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Research Article

Hetero-Molecular Interactions in Polar-Nonpolar Binary Mixture of Different Compositions and Studies on Their Thermodynamic Properties

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Abstract

The thermodynamic properties of binary liquid mixture of 2-Bu-OH and Cumene (isopropylbenzene) have been determined at different temperatures (298.15-323.15) K by 5 K intervals over the whole composition range. The data have been utilized to estimate the excess thermodynamic properties (excess enthalpy, excess entropy, excess free energy). The result of excess properties viz: excess enthalpy of activation ($\Delta H^{\#E}$), excess entropy of activation ($\Delta S^{\#E}$) and excess free energy of activation ($\Delta G^{\#E}$) were fitted to the Redlich-Kister equation and plotted by graphical presentation. The excess values have been found to be useful in estimating the type and strength of the interactions between the polar-nonpolar binary mixture.

Keywords: Binary mixtures; Thermodynamic properties; Polar-nonpolar interactions; 2-Butanol; Cumene; Isopropylbenzene

1. Introduction

From the past few decades liquids have been studied extensively by both theoretical and experimental techniques using various physico-chemical properties. The practical nature of liquid mixtures rather than single component liquid systems, has gained much importance in assessing the nature of molecular interactions and investigating the physico-chemical behaviors [1,2]. In chemical process industries, materials are normally handled in fluid form and as a consequence, the physical, chemical, and transport properties of fluids draw attentions. Thermodynamic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules and in processing product formulation in several industrial and technological purposes. 2-Butanol (or 2-Bu-OH), is an organic polar compound normally found as an equal mixture of the two stereoisomers [3], a racemic mixture of *(R)*-(−)-2-Bu-OH and *(S)*-(+)-2-Bu-OH [4]. This secondary alcohol is a flammable, colorless liquid that is soluble in water and completely miscible with polar organic solvents such as ethers and other alcohols [5,6]. Cumene is also a colorless, flammable hydrocarbon but nonpolar liquid. It is an aromatic hydrocarbon, based on benzene having isopropyl substituent on the aromatic ring. It is part of the aromatic family and has a distinctive odor. The common uses of cumene are as solvent, dissolvent, fragrance intermediate [7]. Cumene is primarily used as a feedstock in the manufacture of phenol [8]. In view of this importance, it is of interest to study the thermodynamic properties in order to understand the interaction behavior in their binary mixtures of various proportions with the variation of temperature. In this paper, density and viscosity for the binary mixtures of 2-Bu-OH with Cumene at (298.15, 303.15, 308.15, 313.15, 318.15, 323.15) K are provided. From the experimental values of density and viscosity, thermodynamic properties and their excess thermodynamic properties have been estimated. The result of excess properties viz: excess enthalpy of activation ($\Delta H^{\#E}$), excess entropy of activation ($\Delta S^{\#E}$) and excess free energy of activation ($\Delta G^{\#E}$) were fitted to the Redlich-Kister equation [9] and plotted by graphical presentation.

2. Experimental Details

All the chemicals used in this study were purchased from Sigma Aldrich Chemicals Company. According to the manufacturer, the purities of these compounds were >99%. The water used in all experimental work was double distilled water. The binary mixtures of 2-Bu-OH and Cumene were prepared by using an analytical electrical balance with a precision of ± o.1 µg and later were converted to different composition of the mixture using dilution method. Special care was taken to prevent evaporation and the introduction of moisture into the experimental samples. To measure the viscosity Stabinger viscometer (svm-3000-stabinger-viscometer) was used. The temperature was previously set up by 298.15-323.15 K. The measurement was accomplished by the descending of the temperature in the viscometer.

Density of all binary mixtures including pure solvents was measured using an oscillation densimeter (Anton Paar DSA 5000). In both machinery processes the temperature was automatically controlled with an uncertainty of ±0.01K.

3. Theoretical Consideration

3.1 Calculation of different thermodynamic parameters for viscous flow

Liquid in a tube is considered as a combination of layers and that it flows as a rate process. To treat the viscosity as a rate process it is assumed that the motion of liquid layers involve the passage of a molecule from one equilibrium position to another in the same layer. In order to do so, it is necessary that a suitable 'hole' or site should be available and the production of such a 'hole' requires the expenditure of energy, since work must be done in pushing back other molecules. The jump of the moving molecules from one equilibrium position to the next may thus be regarded as equivalent to the passage of the system over a potential barrier. Eyring and his co-workers using absolute reaction rate theory and partition functions, correlated viscosity [10], as follows:

$$\eta = \left(\frac{hN}{V_m}\right).\mathrm{Exp}(\Delta G^{\#})/RT \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, $\Delta G^{\#}$ is the free energy of activation per mole for viscous flow, h is the Planck's constant (= 6.6262 x 10^{-34} J.sec), N is the Avogadro number (= 6.023 x 10^{23} mol^{-1}), R is the molar gas constant (= 8.3145 $JK^{-1}mol^{-1}$) T is the absolute temperature in Kelvin scale and η is the observed viscosity in mPa.s. According to the definition of $\Delta G^{\#}$ eq. (1) reduces to-

$$\eta = (hN/V_m).\exp(-T\Delta S^{\#})/RT \ldots\ldots\ldots\ldots (2)$$

$$\text{or, } \ln\left(\frac{\eta V_m}{hN}\right) = -\frac{\Delta S^{\#}}{R} + \Delta H^{\#}/RT \ldots\ldots\ldots (3)$$

Where, $\Delta H^{\#}$ is the enthalpy of activation per mole and $\Delta S^{\#}$ is the entropy of activation per mole for viscous flow.

