Binary Mixture of Pharmaceutical Residual Solvents and Their Thermodynamic Investigation

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Abstract

Molecular interaction of pharmaceutical residual solvents mixture (2-Butanol with m-Xylene) were studied through deep investigation on thermodynamic properties (Enthalpy, Entropy, Free energy) over the entire range of composition at temperature of 298.15 K to 323.15 K and at atmospheric pressure. Results are interpreted and reported in the light of solvation process which is referred to as the transition of molecules from their own environment. Next, the excess thermodynamic properties were calculated, and these excess properties were fitted by the Redlich–Kister polynomial equation. The calculated excess properties are discussed in terms of molecular interactions between 2-Butanol and m-Xylene.

Keywords: Residual solvent; Thermodynamic property; Binary mixture; 2-Butanol; m-Xylene

1. Introduction

The pharmaceutical industry is one of the largest users of organic solvents per amount of the final product [1-3]. Organic solvents are constantly present in the pharmaceutical production processes and the properties of binary liquid mixtures are of interest to pharmacist, medicinal scientists, condensed-matter theorists, experimental chemists, and physicists etc. An understanding of the intermolecular forces which give rise to the diverse phenomena observed experimentally is important for both practical and applications-oriented reasons. In chemical process industries, materials are normally handled in fluid form and therefore, the physical, chemical, and transport properties of fluids draw attention. Thermodynamic investigation of liquid mixtures consisting of polar and nonpolar components is of considerable importance in understanding the

intermolecular interaction between the component molecules and in processing product formulation in several industrial and technological purposes. Residual solvents testing become one of the important parts of quality control in pharmaceuticals [4, 5].

Residual solvents in pharmaceutical products are defined as organic volatile compounds that are used or produced in the manufacturing of drug substances or excipients, or in the preparation of drug products. Among the residual solvents 2-Butanol (or 2-Bu-OH) and xylene are very significant in the view of pharmaceutical importance [6, 7]. 2-Bu-OH is an organic polar compound normally found as an equal mixture of the two stereoisomers, a racemic mixture of *(R)*-(−)-2-Bu-OH and *(S)*-(+)-2-Bu-OH. 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 [8, 9]. Xylene is used in medical technology, dentistry and in industry as a solvent and in the manufacture of pesticides, chemical and pharmaceutical products [10, 11]. m-Xylene (or m-Xln), the most important type of xylene, is an aromatic hydrocarbon, based on benzene with two methyl substituents where "m" stands for meta, meaning the two methyl substituents are at location 1 and 3 on the aromatic ring.

The practical importance of liquid mixtures rather than single component liquid systems, has gained much importance in assessing the nature of molecular interactions and in investigating the physico-chemical behaviors of such systems [12, 13, 14]. The systematic survey of literature shows that there is no systematic study specially on thermodynamic

properties present in the binary mixture containing 2-Bu-OH and m-Xln with highly intensive observation of every specific proportion. 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. From the experimental values of density and viscosity, thermodynamic properties and their excess thermodynamic properties have been estimated at 298.15 K to 323.15 K. 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 [15] and plotted by graphical presentation.

2. Experimental details

2-Bu-OH and m-Xln used in this research 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 in quality. The binary mixtures of 2-Bu-OH and m-Xln 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.

Density of all binary mixtures including pure solvents was measured using an oscillation densimeter (Anton Paar DSA 5000). 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. In both machinery processes the

temperature was automatically controlled with an uncertainty of ±0.01 K.

3. Theoretical aspects

3.1 Calculation of different thermodynamic parameters for viscous flow:

Fluidity of liquid follows some mechanisms as liquid is considered as a combination of layers and so it flows as a rate process. To treat the viscosity as a rate process it is assumed that the motion of liquid layers involves the passage of a molecule from one equilibrium position to another in the same layer. 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 [16] as follows:

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

Where, $\Delta G^{\#}$ is the free energy of activation per mole for viscous flow, h the Planck's constant (=6.6262 x 10^{-34} J.sec), N the Avogadro number (= 6.023 x 10^{23} mol^{-1}), R the molar gas constant (= 8.3145 JK^{-1}mol^{-1}) T 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

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

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

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

The plot of $\mathbf{ln\left(\dfrac{\eta V_m}{hN}\right)}$ 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,

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

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

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

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad \text{.......…..… (6)}$$

3.2 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,

$$\Delta G^{\#E} = \Delta G^{\#} - \Delta G_{id}^{\#} \qquad \text{………................. (7)}$$

$$or, \ \Delta G^{\#E} = \Delta G^{\#} - (X_1\Delta G_1^{\#} + X_2\Delta G_2^{\#}) \text{.............(8)}$$

$$\Delta H^{\#E} = \Delta H^{\#} - \Delta H_{id}^{\#} \qquad \text{………................. (9)}$$

$$or, \ \Delta H^{\#E} = \Delta H^{\#} - (X_1\Delta H_1^{\#} + X_2\Delta H_2^{\#}) \quad \text{…...(10)}$$

$$And \quad \Delta S^{\#E} = \Delta S^{\#} - \Delta S_{id}^{\#} \qquad \text{…………….. (11)}$$

$$or, \Delta S^{\#E} = \Delta S^{\#} - (X_1\Delta S_1^{\#} + X_2\Delta S_2^{\#}) \text{ ……....(12)}$$

