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Volumetric Behaviour of Binary Mixtures of Diethyl Ether + (C_1 – C_4) Alkoxyethanols at Different Temperatures

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Abstract:- Densities of pure liquids and binary mixtures of diethyl ether (DEE) with 2-alkoxyethanols (2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol) have been determined over the entire range of solvent compositions at (293.15, 298.15 and 303.15) K. Excess molar volumes (V_m^E) have been calculated from the density data and were fitted into the Redlich-Kister type polynomial equation to obtain the fitting parameters A_i. The values of excess molar volumes, V_m^E were negative in regions of low diethyl ether (DEE) composition and small positive values were observed in regions of high diethyl ether (DEE) compositions in all the systems studied. V_m^E values were also found to decrease with increase in temperature and increase in chain length of the 2-alkoxyethanols. The above trends were attributed to the combined effects of disruption and formation of hydrogen bonds between like molecules of 2-alkoxyethanols and unlike molecules of diethyl ether (DEE), respectively.

Keywords:- *density, excess molar volumes, hydrogen bonding, intermolecular interactions.*

I. INTRODUCTION

We have been investigating the nature and strengths of intermolecular interactions, and possible structural changes associated with the mixing of binary mixtures of aliphatic C_4 ethers (tetrahydrofuran and diethyl ether) and 2-alkoxyethanols. In an earlier study (Jumbo et al., 2019)[1], reported the results of our findings on the volumetric behavior of tetrahydrofuran and 2-alkoxyethanols at (293.15, 298.15 and 303.15) K. The result of that study revealed that strong interactions existed between the THF molecules and the 2-alkoxyethanols. This was deduced from the fact that the excess molar volumes were negative and at all temperatures. These strong interactions were attributed to the possibility of the existence of hydrogen bonds between the ethereal oxygen of THF and the hydroxyl hydrogen of the 2-alkoxyethanols.

In this present work, there is strong expectation that interactions of the type observed between THF and 2-alkoxyethanols, i.e. hydrogen bonding, will be observed between diethyl ether (DEE) and 2-alkoxyethanols, under same conditions of temperature and mole fractions of mixing. This anticipated similarity is due to the chemical resemblance between the molecules, THF and DEE. They are both ethers, their molecular weights differ only by two hydrogen atoms (72.12g and 74.12g) respectively, and each of them contains four carbon atoms. They are used interchangeably as solvents in the production of plastics (Karas and Piel, 2004)[2].

However, THF and DEE differ in one respect, i.e., in their chemical structure. While THF is a cyclic ether, DEE is acyclic. Interestingly, this structural distinction should introduce some variation in the magnitude of interactions between the component molecules of their respective mixtures with 2-alkoxyethanols. Would the interactions between THF and the named alkoxyethanols be stronger than that between DEE and the alkoxyethanols?

It is the aim of this present paper to provide empirical answers to that question, and by extension add to the already available plethora of useful experimental data on the densities of pure liquid and liquid mixtures.

Diethyl ether (DEE) is used in the production of cellulosic plastics. It is also used as a starting fluid as a component of a mixture with petroleum distillates for gasoline and diesel engines due to its high cetane number of (89 - 96), and having high volatility and low flash point (Dirgha and Nisha, 2019)[3]. For the same reasons, it is also used as a component of fuel mixture for carbureted compression ignition model engines. DEE has also found broad applications in medicine and pharmacy due to its anesthetic effect, with the advantage of having a relatively wide gap between therapeutic and toxic doses, compared to chloroform (Bovil, 2008)[4]. The applications of 2-alkoxyethanols have been reported elsewhere (Jumbo et al., 2019)**[1]** and (Kemeakegha et al., 2015)[5].

II. MATERIALS AND METHOD

The reagents 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol were products of Lobachemie, India, with minimum assay of 99%. Diethyl ether (DEE) (98.5%) was a product of Merck, Germany. All the reagents were used without further purification. The densities of pure solvents and binary mixtures were determined using a single stem capillary pyknometer with a bulb volume of $10cm^3$. The pyknometer was calibrated with doubly distilled water at all working temperatures. All preparations and measurements were carried out in triplicates, and the average taken. The density values were reproducible to within $\pm 0.0002 gcm^{-3}$.

