

# Densities and Viscosities of Binary Mixtures of Ethyl Acetoacetate, Ethyl Isovalerate, Methyl Benzoate, Benzyl Acetate, Ethyl Salicylate, and Benzyl Propionate with Ethanol at $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$

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Densities and viscosities for six binary mixtures formed by the flavor esters (ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, and benzyl propionate) with ethanol over the whole composition range were measured at four different temperatures (288.15, 298.15, 308.15, and 318.15) K and atmospheric pressure. Densities were determined using a vibrating-tube density meter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. Excess molar volumes ( $V^E$ ) and deviations in the viscosity from mole fraction average ( $\Delta\eta$ ) for the binary mixtures were derived from experimental data. The binary data of  $V^E$  and  $\Delta\eta$  were correlated as function of the mole fraction by using the Redlich–Kister equation. Furthermore, McAllister's multi-body interaction models are used to correlate the binary kinematic viscosities.

## Introduction

The thermophysical study of esters is increasing interest due to their wide usage in flavoring, perfumery, artificial essences, and cosmetics. Esters are also important solvents in the pharmaceutical, paint, and plastic industries. Among different type of esters, ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, and benzyl propionate are important flavor compounds used in the flavor and fragrance industries, and ethanol is the most common alcohol component. On the other hand, ethanol is a versatile solvent with protic and self-associated properties, which is often used to study the hydrophobic effect. Several studies for binary mixtures of the thermophysical properties involving the above ester compounds have been conducted recently.<sup>1–6</sup> However, no studies on the properties such as density and viscosity for the binary systems formed by the above esters with ethanol have been reported in the literature.

Therefore, in the present paper we undertake to obtain reliable density and viscosity data for binary mixtures of ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, and benzyl propionate respectively with ethanol at  $T = (288.15, 298.15, 308.15, \text{ and } 318.15) \text{ K}$  and atmospheric pressure. The experimental results are used to calculate excess molar volumes and deviations in the viscosity from mole fraction average. The calculated binary excess molar volumes and viscosity deviations are fitted with the Redlich–Kister equation to determine the coefficients. Furthermore, McAllister's equation is used to correlate the binary kinematic viscosities.

## Experimental Section

**Materials.** The chemicals used were of analytical grade and were used without further purification. The purity of these chemicals was analyzed by gas chromatography (Perkin-Elmer Autosystem). The mass percent purities as determined by the major peak areas on gas chromatography together with the sources and the CAS Registry Numbers (CASRN) of chemicals

**Table 1. Sources and Mass Fraction ( $w$ ) Purities of the Esters Used in This Study**

compounds	molecular formula	sources	CASRN	100 $w$
ethyl acetoacetate	C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>	Acros (USA)	141-97-9	99.2
ethyl isovalerate	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	Acros (USA)	108-64-5	99.0
methyl benzoate	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	Lancaster (U.K.)	93-58-3	99.2
benzyl acetate	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	Acros (USA)	140-11-4	99.6
ethyl salicylate	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	Acros (USA)	118-61-6	99.6
benzyl propionate	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	TCI (Japan)	122-63-4	99.4
ethanol	C <sub>2</sub> H <sub>6</sub> O	Merck (Germany)	64-17-5	99.9

are given in Table 1. The purity of solvents was further ascertained by comparing their densities, viscosities, and refractive indices at a temperature of 298.15 K, and the results are generally in agreement with the corresponding values reported in the literature as shown in Table 2. Experimental refractive indices in Table 2 were measured with a digital Abbe refractometer RX-5000 (Atago, Tokyo, Japan), which works at the wavelength (589 nm) corresponding to the D-line of sodium.

**Apparatus and Procedure.** Samples were prepared by mass in a 50 cm<sup>3</sup> Erlenmeyer flask provided with a ground glass joint stopper, using a Precisa 262SMA balance with an uncertainty of  $\pm 3 \times 10^{-5} \text{ g}$ . Densities were measured with an Anton Paar DMA-5000 vibrating-tube density meter (Anton-Paar, Graz, Austria) with a stated accuracy of  $5 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  in the range (0 to 3)  $\text{g}\cdot\text{cm}^{-3}$ , which was thermostatically controlled to within  $\pm 0.01 \text{ K}$  in the range (273.15 to 363.15) K. Calibration was performed periodically under atmospheric pressure, in accordance with specifications, using double-distilled water and dry air. The uncertainty of the density measurements was estimated to be less than  $\pm 3 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ .

The kinematic viscosities were determined with the commercial Ubbelohde capillary viscometers (Cannon Instrument Co., State College, PA) of (0.36, 0.47, 0.53, and 0.83) mm in diameter. The viscometer was kept in a Lauda D20 KP thermostat controlled to  $\pm 0.01 \text{ K}$  with a proportional integral differential regulator. A computer-controlled measuring system (Lauda, Lauda-Königshofen, Germany) with an uncertainty of  $\pm 0.01 \text{ s}$  was used for flow-time measurement. The range of

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**Table 2. Comparison of Measured Densities ( $\rho$ ), Viscosities ( $\eta$ ), and Refractive Indices ( $n_D$ ) of Pure Components with Literature Values at 298.15 K**

compounds	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$		$n_D$	
	exptl	lit.	exptl	lit.	exptl	lit.
ethyl acetoacetate	1.02345	1.0208 <sup>7</sup> 1.02126 <sup>8</sup>	1.581	1.5081 <sup>8</sup>	1.41658	1.4189 <sup>7</sup>
ethyl isovalerate	0.85978	0.86401 <sup>10</sup>	0.739	0.752 <sup>10</sup>	1.39401	
methyl benzoate	1.08392 1.02126 <sup>8</sup>	1.0850 <sup>1</sup> 1.0839 <sup>8</sup> 1.08363 <sup>11</sup> 1.0837 <sup>12</sup>	1.851 1.0839 <sup>8</sup> 1.08363 <sup>11</sup> 1.0837 <sup>12</sup>	1.918 <sup>1</sup> 1.823 <sup>11</sup> 1.8578 <sup>9</sup> 1.810 <sup>12</sup>	1.51467 1.823 <sup>11</sup> 1.8578 <sup>9</sup> 1.810 <sup>12</sup>	1.51457 <sup>8</sup> 1.51466 <sup>11</sup> 1.5152 <sup>12</sup>
benzyl acetate	1.05075		2.056		1.49982	
ethyl salicylate	1.12500		2.831		1.52022	
benzyl propionate	1.02760		2.123		1.49498	
ethanol	0.78500	0.7850 <sup>13</sup> 0.78493 <sup>14</sup> 0.78515 <sup>15</sup> 0.78506 <sup>17</sup>	1.105	1.105 <sup>13</sup> 1.0826 <sup>14</sup> 1.1120 <sup>18</sup>	1.35941	1.3593 <sup>15</sup> 1.3595 <sup>19</sup>