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

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

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

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 can be known by Figure (1-2). The plotting displays the trend of changing these properties. The changes of the properties are evaluated for the changes of each proportion of the mixture component along with the variation of temperatures.
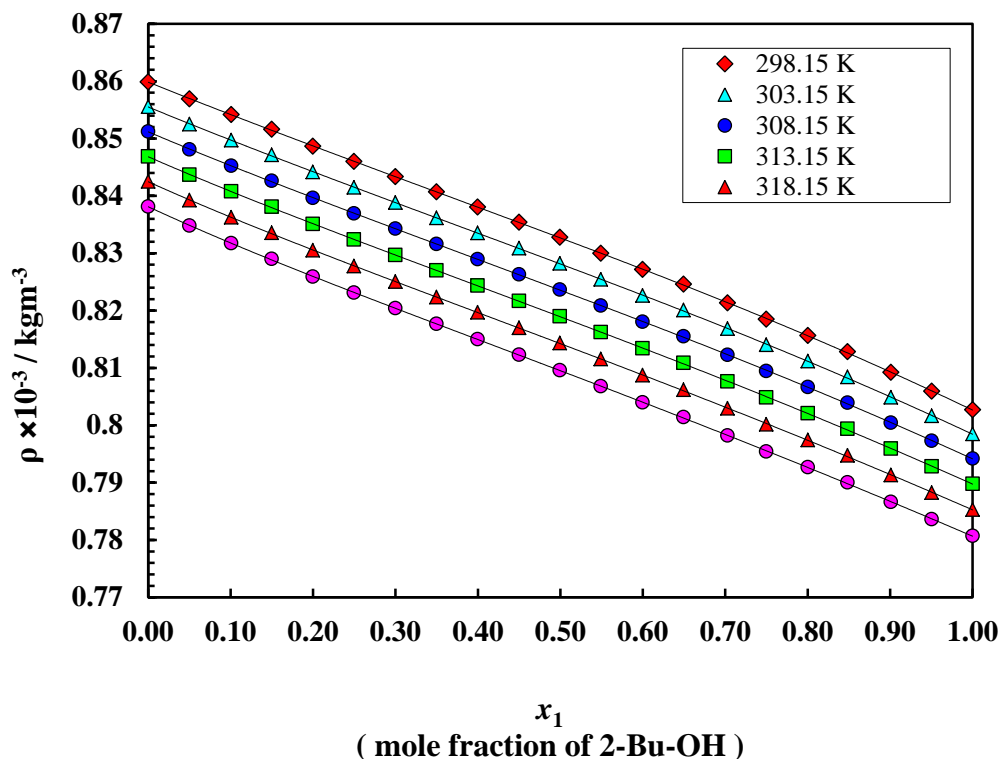

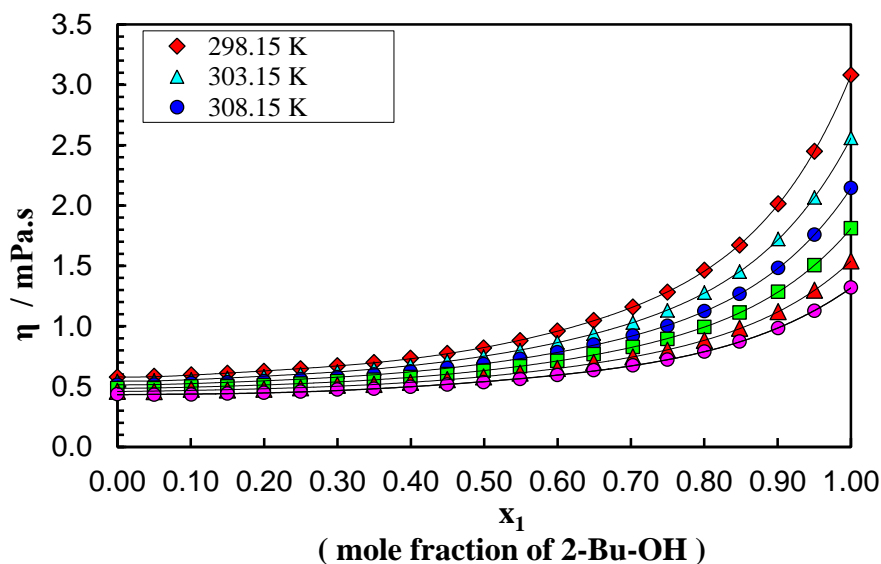**Figure 1:** Density trend analysis of the binary mixture

Figure 2: Viscosity trend analysis of the binary mixture

From Figure 2 it can be observed that viscosity of the binary mixture of 2-Bu-OH + m-Xln increases in very disciplined way with the increasing proportion of 2-Bu-OH but decreases almost linearly with temperature rises. Here the nonpolar m-Xln 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-bond as well as polar-polar interaction. Thus, there was an induction of polarity occurred in m-Xln and become induced dipole and attached to the polar 2-Bu-OH. Thus, the liquid mixture becomes more viscous. From Figure 2 it can be seen that the rising of viscosity first increases slowly but when the polar proportion is higher it rises sharply upward.

