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Volumetric, Viscometric, Ultrasonic, and Refractive Index Properties of Liquid Mixtures of Benzene with Industrially Important Monomers at Different Temperatures

A. Ali · F. Nabi · M. Tariq

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Abstract The densities, ρ, viscosities, η, ultrasonic speeds, u, and refractive indices, n_{D}, of pure benzene, methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), styrene (STY), and their binary liquid mixtures have been measured over the entire composition range at 298.15 K, 303.15 K, 308.15 K, and 313.15 K. The experimental data have been used to calculate excess molar volumes. Partial molar volumes of MA/EA/BA/STY in benzene at infinite dilution and at different temperatures have also been evaluated. The results were discussed in terms of molecular interactions prevailing in the mixtures.

Keywords Alkyl acrylates · Benzene · Binary mixtures · Excess functions · Molecular interactions

1 Introduction

This study is a continuation of our earlier studies [1–5] on molecular interactions of binary non-aqueous liquid mixtures using thermodynamic and transport properties. Here we extend our study to the binary mixtures containing commercially important monomers, methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and styrene (STY) with benzene. A knowledge of thermodynamic and transport properties of these industrially important solutions is often required for industrial applications

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A. Ali (✉) · F. Nabi · M. Tariq
Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi 110025, India
e-mail: anwar_jmi@yahoo.co.in

M. Tariq
Laboratory of Molecular Thermodynamic, Instituto de Technologia Quimicae Bioologia,
Universidade de Nova DE Lisbooa, Oeiras, Portugal

such as making cleaning products, antioxidant agents, amphoteric surfactants, paints, inks, adhesives, dispersions for textiles, papers, polystyrene, etc.

A literature survey indicates that Francesconi and Comelli [6], Gonzalez and Ortega [7], and Liau and co-workers [8] reported density and viscosity data for binary mixtures of esters with alkanols. Bahadur and Sastry [9] measured the density and ultrasonic speed of ternary mixtures of MA + alkanols + hydrocarbons at 308.15 K. Peralta and co-workers [10–13] have measured densities of EA, BA, methyl methacrylate, and STY with toluene/cyclohexane/benzene/1,4-dioxane at a single temperature of 298.15 K. Very recently, densities of 1,2-propanediol carbonate + STY binary mixtures at different temperatures were reported by Wang et al. [14]. These authors used densities or viscosities or ultrasonic speeds, together with the derive excess functions, to investigate the molecular interactions between unlike molecules in these mixtures, mostly at a single temperature. To the best of our knowledge, studies on binary mixtures of benzene with MA, EA, BA, and STY using experimental values of densities, ultrasonic speeds, viscosities, and refractive indices at different temperatures are rarely found.

Benzene is a non-polar, unassociated liquid, and widely used as a solvent in chemical and technological processes. Whereas, acrylic esters, apart from their practical applications, are also interesting theoretically as they have an unsaturated structure along the side of a carbonyl group in the same molecule [15]. Despite the above mentioned industrial and theoretical interests, the thermodynamic and transport behavior of liquid mixtures containing acrylic esters/STY, as one of the components, have not been thoroughly investigated, except for the work of Li et al. [16], who have studied only the excess molar volume of binary mixtures of STY with benzene at a single temperature, 298.15 K.

Thus, keeping both industrial and scientific interests in mind, here we report the measured densities, ρ, ultrasonic speeds, u, viscosities, η, and refractive indices, n_{D}, of pure benzene, MA, EA, BA, STY, and those of their binary mixtures over the entire composition range at 298.15 K, 303.15 K, 308.15 K, and 313.15 K. From the measured ρ data, excess molar volumes, V^{E}, have been calculated at each temperature. Partial molar volumes, $V^0_{\phi,2}$, and partial molar isentropic compressibilities, $K^0_{\phi,2}$, of acrylic esters and STY in benzene have also been calculated. The derived functions, V^{E}, $V^0_{\phi,2}$, and $K^0_{\phi,2}$ have been used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures. We have chosen thermodynamic methods for this study, as these methods are important because changes in properties of the system caused by variations of temperature and composition can be studied without any reference to assumptions, models, or hypotheses [17].

