Viscometric Properties of Binary Mixtures of Tetrahydrofuran + 2–Alkoxyethanols at Temperatures of (293.15, 298.15 & 303.15) K

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Abstract: **Viscosities (η) of pure liquids and binary mixtures of tetrahydrofuran (THF) with 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE) and 2-butoxyethanol (2-BE) have been determined over the entire range of solvent composition at (293.15, 298.15 and 303.15) K. Absolute viscosities were determined by measuring the flow times of the liquids using an Ostwald type viscometer immersed in a thermostated water bath. From the experimental results, the excess viscosity (η^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been derived and presented as functions of composition. Excess viscosities showed both positive and negative deviations from linearity, suggesting the existence of strong intermolecular interactions where positive deviations prevails, and the dominance of disruptive effects of solvent structures, where negative deviations are dominant. Several viscosity correlation models were used to correlate and interpret the viscosity data. The Grunberg-Nissan (G-N), Hind and Ubbelohde (H-U), Katti and Chaudhary (K-C), Heric-Brewer (H-B)and Frenkel (F)models were used to analyze the viscosity result for the interpretation of molecular interactions in the solvent systems. The interaction parameters: d_{12}, H_{12}, K_{12}, Δ_{12} and F_{12}derived from these models served as further proof of the nature, extent and strength of interactions present in the binary mixtures. The predictive abilities of these models have also been tested, with the deviations from the experimental values expressed as average percentage deviations (APD).**

Key Words: **Tetrahydrofuran, alkoxyethanols, molecular interactions, excess viscosity, excess Gibbs free energy**

I. INTRODUCTION

We have been investigating the mixing behaviour of binary mixtures of C_4 aliphatic ethers and (C_1 – C_4)alkoxyethanols at different temperatures. Earlier, we reported the results of our studies on the volumetric properties of mixtures of tetrahydrofuran (THF) with selected alkoxyethanols at (293.15, 298.15 and 303.15) K (Jumbo, et al, 2019)[1]. From the study, it was observed that strong intermolecular interactions through extensive network of hydrogen bonding existed between the components of the mixtures.

In another study, we reported the volumetric behavior of 2-alkoxyethanols in diethyl ether (DEE) (Jumbo and Kemeakegha, 2020)[2]. The mixing properties of DEE and 2-alkoxyethanols were compared with the solvent systems involving THF and 2-alkoxyethanols. This was done to ascertain any structural influence of the ethers on the sign and magnitude of excess molar volumes of the solvent systems. Because both THF and DEE are C_4 aliphatic ethers, the sign of the excess molar volumes in their various solvent systems were the same and changed in identical fashion with increases in chain length of the 2-alkoxyethanols and temperature. However, the magnitude of interactions, as reflected on the value of the excess molar volumes, was noticeably affected by the structure of the ethers.

THF, being cyclic ether, showed greater negative deviations of the excess molar volumes than DEE, a straight-chain aliphatic ether.

In this current study, the viscosities of pure liquids and binary mixtures of THF and 2-alkoxyethanols have been employed for the elucidation of intermolecular interactions in the binary systems. Excess viscosities have been determined to provide information on the structure of liquids and are required in the design of processes which involve mass transfer and fluid flow, etc. (Mariano et al, 2000)[3].

Knowledge of viscosity of liquids is required in different areas of computational and analytical sciences, in the industries for the determination of flow in pipelines and capillaries, heat and mass transfer processes, as well as in the pharmaceutical industries (Mariano et al, 2000)[3]. The employment of thermodynamic excess functions for the study of viscosity of mixed solvents and treatment of their deviations from ideality has been reported by (Mahajan et al, 2012)[4]to be of great theoretical and practical importance.They have been used to serve as useful tools in understanding the nature of molecular interactions in binary liquid mixtures (Nain, 2007)[5].

The last decade has seen a plethora of research efforts aimed at the development of theoretical and practical models for the characterization of mixed solvents and an estimation of their deviations from ideal behaviour. This has necessitated the availability of experimental data for testing the applicability of these models as well as other theories of solutions. Commonly used viscosity correlation models such as the Grunberg-Nissan, the Kendall-Monroe, Hind and Ubbelohde, Katti and Chaudhary, Frenkel, Tamura and –Kurata and the Heric-Brewer models have been employed in this work for the

interpretation of molecular interactions in the binary mixtures of THF and2-alkoxyethanols, as well as in testing their predictive ability (hence their applicability) for these systems.

Numerous studies have been done on the viscometric behaviour of binary mixtures. Li and co. (Li et al., 2010)[6] reported the viscometric properties of binary mixtures of triethylene glycol monomethyl ether (TEGMME) + water mixtures. The excess viscosities and excess Gibbs' free energy of the mixtures were both positive at all temperatures, indicating that there were strong interactions between the componentmolecules of the mixture. TEGMME and 2-alkoxyethanols are identical solvents, albeit the former having three ethereal oxygen, instead of as in *n*-alkoxyethanols, thus a similar type of interaction may be expected between n-alkoxyethanols and THF. Subha and co (Subha et al, 2004)[7] reported the viscometric behaviour of ethoxyethanol with alkyl amines. The excess molar volumes showed large negative deviations and small positive deviations with increasing mole fractions of ethoxyethanol. The effect of chain length of the amines was also determined, and was observed thatthe strength of intermolecular interactions increased with a progressive increase in the chain length of the amines (n-butyalmine < n-hexylamine <n-octylamine). In this work, we have studied extensively the effect of chain length of the 2-alkoxyethanols on the strength of interaction with THF. A similarity can also be drawn between the solvent systems studied by Subha et al[7] and those studied in this present work as both solvent systems are characterized by networks of intra- and intermolecular hydrogen bonds. Koohyar et al (2012)[8] reported the viscosity deviations of aqueous solutions of methanol, ethanol, ethylene glycol, 1-propanol and 1, 2, 3-propantriol. Several authors have also reported the viscometric behaviour of a number of mixed solvents (Beebi et al[9] 2016; Yang et al[10], 2008; Suman[11], 2013; Sihna[12], 2013; Priya[13], 2010; Pavai and Renuka[14], 2012). In spite of the numerous data on viscosity and viscometric properties of binary mixtures, a thorough survey of literature shows a scarcity of experimental data on the solvent systems tetrahydrofuran and 2-alkoxyethanols. The structural features, as well as the importance and usefulness of these solvents have been discussed in our earlier publication (Jumbo et al, 2019)[1]. As earlier stated, the extensive networks of intra- and inter-molecular hydrogen bonds in 2-alkoxyethanols and the intermolecular hydrogen bonds formed between unlike molecules upon mixing with tetrahydrofuran make the solvent combinations very suitable for the testing of the applicability of these correlation models.

II. EXPERIMENTAL SETUP

Materials

The reagents 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol were products of Lobachem, India, with minimum assay of 99%. Tetrahydrofuran (98.5%) was a product of Sigma Aldrich, Germany. All the reagents were used without further purification.

