Volumetric Behavior of Binary Mixtures of Tetrahydrofuran and C_1-C_4 Alkoxyethanols at Different Temperatures

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Abstract: The volumetric behavior of binary mixtures of tetrahydrofuran (THF) +2-methoxyethanol (2-MeOEtOH), + 2-ethoxyethanol (2-EtOEtOH) and 2-butoxyethanol (2-BuOEtOH) were studied at 293.15, 298.15 and 303.15 K to identify the types and strengths of intermolecular interactions taking place in the solvent systems. The densities, ρ, of the pure solvents and the binary mixtures ranging from 0.0003-0.9997 of THF were obtained at the working temperatures. Excess molar volumes, V^E, of the binary mixtures were calculated from the density data. The calculated excess molar volumes were fitted into the Redlich-Kister polynomial and the fitting coefficients, A_i, obtained. The values of excess molar volumes were negative in all the solvent systems and at all temperatures in the mole fraction region of 0.00-0.50 THF. Beyond the mole fraction region of 0.50, the excess molar volumes were slightly positive. The negative excess molar volumes in the region of low THF concentration are attributed to intermolecular hydrogen bonding between unlike molecules of THF and the alkoxyethanols. The magnitudes of the negative excess molar volumes were also found to be dependent upon the chain length of the alkoxy group and the temperature. The results show that the excess molar volumes become more negative when the chain length of the alkoxy group increased and this was attributed to the relative proton-donating ability of the alkoxyethanols investigated.

Keywords: Excess molar volumes, Density, THF, alkoxyethanols

Introduction

There is continued interest in the provision of experimental data on thermodynamic functions such as excess molar volumes, excess viscosities and excess Gibbs' free energies of activation for viscous flow, *etc*. These excess properties have been reported to provide theoretical basis for the testing of theories of solutions[1] development of separation techniques and for industrial applications. Excess thermodynamic functions are also known to find useful applications in processes associated with the flow of masses, heat or fluids and in agriculture and biological systems[2].

The use of binary solvent mixtures rather than their pure components has attracted a lot of interests because binary solvent mixtures have shown to offer a wider range of solvent properties that the pure components do not offer. As a result of the numerous advantages associated with mixed solvents, the last three decades have seen a plethora of research efforts by a number of authors[3-12]. These researchers have focused on providing useful data banks of excess functions for the elucidation of intermolecular interactions in mixed solvent systems involving different classes of solvents. Some of the classes of solvents investigated include alcohols, amides, aldehydes, esters, ethers, carboxylic acids, ketones, amines, thiols, *etc*. A number of researchers have paid special attention to studying various intermolecular interactions in mixed solvents containing ethers. Chanda *et al*.,[13] reported the excess molar volumes of ternary mixtures containing *N,N*-dimethylformamide, benzene and some ethers including tetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, *di*-isopropyl ether and diethyl ether at 298.15 K. The study was undertaken with the aim of providing data for the excess molar volumes, excess viscosities; excess Gibbs' free energies of activation for viscous flow of these ethers with dimethylformamide and benzene. Ali *et al*.,[14] reported the volumetric behavior of tetrahydrofuran, THF, with C_6, C_8 and C_{10} alkanols, in order to interpret the nature of interactions between THF and the alcohols, as well as study the effect of increasing chain length of the alkanols on the strength of the intermolecular interactions. Belandria *et al*.,[15] reported the volumetric properties of tetrahydrofuran + water binary mixtures. The molecular interaction study of binary mixtures of THF with methanol and *o*-cresol was reported by Parveen *et al*.,[16]. Gupta *et al*.,[17] reported the optical and volumetric behavior of binary mixtures of tetrahydrofuran with 1-propanol and 2-propanol. Naorem and Suri[18] reported the volumetric behavior of binary mixtures of furan and some of its derivatives, including tetrahydrofuran, furfural and furfuryl alcohol with benzene, chlorobenzene and bromobenzene at 298.15 K. The study was undertaken to examine the effect of electronegative halogen atoms in the aromatic ring on the excess molar volumes of the binary mixtures. The various studies provided data for the interpretation of intermolecular interactions in the mixed solvent systems.

In spite of the numerous studies that have been reported involving binary mixtures of ethers and alcohols, a thorough survey of the literature shows a paucity of excess thermodynamic data for alkoxyethanols and ethers.

