	0.94840[15]	1.548	1.549[15]
1-Butanol	0.80065	0.80067[18]	2.256	2.257[17]
2-Butanol	0.79853	0.79851*[17]	2.741	2.742*[17]
2-Methyl-1-propanol	0.78965	0.78966[16]	2.455	2.456[14]
2-Methyl-2-propanol	0.77042	0.77039[16]	2.645	2.646[14]

*Uncertainty in density ±0.005 gm·cm^{-3} uncertainty in viscosity ±0.005 mPa·s

*303.15 K

component into air-tight stoppered bottles to minimize evaporation losses. The uncertainty of the mole fraction was $\pm 1\times 10^{-4}$. After mixing the sample, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with temperature accuracy of 303.15 K±0.03 K. The uncertainty density measurement liquid mixtures were $\pm 5\times 10^{-5}$ gm/cm^3. Proper calibration at each temperature was achieved with doubly distilled, deionized water and with air as standards. The viscosities of pure liquids and their mixtures were determined at atmospheric pressure and at 303.15 K,

Table 3. Mole fraction of N-ethylaniline (x_1), density (ρ), excess volumes (V^E),viscosity (η), Theoretical values of Grunberg and Nissan (ηGN), Katti and Chaudhri (ηKC) and (ηH) equations including standard deviation (SD), deviation in viscosities ($\Delta\eta$), excess Gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters (d_{12}), Katti-Chaudhri interaction parameters (W_{vis}/RT), and Hind interaction parameters (H_{12}) at 303.15 K , 308.15 K and 313.15 K

N-ethylaniline (1)+2-methyl-2-propanol (2) 303.15 K

Theoretical values

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.77629	0.0000	3.379	3.379	3.379	3.379	0.000	0.0000				
0.0789	0.79532	−0.1180	3.2872	3.305	3.300	3.287	0.037	0.6765	0.3399	0.3679	2.8169	2.9327
0.1325	0.80766	−0.1898	3.2224	3.246	3.222	3.221	0.060	1.0998	0.3507	0.3782	2.8225	2.9416
0.1974	0.82196	−0.2631	3.1388	3.166	3.135	3.137	0.083	1.5515	0.3599	0.3871	2.8221	2.9461
0.2562	0.83435	−0.3181	3.0614	3.086	3.089	3.057	0.102	1.9261	0.3727	0.3995	2.8275	2.9556
0.3315	0.84944	−0.3691	2.9567	2.973	2.978	2.950	0.120	2.3276	0.3886	0.4152	2.832	2.9657
0.4056	0.86347	−0.3966	2.8483	2.854	2.863	2.839	0.133	2.6374	0.4059	0.4324	2.8368	2.9763
0.4868	0.87795	−0.3994	2.7174	2.714	2.718	2.710	0.135	2.8149	0.4187	0.4454	2.8312	2.9771
0.5626	0.89070	−0.3802	2.5897	2.577	2.580	2.584	0.132	2.8665	0.4336	0.4604	2.828	2.9797
0.6195	0.89980	−0.3509	2.4879	2.471	2.465	2.486	0.123	2.8003	0.4425	0.4696	2.8214	2.9772
0.6889	0.91042	−0.3032	2.3595	2.339	2.335	2.361	0.108	2.6104	0.4539	0.4814	2.813	2.9734
0.7514	0.91955	−0.2484	2.2407	2.219	2.207	2.245	0.092	2.3341	0.4659	0.4939	2.806	2.9705
0.8214	0.92936	−0.1804	2.1025	2.084	2.070	2.110	0.068	1.8706	0.4755	0.504	2.7927	2.9607
0.8914	0.93877	−0.1075	1.9598	1.949	1.938	1.969	0.040	1.2315	0.4737	0.5028	2.7672	2.9367
1.0000	0.95274	0.0000	1.742	1.742	1.742	1.742	0.000	0.0000				
SD				0.0003	0.0314	0.2079						

308.15 K and 313.15 K by using an Ubbelohde viscometer, which was calibrated with benzene, carbon tetrachloride, acetonitrile, and doubly distilled water. The kinetic energy corrections were calculated from these values and found to be negligible. The Ubbelohde viscometer bulb has a capacity of 15 ml and the capillary tube with a length of about 90 mm with 0.5 mm internal diameter. The viscometer was thoroughly cleaned and perfectly dried, filled with the sample liquid by fitting the viscometer to about 30° from the vertical and its limbs were closed with Teflon caps to avoid the evaporation. The viscometer was kept in a transparent walled bath with a thermal stability of ±0.01 K for about 20 minutes to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty ±0.01 s was used for flow time measurements. The viscosity values of pure liquids and mixtures were calculated using the relation:

$$\nu=\eta/\rho=\mathrm{at}-\mathrm{b/t} \tag{1}$$

where a and b are the characteristic constants of the viscometer, ρ is the density and t represents the flow time. The uncertainty of viscosity thus estimated was found to be ±0.005 mPa·s.

RESULTS AND DISCUSSION

The measured densities (ρ) and viscosities (η), calculated excess molar volumes (V^E), viscosity deviation ($\Delta\eta$) and excess Gibbs en-

