

# Volumetric Properties of Binary Systems of Tetrahydrofuran with Isomeric Butanols between 303.15 and 323.15 K

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**Abstract** Densities,  $\rho$ , have been measured for the binary systems of tetrahydrofuran + n-butanol, + sec-butanol and + tert-butanol in the whole range of composition between 303.15 and 323.15 K at an interval of 5 K. From measured  $\rho$ , excess molar volumes,  $V_m^E$ , apparent molal volumes,  $\phi_v$ , thermal expansivities,  $\alpha$ , and excess thermal expansivities,  $\alpha^E$  are estimated. For all systems, measured  $\rho$ ,  $\phi_v$  and  $\alpha$  values are fitted to polynomial equations, whereas,  $V_m^E$  and  $\alpha^E$  are fitted to Redlich-Kister equations. Here, the  $V_m^E$  values are all positive but for tetrahydrofuran + n-butanol system, the values are small and for latter two systems, the values are large.

**Keywords** Tetrahydrofuran, Molar volume, Isomeric butanols, Thermal expansivity

## 1. Introduction

Volumetric properties of binary mixtures depend not only on solute-solute, solvent-solvent and solute-solvent interactions, but also on the structural effects arising from interstitial accommodation due to the difference in molar volume and void space between components present in the solution. Knowledge of the volumetric properties is required for engineering design and for subsequent operations. Moreover, volumetric data help us to understand about molecular interaction among the components of the mixture.

Tetrahydrofuran is a cyclic molecule, which is frequently utilized as a solvent in many pharmaceutical synthetic procedures because of its broad solvency for polar and non-polar compounds and it is excellent solvents of polymers and their application in polymer synthesis[1]. Alkanols are of interest because they serve as a simple example of biologically and industrially important

amphiphilic materials[2]. Among them, butanol isomers are excellent solvents that find use as intermediates in polymerization and other chemical reactions and as cleaning agents for polymer surfaces and electronic materials. Binary systems containing oxygenated compounds, such as, ethers (-O-group) and alkanols (-OH group) are found to be of increasing applications, as these may be used as additives to gasolines, owing to their octane-enriching and pollution-reducing properties[3, 4]. As a continuation of alkanol + ether systems, therefore, the present investigation comprises of three systems involving isomeric butanol with tetrahydrofuran. The choice of these butanols is simple, any variation in studied properties may be correlated to the effect of chain branching and/or the sterical hindrance effect due to increased -CH<sub>3</sub> groups. A good number of literature survey shows that some systematic studies with composition and temperature dependences are still scarce. This paper reports the experimental density results for binary mixtures of tetrahydrofuran + n-butanol, + sec-butanol, + tert-butanol over the whole range of compositions at five temperatures from (303.15 to 323.15) K at atmospheric pressure.

## 2. Experimental Section

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**Table 1.** Comparison of experimental densities,  $\rho$  (g.cm<sup>-3</sup>) of pure liquids with literature values at different temperatures

T/K	Density ( $\rho$ / g.cm <sup>-3</sup> )			
	This work	Literature		
Tetrahydrofuran				
303.15	0.8772	0.8773 <sup>a</sup>	0.8770 <sup>s</sup>	
308.15	0.8717	0.87033 <sup>b</sup>	0.87101 <sup>p</sup>	
313.15	0.8661	0.86567 <sup>c</sup>	0.86623 <sup>t</sup>	
318.15	0.8605	0.86140 <sup>b</sup>		
323.15	0.8550	0.8541 <sup>d</sup>		
n-Butanol				
303.15	0.8022	0.8018 <sup>e</sup>		
308.15	0.7982	0.798242 <sup>q</sup>	0.79820 <sup>h</sup>	0.79811 <sup>i</sup>
313.15	0.7943	0.7941 <sup>e</sup>		
318.15	0.7902	0.79007 <sup>f</sup>	0.79020 <sup>i</sup>	
323.15	0.7862	0.7852 <sup>j</sup>		
sec-Butanol				
303.15	0.7983	0.7984 <sup>e</sup>	0.79818 <sup>k</sup>	0.798513 <sup>q</sup>
308.15	0.7940	0.79392 <sup>g</sup>	0.79398 <sup>i</sup>	0.79378 <sup>k</sup>
313.15	0.7896	0.7895 <sup>e</sup>	0.78965 <sup>r</sup>	
318.15	0.7851	0.78486 <sup>f</sup>	0.78492 <sup>g</sup>	0.78500 <sup>i</sup>
323.15	0.7806	0.78055 <sup>r</sup>		
tert-Butanol				
303.15	0.7758	0.77573 <sup>i</sup>	0.7754 <sup>l</sup>	0.77521 <sup>m</sup>
308.15	0.7707	0.77020 <sup>i</sup>	0.77022 <sup>n</sup>	
313.15	0.7655	0.76484 <sup>i</sup>	0.76469 <sup>m</sup>	0.76507 <sup>r</sup>
318.15	0.7599	0.75941 <sup>i</sup>	0.75965 <sup>n</sup>	0.75952 <sup>o</sup>
323.15	0.7548	0.75401 <sup>m</sup>	0.75419 <sup>r</sup>	