2 Experimental

Benzene and MA (E. Merck, Germany), with purities of 99 %, were used without further purification. EA, BA, and STY (all of Arcos Organics, USA) of AR grade, purities of 99.5 %, were purified by a method similar to that described in the literature [10,11,14]. All the chemicals were stored over 0.4 nm molecular sieves to remove

Table 1 Comparison of experimental densities, ρ, viscosities, η, ultrasonic speeds, u, and refractive indices, n_D, of pure components at 298.15 K (benzene, EA, BA, STY) and at 308.15 K (MA)

Liquid	T (K)	ρ ($kg \cdot m^{-3}$)		η ($mPa \cdot s$)		u ($m \cdot s^{-1}$)		n_D	
		Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Benzene	298.15	873.6	873.6 [12] 873.7 [21]	0.603	0.6028 [18] 0.6036 [22]	1306.0	1310.0 [19] 1304.0 [23]	1.4979	1.4969 [20] 1.4979 [24] 1.4982 [25]
MA	308.15	937.7	935.6 [9]	0.384	0.391 [15]	1145.6	1140.0 [9]	1.3954	1.3981 [15]
EA	298.15	916.2	925.9 [12] 916.3 [26]	0.530	–	1167.5	–	1.4049	–
BA	298.15	894.1	893.7 [12] 894.1 [26]	0.838	–	1207.5	–	1.4119	–
STY	298.15	901.8	901.9 [12] 901.6 [21]	0.695	–	1383.0	–	1.5456	–

traces of water, if any, and degassed just before use. The solutions were prepared by mass in a dry box and were kept in special air-tight bottles. The weighings were done on a Preisa XB 220A (Swiss make) electronic balance with a precision of ±0.0001 g. The probable uncertainty in the mole fraction, x, was estimated to be <0.0001.

The densities of the pure liquids and their mixtures were measured by a single capillary pycnometer as described in our earlier papers [1–5]. The pycnometer was calibrated with triple-distilled water at 298.15 K, 303.15 K, 308.15 K, and 313.15 K. The measured densities were accurate to $0.0001\ g \cdot cm^{-3}$. The ultrasonic speeds in liquid samples were measured by using a single crystal variable path interferometer (Mittal Enterprises, Model M-84, New Delhi) operating at 3 MHz by a method described in the literature [1–5]. The measured ultrasonic speeds were accurate to $1.5\ m \cdot s^{-1}$. Viscosities of pure liquids and their binary mixtures were measured with an Ubbelohde-type suspended level viscometer. The viscometer containing a liquid was allowed to stand for about 30 min. in an electronically thermostatted water bath in order to minimize the thermal fluctuations in the test liquids. The time of flow was measured with an electronic digital stopwatch, which can be read to ±0.01 s. The uncertainty of the viscosity measurements was estimated to be $2 \times 10^{-3}\ mPa \cdot s$. Refractive indices of the liquids were measured using a thermostatically controlled Abbe refractometer (Metrex, India). A minimum of three readings were taken for each sample, and the average value was used in all the calculations. The refractive index data were accurate to 0.0001 units. The temperature control of the thermostatted water bath (JULABO, Model MD, Germany) regulating the pycnometer, viscometer, ultrasonic interferometer, and Abbe-refractometer was better than 0.02 K. The experimental values of densities, ultrasonic speeds, viscosities, and refractive indices of pure liquids at 298.15 K (benzene, EA, BA, and STY) and at 308.15 K (MA, for which data are available at 308.15 K) are compared with reported values available in the literature in Table 1 [9,12,15,18–26].