Table 3. Continued

<table>
<tr><td colspan="13">N-ethylaniline (1)+2-methyl-2-propanol (2) 308.15 K</td></tr>
<tr><td colspan="13">Theoretical values</td></tr>
<tr><td>x_1</td><td>ρ/gm·cm^{-3}</td><td>V^E/cm^3·mol^{-1}</td><td>η/mPa·s</td><td>η GN</td><td>η KC</td><td>η H</td><td>η/mPa·s</td><td>G^{*E}/J·mol^{-1}</td><td>d_{12}</td><td>W_{vis}/RT</td><td>H_{12}</td><td>T_{12}</td></tr>
<tr><td>0.0000</td><td>0.77042</td><td>−0.0000</td><td>2.645</td><td>2.645</td><td>2.645</td><td>2.645</td><td>0.000</td><td>0.0000</td><td></td><td></td><td></td><td></td></tr>
<tr><td>0.0789</td><td>0.78982</td><td>−0.1522</td><td>2.6003</td><td>2.528</td><td>2.621</td><td>2.599</td><td>0.042</td><td>0.6872</td><td>0.3485</td><td>0.3800</td><td>2.3862</td><td>2.4536</td></tr>
<tr><td>0.1325</td><td>0.80231</td><td>−0.2341</td><td>2.5663</td><td>2.453</td><td>2.591</td><td>2.563</td><td>0.067</td><td>1.1089</td><td>0.3556</td><td>0.3877</td><td>2.3874</td><td>2.4591</td></tr>
<tr><td>0.1974</td><td>0.81673</td><td>−0.3112</td><td>2.5222</td><td>2.365</td><td>2.539</td><td>2.516</td><td>0.094</td><td>1.5807</td><td>0.3680</td><td>0.4009</td><td>2.393</td><td>2.4696</td></tr>
<tr><td>0.2562</td><td>0.82918</td><td>−0.3633</td><td>2.4782</td><td>2.289</td><td>2.491</td><td>2.470</td><td>0.114</td><td>1.9559</td><td>0.3788</td><td>0.4124</td><td>2.3967</td><td>2.4781</td></tr>
<tr><td>0.3315</td><td>0.84432</td><td>−0.4065</td><td>2.4141</td><td>2.195</td><td>2.423</td><td>2.404</td><td>0.133</td><td>2.3374</td><td>0.3895</td><td>0.4238</td><td>2.3963</td><td>2.4841</td></tr>
<tr><td>0.4056</td><td>0.85840</td><td>−0.4259</td><td>2.3433</td><td>2.108</td><td>2.351</td><td>2.334</td><td>0.143</td><td>2.6049</td><td>0.3992</td><td>0.4342</td><td>2.3938</td><td>2.4880</td></tr>
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<tr><td>0.6889</td><td>0.90586</td><td>−0.3386</td><td>2.0034</td><td>1.813</td><td>1.989</td><td>2.008</td><td>0.114</td><td>2.4650</td><td>0.4258</td><td>0.4622</td><td>2.3628</td><td>2.4790</td></tr>
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<tr><td>0.8914</td><td>0.93456</td><td>−0.1447</td><td>1.7097</td><td>1.635</td><td>1.697</td><td>1.721</td><td>0.043</td><td>1.1127</td><td>0.4255</td><td>0.4619</td><td>2.3164</td><td>2.4423</td></tr>
<tr><td>1.0000</td><td>0.94843</td><td>−0.0000</td><td>1.548</td><td>1.548</td><td>1.548</td><td>1.548</td><td>0.000</td><td>0.0000</td><td></td><td></td><td></td><td></td></tr>
<tr><td>SD</td><td></td><td></td><td></td><td>0.0300</td><td>0.0192</td><td>0.1754</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td colspan="13">N-ethylaniline (1)+2-methyl-1-propanol (2) 303.15 K</td></tr>
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<tr><td>x_1</td><td>ρ/gm·cm^{-3}</td><td>V^E/cm^3·mol^{-1}</td><td>η/mPa·s</td><td>η GN</td><td>η KC</td><td>η H</td><td>η/mPa·s</td><td>G^{*E}/J·mol^{-1}</td><td>d_{12}</td><td>W_{vis}/RT</td><td>H_{12}</td><td>T_{12}</td></tr>
<tr><td>0.0000</td><td>0.79362</td><td>0.0000</td><td>2.849</td><td>2.849</td><td>2.849</td><td>2.849</td><td>0.000</td><td>0.0000</td><td></td><td></td><td></td><td></td></tr>
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<tr><td>0.1356</td><td>0.82310</td><td>-0.1750</td><td>2.7422</td><td>2.758</td><td>2.777</td><td>2.746</td><td>0.043</td><td>0.8139</td><td></td><td>0.2790</td><td>2.4799</td><td>2.5745</td></tr>
<tr><td>0.1958</td><td>0.83526</td><td>-0.2416</td><td>2.6948</td><td>2.709</td><td>2.717</td><td>2.696</td><td>0.062</td><td>1.1501</td><td>0.2581</td><td>0.2935</td><td>2.4939</td><td>2.5908</td></tr>
<tr><td>0.2654</td><td>0.84862</td><td>-0.3049</td><td>2.6371</td><td>2.647</td><td>2.662</td><td>2.634</td><td>0.082</td><td>1.4932</td><td>0.2731</td><td>0.3077</td><td>2.5054</td><td>2.6059</td></tr>
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<tr><td>0.3956</td><td>0.87166</td><td>-0.3734</td><td>2.5172</td><td>2.515</td><td>2.524</td><td>2.508</td><td>0.106</td><td>1.9630</td><td>0.2960</td><td>0.3299</td><td>2.5174</td><td>2.6261</td></tr>
<tr><td>0.4565</td><td>0.88160</td><td>-0.3803</td><td>2.4541</td><td>2.447</td><td>2.441</td><td>2.444</td><td>0.110</td><td>2.0840</td><td>0.3037</td><td>0.3375</td><td>2.5180</td><td>2.6309</td></tr>
<tr><td>0.5202</td><td>0.89147</td><td>-0.3711</td><td>2.3842</td><td>2.373</td><td>2.361</td><td>2.374</td><td>0.111</td><td>2.1464</td><td>0.3116</td><td>0.3455</td><td>2.5179</td><td>2.6352</td></tr>
<tr><td>0.6021</td><td>0.90342</td><td>-0.3358</td><td>2.2842</td><td>2.272</td><td>2.265</td><td>2.279</td><td>0.102</td><td>2.0762</td><td>0.3140</td><td>0.3482</td><td>2.5078</td><td>2.6303</td></tr>
<tr><td>0.6745</td><td>0.91336</td><td>-0.2865</td><td>2.1936</td><td>2.180</td><td>2.175</td><td>2.191</td><td>0.091</td><td>1.9407</td><td>0.3205</td><td>0.3552</td><td>2.5033</td><td>2.6303</td></tr>
<tr><td>0.7325</td><td>0.92094</td><td>-0.2369</td><td>2.1163</td><td>2.104</td><td>2.089</td><td>2.117</td><td>0.078</td><td>1.7401</td><td>0.3217</td><td>0.3568</td><td>2.4950</td><td>2.6250</td></tr>
<tr><td>0.8025</td><td>0.92970</td><td>-0.1703</td><td>2.0186</td><td>2.011</td><td>1.993</td><td>2.025</td><td>0.058</td><td>1.3909</td><td>0.3168</td><td>0.3526</td><td>2.4784</td><td>2.6109</td></tr>
<tr><td>0.8869</td><td>0.93979</td><td>-0.0885</td><td>1.9027</td><td>1.896</td><td>1.887</td><td>1.908</td><td>0.035</td><td>0.9034</td><td>0.3250</td><td>0.3619</td><td>2.4724</td><td>2.6090</td></tr>
<tr><td>1.0000</td><td>0.95274</td><td>0.0000</td><td>1.742</td><td>1.742</td><td>1.742</td><td>1.742</td><td>0.000</td><td>0.0000</td><td></td><td></td><td></td><td></td></tr>
<tr><td>SD</td><td></td><td></td><td></td><td>0.0001</td><td>0.0246</td><td>0.1853</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