4.2 Thermodynamic properties measurement

The three types of very important thermodynamic properties viz. entropy, enthalpy and free energy were very intensively studied for the binary mixture of polar + nonpolar compound. There excess values were also calculated and fitted in Redlich-kister fitting equation. 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 1) continues to increase 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 graphically 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.

Table 1: Experimental data for Enthalpy of activation of the binary mixture

Mole fraction of		Enthalpy (Expt.) $\Delta H^{\#}$ kJmol^{-1}	Enthalpy (Theor.) $\Delta H^{\neq}_{id}$ kJmol^{-1}	Excess Enthalpy $\Delta H^{\#E}$ kJmol^{-1}	Fitting Value $\Delta H^{\#E*}$ kJmol^{-1}
2-Bu-OH (x_1)	**m-Xln (x_2)**				
0.0000	1.0000	8.2473	8.2473	0.0000	0.0000
0.0500	0.9500	8.8447	9.1483	-0.3036	-0.4519
0.1007	0.8994	8.7808	10.0609	-1.2802	-0.9986
0.1499	0.8501	9.4970	10.9482	-1.4512	-1.5620
0.1998	0.8002	9.8594	11.8470	-1.9876	-2.1274
0.2496	0.7504	10.1993	12.7449	-2.5456	-2.6618
0.2998	0.7002	10.1118	13.6486	-3.5367	-3.1529
0.3498	0.6502	11.0383	14.5502	-3.5119	-3.5863
0.3996	0.6004	11.5978	15.4470	-3.8493	-3.9553
0.4498	0.5502	12.1391	16.3519	-4.2128	-4.2609

0.4993	0.5007	12.7254	17.2432	-4.5178	-4.4925
0.5490	0.4510	13.4728	18.1394	-4.6666	-4.6509
0.5997	0.4003	14.3952	19.0534	-4.6582	-4.7280
0.6493	0.3507	15.0475	19.9470	-4.8995	-4.7104
0.7026	0.2974	16.3868	20.9079	-4.5211	-4.5723
0.7497	0.2503	17.4724	21.7567	-4.2843	-4.3289
0.8001	0.1999	18.9108	22.6649	-3.7542	-3.9175
0.8483	0.1518	19.9537	23.5317	-3.5780	-3.3499
0.9009	0.0991	22.0578	24.4800	-2.4222	-2.4915
0.9503	0.0497	23.9739	25.3712	-1.3973	-1.4104
1.0000	0.0000	26.2660	26.2660	0.0000	0.0000

Enthalpy, Excess Enthalpy and Fitting value of Excess enthalpy of activation for different molar ratios are listed in the table.
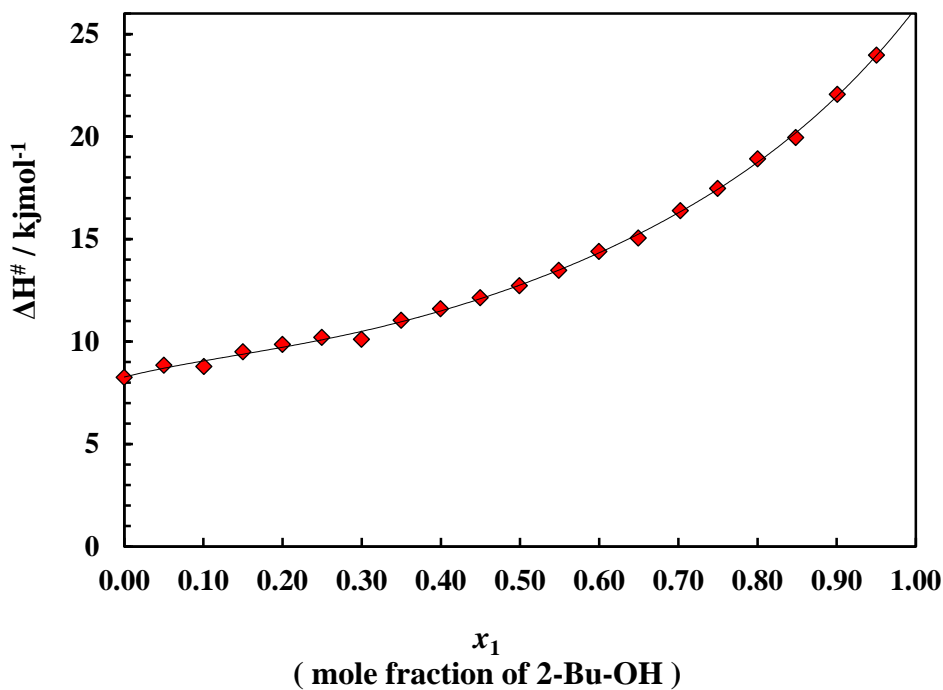