**Table 3. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Ethyl Acetoacetate (1) + Ethanol (2)**

$x_1$	$\rho$				$\eta$				$V^E$				$\Delta\eta$			
	$x_1$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	$\text{cm}^3\cdot\text{mol}^{-1}$
288.15 K																
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.92379	1.250	-0.066	-0.285	0.7000	0.99451	1.536	-0.027	-0.196		
0.0500	0.81878	1.266	-0.043	-0.099	0.4000	0.93631	1.280	-0.060	-0.283	0.7500	1.00207	1.591	-0.019	-0.170		
0.1000	0.84100	1.204	-0.057	-0.189	0.4500	0.94786	1.312	-0.054	-0.279	0.8000	1.00918	1.650	-0.012	-0.139		
0.1500	0.86094	1.190	-0.066	-0.232	0.5000	0.95856	1.349	-0.047	-0.271	0.8500	1.01585	1.709	-0.002	-0.108		
0.2000	0.87893	1.194	-0.069	-0.256	0.5500	0.96853	1.390	-0.044	-0.258	0.9000	1.02216	1.773	0.005	-0.072		
0.2500	0.89525	1.206	-0.069	-0.272	0.6000	0.97779	1.435	-0.039	-0.241	0.9500	1.02815	1.834	0.009	-0.040		
0.3000	0.91015	1.226	-0.069	-0.280	0.6500	0.98640	1.484	-0.030	-0.220	1.0000	1.03392	1.902	0.000	0.000		
298.15 K																
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.91394	1.038	-0.049	-0.234	0.7000	0.98417	1.270	-0.010	-0.168		
0.0500	0.80991	1.042	-0.039	-0.087	0.4000	0.92637	1.061	-0.043	-0.234	0.7500	0.99171	1.316	-0.006	-0.146		
0.1000	0.83189	1.001	-0.049	-0.152	0.4500	0.93783	1.087	-0.036	-0.232	0.8000	0.99879	1.366	-0.001	-0.120		
0.1500	0.85163	0.990	-0.055	-0.186	0.5000	0.94847	1.117	-0.031	-0.226	0.8500	1.00546	1.415	0.003	-0.095		
0.2000	0.86945	0.994	-0.056	-0.206	0.5500	0.95837	1.151	-0.028	-0.216	0.9000	1.01174	1.471	0.009	-0.062		
0.2500	0.88563	1.003	-0.054	-0.221	0.6000	0.96755	1.189	-0.021	-0.202	0.9500	1.01772	1.524	0.009	-0.033		
0.3000	0.90041	1.019	-0.053	-0.229	0.6500	0.97613	1.227	-0.015	-0.187	1.0000	1.02345	1.581	0.000	0.000		
308.15 K																
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.90399	0.878	-0.026	-0.191	0.7000	0.97379	1.073	0.011	-0.144		
0.0500	0.80094	0.869	-0.033	-0.073	0.4000	0.91634	0.898	-0.021	-0.192	0.7500	0.98129	1.112	0.014	-0.126		
0.1000	0.82268	0.841	-0.039	-0.122	0.4500	0.92773	0.921	-0.014	-0.190	0.8000	0.98836	1.154	0.016	-0.105		
0.1500	0.84222	0.832	-0.040	-0.152	0.5000	0.93829	0.947	-0.008	-0.186	0.8500	0.99502	1.199	0.017	-0.082		
0.2000	0.85989	0.837	-0.039	-0.169	0.5500	0.94811	0.974	-0.003	-0.180	0.9000	1.00130	1.247	0.017	-0.055		
0.2500	0.87591	0.846	-0.034	-0.181	0.6000	0.95724	1.004	0.003	-0.171	0.9500	1.00729	1.295	0.012	-0.028		
0.3000	0.89057	0.860	-0.031	-0.188	0.6500	0.96577	1.036	0.009	-0.160	1.0000	1.01300	1.344	0.000	0.000		
318.15 K																
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.89392	0.751	0.000	-0.151	0.7000	0.96333	0.917	0.036	-0.115		
0.0500	0.79180	0.731	-0.027	-0.059	0.4000	0.90618	0.768	0.007	-0.152	0.7500	0.97082	0.948	0.037	-0.103		
0.1000	0.81332	0.713	-0.028	-0.095	0.4500	0.91749	0.789	0.015	-0.150	0.8000	0.97788	0.983	0.035	-0.086		
0.1500	0.83267	0.709	-0.025	-0.118	0.5000	0.92799	0.812	0.021	-0.146	0.8500	0.98454	1.018	0.032	-0.070		
0.2000	0.85017	0.712	-0.020	-0.134	0.5500	0.93775	0.836	0.027	-0.140	0.9000	0.99084	1.059	0.026	-0.048		
0.2500	0.86605	0.721	-0.012	-0.143	0.6000	0.94684	0.861	0.032	-0.134	0.9500	0.99682	1.103	0.017	-0.022		
0.3000	0.88060	0.735	-0.007	-0.148	0.6500	0.95536	0.888	0.034	-0.125	1.0000	1.00254	1.144	0.000	0.000		

the flow time for the liquids investigated varied from 200 s to 920 s. The kinematic viscosities ( $\nu$ ) were determined according to

$$\nu = k(t - \theta) \quad (1)$$

where  $k$  is the viscometer constant,  $t$  is the flow time, and  $\theta$  is the Hagenbach correction. The absolute viscosity ( $\eta$ ) was then calculated from the density by the relation  $\eta = \nu\rho$ . The values of  $k$  were determined by calibrating with pure water at working temperatures. The value  $\theta$ , which is dependent on the flow time and the size of capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible within  $\pm 0.02$  s. The uncertainty of the viscosity measurement was estimated to be less than  $\pm 0.006$  mPa·s.

The densities and viscosities of six binary systems ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate,

ethyl salicylate, and benzyl propionate + ethanol were measured at  $T = (288.15, 298.15, 308.15, \text{ and } 318.15)$  K. A set with the compositions varying from 0.05 to 0.95 mole fractions of alcohol was prepared for each binary system. The uncertainty in the liquid composition was estimated to be  $\pm 1 \times 10^{-4}$ . All measurements described above were performed at least three times at atmospheric pressure ( $100.5 \pm 0.3$ ) kPa, and an average of at least three measurements was calculated for each.

