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Densities, Sound Speeds, Excess Volumes, and Excess Isentropic Compressibilities of Methyl Acrylate + 1-Propanol (or 1-Butanol) + Hydrocarbons (*n*-Hexane, *n*-Heptane, Cyclohexane, Benzene, and Toluene) at 308.15 K

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Densities and sound speeds of ten ternary mixtures of methyl acrylate (1)+ 1-propanol (2) or 1-butanol (2)+*n*-hexane (3), +*n*-heptane (3), +cyclohexane (3), +benzene (3), and +toluene (3) have been measured at 308.15 K. The excess volumes, V^{E}, and excess isentropic compressibilities, κ_s^{E}, have been estimated. These two experimentally derived excess functions were also compared with those predicted by empirical equations of Redlich–Kister, Kohler, and Tsao–Smith. A qualitative analysis of V^{E} and κ_s^{E} data of ternary mixtures reveals that in MA (1)+1-alcohols (2)+*n*-hexane (3), +*n*-heptane (3), and +cyclohexane (3), structure disruptions are more predominant while in MA (1)+1-alcohols (2)+benzene (3) or +toluene (3) mixtures, the weak but specific structure making interactions dominate. A perusal of deviations between the experimental and calculated V^{E} and κ_s^{E} results shows that the predictive expressions give only a rough estimate of the functions for the ten studied mixtures.

KEY WORDS: benzene; 1-butanol; cyclohexane; densities; excess volumes; excess isentropic compressibilities; methyl acrylate; *n*-heptane; *n*-hexane; 1-propanol; sound speeds; ternary mixtures; toluene.

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1. INTRODUCTION

A review of the literature reveals that the thermophysical properties for nonelectrolyte mixtures consisting of binary systems are extensively reported, while the same for the ternary systems in general are scarce and, for higher-order multicomponent systems in particular, are nonexistent. The measurements on multicomponent systems become difficult because they require very sophisticated instruments, and the data, when obtained, may be unreliable due to complex problems associated with the mixing process and unit operations [1]. Acrylic esters are industrially important chemicals because of their wide use as precursors to synthesize important polymers and to produce latex systems. The production of higher homologues of acrylic esters at the industrial scale is carried out by trans-esterification reactions in which an acrylic ester is reacted with selected 1-alcohols in an inert hydrocarbon media. Hence, the availability of data on various thermophysical properties of binary systems of acrylic esters + 1-alcohols, acrylic esters + hydrocarbons, and 1-alcohols +hydrocarbons and ternary mixtures of acrylic esters + 1-alcohols + hydrocarbons would be quite useful to optimize the process parameters for an efficient design of reactors for trans-esterification reactions. Besides this application, acrylic esters are unique molecules with unsaturated structures along side a carbonyl group. Hence, the proximity effects of unsaturation on the carbonyl group interactions with other added components can be determined.

Keeping both the industrial and scientific interests in mind, our laboratory has been actively engaged in the measurements of various thermophysical properties of binary mixtures consisting of either acrylic esters or 1-alcohols as one of the components. The densities, viscosities, sound speeds, and relative permittivities, along with the useful deviation/excess functions derived from them, have been previously reported for the binary systems of methyl methacrylate + 1-alcohols [2, 3], alkyl (methyl, ethyl and butyl) acrylates + 1-alcohols [4, 5], 1-alcohols (1-propanol to 1-dodecanol) + *n*-pentane [6], 1-heptanol + *n*-hexane or + *n*-heptane [7], methyl methacrylate + *n*-alkanes (*n*-pentane to *n*-dodecane) [8], and + aromatic hydrocarbons [9, 10]. In continuation of our earlier work, the present study is undertaken to report the densities, sound speeds, excess volumes, and excess isentropic compressibilities for ten ternary mixtures of methyl acrylate + 1-propanol (or 1-butanol) + *n*-hexane, + *n*-heptane, + cyclohexane, + benzene, and + toluene at $T = 303.15$ K. An attempt has also been made to calculate the ternary excess volumes and excess isentropic compressibilities from the respective constituent binary contributions by using empirical expressions due to Redlisch and Kister [11], Kohler [12], Tsao and Smith [13].

2. EXPERIMENTAL PROCEDURES

Methyl acrylate (MA) was an Aldrich product, and its purity was stated to be better than 99% on a molar basis. It was used as such without any further purification. 1-Propanol and 1-butanol were technical grade chemicals from SD Fine Chemicals.

1-Propanol was purified by refluxing over lime for 5 h and then distilled through a 1 m column. The fraction boiling at 97 to 97.3°C was redistilled in a stream of hydrogen at 40 to 50 mm pressure. 1-Butanol was kept over unslaked lime overnight and distilled. The central portion was further digested over barium oxide, then treated with sodium and fractionally distilled through a 1 m column. *n*-Hexane and *n*-heptane were BDH reagent grade chemicals. *n*-Hexane was treated several times with concentrated sulfuric acid, then by 0.1 $\mathrm{mol \cdot dm^{-3}}$ potassium permanganate in 10 per cent sulfuric acid and as well as 10 per cent sodium hydroxide solutions. After a final washing with distilled water, it was dried over sodium wire and freshly distilled before use.

n-Heptane was shaken twice with concentrated sulfuric acid and then with distilled water and dilute aqueous solution of potassium hydroxide. It was finally distilled after allowing it to stand over potassium hydroxide for 24 h. Cyclohexane, benzene, and toluene were Chiti-Chem, India analytical reagent chemicals. Cyclohexane was washed several times in a cold mixture of concentrated nitric and sulfuric acids to nitrate any benzene that may have been present. After repeated washings with distilled water, it was fractionally distilled over sodium metal. Benzene was further purified by shaking successively with concentrated sulfuric acid until free from thiophene (monitored by the absence of yellow tinge), then with distilled water, dilute sodium hydroxide solution, and two portions of water. The chemical was then dried by distilling over phosphorus pentoxide. Toluene was purified by successive shaking with concentrated sulfuric acid, sodium hydroxide solutions, and mercury. It was dried over phosphorus pentoxide and then finally fractionally distilled over a 1 m column. The gas chromatographically determined purities of all the above chemicals were found to be more than 99.5% on a molar basis.

The measured density and sound speed values for the pure components at $T = 308.15$ K have been found to agree well with literature values. The measured densities (in $\mathrm{g \cdot cm^{-3}}$) at $T = 308.15$ K for various pure components are as follows; methyl acrylate, 0.9356; 1-propanol, 0.7920 (0.7920 [14], 0.7919 [15]); 1-butanol, 0.7980 (0.7980 [16], 0.79799 [17]); *n*-hexane, 0.6458 (0.64586 [18]); *n*-heptane, 0.6709 (0.67088 [19]); cyclohexane, 0.7646 (0.76447 [20]); benzene, 0.8632 (0.86302 [21]); toluene, 0.8518 (0.8517 [22]). Similarly, the sound speeds (in $\mathrm{m \cdot s^{-1}}$) at

$T = 308.15$ K for the pure components are as follows: methyl acrylate, 1140; 1-propanol, 1180 (1184 [23]); 1-butanol, 1210 (1211 [23]); *n*-hexane, 1041; *n*-heptane, 1095; cyclohexane, 1212; benzene, 1260 (1255 [24]) and toluene, 1262 (1262 [24]).