3 Results and Discussion

The experimental densities, ρ, ultrasonic speeds, u, viscosities, η, and refractive indices, n_D of pure benzene, MA, EA, BA, STY and those of their binary mixtures over the

Table 2 Values of experimental density, ρ, viscosity, η, ultrasonic speed, u, and refractive index, n_D, of binary liquid mixtures at different temperatures (x_1 = mole fraction of benzene)

x_1	ρ ($\text{kg} \cdot \text{m}^{-3}$)	$V^E \times 10^7 (\text{m}^3 \cdot \text{mol}^{-1})$	η ($\text{mPa} \cdot \text{s}$)	u ($\text{m} \cdot \text{s}^{-1}$)	n_D
Benzene + methyl acrylate					
$T = 298.15$ K					
0.0000	949.2	0.0000	0.461	1194.5	1.4000
0.1050	940.2	1.1201	0.472	1198.1	1.4075
0.2191	930.9	1.8648	0.485	1204.5	1.4145
0.3452	921.0	2.2993	0.501	1212.8	1.4220
0.4069	916.2	2.4591	0.509	1217.6	1.4265
0.5314	906.8	2.4767	0.526	1229.1	1.4370
0.6457	898.4	2.2332	0.543	1241.1	1.4500
0.7140	893.5	1.9520	0.554	1249.6	1.4600
0.7852	888.5	1.5360	0.565	1260.6	1.4700
0.8977	880.7	0.7458	0.585	1281.5	1.4855
1.0000	873.6	0.0000	0.603	1306.0	1.4979
$T = 303.15$ K					
0.0000	943.4	0.0000	0.420	1172.1	1.3979
0.1050	934.4	1.4560	0.433	1178.8	1.4042
0.2191	925.3	2.3639	0.447	1185.2	1.4110
0.3452	915.6	2.9922	0.462	1194.5	1.4185
0.4069	911.0	3.1433	0.470	1199.7	1.4230
0.5314	901.9	3.2400	0.488	1210.5	1.4345
0.6457	893.8	3.0378	0.505	1222.4	1.4475
0.7140	889.0	2.8589	0.515	1230.6	1.4575
0.7852	884.2	2.4500	0.526	1241.5	1.4670
0.8977	877.0	1.3755	0.545	1262.6	1.4830
1.0000	870.8	0.0000	0.562	1283.6	1.4962
$T = 308.15$ K					
0.0000	937.7	0.0000	0.384	1145.6	1.3954
0.1050	928.6	1.6351	0.398	1153.9	1.4010
0.2191	919.3	2.8235	0.412	1161.4	1.4070
0.3452	909.6	3.5395	0.428	1171.5	1.4150
0.4069	905.0	3.7320	0.436	1176.9	1.4200
0.5314	896.0	3.8083	0.453	1187.8	1.4320
0.6457	887.9	3.6776	0.470	1199.7	1.4450
0.7140	883.1	3.5411	0.481	1208.7	1.4550
0.7852	878.3	3.1737	0.492	1219.5	1.4650
0.8977	871.2	2.0557	0.510	1239.5	1.4812
1.0000	865.7	0.0000	0.526	1257.2	1.4944
$T = 313.15$ K					
0.0000	932.0	0.0000	0.357	1122.1	1.3944
0.1050	922.9	1.7627	0.369	1131.9	1.3990
0.2191	913.6	3.0837	0.382	1140.4	1.4040
0.3452	904.0	3.8380	0.392	1150.6	1.4120
0.4069	899.5	3.9948	0.403	1156.3	1.4170
0.5314	890.6	4.0987	0.418	1168.1	1.4290

