

## Research Article

# Studies on Excess Volume, Viscosity, and Speed of Sound of Binary Mixtures of Methyl Benzoate in Ethers at $T = (303.15, 308.15, \text{ and } 313.15) \text{ K}$

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Densities, viscosities, and speed of sound have been determined at  $T = (303.15, 308.15, \text{ and } 313.15) \text{ K}$  for the binary mixtures of methyl benzoate with tetrahydrofuran, 1,4-dioxane, anisole, and butyl vinyl ether over the entire range of composition. Using these measured values, excess volume  $V^E$ , deviation in viscosities  $\Delta\eta$ , excess Gibbs free energy of activation for viscous flow  $\Delta G^{*E}$ , and deviation in isentropic compressibility  $\Delta k_s$  have been calculated. These calculated binary data have been fitted to Redlich-Kister equation to determine the appropriate coefficients. The values of excess volume  $V^E$  and deviation in viscosities  $\Delta\eta$  are negative over the entire range of composition for all the binary systems at the studied temperatures. The behavior of these parameters with composition of the mixture has been discussed in terms of molecular interactions between the components of liquids.

## 1. Introduction

The excess or deviation properties of liquid-liquid mixtures are useful in several industrial applications owing to their influence upon the effectiveness of the operations. Nowadays, the determination of ultrasonic velocity and the related acoustical parameters derived from it has attracted the attention of several researchers. Much work has been done in solutions of polymers [1–3], pharamaterials [4], electrolytes [5–7], and nonelectrolytes [8–10].

Tetrahydrofuran is a polar ( $\mu = 1.75D$ ), aprotic solvent. Its main use is a precursor to polymers. It is also used as an industrial solvent for PVC and in varnishes. Dye carrier formulations based on methyl benzoate are useful in textile processing. Further methyl benzoate finds its primary uses as a perfume or flavouring agent and also used as a source of benzoyl radical. While ethers are excellent solvents, because they are relatively unreactive, yet they solvate a wide variety of compounds. Tetrahydrofuran, a cyclic ether which is one of the most polar simple ethers, is used as a solvent for polymers and also commercially used for the production of several

compounds. Anisole, an aryl ether, is a major constituent of essential oil of anise seed.

In view of the abovementioned significances, these solvents are chosen with an aim to investigate the effect of the presence of two lone pairs of electrons on the oxygen atom of ether, when it is mixed with methyl benzoate. Moreover, it would be interesting to know the behavior of ether in an environment of aromatic ester molecules. The main objective of the present study is to determine the density  $\rho$ , viscosity  $\eta$ , and speed of sound  $u$  for the binary mixtures formed by the methyl benzoate with ether compounds.

In our earlier papers [11–13], we have reported some data on thermodynamic, transport, acoustical, and optical properties on mixtures of methyl benzoate with hydrocarbons and ketones and analysed the data in terms of molecular interactions. Several authors have also published density, viscosity, and speed of sound data [14–20] of binary mixtures of methyl benzoate with different types of organic solvents. In the present study, we report the results of density  $\rho$ , viscosity  $\eta$ , and speed of sound  $u$  for the binary mixtures of methyl benzoate with ethers, namely, tetrahydrofuran, 1,4-dioxane,

TABLE 1: Comparison of experimental density  $\rho$  and viscosity  $\eta$  of pure liquids with the literature values at (303.15, 308.15, and 313.15) K.

Liquid	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$	
		Exptl.	Lit.	Exptl.	Lit.
Methyl benzoate	303.15	1.0785	1.0788 [18]	1.678	1.673 [28]
			1.0790 [22]		1.656 [18]
	308.15	1.0743	1.0740 [18]	1.517	1.510 [18]
			1.0741 [19]		1.504 [20]
			1.07399 [20]		1.510 [21]
	313.15	1.0696	1.0690 [27]	1.373	1.365 [27]
Tetrahydrofuran	303.15	0.8787	0.8771 [22]	0.439	
	308.15	0.8730	0.87214 [22]	0.429	
	313.15	0.8669	0.86719 [22]	0.390	
1,4-Dioxane	303.15	1.0227	1.02271 [23]	1.090	1.102 [23]
					1.095 [24]
	308.15	1.0178	1.0172 [24]	0.999	1.008 [24]
	313.15	1.0116	1.01132 [23]	0.946	0.946 [23]
Anisole	303.15	0.9853	0.984374 [25]	0.923	0.931 [25]
	308.15	0.9792	0.9788 [26]	0.849	0.849 [26]
	313.15	0.9728		0.764	
Butyl vinyl ether	303.15	0.7741		0.387	
	308.15	0.7682		0.365	
	313.15	0.7633		0.354	

anisole, and butyl vinyl ether measured at (303.15, 308.15, and 313.15) K over the entire mixture composition. To the best of our knowledge, such data on the abovementioned mixtures are not available in the earlier literature. Using the experimental data of  $\rho$ ,  $\eta$ , and  $u$ , various parameters such as excess volume  $V^E$ , deviation in viscosity  $\Delta\eta$ , excess Gibb's free energy of activation for viscous flow  $\Delta G^{*E}$ , and deviation in isentropic compressibility  $\Delta k_s$  were determined. These computed data are discussed to study the nature of behaviors between the components of the mixtures.

## 2. Experimental

**2.1. Materials.** Methyl benzoate (Fluka AG >0.996), tetrahydrofuran, 1,4-dioxane, anisole, and butyl vinyl ether (all Sigma-Aldrich, AR grade) of mass purity >0.997 were used without further purification. These chemicals were kept over molecular sieves for several days before use. The mass fraction purities as determined by gas chromatography (HP 8610) using FID were as follows: methyl benzoate (>0.996), tetrahydrofuran, (>0.996), 1,4-dioxane, (>0.998), anisole, (>0.998), and butyl vinyl ether (>0.997). The purity of the samples was further checked by comparing the measured density  $\rho$  and viscosity  $\eta$  with the literature values [18–28] as shown in Table 1.