Ethers are a class of solvents which contain two organic radicals bonded to the same oxygen atom. Like water, ethers are polar and are widely used in industry. Ethers are good solvents for a wide range of solvents and are relatively chemically inert since they contain no obvious site for nucleophilic or electrophilic attack. Ethers are used as aerosol spray propellants and are a potential renewable alternative fuel for diesel engines. Some ethers have anesthetic properties and are used in medicine for such purposes, as well as in cosmetics and perfumery[19].

Tetrahydrofuran (THF) is cyclic ether. It is an excellent aprotic solvent, soluble in all proportions with water, alcohols, other ethers, phenols and other common solvents[16]. It dissolves in all plastics, except polyamide and is useful in polymerization and other chemical reactions. It is useful in the cleaning of polymer surfaces, electronic materials *etc*., and as a solvent for cleaning and varnishing. It is also used as a thermodynamic additive to decrease operative pressure of gas hydrate formation in many processes like carbon dioxide capture by gas hydrate crystallization[20,21]. THF has been explored as a miscible co-solvent in aqueous solutions to aid in the liquefaction and delignification of plant lignocellulosic biomass[22].

Alkoxyethanols are a very useful class of solvents known by the trademark name "cellosolve". They possess excellent solvent properties as a result of their structural diversity, possessing a polar hydroxyl group, ethereal oxygen and a carbon chain and are therefore bifunctional. This structural diversity makes them the solvent of choice for many reactions where amphiphilicity is desirable. Some of the common and popular 2-alkoxyethanols include; (i) 2-methoxyethanol; (ii) 2-ethoxyethanol; (iii) 2-butoxyethanol, *etc*. The alkoxyethanols, unlike ethers, are reported to be self-associated through intra- and intermolecular hydrogen bonding[23]. Since the alkoxyethanols possess structural diversity, binary mixtures of this class of solvents with the cyclic ether, THF, should provide some interesting results.

2-Methoxyethanol, also called methyl cellosolve, is used mainly as a solvent in varnishes, dyes, resins and as an additive in airplane deicing solutions. 2-Ethoxyethanol, commercially known as "cellosolve", is widely used as a co-emulsifier and stabilizer of emulsions, dyes and lacquers. 2-Butoxyethanol is used as a flame retardant, functional fluid in open systems, as paint and coating additives and as solvent for degreasing. In spite of the popularity of 2-alkoxyethanols and the ethers particularly THF, studies on the binary mixtures of these classes of solvents are deplete.

This paper therefore, is the first constituting results from a number of studies aimed at investigating the nature and strengths of intermolecular interactions in binary mixtures of a named C_4 ether and selected 2-alkoxyethanols for the purpose of providing mixing thermodynamic data for these solvent systems. This paper reports the results of our studies on the volumetric behavior of binary mixtures of tetrahydrofuran with 2-alkoxyethanols of different alkoxy chain lengths and at different temperatures. The alkoxyethanols chosen are 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol, which vary in alkoxy chain length from 1 to 4 carbons.

Experimental

The solvents, 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol were products of Lobachemie, India, with minimum assay of 99%. Tetrahydrofuran (98.5%), was a product of Sigma Aldrich, Germany. All the solvents were dried using molecular sieves and recovered via distillation. The densities of the pure solvents and binary mixtures were determined using a single stem capillary pyknometer with a bulb volume of 10 cm³. The pyknometer was calibrated with doubly distilled water at the working temperatures. All the binary mixtures were prepared in triplicate and the density of each mixture determined. The average density was obtained. The density values were reproducible to within ±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 ±0.001 ^{0}C. Binary mixtures were prepared in the mole fraction range of 0.0003-0.9997 of THF by weight with a Search tech Digital Balance (Model FA 2104A) correct to within ±0.0001g.

The purities of the solvents were checked by comparing the experimental density values at 298.15 K, shown in Table 1, with those reported in the literature.

There was good agreement with the values reported in the literature. The densities of the binary mixtures ranging in solvents composition from 0.0003-0.9997 mole fraction of THF were obtained at the working temperatures and are shown in Table 2. The molecular volumes of the pure solvents were also calculated from the experimental data and are also shown in Table 1.