The desired temperatures were obtained using a water bath with a Bockel Grant digital thermostat (Model GD120; Serial Number 0528020) accurate to within ±0.001ºC. A mercury thermometer was used to confirm the temperature readings on the digital thermostat. Binary mixtures were prepared by weighing calculated masses of the component solvents using Searchtech Digital Balance (Model FA 2104A) correct to within ±0.0001g.

The purities of the solvents were checked by comparing experimental values with those reported in the open literature at 298.15 K and are presented in Table 1. There was good agreement between the two sets of data.

Solvents	**Exptl.**	**Lit.**
Diethyl ether	0.8927	0.8892[a]
2-Methoxyethanol	0.9652	0.9603[b]
2-Ethoxyethanol	0.9274	0.9252[c]
2-Butoxyethanol	0.8995	0.8960[b]

(a) Haynes, W.M[7]; (b) Missopolinou et al[8] ; (c) Patil et al[9]

Table 1:- Densities (ρ/gcm^{-3}) of pure solvents at 298.15K.

III. RESULTS AND DISCUSSION

Excess molar volumes, V_m^E were calculated from the densities of pure liquids and binary mixtures using Eq. 1:

$$V_m^E = \left[\frac{X_1M_1+X_2M_2}{\rho}\right] - \left[\frac{X_1M_1}{\rho_1}+\frac{X_2M_2}{\rho_2}\right] \qquad (1)$$

In Eq. 1, X_1 and X_2 are the mole fractions of components 1 and 2, M_1 and M_2 are their respective molecular weights; ρ, ρ_1 and ρ_2 are the densities of the binary mixtures, components 1 and 2, respectively. The calculated values of pure densities and their excess molar volumes are given in Tables 2a-2c.

X_{DEE}	293.15K		298.15K		303.15K	
	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}
0.0003	0.9754	-0.0077	0.9657	-0.0077	0.9320	-0.0077
0.0714	0.9509	-1.2812	0.9406	-1.2812	0.9089	-1.2812
0.1428	0.9277	-1.6081	0.9168	-1.6081	0.8869	-1.6081
0.2142	0.9061	-1.4137	0.8944	-1.4137	0.8662	-1.4137
0.2856	0.8836	-1.0500	0.8717	-1.0500	0.8453	-1.0500
0.3570	0.8634	-0.4977	0.8510	-0.4977	0.8261	-0.4977
0.4282	0.8439	-0.1775	0.8312	-0.1775	0.8077	-0.1775
0.4998	0.8271	-0.0548	0.8135	-0.0548	0.7909	-0.0548
0.5712	0.8126	0.1093	0.7980	0.1093	0.7759	0.1093
0.6426	0.7997	0.1016	0.7839	0.1016	0.7620	0.1016
0.7140	0.7868	0.0036	0.7699	0.0036	0.7483	0.0036
0.7854	0.7742	0.0021	0.7563	-0.0021	0.7350	0.0021
0.8568	0.7605	0.0591	0.7422	0.0591	0.7217	0.0591
0.9282	0.7465	0.0076	0.7280	0.0076	0.7082	0.0076
0.9997	0.7324	0.0001	0.7134	0.0001	0.6942	0.0001

Table 2a:- Density (ρ/gcm^{-3}) and excess molar volumes (V^E/cm^3mol^{-1}) of binary mixtures of DEE + 2-Methoxyethanol at (293.15, 298.15 and 303.15) K.

X_{DEE}	293.15		298.15		303.15	
	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}
0.0003	0.9320	-0.0091	0.9275	-0.0091	0.9230	-0.0091
0.0714	0.9148	-1.5204	0.9093	-1.5204	0.9038	-1.5204
0.1428	0.8980	-2.0271	0.8917	-2.0271	0.8851	-2.0271
0.2142	0.8819	-1.7158	0.8746	-1.7158	0.8670	-1.7158
0.2856	0.8642	-1.2838	0.8563	-1.2838	0.8481	-1.2838
0.3570	0.8480	-0.9466	0.8394	-0.9466	0.8303	-0.9466
0.4282	0.8320	-0.4479	0.8226	-0.4479	0.8127	-0.4479
0.4998	0.8180	-0.0643	0.8075	-0.0643	0.7965	-0.0643
0.5712	0.8061	0.1691	0.7941	0.1691	0.7817	0.1691
0.6426	0.7954	0.2605	0.7818	0.2605	0.7677	0.2605
0.7140	0.7843	0.2425	0.7691	0.2425	0.7536	0.2425
0.7854	0.7732	0.1626	0.7565	0.1626	0.7396	0.1626
0.8568	0.7602	0.0711	0.7427	0.0711	0.7250	0.0711
0.9282	0.7466	0.0098	0.7284	0.0098	0.7101	0.0098
0.9997	0.9320	0.0005	0.7134	0.0005	0.6942	0.0005