TABLE 2: Values of density  $\rho$ , excess volume  $V^E$ , viscosity  $\eta$ , speeds of sound  $u$ , and isentropic compressibility  $k_s$  for the binary liquid mixtures.

$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_s/\text{Tpa}^{-1}$
Methyl benzoate (1) + tetrahydrofuran (2)					
$T = 303.15\text{ K}$					
0.0689	0.9020	−0.261	0.496	1260	698
0.1417	0.9246	−0.496	0.562	1272	669
0.2202	0.9468	−0.699	0.638	1284	641
0.3030	0.9680	−0.858	0.727	1296	615
0.3932	0.9885	−0.943	0.829	1308	591
0.4930	1.0084	−0.938	0.951	1320	569
0.6018	1.0272	−0.822	1.096	1332	549
0.7225	1.0452	−0.590	1.262	1344	530
0.8535	1.0623	−0.277	1.446	1356	512
$T = 308.15\text{ K}$					
0.0689	0.8964	−0.269	0.484	1232	735
0.1417	0.9192	−0.510	0.546	1236	712
0.2202	0.9413	−0.719	0.616	1244	686
0.3030	0.9627	−0.882	0.699	1256	659
0.3932	0.9833	−0.969	0.790	1268	633
0.4930	1.0033	−0.964	0.904	1284	605
0.6018	1.0222	−0.847	1.032	1300	679
0.7225	1.0403	−0.612	1.181	1316	555
0.8535	1.0575	−0.294	1.343	1336	530
$T = 313.15\text{ K}$					
0.0689	0.8905	−0.283	0.443	1216	759
0.1417	0.9134	−0.538	0.505	1220	736
0.2202	0.9358	−0.749	0.567	1228	709
0.3030	0.9572	−0.913	0.641	1240	679
0.3932	0.9779	−0.999	0.729	1252	652
0.4930	0.9980	−0.990	0.830	1268	623
0.6018	1.0171	−0.877	0.943	1284	596
0.7225	1.0354	−0.645	1.078	1300	572
0.8535	1.0527	−0.317	1.220	1320	545
Methyl benzoate (1) + 1,4-dioxane (2)					
$T = 303.15\text{ K}$					
0.0898	1.0307	−0.059	1.130	1328	550
0.1468	1.0355	−0.105	1.157	1336	541
0.2280	1.0421	−0.185	1.198	1344	531
0.3145	1.0485	−0.254	1.244	1352	521
0.4054	1.0543	−0.281	1.293	1360	513
0.5056	1.0599	−0.278	1.352	1368	504
0.6161	1.0653	−0.242	1.418	1372	499
0.7316	1.0701	−0.161	1.491	1372	496
0.8597	1.0749	−0.062	1.573	1372	494
$T = 308.15\text{ K}$					
0.0898	1.0261	−0.093	1.038	1324	556
0.1468	1.0311	−0.157	1.066	1332	547
0.2280	1.0377	−0.237	1.106	1340	537
0.3145	1.0440	−0.297	1.147	1348	530
0.4054	1.0499	−0.333	1.192	1352	521
0.5056	1.0555	−0.329	1.246	1356	515
0.6161	1.0608	−0.282	1.308	1360	510
0.7316	1.0655	−0.189	1.376	1360	507
0.8597	1.0702	−0.077	1.449	1360	505

TABLE 2: Continued.

$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_s/\text{Tpa}^{-1}$
$T = 313.15\text{ K}$					
0.0898	1.0205	-0.132	0.984	1320	562
0.1468	1.0257	-0.207	1.006	1328	553
0.2280	1.0326	-0.304	1.040	1336	543
0.3145	1.0390	-0.363	1.075	1340	536
0.4054	1.0450	-0.398	1.110	1348	527
0.5056	1.0507	-0.392	1.157	1352	521
0.6161	1.0560	-0.331	1.208	1356	515
0.7316	1.0608	-0.234	1.263	1356	513
0.8597	1.0655	-0.106	1.324	1356	510
Methyl benzoate (1) + Anisole (2)					
$T = 303.15\text{ K}$					
0.0860	0.9950	-0.052	0.974	1388	522
0.1821	1.0056	-0.113	1.038	1380	522
0.2756	1.0157	-0.179	1.101	1372	523
0.3978	1.0282	-0.229	1.187	1368	520
0.4637	1.0347	-0.248	1.234	1368	516
0.5659	1.0442	-0.238	1.307	1368	512
0.6701	1.0534	-0.202	1.391	1368	507
0.7776	1.0624	-0.140	1.480	1368	503
0.8850	1.0710	-0.063	1.572	1368	499
$T = 308.15\text{ K}$					
0.0860	0.9891	-0.062	0.894	1368	540
0.1821	1.0000	-0.145	0.949	1356	544
0.2756	1.0102	-0.209	1.007	1352	542
0.3978	1.0229	-0.264	1.086	1348	538
0.4637	1.0295	-0.285	1.129	1348	535
0.5659	1.0392	-0.282	1.195	1348	530
0.6701	1.0485	-0.242	1.272	1348	525
0.7776	1.0576	-0.175	1.355	1348	520
0.8850	1.0663	-0.093	1.439	1348	516
$T = 313.15\text{ K}$					
0.0860	0.9830	-0.082	0.800	1356	553
0.1821	0.9941	-0.170	0.850	1344	557
0.2756	1.0045	-0.241	0.902	1340	554
0.3978	1.0174	-0.297	0.972	1336	551
0.4637	1.0241	-0.317	1.012	1336	547
0.5659	1.0340	-0.318	1.074	1336	541
0.6701	1.0435	-0.282	1.144	1336	537
0.7776	1.0528	-0.218	1.220	1336	532
0.8850	1.0616	-0.127	1.301	1336	528
Methyl benzoate (1) + Butyl vinyl ether (2)					
$T = 303.15\text{ K}$					
0.1026	0.8056	-0.108	0.437	1104	1019
0.2055	0.8375	-0.260	0.497	1128	938
0.3060	0.8690	-0.423	0.571	1152	867
0.4047	0.8999	-0.544	0.657	1176	804
0.5057	0.9313	-0.605	0.761	1204	741
0.6065	0.9623	-0.596	0.891	1232	685
0.7061	0.9926	-0.524	1.038	1260	635
0.8034	1.0218	-0.388	1.205	1292	586
0.9021	1.0511	-0.201	1.422	1328	540

TABLE 2: Continued.