Table 1. Experimental and literature values of densities, ρ $(g\ cm^{-3})$ and molecular volumes, V_M (cm^3) of pure solvents at 298.15 K

Solvents	ρ		V_M (x 10^{-22})
	Expt.	Lit.	
Tetrahydrofuran	0.8868	0.8850^a.	1.3501
2-Methoxyethanol	0.9652	0.9603^b	1.3081
2-Ethoxyethanol	0.9274	0.9252^c	1.6139
2-Butoxyethanol	0.8995	0.8960^d	2.1810

References: ^{a}[15]; ^{b}[34]; ^{c}[33]; ^{d}[34]

Results and Discussion

Excess molar volumes, V^E for the entire solvents composition range were calculated from the densities of the pure solvents and the binary mixtures using Eq. 1. The calculated excess molar volumes, V^E, are shown in Table 2 for the various solvent systems at the working temperatures.

$$V^E = \left[\frac{X_1 M_1 + X_2 M_2}{\rho} \right] - \left[\frac{X_1 M_1}{\rho_1} + \frac{X_2 M_2}{\rho_2} \right] \tag{1}$$

In Eq. 1, X_1 and X_2 are the mole fractions of THF and the named 2-alkoxyethanol respectively; M_1 and M_2 are their respective molar masses; ρ, ρ_1 and ρ_2 are the densities of the binary mixtures, THF and the named 2-alkoxyethanol, respectively.

Table 2. Densities, ρ, (gcm^{-3}) and excess molar volumes, V^E, $(cm^3 mol^{-1})$ of binary mixtures of THF + 2-alkoxyethanols at 293.15, 298.15 and 303.15 K

X_{THF}	THF + 2-MeOEtOH		THF + 2-EtOEtOH		THF + 2-BuOEtOH	
	ρ	V^E	ρ	V^E	ρ	V^E
293.15 K						
0.0003	0.9755	-0.0082	0.9321	-0.0100	0.9013	-0.0122
0.0714	0.9671	-1.3171	0.9274	-1.6122	0.8979	-1.9807
0.1428	0.9591	-1.6936	0.9222	-2.0762	0.8948	-2.5639
0.2142	0.9519	-1.5310	0.9179	-1.8798	0.8931	-2.3352
0.2856	0.9452	-1.1215	0.9147	-1.3788	0.8913	-1.7248
0.3570	0.9398	-0.6640	0.9126	-0.8161	0.8908	-1.0285
0.4282	0.9347	-0.2792	0.9118	-0.3399	0.8913	-0.4297
0.4998	0.9299	-0.0205	0.9102	-0.0164	0.8925	-0.0134
0.5712	0.9267	0.1023	0.9095	0.1406	0.8937	0.1985
0.6426	0.9233	0.1171	0.9095	0.1636	0.8947	0.2407
0.7140	0.9187	0.0695	0.9071	0.1073	0.8961	0.1766
0.7854	0.9142	0.0096	0.9047	0.0321	0.8961	0.0784
0.8568	0.9069	-0.0239	0.9012	-0.0144	0.8963	0.0068
0.9282	0.9006	-0.0178	0.8972	-0.0147	0.8948	-0.0107
0.9997	0.8929	0.0005	0.8929	0.0003	0.8929	0.0006
298.15 K						
0.0003	0.9659	-0.0077	0.9276	-0.0099	0.8998	-0.0098
0.0714	0.9582	-1.2326	0.9232	-1.5851	0.8960	-1.5841
0.1428	0.9509	-1.5831	0.9182	-2.0384	0.8926	-2.0506

Contd…

0.2142	0.9443	-1.4292	0.9143	-1.8426	0.8906	-1.8677
0.2856	0.9383	-1.0458	0.9111	-1.3497	0.8886	-1.3798
0.3570	0.9327	-0.6191	0.9088	-0.7988	0.8879	-0.8232
0.4282	0.9277	-0.2620	0.9076	-0.3353	0.8881	-0.3448
0.4998	0.9236	-0.0237	0.9057	-0.0238	0.8890	-0.0124
0.5712	0.9195	0.0875	0.9045	0.1250	0.8897	0.1564
0.6426	0.9165	0.0985	0.9049	0.1432	0.8903	0.1896
0.7140	0.9125	0.0530	0.9028	0.0862	0.8912	0.1380
0.7854	0.9085	-0.0020	0.9008	0.0140	0.8909	0.0595
0.8568	0.9011	-0.0302	0.8969	-0.0267	0.8913	0.0026
0.9282	0.8949	-0.0202	0.8921	-0.0202	0.8894	-0.0103
0.9997	0.8870	0.0005	0.8870	0.0001	0.8870	-0.0002