<sup>a</sup>Ref-5, <sup>b</sup>Ref-6, <sup>c</sup>Ref-7, <sup>d</sup>Ref-8, <sup>e</sup>Ref-9, <sup>f</sup>Ref-10, <sup>g</sup>Ref-11, <sup>h</sup>Ref-12, <sup>i</sup>Ref-13, <sup>j</sup>Ref-14, <sup>k</sup>Ref-15, <sup>l</sup>Ref-16, <sup>m</sup>Ref-17, <sup>n</sup>Ref-18, <sup>o</sup>Ref-19, <sup>p</sup>Ref-20, <sup>q</sup>Ref-21, <sup>r</sup>Ref-22, <sup>s</sup>Ref-23, <sup>t</sup>Ref-24

The experimental densities ( $\rho$  / g.cm<sup>-3</sup>) of experimental chemicals that were used to prepare the present binary systems at different temperatures and reported data are tabulated in Table 1. All the liquids were procured from Aldrich Chemical Co. Ltd. with quoted purities tetrahydrofuran (THF): 99.9%, n-butanol (NBA): 99.8%, sec-butanol (SBA): 99% and + tert-butanol (TBA): 99.5%. Densities were measured by using a 10 cm<sup>3</sup> bi-capillary pycnometer. All weighing were made on a College B 204-S, METTLER TOLEDO digital balance with an accuracy of  $\pm 0.0001$ g. A thermostatically controlled water bath, capable of maintaining the temperature constant up to  $\pm 0.05$  K was used in the studies. The mole fraction is found to be accurate up to  $10^{-4}$ , while the uncertainty in the measured density is estimated as  $\pm 1.2 \times 10^{-4}$  g cm<sup>-3</sup>.

In order to find deviations from ideal behavior, excess molar volumes,  $V_m^E$ , for all systems were calculated from measured density data by using the given equation:

$$V_m^E = \left[ \frac{x_1 M_1 + x_2 M_2}{\rho} \right] - \left[ \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right] \quad (1)$$

Here,  $M_1$  &  $M_2$  represent the molar masses,  $\rho_1$  and  $\rho_2$  the densities,  $x_1$  and  $x_2$  are the mole fractions of components 1 & 2, respectively and  $\rho$  is the density of the mixture at the respective composition.

Introducing molal concentration scale replacing mole fraction by molality from the measured density of the solvent, solute and solution the apparent molal volume were determined by following equation (2) and (3) for components 1 and 2.

For component 1,

$$\phi_{v1} = \frac{1000(\rho_2 - \rho_{mix})}{m_1 \rho_{mix} \rho_2} + \frac{M_1}{\rho_{mix}} \quad (2)$$

For component 2,

$$\phi_{v2} = \frac{1000(\rho_1 - \rho_{mix})}{m_2 \rho_{mix} \rho_1} + \frac{M_2}{\rho_{mix}} \quad (3)$$

where,  $m_1 = \frac{1000x_1}{m_2 x_2}$  and  $m_2 = \frac{1000x_2}{m_1 x_1}$  molality of component 1 and 2 respectively.

The average isobaric thermal expansivity,  $\alpha$ , was calculated as:

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_P \quad (4)$$

Excess thermal expansivity,  $\alpha^E$  of a solution was then estimated by following the equation[25–26]:

$$\alpha^E = \alpha - \alpha^{id} = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_P - \sum \phi_i \alpha_i^* \quad (5)$$

where,  $\phi_i$  is the volume fraction,  $\alpha_i^*$  is thermal expansivity of the pure component  $i$  and the rest of the terms have their usual significances.