$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	$u/\text{m}\cdot\text{s}^{-1}$	$k_s/\text{Tpa}^{-1}$
$T = 308.15\text{ K}$					
0.1026	0.8001	-0.141	0.421	1092	1048
0.2055	0.8322	-0.320	0.478	1116	965
0.3060	0.8637	-0.476	0.546	1136	891
0.4047	0.8947	-0.602	0.657	1160	825
0.5057	0.9261	-0.651	0.626	1188	760
0.6065	0.9572	-0.639	0.720	1216	702
0.7061	0.9875	-0.550	0.974	1248	650
0.8034	1.0168	-0.408	1.124	1280	600
0.9021	1.0462	-0.212	1.319	1316	552
$T = 313.15\text{ K}$					
0.1026	0.7954	-0.182	0.400	1084	1070
0.2055	0.8275	-0.367	0.452	1108	984
0.3060	0.8591	-0.541	0.515	1132	908
0.4047	0.8901	-0.667	0.585	1156	841
0.5057	0.9215	-0.713	0.671	1184	774
0.6065	0.9526	-0.697	0.778	1212	715
0.7061	0.9829	-0.601	0.897	1244	657
0.8034	1.0121	-0.439	1.034	1276	607
0.9021	1.0414	-0.221	1.205	1308	561

**2.2. Methods.** Binary mixtures were prepared by mass in airtight ground stoppered bottles. Mass measurements accurate to  $\pm 0.01\text{ mg}$  were made on a digital electronic balance (Mettler AE 240, Switzerland). The resulting uncertainty in mole fraction was estimated to be less than  $\pm 0.0001$ . Each mixture was immediately used after it was well mixed by shaking. The densities of the pure and their binary mixtures were determined by using an Anton Paar density meter (DMA 4100). The uncertainty in the density measurements was found to be less than  $\pm 0.0004\text{ g}\cdot\text{cm}^{-3}$ .

Viscosities were determined using an Ubbelohde viscometer with an uncertainty of  $\pm 0.008\text{ mPa}\cdot\text{s}$ . The detailed method of measurement of viscosity has been reported earlier [11]. The speeds of sound were measured with a single crystal variable path interferometer (Mittal Enterprises, New Delhi, India) at an operating frequency of 2 MHz that had been calibrated with double distilled water and benzene. The uncertainty in speed of sound was estimated to be  $\pm 1\text{ m}\cdot\text{s}^{-1}$ .

### 3. Results and Discussion

The experimental values of densities  $\rho$ , excess volumes  $V^E$ , viscosities  $\eta$ , speeds of sound  $u$ , and isentropic compressibility  $k_s$  of the binary mixtures of methyl benzoate with tetrahydrofuran, 1,4-dioxane, anisole, and butyl vinyl ether at temperatures 303.15, 308.15, and 313.15 K are listed in Table 2.

The excess volume  $V^E$  of the mixtures was deduced from the measured densities using the following relation:

$$V^E = \frac{(x_1 M_1 + x_2 M_2)}{\rho_{12}} - \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right), \quad (1)$$

where  $x$ ,  $M$ , and  $\rho$  are the mole fraction, molar mass, and density, respectively, of pure components 1 and 2.  $\rho_{12}$  is

TABLE 3: Derived parameters of excess functions by Redlich-Kister equation and standard deviations  $\sigma$  of binary liquid mixtures.

Function	T/K	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma$
Methyl benzoate (1) + tetrahydrofuran (2)						
$V^E$	303.15	-3.7342	1.2905	1.1561	—	0.003
	308.15	-3.8390	1.2879	1.1173	—	0.003
	313.15	-3.9542	1.2921	1.9336	—	0.004
$\Delta\eta$	303.15	-0.3703	0.0783	-0.0054	—	0.002
	308.15	-0.2820	0.0762	-0.0017	—	0.002
	313.15	-0.2206	0.0052	-0.0013	—	0.001
$\Delta G^{*E}$	303.15	1303.56	9.2800	-47.1207	-173.82	2.5
	308.15	1332.27	-4.3204	-21.9964	-216.76	3.3
	313.15	1442.68	-177.56	50.2305	-79.613	3.8
$\Delta k_s$	303.15	-17.457	7.2762	-0.2584	1.4106	0.008
	308.15	-11.729	-0.0066	3.5145	-0.134	0.093
	313.15	-11.726	0.5719	4.7747	1.1539	0.090
Methyl benzoate (1) + 1,4-dioxane (2)						
$V^E$	303.15	-1.144	0.290	0.846	—	0.002
	308.15	-1.326	0.425	0.753	—	0.002
	313.15	-1.568	0.552	0.575	—	0.003
$\Delta\eta$	303.15	-0.122	0.018	-0.011	—	0.001
	308.15	-0.096	0.007	0.009	—	0.001
	313.15	-0.062	0.019	0.045	—	0.001
$\Delta G^{*E}$	303.15	152.594	48.243	-4.7463	-34.315	0.7
	308.15	191.571	23.232	37.394	-27.738	2.8
	313.15	201.888	29.749	100.81	-116.35	2.4
$\Delta k_s$	303.15	-8.7386	1.8216	3.7965	-1.7238	0.094
	308.15	-9.2275	2.7930	-0.9078	-0.8437	0.044
	313.15	-11.303	2.1793	-5.0991	-0.8657	0.048
Methyl benzoate (1) + anisole (2)						
$V^E$	303.15	-0.9866	0.2637	0.5566	—	0.003
	308.15	-1.1427	-0.0217	0.4368	—	0.003
	313.15	-1.2778	-0.0899	0.2005	—	0.002
$\Delta\eta$	303.15	-0.1440	0.0055	0.0234	—	0.002
	308.15	-0.1774	-0.0067	-0.0351	—	0.001
	313.15	-0.1602	-0.0069	-0.0270	—	0.002
$\Delta G^{*E}$	303.15	177.724	-46.913	99.649	70.211	2.2
	308.15	116.959	-70.397	12.737	80.252	2.5
	313.15	56.636	-50.389	-50.388	63.520	1.2
$\Delta k_s$	303.15	3.5076	-3.8057	0.9701	5.8130	0.036
	308.15	4.7056	-4.2092	5.0184	4.5773	0.053
	313.15	5.3764	-4.7277	6.5667	2.5075	0.050
Methyl benzoate (1) + butyl vinyl ether (2)						
$V^E$	303.15	-2.4161	-0.7060	1.0922	—	0.004
	308.15	-2.6110	-0.5335	0.9973	—	0.004
	313.15	-2.8690	-0.4280	0.9846	—	0.005
$\Delta\eta$	303.15	-1.0856	-0.3096	-0.1033	—	0.002
	308.15	-0.9534	-0.2594	-0.0654	—	0.003
	313.15	-0.8261	-0.2221	-0.0264	—	0.003
$\Delta G^{*E}$	303.15	-663.33	174.93	-102.07	-27.064	5.8
	308.15	-627.07	153.92	-43.740	-3.6493	7.2
	313.15	-596.84	106.49	131.85	-19.948	5.7
$\Delta k_s$	303.15	-20.411	5.1677	5.1277	-1.1243	0.080
	308.15	-22.018	5.1564	3.8155	-3.0159	0.085
	313.15	-25.224	3.8500	-3.2901	2.8527	0.072