## Results and Discussion

Tables 3 to 8 list the experimental densities, viscosities, excess molar volumes, and deviations in the viscosities for six binary systems ethyl acetoacetate, ethyl isovalerate, methyl benzoate, benzyl acetate, ethyl salicylate, or benzyl propionate + ethanol at temperatures of 288.15 K, 298.15 K, 308.15 K, and 318.15 K. The values of densities and viscosities decrease systematically

**Table 4. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Ethyl Isovalerate (1) + Ethanol (2)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s
288.15 K														
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.83723	0.908	0.063	-0.260	0.7000	0.85827	0.830	0.079	-0.168
0.0500	0.80264	1.229	0.004	-0.084	0.4000	0.84107	0.886	0.070	-0.257	0.7500	0.86046	0.827	0.073	-0.147
0.1000	0.81036	1.125	0.015	-0.164	0.4500	0.84457	0.867	0.074	-0.252	0.8000	0.86252	0.830	0.064	-0.120
0.1500	0.81713	1.057	0.023	-0.207	0.5000	0.84778	0.855	0.077	-0.240	0.8500	0.86444	0.833	0.054	-0.093
0.2000	0.82305	1.002	0.034	-0.238	0.5500	0.85072	0.847	0.079	-0.224	0.9000	0.86627	0.839	0.041	-0.062
0.2500	0.82830	0.966	0.045	-0.250	0.6000	0.85342	0.840	0.082	-0.207	0.9500	0.86803	0.845	0.018	-0.032
0.3000	0.83301	0.935	0.053	-0.257	0.6500	0.85593	0.835	0.081	-0.187	1.0000	0.86966	0.853	0.000	0.000
298.15 K														
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.82765	0.771	0.092	-0.206	0.7000	0.84838	0.713	0.109	-0.136
0.0500	0.79385	1.020	0.007	-0.067	0.4000	0.83142	0.754	0.100	-0.205	0.7500	0.85055	0.714	0.102	-0.117
0.1000	0.80139	0.945	0.023	-0.123	0.4500	0.83487	0.742	0.105	-0.198	0.8000	0.85260	0.716	0.090	-0.096
0.1500	0.80799	0.891	0.037	-0.159	0.5000	0.83802	0.733	0.109	-0.189	0.8500	0.85452	0.722	0.076	-0.072
0.2000	0.81377	0.848	0.052	-0.184	0.5500	0.84093	0.724	0.110	-0.180	0.9000	0.85634	0.727	0.059	-0.049
0.2500	0.81890	0.815	0.067	-0.198	0.6000	0.84359	0.719	0.114	-0.166	0.9500	0.85812	0.729	0.028	-0.028
0.3000	0.82353	0.791	0.078	-0.204	0.6500	0.84606	0.713	0.113	-0.154	1.0000	0.85978	0.739	0.000	0.000
308.15 K														
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.81796	0.663	0.125	-0.160	0.7000	0.83838	0.618	0.146	-0.108
0.0500	0.78495	0.852	0.013	-0.055	0.4000	0.82166	0.653	0.136	-0.156	0.7500	0.84055	0.619	0.135	-0.093
0.1000	0.79229	0.793	0.035	-0.100	0.4500	0.82505	0.645	0.142	-0.150	0.8000	0.84260	0.621	0.118	-0.077
0.1500	0.79873	0.750	0.054	-0.129	0.5000	0.82815	0.638	0.147	-0.143	0.8500	0.84451	0.625	0.101	-0.059
0.2000	0.80439	0.718	0.073	-0.147	0.5500	0.83101	0.631	0.150	-0.137	0.9000	0.84634	0.631	0.077	-0.039
0.2500	0.80939	0.695	0.094	-0.156	0.6000	0.83364	0.624	0.153	-0.130	0.9500	0.84815	0.634	0.037	-0.022
0.3000	0.81392	0.677	0.108	-0.160	0.6500	0.83609	0.620	0.151	-0.120	1.0000	0.84983	0.642	0.000	0.000
318.15 K														
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.80812	0.579	0.163	-0.120	0.7000	0.82828	0.547	0.188	-0.080
0.0500	0.77590	0.715	0.017	-0.046	0.4000	0.81175	0.571	0.177	-0.118	0.7500	0.83044	0.546	0.173	-0.071
0.1000	0.78304	0.668	0.048	-0.082	0.4500	0.81507	0.565	0.188	-0.114	0.8000	0.83248	0.549	0.154	-0.058
0.1500	0.78931	0.638	0.074	-0.102	0.5000	0.81812	0.559	0.195	-0.109	0.8500	0.83444	0.552	0.125	-0.045
0.2000	0.79481	0.618	0.102	-0.112	0.5500	0.82095	0.554	0.198	-0.104	0.9000	0.83627	0.556	0.097	-0.030
0.2500	0.79973	0.600	0.125	-0.120	0.6000	0.82356	0.550	0.200	-0.098	0.9500	0.83810	0.560	0.048	-0.016
0.3000	0.80415	0.587	0.144	-0.122	0.6500	0.82600	0.548	0.195	-0.090	1.0000	0.83981	0.566	0.000	0.000

**Table 5. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Methyl Benzoate (1) + Ethanol (2)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s
288.15 K														
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.95758	1.455	-0.287	-0.218	0.7000	1.04483	1.807	-0.149	-0.202
0.0500	0.82566	1.324	-0.124	-0.061	0.4000	0.97315	1.496	-0.280	-0.225	0.7500	1.05413	1.870	-0.122	-0.187
0.1000	0.85388	1.323	-0.197	-0.110	0.4500	0.98748	1.541	-0.267	-0.228	0.8000	1.06288	1.942	-0.097	-0.163
0.1500	0.87910	1.338	-0.249	-0.143	0.5000	1.00069	1.589	-0.248	-0.228	0.8500	1.07111	2.030	-0.070	-0.123
0.2000	0.90163	1.359	-0.272	-0.170	0.5500	1.01294	1.640	-0.227	-0.225	0.9000	1.07893	2.118	-0.050	-0.083
0.2500	0.92204	1.383	-0.284	-0.194	0.6000	1.02433	1.692	-0.204	-0.221	0.9500	1.08631	2.207	-0.028	-0.042
0.3000	0.94062	1.417	-0.290	-0.208	0.6500	1.03494	1.746	-0.179	-0.215	1.0000	1.09323	2.297	0.000	0.000
298.15 K														
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.94819	1.199	-0.272	-0.167	0.7000	1.03536	1.475	-0.133	-0.152
0.0500	0.81686	1.092	-0.121	-0.050	0.4000	0.96370	1.232	-0.262	-0.171	0.7500	1.04467	1.526	-0.107	-0.138
0.1000	0.84492	1.094	-0.193	-0.086	0.4500	0.97801	1.266	-0.249	-0.175	0.8000	1.05341	1.581	-0.081	-0.121
0.1500	0.86996	1.107	-0.238	-0.110	0.5000	0.99123	1.303	-0.232	-0.175	0.8500	1.06170	1.645	-0.060	-0.094
0.2000	0.89240	1.122	-0.259	-0.132	0.5500	1.00342	1.341	-0.206	-0.174	0.9000	1.06953	1.712	-0.040	-0.064
0.2500	0.91273	1.144	-0.270	-0.148	0.6000	1.01481	1.384	-0.184	-0.169	0.9500	1.07694	1.784	-0.022	-0.030
0.3000	0.93127	1.171	-0.276	-0.158	0.6500	1.02544	1.429	-0.160	-0.161	1.0000	1.08392	1.851	0.000	0.000
308.15 K														
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.93863	1.006	-0.258	-0.128	0.7000	1.02564	1.231	-0.116	-0.117
0.0500	0.80797	0.911	-0.120	-0.040	0.4000	0.95411	1.031	-0.248	-0.134	0.7500	1.03495	1.275	-0.090	-0.103
0.1000	0.83586	0.915	-0.189	-0.067	0.4500	0.96836	1.061	-0.232	-0.135	0.8000	1.04373	1.318	-0.068	-0.091
0.1500	0.86069	0.924	-0.227	-0.089	0.5000	0.98153	1.091	-0.212	-0.135	0.8500	1.05204	1.369	-0.050	-0.071
0.2000	0.88302	0.940	-0.246	-0.103	0.5500	0.99375	1.123	-0.191	-0.134	0.9000	1.05987	1.421	-0.030	-0.049
0.2500	0.90327	0.958	-0.256	-0.116	0.6000	1.00511	1.158	-0.166	-0.129	0.9500	1.06730	1.480	-0.015	-0.021
0.3000	0.92176	0.981	-0.262	-0.123	0.6500	1.01573	1.193	-0.143	-0.124	1.0000	1.07434	1.531	0.000	0.000
318.15 K														
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.92888	0.855	-0.241	-0.100	0.7000	1.01580	1.047	-0.101	-0.092
0.0500	0.79890	0.766	-0.119	-0.031	0.4000	0.94430	0.877	-0.228	-0.104	0.7500	1.02513	1.083	-0.078	-0.082
0.1000	0.82658	0.770	-0.183	-0.054	0.4500	0.95852	0.902	-0.212	-0.106	0.8000	1.03393	1.122	-0.058	-0.070
0.1500	0.85128	0.782	-0.218	-0.068	0.5000	0.97168	0.928	-0.193	-0.106	0.8500	1.04224	1.166	-0.040	-0.052
0.2000	0.87348	0.797	-0.233	-0.079	0.5500	0.98388	0.954	-0.171	-0.106	0.9000	1.05010	1.208	-0.024	-0.036
0.2500	0.89366	0.814	-0.243	-0.089	0.6000	0.99526	0.982	-0.149	-0.105	0.9500	1.05755	1.255	-0.011	-0.016
0.3000	0.91206	0.834	-0.246	-0.095	0.6500	1.00587	1.014	-0.125	-0.099	1.0000	1.06462	1.297	0.000	0.000