Table 3. Continued

N-ethylaniline (1)+2-methyl-1-propanol (2) 308.15 K												
				Theoretical values								
x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.78965	0.0000	2.455	2.455	2.455	2.455	0.000	0.0000				
0.0756	0.80667	−0.1332	2.4141	2.390	2.435	2.417	0.027	0.5119	0.2574	0.2895	2.1982	2.2688
0.1356	0.81941	−0.2188	2.3797	2.377	2.409	2.383	0.048	0.8877	0.2671	0.2994	2.2043	2.2779
0.1958	0.83156	−0.2884	2.3485	2.353	2.364	2.346	0.071	1.2893	0.2914	0.3236	2.2268	2.3024
0.2654	0.84487	−0.3502	2.3069	2.321	2.323	2.299	0.092	1.6799	0.3083	0.3406	2.2388	2.3184
0.3214	0.85503	−0.3848	2.2698	2.270	2.272	2.258	0.106	1.9422	0.3197	0.3520	2.2450	2.3285
0.3956	0.86778	−0.4102	2.2151	2.202	2.214	2.200	0.119	2.2086	0.3327	0.3651	2.2500	2.339
0.4565	0.87768	−0.4150	2.1602	2.145	2.146	2.148	0.119	2.2922	0.3327	0.3652	2.2417	2.3354
0.5202	0.88754	−0.4073	2.1063	2.089	2.079	2.091	0.123	2.3978	0.3472	0.3797	2.2481	2.3466
0.6021	0.89950	−0.3764	2.0292	1.997	2.000	2.013	0.120	2.4025	0.3638	0.3964	2.2525	2.3575
0.6745	0.90947	−0.3334	1.9558	1.944	1.924	1.938	0.113	2.2992	0.3812	0.4139	2.2578	2.3688
0.7325	0.91707	−0.2882	1.8893	1.890	1.850	1.875	0.099	2.0818	0.3872	0.4200	2.2533	2.3684
0.8025	0.92584	−0.2252	1.8113	1.816	1.799	1.796	0.084	1.8012	0.4163	0.4492	2.2670	2.3891
0.8869	0.93585	−0.1352	1.7144	1.719	1.715	1.714	0.064	1.3471	0.4978	0.5308	2.3196	2.4555
1.0000	0.94843	0.0000	1.548	1.548	1.548	1.548	0.000	0.0000				
SD				0.0208	0.0223	0.1647						

N-ethylaniline (1)+2-butanol (2) 303.15 K												
				Theoretical values								
x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.79853	0.0000	2.741	2.741	2.741	2.741	0.000	0.0000				
0.0785	0.81546	−0.0949	2.6821	2.692	2.707	2.686	0.019	0.4214	0.1897	0.2302	2.3741	2.465
0.1325	0.82654	−0.1556	2.6424	2.655	2.672	2.646	0.033	0.7048	0.2027	0.2424	2.3871	2.4789
0.1965	0.83909	−0.2200	2.5955	2.606	2.616	2.596	0.050	1.0255	0.2179	0.2567	2.4016	2.4951
0.2564	0.85028	−0.2710	2.5503	2.556	2.567	2.547	0.065	1.2969	0.2308	0.2689	2.4125	2.5084
0.3214	0.86181	−0.3118	2.4982	2.498	2.505	2.491	0.078	1.5439	0.2423	0.2798	2.4205	2.5196
0.3965	0.87439	−0.3410	2.4327	2.427	2.439	2.423	0.088	1.7506	0.2521	0.2892	2.4247	2.5278
0.4562	0.88383	−0.3475	2.3777	2.367	2.365	2.366	0.092	1.8642	0.2601	0.2970	2.4276	2.5342
0.5124	0.89230	−0.3417	2.3217	2.309	2.296	2.310	0.092	1.9072	0.2648	0.3017	2.4266	2.5365
0.5895	0.90330	−0.3156	2.2397	2.225	2.215	2.231	0.087	1.8751	0.2693	0.3063	2.4224	2.5366
0.6547	0.91208	−0.2780	2.1638	2.152	2.141	2.160	0.077	1.7373	0.2666	0.3038	2.4114	2.5287
0.7325	0.92200	−0.2188	2.0703	2.062	2.049	2.073	0.061	1.4862	0.2621	0.2998	2.3973	2.5175
0.8025	0.93048	−0.1578	1.9832	1.980	1.964	1.991	0.044	1.1684	0.2532	0.2914	2.3799	2.5018
0.8745	0.93884	−0.0941	1.8936	1.894	1.881	1.903	0.026	0.7794	0.2418	0.2807	2.3609	2.4835
1.0000	0.95274	0.0000	1.742	1.742	1.742	1.742	0.000	0.0000				
SD				0.0001	0.0183	0.1786						