the density of the liquid mixture. The Gibbs free energy of activation for viscous flow  $\Delta G^{*E}$  was calculated from the viscosity data using the following relation:

$$\Delta G^{*E} = RT [\ln(\eta\nu) - \{x_1 \ln(\eta_1\nu_1) + x_2 \ln(\eta_2\nu_2)\}], \quad (2)$$

where  $\nu = (x_1 M_1 / \rho_1 + x_2 M_2) / \rho_{12}$  is the molar volume of the mixture and  $\nu_1$  and  $\nu_2$  are the molar volumes of the pure components.

The isentropic compressibilities  $k_s$  were calculated from the densities  $\rho$  and speeds of sound  $u$  using the Newton-Laplace equation:

$$k_s = \frac{1}{u^2 \rho}. \quad (3)$$

The deviation in viscosity  $\Delta\eta$  and deviation in isentropic compressibility  $\Delta k_s$  were calculated using the general equation:

$$\Delta Y = Y_m - x_1 Y_1 - x_2 Y_2, \quad (4)$$

where  $\Delta Y$  is the deviation property in question,  $Y_m$  refers to the property of the mixture, and  $x_1 Y_1$  and  $x_2 Y_2$  refer to the mole fraction and specific property of the pure components 1 and 2, respectively. The results of these excess or deviation properties were fitted by the method of least squares to the Redlich-Kister [29] polynomial type equation:

$$Y = x_1 x_2 \sum_{j=1}^p a_{j-1} (x_1 - x_2)^{j-1}, \quad (5)$$

where  $Y$  is  $V^E$ ,  $\Delta\eta$ ,  $\Delta G^{*E}$ , or  $\Delta k_s$  and  $x_1$  and  $x_2$  are the mole fractions of pure components 1 and 2, respectively.  $a_{j-1}$  is the polynomial coefficient, and  $p$  is the polynomial degree. The degree of (5) was optimised by applying the  $F$ -test. The correlated results are shown in Table 3 in which the tabulated standard deviation  $\sigma$  was calculated using the following relation:

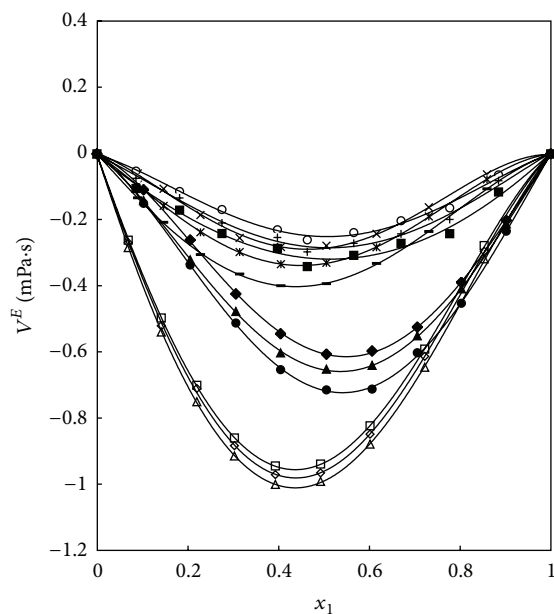
$$\sigma = \left[ \frac{\sum (\gamma_{\text{exp}}^E - \gamma_{\text{cal}}^E)^2}{(n - J)} \right]^{0.5}, \quad (6)$$

where  $n$  is the number of data points and  $j$  is the number of coefficients. The subscripts exp and cal denote experimental and calculated values, respectively.