All the estimated excess properties such as excess molar volume,  $V_m^E$ , for a system as a function of composition are fitted to Redlich-Kister equation[27]:

$$V_m^E = x_2(1-x_2) \sum_{i=0}^n A_i (2x_2 - 1)^i \quad (6)$$

where,  $A_i$  is the fitting coefficient and  $x_2$  is the mole fraction of the aromatic hydrocarbons. The standard deviation,  $\sigma$ , followed the equation:

$$\sigma = \left[ \frac{\sum (V_{obs}^E - V_{cal}^E)^2}{n - p - 2} \right]^{\frac{1}{2}} \quad (7)$$

where,  $V_{obs}^E$  and  $V_{cal}^E$  are the observed and calculated excess molar volumes,  $n$  the total number of compositions for a particular system and  $p$  is the number of coefficients are as shown in Table 4.

Densities ( $\rho$ ) of tetrahydrofuran (THF) + n-butanol (NBA), + sec-butanol (SBA) and + tert-butanol (TBA) in the whole range of composition ( $0 \leq x_2 \leq 1$ ), where,  $x_2$  represents the mole fraction of the butanol under consideration, measured at an interval of 5 K between 303.15 and 323.15 K are summarized in Table 2. At a particular temperature the  $\rho$  values were fitted by a five-degree polynomial equation of the form:

$$\rho / g.cm^{-3} = \sum_{i=0}^n a_i x_2^i \quad (8)$$

All the coefficients  $a_i$  and relevant  $R^2$  are tabulated in Table 3. Densities of the pure butanols are found to follow the order: NBA > SBA > TBA and for the systems follow the same general trend, i.e.,  $\rho$  decreases gradually with the increment of  $x_2$  for all the THF + NBA, THF + SBA and THF + TBA systems.

In alcohols, though the proton accepting capacity increases in the order tertiary > secondary > primary, H-bonding capacity increases in the reverse order. As it is found the fraction of free -OH group is more in isomeric forms than in n-alkanols[28]. That means, NBA, SBA may favour to form more extensive H-bonded networks compared to TBA. Tertiary butanol (TBA) so forms a weaker H-bonding and hence, it is less associated. This is as manifested by the higher density values of NBA and SBA compared to TBA.

### 3. Results and Discussion

**Table 2.** Densities,  $\rho$  ( $g.cm^{-3}$ ) and excess molar volumes,  $V_m^E$  ( $cm^3.mol^{-1}$ ) of the systems of THF ( $x_1$ ) + NBA ( $x_2$ ), + SBA ( $x_2$ ) and + TBA ( $x_2$ ) for different molar ratios at different temperatures

$x_2$	$\rho$	$V_m^E$	$x_2$	$\rho$	$V_m^E$	$x_2$	$\rho$	$V_m^E$
THF ( $x_1$ ) + NBA ( $x_2$ )			THF ( $x_1$ ) + SBA ( $x_2$ )			THF ( $x_1$ ) + TBA ( $x_2$ )		
T=303.15 K								
0.0000	0.8772	0.0000						
0.1001	0.8681	0.0734	0.1001	0.8666	0.1724	0.1064	0.8631	0.1718
0.2003	0.8599	0.0808	0.2000	0.8571	0.2683	0.2003	0.8517	0.2629
0.3004	0.8520	0.0787	0.2999	0.8483	0.3195	0.3001	0.8402	0.3360
0.4014	0.8449	0.0682	0.4001	0.8403	0.3088	0.4001	0.8291	0.4036
0.4996	0.8370	0.0564	0.4989	0.8326	0.2983	0.5001	0.8188	0.4218
0.6142	0.8287	0.0414	0.6006	0.8250	0.2727	0.6000	0.8092	0.3971
0.7011	0.8226	0.0244	0.6999	0.8185	0.1655	0.6999	0.8002	0.3349
0.8003	0.8158	0.0028	0.8002	0.8118	0.0877	0.8000	0.7916	0.2523
0.8912	0.8093	0.0280	0.9001	0.8052	0.0182	0.8998	0.7836	0.1282
1.0000	0.8022	0.0000	1.0000	0.7983	0.0000	1.0000	0.7758	0.0000

