MOLECULAR INTERACTIONS OF BUTYL ETHANOATE + ETHER BINARY MIXTURES

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Keywords: density; viscosity; speed of sound; excess volume; butyl ethanoate; interaction parameters

As part of a study on the molecular interactions between esters and ethers; density, viscosity and speed of sound data were measured for butyl ethanoate + ether mixed solvents. From these data, excess volumes V^E, deviation in viscosity Δη, isentropic compressibility K_S, deviation in isentropic compressibility ΔK_S, intermolecular free length L_f, internal pressure π_i, and the excess intermolecular free length L_f^E, excess internal pressure π_i^E, were deduced. These excess or deviation properties were fitted to the Redlich-Kister type equation. Further the experimental mixture viscosities were correlated using Frenkel, Heric, and McAllister (four-body) models. The studied excess or deviation properties were found to be both positive and negative. These results were interpreted in terms of intermolecular interactions and structural effects.

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Introduction

Intermolecular interactions play an important role in the development of molecular science.

The study of physicochemical properties of liquid mixtures finds extensive applications in chemical, pharmaceutical, and bio-chemical industries. Direct measurement of the characteristic excess or deviation properties of binary non-electrolyte solutions has gained much importance in the recent years.

Butyl ethanoate is often employed in combination with n-butanol in paints, because it enhances resistance to blushing and increase solvency in many cases. Likewise ethers are important industrial solvents. They can be used as scrubbling in cleaning of exhaust air and gas streams from industrial production plants, because of their favorable properties such as low vapor pressure, low viscosity, low toxicity, and high chemical stability. Ethers are increasingly used as additives to gasoline, due to their octane enhancing and pollution reducing properties.

Over the last several years there have been a number of studies on thermophysical properties of liquid mixtures containing butyl ethanoate in various organic solvents.[1-10] Oswal et.al[11,12] have measured viscosity, speed of sound, isentropic compressibilities and excess molar volumes of binary mixtures containing p-dioxane with butyl acetate at 303.15K. Recently Roy et.al[13] have determined excess molar volumes and viscosity deviations of binary mixtures of 1, 3-dioxane and 1, 4-dioxane with butyl acetate at 298.15 K. In order to understand further the molecular interactions of butyl ethanoate mixed with ether binary mixtures and as follow-up of our earlier work[14-16] on thermophysical properties of various types ester containing mixtures, we report here the density, viscosity, and speed of sound for binary mixtures of butyl ethanoate with tetrahydrofuran, 1, 4-dioxane, anisole, and butyl vinyl ether at T=303.15, 308.15, and 313.15 K over the entire range of composition and under atmospheric pressure. Experimental results have been used to calculate the excess molar volumes V^E, deviation in viscosity $\Delta\eta$, isentropic compressibility K_S, deviation in isentropic compressibility ΔK_S, excess intermolecular free length L_f^E, and excess internal pressure π_i^E. The calculated results have been fit to the Redlich-Kister polynomial[17] equation to derive the binary coefficients and standard deviations. Further the experimental (kinematic or dynamic) viscosities were used to test the applicability of the equations proposed by Frankel,[18] Heric,[19] and McAllister (four-body interaction)[20] at the studied temperatures.

Experimental

Chemicals

All the chemicals used in the present study were of analytical grade (Fluka) obtained from S. D. Fine Chemical Ltd. Mumbai, India. The final mass fraction purities as determined by gas chromatography (HP 8610) using FID are shown in Table 1. Prior to the use all liquids were stored over 0.4 nm molecular sieves for 72 h to reduce water content if any and were degassed at low pressure.

Apparatus and procedure

The binary mixtures were prepared by weighing appropriate amounts of butyl ethanoate and ether on an electronic balance (Mettler AE-240, Switzerland) with precision of ± 0.01 mg, by syringing each liquid into airtight stopper bottles in order to minimize evaporation losses. The resulting uncertainty in mole fraction was estimated to be less than ± 0.0001. Each mixture was immediately used after it was well mixed by shaking.

The density of pure liquids and their binary mixtures were determined with density meter (DMA 4500 Anton Paar) with precision of ± 0.00001 g.cm^{-3}. The uncertainty in the density measurements was found to be ± 0.0002 g.cm^{-3}.

Table 1. Chemical specification with purity estimation.

Chemical Name	Source	Initial mole fraction (purity)	Purification method	Final mole fraction (purity)	Analysis Method
Butyl ethanoate	Sigma-Aldrich	0.99	none	0.998	GC[a] (HP-8610)
Tetrahydrofuran	E.Merk	0.98	distillation	0.996	GC (HP-8610)
1,4-Dioxane	E.Merk	0.99	none	0.997	GC (HP-8610)
Anisole	Fluka	0.99	none	0.998	GC (HP-8610)
Butyl vinyl ether	Sigma-Aldrich	0.99	distillation	0.996	GC (HP-8610)

[a] Gas-liquid chromatography

The dynamic viscosities of the pure liquids and their binary mixtures were measured at the required temperature using an Ubbelohde viscometer. The uncertainty in the viscosity measurement was estimated to be ± 0.005 mPa s. In viscosity measurements the temperature of the samples was controlled by using a viscometer bath equipped with a thermostat of accuracy ± 0.01 K.

Speed of sound of pure liquids and their mixtures were determined using a single-crystal variable path interferometer (model F-81, Mittal Enterprises, New Delhi, India), at a frequency of 2 MHz. The uncertainty in speed of sound was estimated to be ± 1 m s^{-1}.