The variations of excess volume  $V^E$  with mole fraction  $x_1$  of methyl benzoate at the studied temperatures for the binary mixtures are displayed in Figure 1. It is observed that all the studied systems exhibit negative deviations. The  $V^E$  data for different components of the mixtures vary in the sequence:

tetrahydrofuran > butyl vinyl ether > 1,4-dioxane > anisole

The effect of temperature on  $V^E$  as displayed in Figure 1 is quite significant, as the negative  $V^E$  values increase with increase in temperature. The behavior of  $V^E$  can be explained



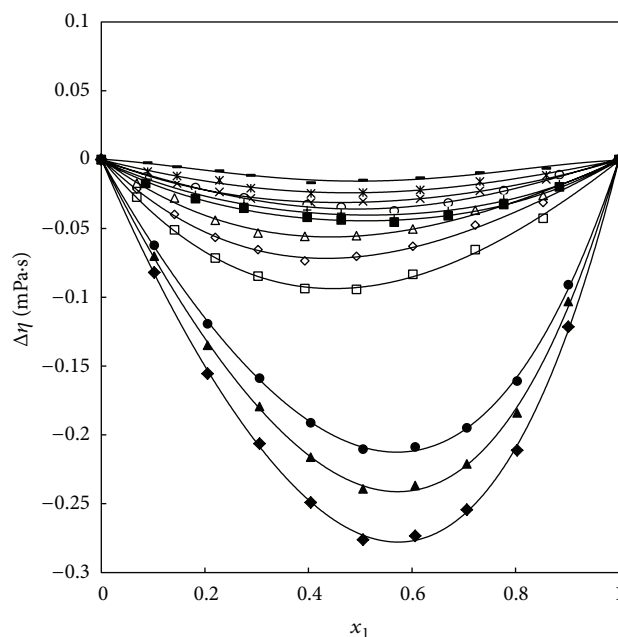
M.b. + THF  
 □ 303.15 K  
 ◇ 308.15 K  
 △ 313.15 K  
 M.b. + anisole  
 ○ 303.15 K  
 + 308.15 K  
 ■ 313.15 K  
 M.b. + 1,4-dioxane  
 × 303.15 K  
 \* 308.15 K  
 — 313.15 K  
 M.b. + BVE  
 ◆ 303.15 K  
 ▲ 308.15 K  
 ● 313.15 K

FIGURE 1: Curves of excess volumes ( $V^E$ ) versus mole fraction for the binary mixtures of methyl benzoate + tetrahydrofuran at (□, 303.15; ◇, 308.15; △, 313.15) K, methyl benzoate + 1,4-dioxane at (×, 303.15; \*, 308.15; —, 313.15) K, methyl benzoate + anisole at (○, 303.15; +, 308.15; ■, 313.15) K, and methyl benzoate + butyl vinyl ether at (◆, 303.15; ▲, 308.15; ●, 313.15) K.

by considering the type of component molecules in pure state and in mixture. In the present case, the negative  $V^E$  values may be attributed to the differences in the dielectric constants of the components. The dielectric constants of methyl benzoate, tetrahydrofuran, 1,4-dioxane, anisole, and butyl vinyl ether are  $\epsilon = 6.02, 7.261, 2.209, 4.33, 3.9$ , respectively. Further, there is a possibility of electron donor-acceptor type or charge transfer interactions [30] between the highly electronegative oxygen of ether and the  $\pi$ -electron of ring of aromatic ester molecule resulting in negative  $V^E$  values. The less negative  $V^E$  values in case of methyl benzoate + anisole may be due to the presence of methyl ( $-\text{CH}_3$ ) group in anisole. This observation suggests that with an increase in methyl group in mixture, the donor-acceptor interactions between the unlike molecules tend to decrease.

The results of  $\Delta\eta$  as displayed in the Figure 2 are all negative over the entire range of composition and the magnitude values of  $\Delta\eta$  vary according to the following sequence:

butyl vinyl ether > tetrahydrofuran > anisole > 1,4-dioxane



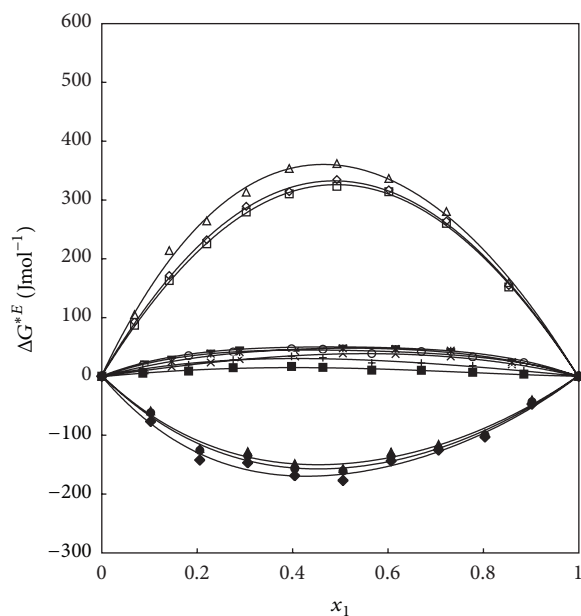
M.b. + THF  
 □ 303.15 K  
 ◇ 308.15 K  
 △ 313.15 K  
 M.b. + anisole  
 ○ 303.15 K  
 + 308.15 K  
 ■ 313.15 K  
 M.b. + 1,4-dioxane  
 × 303.15 K  
 \* 308.15 K  
 — 313.15 K  
 M.b. + BVE  
 ◆ 303.15 K  
 ▲ 308.15 K  
 ● 313.15 K

FIGURE 2: Curves of deviation in viscosity ( $\Delta\eta$ ) versus mole fraction for the binary mixtures of methyl benzoate + tetrahydrofuran at (□, 303.15; ◇, 308.15; △, 313.15) K, methyl benzoate + 1,4-dioxane at (×, 303.15; \*, 308.15; —, 313.15) K, and methyl benzoate + anisole at (○, 303.15; +, 308.15; ■, 313.15) K.

It is observed that negative values of  $\Delta\eta$  decrease with increase in the temperature indicating the effect of temperature on  $\Delta\eta$ . Fort and Moore [31] observed that the negative  $\Delta\eta$  values indicate the dispersion forces without involving the formation of any hetero-molecular complexes. A perusal of Figures 1 and 2 reveals that both  $V^E$  and  $\Delta\eta$  exhibit the negative deviations over the entire range of composition; however, the magnitude values of the studied mixtures follow a different sequence. This type of behavior supports the observation of Rastogi et al. [32] and Kaulgud [33], suggesting that the strength of specific or dispersion forces is not the only factor influencing the  $\Delta\eta$ , but the molecular size and shape of the components are also equally important.