All the mixtures were prepared by mixing weighed amounts of pure liquids in hermetically sealed glass vials. The weighing, with a precision of 1×10^{-5} g, was done using a single-pan Dhona balance (Model 100 DS). Hence, the possible error in the mole fraction was estimated to be less than ± 0.0001. The densities of pure and mixture components were determined by a double-stem Lipkin's type pyknometer. The pyknometer was calibrated with triple distilled water, as well as double distilled cyclohexane. The densities of cyclohexane at different temperatures were taken from the literature [25–27]. The reproducibility in the measured densities with this method was found to be $\pm 0.0001\ \mathrm{g \cdot cm^{-3}}$, and the uncertainties in the measured values was found to be always better than 3 units in the fourth decimal place. An ultrasonic interferometer supplied by Mittal Enterprise, New Delhi was used to determine the sound speed in liquids and their mixtures at a fixed frequency of 2 MHz. The measured values of sound speeds have an estimated uncertainty to within $\pm 1.5\ \mathrm{m \cdot s^{-1}}$ or 0.15%. The details of these measuring methods are described elsewhere [4, 7].

3. RESULTS AND DISCUSSION

3.1. Densities and Excess Volumes

The data for the experimental densities, ρ, and the excess volumes for all ten ternary mixtures are reported in Tables I and II. The ternary excess volume values were also predicted by using the binary data with empirical equations proposed by Redlich and Kister [11], Kohler [12], and Tsao and Smith [13]. The Redlich–Kister (RK) expression for prediction of excess volume of ternary mixtures is given as

$$V^{\mathrm{E}}_{123}(\mathrm{RK}) = V^{\mathrm{E}}_{12} + V^{\mathrm{E}}_{23} + V^{\mathrm{E}}_{13} \tag{1}$$

in which V^{E}_{12}, V^{E}_{23}, and V^{E}_{13} represent the excess molar volumes of constituent binary pairs. The Kohler (K) equation for calculating the excess volume of a ternary mixture is given as

$$V^{\mathrm{E}}_{123} = (x_1 + x_2)^2 V^{\mathrm{E}}_{12} + (x_1 + x_3)^2 V^{\mathrm{E}}_{13} + (x_2 + x_3)^2 V^{\mathrm{E}}_{23} \tag{2}$$

In this equation V^{E}_{ij} refers to the excess volumes for the binary mixtures at compositions x°_i and x°_j such that $x^{\circ}_i = 1 - x^{\circ}_j = x_i/(x_i + x_j)$. The Tsao–

Smith (TS) equation for expressing the excess volumes of ternary mixtures takes the form,

$$V^{\mathrm{E}}_{123} = [x_2 V^{\mathrm{E}}_{12}/(1-x_1)] + [x_3 V^{\mathrm{E}}_{13}/(1-x_1)] + (1-x_1)\,V^{\mathrm{E}}_{23} \tag{3}$$

where V^{E}_{ij} refer to the excess molar volumes for the binary mixtures at compositions x^{o}_i, x^{o}_j such that $x^{\mathrm{o}}_i = x_i$ for the 1, 2 and 1, 3 binary mixtures and $x^{\mathrm{o}}_2 = x_2/(x_2+x_3)$ for the 2, 3 binary mixture. The binary contributions for the respective pairs were calculated using the least squares parameters, a_i listed in Table III. These parameters were obtained by the mathematical representation of compositional variation of experimental binary excess volumes for methyl acrylate + 1-propanol and + 1-butanol, methyl acrylate + n-hexane or + n-heptane (taken from our previous work) and for the rest of the binary mixtures (unpublished results), through an equation of the type,

$$V^{\mathrm{E}}\,(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}) = x_i(1-x_i)\sum_{i=0}^{n=3\text{ or }4} a_i(2x_i-1) \tag{4}$$

The predicted V^{E}_{123} values for all the ternary mixtures are given in columns 6–8 of Tables I and II. The dependence of experimental excess volumes of the ternary mixtures $V^{\mathrm{E}}_{123}(\mathrm{exp.})$ on the composition is expressed by a polynomial equation of type,

$$V^{\mathrm{E}}_{123}(\mathrm{exp.}) = V^{\mathrm{E}}_{123}(b) + x_1x_2x_3[A + B(x_1(x_2-x_3)) + C(x_1^2(x_2-x_3)^2)] \tag{5}$$

where $V^{\mathrm{E}}_{123}(b) = V^{\mathrm{E}}_{12} + V^{\mathrm{E}}_{23} + V^{\mathrm{E}}_{13}$ is the ternary excess volume computed from the binary data through the Redlich–Kister relation, x_1, x_2, and x_3 are the mole fractions of MA, 1-propanol or 1-butanol, and aliphatic/cyclic/aromatic hydrocarbons, respectively. The values of A, B, and C constants were estimated by a multiple regression analysis based on a least squares method, and the summary of the analysis along with the standard deviations between experimental and fitted data are given in Table IV. Columns 9 to 11 of Tables I and II list the difference, $\Delta V^{\mathrm{E}}_{123} = V^{\mathrm{E}}_{123}(\mathrm{exp.}) - V^{\mathrm{E}}_{123}(b)$ between the experimental and predicted ternary excess volumes. It can be seen that the $\Delta V^{\mathrm{E}}_{123}$ values for MA(1) + 1-propanol (2) + hydrocarbons (3) range mostly between −0.291 and 0.126 cm$^3\cdot$mol^{-1}. However, in some compositions the $\Delta V^{\mathrm{E}}_{123}$ is found to be larger than −0.291 and 0.126 cm$^3\cdot$mol^{-1}. Similarly, for MA(1) + 1-butanol (2) + hydrocarbons(3), the $\Delta V^{\mathrm{E}}_{123}$ values range mostly from −0.095 to 0.188 cm$^3\cdot$mol^{-1}, while for some compositions they were found be larger than this limit. Hence, it may be concluded that all three predictive expressions

Table I. Densities, Experimental and Predicted Excess Volumes, and Differences Between Experimental and Predicted Excess Volumes for MA (1) + 1-Propanol (2) + Hydrocarbons (3) at 308.15 K

