VISCOSITIES AND DEVIATIONS IN VISCOSITY FOR BINARY MIXTURES OF TETRAHYDROFURAN + PROPANOL-1 AND TETRAHYDROFURAN + BUTANOL-1 AT 303.15 K

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Abstract

The viscosities, η of pure tetrahydrofuran, propanol-1 and butanol-1and some of their binary mixtures covering the whole composition range have been measured at temperatures 303.15 K. From the experimental η, the deviations in viscosity ($\Delta\eta$) have been calculated. Excess free energy for viscous flow, $\Delta G^{\#E}$ has also been evaluated. The concentration dependences of η were correlated to polynomial expressions, whereas, $\Delta\eta$ and $\Delta G^{\#E}$ were fitted to the Redlich–Kister equation. For all systems, $\Delta\eta$ were found to be negative in the whole range of composition with a single lobe.

Keywords: *Viscosity, Tetrahydrofuran, Propanol-1, Butanol-1.*

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1. INTRODUCTION

As a transport property, application of viscosity are vast including those used in many chemical and industrial processes, such as, design of new processes and process equipments. It has also been used to understand the molecular interactions between the components [1-4]. With the increased popularity of process and reservoir simulators, there is always a need for a consistent, reliable and accurate analytical predictive method for viscosity calculations.

Now a days, binary systems containing oxygenated compounds, such as, ethers (-O- group) and alkanols (-OH group) are found to be of increasing applications. Among them Tetrahydrofuran is commonly used for the synthesis of new compounds in organic chemistry. Also, it has been found to be a super solvent because of its rapid solvent activity, minimum gelation and lower relative viscosities for resin solutions. On the other hand, alcohols are self-associated organic liquids which are widely used as coupling and dispersing agents in the chemical, pharmaceutical and household industries and as carrier and extraction of solvent for natural products.

Previously, Gupta *et al* [5] and Misra et al [6] have studied the viscometric properties of the binary mixtures of tetrahydrofuran with propanol-1 and propanol-2, while Parveen *et al* [7] have reported on tetrahydrofuran + methanol and + o-cresol. A good number of literature survey shows that some systematic studies are still scarce. The present investigation therefore reports on the viscosity and excess thermodynamic properties for tetrahydrofuran + propanol-1 and tetrahydrofuran + butanol-1 in the entire range of composition at 303.15 K.

2. EXPERIMENTAL SECTION

Liquids with quoted purities, tetrahydrofuran (THF): ≥ 99% and butanol-1 (NBL): ≥ 99%, were procured from MERCK and propanol-1 (NPL): 99.5% from DAEJUNG. Binary mixtures of various compositions were prepared by mass mixing pure components at different proportions with the help of an electronic balance (SHIMADZU, model:ATX224) accurate up to ±0.0001 g. The Ostwald viscometer (Technico, PSL BS/U, A-type) was used to measure the viscosity η. The flow time of liquids was recorded by an electronic stopwatch reading up to ±0.1 s. The viscometer was calibrated by doubly distilled water. For all measurements a thermostatic water bath (Model: WBT-400, Spectrolab, UK) controlled up to ±0.01 K was used. The mole fraction was accurate up to $\pm10^{-4}$, while the uncertainty in measured η was estimated as $\pm2\times10^{-3}$ mPa.s. Measured η of pure liquids are compared with reported data as tabulated in Table-1, all of which are found to be in good agreement with the reported data.

Table-1 Comparison of experimental viscosities (η/mPa.s) of pure liquids with literature values at 303.15 k.

Sample	η /mPa.s	
	This work	Literature
Tetrahydrofuran	0.4462	0.438[a]
Propanol-1	1.6388	1.718[b]
Butanol-1	2.2695	2.268[b]

[a]Ref-[8], [b]Ref-[9]

3. RESULTS AND DISCUSSION

3.1 Viscosities

Viscosities, η, of THF + NPL and THF + NBL in the range $0 \leq x_2 \leq 1$ composition measured at 303.15 K are as summarized in Table 2. At a particular temperature η values were fitted to a four-degree polynomial equation of the form:

$$\eta / mPa \cdot S = \sum_{i=0}^{n} a_i x_2^i \qquad (1)$$

where, a_i is the coefficient of polynomial equation. Fig-1 indicates the comparative diagram of η against x_2 of the two systems at temperatures 303.15 K. The η of pure liquids varies in the order: NBL > NPL > THF. For the binary mixtures, η increases systematically as the concentration of the alcohols x_2 increases and the order of increment follows: THF + NBL > THF + NPL.