Table 2 continued

x_1	ρ (kg · m^{-3})	$V^{E} \times 10^7$(m^3 · mol^{-1})	η (mPa · s)	u (m · s^{-1})	n_D
0.6457	882.5	4.0857	0.433	1180.9	1.4420
0.7140	877.8	3.9150	0.442	1189.7	1.4510
0.7852	873.0	3.6178	0.452	1200.4	1.4616
0.8977	865.9	2.6050	0.467	1219.5	1.4780
1.0000	861.0	0.0000	0.480	1233.6	1.4929
Benzene + ethyl acrylate					
$T = 298.15$ K					
0.0000	916.2	0.0000	0.530	1167.5	1.4049
0.1283	911.0	0.7278	0.531	1175.2	1.4110
0.2137	907.4	1.2157	0.533	1180.3	1.4155
0.3255	902.6	1.7552	0.537	1189.5	1.4220
0.4115	898.9	2.0214	0.541	1198.5	1.4270
0.5361	893.6	2.0928	0.550	1213.1	1.4370
0.6109	890.4	2.0145	0.558	1222.8	1.4450
0.7033	886.5	1.7119	0.568	1237.2	1.4565
0.8074	882.3	0.9682	0.579	1255.5	1.4706
0.9025	878.2	0.3835	0.591	1278.3	1.4848
1.0000	873.6	0.0000	0.603	1306.0	1.4979
$T = 303.15$ K					
0.0000	910.6	0.0000	0.502	1145.1	1.4032
0.1283	905.3	0.9603	0.499	1151.0	1.4080
0.2137	901.8	1.4057	0.500	1156.5	1.4124
0.3255	897.1	1.9284	0.501	1165.8	1.4188
0.4115	893.5	2.1562	0.502	1174.5	1.4240
0.5361	888.2	2.3359	0.509	1188.9	1.4336
0.6109	885.1	2.2108	0.516	1198.9	1.4412
0.7033	881.3	1.8773	0.524	1213.0	1.4530
0.8074	877.1	1.2189	0.535	1230.5	1.4676
0.9025	873.1	0.6082	0.548	1251.2	1.4809
1.0000	868.8	0.0000	0.562	1283.6	1.4962
$T = 308.15$ K					
0.0000	904.9	0.0000	0.465	1118.7	1.4014
0.1283	899.4	1.2116	0.461	1123.1	1.4044
0.2137	895.9	1.6591	0.460	1128.9	1.4089
0.3255	891.2	2.1841	0.461	1138.0	1.4155
0.4115	887.6	2.4117	0.462	1146.5	1.4210
0.5361	882.3	2.5894	0.466	1160.9	1.4310
0.6109	879.2	2.4602	0.472	1170.5	1.4380
0.7033	875.4	2.1195	0.481	1184.5	1.4495
0.8074	871.2	1.4494	0.495	1202.2	1.4635
0.9025	867.2	0.8282	0.508	1222.5	1.4782
1.0000	863.1	0.0000	0.526	1257.2	1.4944
$T = 313.15$ K					
0.0000	899.8	0.0000	0.420	1095.1	1.3999
0.1283	894.3	1.4009	0.412	1099.0	1.4012
0.2137	890.8	1.9704	0.410	1104.6	1.4055
0.3255	886.3	2.4181	0.411	1113.5	1.4123
0.4115	882.8	2.6526	0.412	1122.5	1.4182
0.5361	877.7	2.7811	0.415	1136.5	1.4281
0.6109	874.7	2.6470	0.420	1145.9	1.4351
0.7033	871.0	2.3285	0.431	1159.9	1.4460
0.8074	866.9	1.6989	0.444	1176.9	1.4601
0.9025	863.1	1.0011	0.458	1197.1	1.4746
1.0000	859.3	0.0000	0.480	1233.6	1.4929