Results and Discussion

The experimental results of density ρ, excess molar volume V^E, viscosity η, speed of sound u, isentropic compressibility K_S, intermolecular free length L_f, and internal pressure π_i for the binary mixtures of (butyl ethanoate + tetrahydrofuran), (butyl ethanoate + 1,4-dioxane), (butyl ethanoate + anisole), and (butyl ethanoate + butyl vinyl ether) at T= 303.15, 308.15, and 313.15 K and at the atmospheric pressure are reported in Table 2.

The excess molar volumes V^E are calculated from the density data using the following relation.

$$V^{E} = \sum_{i=1}^{2} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (1)$$

where M_i, ρ_i and ρ are the molar mass, density of the i^{th} component and density of the mixture respectively.

Isentropic compressibility, K_S are calculated from the relation

$$K_s = \frac{1}{u^2 \rho} \quad (2)$$

Where u is the speed of sound.

The intermolecular free length L_f was calculated as

$$L_f = K(K_S)^{1/2} \quad (3)$$

Where

K is the temperature dependent Jacobson constant,

K_S is the isentropic compressibility

The internal pressure π_i was calculated from the following relation

$$\pi_i = bRT\left(\frac{K\eta}{u}\right)^{1/2}\left(\frac{\rho^{1/2}}{M_{eff}^{7/6}}\right) \quad (4)$$

where

b is the cubical packing fraction taken as 2 for all the liquids,

R is the universal gas constant,

T is the experimental temperature,

$M_{eff} = \sum x_i M_i$ (x is the mole fraction and M is the molecular weight of i^{th} component) and η is the viscosity.

Excess or deviation values (V^E, $\Delta\eta$, ΔK_S, L_f^E and π_i^E) of all the studied parameters were computed using the general equation

$$Y^{E} = Y_{exp} - (x_1 Y_1 + x_2 Y_2) \quad (5)$$

where

Y represents any parameter,

Y^E its value Y_1 and

Y_2 denote values of parameters for pure liquids, and

Y_{exp} represents the corresponding experimental value for the mixture.

Table 2. Values of density (ρ), excess molar volume (V^E), viscosity (η), speed of sound (u), isentropic compressibility (K_S), intermolecular free length (L_f), internal pressure(π_i) for the binary liquid mixture

x_1	P, g.cm^{-3}	V^E, cm^{3}mol^{-1}	η, mPa.s	u, m.s^{-1}	K_S, TPa^{-1}	L_f x10^8, cm	π_ix10^6 Nm^{-2}
	Butyl ethanoate (1) + tetrahydrofuran(2)						
	***T*/K=303.15**						
0.0000	0.8778		0.4388	1248	731	0.561	3.857
0.0653	0.8769	0.017	0.4564	1228	756	0.571	3.793
0.1123	0.8763	0.029	0.4692	1212	777	0.579	3.748
0.2099	0.8751	0.059	0.4965	1200	794	0.585	3.627
0.2911	0.8743	0.073	0.5129	1188	810	0.591	3.527
0.3800	0.8735	0.088	0.5310	1176	828	0.597	3.420
0.4798	0.8728	0.091	0.5473	1172	834	0.599	3.280
0.5882	0.8722	0.082	0.5656	1168	840	0.602	3.150
0.7096	0.8717	0.058	0.5857	1164	847	0.604	3.017
0.8439	0.8712	0.033	0.6077	1164	847	0.604	2.878
1.0000	0.8707		0.6333	1160	854	0.606	2.740
x_1	***T*/K=308.15**						
0.0000	0.8725		0.4276	1228	760	0.577	3.877
0.0653	0.8715	0.034	0.4456	1212	781	0.585	3.812
0.1123	0.8709	0.052	0.4604	1196	803	0.593	3.769
0.2099	0.8697	0.094	0.4805	1184	820	0.600	3.643
0.2911	0.8689	0.117	0.4951	1172	838	0.606	3.533
0.3800	0.8682	0.131	0.5116	1164	850	0.611	3.417
0.4798	0.8676	0.132	0.5263	1160	857	0.613	3.274
0.5882	0.8671	0.121	0.5411	1156	863	0.615	3.135
0.7096	0.8667	0.095	0.5558	1152	869	0.618	2.991
0.8439	0.8664	0.052	0.5688	1152	870	0.618	2.835
1.0000	0.8661		0.5883	1148	876	0.620	2.683
x_1	***T*/K=313.15**						
0.0000	0.8670		0.3903	1212	785	0.592	3.781
0.0653	0.8659	0.050	0.4118	1200	802	0.598	3.726
0.1123	0.8652	0.082	0.4263	1188	819	0.605	3.689
0.2099	0.8639	0.144	0.4478	1176	837	0.611	3.571
0.2911	0.8631	0.175	0.4641	1168	849	0.616	3.467
0.3800	0.8624	0.198	0.4803	1158	865	0.621	3.352
0.4798	0.8619	0.196	0.4948	1154	871	0.624	3.220
0.5882	0.8615	0.182	0.5093	1148	881	0.627	3.089
0.7096	0.8613	0.138	0.5203	1144	887	0.629	2.939
0.8439	0.8612	0.074	0.5331	1140	893	0.632	2.793
1.0000	0.8611		0.5480	1136	900	0.634	2.641
	Butyl ethanoate(1) +1, 4-dioxane(2)						
x_1	***T*/K=303.15**						
0.0000	1.0227		1.0896	1320	561	0.492	5.179
0.0557	1.0097	0.024	1.0388	1304	582	0.501	4.930
0.1159	0.9966	0.041	0.9800	1284	609	0.512	4.692
0.1841	0.9827	0.062	0.9244	1268	633	0.522	4.434
0.2595	0.9684	0.085	0.8779	1252	659	0.533	4.195
0.3452	0.9535	0.106	0.8318	1236	687	0.544	3.951
0.4401	0.9384	0.098	0.7927	1224	711	0.554	3.717
0.5502	0.9225	0.075	0.7517	1208	743	0.566	3.477
0.6703	0.9068	0.057	0.7157	1196	771	0.576	3.247
0.8230	0.8890	0.033	0.6751	1180	808	0.590	2.993
1.0000	0.8707		0.6333	1160	854	0.606	2.740
x_1	***T*/K=308.15**						
0.0000	1.0174		0.9988	1312	571	0.500	5.026
0.0557	1.0043	0.039	0.9509	1292	597	0.512	4.811
0.1159	0.9912	0.062	0.9041	1272	624	0.523	4.586