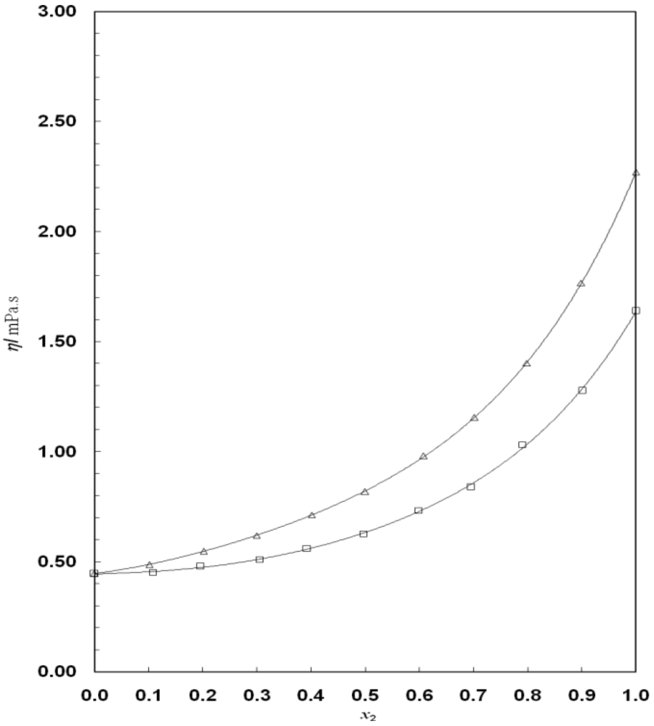

Fig-1. Comparison of viscosity, η as a function of x_2 for the systems of THF (x_1) + NPL (x_2) (□) and THF (x_1) + NBL (x_2) (∆) at 303.15 K

3.2 Deviations in Viscosity

From experimental η, deviations in viscosity, $\Delta\eta$ for the mixtures were calculated as [10-11]:

$$\Delta\eta = \eta - \eta_1 x_1 - \eta_2 x_2 \qquad (2)$$

where, η is the viscosity of solution, η_1 and η_2 are viscosities and x_1 and x_2 are the mole fractions of pure components 1 and 2, respectively. The estimated values of $\Delta\eta$ were correlated well by the Redlich-Kister equation [12]:

$$\Delta\eta = x_2(1 - x_2)\sum_{i=0}^{n} A_i (2x_2 - 1)^i \qquad (3)$$

where, A_i is the fitting coefficient and x_2 is the mole fraction of the alcohols. The standard deviation, σ , followed the equation:

$$\sigma = \left[\frac{\sum(\Delta\eta_{obs} - \Delta\eta_{cal})^2}{n - p - 2}\right]^{\frac{1}{2}} \qquad (4)$$

where, $\Delta\eta_{obs}$ and $\Delta\eta_{cal}$ are the observed and calculated deviations in viscosity, n is the total number of compositions and p is the number of coefficients. The coefficients, A_i and σ are as shown in Table 4. Fig. 2 represents the comparative diagram of $\Delta\eta$ against x_2 at 303.15 K. For all systems, $\Delta\eta$ were negative in the whole range of composition forming a single lobe with minima at x_2~0.7 for THF + NPL and x_2~0.6 for THF + NBL systems. At a particular temperature, $\Delta\eta$ varied in the order: THF + NBL > THF + NPL. Similar results of negative $\Delta\eta$ in THF + NPL system at 303.15 K were observed previously by Gupta et al. [5]. Also, same types of trend are found for THF + MNL (Methanol) by [7].

On mixing of components as fast as structures are broken down, some new H-bonds between alcohols with THF (O-H---O type) are formed simultaneously. During flow, possibly they take more favorable geometrical shapes, and thus enhance the decrement in η values. Thus, the breaking of self-association of alcohols has influences in the deviations in viscosity, thereby suggesting that dispersive forces are operative in THF + NPL and THF + NBL systems exhibiting negative values of $\Delta\eta$. This explanation has been supported from many workers [13-14] where negative values of $\Delta\eta$ indicate dispersive interactions.