Table 2 continued

x_1	ρ (kg · m^{-3})	$V^E \times 10^7$ (m^3 · mol^{-1})	η (mPa · s)	u (m · s^{-1})	n_D
Benzene + butyl acrylate					
$T = 298.15$ K					
0.0000	894.1	0.0000	0.838	1207.5	1.4119
0.1282	891.9	0.7307	0.799	1210.5	1.4155
0.2182	890.1	1.4198	0.773	1213.6	1.4192
0.2926	888.6	1.8603	0.749	1216.2	1.4231
0.4108	886.4	2.0331	0.719	1224.0	1.4307
0.4964	884.7	2.1017	0.699	1230.5	1.4372
0.5923	882.9	1.8355	0.679	1240.0	1.4455
0.7080	880.5	1.5046	0.658	1253.3	1.4570
0.7944	878.7	1.0429	0.641	1265.6	1.4670
0.9032	876.3	0.3304	0.620	1285.0	1.4821
1.0000	873.6	0.0000	0.603	1306.0	1.4979
$T = 303.15$ K					
0.0000	889.2	0.0000	0.781	1185.1	1.4102
0.1282	886.9	1.1713	0.738	1186.5	1.4147
0.2182	885.2	1.9082	0.709	1189.0	1.4188
0.2926	883.9	2.2242	0.686	1191.5	1.4228
0.4108	881.8	2.5304	0.656	1197.5	1.4301
0.4964	880.2	2.6670	0.636	1203.5	1.4364
0.5923	878.4	2.6286	0.618	1212.5	1.4449
0.7080	876.3	2.2100	0.601	1225.7	1.4566
0.7944	874.7	1.7356	0.590	1239.0	1.4666
0.9032	872.6	0.9831	0.574	1258.3	1.4813
1.0000	870.8	0.0000	0.562	1283.6	1.4962
$T = 308.15$ K					
0.0000	884.4	0.0000	0.730	1159.3	1.4084
0.1282	881.8	1.6133	0.683	1158.0	1.4136
0.2182	880.1	2.3144	0.649	1159.9	1.4179
0.2926	878.6	2.8914	0.625	1162.4	1.4218
0.4108	876.5	3.1291	0.595	1168.3	1.4294
0.4964	874.8	3.3500	0.576	1174.8	1.4357
0.5923	872.9	3.3761	0.564	1182.8	1.4440
0.7080	870.6	3.1124	0.554	1195.3	1.4556
0.7944	868.9	2.6755	0.545	1208.5	1.4655
0.9032	866.9	1.7039	0.531	1228.1	1.4800
1.0000	865.7	0.0000	0.526	1257.2	1.4944
$T = 313.15$ K					
0.0000	879.0	0.0000	0.684	1135.1	1.4069
0.1282	876.2	2.0447	0.620	1131.8	1.4126
0.2182	874.5	2.8102	0.585	1132.8	1.4170
0.2926	873.1	3.2915	0.565	1135.3	1.4209
0.4108	870.9	3.7541	0.538	1141.9	1.4285
0.4964	869.3	3.8940	0.524	1147.8	1.4348
0.5923	867.4	3.9855	0.510	1156.3	1.4429
0.7080	865.1	3.7971	0.501	1169.4	1.4545
0.7944	863.4	3.4134	0.496	1181.2	1.4643
0.9032	861.6	2.2799	0.485	1200.9	1.4786
1.0000	861.0	0.0000	0.480	1233.6	1.4929
Benzene + styrene					
$T = 298.15$ K					
0.0000	901.8	0.0000	0.695	1383.0	1.5456
0.1362	898.3	0.5384	0.672	1371.0	1.5375
0.2498	895.1	1.1205	0.654	1359.5	1.5309