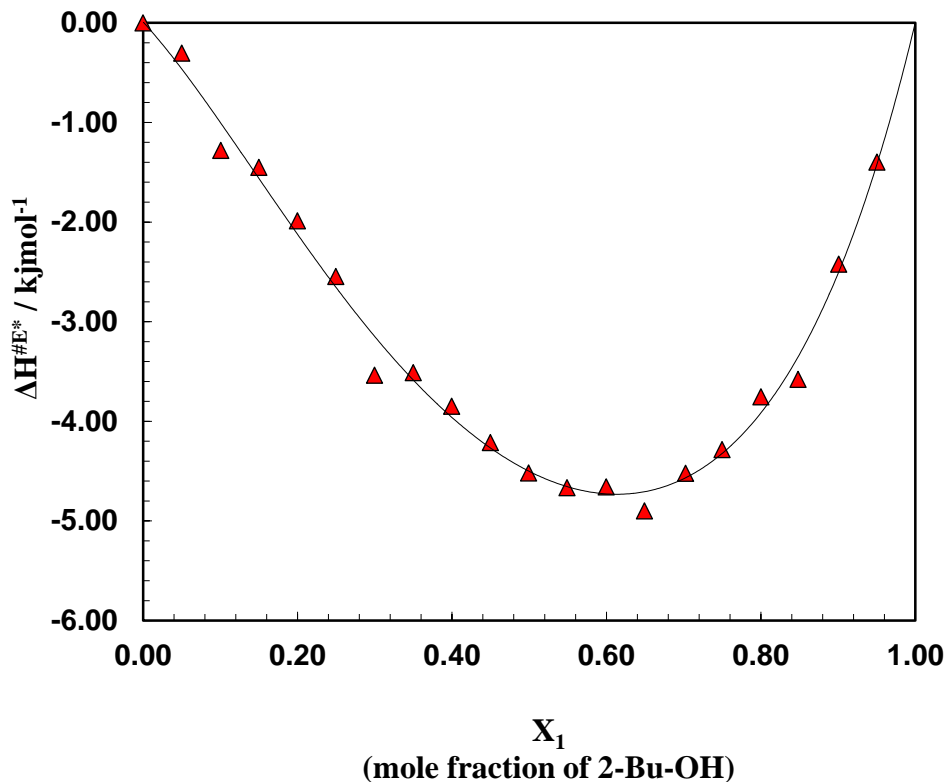**Figure 3:** Enthalpy curve for different mole fractions

Figure 4: Excess enthalpy 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 2. 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.

Figure 5 also reveals that with increase of concentration of alcohol, the negative value decreases

for the binary system of 2-Bu-OH + m-Xln 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 plots 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.

Table 2: Experimental data for Entropy of activation of the binary mixture

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 $\Delta S^{\#E*}$ $Jmol^{-1} K^{-1}$
2-Bu-OH (x_1)	m-Xln (x_2)				
0.0000	1.0000	-53.7654	-53.7654	0.0000	0.0000
0.0500	0.9500	-51.7552	-51.3158	-0.4394	-0.9349
0.1007	0.8994	-71.7320	-48.8346	-3.2086	-2.2531
0.1499	0.8501	-49.7181	-46.4224	-3.2957	-3.6748
0.1998	0.8002	-48.6127	-43.9789	-4.6339	-5.1185
0.2496	0.7504	-47.6356	-41.5379	-6.0977	-6.4842
0.2998	0.7002	-48.1038	-39.0810	-9.0228	-7.7373
0.3498	0.6502	-45.2342	-36.6297	-8.6046	-8.8437
0.3996	0.6004	-43.6499	-34.1915	-9.4584	-9.7901
0.4498	0.5502	-42.1572	-31.7316	-10.4256	-10.5802
0.4993	0.5008	-40.5356	-29.3084	-11.2272	-11.1861
0.5490	0.4510	-38.5053	-26.8720	-11.6333	-11.6068
0.5997	0.4003	-35.9968	-24.3870	-11.6098	-11.8182
0.6493	0.3507	-34.4003	-21.9576	-12.4427	-11.7829
0.7026	0.2974	-30.6157	-19.3452	-11.2704	-11.4360
0.7497	0.2503	-27.6821	-17.0375	-10.6446	-10.8196
0.8001	0.1999	-23.8235	-14.5684	-9.2550	-9.7820
0.8483	0.1518	-21.3038	-12.2120	-9.0918	-8.3609
0.9009	0.0991	-15.6459	-9.6339	-6.0120	-6.2240
0.9503	0.0497	-10.7034	-7.2109	-3.4924	-3.5347
1.0000	0.0000	-4.7782	-4.7782	0.0000	0.0000