The dependence of  $\Delta G^{*E}$  on the mole fraction is shown in Figure 3, where it was observed that  $\Delta G^{*E}$  is positive for mixtures of methyl benzoate with tetrahydrofuran, 1,4-dioxane, and anisole, whereas for mixtures of methyl benzoate + butyl vinyl ether, the values of  $\Delta G^{*E}$  are negative over the entire range of composition. The positive  $\Delta G^{*E}$  values may be an indicative of specific interactions [31, 34, 35] and the negative  $\Delta G^{*E}$  values indicate the presence of dispersive forces in these mixtures.





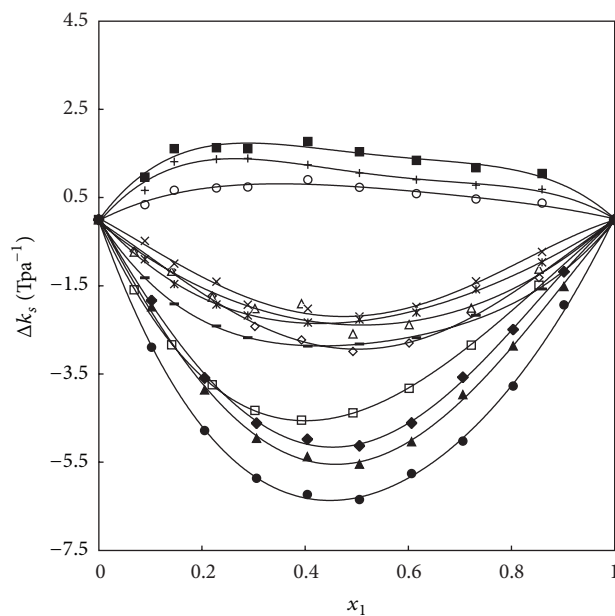
M.b. + THF  
 □ 303.15 K  
 ◇ 308.15 K  
 △ 313.15 K  
 M.b. + 1,4-dioxane  
 × 303.15 K  
 \* 308.15 K  
 — 313.15 K  
 M.b. + anisole  
 ○ 303.15 K  
 + 308.15 K  
 ■ 313.15 K  
 M.b. + BVE  
 ◆ 303.15 K  
 ▲ 308.15 K  
 ● 313.15 K

FIGURE 3: Curves of excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ) versus mole fraction for the binary mixtures of methyl benzoate + tetrahydrofuran at (□, 303.15; ◇, 308.15; △, 313.15) K, methyl benzoate + 1,4-dioxane at (×, 303.15; \*, 308.15; —, 313.15) K, methyl benzoate + anisole at (○, 303.15; +, 308.15; ■, 313.15) K, and methyl benzoate + Butyl vinyl ether at (◆, 303.15; ▲, 308.15; ●, 313.15) K.

The plots of  $\Delta k_s$ , as displayed in Figure 4, show that for methyl benzoate with tetrahydrofuran, 1,4-dioxane, and butyl vinyl ether, the values of  $\Delta k_s$  exhibit negative deviation over the entire range of mixture composition; while for methyl benzoate + anisole, the values of  $\Delta k_s$  exhibit positive deviations. The positive  $\Delta k_s$  values are a sign of weak interaction between component molecules, which may be attributed to the mutual disruption in molecules associated with pure liquids. These positive  $\Delta k_s$  values are accompanied by a decrease in sound velocity over the entire range of composition of ester. The negative values of  $\Delta k_s$  may be attributed to the formation of weak bonds [36–38] by dipole-induced dipole interaction between unlike molecules and the geometrical fitting of component molecules in to each other's structure.

#### 4. Conclusions

The densities  $\rho$ , excess volumes  $V^E$ , viscosities  $\eta$ , speeds of sound  $u$ , and data of binary mixtures methyl benzoate



M.b. + THF  
 □ 303.15 K  
 ◇ 308.15 K  
 △ 313.15 K  
 M.b. + 1,4-dioxane  
 × 303.15 K  
 \* 308.15 K  
 — 313.15 K  
 M.b. + anisole  
 ○ 303.15 K  
 + 308.15 K  
 ■ 313.15 K  
 M.b. + BVE  
 ◆ 303.15 K  
 ▲ 308.15 K  
 ● 313.15 K

FIGURE 4: Curves of deviation in isentropic compressibility ( $\Delta k_s$ ) versus mole fraction for the binary mixture of methyl benzoate + tetrahydrofuran at (□, 303.15; ◇, 308.15; △, 313.15) K, methyl benzoate + 1,4-dioxane at (×, 303.15; \*, 308.15; —, 313.15) K, methyl benzoate + anisole at (○, 303.15; +, 308.15; ■, 313.15) K, and methyl benzoate + Butyl vinyl ether at (◆, 303.15; ▲, 308.15; ●, 313.15) K.

with tetrahydrofuran, 1,4-dioxane, anisole, and butyl vinyl ether have been reported at (303.15, 308.15 and 313.15) K. The excess molar volumes  $V^E$ , deviation in viscosity  $\Delta\eta$ , excess Gibbs free energies of activation for viscous flow  $\Delta G^{*E}$ , and deviation in isentropic compressibility  $\Delta k_s$  were evaluated using the experimental data of  $\rho$ ,  $\eta$ , and  $u$  and discussed in terms of the interactions between the components of the mixtures. Both  $V^E$  and  $\Delta\eta$  exhibit negative deviations, while  $\Delta G^{*E}$  and  $\Delta k_s$  exhibit both positive and negative deviations. It is concluded that the negative  $V^E$  may be attributed to the differences in the dielectric constants of the components and the possibility of the electron donor-acceptor type or charge transfer interactions between the electronegative oxygen of ether and the  $\pi$ -electrons of aromatic ester resulting into contraction in volumes.