					$V^{E}_{123\,cal}$			ΔV^{E}		
x_1	x_2	x_3	ρ_{123} ($\mathrm{g\cdot cm^{-3}}$)	$V^{E}_{123\,exp}$	RK	K ($\mathrm{cm^{3}\cdot mol^{-1}}$)	TS	RK	K ($\mathrm{cm^{3}\cdot mol^{-1}}$)	TS
MA (1) + 1-propanol (2) + *n*-hexane (3)										
0.1533	0.5606	0.2861	0.7511	0.429	0.216	0.194	0.220	0.213	0.235	0.209
0.1233	0.8440	0.0327	0.8040	0.043	−0.001	0.001	0.006	0.0044	0.042	0.037
0.4116	0.1257	0.4627	0.7577	0.211	0.537	0.518	0.588	−0.326	−0.307	−0.377
0.7602	0.0960	0.1438	0.8047	0.266	0.267	0.257	0.302	−0.01	0.009	−0.036
0.8668	0.0642	0.0690	0.8982	0.158	0.145	0.142	0.167	0.013	0.016	−0.009
0.1823	0.2876	0.5301	0.7166	0.430	0.450	0.416	0.462	−0.020	0.014	−0.032
0.2202	0.7474	0.0324	0.8191	0.091	−0.006	−0.003	0.004	0.097	0.094	0.087
0.0600	0.2982	0.6412	0.6867	0.399	0.379	0.366	0.384	0.020	0.033	0.015
0.6194	0.3504	0.0302	0.8768	0.189	0.054	0.053	0.063	0.135	0.136	0.126
MA (1) + 1-propanol (2) + *n*-heptane (3)										
0.0738	0.0854	0.8408	0.6877	0.370	0.404	0.406	0.416	−0.034	−0.036	−0.046
0.0712	0.1752	0.7536	0.6938	0.450	0.485	0.486	0.505	−0.035	−0.036	−0.055
0.0680	0.2544	0.6776	0.6996	0.504	0.520	0.516	0.539	−0.016	−0.012	−0.035
0.0496	0.7671	0.1833	0.7607	0.213	0.183	0.186	0.197	0.030	0.027	0.016
0.1752	0.4787	0.3461	0.7498	0.597	0.475	0.428	0.485	0.122	0.169	0.112
0.1280	0.8441	0.0279	0.8066	0.023	0.011	0.018	0.028	0.012	0.005	−0.005
0.4321	0.1496	0.4183	0.7741	0.229	0.794	0.778	0.880	−0.565	−0.549	−0.651
0.3172	0.6564	0.0264	0.8372	−0.042	0.016	0.016	0.037	−0.058	−0.058	−0.079
0.8744	0.0617	0.0639	0.9000	0.191	0.181	0.176	0.219	0.010	0.015	−0.028
0.2440	0.2207	0.5353	0.7351	0.442	0.749	0.733	0.810	−0.307	−0.291	−0.368
0.6019	0.3042	0.0939	0.8570	0.284	0.246	0.207	0.274	0.038	0.077	0.010
0.5254	0.3144	0.1602	0.8296	0.519	0.385	0.325	0.415	0.134	0.194	0.104
MA (1) + 1-propanol (2) + cyclohexane (3)										
0.0576	0.0720	0.8704	0.7705	0.555	0.592	0.589	0.606	−0.037	−0.034	−0.051
0.0445	0.8806	0.0749	0.7953	0.127	0.160	0.173	0.186	−0.033	−0.046	−0.059
0.0579	0.2008	0.7413	0.7728	0.635	0.733	0.715	0.745	−0.098	−0.080	−0.110
0.1638	0.1989	0.6373	0.7876	0.868	0.991	0.937	1.022	−0.123	−0.069	−0.154
0.1571	0.3190	0.5239	0.7925	0.562	0.844	0.768	0.853	−0.282	−0.206	−0.291
0.1325	0.7941	0.0734	0.8100	0.099	0.136	0.159	0.197	−0.037	−0.060	−0.098
0.2331	0.5687	0.1982	0.8185	0.235	0.386	0.371	0.468	−0.151	−0.136	−0.233
0.4759	0.4066	0.1175	0.8553	0.457	0.330	0.319	0.407	0.127	0.138	0.050
0.6708	0.2871	0.0421	0.8884	0.270	0.159	0.164	0.212	0.111	0.106	0.058
0.2252	0.6615	0.1133	0.8212	0.243	0.217	0.240	0.314	0.026	0.003	−0.071
0.4695	0.1856	0.3449	0.8393	0.785	0.950	0.855	0.996	−0.165	−0.070	−0.211
0.5599	0.1848	0.2553	0.8580	0.522	0.786	0.709	0.824	−0.264	−0.187	−0.302

Table I. *(Continued)*

					$V^{E}_{123\mathrm{cal}}$			ΔV^{E}		
x_1	x_2	x_3	ρ_{123} $(\mathrm{g \cdot cm^{-3}})$	$V^{E}_{123\mathrm{exp}}$	RK $(\mathrm{cm^3 \cdot mol^{-1}})$	K	TS	RK $(\mathrm{cm^3 \cdot mol^{-1}})$	K	TS
				MA (1) + 1-propanol (2) + benzene (3)						
0.0430	0.8627	0.0943	0.8073	−0.021	−0.021	−0.025	−0.025	0.000	0.004	0.004
0.0453	0.1682	0.7865	0.8546	0.176	0.192	0.189	0.196	−0.016	−0.013	−0.020
0.1418	0.1761	0.6821	0.8616	0.156	0.209	0.200	0.221	−0.053	−0.044	−0.065
0.1420	0.2853	0.5727	0.8551	0.124	0.195	0.174	0.195	−0.071	−0.050	−0.071
0.1289	0.7794	0.0917	0.8210	−0.004	−0.025	−0.035	−0.035	0.021	0.031	0.031
0.2247	0.5468	0.2285	0.8448	0.080	0.041	0.007	0.010	0.039	0.073	0.070
0.1753	0.6901	0.1346	0.8311	0.035	−0.011	−0.029	−0.030	0.046	0.064	0.065
0.3903	0.2699	0.3398	0.8758	0.050	0.144	0.114	0.134	−0.094	−0.064	−0.084
0.5897	0.1343	0.2760	0.8984	0.061	0.134	0.128	0.155	−0.073	−0.067	−0.094
0.0460	0.1119	0.8421	0.8584	0.150	0.165	0.164	0.170	−0.015	−0.014	−0.020
0.6112	0.3392	0.0496	0.8878	0.126	0.029	0.025	0.010	0.097	0.101	0.116
				MA (1) + 1-propanol (2) + toluene (3)						
0.8516	0.0609	0.0875	0.9197	0.014	0.039	0.044	0.039	−0.025	−0.030	−0.025
0.6732	0.0621	0.2647	0.9030	0.034	0.040	0.053	0.051	−0.006	−0.017	0.040
0.5799	0.0630	0.3571	0.8945	0.060	0.020	0.035	0.031	0.040	0.025	0.029
0.0568	0.0701	0.8731	0.8532	−0.029	−0.007	−0.006	−0.005	−0.022	−0.023	−0.024
0.0532	0.1890	0.7578	0.8476	−0.026	0.022	0.022	0.023	−0.048	−0.048	−0.049
0.1626	0.1933	0.6441	0.8567	−0.128	−0.026	−0.019	−0.024	−0.102	−0.109	−0.104
0.7199	0.2384	0.0417	0.9013	0.080	0.021	0.023	−0.003	0.059	0.057	0.083
0.2737	0.2687	0.4576	0.8632	−0.223	−0.035	−0.022	−0.047	−0.188	−0.201	−0.176
0.1549	0.3156	0.5295	0.8509	−0.178	−0.030	−0.029	−0.041	−0.148	−0.149	−0.137
0.1344	0.7488	0.1168	0.8237	−0.076	−0.079	−0.082	−0.102	0.003	0.006	0.026

as described above give only a rough estimate of excess volumes of the ternary mixtures studied in the present work.