<div align="center">303.15 K</div>

0.0003	0.9566	-0.0076	0.9231	-0.0076	0.8982	-0.0080
0.0714	0.9496	-1.2178	0.9194	-1.2242	0.8948	-1.3047
0.1428	0.9428	-1.5619	0.9155	-1.5694	0.8916	-1.6887
0.2142	0.9366	-1.4081	0.9121	-1.4138	0.8896	-1.5382
0.2856	0.9307	-1.0290	0.9091	-1.0320	0.8875	-1.1366
0.3570	0.9255	-0.6091	0.9065	-0.6097	0.8865	-0.6787
0.4282	0.9206	-0.2596	0.9044	-0.2586	0.8862	-0.2854
0.4998	0.9159	-0.0284	0.9020	-0.0267	0.8864	-0.0125
0.5712	0.9121	0.07724	0.9005	0.0789	0.8864	0.1257
0.6426	0.9097	0.08505	0.9001	0.0863	0.8864	0.1525
0.7140	0.9063	0.03894	0.8984	0.0396	0.8866	0.1097
0.7854	0.9030	-0.0141	0.8961	-0.0137	0.8860	0.0452
0.8568	0.8953	-0.0385	0.8919	-0.0380	0.8864	-0.0008
0.9282	0.8892	-0.0239	0.8871	-0.0233	0.8839	-0.0102
0.9997	0.8808	-0.0004	0.8808	-0.0002	0.8808	-0.0001

The calculated values of excess molar volumes, V^E were correlated by the Redlich-Kister polynomial using Eq. 2:

$$Y^E = X_1 X_2 \sum_{i=1}^{n} Ai(2X_1 = 1)^{i=1} \tag{2}$$

The values of the parameter, A_i, were obtained by fitting the equation to the experimental values with least-squares method. The standard deviations, σ, for the V^E values were calculated using Eq. 3:

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

In Eq. 3, m is the number of experimental data points and n is the number of coefficients considered. In this work, n was considered to be 4. The subscripts, exp and cal, represent the experimental and calculated values of excess molar volumes respectively. The coefficients and their standard deviations are shown in Table 3.

The variations of the excess molar volumes, V^E of binary mixtures of THF + the named 2-alkoxyethanols as a function of mole fraction of THF at different temperatures are shown in Figures (1-6).

Table 3. Fitting parameters and standard deviations of excess molar volumes at 293.15, 298.15 and 303.15 K