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## References

- [1] J. N. Prassianakis, "Correlation of mechanical and acoustical properties of plasticized epoxy polymers," *Journal of Applied Polymer Science*, vol. 39, no. 10, pp. 2031–2041, 1990.
- [2] V. Kannappan, S. Mahendran, P. Sathyamoorthy, and D. Roop Singh, "Ultrasonic method of determination of glass transition temperatures of certain thermotropic liquid crystalline copolyesters," *Journal of Polymer Materials*, vol. 18, no. 4, pp. 409–416, 2001.
- [3] D. R. Godhani and P. H. Parsania, "Studies on acoustical properties of poly(4,4'-diphenylphthalidodiphenyl-4,4'-disulfonate) at 30°C," *Journal of the Indian Chemical Society*, vol. 79, no. 7, pp. 620–622, 2002.
- [4] M. Levina and M. H. Rubinstein, "The effect of ultrasonic vibration on the compaction characteristics of paracetamol," *Journal of Pharmaceutical Sciences*, vol. 89, no. 6, pp. 705–723, 2000.
- [5] V. K. Syal, V. Bhalla, and S. Chauhan, "Ultrasonic studies of some tetraalkylammonium salts in acetonitrile+dioxane mixtures at 35°C," *Acustica*, vol. 81, no. 3, pp. 276–278, 1995.
- [6] D. Geetha and P. S. Ramesh, "Ultrasonic studies on polymer blend (natural/synthetic) in strong electrolyte solutions," *Journal of Molecular Liquids*, vol. 136, no. 1–2, pp. 50–53, 2007.
- [7] E. S. Balankina and A. K. Lyaschenko, "The acoustical and structural changes of aqueous solutions due to transition to molten supercooled salts," *Journal of Molecular Liquids*, vol. 101, no. 1–3, pp. 273–283, 2002.
- [8] M. Gowrishankar, S. Sivarambabu, P. Venkateswarlu, and K. S. Kumar, "Excess volumes, speeds of sound, isentropic compressibilities and viscosities of binary mixtures of N-ethyl aniline with some aromatic ketones at 303.15 K," *Bulletin of the Korean Chemical Society*, vol. 33, no. 5, pp. 1686–1692, 2012.
- [9] A. C. H. Chandrasekhar, S. K. Ramanjaneyulu, and A. Krishniah, "Volumetric and ultrasonic behaviour of acetophenone and alcohol mixtures," *Physics and Chemistry of Liquids*, vol. 19, no. 3, pp. 171–179, 1989.
- [10] M. Yasmin, K. P. Singh, S. Parveen, M. Gupta, and J. P. Shukla, "Thermoacoustical excess properties of binary liquid mixtures: a comparative experimental and theoretical study," *Acta Physica Polonica A*, vol. 115, no. 5, pp. 890–900, 2009.
- [11] M. V. Rathnam, R. T. Sayed, K. R. Bhanushali, and M. S. S. Kumar, "Molecular interaction study of binary mixtures of methyl benzoate: viscometric and ultrasonic study," *Journal of Molecular Liquids*, vol. 166, pp. 9–16, 2012.
- [12] M. V. Rathnam, S. Mankumare, and M. S. S. Kumar, "Density, viscosity, and speed of sound of (Methyl Benzoate + Cyclohexane), (Methyl Benzoate + *n*-Hexane), (Methyl Benzoate + Heptane), and (Methyl Benzoate + Octane) at temperatures of (303.15, 308.15, and 313.15) K," *Journal of Chemical and Engineering Data*, vol. 55, no. 3, pp. 1354–1358, 2010.
- [13] M. V. Rathnam, S. Mohite, and M. S. Kumar, "Thermophysical properties of isoamyl acetate or methyl benzoate + hydrocarbon binary mixtures, at (303.15 and 313.15) K," *Journal of Chemical and Engineering Data*, vol. 54, no. 2, pp. 305–309, 2009.
- [14] P. J. Raju, K. Rambabu, D. Ramchandran, M. Nagshwar Rao, and C. Rambabu, "Densities, adiabatic compressibility, frelength, viscosities and excess volumes of dimethyl sulfoxide with some aromatic esters at 303.15–318.15 K," *Physics and Chemistry of Liquids*, vol. 34, pp. 51–60, 1997.
- [15] B. Garcia, R. Alcade, S. Aparicio, and J. M. Leal, "Volumetric properties, viscosities and refractive indices of binary mixed solvents containing methyl benzoate," *Physical Chemistry Chemical Physics*, vol. 4, pp. 5833–5840, 2002.
- [16] Y. W. Sheu and C. H. Tu, "Densities, viscosities, refractive indices, and surface tensions for 12 flavor esters from T = 288.15 K to T = 358.15 K," *Journal of Chemical and Engineering Data*, vol. 50, no. 5, pp. 1706–1710, 2005.
- [17] Y. W. Sheu and C. H. Tu, "Densities and viscosities of binary mixtures of ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, and benzyl propionate with ethanol at T = (288.15, 298.15, 308.15, and 318.15) K," *Journal of Chemical and Engineering Data*, vol. 51, no. 2, pp. 545–553.
- [18] T. M. Aminabhavi, S. K. Raikar, and R. H. Balundgi, "Densities, viscosities, refractive indices, and speeds of sound in methyl acetoacetate + methyl acetate, + ethyl acetate, + *n*-butyl acetate, + methyl benzoate, and + ethyl benzoate at 298.15, 303.15, and 308.15 K," *Journal Of Chemical And Engineering Data*, vol. 38, no. 3, pp. 441–445, 1993.
- [19] A. M. Blanco, J. Ortega, B. Garcia, and J. M. Leal, "Studies on densities and viscosities of binary mixtures of alkyl benzoates in *n*-heptane," *Thermochimica Acta*, vol. 222, no. 1, pp. 127–136, 1993.
- [20] B. Garcia, R. Alcade, S. Aparicio, and J. M. Leal, "Thermophysical behavior of methylbenzoate + *n*-alkanes mixed aolvents: application of cubic equations of state and viscosity models," *Industrial and Engineering Chemistry Research*, vol. 41, no. 17, pp. 4399–4408, 2002.
- [21] T. M. Aminabhavi and S. K. Raikar, "Thermodynamic interactions in binary mixtures of 2-methoxyethanol with alkyl and aryl esters at 298. 15, 303. 15 and 308. 15 K," *Collection of Czechoslovak Chemical Communications*, vol. 58, pp. 1761–1776, 1993.
- [22] A. K. Nain, "Densities and volumetric properties of binary mixtures of tetrahydrofuran with some aromatic hydrocarbons at temperatures from 278.15 to 318.15 K," *Journal of Solution Chemistry*, vol. 35, no. 10, pp. 1417–1439, 2006.
- [23] A. G. Oskoei, N. Sataei, and J. Ghasemi, "Densities and viscosities for binary and ternary mixtures of 1, 4-dioxane + 1-hexanol + N,N-dimethylaniline from T = (283.15 to 343.15) K," *Journal of Chemical and Engineering Data*, vol. 53, no. 2, pp. 343–349, 2008.
- [24] J. G. Baragi, M. I. Aralaguppi, T. M. Aminabhavi, M. Y. Kariduraganavar, and S. S. Kulkarni, "Density, viscosity, refractive index, and speed of sound for binary mixtures of 1,4-dioxane with different organic liquids at (298.15, 303.15, and 308.15) K," *Journal of Chemical and Engineering Data*, vol. 50, no. 3, pp. 917–923, 2005.
- [25] J. A. Al-Kandary, A. S. Al-Jimaz, and A.-H. M. Abdul-Latif, "Viscosities, densities, and speeds of sound of binary mixtures of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene with anisole at (288.15, 293.15, 298.15, and 303.15) K," *Journal of Chemical and Engineering Data*, vol. 51, no. 6, pp. 2074–2082, 2006.
- [26] J. N. Nayak, M. I. Aralaguppi, and T. M. Aminabhavi, "Density, viscosity, refractive index, and speed of sound in the binary mixtures of ethyl chloroacetate with aromatic liquids at 298.15, 303.15, and 308.15 K," *Journal of Chemical and Engineering Data*, vol. 47, no. 4, pp. 964–969, 2002.