The plot of $\ln\left(\frac{\eta V_m}{hN}\right)$ vs. **1/T** of eq. (3) gives a straight line with slope, $\Delta H^{\#}/R$ and intercept, $-\Delta S^{\#}/R$ assuming that $\Delta H^{\#}$ and $\Delta S^{\#}$ be almost independent of temperature. Therefore, $\Delta H^{\#}$ and $\Delta S^{\#}$ can easily be calculated from the slope and intercept of eq. (3) as,

$$\Delta H^{\#} = \text{Slope} \times R \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\Delta S^{\#} = -\text{Intercept} \times R \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The free energy of activation, $\Delta G^{\#}$, for viscous flow has been calculated by using the simple thermodynamic relation,

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Calculation of different excess thermodynamic parameters for viscous flow:

The excess free energy of activation ($\Delta G^{\#E}$), excess enthalpy of activation ($\Delta H^{\#E}$) and excess entropy of activation ($\Delta S^{\#E}$) for viscous flow were calculated by using the following relations,

$$\Delta G^{\#E} = \Delta G^{\#} - \Delta G^{\#}_{id} \ldots\ldots\ldots\ldots\ldots (7)$$

$$\text{or, } \Delta G^{\#E} = \Delta G^{\#} - (X_1\Delta G^{\#}_1 + X_2\Delta G^{\#}_2) \ldots\ldots\ldots\ldots (8)$$

$$\Delta H^{\#E} = \Delta H^{\#} - \Delta H^{\#}_{id} \ldots\ldots\ldots\ldots (9)$$

$$\text{or, } \Delta H^{\#E} = \Delta H^{\#} - (X_1\Delta H^{\#}_1 + X_2\Delta H^{\#}_2) \ldots\ldots\ldots\ldots (10)$$

$$\text{and } \Delta S^{\#E} = \Delta S^{\#} - \Delta S^{\#}_{id} \ldots\ldots\ldots (11)$$

$$\text{or, } \Delta S^{\#E} = \Delta S^{\#} - (X_1\Delta S^{\#}_1 + X_2\Delta S^{\#}_2) \ldots\ldots\ldots (12)$$

Where, the subscripts 1 and 2 represent the pure components of the mixture.

The experimentally obtained values of excess properties for a system can be fitted by the least square method using Redlich-Kister Eq. (13) of the form:

$$(Y)^{E} = x_1 x_2 \sum_{i\geq 0}(1 - 2x_1)B_i \quad \text{.....} \quad (13)$$

4. Results and Discussion

4.1 Density and Viscosity of the binary mixture

The density and viscosity values of binary mixture as a function of the mole fraction of 2-Bu-OH(x_1) respectively at temperatures (298.15 to 323.15) K are listed in tables 1 and 2. The corresponding plotting of these values are displayed to observe the trend of changing these properties by figures 1 and 2. The changes of the properties are evaluated for the changes of each proportion of the mixture component along with the variation of temperatures.

Mole fraction of X		**Experimental Density r $\times 10^{-3}$ / kgm^{-3}**					
2-Bu-OH	**Cumene**	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
x1	**x2**						
0	1	0.8577	0.8535	0.8492	0.8449	0.8406	0.8363
0.05	0.95	0.8552	0.8509	0.8465	0.8422	0.8378	0.8334
0.1	0.9	0.8526	0.8483	0.8439	0.8395	0.835	0.8306
0.15	0.85	0.8503	0.8459	0.8415	0.8371	0.8326	0.8281
0.2001	0.7999	0.8479	0.8435	0.839	0.8345	0.83	0.8255
0.2503	0.7497	0.8454	0.841	0.8365	0.832	0.8275	0.823
0.3001	0.6999	0.843	0.8386	0.8341	0.8296	0.825	0.8205
0.3502	0.6498	0.8407	0.8362	0.8317	0.8272	0.8226	0.818
0.3992	0.6008	0.8385	0.834	0.8295	0.825	0.8204	0.8158
0.4502	0.5498	0.8361	0.8317	0.8271	0.8226	0.818	0.8134
0.5002	0.4998	0.8333	0.8288	0.8243	0.8198	0.8152	0.8105
0.5503	0.4497	0.8306	0.8261	0.8216	0.8171	0.8124	0.8078
0.5999	0.4001	0.8279	0.8234	0.8189	0.8143	0.8097	0.805
0.6502	0.3498	0.8251	0.8206	0.8161	0.8115	0.8068	0.8021
0.7001	0.2999	0.8223	0.8178	0.8133	0.8087	0.8041	0.7994
0.7503	0.2497	0.8193	0.8149	0.8104	0.8058	0.8011	0.7964
0.8001	0.1999	0.8163	0.8118	0.8073	0.8028	0.7981	0.7934
0.85	0.15	0.8131	0.8088	0.8043	0.7997	0.7951	0.7904
0.9001	0.1	0.8096	0.8053	0.8009	0.7964	0.7918	0.7871
0.9499	0.0501	0.8055	0.8013	0.7969	0.7925	0.788	0.7833
1	0	0.8027	0.7985	0.7942	0.7898	0.7853	0.7807

Table 1: Density (ρ) of 2-Bu-OH + Cumene system for different molar ratios at 298.15 K to 323.15 K by 5 K intervals