T/K	A_0	A_1	A_2	A_3	σ
THF + 2-MeOEtOH					
293.15 K	-0.1858	-0.0015	-6.1895	-0.0014	0.02
298.15 K	-0.2160	-0.0013	-5.7979	-0.0014	0.03
303.15 K	-0.2601	-0.0013	-5.7341	-0.0014	0.03
THF + 2-EtOEtOH					
293.15 K	-0.2160	-0.0013	-5.7979	-0.0014	0.04
298.15 K	-0.2114	-0.0018	-7.4466	-0.0017	0.03
303.15 K	-0.2439	-0.0013	-5.7660	-0.0014	0.03
THF + 2-BuOEtOH					
293.15 K	-0.2601	-0.0013	-5.7341	-0.0014	0.03
298.15 K	-0.1092	-0.0019	-7.4239	-0.0016	0.03
303.15 K	-0.1115	-0.0016	-6.1167	-0.0013	0.02
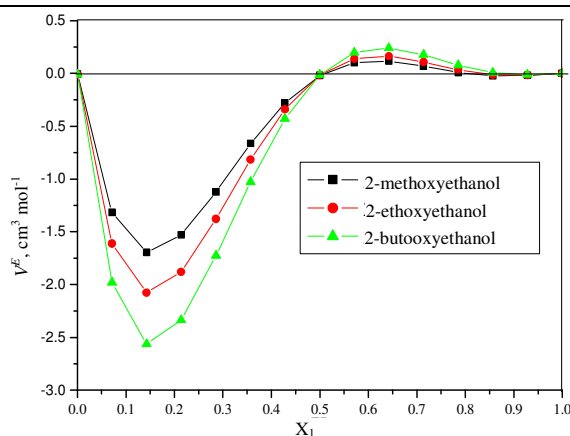
Figure 1. Plots of excess molar volumes of binary mixtures of THF + alkoxyethanols as a function of mole fraction of THF at 293.15 K
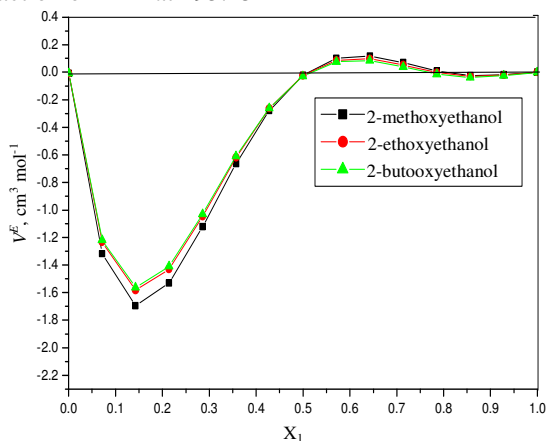
Figure 2. Plots of excess molar volumes of binary mixtures of THF + alkoxethanols as a function of mole fraction of THF at 298.15 K
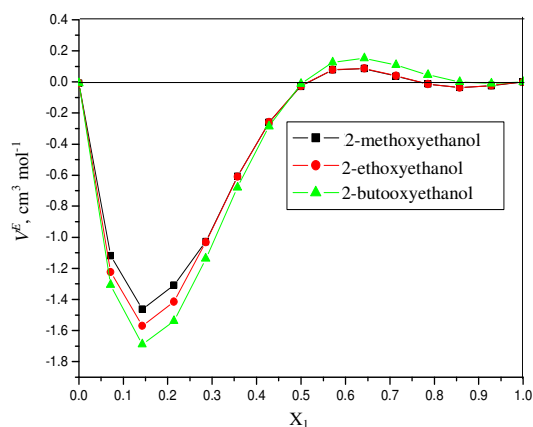
Figure 3. Plots of excess molar volumes of binary mitures of THF + alkoxyethanols as a function of mole fraction of THF at 303.15 K
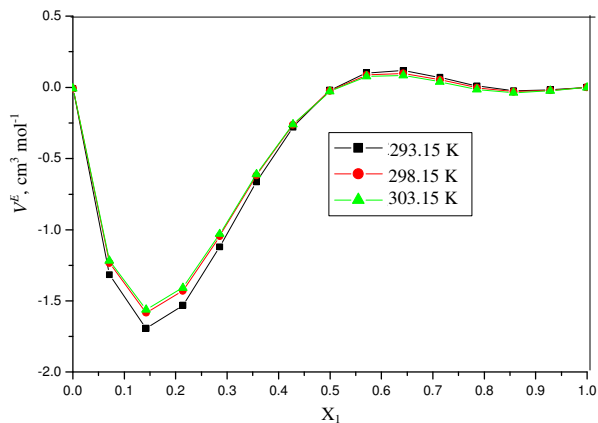

Figure 4. Plots of excess molar volumes of binary mixtures of THF + 2-methoxyethanol as afuntion of mole fraction of THF at selected temperatures (293.15, 298.15 and 303.15 K)
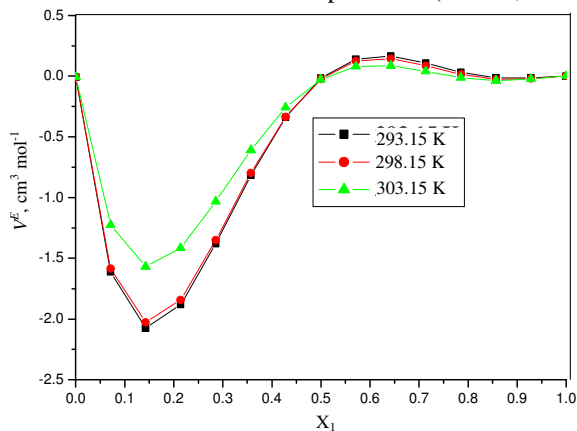