0.1841	0.9773	0.080	0.8533	1248	657	0.537	4.349
0.2595	0.9631	0.110	0.8117	1230	686	0.549	4.122
0.3452	0.9483	0.119	0.7684	1208	723	0.563	3.891
0.4401	0.9333	0.119	0.7320	1196	749	0.573	3.659
0.5502	0.9175	0.095	0.6957	1184	777	0.584	3.422
0.6703	0.9019	0.075	0.6644	1172	807	0.595	3.201
0.8230	0.8842	0.050	0.6283	1160	840	0.607	2.950
1.0000	0.8661		0.5883	1148	876	0.620	2.683
x_1			***T*/K=313.15**				
0.0000	1.0111		0.9458	1304	582	0.510	4.977
0.0557	0.9980	0.058	0.9000	1280	612	0.523	4.759
0.1159	0.9848	0.094	0.8565	1260	640	0.534	4.538
0.1841	0.9711	0.116	0.8134	1236	674	0.549	4.318
0.2595	0.9570	0.130	0.7728	1216	707	0.562	4.093
0.3452	0.9423	0.142	0.7307	1116	742	0.576	3.858
0.4401	0.9275	0.136	0.6954	1184	769	0.586	3.628
0.5502	0.9118	0.117	0.6582	1172	798	0.597	3.386
0.6703	0.8964	0.102	0.6260	1160	829	0.608	3.161
0.8230	0.8789	0.072	0.5893	1148	863	0.621	2.906
1.0000	0.8611		0.5480	1136	900	0.634	2.641
Butyl ethanoate (1) + anisole(2)							
x_1			***T*/K=303.15**				
0.0000	0.9854		0.9225	1388	527	0.476	3.568
0.0829	0.9746	-0.064	0.8794	1380	539	0.482	3.450
0.1685	0.9640	-0.150	0.8431	1372	551	0.487	3.342
0.2588	0.9531	-0.228	0.8112	1360	567	0.494	3.241
0.3527	0.9421	-0.301	0.7797	1342	589	0.504	3.149
0.4499	0.9309	-0.347	0.7486	1324	613	0.514	3.049
0.5499	0.9196	-0.353	0.7218	1300	644	0.527	2.978
0.6545	0.9077	-0.314	0.6951	1272	681	0.542	2.911
0.7642	0.8955	-0.226	0.6724	1244	722	0.558	2.842
0.8786	0.8832	-0.117	0.6499	1204	781	0.580	2.786
1.0000	0.8707		0.6333	1160	854	0.606	2.740
x_1			***T*/K=308.15**				
0.0000	0.9793		0.8495	1368	546	0.489	3.526
0.0829	0.9690	-0.104	0.8083	1360	558	0.495	3.409
0.1685	0.9586	-0.198	0.7705	1348	674	0.502	3.293
0.2588	0.9479	-0.284	0.7373	1336	591	0.509	3.186
0.3527	0.9370	-0.352	0.7085	1320	613	0.518	3.092
0.4499	0.9259	-0.394	0.6800	1300	639	0.529	2.972
0.5499	0.9146	-0.395	0.6579	1276	672	0.543	2.921
0.6545	0.9030	-0.363	0.6358	1250	709	0.558	2.846
0.7642	0.9108	-0.284	0.6158	1224	749	0.573	2.775
0.8786	0.8788	-0.170	0.5998	1188	806	0.595	2.731
1.0000	0.8661		0.5883	1148	876	0.620	2.683
x_1			***T*/K=313.15**				
0.0000	0.9729		0.7636	1348	566	0.503	3.478
0.0829	0.9630	-0.135	0.7220	1336	582	0.510	3.367
0.1685	0.9529	-0.250	0.6879	1324	599	0.517	3.259
0.2588	0.9424	-0.345	0.6581	1312	616	0.525	3.159
0.3527	0.9316	-0.411	0.6326	1294	641	0.535	3.066
0.4499	0.9206	-0.449	0.6094	1276	667	0.546	2.874
0.5499	0.9095	-0.460	0.5923	1252	701	0.560	2.900
0.6545	0.8980	-0.425	0.5752	1228	739	0.574	2.831
0.7642	0.8861	-0.341	0.5599	1220	784	0.592	2.756
0.8786	0.8739	-0.207	0.5504	1170	836	0.611	2.697
1.0000	0.8611		0.5480	1136	900	0.634	2.641