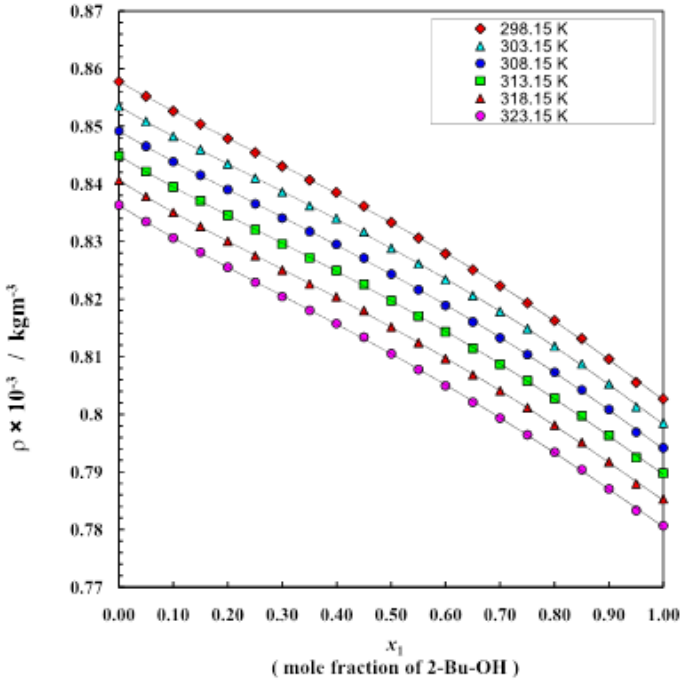

Figure 1: Density change for different mole fractions at different temperatures

Mole fraction of X		Experimental Viscosity (η) mPa.s					
2-Bu-OH	Cumene	298.15	303.15	308.15	313.15	318.15	323.15
x1	x2						
0	1	0.7267	0.68	0.6376	0.599	0.5637	0.5316
0.05	0.95	0.7189	0.6713	0.6282	0.5892	0.5536	0.5212
0.1	0.9	0.7244	0.6749	0.6303	0.5899	0.5531	0.5192
0.15	0.85	0.7356	0.6839	0.6372	0.5949	0.5564	0.5223
0.2001	0.7999	0.7495	0.6953	0.6465	0.6026	0.5626	0.5265
0.2503	0.7497	0.7668	0.7098	0.6588	0.6125	0.5706	0.5328
0.3001	0.6999	0.7867	0.7267	0.6729	0.6244	0.5805	0.5419
0.3502	0.6499	0.8107	0.7469	0.6899	0.6386	0.5924	0.552
0.3992	0.6008	0.8396	0.7704	0.7085	0.6542	0.6063	0.5612
0.4502	0.5498	0.8795	0.8028	0.7357	0.6763	0.6238	0.5785
0.5002	0.4998	0.9207	0.8376	0.7649	0.7007	0.6439	0.5948
0.5503	0.4497	0.997	0.8965	0.8097	0.7348	0.6711	0.6182
0.5999	0.4001	1.0685	0.9534	0.855	0.7714	0.7009	0.6429
0.6502	0.3498	1.1355	1.012	0.9064	0.816	0.7389	0.6742
0.7001	0.2999	1.2462	1.1024	0.9796	0.8751	0.7868	0.7138

0.7503	0.2497	1.3628	1.1994	1.0617	0.945	0.8457	0.7631
0.8001	0.1999	1.5256	1.3327	1.1714	1.0357	0.9212	0.8244
0.85	0.15	1.7423	1.5062	1.3112	1.1487	1.0122	0.9
0.9001	0.1	2.0491	1.7512	1.5072	1.3059	1.1387	1.0024
0.9499	0.0501	2.4528	2.0719	1.7634	1.5121	1.306	1.1392
1	0	3.0807	2.5601	2.1443	1.8103	1.5401	1.3207

Table 2: Viscosity of 2-Bu-OH + Cumene system for different molar ratios at 298.15 K to 323.15 K by 5 K intervals

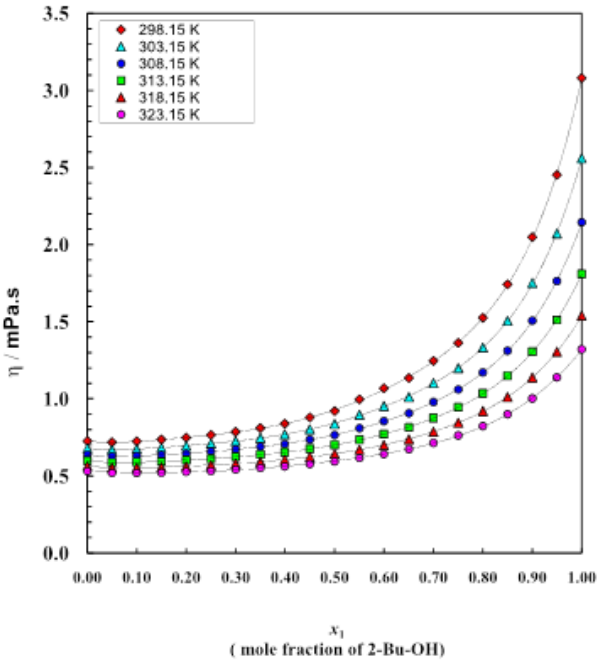

Figure 2: Viscosity curve for different mole fractions at different temperatures

4.2 Thermodynamic properties measurement

The three types of very important thermodynamic properties viz. enthalpy, entropy, and free energy were very intensively studied for the binary mixture of polar + nonpolar interaction. There excess values were also calculated and fitted in Redlich-kister fitting equation (eq.13). The overall data are provided by tables 3-10. The trend of changing due to miscibility is displayed by figures 3-8. Table 3 is for enthalpy study and its corresponding plots are by figures 3,4. Table 4 is for entropy study and it's corresponding plots are by figures 5,6. Data for the free energy study of this binary mixture were provided by tables 5-10 and corresponding plotting are shown by figures 7,8.

Mole fraction of		Enthalpy (Expt.)	Enthalpy (Theor.)	Excess Enthalpy	Fitting
2-Bu-OH	Cumene	$\Delta H^{\#}$ kJmol^{-1}	$\Delta H^{\neq}_{id}$ kJmol^{-1}	$\Delta H^{\#E}$ kJmol^{-1}	$\Delta H^{\#E*}$ kJmol^{-1}
x_1	x_2				
0	1	9.21	9.21	0	0
0.05	0.95	9.4792	10.0624	-0.5833	-0.6385
0.1	0.9	9.823	10.9158	-1.0928	-1.0867
0.15	0.85	10.1411	11.769	-1.6279	-1.5668
0.2001	0.7999	10.4602	12.623	-2.1628	-2.1274
0.2503	0.7497	10.8045	13.4785	-2.674	-2.726
0.3001	0.6999	11.0943	14.3285	-3.2342	-3.2848
0.3502	0.6498	11.4636	15.1822	-3.7186	-3.7445
0.3992	0.6008	12.0004	16.0194	-4.019	-4.0609
0.4502	0.5498	12.5615	16.8889	-4.3274	-4.2463
0.5002	0.4998	13.1307	17.7421	-4.6113	-4.3137
0.5503	0.4497	14.4789	18.5959	-4.117	-4.3121
0.5999	0.4001	15.4402	19.4413	-4.001	-4.2859
0.6502	0.3498	15.8413	20.3005	-4.4592	-4.2614
0.7001	0.2999	17.0098	21.1514	-4.1416	-4.2341
0.7503	0.2497	17.7091	22.0067	-4.2977	-4.1578
0.8001	0.1999	18.8262	22.856	-4.0297	-3.9493
0.85	0.15	20.2898	23.7076	-3.4177	-3.4981
0.9001	0.1	22.043	24.5613	-2.5183	-2.6984
0.9499	0.0501	23.714	25.4111	-1.6971	-1.5093
1	0	26.266	26.266	0	0

Table 3: Enthalpy ($\Delta H^{\#}$), Excess Enthalpy ($\Delta H^{\#E}$) and Fitting value ($\Delta H^{\#E*}$) of activation for viscous flow for different molar ratios