T=308.15 K								
0.0000	0.8717	0.0000						
0.1001	0.8627	0.0817	0.1001	0.8612	0.1785	0.1064	0.8577	0.1677
0.2003	0.8547	0.0862	0.2000	0.8518	0.2792	0.2003	0.8464	0.2551
0.3004	0.8470	0.0805	0.2999	0.8432	0.3240	0.3001	0.8350	0.3192
0.4014	0.8394	0.0760	0.4001	0.8353	0.3159	0.4001	0.8240	0.3772
0.4996	0.8322	0.0694	0.4989	0.8277	0.3074	0.5001	0.8138	0.3980
0.6142	0.8241	0.0509	0.6006	0.8202	0.2836	0.6000	0.8042	0.3765
0.7011	0.8182	0.0254	0.6999	0.8138	0.1766	0.6999	0.7952	0.3108
0.8003	0.8115	0.0075	0.8002	0.8072	0.0992	0.8000	0.7868	0.2119
0.8912	0.8051	0.0353	0.9001	0.8007	0.0297	0.8998	0.7787	0.1012
1.0000	0.7982	0.0000	1.0000	0.7940	0.0000	1.0000	0.7707	0.0000
T=313.15 K								
0.0000	0.8661	0.0000						
0.1001	0.8573	0.0827	0.1001	0.8557	0.1848	0.1064	0.8523	0.1554
0.2003	0.8494	0.0966	0.2000	0.8465	0.2803	0.2003	0.8410	0.2461
0.3004	0.8418	0.0997	0.2999	0.8379	0.3390	0.3001	0.8296	0.3187
0.4014	0.8345	0.0829	0.4001	0.8302	0.3231	0.4001	0.8188	0.3635
0.4996	0.8275	0.0730	0.4989	0.8227	0.3167	0.5001	0.8086	0.3787
0.6142	0.8195	0.0641	0.6006	0.8153	0.2948	0.6000	0.7991	0.3495
0.7011	0.8138	0.0317	0.6999	0.8090	0.1880	0.6999	0.7902	0.2816
0.8003	0.8072	0.0197	0.8002	0.8025	0.1109	0.8000	0.7817	0.1926
0.8912	0.8010	0.0406	0.9001	0.7961	0.0415	0.8998	0.7736	0.0853
1.0000	0.7943	0.0000	1.0000	0.7896	0.0000	1.0000	0.7655	0.0000
T=318.15 K								
0.0000	0.8605	0.0000						
0.1001	0.8518	0.0912	0.1001	0.8501	0.2000	0.1064	0.8468	0.1465
0.2003	0.8441	0.1023	0.2000	0.8411	0.2892	0.2003	0.8356	0.2270
0.3004	0.8367	0.1017	0.2999	0.8327	0.3402	0.3001	0.8242	0.2996
0.4014	0.8295	0.0909	0.4001	0.8251	0.3257	0.4001	0.8134	0.3442
0.4996	0.8226	0.0863	0.4989	0.8177	0.3202	0.5001	0.8033	0.3475
0.6142	0.8148	0.0739	0.6006	0.8104	0.2990	0.6000	0.7938	0.3173
0.7011	0.8093	0.0326	0.6999	0.8041	0.2026	0.6999	0.7850	0.2359
0.8003	0.8028	0.0246	0.8002	0.7977	0.1249	0.8000	0.7765	0.1449
0.8912	0.7967	0.0481	0.9001	0.7914	0.0545	0.8998	0.7682	0.0606
1.0000	0.7902	0.0000	1.0000	0.7851	0.0000	1.0000	0.7599	0.0000
T=323.15 K								
0.0000	0.8550	0.0000						
0.1001	0.8464	0.1000	0.1001	0.8446	0.2143	0.1064	0.8415	0.1334
0.2003	0.8389	0.1081	0.2000	0.8357	0.3061	0.2003	0.8303	0.2161
0.3004	0.8316	0.1142	0.2999	0.8274	0.3589	0.3001	0.8190	0.2819
0.4014	0.8246	0.0990	0.4001	0.8198	0.3558	0.4001	0.8082	0.3309
0.4996	0.8178	0.0998	0.4989	0.8126	0.3397	0.5001	0.7982	0.3332
0.6142	0.8102	0.0839	0.6006	0.8054	0.3184	0.6000	0.7888	0.2897
0.7011	0.8048	0.0448	0.6999	0.7992	0.2205	0.6999	0.7800	0.2127
0.8003	0.7985	0.0295	0.8002	0.7929	0.1411	0.8000	0.7715	0.1266
0.8912	0.7925	0.0558	0.9001	0.7867	0.0688	0.8998	0.7631	0.0558
1.0000	0.7862	0.0000	1.0000	0.7806	0.0000	1.0000	0.7548	0.0000

**Table 3.** Coefficients,  $a_i$  of polynomial equation (1) for density,  $\rho$  ( $\text{g.cm}^{-3}$ ) and coefficients,  $A_i$  and standard deviation,  $\sigma$  for excess molar volumes,  $V_m^E$  ( $\text{cm}^3.\text{mol}^{-1}$ ) of the systems of THF ( $x_1$ ) + NBA ( $x_2$ ), + SBA ( $x_2$ ) and + TBA ( $x_2$ ) at different temperatures