A perusal of column 5 of Tables I and II shows that V^{E}_{123}(exp.) values are mostly positive in MA + 1-alcohol + *n*-hexane or *n*-heptane or cyclohexane mixtures. The algebraic sum of V^{E}_{123}(exp.) values (within the compositions taken), however, are higher for ternary mixtures containing *n*-heptane than *n*-hexane. The V^{E}_{123}(exp.) for ternary mixtures of ester + 1-alcohol + cyclohexane are large and more positive than that with aliphatic hydrocarbons. The positive values of ternary excess volumes suggest that structure breaking interactions in the form of depolymerization of 1-alcohol associates into multimers, cyclic-, tetra-, tri-, di-, or monomers, etc. are predominant. Cyclohexane is found to be an effective structure breaker compared to *n*-hexane or *n*-heptane molecules. The replacement of

Table II. Densities, Experimental and Predicted Excess Volumes, and Differences Between Experimental and Predicted Excess Volumes for MA (1) + 1-Butanol (2) + Hydrocarbons (3) at 308.15 K

					$V^{E}_{123\mathrm{cal}}$			ΔV^{E}		
x_1	x_2	x_3	ρ_{123} ($\mathrm{g \cdot cm^{-3}}$)	$V^{E}_{123\mathrm{exp}}$	RK ($\mathrm{cm^3 \cdot mol^{-1}}$)	K	TS	RK ($\mathrm{cm^3 \cdot mol^{-1}}$)	K	TS
MA (1) + 1-butanol (2) + *n*-hexane (3)										
0.1926	0.1871	0.6203	0.7090	0.515	0.437	0.411	0.446	0.078	0.104	0.069
0.1646	0.5274	0.3080	0.7571	0.310	0.193	0.148	0.158	0.117	0.162	0.152
0.1661	0.6052	0.2287	0.7719	0.311	0.143	0.106	0.112	0.168	0.205	0.199
0.1734	0.7833	0.0433	0.8121	0.180	0.080	0.073	0.073	0.100	0.107	0.107
0.4238	0.1176	0.4586	0.7576	0.744	0.522	0.496	0.548	0.222	0.248	0.196
0.3567	0.6024	0.0409	0.8346	0.438	0.133	0.123	0.119	0.305	0.315	0.319
0.5823	0.0559	0.3618	0.7934	0.666	0.491	0.479	0.524	0.175	0.187	0.142
0.7651	0.0816	0.1533	0.8622	0.316	0.292	0.276	0.305	0.024	0.040	0.011
0.8738	0.0543	0.0719	0.8976	0.167	0.157	0.151	0.163	0.010	0.016	0.004
0.2851	0.4436	0.2713	0.7770	0.469	0.280	0.220	0.232	0.189	0.249	0.237
0.1200	0.3562	0.5238	0.7165	0.334	0.290	0.256	0.276	0.044	0.078	0.058
0.1877	0.2472	0.5651	0.7168	0.467	0.408	0.373	0.406	0.059	0.094	0.061
0.6149	0.1131	0.2720	0.8161	0.507	0.427	0.400	0.446	0.080	0.107	0.061
MA (1) + 1-butanol (2) + *n*-heptane (3)										
0.0752	0.0749	0.8499	0.6822	0.426	0.469	0.464	0.480	−0.043	−0.038	−0.054
0.0784	0.2346	0.6870	0.7044	0.444	0.530	0.510	0.536	−0.086	−0.066	−0.092
0.0674	0.3381	0.5945	0.7139	0.364	0.455	0.436	0.458	−0.091	−0.072	−0.094
0.0565	0.7331	0.2104	0.7669	0.159	0.186	0.173	0.183	−0.027	−0.014	−0.024
0.2030	0.2025	0.5945	0.7260	0.571	0.758	0.712	0.775	−0.187	−0.141	−0.204
0.1852	0.4327	0.3821	0.7534	0.362	0.516	0.469	0.524	−0.154	−0.107	−0.162
0.1777	0.5285	0.2938	0.7662	0.330	0.411	0.371	0.419	−0.081	−0.041	−0.089
0.1532	0.8129	0.0339	0.8624	0.125	0.104	0.087	0.095	0.021	0.038	0.030
0.4426	0.1263	0.4311	0.7713	0.733	0.875	0.816	0.917	−0.142	−0.083	−0.184
0.3569	0.6106	0.0325	0.8379	0.317	0.164	0.141	0.155	0.153	0.176	0.162
0.4704	0.4648	0.0648	0.8438	0.501	0.245	0.206	0.241	0.256	0.295	0.260
0.5128	0.4545	0.0327	0.8580	0.367	0.185	0.162	0.179	0.182	0.205	0.188
0.3979	0.3812	0.2209	0.8031	0.482	0.508	0.437	0.520	−0.026	0.045	−0.038
0.7854	0.0808	0.1338	0.8696	0.322	0.387	0.352	0.417	−0.065	−0.030	−0.095
0.8825	0.0531	0.0644	0.9004	0.176	0.196	0.182	0.216	−0.020	−0.006	−0.040
0.1707	0.6209	0.2084	0.7797	0.310	0.311	0.274	0.312	−0.001	0.036	−0.002
MA (1) + 1-butanol (2) + cyclohexane (3)										
0.0576	0.0588	0.8836	0.7714	0.474	0.462	0.460	0.470	0.012	0.014	0.004
0.0521	0.8596	0.0883	0.8018	0.190	0.163	0.154	0.167	0.027	0.036	0.023
0.0574	0.1746	0.7680	0.7738	0.651	0.601	0.593	0.616	0.050	0.058	0.035
0.1695	0.1710	0.6595	0.7880	1.011	0.923	0.894	0.967	0.088	0.117	0.044
0.1674	0.2777	0.5549	0.7914	1.024	0.887	0.840	0.934	0.137	0.184	0.090
0.1533	0.7562	0.0905	0.8140	0.315	0.243	0.215	0.254	0.072	0.100	0.061
0.2614	0.5211	0.2175	0.8186	0.774	0.564	0.490	0.601	0.210	0.284	0.173
0.3585	0.5551	0.0864	0.8402	0.442	0.327	0.293	0.351	0.115	0.149	0.091