Binary mixtures were prepared volumetrically, by mixing appropriate volumes of the components. An Ostwald type, double stem viscometer was used for measuring the flow times of the liquids and binary mixtures. The viscometer was calibrated with *n*-hexane and doubly distilled water at all working temperatures. The desired temperatures for measurements were obtained using a water bath with a Bockel Grant digital thermostat (Model GD120; Serial Number 0528020) accurate to within $\pm0.001^0$C. All preparations and measurements were done in triplicates, the average taken to check possible errors. The accuracy of the method employed was checked by comparing the viscosity results obtained experimentally with those reported in the open literature and is presented in Table 1.

Table 1: Absolute viscosities *(η/mPa.s)* of pure solvents at 298.15K.

Solvents	Exptl.	Lit.	
Tetrahydrofuran	0.2244	0.2253[a]	
2-Methoxyethanol	1.3997	1.3985[c]	1.3847[b]
2-Ethoxyethanol	2.1238	2.1230[b]	
2-Butoxyethanol	2.7293	2.7286[a]	2.7304[b]

[a]Haynes, W.M[15]; [b]Patil et al[16]; [c]Missopolinou et al[17]

III. RESULTS AND DISCUSSION

Excess viscosities, η^E of the binary mixtures of THF with 2-alkoxyethanols have been calculated from the experimental viscosity data using Equation 1.

$$\eta^E = \eta - x_1\eta_1 - x_2\eta_2 \text{ --------- Eq. 1}$$

Where η, η_1 andη_2 are the absolute viscosities of the binary mixtures and the pure components 1 and 2, respectively; x_1 and x_2 are their respective mole fractions.

The excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the viscosity data using Eq. 4:

$$\Delta G^{*E} = RT\left[\ln \eta V - x_1 lnV_1 - x_2 lnV_2\right] \quad \text{----- Eq. 2}$$

Where *R, T* and *V* are the terms representing gas constant, absolute temperature, and molar volumes respectively; the subscripts 1 and 2 represent the pure components 1 and 2 respectively.

The composition dependence ofη^E and ΔG^{*E} values were fitted to the Redlich-Kister nonlinear polynomial type equation (Redlich and Kister[18], 1948) by least-squares fitting.

$$Y^E = X_1 X_2 \sum_{i=1}^{n} A_i(2X_1 - 1)^{i-1} \quad \text{--Eq. 3}$$

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of standard deviation $\sigma(Y^E)$ as calculated using Equation 4:

$$\sigma(Y^E) = \left[\frac{\Sigma \; \overline{Y^E_{exp} - Y^E_{cal}}^2}{m-n} \right]^{1/2}$$

Eq. 4

Where m is the number of experimental data points and n is the number of coefficients ($n = 4$ in this present case). The subscripts *exp.* and *cal.* represent the experimental and calculated values of excess viscosity or excess Gibbs free energy of activation of viscous flow respectively. The coefficients together with their standard deviations are given in Table 3.

The values of η^E and ΔG^{*E} obtained using Eqs. 1 and 2 are listed as a function of composition in Table 2.

Table 2: Dynamic viscosities (η), excess viscosity (η^E) and excess Gibbs' free energy of activation of viscous flow (ΔG^{*E}) of binary mixtures of Tetrahydrofuran + (C_1–C_4) 2-alkoxyethanols at different temperatures.

X_1	293.15K			298.15K			303.15K		
	η (mPa.s)	η^E (mPa.s)	ΔG^{*E} (Jmol^{-1})	η (mPa.s)	η^E (mPa.s)	ΔG^{*E} (Jmol^{-1})	η (mPa.s)	η^E (mPa.s)	ΔG^{*E} (Jmol^{-1})
Tetrahydrofuran (1) + 2-methoxyethanol (2)									
0.0003	1.7286	0.0023	0.0040	1.5249	0.0032	0.0081	1.3783	0.0044	0.0015
0.0714	1.5433	0.3830	3.7689	1.3077	0.5285	7.3301	1.1199	0.7136	14.8145
0.1428	1.4081	0.5009	6.7521	1.1597	0.6912	13.2484	0.9551	0.9333	27.0892
0.2142	1.2619	0.4620	9.0577	0.9964	0.6375	17.9043	0.7695	0.8608	36.9953
0.2856	1.1325	0.3466	10.7662	0.8563	0.4782	21.4087	0.6153	0.6458	44.6512
0.3570	1.0059	0.2108	11.9336	0.7202	0.2908	23.8391	0.4665	0.3928	50.1316
0.4282	0.9461	0.0905	12.5942	0.6761	0.1247	25.2419	0.4417	0.1686	53.4658
0.4998	0.9521	0.0031	12.7701	0.7229	0.0042	25.6503	0.5399	0.0058	54.6754
0.5712	0.9336	-0.0450	12.4630	0.7359	-0.0623	25.0636	0.5923	-0.0841	53.7218
0.6426	0.8884	-0.0591	11.6694	0.7121	-0.0817	23.4782	0.5951	-0.1103	50.5717
0.7140	0.8040	-0.0497	10.3786	0.6341	-0.0687	20.8793	0.5247	-0.0927	45.1744
0.7854	0.7351	-0.0298	8.5775	0.5775	-0.0413	17.2488	0.4832	-0.0557	37.4754
0.8568	0.6800	-0.0115	6.2541	0.5401	-0.0160	12.5703	0.4676	-0.0217	27.4222
0.9282	0.6187	-0.0020	3.4014	0.4939	-0.0029	6.8338	0.4402	-0.0039	14.9697
0.9997	0.5685	0.0000	0.0000	0.4634	0.0000	0.0000	0.4341	0.0000	0.0000
Tetrahydrofuran (1) + 2-ethoxyethanol (2)									
0.0003	2.0984	0.0033	1.0202	2.2567	0.0042	2.0147	2.4107	0.0056	4.5885
0.0714	1.8426	0.5478	5.0937	1.9410	0.7011	7.5089	2.0238	0.9194	10.6838
0.1428	1.6587	0.7165	9.1091	1.7173	0.9170	13.4857	1.7573	1.2024	19.2297
0.2142	1.4587	0.6608	12.2012	1.4732	0.8457	18.1285	1.4641	1.1089	25.8975
0.2856	1.2828	0.4957	14.4848	1.2598	0.6344	21.5843	1.2112	0.8319	30.8801
0.3570	1.1111	0.3015	16.0402	1.0518	0.3858	23.9559	0.9653	0.5059	34.3123
0.4282	1.0347	0.1294	16.9167	0.9659	0.1654	25.3059	0.8793	0.2170	36.2758
0.4998	1.0525	0.0045	17.1452	1.0004	0.0055	25.6753	0.9511	0.0074	36.8254
0.5712	1.0352	-0.0645	16.7286	0.9900	-0.0827	25.0664	0.9642	-0.1083	35.9630
0.6426	0.9799	-0.0846	15.6618	0.9310	-0.1085	23.4732	0.9135	-0.1421	33.6811
0.7140	0.8683	-0.0711	13.9297	0.8001	-0.0912	20.8762	0.7685	-0.1194	29.9541
0.7854	0.7790	-0.0427	11.5133	0.6974	-0.0548	17.2513	0.6607	-0.0717	24.7505