**Table 6. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Benzyl Acetate (1) + Ethanol (2)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s
288.15 K														
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.94782	1.543	-0.265	-0.212	0.7000	1.02155	2.003	-0.143	-0.169
0.0500	0.82552	1.317	-0.120	-0.080	0.4000	0.96141	1.601	-0.262	-0.213	0.7500	1.02905	2.081	-0.114	-0.151
0.1000	0.85286	1.328	-0.188	-0.128	0.4500	0.97374	1.661	-0.252	-0.213	0.8000	1.03605	2.163	-0.085	-0.128
0.1500	0.87656	1.357	-0.220	-0.159	0.5000	0.98492	1.724	-0.231	-0.209	0.8500	1.04259	2.249	-0.056	-0.102
0.2000	0.89758	1.393	-0.250	-0.183	0.5500	0.99520	1.789	-0.210	-0.204	0.9000	1.04878	2.339	-0.035	-0.072
0.2500	0.91618	1.439	-0.262	-0.196	0.6000	1.00468	1.859	-0.189	-0.194	0.9500	1.05457	2.440	-0.011	-0.030
0.3000	0.93286	1.489	-0.269	-0.206	0.6500	1.01340	1.929	-0.163	-0.183	1.0000	1.06011	2.530	0.000	0.000
298.15 K														
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.93844	1.274	-0.250	-0.164	0.7000	1.01210	1.629	-0.130	-0.142
0.0500	0.81673	1.089	-0.118	-0.064	0.4000	0.95200	1.319	-0.247	-0.166	0.7500	1.01958	1.691	-0.099	-0.127
0.1000	0.84391	1.098	-0.184	-0.102	0.4500	0.96429	1.365	-0.235	-0.168	0.8000	1.02661	1.760	-0.074	-0.106
0.1500	0.86747	1.123	-0.213	-0.125	0.5000	0.97544	1.413	-0.212	-0.167	0.8500	1.03316	1.830	-0.046	-0.083
0.2000	0.88840	1.154	-0.241	-0.141	0.5500	0.98572	1.465	-0.192	-0.163	0.9000	1.03939	1.906	-0.031	-0.055
0.2500	0.90692	1.191	-0.251	-0.152	0.6000	0.99521	1.518	-0.173	-0.158	0.9500	1.04521	1.987	-0.011	-0.021
0.3000	0.92354	1.231	-0.257	-0.159	0.6500	1.00392	1.571	-0.146	-0.152	1.0000	1.05075	2.056	0.000	0.000
308.15 K														
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.92898	1.067	-0.232	-0.128	0.7000	1.00256	1.360	-0.108	-0.108
0.0500	0.80783	0.910	-0.115	-0.050	0.4000	0.94250	1.104	-0.226	-0.130	0.7500	1.01007	1.409	-0.080	-0.098
0.1000	0.83485	0.920	-0.177	-0.079	0.4500	0.95476	1.142	-0.212	-0.131	0.8000	1.01713	1.463	-0.058	-0.084
0.1500	0.85828	0.942	-0.203	-0.096	0.5000	0.96591	1.182	-0.190	-0.130	0.8500	1.02371	1.524	-0.034	-0.062
0.2000	0.87910	0.967	-0.227	-0.110	0.5500	0.97617	1.223	-0.168	-0.128	0.9000	1.02998	1.588	-0.024	-0.037
0.2500	0.89757	0.998	-0.236	-0.119	0.6000	0.98566	1.268	-0.150	-0.122	0.9500	1.03584	1.652	-0.009	-0.012
0.3000	0.91412	1.031	-0.239	-0.125	0.6500	0.99438	1.312	-0.124	-0.117	1.0000	1.04139	1.703	0.000	0.000
318.15 K														
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.91938	0.906	-0.208	-0.096	0.7000	0.99296	1.156	-0.082	-0.078
0.0500	0.79878	0.766	-0.113	-0.038	0.4000	0.93288	0.937	-0.201	-0.098	0.7500	1.00051	1.197	-0.058	-0.070
0.1000	0.82563	0.779	-0.170	-0.058	0.4500	0.94512	0.971	-0.185	-0.097	0.8000	1.00760	1.241	-0.039	-0.059
0.1500	0.84894	0.796	-0.191	-0.074	0.5000	0.95627	1.005	-0.163	-0.096	0.8500	1.01422	1.289	-0.019	-0.044
0.2000	0.86966	0.821	-0.211	-0.082	0.5500	0.96652	1.040	-0.139	-0.095	0.9000	1.02053	1.341	-0.013	-0.025
0.2500	0.88807	0.846	-0.218	-0.090	0.6000	0.97603	1.077	-0.122	-0.091	0.9500	1.02644	1.392	-0.005	-0.007
0.3000	0.90456	0.875	-0.218	-0.094	0.6500	0.98476	1.116	-0.096	-0.085	1.0000	1.03203	1.432	0.000	0.000