T/K	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$R^2$	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
THF ( $x_1$ ) + NBA ( $x_2$ )													
303.15	0.877	-0.098	0.083	-0.155	0.142	-0.048	1.0000	0.2409	-0.3220	-0.2789	-0.0659	1.1717	0.0077
308.15	0.871	-0.092	0.050	-0.065	0.047	-0.013	1.0000	0.0280	-0.3159	-0.5580	-0.0881	1.7333	0.0069
313.15	0.866	-0.091	0.047	-0.053	0.029	-0.005	1.0000	0.3103	-0.3563	-0.0342	0.0122	1.2360	0.0095
318.15	0.860	-0.089	0.050	-0.059	0.037	-0.008	1.0000	0.3585	-0.3510	-0.5181	-0.0085	1.8087	0.0098
323.15	0.855	-0.088	0.053	-0.066	0.044	-0.010	1.0000	0.4079	-0.3428	-0.5837	-0.0396	1.9862	0.0108
THF ( $x_1$ ) + SBA ( $x_2$ )													
303.15	0.877	-0.113	0.085	-0.124	0.125	-0.052	1.0000	1.2100	-0.6808	-0.3198	-0.6816	0.1287	0.0144
308.15	0.871	-0.113	0.090	-0.134	0.133	-0.053	1.0000	1.2445	-0.6513	-0.2816	-0.6956	0.2368	0.0148
313.15	0.866	-0.111	0.090	-0.136	0.134	-0.053	1.0000	1.2855	-0.6509	-0.2576	-0.6138	0.3109	0.0164
318.15	0.860	-0.112	0.106	-0.174	0.170	-0.065	1.0000	1.3105	-0.6087	0.2080	-0.6744	0.5490	0.0121
323.15	0.855	-0.112	0.105	-0.165	0.156	-0.058	1.0000	1.3911	-0.6157	-0.2027	-0.6638	0.7276	0.0122
THF ( $x_1$ ) + TBA ( $x_2$ )													
303.15	0.877	-0.137	0.061	-0.067	0.070	-0.029	1.0000	1.6831	0.0490	-0.5286	-0.4035	0.7200	0.0065
308.15	0.871	-0.137	0.070	-0.097	0.111	-0.047	1.0000	1.5919	0.0192	-0.5656	-0.6748	0.5416	0.0047
313.15	0.866	-0.134	0.055	-0.056	0.066	-0.030	1.0000	1.5079	-0.1320	-0.5086	-0.4554	0.2898	0.0023
318.15	0.860	-0.132	0.044	-0.033	0.044	-0.024	1.0000	1.4042	-0.2956	-0.9200	-0.3929	0.7158	0.0031
323.15	0.855	-0.129	0.026	0.014	-0.007	-0.004	1.0000	1.3328	-0.4244	-1.0291	-0.1115	0.8326	0.0030

Fig. 1 represents  $V_m^E$  of the three systems against  $x_2$  at 303.15 and 323.15 K. For each system,  $V_m^E$  at different temperatures have been fitted well by Redlich-Kister equation[27] and the relevant fitting coefficients being shown in Table 3. In THF + NBA system, as the values are small the variation of  $V_m^E$  against  $x_2$  are not so smooth. Moreover,  $V_m^E$  forms a small maximum in the NBA-rich region near  $x_2 = 0.9$ . On the other hand,  $V_m^E$  vs.  $x_2$  forms a large positive lobes with maximum at  $x_2 \sim 0.4$  and 0.5 for THF + SBA and + TBA systems, respectively.

The above behaviors can be explained as follows. It may be stated that, addition of small amount of NBA in THF initially involves complete rupture of O-H--O type bonding

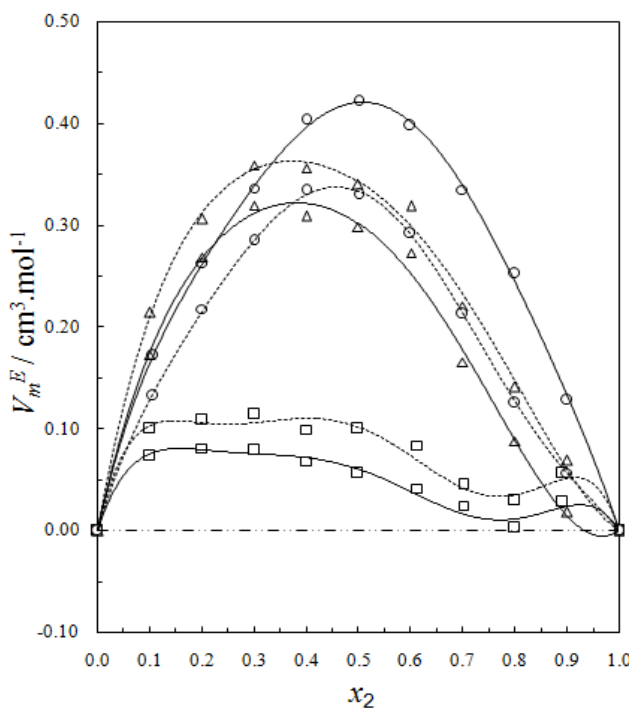
in NBA, together with dispersion in THF. But as fast as monomeric NBA species are formed, intermolecular interaction due to dipole-dipole and/or H-bonding between NBA and THF molecules may also occur, contributing negatively to the  $V_m^E$ . However, the former factors