0.8568	0.7095	-0.0166	8.3956	0.6203	-0.0214	12.5766	0.5862	-0.0279	18.0414
0.9282	0.6310	-0.0029	4.5663	0.5316	-0.0038	6.8391	0.4966	-0.0050	9.8099
0.9997	0.5685	0.0000	0.1245	0.4634	0.0000	0.2458	0.4341	0.0000	1.1254
Tetrahydrofuran (1) + 2-butoxyethanol (2)									
0.0003	3.2986	0.0066	0.0547	2.9445	0.0084	0.9755	2.5017	0.0109	3.0125
0.0714	2.8249	1.0758	6.6684	2.4133	1.3664	10.8361	1.8938	1.7750	23.5857
0.1428	2.4877	1.3967	11.7219	2.0555	1.7740	19.2558	1.5113	2.3056	42.4899
0.2142	2.1203	1.2765	15.4742	1.6592	1.6213	25.6456	1.0789	2.1073	57.2929
0.2856	1.7986	0.9465	18.1567	1.3211	1.2022	30.2728	0.7220	1.5627	68.4116
0.3570	1.5754	0.5664	19.9290	1.1081	0.7195	33.4257	0.5278	0.9352	76.1821
0.4282	1.4953	0.2361	20.8888	1.0766	0.3001	35.8727	0.5692	0.3900	80.6604
0.4998	1.5093	0.0029	21.0904	1.1649	0.0038	35.6562	0.7670	0.0050	81.9508
0.5712	1.5048	-0.1196	20.5402	1.2296	-0.1518	34.7753	0.9337	-0.1976	80.0868
0.6426	1.4085	-0.1488	19.2234	1.1778	-0.1890	32.5353	0.9490	-0.2456	75.0376
0.7140	1.1737	-0.1174	17.1071	0.9500	-0.1491	28.9727	0.7355	-0.1936	66.7491
0.7854	0.9928	-0.0636	14.1532	0.7906	-0.0808	23.9489	0.6110	-0.1047	55.1402
0.8568	0.8280	-0.0200	10.3291	0.6517	-0.0255	17.4572	0.5131	-0.0327	40.1845
0.9282	0.6231	-0.0027	5.6187	0.4620	-0.0035	9.4924	0.3491	-0.0042	21.8407
0.9997	0.5685	0.0000	0.9874	0.4634	0.0000	2.0245	0.4341	0.0000	4.8560

An examination of Table2 shows that the excess viscosities were large and positive at regions of low THF composition and small negative at regions of high THF for the binary mixtures of MOE, EOE and BOE with THF at the studied temperatures in the whole range of solvent compositions and shown in Figs. (1-3), this result agrees well with the reported negative and positive excess molar volumes reported in our earlier work (Jumbo et al, 2019)[1] on the volumetric behavior of THF + 2-alkoxyethanol mixtures at the same temperatures and mole fraction ranges.

Excess Viscosity

Generally, positive values of excess viscosity indicate strong specific interactions andnegative values of η^E indicate the presence of dispersion forces or mutual loss of specific interactions in molecules operating in the systems arising due to weak intermolecular interactions. The dependence of ηE on composition for the binary mixtures THF + 2-alkoxyethanols under study may be explained in terms of the following factors: physical, chemical and structural contributions [Bhatia et al[19], Cwiklinska and Kinart][20]. The physical contributions comprise of dispersion forces and non-specific physical interactions and the sign of excess viscosity may be negative. The chemical contributions takes into consideration the breaking up of hydrogen bond structure which gives negative η^E and specific interactions such as H-bond formation, charge-transfer complex formation and dipole– dipole interactions that gives to positive η^E values, while the structural contribution takes into account the difference in molar volumes and free volumes of liquid components, geometry of molecules, which favours fitting of the component molecules within the voids of each other which gives positive values to excess viscosity as reported by Kaufman and Eyring[21]. The sign and magnitude of η^E depend on the combined effect of various factors such as molecular size, shape, and intermolecular forces.

Many authors (Dikio et al[22], 2012; Li et al[6], 2010; Mahendra et al[23], 2009) have reported negative excess viscosities where excess molar volumes were positive, and positive excess viscosities where excess molar volumes were negative. Positive η^E values have been reported by (Subha et al[7], 2004; Peshwe et al[24], 2009) to be indicative of the presence of strong interactions between component molecules. [Awasthi and Awasthi][25] reported on the intermolecular interactions between formamide and 2-alkoxyethanols in terms of viscometric study. The authors concluded that 2-alkoxyethanol and formamide interaction predominate than those between 2-alkoxyethanol molecules which contributes to positive η^E values. In this present work, the large positive values of η^E are attributable to the existence of strong dipole-dipole interactions (Reddy and Reddy[26], 2014) such as hydrogen bonding between the ethereal oxygen of THF and the O-H group of 2-alkoxyethanols. The slightly negative values of η^E at higher mole fraction ranges of THF corroborates thoroughly with the reported small positive V_m^E

values reported for the solvent systems at the same temperatures in our earlier publication, and supports our earlier proposition of the presence and dominance of disruptive effects over specific interactions (Parthasarathi et al[27], 2011, Ponchomi et al[28], 2015) in the named systems.

The dependence of excess viscosity on temperature has been studied and is presented graphically in Figures 1-3
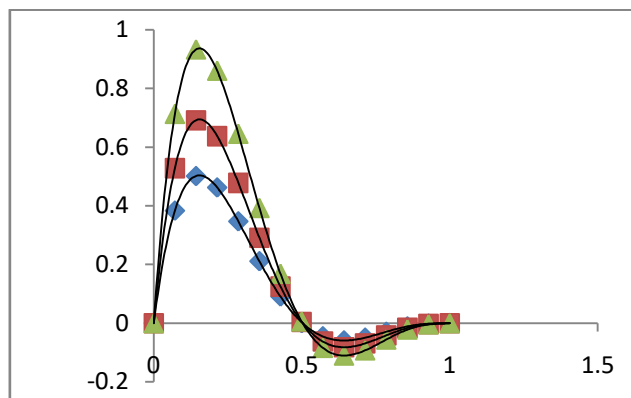

Figure 1. Plot of excess viscosity (η^E) for binary mixtures of THF + 2-methoxyethanol as a function of mole fraction of THF at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).
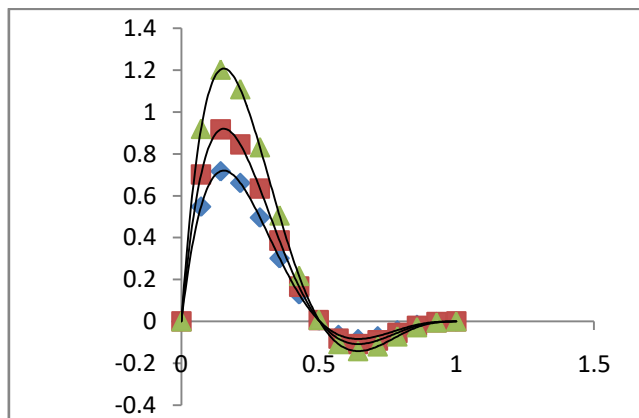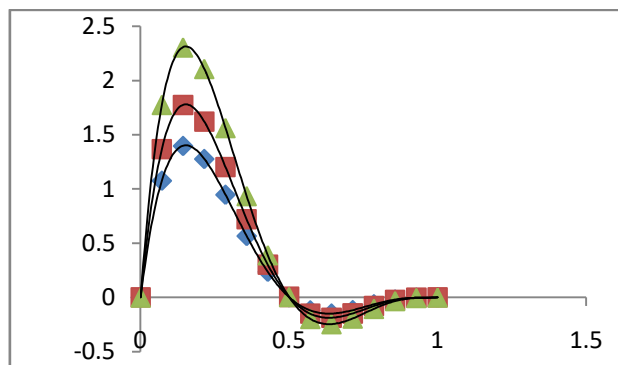

Figure 2.Plot of excess viscosity (η^E) for binary mixtures of THF + 2-ethoxyethanol as a function of mole fraction of THF at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).