ergy of activation of viscous flow (G^{*E}) for binary mixtures of N-ethylaniline with isomeric butanols at different temperatures 303.15, 308.15 and 313.15 K. are shown in Table 3 and also excess/deviation properties are graphically represented in Figs. 1-9, respectively V^E, η, and G^{*E} are calculated from the experimental measurements by Eqs. (2)-(4):

$$V^E/\mathrm{cm^3\cdot mol^{-1}}=[x_1M_1+x_2M_2]/\rho-[x_1M_1/\rho_1+x_2M_2/\rho_2] \tag{2}$$

$$\Delta\eta/\mathrm{mPA\cdot s}=\eta-[x_1\ \eta_1+x_2\ \eta_2] \tag{3}$$

$$G^{*E}/\mathrm{J\cdot mol^{-1}}=RT\ [\ln\eta V-(x_1\ln\eta_1 V_1+x_2\ln\eta_2 V_2)] \tag{4}$$

where for each equation, ρ, V, and η are the density, the molar volume and the dynamic viscosity of the mixtures and x_i, V_i, M_i, and η_i (i=1, 2) are the mole fraction, molar volume, the molar mass and the dynamic viscosity of the components N-ethyl aniline (1) and alcohols (2), respectively. R is the gas constant and T the absolute temperature.

1. Excess Molar Volumes

The magnitude and the sign of V^E can arise from two opposing factors: (i) the positive contribution is a consequence of the disruption of the hydrogen bonds in the self-associated alcohol and the dipole-dipole interactions between alcohol monomer and multimer; (ii) negative contributions arise from strong intermolecular interactions attributed to charge-transfer, dipole-dipole interactions and hy-

Table 3. Continued

N-ethylaniline (1)+2-butanol (2) 308.15 K

Theoretical values

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.79403	0.0000	2.128	2.128	2.128	2.128	0.000	0.0000				
0.0785	0.81111	−0.1133	2.1047	2.097	2.124	2.109	0.022	0.4221	0.1931	0.2307	1.9917	2.0415
0.1325	0.82227	−0.1837	2.0888	2.075	2.112	2.093	0.038	0.7035	0.2051	0.2419	2.0018	2.0532
0.1965	0.83489	−0.2564	2.0708	2.046	2.085	2.072	0.057	1.0371	0.2235	0.2596	2.0178	2.0712
0.2564	0.84613	−0.3132	2.0517	2.017	2.063	2.049	0.072	1.3121	0.2364	0.2720	2.0279	2.0841
0.3214	0.85770	−0.3583	2.0277	1.983	2.032	2.021	0.086	1.5603	0.2476	0.2828	2.0354	2.0951
0.3965	0.87030	−0.3890	1.9953	1.942	1.998	1.985	0.097	1.7746	0.2582	0.2931	2.0412	2.1055
0.4562	0.87976	−0.3969	1.9644	1.908	1.953	1.954	0.101	1.8674	0.2627	0.2975	2.0416	2.1096
0.5124	0.88824	−0.3912	1.9323	1.875	1.911	1.922	0.101	1.9045	0.2665	0.3013	2.0411	2.1128
0.5895	0.89924	−0.3631	1.8823	1.827	1.862	1.874	0.096	1.8559	0.2682	0.3031	2.0368	2.1132
0.6547	0.90802	−0.3236	1.8347	1.786	1.816	1.831	0.086	1.7200	0.2656	0.3007	2.0292	2.1092
0.7325	0.91793	−0.2607	1.7734	1.734	1.757	1.775	0.070	1.4619	0.2593	0.2949	2.0173	2.1010
0.8025	0.92639	−0.1946	1.7141	1.687	1.700	1.720	0.052	1.1330	0.2465	0.2826	2.0006	2.0865
0.8745	0.93469	−0.1205	1.6528	1.637	1.643	1.661	0.032	0.7487	0.2330	0.2696	1.9838	2.0712
1.0000	0.94843	0.0000	1.548	1.548	1.548	1.548	0.000	0.0000				
SD				0.0099	0.0143	0.1498						

N-ethylaniline (1)+1-butanol (2) 303.15 K

Theoretical values

x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.80201	0.0000	2.227	2.227	2.227	2.227	0.000	0.0000				
0.0702	0.81685	−0.0757	2.2028	2.210	2.209	2.208	0.010	0.2334	0.1000	0.1437	2.0632	2.1176
0.1296	0.82881	−0.1363	2.1867	2.193	2.181	2.191	0.023	0.4624	0.1220	0.1647	2.0862	2.1396
0.1901	0.84044	−0.1917	2.1727	2.174	2.182	2.172	0.038	0.7124	0.1441	0.1859	2.1086	2.1621
0.2568	0.85263	−0.2427	2.1538	2.151	2.163	2.148	0.052	0.9369	0.1562	0.1972	2.1197	2.1751
0.3204	0.86366	−0.2801	2.1322	2.126	2.135	2.134	0.061	1.0985	0.1623	0.2027	2.1242	2.1821
0.3725	0.87228	−0.3015	2.1144	2.104	2.107	2.112	0.068	1.2217	0.1701	0.2100	2.1305	2.1906
0.4414	0.88311	−0.3143	2.0846	2.073	2.067	2.072	0.072	1.2997	0.1722	0.2118	2.1302	2.1935
0.5136	0.89382	−0.3111	2.0468	2.037	2.040	2.048	0.069	1.2869	0.1677	0.2070	2.1226	2.1892
0.5841	0.90367	−0.2899	2.0074	2.000	1.999	2.002	0.064	1.2268	0.1636	0.2029	2.1158	2.1852
0.6525	0.91272	−0.2565	1.9698	1.962	1.964	1.965	0.059	1.1585	0.1659	0.2053	2.1153	2.1876
0.7225	0.92150	−0.2101	1.9261	1.921	1.918	1.925	0.050	1.0031	0.1614	0.2010	2.1081	2.1827
0.7954	0.93019	−0.1531	1.8725	1.877	1.871	1.880	0.031	0.7103	0.1354	0.1754	2.0806	2.1552
0.8741	0.93914	−0.0890	1.8195	1.826	1.815	1.812	0.017	0.4253	0.1148	0.1553	2.0592	2.1334
1.0000	0.95274	0.0000	1.7420	1.742	1.742	1.742	0.000	0.0000				
SD				0.0001	0.0157	0.1554						

drogen bonding between unlike molecules. Hence, the negative V^E values of the investigated systems assume heteroassociated complexes formation through hydrogen bonding between the nitrogen atom of amine group and the hydrogen atom of alcohols.