D_0	D_1	D_2	D_3	D_4	D_5	SD
-17.2544	-1.0101	-3.41	-33.4203	-3.8964	27.3415	0.17052

Table 3(a): Redlich-Kister equation constants

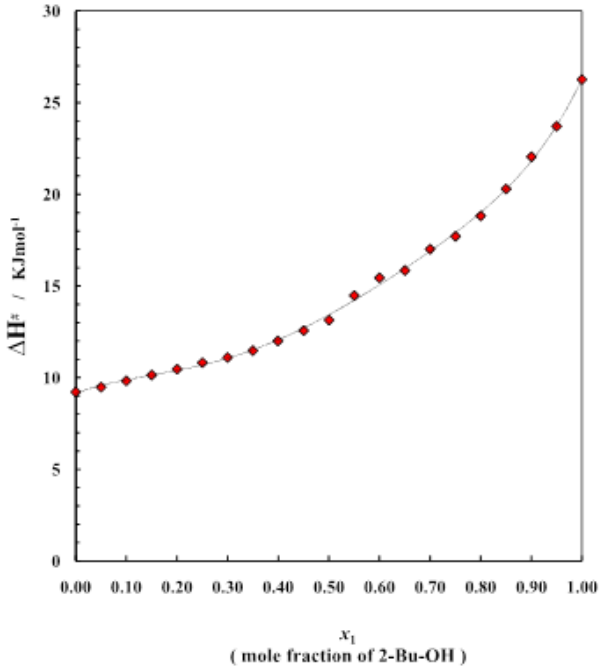

Figure 3: Enthalpy curve for different mole fractions

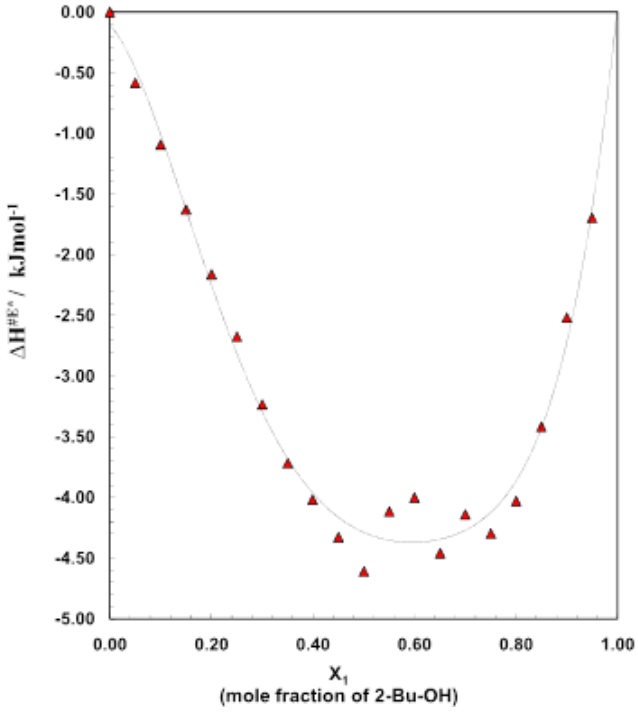

Figure 4: Excess enthalpy curve for different mole fractions

Figure 3 shows the plot of enthalpy of activation $\Delta H^{\#}$ for the transport process vs. mole fraction of alcohol for the system over the whole range of composition (0 to 1). It is noticed that for the binary system $\Delta H^{\#}$ value (table 3) continues to rise on addition of alcohol and eventually reach the value of pure 2-Bu-OH because H-bonded liquids, like 2-Bu-OH always require higher enthalpy for activation than that of the other low polar or nonpolar liquids. The excess enthalpies of the binary mixtures of aromatic hydrocarbons with 2-Bu-OH are represented by the figure 4. The excess enthalpy of activation for viscous flow ($\Delta H^{\#E}$) show the negative values extended over a considerable region of concentrations.

Mole fraction of		Entropy (Expt.) $\Delta S^{\#}$ $Jmol^{-1}$ K^{-1}	Entropy (Theor.) $\Delta S^{\#}_{id}$ $Jmol^{-1}$ K^{-1}	Excess Entropy $\Delta S^{\#E}$ $Jmol^{-1}$ K^{-1}	Fitting Value
2-Bu-OH	Cumene				
x_1	x_2				
0	1	-53.478	-53.47797	0	0
0.05	0.95	-52.3478	-51.04396	-1.3038	-1.3038
0.1	0.9	-51.1202	-48.60734	-2.5129	-2.5129
0.15	0.85	-50.0343	-46.17127	-3.863	-3.863
0.2001	0.7999	-48.9736	-43.73286	-5.2408	-5.2408
0.2503	0.7497	-47.8593	-41.29028	-6.569	-6.569
0.3001	0.6999	-46.9438	-38.86318	-8.0807	-8.0807
0.3502	0.6498	-45.7949	-36.42566	-9.3693	-9.3693
0.3992	0.6008	-44.1219	-34.03524	-10.0867	-10.0867
0.4502	0.5498	-42.4454	-31.55254	-10.8928	-10.8928
0.5002	0.4998	-40.7529	-29.11651	-11.6364	-11.6364
0.5503	0.4497	-36.6974	-26.67861	-10.0188	-10.0188
0.5999	0.4001	-33.8644	-24.26473	-9.5997	-9.5997
0.6502	0.3498	-32.8549	-21.81155	-11.0433	-11.0433
0.7001	0.2999	-29.5224	-19.38178	-10.1406	-10.1406
0.7503	0.2497	-27.7299	-16.93968	-10.7902	-10.7902
0.8001	0.1999	-24.7277	-14.51492	-10.2128	-10.2128
0.85	0.15	-20.717	-12.08335	-8.6336	-8.6336
0.9001	0.1	-15.9815	-9.64578	-6.3358	-6.3358
0.9499	0.0501	-11.6634	-7.21941	-4.444	-4.444
1	0	-4.7782	-4.77824	0	0

Table 4: Entropy ($\Delta S^{\#}$), Excess Entropy ($\Delta S^{\#E}$) and Fitting value ($\Delta S^{\#E^*}$) of Activation for viscous flow for different molar ratios