Figure 3.Plot of excess viscosity (η^E) for binary mixtures of THF + 2-butoxyethanol as a function of mole fraction of THF at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).

The figures above reveal that the excess viscosities increase with increase in temperature in all the systems studied.This increment in excess viscosities suggest the strengthening of interactions between unlike molecules, a consequence of weakening self-association through hydrogen bonds in the 2-alkoxyethanols. A similar observation was made by Bhudpesh and co-workers (Bhudpesh et al[29], 2009) in their study of the dielectric behaviour of chloroaniline with 2-methoxyethanol and 2-ethoxyethanol.

The structural effects of excess viscosity have been studied by varying the chain length of the 2-alkoxyethanols (from 2-methoxy- to 2-butoxyethanol), and is presented graphically in Figures (4-6):
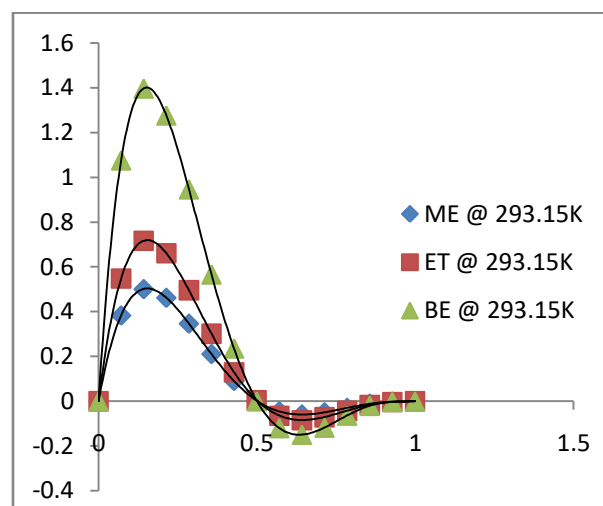

Figure 4. : Plots of excess viscosity vs. mole fraction of THF for binary mixtures of THF + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 293.15K.
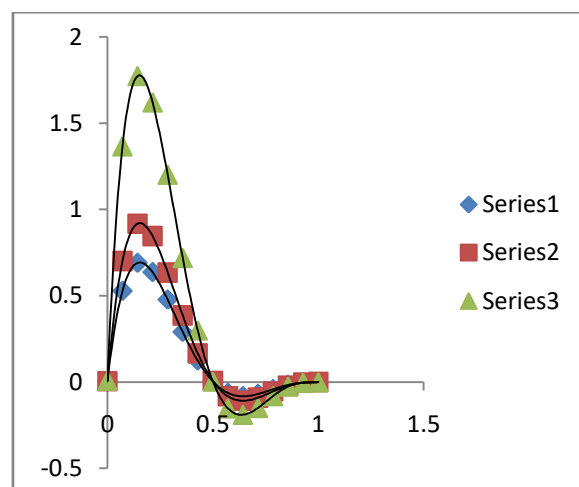

Figure 5. Plots of excess viscosity vs. mole fraction of THF for binary mixtures of THF + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 298.15K.
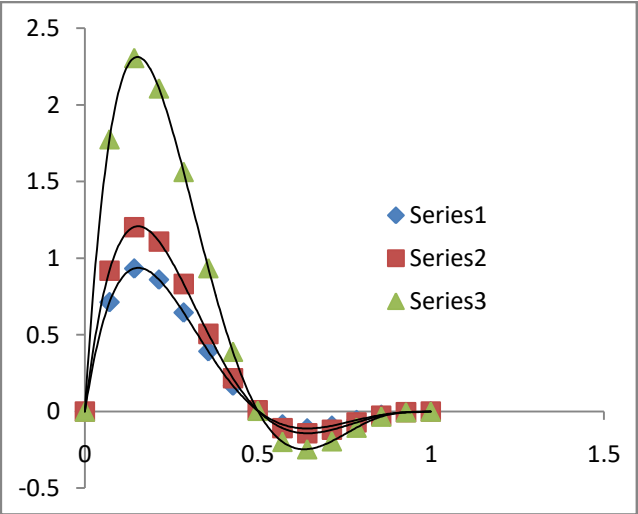
Figure 6. Plots of excess viscosity vs. mole fraction of THF for binary mixtures of THF + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 303.15K.

Increasing the alkoxy- chain length of the 2-alkoxyethanols results in an increase in excess viscosity, which agrees well with the reported values of excess molar volumes of the systems THF +2-alkoxyethanols in our previous study (Jumbo et al., 2019)[1]. The strengths of interaction in the binary mixtures follow the previously established order: THF + BOE > EOE > MOE.

Table 3: Fitting parameters, A_i, of the Redlich-Kister polynomial equation and standard deviations, σ, of excess viscosities, η^E and excess Gibbs free energy of activation for viscous flow, ΔG^{*E}, of binary mixtures of THF + 2-alkoxyethanols at different temperatures.

T/K	Property	A_0	A_1	A_2	A_3	σ
		Tetrahydrofuran (1) + 2-methoxyethanol (2)				
293.15K	η^E (mPa.s)	0.0279	0.0005	1.7731	0.0004	0.3200
	ΔG^{*E} (Jmol^{-1})	118.6460	0.0005	1.7735	0.0004	0.9200
298.15K	η^E (mPa.s)	0.0372	0.0007	2.4471	0.0005	0.4900
	ΔG^{*E} (Jmol^{-1})	238.3130	0.0007	2.4471	0.0005	1.3900
303.15K	η^E (mPa.s)	0.0511	0.0010	3.3038	0.0007	0.7500
	ΔG^{*E} (Jmol^{-1})	507.9889	0.0010	3.3038	0.0007	1.7500
		Tetrahydrofuran (1) + 2-ethoxyethanol (2)				
293.15K	η^E (mPa.s)	0.0395	0.0008	2.5364	0.0005	0.9500
	ΔG^{*E} (Jmol^{-1})	159.2940	0.0008	2.5364	0.0005	1.9400
298.15K	η^E (mPa.s)	0.0488	0.0009	3.2465	0.0006	1.2400
	ΔG^{*E} (Jmol^{-1})	238.5460	0.0010	3.2465	0.0007	2.4600
303.15K	η^E (mPa.s)	0.0488	0.0013	4.2566	0.0008	1.9600
	ΔG^{*E} (Jmol^{-1})	342.1399	0.0013	4.2571	0.0008	2.9800
		Tetrahydrofuran (1) + 2-butoxyethanol (2)				
293.15K	η^E (mPa.s)	0.0232	0.0014	5.0099	0.0011	1.8200
	ΔG^{*E} (Jmol^{-1})	195.9470	0.0014	5.0099	0.0011	1.8700
298.15K	η^E (mPa.s)	0.0302	0.0018	6.3627	0.0014	2.0600
	ΔG^{*E} (Jmol^{-1})	330.9910	0.0018	6.3627	0.0014	2.0600
303.15K	η^E (mPa.s)	0.0395	0.0023	8.2710	0.0018	2.2200
	ΔG^{*E} (Jmol^{-1})	761.3948	0.0023	8.2710	0.0018	2.1600