An examination of data in the Table 3 suggests that the excess volume data for all the binary systems are negative over the entire composition range at 303.15, 308.15 and 313.15 K and atmospheric pressure.

The plots of V^E versus x_1 are presented in Figs. 1, 2 and 3. These figures show that in each case the plots are parabolic and characterized by well-defined minima that occur at x_1=0.5, indicating the presence of complex formation between the mixing components [19].

The more negative V^E values for N-ethyl aniline+2-Alkanols when composed to N-ethyl aniline+1-Alkanols may be because in 2-Alkanols the presence of -CH_3 groups at the α-carbon atom increases the electron density at the oxygen atom of hydroxyl group to a greater extent than in 1-alkanols, which has one alkyl group on the α-carbon atom, resulting in stronger interaction (H-bonding) in former. Furthermore, the more negative V^E values for N-ethyl aniline with 2-methyl-2-propanol mixture when compared to N-ethyl aniline with 2-methyl-1-propanol may be ascribed to the fact that, in 2-methyl-2-propanol, the presence of three -CH_3 groups at the α-carbon atom increases the electron density at the oxygen atom to a greater extent

Table 3. Continued

N-ethylaniline (1)+1-butanol (2) 308.15 K												
Theoretical values												
x_1	ρ/gm·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	η GN	η KC	η H	η/mPa·s	G^{*E}/J·mol^{-1}	d_{12}	W_{vis}/RT	H_{12}	T_{12}
0.0000	0.80065	0.0000	2.	2.254	2.254	2.254	0.000	0.0000				
0.0702	0.81542	−0.0961	2.2211	2.218	2.242	2.229	0.016	0.3549	0.1769	0.2184	2.0266	2.0927
0.1296	0.82724	−0.1641	2.1906	2.184	2.226	2.205	0.028	0.6146	0.1777	0.2189	2.0245	2.0932
0.1901	0.83882	−0.2379	2.1645	2.169	2.193	2.177	0.044	0.9192	0.2001	0.2399	2.0456	2.1148
0.2568	0.85081	−0.2916	2.1318	2.141	2.135	2.144	0.059	1.1993	0.213	0.2525	2.0554	2.1271
0.3204	0.86170	−0.3370	2.1013	2.096	2.125	2.109	0.073	1.4585	0.2303	0.2691	2.0695	2.1437
0.3725	0.87014	−0.3569	2.0732	2.071	2.077	2.078	0.082	1.6253	0.2407	0.2794	2.0765	2.1535
0.4414	0.88077	−0.3717	2.0312	1.999	2.032	2.035	0.089	1.7711	0.2502	0.2886	2.0809	2.1617
0.5136	0.89122	−0.3635	1.9792	1.981	1.978	1.985	0.088	1.8041	0.2518	0.2902	2.0766	2.1615
0.5841	0.90083	−0.3383	1.9257	1.928	1.922	1.932	0.084	1.7755	0.2552	0.2937	2.0739	2.1628
0.6525	0.90965	−0.3006	1.8672	1.876	1.865	1.878	0.074	1.6328	0.2508	0.2893	2.0638	2.1558
0.7225	0.91815	−0.2432	1.8022	1.802	1.799	1.819	0.058	1.3831	0.2381	0.2772	2.0463	2.1405
0.7954	0.92660	−0.1803	1.7308	1.744	1.731	1.753	0.038	1.0238	0.2133	0.2528	2.0188	2.1134
0.8741	0.93527	−0.1061	1.6597	1.651	1.660	1.658	0.023	0.666	0.2031	0.2432	2.0046	2.1004
1.0000	0.94843	0.0000	1.548	1.548	1.548	1.548	0.000	0.0000				
SD				0.0148	0.0213	0.1553						

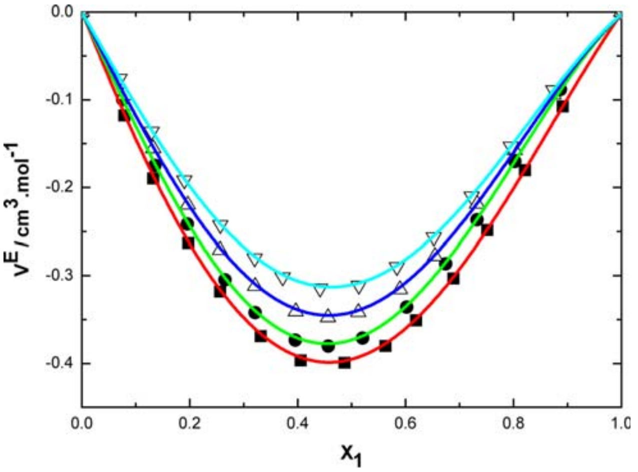

Fig. 1. Variation of excess molar volume (V^E) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 303.15 K.

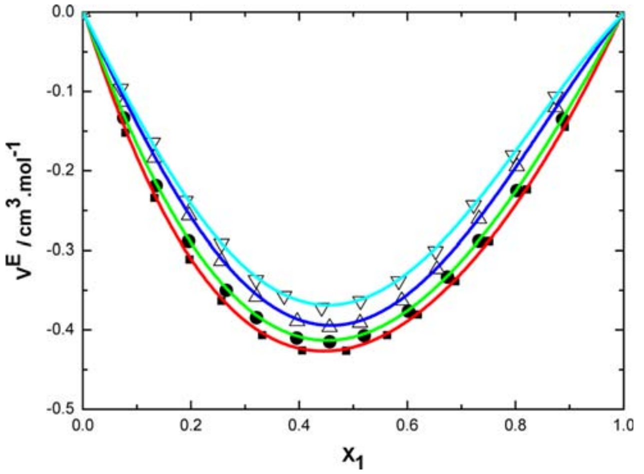

Fig. 2. Variation of excess molar volume (V^E) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 308.15 K.

than that in 2-methyl-1-propanol, which has two-CH_3 groups on the β-carbon atom, resulting in stronger interaction in the N-ethyl aniline+2-methyl-2-propanol mixture. Hence, it may be concluded that the interaction between N-ethyl aniline and alcohols under study increases when a hydroxyl group is attached to a carbon atom with a greater number of -CH_3 groups, i.e., an increase in the number of -CH_3 groups at the α-carbon atom of alkanols. Similar results have been reported for N-methyl acetamide with aromatic hydrocarbon [20] phenyl acetonitrile with aliphatic alcohol [21] and aniline with 1-alkanols [16].