**Table 7. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Ethyl Salicylate (1) + Ethanol (2)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s
288.15 K														
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.99322	1.902	-0.281	-0.260	0.7000	1.08651	2.664	-0.146	-0.323
0.0500	0.83547	1.398	-0.141	-0.057	0.4000	1.01045	2.001	-0.271	-0.279	0.7500	1.09597	2.800	-0.120	-0.305
0.1000	0.87102	1.467	-0.210	-0.106	0.4500	1.02608	2.104	-0.257	-0.294	0.8000	1.10472	2.943	-0.088	-0.280
0.1500	0.90189	1.533	-0.253	-0.158	0.5000	1.04036	2.209	-0.243	-0.306	0.8500	1.11293	3.100	-0.062	-0.240
0.2000	0.92898	1.615	-0.281	-0.193	0.5500	1.05340	2.317	-0.225	-0.316	0.9000	1.12061	3.268	-0.035	-0.190
0.2500	0.95287	1.708	-0.290	-0.218	0.6000	1.06537	2.428	-0.204	-0.323	0.9500	1.12785	3.503	-0.013	-0.073
0.3000	0.97413	1.800	-0.288	-0.244	0.6500	1.07635	2.543	-0.174	-0.326	1.0000	1.13472	3.694	0.000	0.000
298.15 K														
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.98364	1.526	-0.274	-0.183	0.7000	1.07667	2.096	-0.128	-0.217
0.0500	0.82663	1.145	-0.142	-0.046	0.4000	1.00081	1.598	-0.261	-0.197	0.7500	1.08612	2.187	-0.102	-0.212
0.1000	0.86200	1.197	-0.211	-0.081	0.4500	1.01638	1.677	-0.245	-0.205	0.8000	1.09488	2.288	-0.071	-0.198
0.1500	0.89270	1.258	-0.252	-0.106	0.5000	1.03063	1.757	-0.231	-0.211	0.8500	1.10309	2.398	-0.045	-0.174
0.2000	0.91964	1.322	-0.276	-0.128	0.5500	1.04363	1.838	-0.211	-0.216	0.9000	1.11081	2.522	-0.023	-0.136
0.2500	0.94342	1.388	-0.284	-0.148	0.6000	1.05557	1.921	-0.188	-0.220	0.9500	1.11807	2.706	-0.004	-0.039
0.3000	0.96462	1.455	-0.282	-0.168	0.6500	1.06653	2.006	-0.158	-0.221	1.0000	1.12500	2.831	0.000	0.000
308.15 K														
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.97396	1.254	-0.261	-0.133	0.7000	1.06679	1.695	-0.106	-0.158
0.0500	0.81770	0.953	-0.142	-0.035	0.4000	0.99108	1.313	-0.247	-0.141	0.7500	1.07624	1.766	-0.080	-0.154
0.1000	0.85286	0.998	-0.209	-0.056	0.4500	1.00661	1.373	-0.229	-0.147	0.8000	1.08502	1.846	-0.051	-0.141
0.1500	0.88341	1.043	-0.249	-0.078	0.5000	1.02080	1.435	-0.211	-0.152	0.8500	1.09324	1.932	-0.026	-0.121
0.2000	0.91021	1.094	-0.270	-0.093	0.5500	1.03379	1.498	-0.191	-0.156	0.9000	1.10100	2.030	-0.010	-0.090
0.2500	0.93390	1.147	-0.276	-0.107	0.6000	1.04570	1.561	-0.166	-0.159	0.9500	1.10831	2.163	0.003	-0.023
0.3000	0.95501	1.198	-0.271	-0.123	0.6500	1.05665	1.627	-0.135	-0.160	1.0000	1.11529	2.253	0.000	0.000
318.15 K														
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.96415	1.045	-0.243	-0.101	0.7000	1.05685	1.403	-0.079	-0.118
0.0500	0.80861	0.802	-0.143	-0.023	0.4000	0.98122	1.093	-0.226	-0.106	0.7500	1.06631	1.463	-0.053	-0.111
0.1000	0.84356	0.836	-0.206	-0.042	0.4500	0.99672	1.141	-0.207	-0.112	0.8000	1.07511	1.527	-0.026	-0.101
0.1500	0.87395	0.877	-0.242	-0.055	0.5000	1.01088	1.192	-0.186	-0.114	0.8500	1.08337	1.596	-0.005	-0.085
0.2000	0.90063	0.915	-0.261	-0.070	0.5500	1.02385	1.242	-0.165	-0.118	0.9000	1.09117	1.678	0.008	-0.057
0.2500	0.92422	0.957	-0.263	-0.082	0.6000	1.03576	1.294	-0.140	-0.120	0.9500	1.09855	1.781	0.012	-0.007
0.3000	0.94525	0.999	-0.255	-0.093	0.6500	1.04670	1.347	-0.107	-0.120	1.0000	1.10560	1.842	0.000	0.000