Entropy, Excess entropy and Fitting value of excess entropy of activation for different molar ratios are listed in the table.
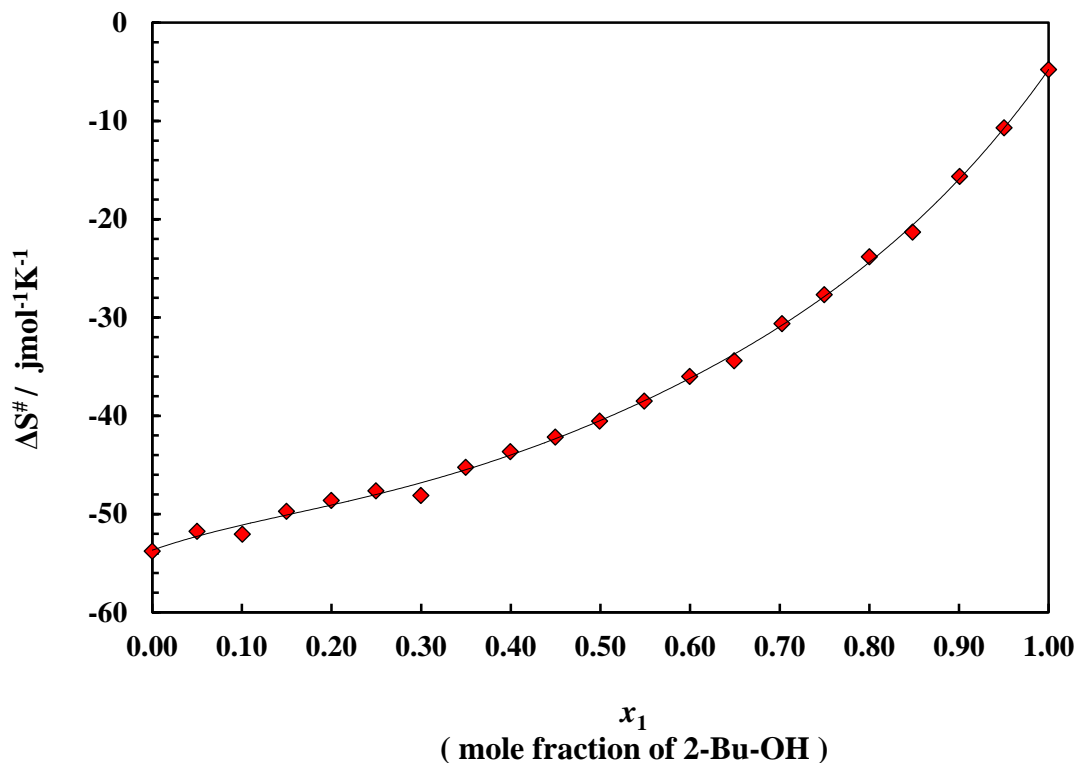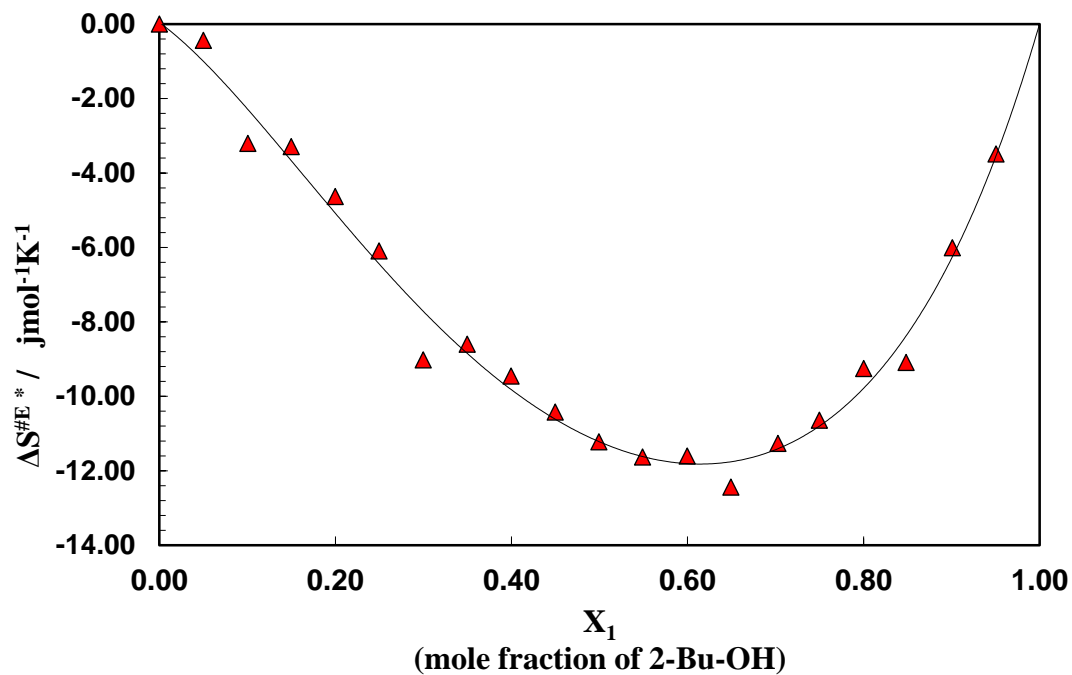
Figure 5: Entropy curve for different mole fractions

Figure 6: Excess entropy curve for different mole fractions

Table (3-8) shows 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 the 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 (m-Xln) 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 to 323.15 K over the whole composition range for this binary system (Table 3-8). 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 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. The excess values throughout the whole concentration range are negative with minima falling around 0.6 mole fraction of 2-Bu-OH. The negative excess free energy indicates the reduction of energy barrier height and hence increases of viscous flow.