One parameter correlating equations given by Grunberg and Nissan [15] has been used to correlate the viscosity of liquid mixtures.

$$ln\eta = x_1\, ln\eta_1 + x_2\, ln\eta_2 + x_1 x_2 \varepsilon \qquad (5)$$

where ε is a parameter proportional to the interchange energy. All the values of ε are negative for both the systems as listed in Table 2 and their magnitude increases with the rise of temperature. According to Fort and Moore [16], ε is termed as an approximate index for estimating strength of interaction between dissimilar components in flow. If $\Delta\eta < 0$ and $\varepsilon < 0$ and their magnitudes are large, specific interaction would be absent or only dispersion forces would dominant.

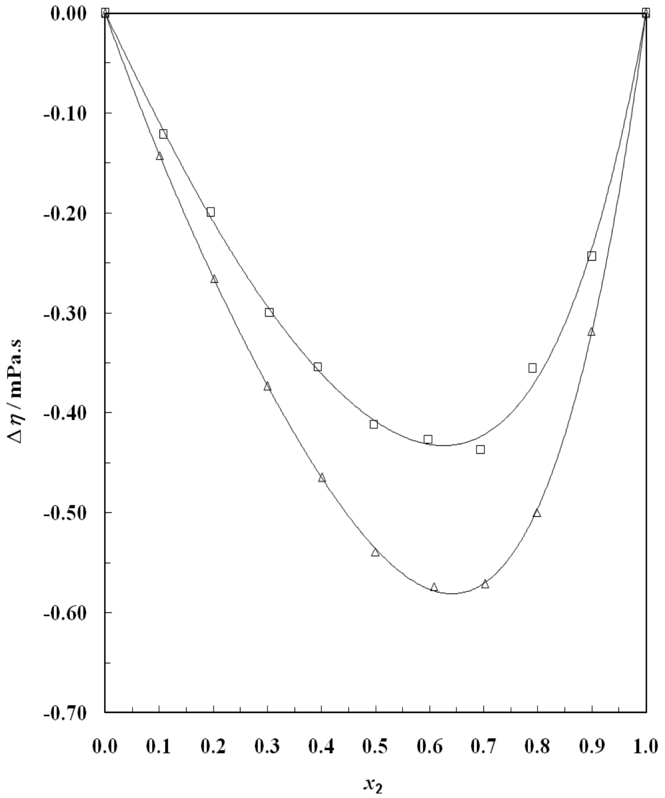

Fig-2. Comparative diagrams of deviation in viscosity, $\Delta\eta$ as a function of x_2 for the systems of THF (x_1) + NPL (x_2) (□) and THF (x_1) + NBL (x_2) (Δ) at 303.15 K.

Table-2 Viscosities, η (mPa.s) and interaction parameter (ε **)** of the systems of THF (x_1) + NPL (x_2) and THF (x_1) + NBL (x_2) at different molar ratios at 303.15 K.

x_2	η	ε	x_2	η	ε
THF (x_1) + NPL (x_2)			THF (x_1) + NBL (x_2)		
0.0000	0.4462	0.0000	0.0000	0.4462	0.0000
0.1071	0.4524	-0.0151	0.1007	0.4871	-0.0085
0.1953	0.4796	-0.0441	0.2013	0.5479	-0.0308
0.3048	0.5105	-0.1148	0.2996	0.6195	-0.0681
0.3929	0.5611	-0.1825	0.4011	0.7129	-0.1231
0.4967	0.6274	-0.3014	0.4996	0.8181	-0.2061
0.5981	0.7331	-0.4190	0.6077	0.9803	-0.3119
0.6949	0.8385	-0.6222	0.7019	1.1551	-0.4485
0.7900	1.0328	-0.7091	0.7987	1.4028	-0.6097
0.9007	1.2765	-1.0944	0.8991	1.7671	-0.7672
1.0000	1.6388	0.0000	1.0000	2.2695	0.0000

Table-3 Coefficients, a_i of polynomial equation (1) for viscosity, η (mPa.s) of the systems of THF (x_1) + NPL (x_2) and THF (x_1) + NBL (x_2) at 303.15 K

a_0	a_1	a_2	a_3	a_4	a_5	R^2
THF (x_1) + NPL (x_2)						
0.446	0.307	1.114	-0.874	0.411	0.865	1.000
THF (x_1) + NBL (x_2)						
0.445	0.084	0.044	1.970	-2.643	1.734	0.999

Table-4 Polynomial fitting coefficients using equation (3) of $\Delta\eta$ / mPa.s and $\Delta G^{\#E}$ / kJ mol^{-1} and standard deviations, σ in equation (4) for the systems of THF (x_1) + NPL (x_2) and THF (x_1) + NBL (x_2) at 303.15 K.