**Table 8. Experimental Densities ( $\rho$ ), Viscosities ( $\eta$ ), Excess Molar Volumes ( $V^E$ ), and Viscosity Deviations ( $\Delta\eta$ ) for System Benzyl Propionate (1) + Ethanol (2)**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s	$x_1$	$\rho$ g·cm <sup>-3</sup>	$\eta$ mPa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta\eta$ mPa·s
288.15 K														
0.0000	0.79360	1.337	0.000	0.000	0.3500	0.94083	1.631	-0.248	-0.131	0.7000	1.00481	2.088	-0.125	-0.098
0.0500	0.82563	1.352	-0.114	-0.046	0.4000	0.95287	1.694	-0.238	-0.128	0.7500	1.01109	2.158	-0.095	-0.089
0.1000	0.85243	1.379	-0.179	-0.079	0.4500	0.96372	1.757	-0.228	-0.126	0.8000	1.01698	2.230	-0.074	-0.077
0.1500	0.87521	1.420	-0.214	-0.099	0.5000	0.97357	1.821	-0.218	-0.123	0.8500	1.02250	2.305	-0.059	-0.063
0.2000	0.89495	1.466	-0.237	-0.114	0.5500	0.98243	1.886	-0.196	-0.118	0.9000	1.02759	2.383	-0.036	-0.046
0.2500	0.91216	1.516	-0.247	-0.124	0.6000	0.99054	1.952	-0.174	-0.113	0.9500	1.03237	2.463	-0.017	-0.026
0.3000	0.92738	1.571	-0.253	-0.130	0.6500	0.99798	2.019	-0.151	-0.106	1.0000	1.03686	2.550	0.000	0.000
298.15 K														
0.0000	0.78500	1.105	0.000	0.000	0.3500	0.93154	1.348	-0.234	-0.113	0.7000	0.99544	1.737	-0.108	-0.081
0.0500	0.81686	1.115	-0.113	-0.041	0.4000	0.94355	1.401	-0.223	-0.111	0.7500	1.00173	1.797	-0.079	-0.071
0.1000	0.84350	1.140	-0.176	-0.067	0.4500	0.95439	1.454	-0.213	-0.109	0.8000	1.00763	1.858	-0.060	-0.061
0.1500	0.86617	1.173	-0.208	-0.085	0.5000	0.96422	1.509	-0.202	-0.105	0.8500	1.01315	1.921	-0.045	-0.049
0.2000	0.88582	1.211	-0.229	-0.098	0.5500	0.97307	1.564	-0.179	-0.101	0.9000	1.01825	1.986	-0.024	-0.035
0.2500	0.90296	1.253	-0.236	-0.107	0.6000	0.98117	1.621	-0.157	-0.095	0.9500	1.02306	2.053	-0.009	-0.019
0.3000	0.91813	1.298	-0.241	-0.112	0.6500	0.98861	1.678	-0.134	-0.089	1.0000	1.02760	2.123	0.000	0.000
308.15 K														
0.0000	0.77631	0.921	0.000	0.000	0.3500	0.92217	1.127	-0.214	-0.097	0.7000	0.98604	1.457	-0.085	-0.070
0.0500	0.80799	0.929	-0.111	-0.035	0.4000	0.93416	1.171	-0.202	-0.096	0.7500	0.99235	1.509	-0.058	-0.061
0.1000	0.83448	0.949	-0.170	-0.059	0.4500	0.94497	1.217	-0.189	-0.094	0.8000	0.99828	1.562	-0.042	-0.052
0.1500	0.85703	0.976	-0.198	-0.075	0.5000	0.95479	1.263	-0.177	-0.091	0.8500	1.00382	1.617	-0.030	-0.040
0.2000	0.87660	1.009	-0.216	-0.085	0.5500	0.96363	1.310	-0.153	-0.087	0.9000	1.00896	1.674	-0.014	-0.026
0.2500	0.89368	1.044	-0.221	-0.094	0.6000	0.97174	1.358	-0.131	-0.083	0.9500	1.01380	1.729	-0.003	-0.015
0.3000	0.90880	1.084	-0.224	-0.097	0.6500	0.97919	1.407	-0.109	-0.077	1.0000	1.01838	1.787	0.000	0.000
318.15 K														
0.0000	0.76744	0.771	0.000	0.000	0.3500	0.91269	0.950	-0.191	-0.081	0.7000	0.97658	1.233	-0.058	-0.059
0.0500	0.79897	0.777	-0.111	-0.031	0.4000	0.92465	0.988	-0.176	-0.081	0.7500	0.98293	1.278	-0.035	-0.051
0.1000	0.82530	0.795	-0.163	-0.050	0.4500	0.93546	1.027	-0.163	-0.079	0.8000	0.98888	1.323	-0.020	-0.043
0.1500	0.84775	0.819	-0.187	-0.064	0.5000	0.94528	1.067	-0.150	-0.076	0.8500	0.99446	1.370	-0.013	-0.033
0.2000	0.86725	0.848	-0.202	-0.072	0.5500	0.95412	1.107	-0.124	-0.073	0.9000	0.99964	1.419	-0.001	-0.022
0.2500	0.88427	0.879	-0.204	-0.078	0.6000	0.96224	1.148	-0.102	-0.069	0.9500	1.00453	1.468	0.002	-0.010
0.3000	0.89934	0.913	-0.203	-0.081	0.6500	0.96971	1.190	-0.081	-0.065	1.0000	1.00915	1.515	0.000	0.000

from 288.15 K to 318.15 K through the whole range of mole fractions. The molar excess volumes ( $V^E$ ) were calculated from density data according to

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

where  $x_i$ ,  $M_i$ , and  $\rho_i$  are the mole fraction, molar mass, and density of the pure component  $i$ , respectively.  $\rho$  is the density of mixture. The deviation of the viscosity from the mole fraction average ( $\Delta\eta$ ) is given by

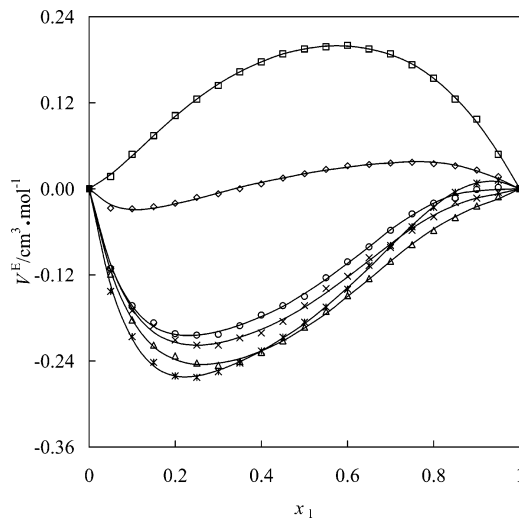
$$\Delta\eta = \eta - \sum_{i=1}^2 x_i \eta_i \quad (3)$$

where  $\eta$  is the absolute viscosities of the mixtures and  $\eta_i$  is the absolute viscosities of pure component  $i$ .

The values of excess molar volumes  $V^E$  increase with a rise in temperature for all of the mixtures. The  $V^E$  values are graphically represented as a function of mole fraction at 298.15 K in Figure 1. It is observed that the  $V^E$  values are negative for the systems methyl benzoate + ethanol, benzyl acetate + ethanol, ethyl salicylate + ethanol, and benzyl propionate + ethanol over the whole composition range, while the positive values were observed for the system ethyl isovalerate + ethanol. For the system of ethyl acetoacetate + ethanol, the values of  $V^E$  are negative except that some positive values were observed in the lower composition region of ethanol. The excess molar volume  $V^E$  ( $x = 0.5$ ) show the order as the sequence: ethyl isovalerate + ethanol > ethyl acetoacetate + ethanol > benzyl propionate + ethanol > benzyl acetate + ethanol > ethyl salicylate + ethanol > methyl benzoate + ethanol. The values

of  $V^E$  ( $x = 0.5$ ) at 298.15 K vary from  $-0.231$  cm<sup>3</sup>·mol<sup>-1</sup> to  $0.109$  cm<sup>3</sup>·mol<sup>-1</sup>.

The dependence of  $V^E$  on both composition and temperature for the present mixtures may be explained as a balance between positive contributions (hydrogen bond rupture, dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components). In the present investigation, alcohols are



**Figure 1.** Change of excess molar volume  $V^E$  with mole fraction  $x_1$  at  $T = 298.15$  K:  $\diamond$ , ethyl acetoacetate + ethanol;  $\square$ , ethyl isovalerate + ethanol;  $\Delta$ , methyl benzoate + ethanol;  $\times$ , benzyl acetate + ethanol;  $*$ , ethyl salicylate + ethanol;  $\circ$ , benzyl propionate + ethanol. Solid curves were calculated from Redlich–Kister equation.