Butyl ethanoate(1) + butyl vinyl ether(2)							
x_1	***T*/K=303.15**						
0.0000	0.7734		0.3865	1084	1100	0.689	2.432
0.0969	0.7841	-0.168	0.3997	1100	1054	0.674	2.434
0.1944	0.7944	-0.267	0.4135	1116	1011	0.660	2.436
0.2931	0.8046	-0.338	0.4308	1128	977	0.649	2.450
0.3929	0.8146	-0.383	0.4466	1136	951	0.640	2.463
0.4941	0.8247	-0.399	0.4679	1148	920	0.630	2.484
0.5934	0.8344	-0.406	0.5001	1152	903	0.624	2.531
0.6942	0.8440	-0.383	0.5275	1156	887	0.618	2.580
0.7960	0.8534	-0.324	0.5625	1160	871	0.612	2.630
0.8981	0.8624	-0.209	0.5962	1164	856	0.607	2.685
1.0000	0.8707		0.6333	1160	854	0.606	2.740
x_1	***T*/K=308.15**						
0.0000	0.7682		0.3647	1072	1132.	0.705	2.399
0.0969	0.7788	-0.146	0.3797	1084	1093	0.692	2.418
0.1944	0.7891	-0.238	0.3966	1100	1047	0.678	2.432
0.2931	0.7993	-0.301	0.4139	1112	1012	0.666	2.448
0.3929	0.8094	-0.338	0.4314	1120	985	0.657	2.467
0.4941	0.8195	-0.361	0.4510	1132	952	0.646	2.486
0.5934	0.8292	-0.358	0.4761	1136	935	0.640	2.517
0.6942	0.8389	-0.341	0.5016	1140	917	0.634	2.560
0.7960	0.8484	-0.287	0.5294	1144	901	0.629	2.601
0.8981	0.8575	-0.176	0.5574	1148	885	0.623	2.643
1.0000	0.8661		0.5883	1148	876	0.620	2.683
x_1	***T*/K=313.15**						
0.0000	0.7633		0.3541	1060	1166	0.721	2.411
0.0969	0.7738	-0.133	0.3680	1072	1125	0.709	2.422
0.1944	0.7840	-0.212	0.3829	1084	1085	0.696	2.435
0.2931	0.7941	-0.262	0.3980	1096	1048	0.684	2.447
0.3929	0.8041	-0.285	0.4151	1104	1020	0.675	2.467
0.4941	0.8141	-0.294	0.4325	1116	986	0.664	2.481
0.5934	0.8238	-0.294	0.4500	1120	968	0.657	2.503
0.6942	0.8335	-0.279	0.4731	1124	950	0.651	2.538
0.7960	0.8430	-0.225	0.4966	1128	932	0.645	2.572
0.8981	0.8523	-0.145	0.5222	1132	916	0.639	2.608
1.0000	0.8611		0.5480	1136	900	0.634	2.641

For each binary mixture, the composition dependence of V^E, $\Delta\eta$, ΔK_S, L_f^E and π_i^E versus mole fraction x_i can be expressed by using Redlich-Kister polynomial[17] equation.

$$Y = x_1 x_2 \sum_{K=0}^{m} A_i (x_1 - x_2)^{i-1} \qquad (6)$$

Where m is the number of estimated parameters. The coefficients A_i of equation (6) along with the standard deviation $\sigma(Y^E)$ are given in Table 3. These coefficients are adjustable parameters to get best fit value of Y^E. The standard deviation σ (Y^E) was calculated by using the relation

$$\sigma(Y^E) = [\sum \frac{(Y_{exp} - Y_{cal})^2}{(n-m)}]^{1/2} \qquad (7)$$

where n and m represent the number of experimental data points and that of estimated parameters used in the equation (6)

Semi empirical models for analyzing mixture viscosities

In this paper we have selected some of the semi empirical relations to represent the dependence of viscosity on concentration of the component in the mixtures, which are suited for practical engineering use. The methods were chosen because they are well known and accepted or appear potentially promising. The methods are categorized according to the number of adjustable parameters. An attempt has been made to check the suitability of equations for the present experimental data fits by taking into account the number of empirical adjustment coefficients.

The applicability and average relative deviations for each method are discussed with the recommended method identified.

The equations discussed are:

Frankel[18]

$$\log\eta = x_1^2\log\eta_1 + x_2^2\log\eta_2 + 2x_1x_2\log\eta_{12} \quad (8)$$

Where η is the viscosity coefficient and η_{12} is the interaction parameter.

Heric[19]

Heric proposed a two parameter model of the form

$$\ln(\eta_{mix}) = x_1\ln(\eta_1) + x_2\ln(\eta_2) + x_1\ln(M_1) + x_2\ln(M) - \ln(x_1M_1 + x_2M_2) + x_1x_2[\gamma_{12} + \gamma_{21}(x_1 - x_2)] \quad (9)$$

Where

M_1 and M_2 are the molecular weights of pure components,

γ_{12} and γ_{21} are the adjustable parameters.