The algebraic negative V^E values of N-ethylaniline with isomeric butanols fall in the order:

1-butanol<2-butanol<2-methyl-1-propanol<2-methyl-2-propanol.

Table 3 shows that the values of $\Delta\eta$, and G^{*E} are positive for all the binary systems over the entire composition range at 303.15, 308.15 and 313.15 K and atmospheric pressure.

According to Fort and Moore (22), viscosity deviation tends to become more positive as the strength of the interaction increases. The deviation in viscosity variation gives a qualitative estimation of the strength of the intermolecular interactions. The viscosity deviation may be generally explained by considering the following factors [23]: (i) The difference in size and shape of the component molecules and the loss of dipolar association in pure component may

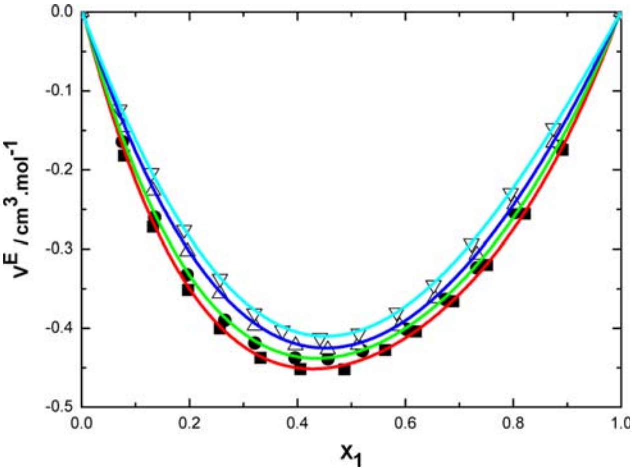

Fig. 3. Variation of excess molar volume (V^E) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 313.15 K.

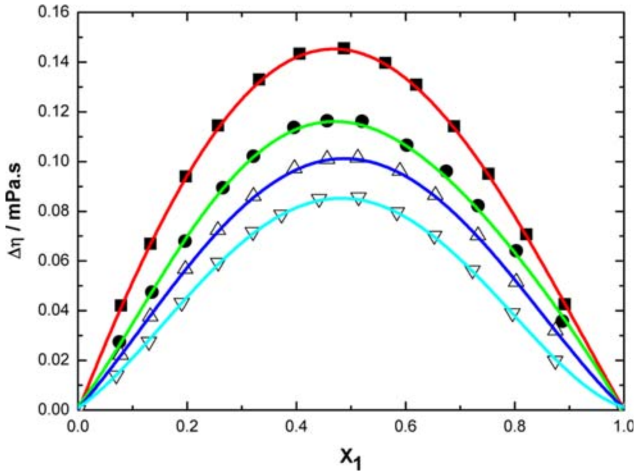

Fig. 5. Deviation in viscosity $\Delta\eta$ with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 308.15 K.

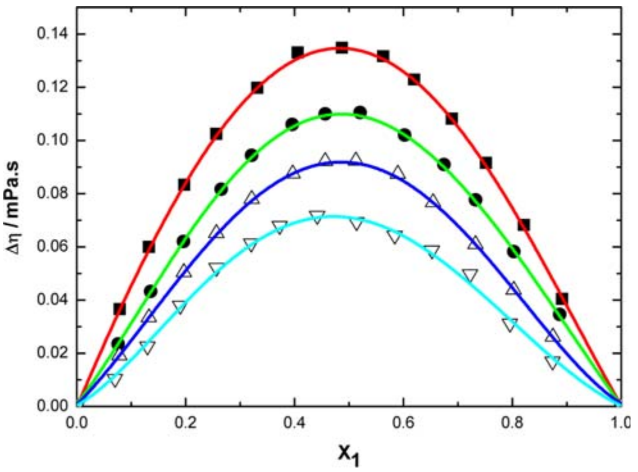

Fig. 4. Deviation in viscosity $\Delta\eta$ with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 303.15 K.

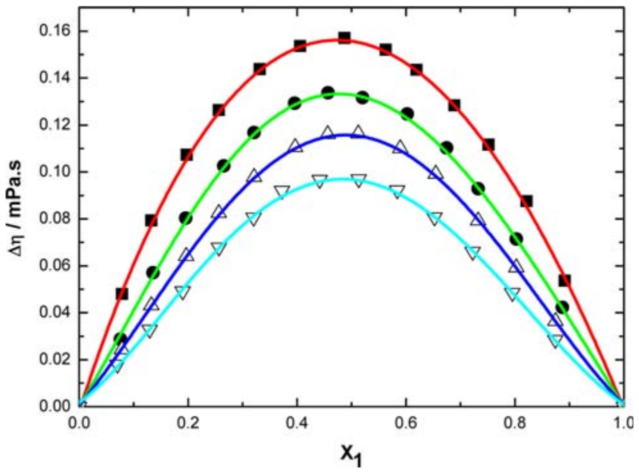

Fig. 6. Deviation in viscosity $\Delta\eta$ with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 313.15 K.

contribute to a decrease in viscosity, and (ii) specific interactions between unlike components such as hydrogen bond formation and charge-transfer complexes may cause increase in viscosity in mixtures compared to in pure components. The former effect produces negative deviation in viscosity and latter effect produces positive viscosity deviation. The positive values of viscosity deviation for the binary systems investigated suggest that the viscosities of associates formed between unlike molecules are relatively more than those of the pure components.