Table 2b:- Density (ρ/gcm^{-3}) and excess molar volumes (V^E/cm^{3}mol^{-1}) of binary mixtures of DEE + 2-Ethoxyethanol at (293.15, 298.15 and 303.15) K.

X_{DEE}	293.15		298.15		303.15	
	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}	ρ/gcm^{-3}	V^E/cm^3mol^{-1}
0.0003	0.9013	-0.0123	0.8997	-0.0123	0.8981	-0.0123
0.0714	0.8894	-0.8486	0.8872	-0.8486	0.8847	-0.8486
0.1428	0.8776	-2.3296	0.8745	-2.3296	0.8712	-2.3296
0.2142	0.8658	-2.1769	0.8618	-2.1769	0.8575	-2.1769
0.2856	0.8519	-1.6942	0.8473	-1.6942	0.8424	-1.6942
0.3570	0.8390	-0.9709	0.8336	-0.9709	0.8278	-0.9709
0.4282	0.8256	-0.2999	0.8194	-0.2999	0.8128	-0.2999
0.4998	0.8150	-0.0086	0.8074	-0.0086	0.7992	-0.0086
0.5712	0.8043	0.0282	0.7952	0.0282	0.7855	0.0282
0.6426	0.7956	0.1498	0.7844	0.1498	0.7728	0.1498
0.7140	0.7860	0.0847	0.7728	0.0847	0.7592	0.0847
0.7854	0.7759	0.0107	0.7607	0.0107	0.7452	0.0107
0.8568	0.7627	0.0946	0.7463	0.0946	0.7295	0.0946
0.9282	0.7482	0.0129	0.7305	0.0129	0.7125	0.0129
0.9997	0.7325	0.0004	0.7135	0.0004	0.6943	0.0004

Table 2c:- Density (ρ/gcm^{-3}) and excess molar volumes (V^E/cm^{3}mol^{-1}) of binary mixtures of DEE + 2-Butoxyethanol at (293.15, 298.15 and 303.15) K.

The values of V_m^E were correlated by the Redlich-Kister polynomial equation[6] (Eq. 2):

$$Y^E = X_1 X_2 \sum_{i=1}^{n} A_i (2X_1 - 1)^{i-1} \qquad (2)$$

The values of the parameters A_i were obtained by fitting the equation to the experimental values using least-squares method. The standard deviations for V_m^E were calculated using Eq. 3:

$$\sigma(Y^E) = \left[\frac{\Sigma\ Y_{\exp}^E - Y_{cal}^E \ ^2}{m-n} \right]^{1/2} \qquad (3)$$

Where m is the number of experimental data points and n is the number of coefficients considered. The subscripts *exp* and *cal* represent the experimental and calculated values of excess molar volumes respectively. The coefficients together with their standard deviations are given in Table 3.

T/K	A_0	A_1	A_2	A_3	$\sigma(V^E)$
DEE + 2-MeOEtOH					
293.15K	-0.4994	-0.0021	-5.8207	-0.0009	0.0600
298.15K	-0.4088	-0.0017	-4.7413	-0.0008	0.0900
303.15K	-0.3205	-0.0013	-3.6919	-0.0006	0.0900
DEE + 2-EtOEtOH					
293.15K	-0.5900	-0.0024	-6.9046	-0.0011	0.0400
298.15K	0.4831	-0.0020	-5.6203	-0.0009	0.0300
303.15K	0.3763	-0.0015	-4.3614	-0.0007	0.0100
DEE + 2-BuOEtOH					
293.15K	-0.7758	-0.0033	-9.3094	-0.0015	0.0500
298.15K	-0.6318	-0.0026	-7.5605	-0.0012	0.0500
303.15K	-0.4901	-0.0020	-5.8434	-0.0010	0.0200

Table 3:- Fitting parameters, A_i, of the Redlich-Kister polynomial equation and standard deviations, σ, of excess molar volumes, V^E, of binary mixtures of DEE + 2-alkoxyethanols at different temperatures.