McAllister (four-body)[20]

McAllister four-body interaction model is a three parameter equation

$$\begin{aligned}\ln v &= x_1^4 \ln v_1 + 4x_1^3x_2 \ln v_{1112} + 6x_1^2x_2^2 \ln v_{1122} + 4x_1x_2^3 \ln v_{2221} + x_2^4 \ln v_2 - \ln[x_1 + (\frac{x_2M_2}{M_1})] \\ &+ 4x_1^3x_2 \ln[\frac{\{3 + (M_2/M_1)\}}{4}] + 6x_1^2x_2^2 \ln[\frac{\{1 + (M_2/M_1)\}}{2}] \\ &+ 4x_1x_2^3 \ln[\frac{\{1 + (3M_2/M_1)\}}{4}] + x_2^4 \ln(M_2/M_1)\end{aligned} \quad (10)$$

These three adjustable parameters v_{1112}, v_{1122}, and v_{2221} are determined from the kinematic viscosity-composition data. The correlating ability of equations (8-10) was tested by calculating the average relative deviation (ARD) between the experimental and the calculated viscosities as obtained by relation

$$\sigma(\%) = [(\frac{1}{(n-k)}\frac{\Sigma\{100(\eta_{exp} - \eta_{cal})\}^2}{\eta_{exp}}]^{1/2} \quad (11)$$

where,

n, represents the number of data points in each set and,
k, is the number of adjustable parameters in Eqs. (8-10).

The values of parameters of equations (8-10) and the ARD values of equation (11) are given in the Table 4. Comparison of ARD values in Table 3 reveals that these values lie in the range (0.011-0.129) for the one-parameter model of Frankel, (0.012–0.034) for two-parameter model of Heric, and (0.004–0.008) for three-parameter model of McAllister (4-body). From this it is apparent that McAllister model with more number of adjustable parameters has the good predictive ability as compared to one, and two parameter models; however McAllister model is a correlative in nature, severely limits its predictability and usefulness. This is mainly because costly and time consuming data are required for the determination of the adjustable parameters contained in the model. Figure 1 shows the variation of V^E of binary mixtures at T= 303.15, 308.15, and 313.15 K

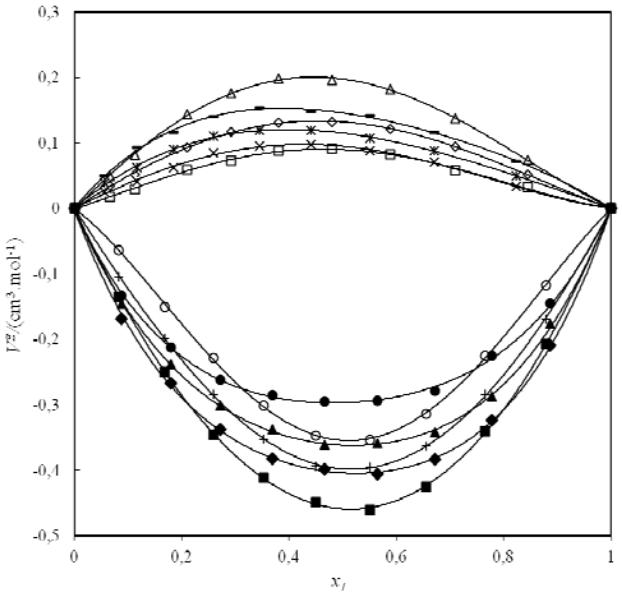

Figure 1. Curves of excess molar volume V^E versus mole fraction X_1 for the binary mixtures butyl ethanoate + tetrahydrofuran at (□, 303.15 ; ◊, 308.15 ; Δ, 313.15) K, butyl ethanoate + 1,4-dioxane at (×, 303.15 ; ж, 308.15; ▬, 313.15) K, butyl ethanoate + anisole at (O, 303.15 ; + 308.15 ; ■, 313.15) K, butyl ethanoate + butyl vinyl ether (♦, 303.15; ▲, 308.15; ●, 313.15) K.

In the present study the values of V^E were found to be positive for (butyl ethanoate + tetrahydrofuran) and (butyl ethanoate +1, 4-dioxane) systems, where as in case of (butyl ethanoate + anisole) and (butyl ethanoate + butyl vinyl ether) systems V^E is negative over the entire range of composition at all the temperatures studied. The effect of temperature is noteworthy as the magnitude of V^E either increase or decrease with increase in temperature. The positive V^E values indicate the dispersive interactions between unlike molecules are weaker than those between like molecules.[21] While the negative V^E values may be attributed to charge transfer complex, dipole-dipole interactions and structural effects that arise from proper interstitial accommodation leading to more compact structure and greater packing in the mixture due to higher molar volume[22] of the solvent butyl ethanoate.

Table 3. Derived parameters of excess functions and standard deviation of binary liquid mixtures