Table 2 continued

x_1	ρ (kg · m^{-3})	$V^E \times 10^7$(m^3 · mol^{-1})	η (mPa · s)	u (m · s^{-1})	n_D
0.3047	893.5	1.3917	0.645	1353.9	1.5275
0.4109	890.5	1.6610	0.633	1344.7	1.5225
0.5207	887.4	1.7425	0.623	1335.9	1.5171
0.5834	885.7	1.6197	0.618	1332.0	1.5144
0.7114	882.1	1.3145	0.608	1323.8	1.5085
0.7924	880.0	0.7867	0.605	1318.6	1.5052
0.8831	877.4	0.3348	0.604	1313.1	1.5025
1.0000	873.6	0.0000	0.603	1306.0	1.4979
$T = 303.15$ K					
0.0000	897.1	0.0000	0.654	1360.0	1.5445
0.1362	893.6	0.8107	0.629	1346.9	1.5353
0.2498	890.6	1.3751	0.610	1335.9	1.5291
0.3047	889.1	1.6377	0.600	1330.5	1.5257
0.4109	886.3	1.8882	0.589	1321.7	1.5205
0.5207	883.4	1.9678	0.577	1312.6	1.5151
0.5834	881.8	1.8639	0.570	1308.6	1.5122
0.7114	878.5	1.5008	0.560	1300.5	1.5063
0.7924	876.5	1.0422	0.556	1295.3	1.5030
0.8831	874.1	0.5805	0.555	1290.0	1.4997
1.0000	870.8	0.0000	0.562	1283.6	1.4962
$T = 308.15$ K					
0.0000	892.0	0.0000	0.618	1334.0	1.5437
0.1362	888.3	1.0744	0.590	1319.6	1.5339
0.2498	885.3	1.6392	0.570	1309.0	1.5274
0.3047	883.8	1.9019	0.560	1304.0	1.5241
0.4109	881.0	2.1496	0.548	1295.3	1.5188
0.5207	878.1	2.2243	0.537	1286.2	1.5132
0.5834	876.5	2.1159	0.530	1282.1	1.5103
0.7114	873.1	1.8541	0.520	1274.0	1.5043
0.7924	871.0	1.4936	0.515	1268.7	1.5005
0.8831	868.8	0.8017	0.514	1262.5	1.4970
1.0000	865.7	0.0000	0.526	1257.2	1.4944
$T = 313.15$ K					
0.0000	887.3	0.0000	0.573	1310.0	1.5429
0.1362	883.4	1.3431	0.540	1295.2	1.5322
0.2498	880.4	1.9077	0.518	1284.5	1.5256
0.3047	879.0	2.0458	0.510	1280.0	1.5225
0.4109	876.2	2.2932	0.499	1271.6	1.5172
0.5207	873.3	2.3658	0.487	1262.8	1.5115
0.5834	871.7	2.2546	0.480	1258.3	1.5085
0.7114	868.3	1.9867	0.470	1249.8	1.5023
0.7924	866.1	1.7316	0.466	1244.5	1.4984
0.8831	863.9	1.0273	0.465	1238.5	1.4945
1.0000	861.0	0.0000	0.480	1233.6	1.4929

entire composition range, expressed by the mole fraction, x_1 of benzene at 298.15 K, 303.15 K, 308.15 K, and 313.15 K are presented in Table 2. Excess molar volumes, which are a measure of the deviations of the actual property from the property if the system behaves ideally, give information on molecular interactions between the component molecules of the mixture and are influenced by effects such as (i) differences in shape and size of the component molecules, (ii) reorientation of the component

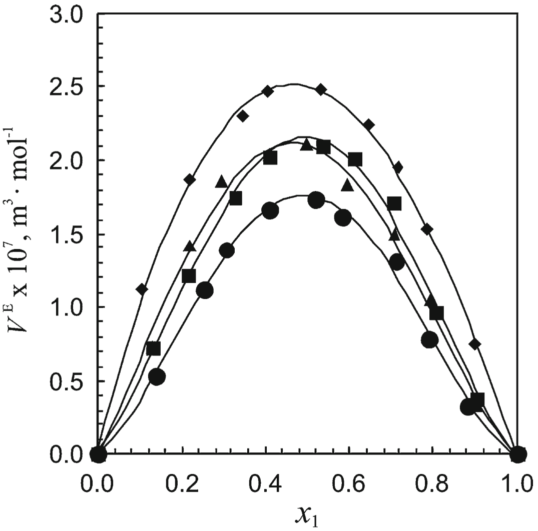

Fig. 1 Plots of excess molar volumes (V^E) against mole fraction x_1 of benzene with MA (◆), EA (■), BA (▲), and STY (●) at 298.15 K

molecules in the mixture, and (iii) intermolecular interactions [27,28]. Thus, excess molar volumes, V^E, were calculated with

$$V^E = V - (x_1 V_1 + x_2 V_2) \tag{1}$$

where subscripts 1 and 2 stand for the pure components benzene and MA/EA/BA/STY, respectively. V is the molar volume, and can be evaluated by the following relation:

$$V = (x_1 M_1 + x_2 M_2)/\rho \tag{2}$$

where M is the molar mass of the pure components. The mole fraction, x, was used for calculating V^E .