IV. DISCUSSION

The excess molar volumes, V_m^E show negative deviations in regions of low diethyl ether (DEE) composition, (x_1 = 0.0003 to 0.4998) and exhibited positive deviations in regions of high DEE composition, (x_1 = 0.57122 to 0.9997) in all the solvent systems studied and at all temperatures. Similar trend have been reported by Parveen and co-workers for the system THF + methanol at 293.15K (Parveen et al, 2009)[10]. Excess molar volumes have been reported to be dependent on several opposing effects. According to Sham (2011)[11] these effects are classified into chemical, physical and structural contributions. Physical factors, which may include mainly nonspecific interactions due to dispersive forces, dipole-dipole interactions, etc. which contribute positively to the values of V_m^E, and usually occur as a result of the breakage of liquid order on mixing. Chemical factors, such as complex formation, hydrogen bonding between constituent molecules and charge transfer impart negatively on excess molar volumes. Structural effects on the other hand arises from interstitial accommodation of smaller molecules fitting into the lattices of larger molecules due to differences in molecular volumes and free volumes between component molecules that causes negative deviations (Matos and Trenzado, 2001)[12]. The sign and magnitude of V_m^E depends on the relative strengths of these effects (Sinha et al, 2013)[13].

An examination of Figs. 1 - 3 show a decrease in excess molar volumes, V_m^E with increase in temperature,

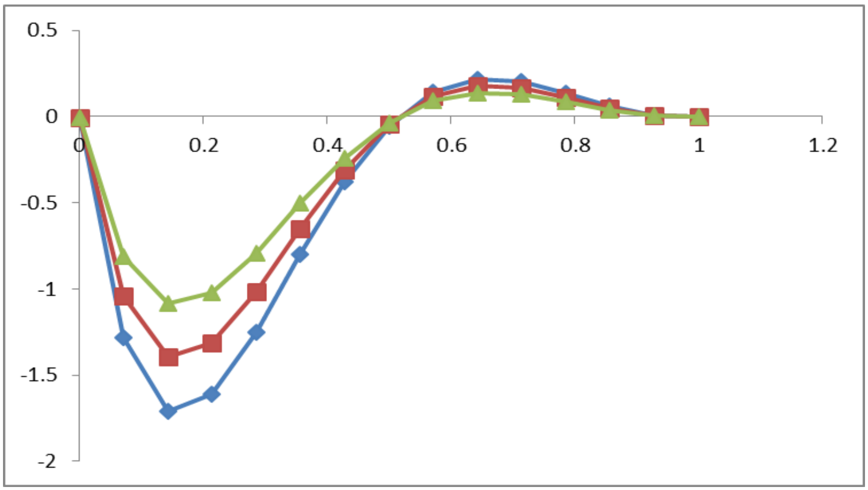

Fig 1:- Plot of excess molar volumes (V_m^E) for binary mixtures of DEE + 2-methoxyethanol as a function of mole fraction of DEE at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).