Table 3: Experimental data for Free energy of activation of the binary mixture at 298.15 K

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 (x_1)	m-Xln (x_2)				
0.0000	1.0000	24.2774	24.2774	0.0000	0.0000
0.0500	0.9500	24.2755	24.4481	-0.1726	-0.1732
0.1007	0.8994	24.2974	24.6210	-0.3235	-0.3268
0.1499	0.8501	24.3205	24.7890	-0.4686	-0.4664
0.1998	0.8002	24.3533	24.9593	-0.6060	-0.6013
0.2496	0.7504	24.4018	25.1294	-0.7276	-0.7286
0.2998	0.7002	24.4540	25.3006	-0.8466	-0.8460
0.3498	0.6502	24.5249	25.4714	-0.9465	-0.9495

0.3996	0.6004	24.6120	25.6412	-1.0293	-1.0364
0.4498	0.5502	24.7083	25.8127	-1.1044	-1.1064
0.4993	0.5008	24.8111	25.9815	-1.1704	-1.1573
0.5490	0.4510	24.9531	26.1512	-1.1981	-1.1903
0.5997	0.4003	25.1277	26.3244	-1.1967	-1.2044
0.6493	0.3507	25.3040	26.4937	-1.1897	-1.1974
0.7026	0.2974	25.5149	26.6757	-1.1608	-1.1627
0.7497	0.2503	25.7259	26.8365	-1.1106	-1.1031
0.8001	0.1999	26.0137	27.0085	-0.9948	-1.0010
0.8483	0.1518	26.3054	27.1727	-0.8673	-0.8571
0.9009	0.0991	26.7226	27.3523	-0.6297	-0.6358
0.9503	0.0497	27.1651	27.5212	-0.3560	-0.3565
1.0000	0.0000	27.6907	27.6907	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 298.15 K are listed in the table.

Table 4: Experimental data for Free energy of activation of the binary mixture at 303.15 K

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 (x_1)	m-Xln (x_2)				
0.0000	1.0000	24.5462	24.5462	0.0000	0.0000
0.0500	0.9500	24.5343	24.7047	-0.1704	-0.1685
0.1007	0.8994	24.5577	24.8651	-0.3075	-0.3156
0.1499	0.8501	24.5691	25.0212	-0.4521	-0.4480
0.1998	0.8002	24.5963	25.1792	-0.5829	-0.5757
0.2496	0.7504	24.6400	25.3371	-0.6971	-0.6961
0.2998	0.7002	24.6945	25.4960	-0.8015	-0.8074
0.3498	0.6502	24.7511	25.6545	-0.9035	-0.9053
0.3996	0.6004	24.8302	25.8122	-0.9820	-0.9874
0.4498	0.5502	24.9191	25.9713	-1.0523	-1.0535
0.4993	0.5008	25.0138	26.1280	-1.1142	-1.1014

0.5490	0.4510	25.1457	26.2856	-1.1399	-1.1323
0.5997	0.4003	25.3077	26.4463	-1.1387	-1.1453
0.6493	0.3507	25.4760	26.6035	-1.1275	-1.1385
0.7026	0.2974	25.6679	26.7724	-1.1045	-1.1055
0.7497	0.2503	25.8643	26.9217	-1.0574	-1.0490
0.8001	0.1999	26.1328	27.0814	-0.9485	-0.9520
0.8483	0.1518	26.4119	27.2338	-0.8218	-0.8153
0.9009	0.0991	26.8009	27.4005	-0.5997	-0.6046
0.9503	0.0497	27.2187	27.5572	-0.3385	-0.3388
1.0000	0.0000	27.7145	27.7145	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 303.15 K are listed in the table.

Table 5: Experimental data of Free energy of activation of the binary mixture at 308.15 K

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 (x_1)	m-Xln (x_2)				
0.0000	1.0000	24.8151	24.8151	0.0000	0.0000
0.0500	0.9500	24.7931	24.9613	-0.1682	-0.1639
0.1007	0.8994	24.8179	25.1093	-0.2914	-0.3043
0.1499	0.8501	24.8177	25.2533	-0.4356	-0.4297
0.1998	0.8002	24.8394	25.3991	-0.5597	-0.5502
0.2496	0.7504	24.8782	25.5448	-0.6666	-0.6637
0.2998	0.7002	24.9350	25.6914	-0.7564	-0.7687
0.3498	0.6502	24.9772	25.8377	-0.8604	-0.8611
0.3996	0.6004	25.0485	25.9832	-0.9347	-0.9385
0.4498	0.5502	25.1298	26.1300	-1.0001	-1.0006
0.4993	0.5008	25.2165	26.2746	-1.0581	-1.0455
0.5490	0.4510	25.3382	26.4200	-1.0818	-1.0743
0.5997	0.4003	25.4877	26.5683	-1.0806	-1.0863
0.6493	0.3507	25.6480	26.7132	-1.0653	-1.0796

0.7026	0.2974	25.8210	26.8691	-1.0481	-1.0483
0.7497	0.2503	26.0027	27.0069	-1.0042	-0.9949
0.8001	0.1999	26.2520	27.1542	-0.9022	-0.9031
0.8483	0.1518	26.5184	27.2948	-0.7764	-0.7735
0.9009	0.0991	26.8791	27.4487	-0.5696	-0.5735
0.9503	0.0497	27.2722	27.5933	-0.3211	-0.3212
1.0000	0.0000	27.7384	27.7384	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 308.15 K are listed in the table.