Figure 5. Plots of excess molar volumes of binary mixtures of THF + 2-ethoxyethanol as a function of mole fraction THF at selected temperatures (293.15, 298.15 and 303.15 K)
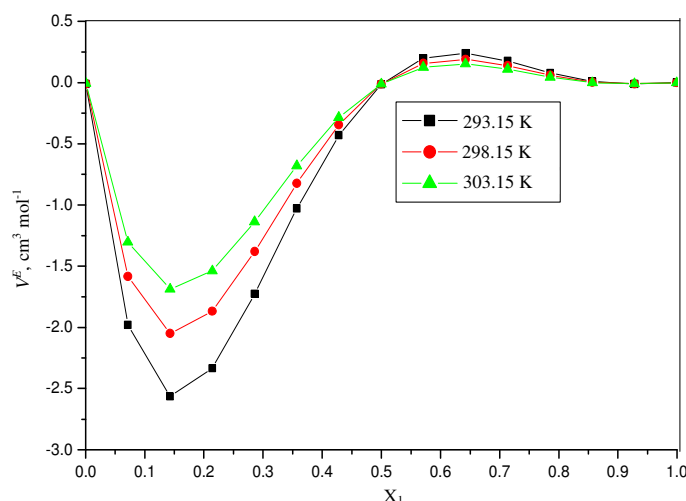
Figure 6. Plots of excess moar excess volumes of binary mixtures of THF +2-butoxyethanol as a function of mole fraction of THF at selected tempetures (293.15, 298.15 and 303.15 K)

All the plots show that the excess molar volumes are negative in the mole fraction region of 0.00-0.50 THF. Beyond the mole fraction of 0.50 THF, the excess molar volumes are slightly positive. Similar results showing negative excess molar volumes in regions of low THF concentration and slightly positive excess molar volumes in regions rich in THF have been reported by Parveen *et al*.,[16] for binary solvent systems of THF + methanol and by Subha *et al*.,[24] for the binary solvent mixtures of ethoxyethanol + *n-, sec-, tert*-butylamine, *n*-hexylamine, *n*-octylamine and cyclohexylamine. In binary mixtures of 2-alkoxyethanols and some aliphatic and aromatic amines, we had earlier reported that the excess molar volumes were all negative over the entire range of solvent composition. Plots of the excess molar volumes as a function of the mole fraction of 2-alkoxyethanols showed different minima values that were dependent on the chain length and degree of branching of the aliphatic amines. The negative excess molar volumes were attributed to the formation of stronger hydrogen bonds between unlike molecules than between like molecules.

The sign and magnitude of excess molar volumes are often attributed to a number of factors which are classified into chemical, physical and structural contributions[16,25]. Physical factors involving nonspecific interactions due to dispersive forces, dipole-dipole interactions, result in positive excess molar volumes which are indicative of the breaking of liquid order or bonds upon mixing. Chemical factors (such as complex formation and charge transfer) and hydrogen bonding between unlike molecules often lead to negative excess molar volumes. Structural effects arise from interstitial fittings of molecules with smaller molecular volumes into molecules of larger molecular volumes and result in negative excess molar volumes[26]. Steric hindrance between unlike molecules often leads to positive excess molar volumes. The sign and magnitude of the excess molar volumes, V^E, of a given solvent system depend upon which of the aforelisted factors is dominant[27].

Effect of alkoxy chain length on magnitude of excess molar volumes, V^E

Figures (1-3) show variations of excess molar volumes for the binary mixtures of THF + alkoxyethanols at various temperatures. The figures show that the values of the excess molar volumes are all negative in the solvents composition region 0.00-0.50 mole fraction of THF.

The minimum of all the plots is at about 0.14 mole fraction of THF. A close examination of the minima of the plots suggests that the magnitudes of the negative excess molar volumes are alkoxy chain length dependent. The magnitudes of the minima of the plots are in the order THF + 2-BuOEtOH >+ 2-EtOEtOH >+ 2-MeOEtOH. The negative values of the excess molar volumes in this region of solvent composition may be due to a number of factors including interstitial fitting of molecules of smaller molecular volumes into molecules of larger molecular volumes and hydrogen bonding between unlike molecules. The calculated molecular volumes of the pure solvents at 298.15 K are shown in Table 1. The values show that except for 2-methoxyethanol the molecular volumes of 2-ethoxyethanol and 2-butoxyethanol are larger than the value for THF. The magnitudes of the molecular volumes of the alkoxyethanols are in the order: 2-BuOEtOH > 2-EtOEtOH > 2-MeOEtOH. It is therefore tempting to conclude that interstitial fitting of the smaller THF molecules into the larger alkoxyethanol molecules account for the negative excess molar volumes in this region of low THF composition. However, the mixing of THF with 2-alkoxyethanol molecules results in intermolecular hydrogen bonding between unlike molecules. This is as a result of the fact that the hydrogen of the –OH group in the alkoxyethanol binds to the oxygen atom of THF, which has lone pairs of electrons, via hydrogen bonding forming an O---H---O link between unlike molecules. In other words, the hydrogen of the –OH group of the alkoxyethanols can be donated as a proton and accepted by the lone pairs on the oxygen of THF. An acid-base type of reaction can therefore be said to take place when unlike molecules of THF and alkoxyethanol are mixed. The magnitudes of the negative excess molar volumes of the binary mixtures of THF and the 2-alkoxyethanols suggest that the O---H---O link arising from hydrogen bonding between unlike molecules of THF + 2-butoxyethanol is strongest, followed by that between THF +2-ethoxyethanol and the least being that of THF + 2-methoxyethanol. Similar trends in the relative negative values of excess molar volumes were reported by Pal *et al.,*[28] in their studies of binary mixtures of 2-pyrrolidinone and *N*-methyl pyrrolidinone with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol. The authors attributed the trend to the presence of relatively strong interactions between 2-butoxyethanol and pyrrolidinone. In this study, we attribute the trend to the chain lengths of the alkoxy group of the alkoxyethanols which increase the proton donating ability of the –OH group as the chain length of the alkoxy group increases. The hydrogen bonding between THF and the alkoxyethanols can be described with the following Scheme 1.