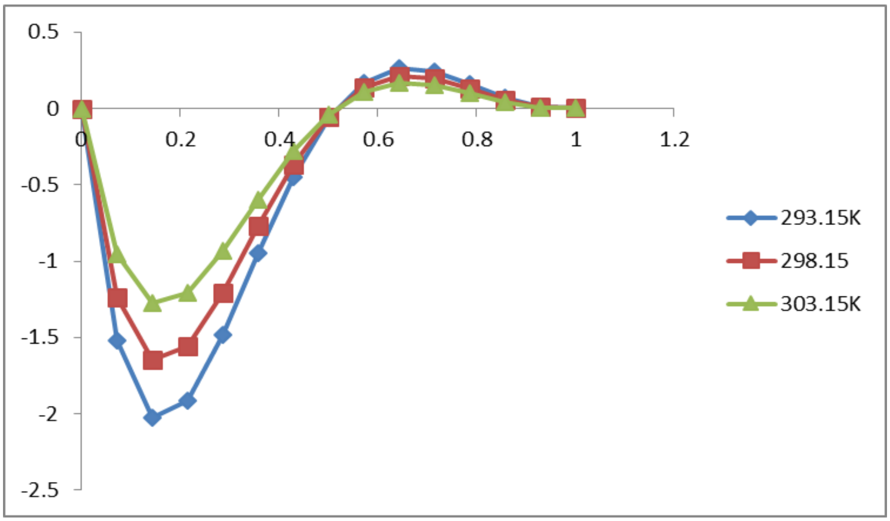

Fig 2:- Plot of excess molar volumes (V_m^E) for binary mixtures of DEE + 2-ethoxyethanol as a function of mole fraction of DEE at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).

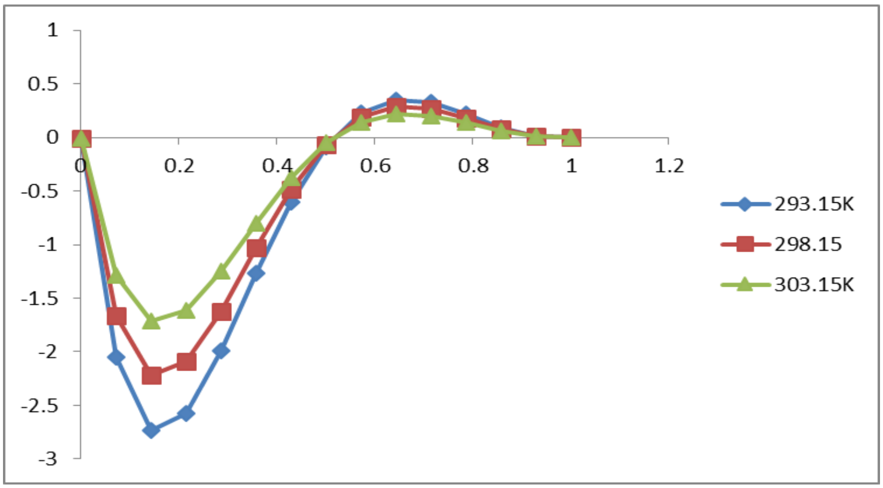

Fig 3:- Plot of excess molar volumes (V_m^E) for binary mixtures of DEE + 2-butoxyethanol as a function of mole fraction of DEE at different temperatures. T: 293.15K (♦); 298.15K (■); 303.15K (▲).

i.e. excess molar volumes, V_m^E becomes less negative at lower mole fractions of diethyl ether and at higher mole fractions of diethyl ether (DEE), the excess molar volumes found to be less positive with increase in temperature. This is in conformity with generally expected trends as intermolecular interactions due to hydrogen bonds formation, dipolar associations and dispersive forces tend to weaken with rise in temperature caused by increased thermal agitation of molecules (Parthasarathi et al, 2011)[14]. Peshwe et al[15] reported the same variation with temperature for the systems N, N-dimethylacetamide and methanol.

The variation of excess molar volumes with increase in chain length of the alkoxyethanol (2-methoxy-, 2-ethoxy- and 2-butoxyethanol) have been represented graphically in Figs. 4-6.