The excess Gibbs free energy of activation of viscous flow

The excess Gibbs free energy of activation of viscous flow, like excess viscosity, can be used to investigate the molecular interactions of solvent systems [Mariano and Postigo][30]. The change of excess Gibbs free energy of activation of viscous flow with mole fraction of THF for the binaries of MOE, EOE and BOE with THF is shown in Figures (7–9). The excess Gibbs free energy of activation of viscous flow is positive for

THF + 2–alkoxyethanols binary systems over the entire composition range and at all the temperatures. It is well known fact that negative values of ΔG^{*E} indicate the presence of weak physical forces in the system [Nayeem et al][31]. On the other hand, positive values of ΔG^{*E} suggest strong specific interactions (like hydrogen bonding and dipole-dipole interactions) between unlike molecules. The positive values of

ΔG^{*E} in the binary liquids of THF with 2–alkoxyethanols also support the conclusion drawn from the excess viscosity.
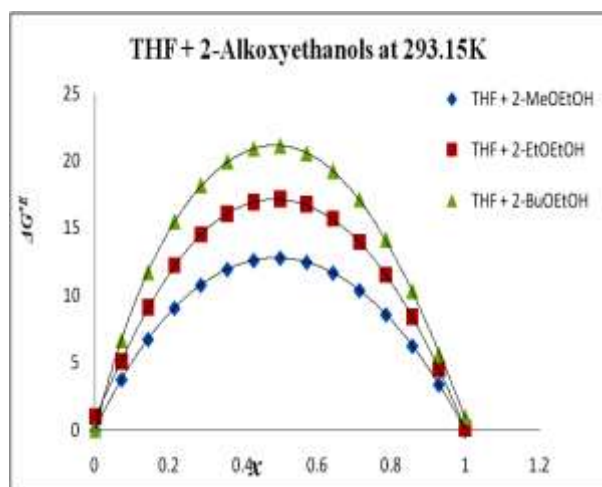

Figure 7.Plots of excess Gibbs free energies of activation of viscous flow(ΔG^{*E}) vs. mole fraction of binary mixtures of THF + 2-alkoxyethanols at 293.15K.
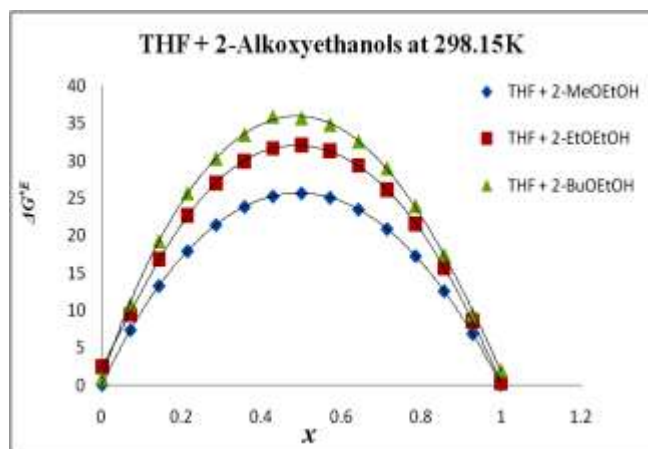

Figure 8.Plots of excess Gibbs free energies of activation of viscous flow (ΔG^{*E}) vs. mole fraction of binary mixtures of THF + 2-alkoxyethanols at 298.15K.
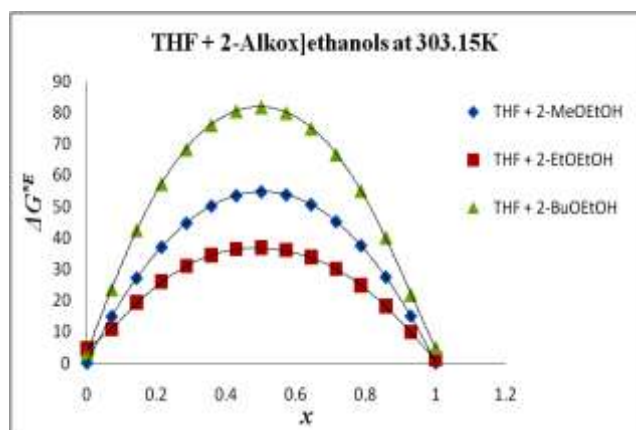

Figure 9.Plots of excess Gibbs free energies of activation of viscous flow(ΔG^{*E}) vs. mole fraction of binary mixtures of THF + 2-alkoxyethanols at 303.15K.

The figuresof ΔG^{*E} show that the strength of interaction increases with increase in chain length of the 2-alkoxyethanol, although the profiles of the curve are identical. This suggests that, the type of interactions in these solvent systems are governed by their identical chemical functional group, the physical structure of the components affect the magnitude and extent of these interactions.

Analyzing viscosity of binary mixtures by semi empirical models

Several semi-empirical correlation models have been used to analyze the viscosity data, and their predictive ability tested on the basis of their percentage standard deviations.

Grunberg and Nissan[32] suggested the following logarithmic relation between viscosity of binary mixtures and their pure components:

$$\ln \eta = x_1 ln\eta_1 + x_2 ln\eta_2 + x_1 x_2 d_{12} \qquad (5)$$

Where d_{12} is a constant proportional to interaction energy and is an approximate measure of the strength of the intermolecular interactions between the components in a binary mixture.

Hind and Ubbelohde[33] suggested the following equation for the viscosity of binary mixtures:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \qquad (6)$$

Where H_{12} is the Hind interaction parameter.

Frenkel[34] proposed the following equation for the correlation of viscosity data:

$$\ln \eta = x_1^2 ln\eta_1 + x_2^2 ln\eta_2 + 2x_1 x_2 ln F_{12} \qquad (7a)$$

Where F_{12} is a constant attributed to unlike pair interactions, its value is obtained from:

$$F_{12} = 0.5\eta_1 + 0.5\eta_2 \qquad (7b)$$

Katti and Chaudhary[35] suggested the following equation for the interpretation of intermolecular interactions in binary mixtures:

$$\ln(\eta V) = x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2 + x_1 x_2 {}^{W_{vis}}/_{RT} \qquad (8)$$

Where ${W vis}/_{RT}$ is an interaction term,R the gas constant and T the temperature.

The nature of interactions in binary mixtures, according to Heric and Brewer[36] follows the equation:

$$ln\eta = x_1 ln\eta_1 + x_2 ln\eta_2 + x_1 lnM_1 + x_2 lnM_2 - ln(x_1 M_1 + x2 M2 + \Delta 12 \qquad (9)$$

Where Δ_{12} is a function representing molecular interactions and $\alpha_{12}=\alpha_{21}$is the interaction parameter. Heric and Brewer expressed α_{12} as a function of composition.