Table II. *(Continued)*

x_1	x_2	x_3	ρ_{123} $(\mathrm{g \cdot cm^{-3}})$	$V^{\mathrm{E}}_{123\,\mathrm{exp}}$	$V^{\mathrm{E}}_{123\,\mathrm{cal}}$			ΔV^{E}		
					RK	K	TS	RK	K	TS
					$(\mathrm{cm^3 \cdot mol^{-1}})$			$(\mathrm{cm^3 \cdot mol^{-1}})$		
MA (1) + 1-butanol (2) + cyclohexane (3)										
0.3804	0.1676	0.4520	0.8203	1.161	1.047	0.993	1.131	0.114	0.168	0.030
0.5142	0.3583	0.1275	0.8569	0.638	0.474	0.436	0.523	0.164	0.202	0.115
0.7100	0.2477	0.0423	0.8909	0.282	0.232	0.227	0.260	0.070	0.055	0.022
0.8607	0.0530	0.0863	0.9075	0.376	0.353	0.351	0.405	0.023	0.025	−0.029
0.4595	0.4514	0.0891	0.8530	0.490	0.361	0.331	0.393	0.128	0.159	0.097
0.2580	0.6149	0.1271	0.8244	0.516	0.378	0.328	0.401	0.138	0.188	0.115
0.5000	0.1287	0.3713	0.8393	1.086	0.993	0.952	1.083	0.093	0.134	0.003
0.6236	0.2032	0.1732	0.8678	0.750	0.610	0.580	0.689	0.140	0.170	0.061
MA (1) + 1-butanol (2) + benzene (3)										
0.0513	0.8613	0.0874	0.8119	0.069	0.065	0.064	0.067	0.004	0.005	0.002
0.0489	0.1464	0.8047	0.8553	0.221	0.221	0.217	0.228	0.000	0.004	−0.007
0.1482	0.1477	0.7041	0.8623	0.240	0.248	0.236	0.267	−0.008	0.004	−0.027
0.1495	0.2461	0.6044	0.8559	0.264	0.273	0.250	0.287	−0.009	0.014	−0.023
0.1502	0.7457	0.1041	0.8255	0.157	0.108	0.102	0.112	0.049	0.055	0.045
0.2497	0.4947	0.2556	0.8473	0.281	0.194	0.160	0.192	0.087	0.121	0.089
0.3502	0.5435	0.1063	0.8513	0.304	0.149	0.138	0.151	0.155	0.166	0.153
0.3483	0.1478	0.5039	0.8770	0.225	0.237	0.215	0.273	−0.012	0.010	−0.048
0.5008	0.3481	0.1511	0.8746	0.293	0.174	0.155	0.174	0.119	0.138	0.119
0.7021	0.2478	0.0501	0.8966	0.173	0.115	0.111	0.118	0.058	0.062	0.055
0.8493	0.0490	0.1017	0.9208	0.086	0.084	0.081	0.111	0.002	0.005	−0.025
0.4487	0.4485	0.1028	0.8642	0.324	0.156	0.145	0.156	0.168	0.179	0.168
0.1994	0.6484	0.1522	0.8345	0.228	0.140	0.125	0.143	0.088	0.103	0.085
0.3384	0.1908	0.4708	0.8735	0.228	0.248	0.218	0.278	−0.020	0.010	−0.050
0.6465	0.0508	0.3028	0.9055	0.151	0.149	0.143	0.188	0.002	0.008	−0.037
MA (1) + 1-butanol (2) + toluene (3)										
0.0573	0.0566	0.8861	0.8553	0.018	0.025	0.024	0.028	−0.007	−0.006	−0.010
0.0526	0.8592	0.0882	0.8124	0.006	0.008	0.012	0.008	−0.002	−0.006	−0.002
0.0567	0.1684	0.7749	0.8477	0.067	0.084	0.079	0.086	−0.017	−0.012	−0.019
0.2427	0.2444	0.5129	0.8591	−0.037	0.046	0.033	0.034	−0.083	−.070	−0.071
0.1651	0.2706	0.5643	0.8517	−0.015	0.048	0.033	0.038	−0.063	−0.048	−0.053
0.1522	0.7565	0.0913	0.8253	0.055	0.037	0.048	0.036	0.018	0.007	0.019
0.3525	0.5552	0.0923	0.8510	0.162	0.079	0.091	0.065	0.083	0.071	0.097
0.3784	01637	0.4579	0.8736	−0.039	0.049	0.044	0.051	−0.088	−0.083	−0.090
0.5150	0.3563	0.1287	0.8744	0.153	0.097	0.098	0.062	0.056	0.055	0.091
0.5895	0.2070	0.2035	0.8885	0.056	0.094	0.086	0.065	−0.038	−0.030	−0.009
0.8581	0.0525	0.0894	0.9194	0.045	0.054	0.051	0.058	−0.009	−0.006	−0.013
0.4340	0.4785	0.0875	0.8614	0.183	0.093	0.102	0.074	0.090	0.081	0.109
0.2061	0.6615	0.1324	0.8345	0.074	0.038	0.050	0.029	0.036	0.024	0.045
0.6785	0.0519	0.2696	0.9032	0.037	0.066	0.065	0.087	−0.029	−0.028	−0.050
0.2663	0.3700	0.3637	0.8548	−0.014	.042	0.029	0.007	−0.056	−0.043	−0.021

Table III. Values of the Coefficients, a_i, Obtained by the Representation (Eq. (4)) of Excess Volumes of Binary Systems at 308.15 K

System	a_0	a_1	a_2	a_3	σ
MA (1) + 1-propanol (2)	−0.065	0.303	−0.021	–	0.004
1-Propanol (2) + *n*-hexane (3)	0.947	−0.975	0.982	–	0.005
1-Propanol (2) + *n*-heptane (3)	1.403	−1.064	0.320	1.183	0.001
1-Propanol (2) + cyclohexane (3)	1.553	−1.015	2.651	–	0.004
1-Propanol (2) + benzene (3)	0.393	−1.021	0.394	–	0.003
1-Propanol (2) + toluene (3)	−0.052	−0.759	0.000	–	0.006
MA (1) + *n*-hexane (3)	2.125	−0.220	0.262	–	0.006
MA (1) + *n*-heptane (3)	3.651	−0.909	0.010	–	0.005
MA (1) + cyclohexane (3)	4.560	−1.084	1.103	–	0.006
MA (1) + benzene (3)	0.511	−0.026	0.377	–	0.004
MA (1) + toluene (3)	−0.087	0.758	−0.117	–	0.005
MA (1) + 1-butanol (2)	0.468	0.010	−0.006	−0.215	0.003
1-Butanol (2) + *n*-hexane (3)	0.222	−1.169	0.567	–	0.007
1-Butanol (2) + *n*-heptane (3)	0.948	−0.717	0.892	−1.081	0.001
1-Butanol (2) + cyclohexane (3)	1.753	−0.705	0.291	–	0.004
1-Butanol (2) + benzene (3)	0.738	−0.779	0.539	–	0.004
1-Butanol (2) + toluene (3)	0.030	−0.833	0.693	–	0.004

n-hexane with aromatic hydrocarbons, viz. benzene or toluene, is found to decrease the ternary excess volumes almost by a factor of 3 to 4 and even result in negative values in ester + 1-alcohol + toluene mixtures. The highly diminished positive or negative V^{E}_{123}(exp.) values indicate that besides structure disruptions, the weak but specific interactions of –OH-----π type between the hydroxyl group of 1-alcohol and π electrons of aromatic ring