$$R — \overline{\underline{O}} — C_2H_4 — O–H$$
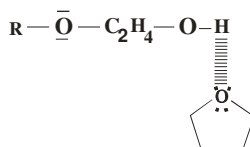
Scheme 1.

The alkoxyethanols are known to have proton donating ability which is said to be associated with the hydroxyl group[29]. According to Pal *et al.,*[28], this ability of proton donation increases with chain length of the alkoxy group of the cellosolves. The proton donating ability of the alkoxyethanols studied is therefore in the order: 2-BuOEtOH >2-EtOEtOH > 2-MeOEtOH. This order confirms that the O---H---O link between THF and 2-butoxyethanol is strongest and decreases as the chain length of the alkoxy group decreases. The relative negative values of the excess molar volumes of binary mixtures of THF + the named alkoxyethanols in the solvents composition region of low THF is therefore in agreement with the strength of the O-H---O link between THF and the alkoxyethanol molecules.

The slightly positive values of excess molar volumes, V^E in the THF rich region and low alkoxyethanol concentration of solvent composition may be due to the disruption or breaking of intra- and intermolecular hydrogen bonds between like molecules of the alkoxyethanols and the dispersive forces in THF.

Effect of temperature on the magnitude of excess molar volumes, V^E

Figures (4-6) show variations of the excess molar volumes, V^E of binary mixtures of THF + a named alkoxyethanol as a function of mole fraction of THF at the three working temperatures. The profiles of the plots are similar at all temperatures having the minima and maxima occurring at about the mole fractions of 0.14 and 0.60 THF, respectively. An examination of the plots for each of the solvent systems however, shows that the relative magnitudes of the excess molar volumes are less negative with increase in temperature. A number of authors[30-39] have reported similar trends in other binary solvent systems. Intermolecular hydrogen bonding between unlike molecules was said to account for the negative excess molar volumes of binary mixtures of THF and the alkoxyethanols. Under such circumstances, when temperatures increase, intermolecular hydrogen bonds weaken arising from increased thermal agitation of molecules and lead to a weakening of O---H---O links between THF and alkoxyethanol molecules. The less negative excess molar volumes at higher temperatures in all binary mixtures of THF and the named alkoxyethanols are therefore consistent with the formation of weaker hydrogen bonds with unlike molecules in binary mixed solvent systems of THF + 2-alkoxyethanols.

Conclusion

The results of the study show that the volumetric behavior of binary mixtures of THF + 2-alkoxyethanols is largely dependent on the ethereal oxygen of THF, proton donation from the -OH group of the alkoxyethanols and the chain length of the alkoxy group. The results suggest that an acid-base type reaction leading to hydrogen bonding takes place in the binary mixtures of THF and 2-alkoxyethanols which lead to negative excess molar volumes. The ease of donation of protons from the alkoxyethanols is influenced by the chain length of the alkoxy group. Proton donation and acceptance result in O----H----O links between unlike molecules of different strengths in different regions of solvents composition which bring about deviations in excess molar volumes. Thermal agitations of molecules in the solvent systems also weaken intermolecular hydrogen bonds which are evidenced in less negative values of excess molar volumes at higher temperatures. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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