The curves in Fig. 1 reveal that the values of V^E are positive over the entire mole fraction of benzene for all the four systems investigated and follow the sequence: MA > EA > BA > STY. This can be explained by considering the fact that mixing of benzene with esters or STY will lead to (i) the loss of dipolar association in the esters/STY molecules, (ii) weak interactions of $n \ldots\ldots \pi$ type between the lone pair of electrons of the oxygen atom of the carbonyl group of ester and π–electron cloud of the benzene molecule and $\pi \ldots \pi$ interactions between π–electrons of benzene rings of STY and benzene, and (iii) the interstitial accommodation of the smaller molecules into the voids created by large molecules due to the difference in molar volumes. The first two effects lead to an expansion in volume, resulting in positive V^E values. Positive values in V^E may also occur when component molecules interact less strongly. The third effect contributes to a contraction in volume, thereby, resulting in negative V^E values. Further, it is noted from Fig. 1 that, for the binary mixtures investigated, the values of V^E become less positive as we move from MA to STY. The observed positive V^E values suggest that the combined effects (i) and

(ii) due to the breaking up of the dipolar association of the ester/STY molecules and the interaction of benzene with ester/STY molecules exceeds the (iii) effect due to the packing of smaller molecules of benzene (molar volume $= 89.2875\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) into the voids created by larger molecules of EA, BA, and STY having molar volumes of $109.2774\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, $143.3508\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, and $115.3249\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ at 298.15 K, respectively. It has been reported [29–31] that liquids of different molecular sizes mix into each other's structure and, thereby, decrease the volume of the mixture. This is the case with mixtures of benzene with EA, BA, and STY. On the other hand, unfavorable packing of MA (molar volume $= 90.7290\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) and benzene molecules into each other's structure due to almost equal molecular size is quite obvious, resulting in an increase in volume of the mixture and, hence, showing the largest positive V^{E} values. For the mixtures of benzene + STY, the smallest positive V^{E} values are due to the fact that, in addition to the larger difference in the molar volumes of benzene and STY, both have plate-like molecules which further promote packing of unlike molecules into each other's structure. Thus, a decrease in V^{E} values as we move from MA to STY clearly suggests increasingly better packing of the component molecules in the mixture than in the pure state. As the size of the alkyl group increases from MA to BA, the steric hindrance also increases, resulting in a decreased interaction between benzene and ester molecules, and hence, the strength of the $n\ldots\ldots\pi$ interactions should follow the order: MA > EA > BA. A similar behavior in V^{E} with composition has also been reported for cyclohexane + acrylic esters [11] and ethylbenzene + acrylic esters [32]. As the temperature increases, V^{E} values increase for all the mixtures over the entire mole fraction range and, thereby, suggest a decrease in the strength of interactions between the component molecules.

Furthermore, the extent of interactions between the component molecules in a mixture is well reflected in the parameters like apparent molar volume, apparent molar compressibility, partial molar volume, and partial molar compressibility [33,34]. The apparent molar volumes, $V_{\phi,2}$ of MA, EA, BA, and STY in benzene were calculated by using [33]

$$V_{\phi,2} = V_2^* + (V^{\mathrm{E}}/x_2) \tag{3}$$

where V_2^* is the molar volume of MA/EA/BA/STY. The partial molar volumes, $V_{\phi,2}^0$ of MA, EA, BA, and STY in benzene at infinite dilution were obtained by the method described earlier [34,35]. The deviations in $V_{\phi,2}$ at infinite dilution, ΔV, were calculated by using [34]

$$\Delta V = \bar{V}_{\phi,2}^0 - V_2^* \tag{4}$$

The values of $V_{\phi,2}^0$, V^*, and ΔV are listed in Table 3. It is clear from Table 3 that the values of ΔV are positive (i.e., the partial molar volumes, $V_{\phi,2}^0$, of MA/EA/BA/STY in benzene at infinite dilution are greater than their corresponding molar volumes in the pure state, V_2^*), suggesting that on mixing there is an expansion in the volume of the mixture, which may be due to the presence of weak interactions between the component molecules, as mentioned above. However, as the temperature increases,