Table 6: Experimental data of Free energy of activation of the binary mixture at 313.15 K

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 (x_1)	m-Xln (x_2)				
0.0000	1.0000	25.0839	25.0839	0.0000	0.0000
0.0500	0.9500	25.0518	25.2178	-0.1660	-0.1592
0.1007	0.8994	25.0781	25.3535	-0.2754	-0.2930
0.1499	0.8501	25.0663	25.4854	-0.4191	-0.4113
0.1998	0.8002	25.0825	25.6190	-0.5365	-0.5246
0.2496	0.7504	25.1164	25.7525	-0.6361	-0.6313
0.2998	0.7002	25.1755	25.8868	-0.7113	-0.7300
0.3498	0.6502	25.2034	26.0208	-0.8174	-0.8169
0.3996	0.6004	25.2667	26.1541	-0.8874	-0.8896
0.4498	0.5502	25.3406	26.2886	-0.9480	-0.9477
0.4993	0.5008	25.4191	26.4211	-1.0020	-0.9896
0.5490	0.4510	25.5307	26.5543	-1.0236	-1.0162
0.5997	0.4003	25.6676	26.6902	-1.0226	-1.0272
0.6493	0.3507	25.8200	26.8230	-1.0030	-1.0206
0.7026	0.2974	25.9741	26.9659	-0.9918	-0.9912
0.7497	0.2503	26.1411	27.0920	-0.9510	-0.9408

0.8001	0.1999	26.3711	27.2270	-0.8560	-0.8542
0.8483	0.1518	26.6250	27.3559	-0.7309	-0.7317
0.9009	0.0991	26.9573	27.4968	-0.5395	-0.5424
0.9503	0.0497	27.3257	27.6293	-0.3036	-0.3035
1.0000	0.0000	27.7623	27.7623	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 313.15 K are listed in the table.

Table 7: Experimental data for Free energy of activation of the binary mixture at 318.15 K

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 (x_1)	**m-Xln (x_2)**				
0.0000	1.0000	25.3527	25.3527	0.0000	0.0000
0.0500	0.9500	25.3106	25.4744	-0.1638	-0.1545
0.1007	0.8994	25.3383	25.5977	-0.2594	-0.2818
0.1499	0.8501	25.3149	25.7175	-0.4026	-0.3929
0.1998	0.8002	25.3255	25.8389	-0.5134	-0.4990
0.2496	0.7504	25.3546	25.9601	-0.6056	-0.5989
0.2998	0.7002	25.4160	26.0822	-0.6661	-0.6913
0.3498	0.6502	25.4296	26.2040	-0.7744	-0.7727
0.3996	0.6004	25.4850	26.3251	-0.8401	-0.8406
0.4498	0.5502	25.5514	26.4473	-0.8959	-0.8948
0.4993	0.5008	25.6218	26.5676	-0.9458	-0.9336
0.5490	0.4510	25.7232	26.6887	-0.9654	-0.9582
0.5997	0.4003	25.8476	26.8121	-0.9645	-0.9681
0.6493	0.3507	25.9920	26.9328	-0.9408	-0.9617
0.7026	0.2974	26.1272	27.0626	-0.9354	-0.9340
0.7497	0.2503	26.2795	27.1772	-0.8977	-0.8867
0.8001	0.1999	26.4902	27.2999	-0.8097	-0.8053
0.8483	0.1518	26.7315	27.4169	-0.6855	-0.6899
0.9009	0.0991	27.0355	27.5450	-0.5095	-0.5113

0.9503	0.0497	27.3792	27.6654	-0.2862	-0.2858
1.0000	0.0000	27.7862	27.7862	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 318.15 K are listed in the table.

Table 8: Experimental data for Free energy of activation of the binary mixture at 323.15 K

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 (x_1)	m-Xln (x_2)				
0.0000	1.0000	25.6216	25.6216	0.0000	0.0000
0.0500	0.9500	25.5694	25.7310	-0.1616	-0.1498
0.1007	0.8994	25.5985	25.8418	-0.2433	-0.2705
0.1499	0.8501	25.5634	25.9496	-0.3862	-0.3745
0.1998	0.8002	25.5686	26.0588	-0.4902	-0.4734
0.2496	0.7504	25.5927	26.1678	-0.5751	-0.5665
0.2998	0.7002	25.6566	26.2776	-0.6210	-0.6526
0.3498	0.6502	25.6557	26.3871	-0.7314	-0.7284
0.3996	0.6004	25.7032	26.4960	-0.7928	-0.7917
0.4498	0.5502	25.7622	26.6059	-0.8438	-0.8419
0.4993	0.5008	25.8245	26.7142	-0.8897	-0.8777
0.5490	0.4510	25.9158	26.8230	-0.9073	-0.9002
0.5997	0.4003	26.0276	26.9341	-0.9065	-0.9090
0.6493	0.3507	26.1640	27.0426	-0.8786	-0.9028
0.7026	0.2974	26.2803	27.1593	-0.8791	-0.8768
0.7497	0.2503	26.4179	27.2624	-0.8445	-0.8326
0.8001	0.1999	26.6093	27.3727	-0.7634	-0.7564
0.8483	0.1518	26.8380	27.4780	-0.6400	-0.6480
0.9009	0.0991	27.1138	27.5932	-0.4794	-0.4802
0.9503	0.0497	27.4327	27.7014	-0.2687	-0.2681
1.0000	0.0000	27.8101	27.8101	0.0000	0.0000