According to Reed et al. [24], the G^{*E} parameter may be considered as a reliable criterion to detect or exclude the presence of interaction between unlike molecules. According to the authors, positive values and the magnitude are excellent indicators of the strength of specific interactions.

The positive values of excess Gibbs energy of activation of viscous flow for the binary systems investigated suggest the specific interactions of hydrogen bonding resulting in the formation of complexes between the component molecules. Thus, the values of viscosity deviation and excess Gibbs energy of activation of viscous flow are dependent on the position of the -OH group in the alcohol molecule, indicating a different extent of molecular interactions in isomeric butanols.

The increase of temperature leads to an increase in the kinetic energy of the self-associated molecules of N-substituted amines, promoting their dissociation. However, the temperature rise has the same influence on the complex between the components of the mixture. The observed results indicate that the increase in temperature has a greater effect on characteristic self-association reactions of amines and alcohols than it has on complex formation between the amine and alcohol. This assumption can be confirmed by the hydrogen bonding enthalpy data and has been discussed extensively previously. The enthalpy for dimerization for some lower primary

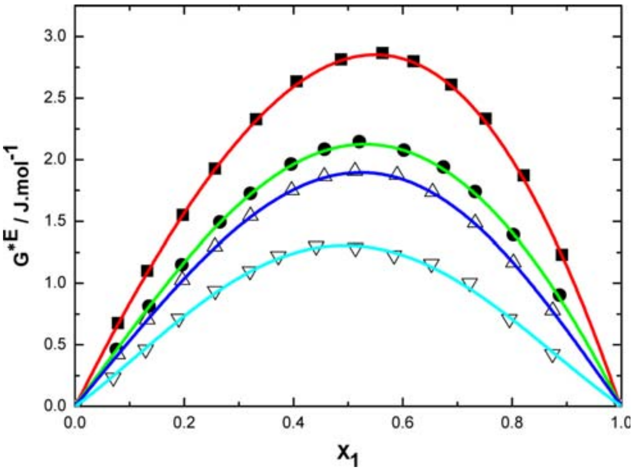

Fig. 7. Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 303.15 K.

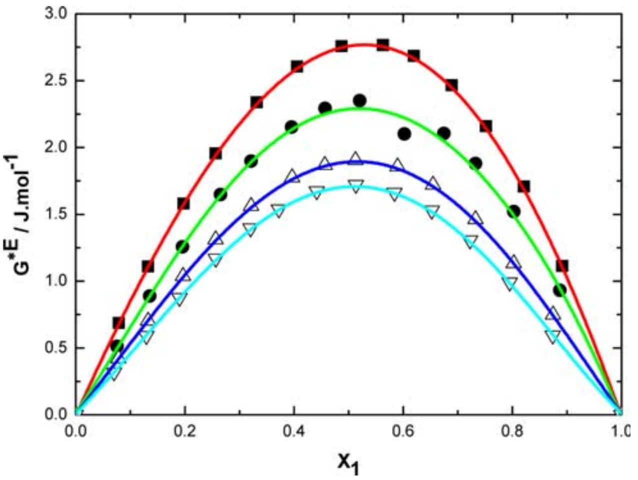

Fig. 8. Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 308.15 K.

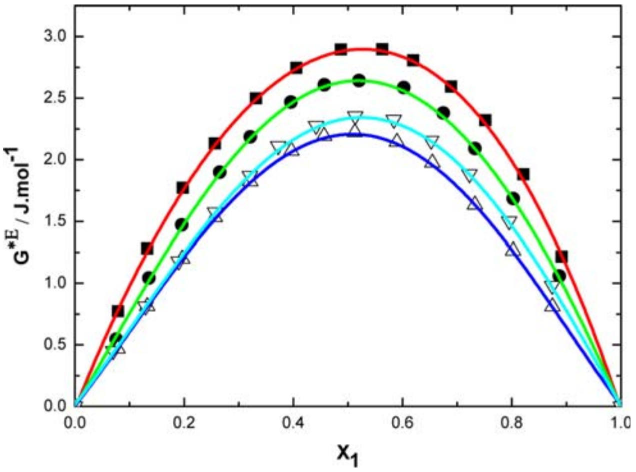

Fig. 9. Excess Gibbs energy of activation of viscous flow (G^{*E}) with mole fraction (x_1) of N-ethylaniline in the binary liquid mixtures of N-ethylaniline with tert-butanol (■), iso-butanol (●), 2-butanol (△), and 1-butanol (▽) at 313.15 K.

alcohols is in the interval from 11 to 14 kJ mol^{-1} [25], whereas the value of interaction energy of the hydrogen bond of O H----N is −39.3 kJ mol^{-1}. Consequently, the increase in temperature disturbs the simultaneous equilibria: self-association of secondary amines, self-association of alcohols and complex formation between the secondary amines and alcohol. As a result, the complex formation equilibrium is more shifted toward the complex and V_m^E becomes more negative.

The variation of V^E, and $\Delta\eta$ with mole fraction were fitted to the Redlich-Kister polynomial equation [26] of the type,

$$Y^E=x_1x_2[a_0+a_1(x_1-x_2)+a_2(x_1-x_2)^2] \tag{5}$$

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

$$\sigma(Y^E)=[(Y^E_{obs}-Y^E_{cal})^2/(n-m)]^{1/2} \tag{6}$$

where n is the total number of experimental points and m is the number of coefficients. The values of a_0, a_1 and a_2 are the coefficients determined by a multiple-regression analysis on the least square method and summarized along with the standard deviations between the experimental and fitted values of V^E, and $\Delta\eta$ (Table 4).

2. The Viscosity Data Correlation

Knowledge of the viscosity of pure liquids and respective mixtures and study of the viscosity calculation methods are important for practical and theoretical purposes. Numerous equations for liquid mixture viscosity have been proposed, and methods concerning viscosity modeling can be found in the literature [27,28]. We used three typical semi-empirical relations to correlate the experimental viscosity data of the investigated binary systems.