E_0	E_1	E_2	E_3	E_4	E_5	SD
-42.8451	1.3533	-8.362	-103.6268	-9.7473	83.7869	0.53364

Table 4(a): Redlich-Kister equation constants

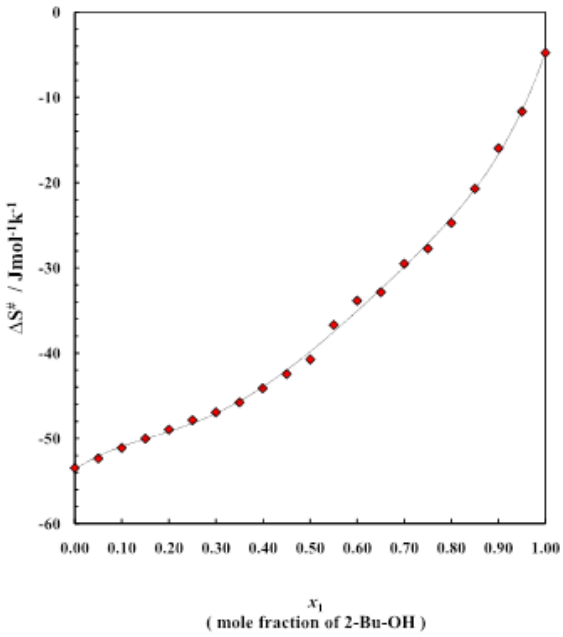

Figure 5: Entropy curve for different mole fractions

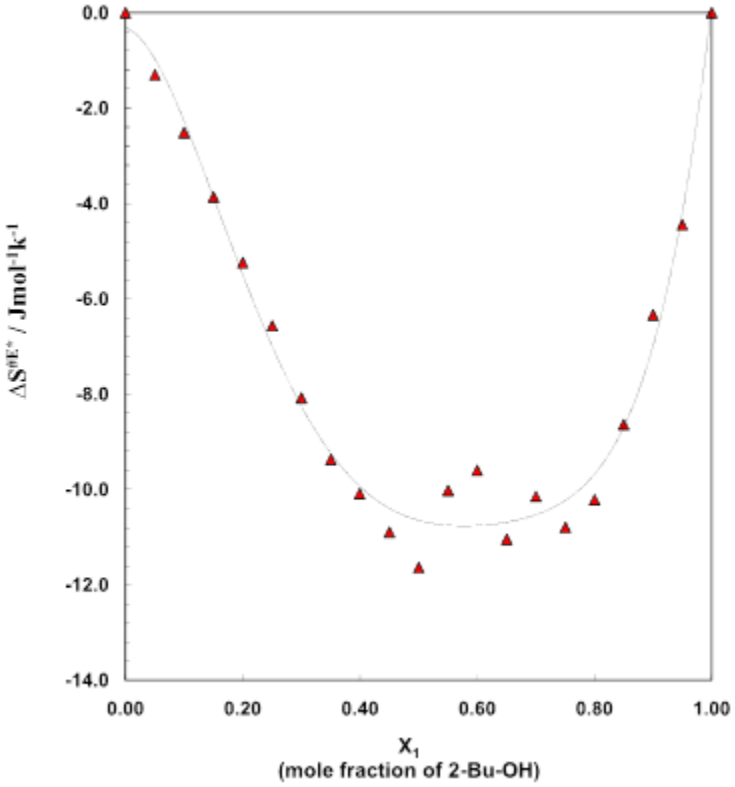

Figure 6: Excess entropy curve for different mole fractions

Figure 5 is for the plots of entropy of activation $\Delta S^{\#}$ for the viscous flow vs. mole fraction of alcohol for this binary system. The corresponding data are listed in table 4. The typical nature of the small and negative ($\Delta S^{\#}$) value of alcohol indicates that during the viscous flow of initial H-bonded order breaks down to form the activated complex of little ordered structure. On the other hand, negative ($\Delta S^{\#}$) value for the aromatic hydrocarbons revealed that during the flow process the activated complex formed, are much more ordered than of the initial state. Figure 5 also reveals that with increases of concentration of alcohol, the negative value decreases for the binary system of 2-Bu-OH + Cumene respectively. It indicates that during the flow process at the certain composition of mixtures, the molecular order of the activated and inactivated state for each of the mixtures is same. The excess entropy $\Delta S^{\#E}$ of activation for the system are shown (Figure 6) as a function of mole fraction of 2-Bu-OH. The plot of $\Delta S^{\#E}$ vs. mole fraction of 2-Bu-OH (Figure 6) for the binary mixture show an almost similar trend at those of the excess enthalpy ($\Delta H^{\#E}$). The curve has been found to be concave in nature. The negative excess entropy signifies that the species formed in the activated state are more ordered than what is to be expected to the additive law.

Mole fraction of		Free Energy (Expt.) $\Delta G^{\#}$ kJmol^{-1}	Free Energy (Theor.) $\Delta G^{\#}_{id}$ kJmol^{-1}	Excess Free Energy $\Delta G^{\#E}$ kJmol^{-1}	Fitting Value $\Delta G^{\#E*}$ kJmol^{-1}
2-Bu-OH	Cumene				
x_1	x_2				
0	1	25.1544	25.1544	0	0
0.05	0.95	25.0867	25.2812	-0.1945	-0.1973
0.1	0.9	25.0645	25.4081	-0.3436	-0.3441
0.15	0.85	25.0588	25.535	-0.4761	-0.473
0.2001	0.7999	25.0616	25.6619	-0.6003	-0.5969
0.2503	0.7497	25.0737	25.7892	-0.7154	-0.7174
0.3001	0.6999	25.0906	25.9156	-0.825	-0.8296
0.3502	0.6499	25.1174	26.0425	-0.9251	-0.9294
0.3992	0.6008	25.1554	26.167	-1.0116	-1.0108
0.4502	0.5498	25.2166	26.2963	-1.0797	-1.0758
0.5002	0.4998	25.2812	26.4231	-1.1419	-1.1202
0.5503	0.4497	25.4203	26.5501	-1.1298	-1.1469
0.5999	0.4001	25.5369	26.6758	-1.1389	-1.1569
0.6502	0.3498	25.637	26.8036	-1.1666	-1.1504
0.7001	0.2999	25.8119	26.9301	-1.1182	-1.1245
0.7503	0.2497	25.9768	27.0573	-1.0806	-1.0721
0.8001	0.1999	26.1988	27.1836	-0.9848	-0.9836
0.85	0.15	26.4666	27.3102	-0.8436	-0.8448
0.9001	0.1	26.8079	27.4372	-0.6293	-0.6408
0.9499	0.0501	27.1914	27.5635	-0.3721	-0.3614
1	0	27.6907	27.6907	0	0