outweigh the later ones, so that, the overall  $V_m^E$  though small, is positive for the THF + NBA. Similar results of positive  $V_m^E$  in the three systems were also observed previously by Alonso et al[29], Brocos[30] and Aminabhavi et al[31]. With the increase in alkanol concentration ( $x_2$ ), NBA molecules undergo restructuring through H-bonding as well as dipole-dipole interactions among themselves. As a result positive  $V_m^E$  values start to decrease correspondingly.

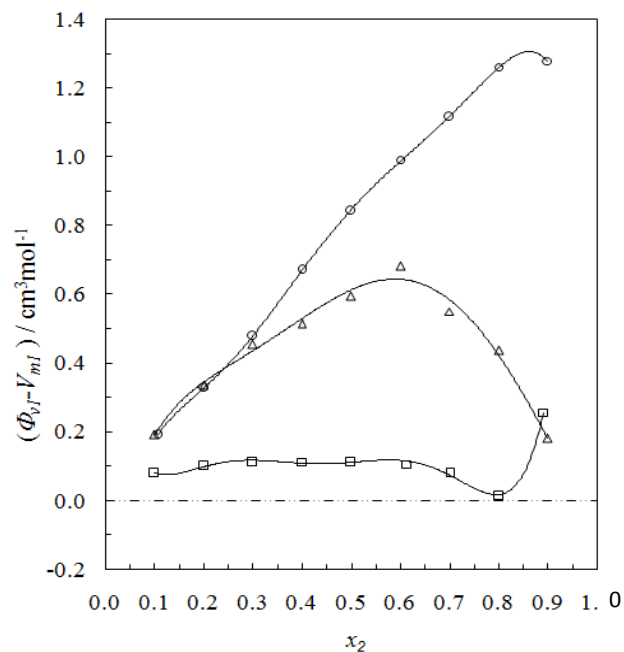
Again, when each of SBA and TBA to THF, destruction of

SBA-SBA and TBA-TBA H-bonding occurs more easily due to the steric hindrance effect through increasing  $-\text{CH}_3$  groups compared to NBA and subsequently all the monomeric or segregated species are more dispersed weakening the dipole-dipole interaction in THF further. As a result, in THF + SBA and THF+TBA systems, factors that cause volume expansion seem to exert greater influence over those of volume contraction at all temperatures over the whole range of composition. Again the comparative diagram of Fig. 1 shows that,  $V_m^E$  values vary as  $\text{THF} + \text{TBA} > \text{THF} + \text{SBA} > \text{THF} + \text{NBA}$ . With the rise of temperature, structure-breaking processes dominate over the structure making interactions. So that, in the whole range of composition,  $V_m^E$  values increase proportionately leading to positive  $\frac{dV_m^E}{dT}$  for the THF + NBA system.

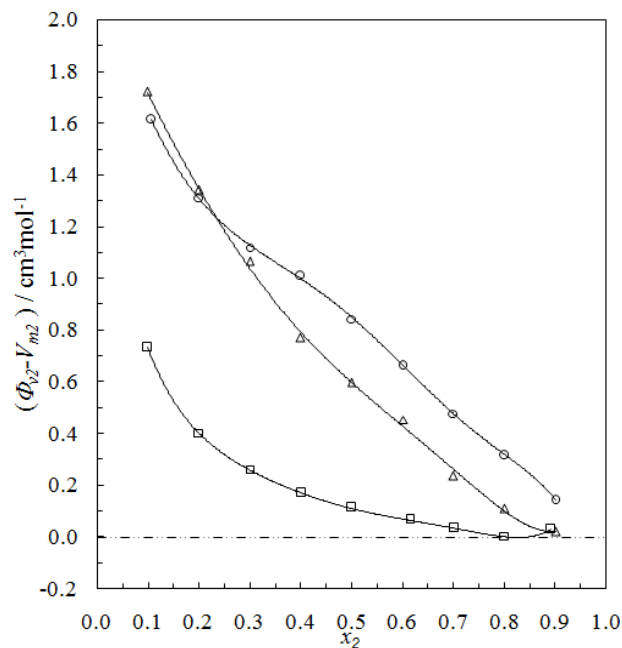
The apparent molal volumes,  $\phi_{v1}$  and  $\phi_{v2}$  of component 1 and 2, in their binary mixtures as calculated by the equations (2) and (3) respectively, and the difference between apparent molal volume and molar volume of each of components 1 and 2, i.e.;  $(\phi_{v1} - V_{m1})$  and  $(\phi_{v2} - V_{m2})$  were estimated at 303.15 K and graphically represented by Figs. 2-3. For both the components, these differences are positive indicating the dominance of dispersive forces almost over all compositions.