The predictability of these models was tested by comparing the experimental viscosity values to the model-derived values at 298.15K as shown in Tables 4.

Table 4: Experimental (η_{expt}) and predicted values (η_{calc}) of absolute viscosities for binary mixtures of   THF + 2-Alkoxyethanol at 298.15K.

			298.15K			
	η_{expt}	η_{calc}				
		G-N	H-U	K-C	H-B	F
X_1		Tetrahydrofuran (1) + 2-methoxyethanol (2)				
0.0003	1.5249	2.9429	2.9427	2.9428	2.9602	2.9389
0.0714	1.3077	3.6760	2.7425	3.5790	6.6741	3.7837
0.1428	1.1597	5.1811	2.6224	4.9029	7.8326	4.9591
0.2142	0.9964	5.4635	2.3501	5.1182	6.3411	5.8264
0.2856	0.8563	4.2002	1.9310	3.9557	4.3473	5.9948
0.3570	0.7202	2.7037	1.4648	2.5809	2.8890	5.3732
0.4282	0.6761	1.7161	1.0562	1.6595	2.0125	4.2151
0.4998	0.7229	1.1959	0.7637	1.1659	1.5127	2.9201
0.5712	0.7359	0.9514	0.5987	0.9297	1.2276	1.8325
0.6426	0.7121	0.8387	0.5263	0.8194	1.0495	1.0914
0.7140	0.6341	0.7706	0.4961	0.7542	0.9146	0.6843
0.7854	0.5775	0.6986	0.4689	0.6864	0.7878	0.5163
0.8568	0.5401	0.6125	0.4364	0.6061	0.6603	0.4498
0.9282	0.4939	0.5297	0.4238	0.5268	0.5443	0.4037
0.9997	0.4634	0.4637	0.4631	0.4636	0.4636	0.3421
		Tetrahydrofuran (1) + 2-ethoxyethanol (2)				
0.0003	2.2567	2.2556	2.2554	2.2557	2.2637	2.2535
0.0714	1.9410	2.3308	2.0870	2.3162	3.5979	3.2419
0.1428	1.7173	2.5369	1.9905	2.5017	3.8600	4.6786
0.2142	1.4732	2.4555	1.8071	2.4131	3.3147	5.9582
0.2856	1.2598	2.0845	1.5297	2.0496	2.5773	6.5358
0.3570	1.0518	1.6390	1.2152	1.6170	1.9670	6.1336
0.4282	0.9659	1.2766	0.9284	1.2656	1.5430	4.9326
0.4998	1.0004	1.0308	0.7093	1.0253	1.2642	3.4081
0.5712	0.9900	0.8799	0.5704	0.8776	1.0811	2.0432
0.6426	0.9310	0.7861	0.4956	0.7868	0.9499	1.0709
0.7140	0.8001	0.7175	0.4575	0.7183	0.8404	0.5082
0.7854	0.6974	0.6530	0.4330	0.6543	0.7351	0.3486
0.8568	0.6203	0.5857	0.4158	0.5866	0.6303	0.4086
0.9282	0.5316	0.5204	0.4193	0.5208	0.5346	0.4065
0.9997	0.4634	0.4636	0.4631	0.4636	0.4636	0.0390
		Tetrahydrofuran (1) + 2-butoxyethanol (2)				
0.0003	2.9445	2.9429	2.9427	2.9428	2.9602	2.9389
0.0714	2.4133	3.6760	2.7425	3.5790	6.6741	3.7837
0.1428	2.0555	5.1811	2.6224	4.9029	7.8326	4.9591
0.2142	1.6592	5.4635	2.3501	5.1182	6.3411	5.8264
0.2856	1.3211	4.2002	1.9310	3.9557	4.3473	5.9948
0.3570	1.1081	2.7037	1.4648	2.5809	2.8890	5.3732
0.4282	1.0766	1.7161	1.0562	1.6595	2.0125	4.2151

0.4998	1.1649	1.1959	0.7637	1.1659	1.5127	2.9201
0.5712	1.2296	0.9514	0.5987	0.9297	1.2276	1.8325
0.6426	1.1778	0.8387	0.5263	0.8194	1.0495	1.0914
0.7140	0.9500	0.7706	0.4961	0.7542	0.9146	0.6843
0.7854	0.7906	0.6986	0.4689	0.6864	0.7878	0.5163
0.8568	0.6517	0.6125	0.4364	0.6061	0.6603	0.4498
0.9282	0.4620	0.5297	0.4238	0.5268	0.5443	0.4037
0.9997	0.4634	0.4637	0.4631	0.4636	0.4636	0.3421

Fig.(10 – 12) present a graphical representation of the extent of deviations of the derived values from the experimental values. The models by Grunberg-Nissan, Hind-Ubbelohde, and Katti- Chaudhary reproduced the viscosity data better than the models proposed by Heric-Brewer and Frenkel model.
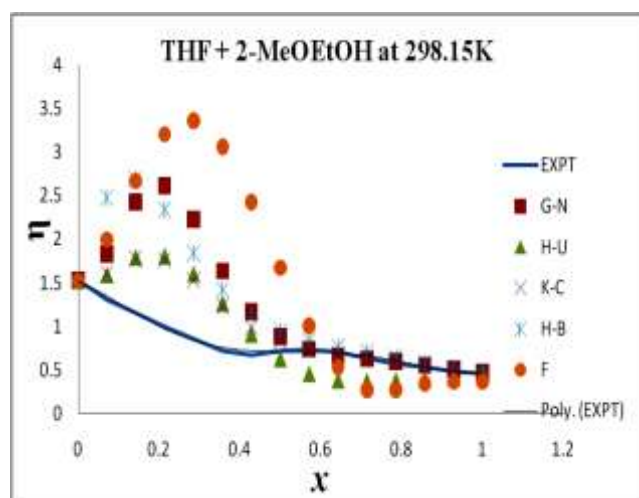

Figure 10. Plots of experimental and predicted values of absolute viscosities vs. mole fraction of binary mixtures of THF + 2-methoxyethanol at 298.15K.
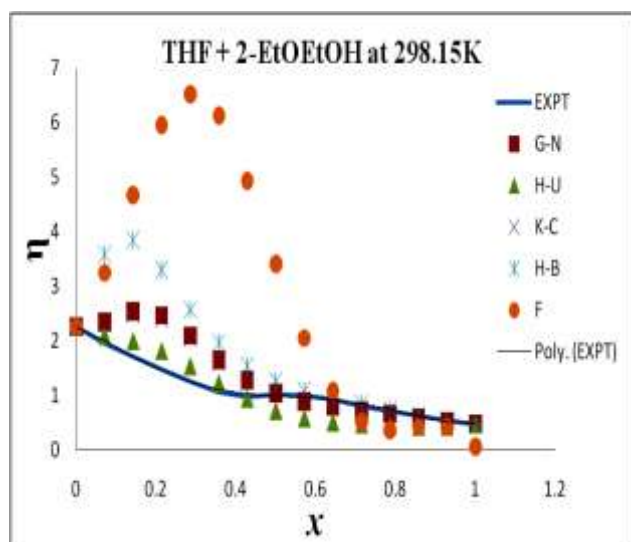