Table IV. Values of the Ternary Parameters A, B, and C (Eq. (5)) and the Standard Deviation $\sigma(\Delta V^{E}_{123})$ for the Ternary Systems at 308.15 K

System	A	B	C	σ
MA (1) + 1-propanol (2) + *n*-hexane (3)	4.029	108.648	−129.212	0.004
MA (1) + 1-propanol (2) + *n*-heptane (3)	2.302	103.982	−840.415	0.004
MA (1) + 1-propanol (2) + cyclohexane (3)	−12.586	−14.956	1061.291	0.004
MA (1) + 1-propanol (2) + benzene (3)	−1.893	33.997	174.148	0.002
MA (1) + 1-propanol (2) + toluene (3)	−5.492	29.328	471.429	0.004
MA (1) + 1-butanol (2) + *n*-hexane (3)	2.498	38.072	604.793	0.005
MA (1) + 1-butanol (2) + *n*-heptane (3)	−5.906	53.896	385.293	0.005
MA (1) + 1-butanol (2) + cyclohexane (3)	6.153	13.703	−58.985	0.004
MA (1) + 1-butanol (2) + benzene (3)	0.581	25.031	141.096	0.003
MA (1) + 1-butanol (2) + toluene (3)	−1.586	23.253	89.535	0.004

Table V. Sound Speeds, Experimental and Predicted Excess Isentropic Compressibilities, and Deviations Between Experimental and Predicted Excess Isentropic Compressibilities for MA (1) + 1-Propanol (2) + Hydrocarbons (3) at 308.15 K

			u_{exp}	$\kappa_{s\,\mathrm{exp}}^{\mathrm{E}}$	$\kappa_{s\,\mathrm{cal}}^{\mathrm{E}}$ $(\mathrm{TPa})^{-1}$			$\Delta\kappa_{s}^{\mathrm{E}}$ $(\mathrm{TPa})^{-1}$		
x_1	x_2	x_3	$(\mathrm{m \cdot s^{-1}})$	$(\mathrm{TPa})^{-1}$	RK	K	TS	RK	K	TS
MA(1) + 1-propanol (2) + *n*-hexane (3)										
0.1533	0.5606	0.2861	1043	−29	−31	−36	−38	2	7	9
0.1233	0.8440	0.0327	1129	−5	−6	−8	−9	1	3	4
0.4116	0.1257	0.4627	995	−56	−57	−61	−61	1	5	5
0.7602	0.0960	0.1438	1068	−29	−29	−29	−35	0	0	6
0.8668	0.0642	0.0690	1039	−14	−14	−14	−18	0	0	4
0.1823	0.2876	0.5301	995	−34	−34	−39	−40	0	5	6
0.2202	0.7474	0.0324	1116	−4	−4	−6	−9	0	2	5
0.0606	0.2982	0.6412	985	−21	−20	−22	−22	−1	1	1
0.6194	0.3504	0.0302	1073	−5	−5	−5	−11	0	0	6
MA(1) + 1-propanol (2) + *n*-heptane (3)										
0.0738	0.0854	0.8408	1013	19	20	19	20	−1	0	−1
0.0712	0.1752	0.7536	1017	24	23	21	23	1	3	1
0.0680	0.2544	0.6776	1023	22	21	20	21	1	2	1
0.0496	0.7671	0.1833	1094	8	8	7	8	0	1	0
0.1752	0.4787	0.3461	1051	14	12	6	13	2	−2	1
0.1280	0.8441	0.0279	1132	2	2	1	2	0	1	0
0.4321	0.1496	0.4183	1029	−9	−7	−16	−6	−2	7	−3
0.3172	0.6564	0.0264	1107	3	3	1	2	0	2	1
0.8744	0.0617	0.0639	1050	−11	−12	−13	−11	1	2	0
0.2440	0.2207	0.5353	1024	13	13	6	13	0	7	0
0.6019	0.3042	0.0939	1064	−4	−5	−10	−4	1	6	0
0.5254	0.3144	0.1602	1057	−2	−5	−14	−4	3	12	2
MA(1) + 1-propanol (2) + *n*-cyclohexane (3)										
0.0576	0.0720	0.8704	1184	32	30	31	31	1	1	1
0.0445	0.8806	0.0749	1168	−5	−6	−8	−8	1	3	3
0.0579	0.2008	0.7413	1173	36	34	34	35	2	2	1
0.1638	0.1989	0.6373	1150	62	54	51	56	8	11	6
0.1571	0.3190	0.5239	1146	56	47	41	47	9	15	9
0.1325	0.7941	0.0734	1158	4	1	−4	−4	3	8	8
0.2331	0.5687	0.1982	1144	28	20	8	11	8	20	17
0.4759	0.4066	0.1175	1137	25	20	16	11	5	9	14
0.6708	0.2871	0.0421	1138	12	10	11	5	2	1	7
0.2252	0.6615	0.1133	1150	14	10	1	1	4	13	13
0.4695	0.1856	0.3449	1128	61	50	48	52	11	15	9
0.5599	0.1848	0.2553	1127	51	42	42	43	9	9	8

Table V. *(Continued)*

			u_{exp}	$\kappa^{\mathrm{E}}_{s\,\mathrm{exp}}$	$\kappa^{\mathrm{E}}_{s\,\mathrm{cal}}$ (TPa)$^{-1}$			$\Delta\kappa^{\mathrm{E}}_{s}$ (TPa)$^{-1}$		
x_1	x_2	x_3	(m·s^{-1})	(TPa)$^{-1}$	RK	K	TS	RK	K	TS
MA(1) + 1-propanol (2) + benzene (3)										
0.0430	0.8627	0.0943	1176	−10	−4	−5	−5	−6	−5	−5
0.0453	0.1682	0.7865	1230	6	15	15	16	−9	−9	−10
0.1418	0.1761	0.6821	1214	10	20	19	21	−10	−9	−11
0.1289	0.7794	0.0917	1173	−12	0	−3	−3	−12	−9	−9
0.5897	0.1343	0.2760	1167	7	13	12	15	−6	−5	−8
0.0460	0.1119	0.8421	1236	7	13	13	13	−6	−6	−6
0.6112	0.3392	0.0496	1138	17	4	3	1	13	14	16
MA(1) + 1-propanol (2) + toluene (3)										
0.8516	0.0609	0.0875	1151	1	3	3	0	−2	−2	1
0.6732	0.0621	0.2647	1171	3	3	3	2	0	0	1
0.5799	0.0630	0.3571	1181	5	2	2	2	3	3	3
0.0568	0.0701	0.8731	1247	0	2	2	2	−2	−2	−2
0.0532	0.1890	0.7578	1238	−5	−1	−2	−2	−4	−3	−3
0.1626	0.1933	0.6441	1227	−10	−1	−2	−2	−9	−8	−8
0.7199	0.2384	0.0417	1142	8	1	1	−2	7	7	10
0.1344	0.7488	0.1168	1171	−5	−7	−7	−9	2	2	4