Table 5: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 298.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-4.4802	-1.4136	-0.9169	-2.5236	-0.9902	2.3599	0.0118

Table 5(a): Redlich-Kister equation constants

Mole fraction of		Free Energy (Expt.) $\Delta G^{\#}$ kJmol^{-1}	Free Energy (Theor.) $\Delta G^{\#}_{id}$ kJmol^{-1}	Excess Free Energy $\Delta G^{\#E}$ kJmol^{-1}	Fitting Value $\Delta G^{\#E*}$ kJmol^{-1}
2-Bu-OH	Cumene				
x_1	x_2				
0	1	25.4218	25.4218	0	0
0.05	0.95	25.3484	25.5364	-0.188	-0.1962
0.1	0.9	25.3201	25.6511	-0.3311	-0.3669
0.15	0.85	25.309	25.7658	-0.4568	-0.5164

0.2001	0.7999	25.3065	25.8806	-0.5741	-0.6457
0.2503	0.7497	25.313	25.9956	-0.6826	-0.756
0.3001	0.6999	25.3253	26.1099	-0.7846	-0.8479
0.3502	0.6499	25.3464	26.2246	-0.8783	-0.924
0.3992	0.6008	25.376	26.3372	-0.9612	-0.9841
0.4502	0.5498	25.4288	26.454	-1.0252	-1.0328
0.5002	0.4998	25.485	26.5687	-1.0837	-1.0666
0.5503	0.4497	25.6038	26.6835	-1.0797	-1.0854
0.5999	0.4001	25.7062	26.7971	-1.0909	-1.0885
0.6502	0.3498	25.8013	26.9126	-1.1114	-1.0762
0.7001	0.2999	25.9595	27.027	-1.0675	-1.0393
0.7503	0.2497	26.1154	27.142	-1.0266	-0.9777
0.8001	0.1999	26.3224	27.2562	-0.9337	-0.8769
0.85	0.15	26.5702	27.3706	-0.8004	-0.7279
0.9001	0.1	26.8878	27.4854	-0.5976	-0.5164
0.9499	0.0501	27.2497	27.5996	-0.3499	-0.2575
1	0	27.7145	27.7145	0	0

Table 6: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 303.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-4.2659	-1.4204	-0.8751	-2.0055	-0.9414	1.941	0.0092

Table 6(a): Redlich-Kister equation constants

Mole fraction of		**Free Energy (Expt.)** $\Delta G^{\#}$ **kJmol^{-1}**	**Free Energy (Theor.)** $\Delta G^{\#}_{id}$ **kJmol^{-1}**	**Excess Free Energy** $\Delta G^{\#E}$ **kJmol^{-1}**	**Fitting Value** $\Delta G^{\#E*}$ **kJmol^{-1}**
2-Bu-OH	**Cumene**				
x_1	x_2				
0	1	25.6892	25.6892	0	0
0.05	0.95	25.6102	25.7916	-0.1815	-0.1825
0.1	0.9	25.5757	25.8942	-0.3185	-0.3192
0.15	0.85	25.5592	25.9967	-0.4375	-0.4363
0.2001	0.7999	25.5514	26.0993	-0.5479	-0.5455
0.2503	0.7497	25.5523	26.2021	-0.6497	-0.65
0.3001	0.6999	25.56	26.3042	-0.7442	-0.7472
0.3502	0.6499	25.5753	26.4068	-0.8314	-0.835
0.3992	0.6008	25.5966	26.5073	-0.9108	-0.9085

0.4502	0.5498	25.641	26.6118	-0.9708	-0.9694
0.5002	0.4998	25.6888	26.7143	-1.0255	-1.0131
0.5503	0.4497	25.7873	26.8169	-1.0297	-1.0407
0.5999	0.4001	25.8756	26.9185	-1.0429	-1.052
0.6502	0.3498	25.9655	27.0217	-1.0562	-1.0461
0.7001	0.2999	26.1071	27.1239	-1.0168	-1.0202
0.7503	0.2497	26.254	27.2267	-0.9727	-0.9686
0.8001	0.1999	26.4461	27.3287	-0.8827	-0.8841
0.85	0.15	26.6738	27.431	-0.7573	-0.7558
0.9001	0.1	26.9677	27.5336	-0.5659	-0.5718
0.9499	0.0501	27.308	27.6357	-0.3277	-0.3229
1	0	27.7384	27.7384	0	0

Table 7: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 308.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-4.0517	-1.4272	-0.8333	-1.4873	-0.8927	1.522	0.0067

Table 7(a): Redlich-Kister equation constants

Mole fraction of		**Free Energy (Expt.)** $\Delta G^{\#}$ **kJmol^{-1}**	**Free Energy (Theor.)** $\Delta G^{\#}_{id}$ **kJmol^{-1}**	**Excess Free Energy** $\Delta G^{\#E}$ **kJmol^{-1}**	**Fitting Value** $\Delta G^{\#E*}$ **kJmol^{-1}**
2-Bu-OH	**Cumene**				
x_1	x_2				
0	1	25.9566	25.9566	0	0
0.05	0.95	25.8719	26.0469	-0.175	-0.1751
0.1	0.9	25.8313	26.1372	-0.3059	-0.3067
0.15	0.85	25.8093	26.2275	-0.4182	-0.4179
0.2001	0.7999	25.7962	26.3179	-0.5217	-0.5199
0.2503	0.7497	25.7916	26.4085	-0.6169	-0.6163
0.3001	0.6999	25.7948	26.4985	-0.7037	-0.7061
0.3502	0.6499	25.8043	26.5889	-0.7846	-0.7878
0.3992	0.6008	25.8172	26.6775	-0.8603	-0.8573
0.4502	0.5498	25.8533	26.7696	-0.9163	-0.9163
0.5002	0.4998	25.8925	26.8599	-0.9674	-0.9595
0.5503	0.4497	25.9707	26.9503	-0.9796	-0.9876
0.5999	0.4001	26.0449	27.0398	-0.9949	-0.9995
0.6502	0.3498	26.1298	27.1308	-1.001	-0.9939
0.7001	0.2999	26.2547	27.2208	-0.9661	-0.968