Figurer 11. Plots of experimental and predicted values of absolute viscosities vs. mole fraction of binary mixtures of THF + 2-ethoxyethanol at 298.15K.
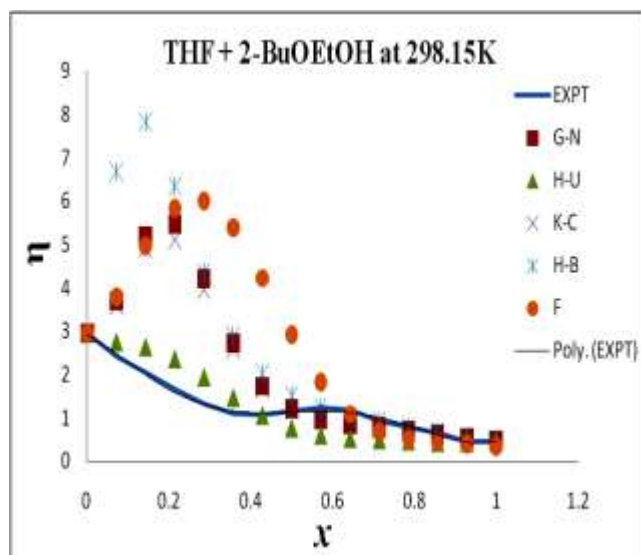

Figure 12.Plots of experimental and predicted values of absolute viscosities vs. mole fraction of binary mixtures of THF + 2-butoxyethanol at 298.15K.

The parameters of Grunberg-Nissan (G_{12})and *Katti-Chaudhary* (K_{12}) showed positive deviations in regions of low THF composition and slight negative deviations in high THF rich regions. Positive G_{12} indicates the presence of strong interactions between unlike molecules (Ali and Tariq, 2009)[37], and the small negative values confirm the slight dominance of disruptive effects in those regions. The parameters of Heric-Brewer($Δ_{12}$), Hind-Ubbelohde (H_{12}) and Frenkel's model all show positive deviations, although there is considerable linearity towards the THF rich mole fraction regions.

A close examination of the figures reveal that the model by Hind-McLaughlin-Ubbelohde reproduced the viscosity data most accurately. The accuracy of the predicted viscosities by the correlation models are summarized in terms of their average percentage deviations (APDs) and are shown in Table 5. From the table, it was observed that the values predicted by the Hind-Ubbelohde model gave the lowest APDs: 0.3746, 0.2809 and 0.3765% as compared to 2.8068, 2.6882 and 1.5312 for the Frenkel model for the binary mixtures of THF + 2-butoxyethanol at 293.15K.

Table 5. Average percentage deviations (APD) for calculated values of absolute viscosities for binary mixtures of THF + 2-alkoxyethanols at T: (293.15, 298.15 and 303.15) K.

Temp/K	APD (%)				
	G-N	*H-U*	*K-C*	*H-B*	*F*
THF + 2-MeOEtOH					
293.15	0.2538	0.3746	0.6119	0.5688	2.8068
298.15	0.8236	0.4630	0.4160	0.8103	1.4691
303.15	1.1938	0.5946	1.1298	1.4305	0.8634
THF + 2-EtOEtOH					
293.15	0.3739	0.2809	0.3644	0.8595	2.6882
298.15	0.5182	0.3016	0.4969	1.1166	3.1239
303.15	0.8141	0.3469	0.7991	1.5957	2.0664
THF + 2-BuOEtOH					
293.15	1.5436	0.3765	1.3656	1.9735	1.5312
298.15	1.8419	0.4998	1.6829	2.8091	2.7172
303.15	2.7834	1.0056	4.2950	6.2994	2.5992

IV. CONCLUSION

The viscosities of pure solvents, tetrahydrofuran, 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol, and the binary mixtures of tetrahydrofuran in the alkoxyethanols were determined at three temperatures. The viscosity data have been used to estimate the excess viscosities and excess Gibbs' free energies of activation of viscous flow. These excess functions have been used to elucidate the nature and strengths of intermolecular interactions in the binary mixtures.

The excess viscosities were relatively large and positive in the regions of low tetrahydrofuran compositions, and slightly negative in regions of high tetrahydrofuran compositions. Excess Gibbs' free energies were mostly positive. The magnitudes of the excess functions were found to be dependent on the chain length of the alkoxyethanols, and increased in magnitude in the order: 2-BuOEtOH > 2-EtOEtOH > 2-MeOEtOH.

Several viscosity correlation and interaction models were employed to correlate interpret as well as predict the experimental viscosity such as Grunberg–Nissan,Hind–Ubbelohde, Frenkel, Katti and Chaudhary andHeric and Brewer.The adjustable parameters of these models were used to predict the viscosity deviation of the binaries. Positive value of Grunberg–Nissan indicates strong interaction in the studied binaries. Of the models employed, the model proposed by Hind-Ubbelohde gave the most accurate predictions of the experimental viscosities.

REFERENCES

[1] Jumbo A.B., Kemeakegha A.J., Abasi C.Y. (2019) Volumetric behavior of binary mixtures of tetrahydrofuran and C1 – C4 alkoxyethanols at different temperatures, Chem. Sci. Trans., 8(4), 448–458.

[2] Jumbo A.B., Kemeakegha A.J. (2020) Volumetric behavior of binary mixtures of diethyl ether + (C1 – C4) alkoxyethanols at different temperatures. Int. J. Inn. Sci. & Res., 5(8) 1166–1173

[3] Mariano A., Camacho A.A., Postigo M., Valen A., Artigas H, Royo F.M., Urieta J.S. (2000) Viscosities and excess energy of activation for viscous flow for binary mixtures of tetrahydrofuran with 1-butanol, 2-butanol and 1-chlorobutane at 283.15, 298.15 and 313.15K. Brazilian J. Chem. Eng. 17(4-7), 459–470

[4] Mahajan A.R, Mirgane S.R and Deshmukh S. B, (2012), Excess molar volumes and viscosities for the binary mixtures of n-octane, n-decane, n-dodecane and n-tetradecane with octan-2-ol at 298.15K, J Mol Liq., 44, 175.

[5] Nain A.K. (2007), Densities and volumetric properties of binary mixtures of formamide with 1-butanol, 2-butanol, 1,3-butanediol and 1,4–butanediol at temperatures between 293.15 and 318.15 K, J. Sol. Chem., 36, 497-516.

[6] Li X, Fan G, Wang Y, Zhang M and Lu Y (2010), "Volumetric and viscometric properties of the binary mixture of triethylene glycol monomethyl ether + water at T = (293.15, 303.15, 313.15, 323.15, 333.15)K under atmospheric pressure", J Molecular Liquids, 151, 62-66.

[7] Subha M. C. S., Swamy G. N., Bai M. E. and KrishnaRao K. S. V. (2004), Excess volume and viscosity of ethoxyethanol with n-butylamine, n-hexylamine, n-octylamine and cyclohexylamine, Ind J Chem, 43A, 1876-1881.