Function	*T*/K	A_0	A_1	A_2	σ
	Butyl ethanoate (1) + tetrahydrofuran(2)				
V^E	303.15	0.3590	-0.0738	-0.1730	0.002
	308.15	0.5294	-0.1215	-0.1159	0.002
	313.15	0.7909	-0.2128	-0.1816	0.002
$\Delta\eta$	303.15	0.6309	-0.0552	0.0156	0.001
	308.15	0.8929	-0.0582	-0.0020	0.001
	313.15	0.1129	-0.6219	0.1673	0.001
ΔK_S	303.15	17.360	-10.763	1.7488	0.306
	308.15	16.390	-10.627	1.5757	0.257
	313.15	12.645	-6.658	1.1139	0.187
L_f^E	303.15	0.0657	-0.0401	0.0097	0.001
	308.15	0.0606	-0.0392	0.0032	0.001
	313.15	0.0479	-0.0260	0.0056	0.001
π_i^E	303.15	-0.1563	-0.2709	0.151	0.004
	308.15	-0.1175	-0.2851	0.176	0.004
	313.15	-0.0638	-0.3059	0.198	0.004
	Butyl ethanoate (1) + 1, 4-dioxane(2)				
V^E	303.15	0.3812	-0.1567	-0.1322	0.002
	308.15	0.4578	-0.2025	0.0421	0.002
	313.15	0.5823	-0.2327	0.1739	0.004
$\Delta\eta$	303.15	-0.3698	0.2043	-0.0679	0.001
	308.15	-0.3304	0.1817	-0.0161	0.001
	313.15	-0.2905	0.1527	-0.0189	0.001
ΔK_S	303.15	8.6603	-6.1010	-1.5477	0.118
	308.15	12.1419	-6.5438	-2.2169	0.268
	313.15	13.2142	-8.3458	0.2736	0.229
L_f^E	303.15	0.0456	-0.0265	-0.0025	0.001
	308.15	0.0794	-0.0299	-0.0179	0.001
	313.15	0.0846	-0.0397	-0.0075	0.001
π_i^E	303.15	-1.5226	0.5562	-0.1563	0.003
	308.15	-1.3132	0.4867	-0.0006	0.004
	313.15	-1.2596	0.3885	-0.0864	0.004
	Butyl ethanoate (1) + anisole(2)				
V^E	303.15	-1.4168	-0.0985	0.7042	0.003
	308.15	-1.5918	-0.1146	0.2101	0.003
	313.15	-1.8355	-0.1081	-0.0391	0.002
$\Delta\eta$	303.15	-0.1704	0.0338	-0.0465	0.001
	308.15	-0.2009	0.0466	-0.0393	0.001
	313.15	-0.2203	0.0493	-0.0698	0.001
ΔK_S	303.15	-24.9284	-6.5334	-2.8797	0.147
	308.15	-22.4828	-5.1904	-2.8797	0.151
	313.15	-19.6285	-2.8968	-2.9539	0.103
L_f^E	303.15	-0.0846	-0.0168	-0.0106	0.001
	308.15	-0.0753	-0.0114	-0.0040	0.001
	313.15	-0.0626	-0.0018	0.0053	0.001

π_i^E	303.15	-0.5720	0.0831	-0.1326	0.002
	308.15	-0.5908	0.0863	-0.0434	0.003
	313.15	-0.6607	0.0958	-0.1189	0.003
Butyl ethanoate (1) + butyl vinyl ether(2)					
V^E	303.15	-1.6076	-0.2401	-0.7241	0.003
	308.15	-1.4378	-0.1988	-0.5664	0.002
	313.15	-1.1857	-0.0542	-0.5552	0.003
$\Delta\eta$	303.15	-0.1536	-0.0041	0.0700	0.001
	308.15	-0.1058	0.0036	-3.97E-04	0.001
	313.15	-0.0721	-0.0030	0.0288	0.001
ΔK_S	303.15	-21.874	3.9882	-4.3763	0.261
	308.15	-20.190	3.4373	2.2346	0.287
	313.15	-17.867	4.1050	5.1867	0.205
L_f^E	303.15	-0.1050	0.0011	-0.0224	0.001
	308.15	-0.1004	0.0014	-0.0028	0.001
	313.15	-0.0937	0.0024	0.0137	0.001
π_i^E	303.15	-0.3728	0.0554	0.1508	0.004
	308.15	-0.2018	-0.0116	0.1639	0.002
	313.15	-0.1714	-0.0066	0.1008	0.003

Table 4. Adjustable parameters and average relative deviations of viscosity models for binary mistures

T/K	Frenkel		Heric			McAllister-4-body			
	η_{12}	σ%	γ_{12}	γ_{21}	σ%	ν_{1112}	ν_{1122}	ν_{2221}	σ%
	Butyl ethanoate (1) + tetrahydrofuran(2)								
303.15	-0.540	0.011	0.3041	-0.1582	0.022	4.802	4.6988	4.5752	0.007
308.15	-0.573	0.011	0.3370	-0.1633	0.018	4.808	4.7048	4.5816	0.007
313.15	-0.615	0.014	0.4138	-0.2032	0.037	4.814	4.7116	4.5886	0.007
Butyl ethanoate (1) +1, 4-dioxane(2)									
303.15	-0.349	0.119	-0.2739	0.1555	0.017	4.810	4.708	4.599	0.005
308.15	-0.421	0.113	-0.2577	0.1458	0.022	4.816	4.712	4.605	0.005
313.15	-0.464	0.097	-0.2206	0.1265	0.013	4.822	4.718	4.612	0.005
Butyl ethanoate (1) + anisole(2)									
303.15	-0.3502	0.024	-0.1602	0.0820	0.025	4.849	4.795	4.750	0.004
308.15	-0.4611	0.023	-0.2256	0.0189	0.018	4.853	4.802	4.755	0.004
313.15	-0.5907	0.037	-0.3069	0.0252	0.034	4.858	4.808	4. 760	0.004
Butyl ethanoate (1) + butyl vinyl ether(2)									
303.15	-0.793	0.061	-0.1707	0.051	0.051	4.881	4.879	4.867	0.009
308.15	-0.811	0.030	-0.1341	-0.012	0.049	4.887	4.885	4.8740	0.009
313.15	-0.850	0.025	-0.0509	-0.013	0.022	4.894	4.892	4.8806	0.009

Figure 2 depicts the variation of $\Delta\eta$ with mole fraction of butyl ethanoate. The $\Delta\eta$ values for all the studied systems except for (butyl ethanoate + tetrahydrofuran) are negative at all the studied temperatures. For the mixtures of tetrahydrofuran the $\Delta\eta$ values are positive. The minima of the ($\Delta\eta$ - x_1) curves occur at about $x_1 \sim 0.375$. Like V^E the magnitude of $\Delta\eta$ values also vary with temperature indicating the effect of temperature on $\Delta\eta$. In our present case the components have different molecular structure, the molar volume of the solvent butyl ethanoate (133.32 cm^3 mol^{-1}) being large, the inclusion of smaller molecules of solute in the structure of larger molecules causes the $\Delta\eta$ values negative.