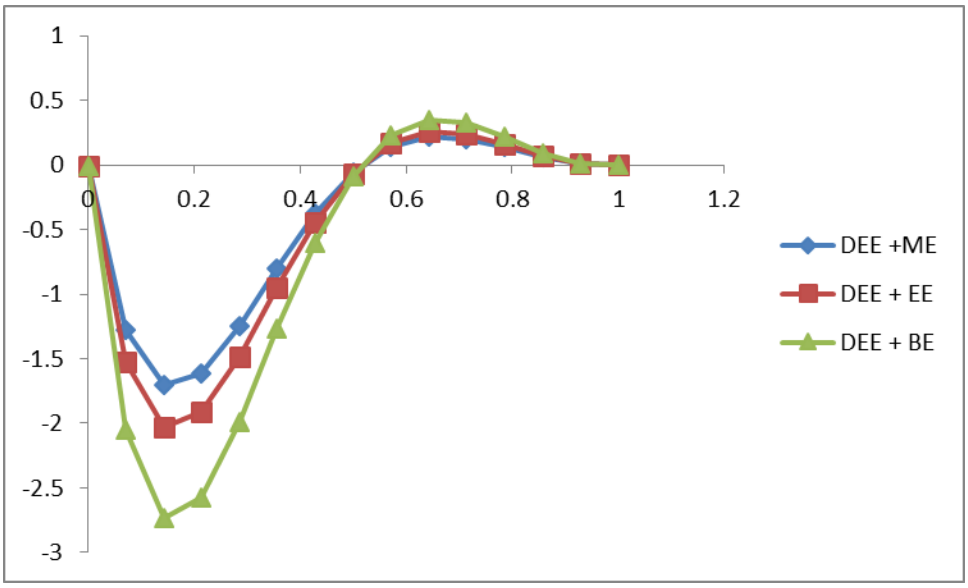

Fig 4:- Plots of excess molar volumes vs. mole fraction of DEE for binary mixtures of DEE + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 293.15K.

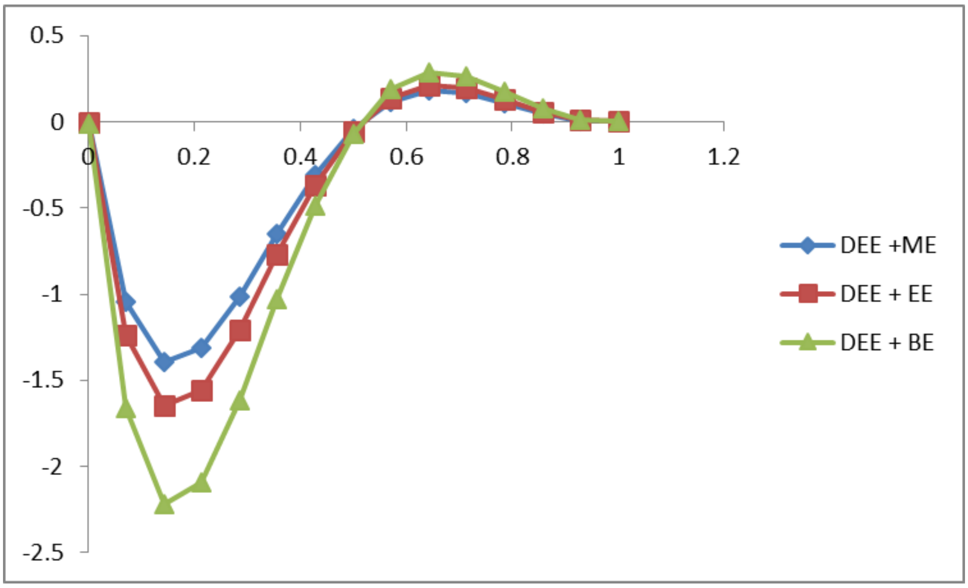

Fig 5:- Plots of excess molar volumes vs. mole fraction of DEE for binary mixtures of DEE + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 298.15K