[8] Koohyar F, Kiani F, Sharifi S, Sharifirad M, Rahmanpour H.S., (2012), Study on the change of refractive indices on mixing, excess molar volumes and viscosity deviation for aqueous solution of methanol, ethanol, ethylene glycol, 1-propanol and 1,2,3-propantriol at T = 292.15K and atmospheric pressure. Res. J. Appl. Sci. Eng. Tech., 4(17): 3095 – 3101.

[9] BeebiS. K, Nayeem S K. M, Satyanarayana G. R, Venkateshwara A Rao, Bala D and Rambabu, C, (2016), Viscometric Study of Molecular Interactions in Dimethyl Carbonate + n-Alkoxyethanol Mixtures at Different Temperatures, Journal of Therm & Cat., 7(4),

[10] Yang C., Guanghu H, Yifu H andPeisheng M, (2008) Densities and viscosities of N,N-dimethyl formamide + N-methyl-2-pyrrolidinone and + dimethyl sulfoxide in the temperature range (303.15 to 353.15)K. J. Chem. Eng. Data, 53; 1639 – 1642.

[11] Suman (2013), Excess Molar volume of binary mixtures of 2-butanone with aromatic hydrocarbons and cyclohexane at T = 298.15K. Int. J. Sci. Tech. Management, 1(4); 19–25.

[12] Sihna B, Pradhan R., Saha S, Brahman D, Sarkar A, (2013) Thermophysical properties of binary mixtures of N,N-dimethylformamide with three cyclic ethers. J. Serb. Chem. Soc. 78(9); 1443 – 1460.

[13] Priya C.S, (2010). Molecular interaction studies in liquid mixtures using ultrasonic technique. Int. J. Adv. Sci. Tech., 18; 59–74.

[14] Pavai R.E and Tenuka S, (2012). Study of molecular interaction in ternary mixture of propyl acetate in cyclohexane with 2-methoxyethanol at 303, 308 and 313K. Int. J. Res. Phys. Chem. 1(1); 32–37.

[15] Haynes, W.M. (ed.) CRC Handbook of Chemistry and Physics. 91st ed. Boca Raton, FL: CRC Press Inc., 201–2011, pp. 3–76

[16] Patil P P, Patil S R, Borse A U and Hundiwale D G, Rasayan J Chem., 2011, 4(2), 599-604.

[17] Missopolinou D, Tsinvintzelis I and Panayiotou C, (2006), Fluid Phase Equilibria, 245(2), 2006, 89-101; DOI:10.1016/j.fluid.2006.04.016

[18] Redlich O. J. and Kister A. T, (1948), Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, Ind. Eng. Chem., 40, 345–348.

[19] Bhatia SC, Bhatia R, Dubey GP (2009) Studies on transport and thermodynamic properties of binary mixtures of octan-1-ol with chloroform, 1, 2-dichloroethane and 1, 1, 2, 2-tetrachloroethane at 298.15 and 308.15 K. J Mol Liq., 144: 163- 171.

[20] Ćwiklińska A, Kinart CM (2011) Thermodynamic and physicochemical properties of binary mixtures of nitromethane with {2-methoxyethanol+ 2-butoxyethanol} systems at T=(293.15,

298.15, 303.15, 308.15, and 313.15) K. J Chem Thermodyn., 43: 420-429.

[21] Kauzmann W, Eyring H (1940),"The viscous flow of large molecules". J Am Chem Soc., 62: 3113-3125.

[22] Dikio E. D., Nelana S. M., Isabirye A. D., Ebenso E. E. (2012), Density, dynamic viscosity and derived properties of binary mixtures of methanol, ethanol, n-propanol, and n-butanol with pyridine at T = (293.15, 303.15, 313.15 and 323.15)K, Int J ElectrochemSci, **7**, 11101-11122.

[23] Mahendra R. N., Sarkar L and Dewan R (2009), Molecular interactions with reference to manifestation of solvation effects in binary mixtures of ethyl acetoacetate with some methane derivatives by physicochemical techniques, Bull ChemSoc Ethiop, **5**, 103-114.

[24] Peshwe A. G., Arbad B. R. and Pachaling S. P. (2009), Volumetric and viscometric studies on N,N-dimethylacetamide and methanol binary mixtures at different temperatures, Int J Chem, **7**(3), 1505-1517.

[25] Awasthi A, Awasthi A (2012) Intermolecular interactions in formamide+ 2-alkoxyethanols: viscometric study. ThermochimActa, 537: 57-64

[26] Reddy G.S. and Reddy M.M. (2014), Thermodynamic properties of binary liquid mixtures of toluene with benzene, Int'l. J. Pharm. Bio Sci., **5**(1), 1064 – 1073.

[27] Parthasarathi S, Saravanakuamr K, BaskaranR and Kubendran T. R. (2011), Volumetric and viscosity study for the binary mixtures of dimethylsulfoxide with benzene, ethyl benzene, chlorobenzene and bromobenzene at temperatures of (303.15, 308.15 and 313.15)K and a pressure of 0.1MPa, Int J Sci Tech, **1**(2), 96–101.

[28] PonchomiRaha, Mahmuda Sultana, M. Kamrul Hossain, M. AbdurRahaman, (2015), Viscosities and deviations in viscosity for

binary mixtures of tetrahydrofuran + propanol-1 and tetrahydrofuran + butanol-1 at 303.15 K. International Journal of Research in Engineering and Technology, 4(5), 152–156.

[29] Bhupesh G. N., Kalyankar V. and Kadam P. L. (2013), "Dielectric behavior of binary mixture of 2-chloroaniline with 2-methoxyethanol and 2-ethoxyethanol", Orbital Elec J Chem, **5**(1), 1-6.

[30] Mariano A and Postigo M (2006) Excess molar volume and viscosity study for the ternary system tetrahydrofuran (1)+ 1-chlorobutane (2)+ 2-butanol (3) at 283.15, 298.15 and 313.15 K. Fluid Phase Equilib 239: 146-155.

[31] Nayeem M, Kondaiah M, Sreekanth K and Krishna Rao D, (2014) Thermoacoustic, volumetric, and viscometric investigations in binary liquid system of cyclohexanone with benzyl benzoate at T= 308.15, 313.15, and 318.15 K. J Thermodyn 2014: 487403.

[32] Grunberg L. and Nissan A. H, (1949), Mixture Law for Viscosity, Nature 164, 799.

[33] Hind R. K, McLaughlin E and Ubbelohde A. R, (1960), "Structure and viscosity of liquids camphor + pyrene mixtures," Transactions of the Faraday Society, vol. 56, 328–330.

[34] FrenkelYa I and Gubanov A, (1946),J. Exp. Theor. Phys. (Russ.), 16, 435

[35] Katti P. K, Chaudhri M. M, and PrakashO, (1966), "Viscosities of binary mixtures involving benzene, carbon tetrachloride, and cyclohexane," J. Chem and Eng Data, vol. 11, no. 4, pp. 593–594.

[36] Heric E. L and Brewer J. G, (1967), Viscosity of some binary liquid nonelectrolyte mixtures,J. Chem. Eng. Data, 12, 574–583.

[37] Ali A and Tariq M, (2007), Indian J ChemTechn, 14(2), 189–194.