It was observed that the speed of sound values (Table 2) for (butyl ethanoate + tetrahydrofuran) and (butyl ethanoate +1, 4-dioxane) and (butyl ethanoate + anisole) decrease with increase in temperature at any given concentration of ester, while for (butyl ethanoate + butyl vinyl ether) these values increase with increase in temperature. The decreasing trend with increase in temperature indicates breaking of hetero and homo molecular clusters at high temperature.[23]

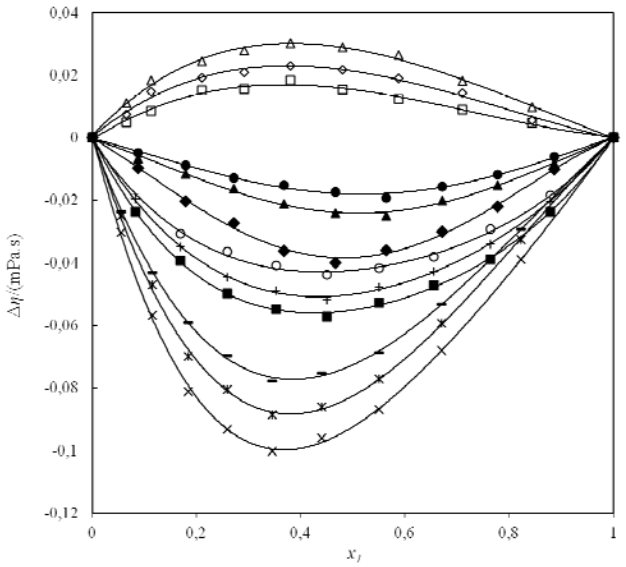

Figure 2. Curves of deviation in viscosity $\Delta\eta$ Vs mole fraction for the binary mixtures. Butyl ethanoate+ tetrahydrofuran at (□, 303.15 ; ◊, 308.15 ; Δ, 313.15) K, butyl ethanoate + 1,4-dioxane at (×, 303.15 ; ж, 308.15 ; ▬, 313.15) K, butyl ethanoate + anisole at (O, 303.15 ; +, 308.15 ; ■, 313.15) K, butyl ethanoate + butyl vinyl ether at (♦, 303.15; ▲, 308.15; ●, 313.15) K

The speed of sound will decrease if the intermolecular free length increases with temperature and vice – versa. This phenomenon of interdependence of intermoleculat free length and speed of sound was explained by Kincaid and Eyring[24]

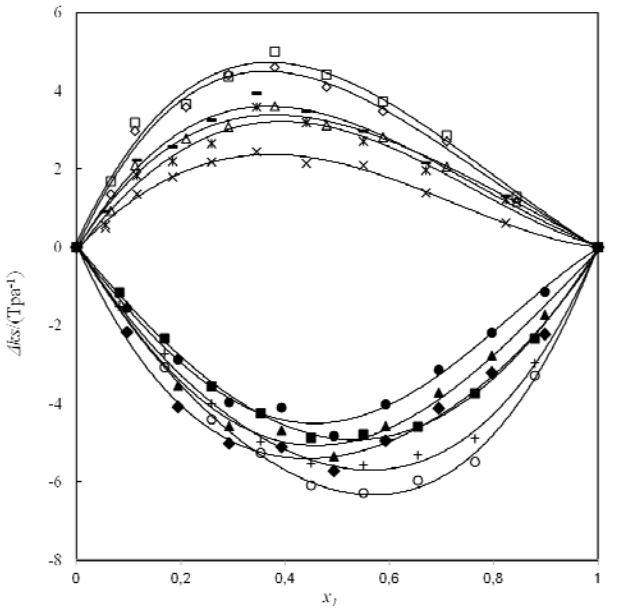

Figure 3. Curves of deviations in isentropic compressibility ΔK_S vs mole fraction for the binary mixture butyl ethanoate + tetrahydrofuran at (□, 303.15; ◊, 308.15; δ,313.15) K, butyl ethanoate +1, 4-dioxane at (×,303.15; ж, 308.15; ▬, 313.15) K, butyl ethanoate +anisole at (o,303.15; +, 308.15; ■, 313.15) K, butyl ethanoate + butyl vinyl ether (♦, 303.15; ▲, 308.15; ●, 313.15) K.

Figure 3 represents the variation of ΔK_S values with mole the fraction of butyl ethanoate. The ΔK_S values show positive deviations for tetrahydrofuran and 1, 4-dioxane systems, while for anisole and butyl vinyl ether ΔK_S values show negative deviations. The magnitude of ΔK_S values change with rise in temperature.The negative ΔK_S for anisole and butyl vinyl ether systems in our present study may be attributed to the dipole – dipole interactions.