The equations of Grunberg-Nissan, Katti and Chaudhri, Hind et al., and Tamara and Kurata have one adjustable parameter.

Grunberg-Nissan provided the following empirical equation containing one adjustable parameter [29]. The equation is

$$\ln\eta=x_1\ln\eta_1+x_2\ln\eta_2+x_1x_2d_{12} \tag{7}$$

where d_{12} may be regarded as a parameter proportional to the interchange energy also an approximate measure of the strength of the interaction between the components.

Katti and Chaudhri [30] derived the following equation:

$$\ln\eta V=x_1\ln V_1\eta_1+x_2\ln V_2\eta_2+x_1x_2W_{vis}/RT \tag{8}$$

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

Hind et al. [31], proposed the following equation:

$$\eta=x_1^2\eta_1+x_2^2\eta_2+2x_1x_2H_{12} \tag{9}$$

where H_{12} is the Hind interaction parameter and is attributed to unlike pair interactions.

The one-parameter equation due to Tamura and Kurata [32] gave the equation of the form

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

Binary mixtures	Functions	a_0	a_1	a_2	σ
	303.15 K				
N-ethylaniline+2-methyl-2-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.590	0.336	0.353	0.001
	$\Delta\eta/mPa\cdot s$	0.542	−0.055	−0.120	0.001
N-ethylaniline+2-methyl-1-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.504	0.379	0.546	0.001
	$\Delta\eta/mPa\cdot s$	0.442	−0.016	−0.154	0.001
N-ethylaniline+2-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.376	0.330	0.487	0.001
	$\Delta\eta/mPa\cdot s$	0.370	−0.033	−0.193	0.001
N-ethylaniline+1-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.250	0.264	0.433	0.001
	$\Delta\eta/mPa\cdot s$	0.291	−0.035	−0.206	0.002
	308.15 K				
N-ethylaniline+2-methyl-2-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.696	0.361	−0.137	0.001
	$\Delta\eta/mPa\cdot s$	0.582	−0.087	−0.111	0.001
N-ethylaniline+2-methyl-1-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.644	0.345	0.048	0.001
	$\Delta\eta/mPa\cdot s$	0.477	−0.029	−0.162	0.001
N-ethylaniline+2-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.574	0.332	0.405	0.001
	$\Delta\eta/mPa\cdot s$	0.406	−0.025	−0.173	0.001
N-ethylaniline+1-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.467	0.355	0.429	0.002
	$\Delta\eta/mPa\cdot s$	0.343	−0.043	−0.228	0.001
	313.15 K				
N-ethylaniline+2-methyl-2-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.782	0.400	−0.537	0.002
	$\Delta\eta/mPa\cdot s$	0.630	−0.067	−0.012	0.001
N-ethylaniline+2-methyl-1-propanol	$V^E/cm^3\cdot mol^{-1}$	−1.734	0.370	−0.4160	0.001
	$\Delta\eta/mPa\cdot s$	0.539	−0.040	−0.182	0.002
N-ethylaniline+2-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.694	0.313	−0.092	0.001
	$\Delta\eta/mPa\cdot s$	0.466	−0.027	−0.214	0.001
N-ethylaniline+1-butanol	$V^E/cm^3\cdot mol^{-1}$	−1.630	0.335	0.078	0.002
	$\Delta\eta/mPa\cdot s$	0.3869	−0.030	−0.188	0.001

$$\eta = x_1\Phi_1\eta_1 + x_2\Phi_2\eta_2 + 2(x_1x_2\Phi_1\Phi_2)^{1/2}T_{12} \qquad (10)$$

where Φ_1 and Φ_2 are the volume fractions of components 1 and 2, respectively, T_{12} is the Tamura and Kurata constant.

The interaction parameter d_{12} is positive for binary systems. Nigam and Mahl [33] concluded from the study of binary mixtures that (i) if $\Delta\eta>0$, $d_{12}>0$ and the magnitude of both is large, then strong specific interaction; (ii) if $\Delta\eta<0$, $d_{12}>0$ then weak specific interaction; (iii) if $\Delta\eta<0$, $d_{12}<0$ the magnitude of both is large, then the dispersion force would be dominant. Fort and Moore [22] reported that for any binary liquid mixture, a positive value of d_{12} indicates the presence of specific interactions and a negative value of d_{12} indicates the presence of weak interactions between the unlike molecules. On this basis, we can say that there is a strong interaction in the binary system studied.

Interaction parameter $W_{vis/RT}$ shows almost the same trend as that of d_{12}. In fact, one could say that the parameters d_{12} and $W_{vis/RT}$ exhibit almost similar behavior, which is not unlikely in view of the logarithmic nature of both equations. Tamara and Kurata and Hind et al. represent the binary mixtures satisfactorily as compared to Grunberg-Nissan and Katti and Chaudhri. The experimental and theoretical values of viscosity of the liquid mixtures calculated using Eqs. (7)-(9) including standard deviation are presented in Table 3. All the empirical relations gave a reasonable fit, but the viscosity values calculated using Grunberg-Nissan, and Katti-Chaudhri, relation are in good agreement with the experimental values.

CONCLUSIONS

Experimental data of viscosity and density are reported for binary mixtures of N-ethyl aniline with isomeric butanols over the entire range of mole fraction at 303.15, 308.15 and 313.15 K. Calculated viscosity deviation, excess molar volume, and excess Gibbs energy of activation of viscous flow are fitted with a Redlich-Kister type polynomial equation. Positive values of viscosity deviation and excess Gibbs energy of activation of viscous flow, and negative values of excess molar volume over the whole composition range are observed for all the investigated binary systems. Thermodynamic functions of activation have been estimated for each binary mixture. The viscosity data have been correlated with several semi-empirical equations (Grunberg-Nissan, Katti-Chaudhri, and Hind et al.). The excess/deviation properties and positive values of viscosity interaction parameter can be interpreted by considering the intermolecular hydrogen bonding, molecular size and shapes of the components. The strong intermolecular interactions have a significant effect on the thermodynamic and transport properties of the investigated binary mixtures.

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