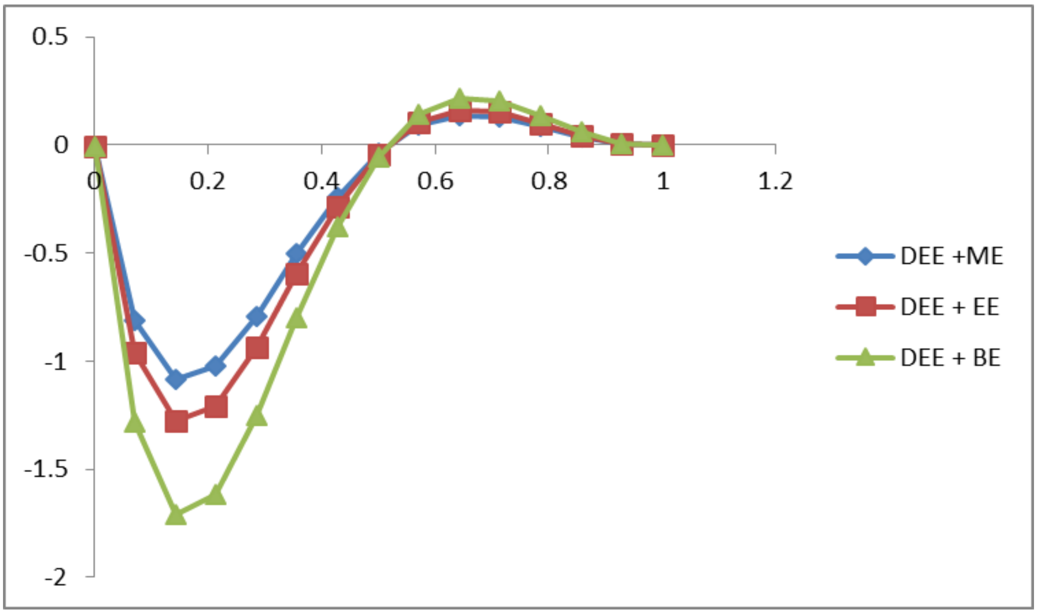

Fig 6:- Plots of excess molar volumes vs. mole fraction of DEE for binary mixtures of DEE + 2-methoxyethanol (♦); + 2-ethoxyethanol (■); and + 2-butoxyethanol (▲) at 303.15K.

A perusal of Figs. 4 - 6 show that the excess molar volumes increase with increases in alkoxy chain length of 2-alkoxyethanols and fall in the order BE > EE > ME. The greater negative values reported in DEE + 2-butoxyethanol mixtures could partly be due to the interstitial accommodation of smaller DEE molecules (molecular volume = 1.7251×10^{-22} cm^3) into the interstitials holes of the larger 2-butoxyethanol molecules (molecular volume = 2.1774×10^{-22} cm^3). Interstitial fittings of smaller molecules into larger ones have been reported for 2-pyrrolidinone and (C_6 – C_{10}) *n*-alkanols by Garcia et al (1996) [16], for the systems formamide and ethanol mixtures by Ali and Nain (1996) [17], dimethyl sulfoxide and alcohols by Ali et al (1999)[18], aliphatic ketones and ethylacetoacetate by Izonfuo and Kemeakegha (2009) [19]. Kemeakegha et al, (2015)[5] also reported the same trend in their study “volumetric behavior of binary mixtures of alkoxyethanols and some selected amines”. Subha et al (2004)[20] reported an increase in excess molar volumes with increase in chain length for the systems, 2-ethoxyethanol with *n*-butylamine, sec-butylamine, tert-butylamine, *n*-hexylamine, *n*-octylamine and cyclohexylamine binary systems. According to the authors, as the chain length of the normal amines increases, the interaction ability of the amines with ethoxyethanol increases, hence the increase in negative excess molar volumes.

A comparison of the results of our previous study (Jumbo et al., 2019)[1] on the volumetric behavior of THF + 2-alkoxyethanols and this work reveals a striking similarity in the profiles of the V_m^E vs. mole fraction plots for both solvent systems. The excess molar volumes, V_m^E values are, however, larger in THF mixtures than in DEE mixtures. This is indicative of stronger intermolecular interactions between THF and the 2-alkoxyethanols than in DEE and 2-alkoxyethanols. We have attributed this difference to the fact that THF is more susceptible to interactions than DEE due to the inherent ring strain of THF, as opposed to the two ethyl groups in DEE. According to DeRuiter (2005) [21], the ethyl groups in DEE interfere with hydrogen bonding and other interactions on the ethereal oxygen. In the case of THF, the hydrocarbon portion (alkyl groups on oxygen) are “tied back" in the cyclic structure, exposing the oxygen atom for optimal hydrogen bonding interactions with water with little interference from the non-polar hydrocarbon portion of the molecule.

V. CONCLUSION

The observed experimental values of excess molar volumes reveal that strong intermolecular interactions exist between the molecules of diethyl ether (DEE) and 2-alkoxyethanols. The strengths of these interactions are enhanced by increasing alkyl chain length of the 2-alkoxyethanol and low temperatures. The values in this work compare with that in our earlier studies, between THF and the named co-solvents with the results displaying close resemblance in trends but differ slightly in magnitude. The higher excess molar values reported for THF + 2-alkoxyethanol binary mixtures suggest that the intermolecular interactions are stronger in the systems involving THF and 2-alkoxyethanols than between DEE and 2-alkoxyethanols.

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