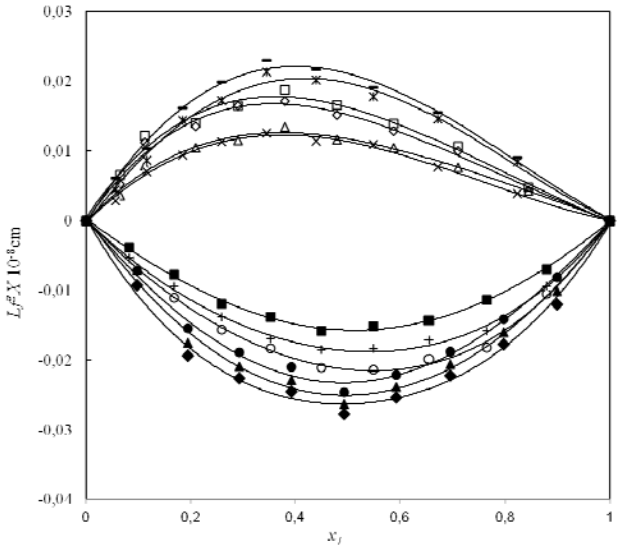

Figure 4. Curves of excess intermolecular free length L_f^E vs mole fraction for the binary mixtures butyl ethanoate + tetrahydrofuran at (□, 303.15; ◊,308.15; δ, 313.15) k, butyl ethanoate + 1,4-dioxane at (×, 303.15 ; ж, 308.15; ▬,313.15) k, butyl ethanoate +anisole at (o, 303.15 ; +,308.15 ;■,313.15) k, butyl ethanoate + butyl vinyl ether (♦, 303.15; ▲, 308.15; ●, 313.15) K.

Figure 4 shows the variation of L_f^E with x_1. Like ΔK_S the L_f^E values for tetrahydrofuran and 1, 4-dioxane systems are positive, while for anisole and butyl vinyl ether the L_f^E values are negative over the entire composition range of butyl ethanoate. According to Ramamurthy and Sastry[25] the negative values of L_f^E indicate that sound wave has to travel a larger distance due to the dominant nature of interactions between unlike molecules.

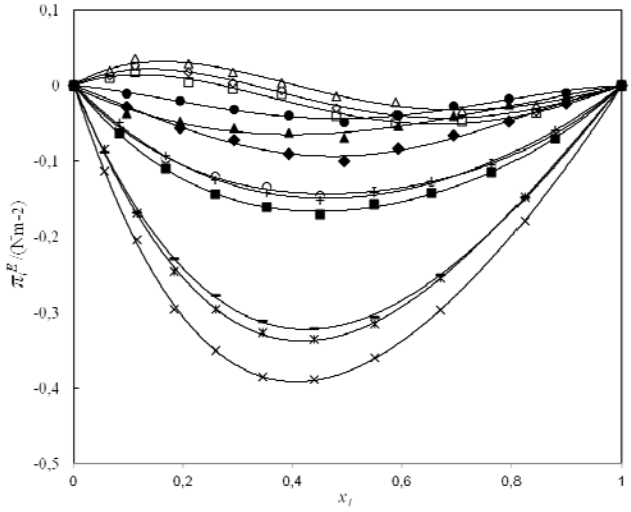

Figure 5. Plots of excess internal pressure π_i^E Vs mole fraction for the binary mixture butyl ethanoate + tetrahydrofuran at (□,303.15 ; ◊, 308.15 ; δ,313.15) K, butyl ethanoate+ 1,4-dioxane at (×, 303.15 ; ж, 308.15 ; ▬, 313.15) K, butyl ethanoate + anisole at (o, 303.15 ; +, 308.15 ; ■, 313.15) K, butyl ethanoate + butyl vinyl ether (♦, 303.15; ▲, 308.15; ●, 313.15) K.

Figure 5 shows the variation of π_i^E versus mole fraction of butyl ethanoate, wherein it is observed that the π_i^E values except for (butyl ethanoate + tetrahydrofuran) system, exhibit negative deviation over the entire range of composition at all the studied temperatures. For the mixtures of tetrahydrofuran inversion of sign of π_i^E from positive to negative occurs at about $x_1 \sim 0.275$. It is also observed that the values of π (Table 2) except for (butyl ethanoate + butyl vinyl ether) decrease with increase in concentration of butyl ethanoate. The decrease in internal pressure with increase in concentration of ester may be explained as the addition of monomer (solute) decreases the cohesive forces of the solvent. Whereas for butyl vinyl ether the π values increase with increase in concentration of ester. Similar behavior has been noticed in the earlier studies.[26, 27]

Conclusions

Density, viscosity and speed of sound for the binary mixtures of butyl ethanoate with tetrahydrofuran, 1, 4-dioxane, anisole, and butyl vinyl ether were determined over the entire range of composition at T=303.15, 308.15, and 313.15 K. The various excess or deviation parameters (V^E, $\Delta\eta$, ΔK_S, L_f^E and π_i^E) were evaluated from the measured data. All these parameters were correlated by the Redlich-Kister polynomial equation to derive the coefficients and standard errors. These properties exhibit either positive or negative deviations from ideality. The results were interpreted in terms of intermolecular interactions and structural effects. It is observed that the interactions involved in the present study are mostly of dipolar-dipolar type. Finally we have employed some of the available semi-empirical equations to correlate the experimental viscosity data and compared their predictive abilities. From the analysis it was concluded that McAllister equation with three adjustable parameters has a good predictive ability as compared to one, and two adjustable parameter models.

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Received: 17.04.2014.
Accepted: 04.06.2014.