- [27] T. M. Aminabhavi, H. T. S. Phayde, R. S. Khinnavar, B. Gopalakrishna, and K. C. Hansen, "Densities, refractive indices, speeds of sound, and shear viscosities of diethylene glycol dimethyl ether with ethyl acetate, methyl benzoate, ethyl benzoate, and diethyl succinate in the temperature range from 298.15 to 318.15 K," *Journal of Chemical and Engineering Data*, vol. 39, no. 2, pp. 251–260, 1994.
- [28] J. A. Reddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents, Physical Properties and Method of Purification, Techniques of Chemistry, II*, Wiley-Interscience, New York, NY, USA, 1986.
- [29] O. Redlich and A. T. Kister, "Algebraic representation of thermodynamic properties and the classification of solutions," *Industrial and Engineering Chemistry Research*, vol. 40, no. 2, pp. 345–348.
- [30] C. Yang, P. Ma, and Q. Zhou, "Excess molar volumes and viscosities of binary mixtures of sulfolane with benzene, toluene, ethylbenzene, *p*-Xylene, *o*-Xylene, and *m*-Xylene at 303.15 and 323.15 K and atmospheric pressure," *Journal of Chemical and Engineering Data*, vol. 49, pp. 881–885, 2004.
- [31] R. J. Fort and W. R. Moore, "Viscosities of binary liquid mixtures," *Transactions of the Faraday Society*, vol. 62, pp. 1112–1119, 1966.
- [32] R. P. Rastogi, J. Nath, and J. Misra, "Thermodynamics of weak interactions in liquid mixtures. I. Mixtures of carbon tetrachloride, benzene, toluene, and *p*-xylene," *Journal of Physical Chemistry*, vol. 71, no. 5, pp. 1277–1286, 1967.
- [33] M. V. Kaulgud, "Ultrasonic velocity and compressibility in Binary liquid mixtures," *Zeitschrift Für Physikalische Chemie*, vol. 36, pp. 365–370, 1963.
- [34] R. PalePu, J. Oliver, and B. Mackinnon, "Viscosities and densities of binary liquid mixtures of *m*-cresol with substituted anilines," *Canadian Journal of Chemistry*, vol. 63, no. 5, pp. 1024–1030, 1985.
- [35] T. M. Reed III and T. E. Taylor, "Viscosities of liquid mixtures," *Journal of Physical Chemistry*, vol. 63, no. 1, pp. 58–67, 1959.
- [36] R. Mehra and M. Pancholi, "Effect of temperature variation on acoustic and thermodynamic properties in the multicomponent system of heptane + 1-dodecanol + cyclohexane at 298, 308 and 318 K and suitability of different theories of sound speed," *Journal of the Indian Chemical Society*, vol. 83, no. 11, pp. 1149–1152, 2006.
- [37] A. Ali, A. K. Nain, D. Chand, and B. Lal, "Molecular interactions in binary mixtures of anisole with benzyl chloride, chlorobenzene and nitrobenzene at 303.15 K: an ultrasonic, volumetric, viscometric and refractive index study," *Indian Journal of Chemistry A*, vol. 44, no. 3, pp. 511–515, 2005.
- [38] R. Palani and K. Meenakshi, "Investigation of molecular interactions in ternary liquid mixtures using ultrasonic velocity," *Indian Journal of Chemistry A*, vol. 46, no. 2, pp. 252–257, 2007.