0.7503	0.2497	26.3927	27.3114	-0.9187	-0.9168
0.8001	0.1999	26.5697	27.4013	-0.8316	-0.8344
0.85	0.15	26.7774	27.4915	-0.7141	-0.7113
0.9001	0.1	27.0476	27.5818	-0.5342	-0.5372
0.9499	0.0501	27.3664	27.6718	-0.3055	-0.3036
1	0	27.7623	27.7623	0	0

Table 8: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 313.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-3.8375	-1.4339	-0.7915	-0.9693	-0.8439	1.1032	0.0045

Table 8(a): Redlich-Kister equation constants

Mole fraction of		**Free Energy (Expt.)** $\Delta G^{\#}$ **kJmol^{-1}**	**Free Energy (Theor.)** $\Delta G^{\#}_{id}$ **kJmol^{-1}**	**Excess Free Energy** $\Delta G^{\#E}$ **kJmol^{-1}**	**Fitting Value** $\Delta G^{\#E*}$ **kJmol^{-1}**
2-Bu-OH	**Cumene**				
x_1	x_2				
0	1	26.224	26.224	0	0
0.05	0.95	26.1336	26.3021	-0.1684	-0.1677
0.1	0.9	26.0869	26.3802	-0.2934	-0.2943
0.15	0.85	26.0595	26.4584	-0.3989	-0.3996
0.2001	0.7999	26.0411	26.5366	-0.4955	-0.4942
0.2503	0.7497	26.0309	26.615	-0.584	-0.5826
0.3001	0.6999	26.0295	26.6928	-0.6633	-0.6649
0.3502	0.6499	26.0333	26.771	-0.7377	-0.7406
0.3992	0.6008	26.0378	26.8477	-0.8099	-0.8062
0.4502	0.5498	26.0655	26.9273	-0.8618	-0.8631
0.5002	0.4998	26.0963	27.0055	-0.9092	-0.906
0.5503	0.4497	26.1542	27.0837	-0.9295	-0.9345
0.5999	0.4001	26.2142	27.1611	-0.9469	-0.9471
0.6502	0.3498	26.2941	27.2398	-0.9457	-0.9418
0.7001	0.2999	26.4024	27.3178	-0.9154	-0.9159
0.7503	0.2497	26.5313	27.3961	-0.8648	-0.8651
0.8001	0.1999	26.6933	27.4739	-0.7805	-0.7847
0.85	0.15	26.8809	27.5519	-0.6709	-0.6668
0.9001	0.1	27.1275	27.6301	-0.5026	-0.5027
0.9499	0.0501	27.4247	27.7079	-0.2832	-0.2844
1	0	27.7862	27.7862	0	0

Table 9: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 318.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-3.6233	-1.4407	-0.7497	-0.4511	-0.7952	0.6842	0.003

Table 9(a): Redlich-Kister equation constants

Mole fraction of		**Free Energy (Expt.)** $\Delta G^{\#}$ **kJmol^{-1}**	**Free Energy (Theor.)** $\Delta G^{\#}_{id}$ **kJmol^{-1}**	**Excess Free Energy** $\Delta G^{\#E}$ **kJmol^{-1}**	**Fitting Value** $\Delta G^{\#E*}$ **kJmol^{-1}**
2-Bu-OH	**Cumene**				
x_1	x_2				
0	1	26.4914	26.4914	0	0
0.05	0.95	26.3954	26.5573	-0.1619	-0.1603
0.1	0.9	26.3425	26.6233	-0.2808	-0.2818
0.15	0.85	26.3097	26.6892	-0.3796	-0.3812
0.2001	0.7999	26.286	26.7553	-0.4693	-0.4685
0.2503	0.7497	26.2702	26.8214	-0.5512	-0.5489
0.3001	0.6999	26.2642	26.8871	-0.6229	-0.6237
0.3502	0.6499	26.2623	26.9531	-0.6909	-0.6934
0.3992	0.6008	26.2584	27.0179	-0.7595	-0.755
0.4502	0.5498	26.2777	27.0851	-0.8074	-0.8099
0.5002	0.4998	26.3001	27.1511	-0.851	-0.8524
0.5503	0.4497	26.3377	27.2171	-0.8794	-0.8814
0.5999	0.4001	26.3835	27.2824	-0.8989	-0.8946
0.6502	0.3498	26.4584	27.3489	-0.8905	-0.8896
0.7001	0.2999	26.55	27.4147	-0.8647	-0.8637
0.7503	0.2497	26.67	27.4808	-0.8108	-0.8133
0.8001	0.1999	26.817	27.5465	-0.7295	-0.7349
0.85	0.15	26.9845	27.6123	-0.6278	-0.6223
0.9001	0.1	27.2074	27.6783	-0.4709	-0.4682
0.9499	0.0501	27.483	27.744	-0.261	-0.2651
1	0	27.8101	27.8101	0	0

Table 10: Free energy ($\Delta G^{\#}$), Excess Free energy ($\Delta G^{\#E}$) and Fitting value ($\Delta G^{\#E*}$) of Activation for viscous flow at 323.15 K