Table 3 Values of $\bar{V}_2^0$, V_2^*, ΔV_2, $\bar{K}_2^0$, K_2^*, and ΔK_2 for the binary liquid mixtures at different temperatures

T (K)	$\bar{V}_2^0$	V_2^*	ΔV_2	$\bar{K}_2^0$	K_2^*	ΔK_2
	$(10^{-5}\text{m}^3 \cdot \text{mol}^{-1})$			$(10^{-14}\text{m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1})$		
Benzene + methyl acrylate						
298.15	9.1592	9.0697	0.0895	8.0009	6.6968	1.3041
303.15	9.2715	9.1255	0.1460	8.2299	7.0410	1.1889
308.15	9.3796	9.1810	0.1986	8.4911	7.4603	1.0308
313.15	9.4735	9.2371	0.2364	8.6565	7.8715	0.7850
Benzene + ethyl acrylate						
298.15	10.9906	10.9277	0.0629	9.9272	8.7504	1.1768
303.15	11.0748	10.9949	0.0799	10.8191	9.2083	1.6108
308.15	11.1618	11.0642	0.0976	11.7454	9.7699	1.9755
313.15	11.2396	11.1269	0.1127	12.6134	10.3115	2.3019
Benzene + butyl acrylate						
298.15	14.3945	14.3351	0.0594	11.7709	10.9961	0.7748
303.15	14.5353	14.4141	0.1212	12.9164	11.5419	1.3745
308.15	14.6860	14.4923	0.1937	14.2278	12.1926	2.0352
313.15	14.8325	14.5813	0.2512	15.5295	12.8748	2.6547
Benzene + styrene						
298.15	11.5982	11.5491	0.0491	7.0629	6.6957	0.3672
303.15	11.6761	11.6096	0.0665	7.4615	6.9968	0.4647
308.15	11.7651	11.6760	0.0891	7.9414	7.3556	0.5858
313.15	11.8424	11.7379	0.1045	8.3848	7.7086	0.6762

ΔV becomes more positive, thereby, indicating weakening of the interactions between the component molecules of the mixture.

The apparent molar compressibilities, $K_{\phi,2}$, of MA, EA, BA, and STY in benzene were calculated using [33]

$$K_{\phi,2} = K_2^* + (K_s^{\text{E}}/x_2) \tag{5}$$

where $K_{\text{s}}^{\text{E}}[=(k_{\text{s}}V)^{\text{E}}]$ is the excess molar compressibility of the mixture; x_2 and K_2^* are the mole fraction and molar isentropic compressibility of MA/EA/BA/STY, respectively. The partial molar compressibilities, $K_{\phi,2}^0$, of MA, EA, BA, and STY in benzene at infinite dilution were obtained by using the method described elsewhere [33,34]. The deviations in $K_{\phi,2}$ at infinite dilution, ΔK, were obtained by using the relation [33],

$$\Delta K = \bar{K}_{\phi,2}^0 - K_2^* \tag{6}$$

The values of $\bar{K}_{\phi,2}^0$, K_2^*, and ΔK are also included in Table 3. The partial molar compressibilities, $\bar{K}_{\phi,2}^0$, of MA, EA, BA, and STY in benzene at infinite dilution, characterize the compressibilities of their molecules in the mixture, whereas molar isentropic compressibilities, K_2^*, of pure components MA/EA/BA/STY can be considered as partial molar isentropic compressibilities of these molecules when dissolved in itself. It is worth mentioning that all the values of ΔK (Table 3) for four binary mixtures studied are positive and increase with temperature. Positive values of ΔK

are indicative of weak interactions between the component molecules in the mixture. This further supports our earlier finding.

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