**Figure 1.** Comparison of excess molar volumes,  $V_m^E$ , for the systems of THF ( $x_1$ ) + NBA ( $x_2$ ) (□), + SBA ( $x_2$ ) (Δ) and + TBA ( $x_2$ ) (○) at 303.15 K (—) and 323.15 K (---)



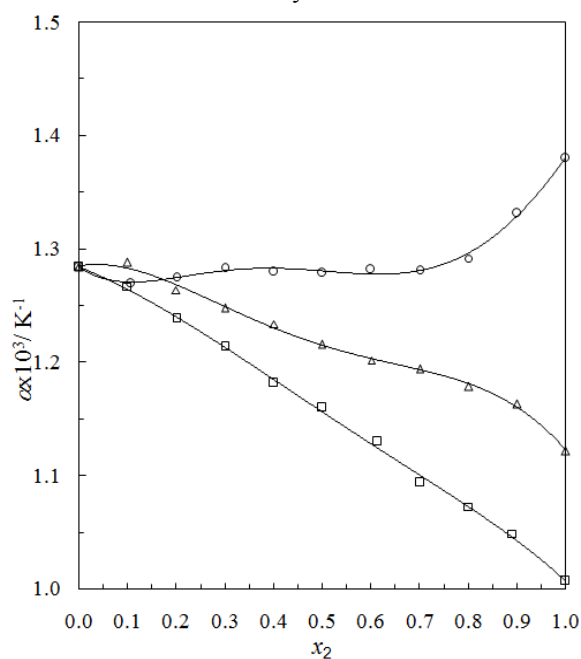
**Figure 2.** Plot of  $(\phi_{v1} - V_{m1})$  of component 1 in the systems of THF ( $x_1$ ) + NBA ( $x_2$ ) (□), + SBA ( $x_2$ ) (Δ) and + TBA ( $x_2$ ) (○) at 303.15 K



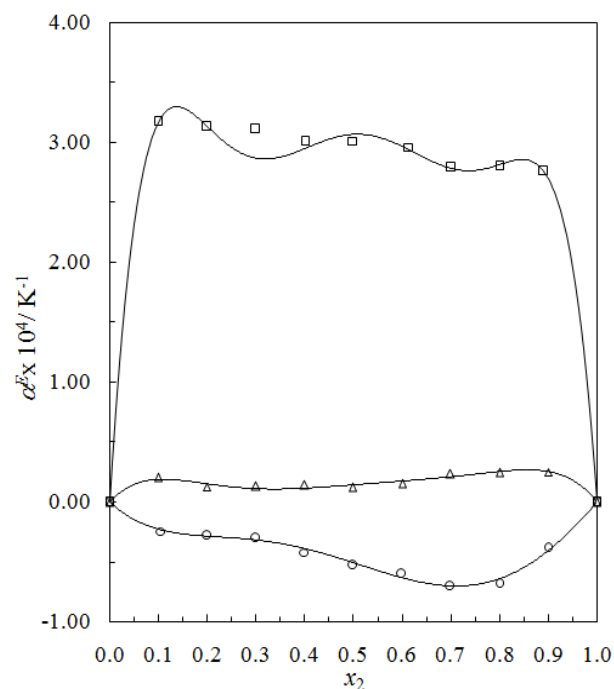
**Figure 3.** Plot of  $(\phi_{v2} - V_{m2})$  of component 2 in the systems of THF ( $x_1$ ) + NBA ( $x_2$ ) (□), + SBA ( $x_2$ ) (Δ) and + TBA ( $x_2$ ) (○) at 303.15 K