**Table 9.** Coefficients and Standard Deviations ( $\sigma$ ) of  $V^E$  and  $\Delta\eta$  for the Binary Mixtures from  $T = 288.15$  K to  $T = 318.15$  K

$Y$	$T/K$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$\sigma \cdot 10^4$
Ethyl Acetoacetate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	-0.1969	0.1826	-0.1570	0.3911		25
	298.15	-0.1253	0.1870	-0.1598	0.3329		24
	308.15	-0.0286	0.1999	-0.1351	0.2877		26
	318.15	0.8871	0.2079	-0.1363	0.2636		25
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-1.0693	0.4256	-0.5031	0.5141		41
	298.15	-0.8917	0.2934	-0.4042	0.4578		27
	308.15	-0.7398	0.1917	-0.3519	0.4132		14
	318.15	-0.5805	0.1546	-0.3143	0.2692		15
Ethyl Isovalerate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	0.3148	0.1560	-0.0220			18
	298.15	0.4428	0.1967	0.0043			28
	308.15	0.5979	0.2352	0.0172			30
	318.15	0.7851	0.2744	0.0096			32
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-0.9511	0.5910	-0.4397			47
	298.15	-0.7609	0.4450	-0.3064			27
	308.15	-0.5817	0.3502	-0.3181			34
	318.15	-0.4373	0.2801	-0.2781			33
Methyl Benzoate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	-0.99710	0.76361	-0.19892	0.43462	-0.63822	14
	298.15	-0.92303	0.77620	-0.17788	0.44298	-0.64247	15
	308.15	-0.85588	0.78446	-0.12316	0.46484	-0.69039	23
	318.15	-0.77712	0.77103	-0.15509	0.49496	-0.67005	27
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-0.92208	0.07188	-0.28297			51
	298.15	-0.70278	0.07240	-0.21369			36
	308.15	-0.54168	0.07484	-0.16696			31
	318.15	-0.42856	0.05416	-0.09981			33
Benzyl Acetate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	-0.9171	0.6641	-0.4036	0.5949		50
	298.15	-0.8465	0.6833	-0.4310	0.5702		54
	308.15	-0.7534	0.7139	-0.4459	0.5235		6
	318.15	-0.6403	0.7412	-0.4656	0.5106		63
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-0.8333	0.1541	-0.3945	0.3879		23
	298.15	-0.6658	0.0266	-0.3066	0.4695		20
	308.15	-0.5208	0.0235	-0.2078	0.3954		25
	318.15	-0.3873	0.0355	-0.1388	0.3013		19
Ethyl Salicylate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	-0.9569	0.6895	-0.5901	0.8560		46
	298.15	-0.9058	0.7435	-0.5529	0.9155		48
	308.15	-0.8300	0.8141	-0.5379	0.9328		50
	318.15	-0.7315	0.8729	-0.5164	0.9941		55
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-1.2351	-0.4658	-0.6115			79
	298.15	-0.8483	-0.3207	-0.4535			87
	308.15	-0.6161	-0.2169	-0.2897			68
	318.15	-0.4709	-0.1364	-0.1263			67
Benzyl Propionate (1) + Ethanol (2)							
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	288.15	-0.8610	0.6676	-0.6399	0.4991	-0.7141	24
	298.15	-0.7956	0.6812	-0.4941	0.5678	-0.6935	25
	308.15	-0.6960	0.7180	-0.6071	0.5546	-0.6947	28
	318.15	-0.5854	0.7507	-0.3095	0.5692	-0.7719	31
$\Delta\eta/\text{mPa} \cdot \text{s}$	288.15	-0.4910	0.1952	-0.3074			14
	298.15	-0.4214	0.1952	-0.2222			15
	308.15	-0.3657	0.1790	-0.1790			20
	318.15	-0.3063	0.1539	-0.1511			21

strongly self-associated through hydrogen bonding with degrees of association depending on such variables as chain length, the position of the -OH group, temperature, and dilution by other substances. The ester molecules do not exhibit this property because they have no groups having that ability. The interactions of ethanol with ethyl isovalerate molecules involve mainly dispersion force giving a positive contribution to  $V^E$ . The interactions between ethanol and other ester molecules lead to hydrogen bond effects and/or weak dispersion type, giving a negative contribution to  $V^E$ .

In the system studied, the values of viscosity deviation  $\Delta\eta$  are negative and increase with a rise in temperature for all of the mixtures. The  $\Delta\eta$  values are also graphically represented as a function of mole fraction at 298.15 K in Figure 2. It is observed that the  $\Delta\eta$  values are negative over the whole composition range for all of the systems. The minimum value

of  $\Delta\eta$  in the ethyl salicylate + ethanol system is shifted toward higher mole fraction (i.e., at  $x_1 \approx 0.7$ ) and the curve is somewhat skewed. This is suggestive of the specific interaction between ethyl salicylate and ethanol molecules. The values of  $\Delta\eta$  ( $x = 0.5$ ) at 298.15 K vary from  $-0.226$  mPa·s to  $-0.105$  mPa·s. The smallest value of  $\Delta\eta$  ( $x = 0.5$ ) at 298.15 K was found for the system ethyl acetoacetate + ethanol, and the largest value of  $\Delta\eta$  ( $x = 0.5$ ) at 298.15 K was corresponding to the system benzyl propionate + ethanol.

The temperature dependence of  $V^E$  and  $\Delta\eta$  at  $x = 0.5$  for all of the systems studied is shown in Figures 3 and 4. It can be seen that the values of  $V^E$  and  $\Delta\eta$  at  $x = 0.5$  increase as temperature increases for all of the systems. To the best of our knowledge, the mixture properties presented here have not been published earlier; hence, we cannot compare the present results with the literature findings.

Table 10. Parameters of McAllister's Three-Body and Four-Body Interaction Models and Standard Deviations ( $\sigma$ ) for Kinematic Viscosities