Property	A_0	A_1	A_2	A_3	σ
THF (x_1) + NPL (x_2)					
$\Delta\eta$	-1.6332	-0.7281	-0.4388	-0.2267	0.0116
$\Delta G^{\#E}$	-2.9342	-0.0373	-0.1085	-0.0726	0.0336
THF (x_1) + NBL (x_2)					
$\Delta\eta$	-2.1440	-1.1630	-0.6416	-0.1046	0.0030
$\Delta G^{\#E}$	-2.0041	-0.5756	-0.3393	0.5315	0.0075

3.3 Excess Free Energy

Excess free energy for viscous flow, $\Delta G^{\#E}$ is conveniently considered as a real index for estimating the energy barrier for activating in viscous flow. It is calculated by using the equation [17]

$$\Delta G^{\#E} = RT\left[\ln \eta V - \sum x_i \ln(\eta_i V_i)\right] \qquad (6)$$

Here, η, V, η_i and V_i, denote the viscosity and molar volume of the mixture and pure components, respectively, and R is the gas constant and T is the experimental temperature. Fig.3 represents the comparative diagram of $\Delta G^{\#E}$ against x_2 at 303.15 K. For the present systems the fact $\Delta G^{\#E}$ are all negative in the whole range of composition, leads to suggest that irrespective of volume expansion and contraction, all the flowing species surpass smaller energy barriers than it is expected from additivity rule.

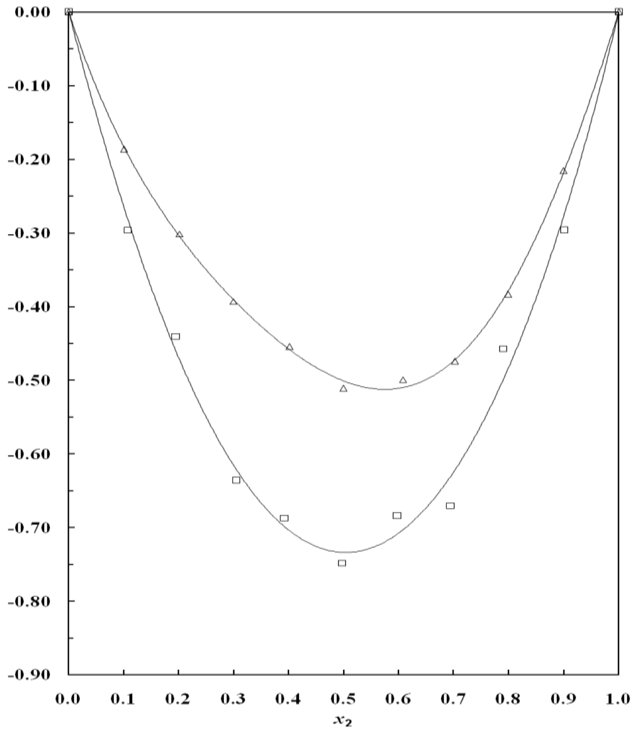

Fig-3 Comparison of excess free energies of activation for viscous flow, $\Delta G^{\#E}$ as a function of x_2 for the systems of THF (x_1) + NPL (x_2) (□) and THF (x_1) + NBL (x_2) (Δ) at 303.15 K.

4. CONCLUSION

The present study reports on measurements of viscosity, η for the tetrahydrofuran + alcanols-1 systems at compositions $0 \leq x_2 \leq 1$ and at 303.15K. From measured η the interaction parameter ε and deviations $\Delta\eta$ were also calculated. In order to obtain relevant coefficients and the standard deviations, concentration dependences of η was correlated to polynomial expressions, whereas, $\Delta\eta$ was fitted to the Redlich– Kister equations. An analysis of viscosity data based on the Grunberg_Nissan treatment shows that no specific interaction exists among the component molecules.

ACKNOWLEDGEMENTS

The authors are gratefully acknowledging the financial grants from the department of chemistry, Mawlana Bhashani Science and Technology University, Santosh, Tangail-1902, Bangladesh.

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