Table 4 represents thermal expansivity,  $\alpha$ , and its excess value,  $\alpha^E$ , estimated by equation (4) & (5) respectively; the relevant coefficients being summarized as in Table 5. Figs. 4 and 5 indicate  $\alpha$  and  $\alpha^E$  of the three systems against  $x_2$ .  $\alpha$  of THF + NBA and THF + SBA decreases

with the increase of alcohols in the whole range of concentration, but in THF + TBA it largely increases in the alcohol rich region and follow the order: THF + TBA > + SBA > + NBA. On the other hand,  $\alpha^E$  values are positive for THF + NBA and THF + SBA systems, but negative for THF + TBA system. Positive  $\alpha^E$  signifies that structure breaking effects are more at high temperatures, whereas, under similar conditions structure making effects seem to be favorable in the THF + TBA system.



**Figure 4.** Plot of thermal expansivities,  $\alpha$ , of the systems of THF ( $x_1$ ) + NBA ( $x_2$ ) ( $\square$ ), + SBA ( $x_2$ ) ( $\Delta$ ) and + TBA ( $x_2$ ) ( $\circ$ )



**Figure 5.** Plot of excess thermal expansivities,  $\alpha^E$ , of the systems of THF ( $x_1$ ) + NBA ( $x_2$ ) ( $\square$ ), + SBA ( $x_2$ ) ( $\Delta$ ) and + TBA ( $x_2$ ) ( $\circ$ )

**Table 4.** Thermal expansivity,  $\alpha$  ( $K^{-1}$ ) and excess thermal expansivity,  $\alpha^E$  ( $K^{-1}$ ) of the systems of THF ( $x_1$ ) + NBA ( $x_2$ ), + SBA ( $x_2$ ) and + TBA ( $x_2$ ) for different molar ratios

THF ( $x_1$ )+NBA ( $x_2$ )			THF ( $x_1$ )+SBA ( $x_2$ )			THF ( $x_1$ )+TBA ( $x_2$ )		
$x_2$	$\alpha \times 10^3$	$\alpha^E \times 10^4$	$x_2$	$\alpha \times 10^3$	$\alpha^E \times 10^4$	$x_2$	$\alpha \times 10^3$	$\alpha^E \times 10^4$
0.0000	1.284	0.0000	0.0000	1.284	0.0000	0.0000	1.284	0.0000
0.1001	1.267	3.1770	0.1001	1.288	0.2023	0.1064	1.270	-0.2461
0.2003	1.239	3.1356	0.2000	1.264	0.1257	0.2003	1.275	-0.2847
0.3004	1.214	3.1116	0.2999	1.248	0.1296	0.3001	1.283	-0.3017
0.4014	1.182	3.0101	0.4001	1.234	0.1437	0.4001	1.280	-0.4217
0.4996	1.160	3.0132	0.4989	1.216	0.1236	0.5001	1.279	-0.5301
0.6142	1.130	2.9637	0.6006	1.202	0.1530	0.6000	1.282	-0.5988
0.7011	1.094	2.7926	0.6999	1.194	0.2348	0.6999	1.281	-0.7022
0.8003	1.073	2.8030	0.8002	1.179	0.2444	0.8000	1.292	-0.6840
0.8912	1.049	2.7627	0.9001	1.163	0.2494	0.8998	1.332	-0.3841
1.0000	1.007	0.0000	1.0000	1.122	0.0000	1.0000	1.380	0.0000

**Table 5.** Coefficients,  $b_i$  of polynomial equation for thermal expansivity,  $\alpha \times 10^3$  and Fitting coefficients,  $B_i$  & standard deviation,  $\sigma$  for excess thermal expansivity,  $\alpha^E \times 10^4 \text{ (K}^{-1}\text{)}$  of the systems of THF ( $X_1$ ) + NBA ( $X_2$ ), + SBA ( $X_2$ ) and + TBA ( $X_2$ )

$b_0$	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	$R^2$	$B_0$	$B_1$	$B_2$	$B_3$	$B_4$	$\sigma$
THF ( $X_1$ ) + NBA ( $X_2$ )												
1.284	-0.173	-0.272	0.178	0.167	-0.176	0.998	12.2869	-0.7300	2.0858	-3.7389	45.7148	0.08552
THF ( $X_1$ ) + SBA ( $X_2$ )												
1.285	0.076	-1.151	1.997	-1.166	0.080	0.997	0.5676	0.5530	0.8010	-0.1405	3.2645	0.02936
THF ( $X_1$ ) + TBA ( $X_2$ )												
1.283	-0.288	2.028	-5.027	5.003	-1.619	0.994	-2.0447	-2.6187	-2.6466	2.1365	0.5102	0.03639

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