F_0	F_1	F_2	F_3	F_4	F_5	SD
-3.409	-1.4475	-0.7079	0.0671	-0.7465	0.2652	0.0035

Table 10(a): Redlich-Kister equation constants

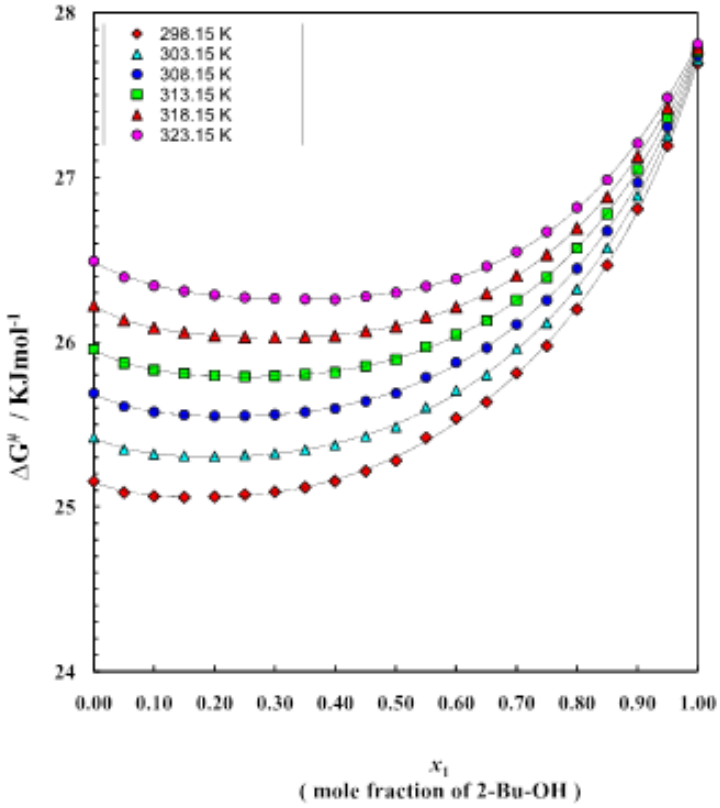

Figure 7: Free energy curve for different mole fractions at different temperatures

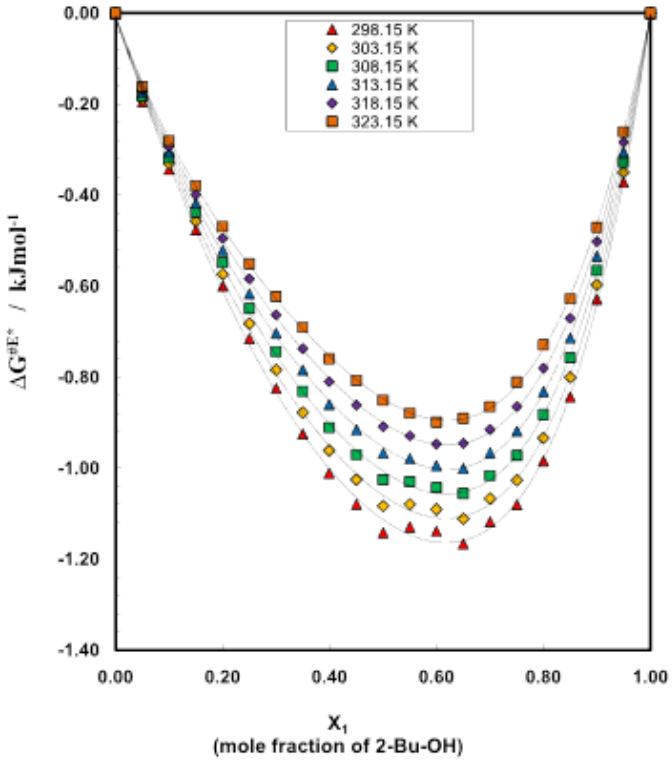

Figure 8: Excess free energy curve for different mole fractions at different temperatures

Tables 5-10 show the variation of free energy of activation $\Delta G^{\#}$ for the viscous flow of the system as a function of 2-Bu-OH under the whole range of composition at temperature 298.15 K to 323.15 K. And trend of changing this thermodynamic property are given by figure 7. The $\Delta G^{\#}$ values increase very slowly in the initial stage which is followed by a relatively greater rise with increasing concentration of 2-Bu-OH. The curves for $\Delta G^{\#}$ for the system are found to be smooth and similar. But a crossover of curves between temperature 298.15 K and 323.15 K is noticed in the system at higher mole fraction of 2-Bu-OH. It is also revealed from the figure 7 that the nonpolar (Cumene) rich region the $\Delta G^{\#}$ values increase slightly with the rise of temperature but at the alcohol rich region it is vice versa. Figure 8 shows the variation of excess free energy $\Delta G^{\#E}$ of activation at 298.15 K to 323.15 K over the whole composition range for this binary system (Table 5-10). In each case, the $\Delta G^{\#E}$ values are negative, but with the rise of temperature, the values are less negative, i.e., $(\delta\Delta G^{\#E}/\Delta T)_p$ is positive. The general nature of the curves does not virtually change with the variation of temperature. The negative excess free energies indicate according to the Eyring $\ln\left(\frac{\eta V_m}{hN}\right) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R}$ that the viscous flow of the solutions of the aromatic hydrocarbons in 2-Bu-OH is enhanced, causing the viscosity to decrease from the values expected ideally.

The excess values throughout the whole concentration range are negative with minima falling around 0.62 mole fraction of 2-Bu-OH. The free energy of activation is often regarded to be an energy barrier that a molecule must surmount in order to make a hole which is a necessary requirement for a molecule to flow through [11]. The negative excess free energy indicates the reduction of energy barrier height and hence increases of viscous flow.

5. Conclusion

The properties of binary liquid mixtures are of interest to experimental chemists and physicists and to the pharmaceutical as well as chemical industries [12,13]. An understanding of the thermodynamic properties of 2-Bu-OH and Cumene and their binary system have been measured at temperatures (298.15 to 323.15) K and in atmospheric pressure. Excess thermodynamic properties of binary mixture solvents were calculated and fitted with the Redlich–Kister equation. Besides knowing the very important thermodynamic behaviors of the liquid mixture at different proportions we also got some ideas about the polar-nonpolar interactions between these mixing components which are mainly for dipole–induced dipole interaction thus breaking of self-network built by H-bond among the polar molecules and rising dispersion force of nonpolar liquid. The observed excess values (excess enthalpy, excess entropy, excess free energy) in all the mixture indicate the significant interaction between the unlike molecules. Cumene is comparatively highly densed than 2-Bu-OH and the almost linear decreasing trend is observed with the addition of 2-Bu-OH as well as with the increasing of temperature (Figure 1). From table 2 and figure 2 it can be observed that viscosity of the binary mixture of 2-Bu-OH + Cumene increases in very disciplined way with the increasing proportion of 2-Bu-OH but decreases almost linearly with temperature rises. Here the nonpolar Cumene is low viscous liquid and when it interacts with the polar one it breaks the intermolecular network of the 2-Bu-OH which was built due to a lot of H-bonds and by polar-polar interactions between adjacent molecules. There was an induction of polarity occurred in Cumene and become induced dipole and attached to the polar 2-Bu-OH. Thus, the liquid mixture becomes more viscous than individual Cumene. From figure 2 the rising of viscosity was first observed slowly but when the polar proportion is higher it rises sharply upward.

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