and n-----π interactions between the carbonyl group of ester and π electrons of aromatic ring are more predominant in these mixtures. One can also imagine additional dipole-induced dipole interactions in MA + 1-alcohol + toluene mixtures. Thus, it can be reasonably concluded that the interactions between the 1-alcohol + aliphatic/cyclic/aromatic hydrocarbons and also between ester + hydrocarbons contribute equally for the ternary excess volume data.

3.2. Sound Speeds and Excess Isentropic Compressibilities

The sound speeds, u, isentropic compressibilities, κ_s, isentropic compressibilities in ideal state, κ_s^{id}, and excess isentropic compressibilities, κ_s^{E}, for ten ternary mixtures at 308.15 K are listed in Tables V and VI. The κ_s^{id} values were calculated using expressions proposed by Benson and Kiyohara [28] and Douheret et al. [29]. The excess isentropic compressibilities, κ_s^{E}, of ternary mixtures were also predicted from the respective binary values by RK, K, and TS equations. The κ_s^{E} contributions of the respective binary pairs were estimated using the values of the coefficients, a_i, as listed in

Table VI. Sound Speeds, Experimental and Predicted Excess Isentropic Compressibilities, and Deviations Between Experimental and Predicted Excess Isentropic Compressibilities for MA (1) + 1-Butanol (2) + Hydrocarbons (3) at 308.15 K

			u_{exp}	$\kappa^{\mathrm{E}}_{s\,\mathrm{exp}}$	$\kappa^{\mathrm{E}}_{s\,\mathrm{cal}}$ $(\mathrm{TPa})^{-1}$			$\Delta\kappa^{\mathrm{E}}_{s}$ $(\mathrm{TPa})^{-1}$		
x_1	x_2	x_3	$(\mathrm{m \cdot s^{-1}})$	$(\mathrm{TPa})^{-1}$	RK	K	TS	RK	K	TS
MA(1) + 1-butanol (2) + *n*-hexane (3)										
0.1926	0.1871	0.6203	993	−47	−47	−51	−52	0	4	5
0.1646	0.5274	0.3080	1066	−49	−48	−56	−61	−1	7	12
0.1661	0.6052	0.2287	1091	−45	−42	−49	−55	−3	4	10
0.1734	0.7833	0.0433	1156	−11	−10	−12	−14	−1	1	3
0.4238	0.1176	0.4586	1006	−66	−67	−70	−74	1	4	8
0.3567	0.6024	0.0409	1130	−12	−11	−12	−17	−1	0	5
0.5823	0.0559	0.3618	1011	−69	−68	−68	−72	−1	−1	3
0.7651	0.0816	0.1533	1034	−34	−35	−34	−43	1	0	9
0.8738	0.0543	0.0719	1042	−17	−16	−16	−22	−1	−1	5
0.2851	0.4436	0.2713	1063	−49	−46	−55	−64	−3	6	15
0.1200	0.3562	0.5238	1018	−48	−48	−52	−55	0	4	7
0.1877	0.2472	0.5651	1004	−50	−48	−53	−56	−2	3	6
0.6149	0.1131	0.2720	1025	−56	−56	−56	−65	0	0	9
MA(1) + 1-butanol (2) + *n*-heptane (3)										
0.0752	0.0749	0.8499	1016	15	14	13	14	1	2	1
0.0784	0.2346	0.6870	1030	15	14	12	14	1	3	1
0.0674	0.3381	0.5945	1043	11	10	8	9	1	3	2
0.0565	0.7331	0.2104	1123	0	0	−1	0	0	1	0
0.2030	0.2025	0.5945	1029	13	11	4	10	2	9	3
0.1852	0.4327	0.3821	1063	5	5	−3	3	0	8	2
0.1777	0.5285	0.2938	1082	3	3	−4	1	0	7	2
0.1532	0.8129	0.0339	1128	2	2	0	1	0	2	1
0.4426	0.1263	0.4311	1036	−14	−14	−22	−13	0	8	−1
0.3569	0.6106	0.0325	1133	0	−1	−4	−2	1	4	2
0.4704	0.4648	0.0648	1108	−6	−5	−10	−6	−1	4	0
0.5128	0.4545	0.0327	1111	−4	−4	−7	−5	0	3	1
0.3979	0.3812	0.2209	1075	−7	−6	−17	−8	−1	10	1
0.7854	0.0808	0.1338	1053	−23	−22	−25	−23	−1	2	0
0.8825	0.0531	0.0644	1053	−14	−14	−15	−14	0	1	0
0.1707	0.6209	0.2084	1103	2	2	−4	1	0	6	1
MA(1) + 1-butanol (2) + cyclohexane (3)										
0.0576	0.0588	0.8836	1188	31	30	29	30	1	2	1
0.0521	0.8596	0.0883	1198	9	7	5	7	2	4	2
0.0574	0.1746	0.7680	1184	34	32	31	32	2	3	2
0.1695	0.1710	0.6595	1163	56	54	50	55	2	6	1
0.1674	0.2777	0.5549	1162	56	49	44	51	7	12	5
0.1533	0.7562	0.0905	1186	16	11	8	11	5	8	5
0.3804	0.1676	0.4520	1147	59	55	50	58	4	9	1
0.7100	0.2477	0.0423	1152	11	6	9	6	5	2	5
0.8607	0.0530	0.0863	1133	25	24	26	26	1	−1	−1
0.5000	0.1287	0.3713	1142	53	51	49	54	2	4	−1
0.6236	0.2032	0.1732	1136	37	28	32	31	9	5	6