Free energy, Excess free energy, and Fitting value of excess free energy for different molar ratios at 323.15 K are listed in the table.
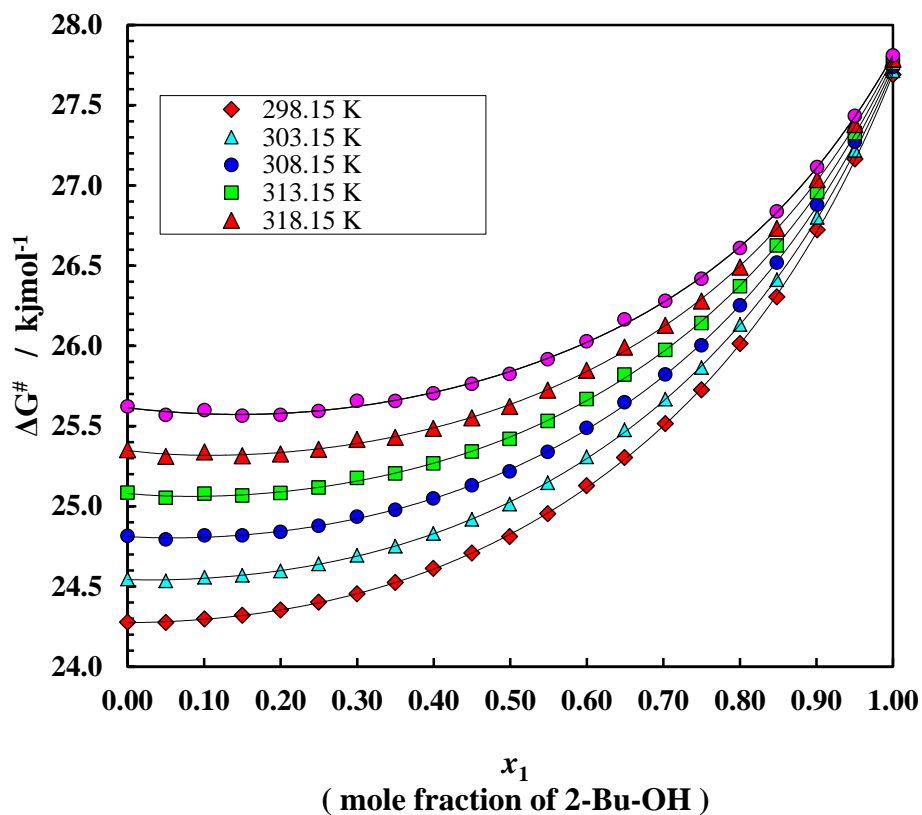
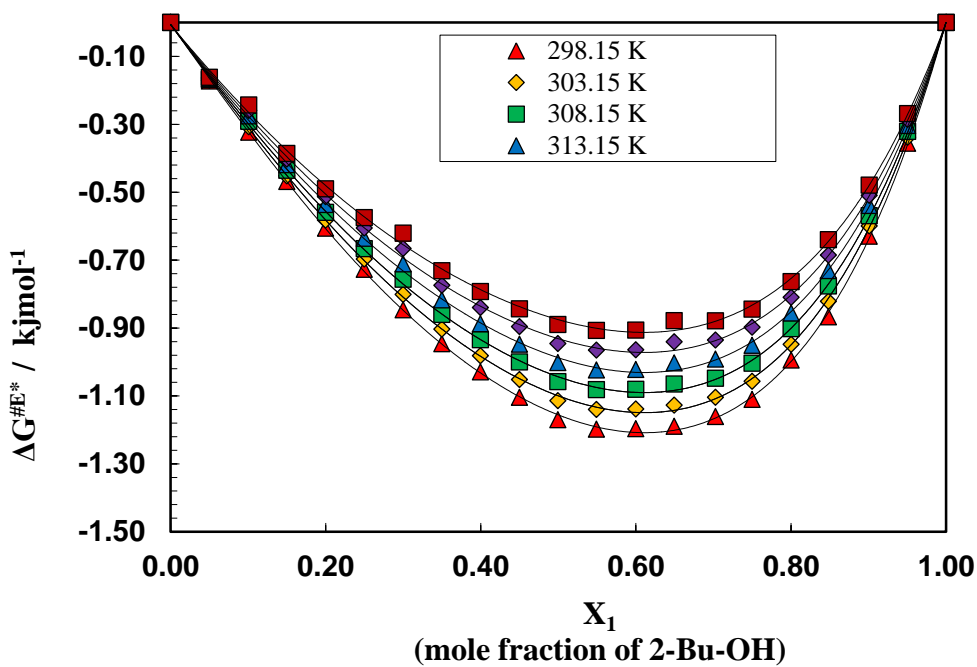**Figure 7:** Free energy curves for different mole fractions at different temperatures

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

5. Conclusion

Studies on thermodynamic properties along with their respective excess values in liquids and liquid mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models [17] as well as engineering applications in pharmaceutical process industries. An understanding of the thermodynamic properties of 2-Bu-OH and m-Xln 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. Thermodynamic properties derived from viscosity and its related parameters are also important in designing industrial equipments with better precision [18]. In these mixtures, the predominance of physical effect may arise due to dipole-induced dipole interaction resulting in disruption in the favorable orientation due to breaking of self-network built by H-bond among the polar molecules and rising dispersion force of nonpolar liquid. The observed excess thermodynamic values in all the mixture indicate the significant interaction between the unlike molecules.

Acknowledgement

Abbreviations

2-Bu-OH = 2-Butanol

m-Xln = m-Xylene (or meta-Xylene)

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