Table VI. *(Continued)*

			u_{exp}	$\kappa^{\mathrm{E}}_{s\,\mathrm{exp}}$	$\kappa^{\mathrm{E}}_{s\,\mathrm{cal}}$ (TPa)$^{-1}$			$\Delta\kappa^{\mathrm{E}}_{s}$ (TPa)$^{-1}$		
x_1	x_2	x_3	(m·s^{-1})	(TPa)$^{-1}$	RK	K	TS	RK	K	TS
			MA(1) + 1-butanol (2) + benzene (3)							
0.0513	0.8613	0.0874	1206	6	3	3	3	3	3	3
0.0489	0.1464	0.8047	1238	11	8	8	8	3	3	3
0.1482	0.1477	0.7041	1217	21	13	12	14	8	9	7
0.1495	0.2461	0.6044	1209	25	13	12	14	12	13	11
0.1502	0.7457	0.1041	1193	15	5	4	5	10	11	10
0.3483	0.1478	0.5039	1189	27	14	12	15	13	15	12
0.7021	0.2478	0.0501	1157	8	−1	−1	0	9	9	8
0.8493	0.0790	0.1017	1150	7	5	5	6	2	2	1
0.6465	0.0508	0.3027	1166	16	11	11	11	5	5	5
			MA(1) + 1-butanol (2) + toluene (3)							
0.0573	0.0566	0.8861	1245	5	5	5	5	0	0	0
0.0526	0.8592	0.0882	1203	8	8	8	8	0	0	0
0.0567	0.1684	0.7749	1236	9	10	9	10	0	0	−1
0.2427	0.2444	0.5129	1209	9	9	7	11	2	2	−2
0.1651	0.2706	0.5643	1217	9	11	9	12	0	0	−3
0.1522	0.7565	0.0913	1197	7	7	8	9	−1	−1	−2
0.3525	0.5552	0.0923	1179	13	3	5	7	8	8	6
0.3784	0.1637	0.4579	1194	15	−5	4	7	11	11	8
0.5150	0.3563	0.1287	1177	4	1	2	5	3	2	−1
0.5895	0.2070	0.2035	1181	−4	2	2	5	−6	−6	−9
0.8581	0.0525	0.0894	1154	1	2	2	3	−1	−1	−2
0.4340	0.4785	0.0875	1174	12	1	3	5	11	9	7
0.2061	0.6615	0.1324	1194	8	7	8	10	1	0	−2
0.6785	0.0519	0.2696	1169	10	3	3	5	7	7	5
0.2663	0.3700	0.3637	1207	−1	8	7	11	−9	−8	−12

Table VII and Eq. (1). Columns 8 to 10 of Tables V and VI list the calculated $\kappa^{\mathrm{E}}_{s\,123}$ values and columns 11 to 13 list the deviations $\Delta\kappa^{\mathrm{E}}_{s\,123}$ between the experimental and predicted values. The dependence of experimental $\kappa^{\mathrm{E}}_{s\,123}$ values of all the six ternary mixtures on the composition was also mathematically expressed by Eq. (5). The values of the constants *A*, *B*, and *C* as evaluated by multiple regression analysis along with the standard deviations, σ, are summarized in Table VIII.

Close examination of columns 8 to 10 of Tables V and VI shows that $\kappa^{\mathrm{E}}_{s\,123}$ for MA (1) + 1-propanol (2) or + 1-butanol (2) + *n*-hexane(3) are negative and for the ternary mixtures containing *n*-heptane (3) are positive and negative depending on the composition. This trend indicates that *n*-hexane can be interstitially accommodated into MA + 1-alcohol associates. For the *n*-cyclohexane containing ternary mixtures, the values are found to be large and positive. The large positive $\kappa^{\mathrm{E}}_{s\,123}$ data may be

Table VII. Values of the Parameters a_i Obtained by the Representation (Eq. (4)) of Excess Isentropic Compressibilities of Binary Systems

System	a_0	a_1	a_2	a_3	σ
MA (1) + 1-propanol (2)	10.2	−7.4	−10.6	–	1.0
1-Propanol (2) + *n*-hexane (3)	−115.8	−95.1	42.3	−136.7	0.4
1-Propanol (2) + *n*-heptane (3)	53.4	−23.9	82.2	−107.8	0.6
1-Propanol (2) + cyclohexane (3)	33.1	−133.5	−88.5	–	1.6
1-Propanol (2) + benzene (3)	32.8	−95.7	−31.1	–	1.5
1-Propanol (2) + toluene (3)	−67.1	−64.9	33.1	–	0.9
MA + (1) + cyclohexane (3)	262.7	−69.7	241.8	–	0.5
MA (1) + benzene (3)	56.3	−20.7	53.7	–	0.7
MA (1) + *n*-hexane (3)	−316.2	4.7	133.8	–	0.9
MA (1) + *n*-heptane (3)	−120.5	−195.3	64.7	–	0.6
MA (1) + toluene (3)	4.2	16.0	35.0	–	0.4
MA (1) + 1-butanol (2)	−9.9	−27.8	11.3	–	0.8
1-Butanol (2) + *n*-hexane (3)	−216.9	−136.5	2.8	–	0.6
1-Butanol (2) + *n*-heptane (3)	2.3	−50.9	67.3	−46.3	1.0
1-Butanol (2) + cyclohexane (3)	56.1	−17.0	−5.5	–	0.9
1-Butanol (2) + benzene (3)	27.4	−3.9	−6.7	–	0.9
1-Butanol (2) + toluene (3)	55.5	10.2	40.8	–	0.5

attributed to the predominance of structure breaking interactions in which the depolymerization of 1-alcohol associates occurs. The dissociated state is expected to occupy more volume and, hence, the compressibilities in the mixed state can be expected to be large. Interestingly, the $\kappa^{\mathrm{E}}_{s\,123}$ values are found to become less positive or even negative when *n*-cyclohexane is replaced by aromatic hydrocarbons, namely, benzene or toluene. The

Table VIII. Values of the Ternary Parameters *A*, *B*, and *C* (Eq. (5)) and the Standard Deviation $\sigma(\Delta K^{E}_{s\,123})$ for the Ternary Systems at 308.15 K

System	*A*	*B*	*C*	σ
MA (1) + 1-propanol (2) + *n*-hexane (3)	42.4	315.8	−1318.5	0.9
MA (1) + 1-propanol (2) + *n*-heptane (3)	75.1	688.9	−6068.4	0.8
MA (1) + 1-propanol (2) + cyclohexane (3)	329.5	−187.6	−2126.1	0.7
MA (1) + 1-propanol (2) + benzene (3)	−1731.8	−6323.3	131140.0	0.1
MA (1) + 1-propanol (2) + toluene (3)	−441.5	3499.0	45328.1	0.4
MA (1) + 1-butanol (2) + *n*-hexane (3)	−70.9	−418.0	8.9	0.9
MA (1) + 1-butanol (2) + *n*-heptane (3)	−12.9	60.5	674.0	0.9
MA (1) + 1-butanol (2) + cyclohexane (3)	360.3	2119.3	−1483.1	0.7
MA (1) + 1-butanol (2) + benzene (3)	606.3	1973.6	8335.2	0.1
MA (1) + 1-butanol (2) + toluene (3)	−207.5	−1125.2	34934.7	0.6

highly smaller and even negative $\kappa_{s\,123}^{\mathrm{E}}$ values for the latter mixtures support the dominance of weak but specific structure making interactions of $n\cdots\cdots\pi$ type between the lone pair of electrons on oxygen of either hydroxyl functional group of 1-alcohol or carbonyl group of ester species and π electrons of aromatic ring of benzene or toluene.

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