$T$ K	three-body			four-body			
	$\nu_{12}$ $\text{mm}^2\cdot\text{s}^{-1}$	$\nu_{21}$ $\text{mm}^2\cdot\text{s}^{-1}$	$10^3\sigma$ $\text{mm}^2\cdot\text{s}^{-1}$	$\nu_{1112}$ $\text{mm}^2\cdot\text{s}^{-1}$	$\nu_{1122}$ $\text{mm}^2\cdot\text{s}^{-1}$	$\nu_{2221}$ $\text{mm}^2\cdot\text{s}^{-1}$	$10^3\sigma$ $\text{mm}^2\cdot\text{s}^{-1}$
Ethyl Acetoacetate (1) + Ethanol (2)							
288.15	1.5932	1.1389	27	1.4747	1.6299	1.0987	8.4
298.15	1.3734	0.9473	16	1.3018	1.2896	0.9505	8.2
308.15	1.1581	0.8216	14	1.0960	1.1168	0.8127	7.1
318.15	1.0258	0.7143	11	0.9805	0.9403	0.7185	8.4
Ethyl Isovalerate (1) + Ethanol (2)							
288.15	0.9865	0.9658	8.2	0.9374	1.0419	1.0418	3.9
298.15	0.8553	0.8412	5.1	0.8247	0.8861	0.9090	2.5
308.15	0.7558	0.7393	7.4	0.7107	0.8145	0.7721	2.8
318.15	0.6797	0.6577	7.6	0.6325	0.7398	0.6726	2.8
Methyl Benzoate (1) + Ethanol (2)							
288.15	1.7334	1.4350	11	1.7358	1.6721	1.4036	5.9
298.15	1.4316	1.1998	8.3	1.4317	1.3829	1.1765	4.4
308.15	1.2131	1.0192	6.8	1.2111	1.1689	0.9996	3.9
318.15	1.0415	0.8840	5.1	1.0482	0.9923	0.8698	3.9
Benzyl Acetate (1) + Ethanol (2)							
288.15	2.0445	1.5396	17	1.9849	1.9480	1.4417	8.5
298.15	1.6668	1.2969	14	1.6266	1.6036	1.2165	9.0
308.15	1.4054	1.1041	11	1.3808	1.3369	1.0426	8.0
318.15	1.2086	0.9573	7.8	1.1933	1.1378	0.9059	5.7
Ethyl Salicylate (1) + Ethanol (2)							
288.15	2.3778	2.0514	15	2.4464	2.3396	1.8110	8.6
298.15	1.8895	1.6664	13	1.9352	1.8717	1.4852	8.6
308.15	1.5330	1.3839	8.9	1.5950	1.5229	1.2487	6.9
318.15	1.3074	1.1647	6.3	1.3598	1.2421	1.0714	6.4
Benzyl Propionate (1) + Ethanol (2)							
288.15	1.8612	1.7426	5.6	1.8419	1.8125	1.6447	4.7
298.15	1.5599	1.4782	3.4	1.5511	1.5167	1.3959	3.0
308.15	1.3259	1.2774	2.9	1.3218	1.2968	1.2005	2.7
318.15	1.1420	1.1321	1.3	1.1532	1.1118	1.0631	1.3

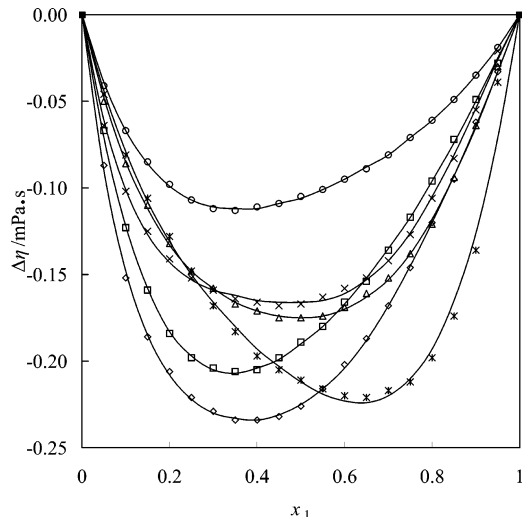


Figure 2. Change of viscosity  $\Delta\eta$  with mole fraction  $x_1$  at  $T = 298.15$  K:  $\diamond$ , ethyl acetoacetate + ethanol;  $\square$ , ethyl isovalerate + ethanol;  $\triangle$ , methyl benzoate + ethanol;  $\times$ , benzyl acetate + ethanol;  $*$ , ethyl salicylate + ethanol;  $\circ$ , benzyl propionate + ethanol. Solid curves were calculated from Redlich–Kister equation.

The mixing functions  $V^E$  and  $\Delta\eta$  were represented mathematically by the Redlich–Kister equation for correlating the experimental data:<sup>20</sup>

$$Y = x_1(1 - x_1) \sum_{k=0}^m a_k(2x_1 - 1)^k \quad (4)$$

where  $Y$  refers to  $V^E/\text{cm}^3\cdot\text{mol}^{-1}$  or  $\Delta\eta/\text{mPa}\cdot\text{s}$ ,  $x_1$  is the mole fraction of component 1, and  $a_k$  is the  $k$ th fitting parameter.

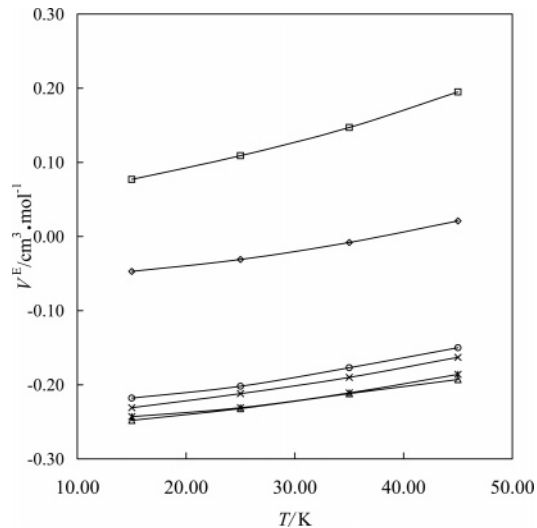
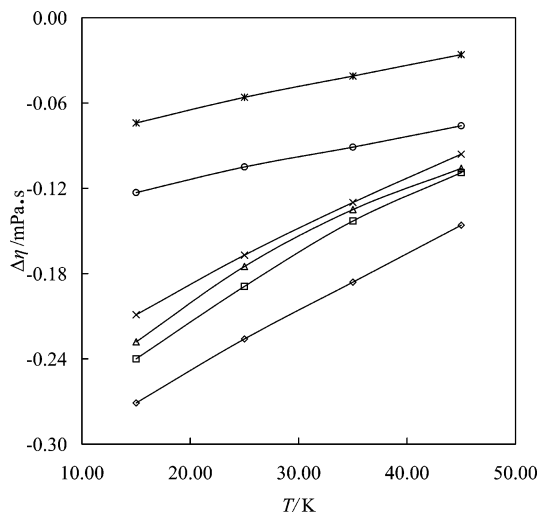


Figure 3. Variation of excess molar volume  $V^E$  at  $x = 0.5$  from  $T = 288.15$  K to  $T = 318.15$  K:  $\diamond$ , ethyl acetoacetate + ethanol;  $\square$ , ethyl isovalerate + ethanol;  $\triangle$ , methyl benzoate + ethanol;  $\times$ , benzyl acetate + ethanol;  $*$ , ethyl salicylate + ethanol;  $\circ$ , benzyl propionate + ethanol. Solid curves were calculated from Redlich–Kister equation.

The values of coefficients  $a_k$  were determined by a nonlinear regression analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 9. The standard deviation ( $\sigma$ ) is defined by

$$\sigma = \left[ \sum_{i=1}^n \frac{(Y_i^{\text{exptl}} - Y_i^{\text{calcd}})^2}{n - p} \right]^{1/2} \quad (5)$$



**Figure 4.** Variation of viscosity deviations  $\Delta\eta$  at  $x = 0.5$  from  $T = 288.15\text{K}$  to  $T = 318.15\text{K}$ :  $\diamond$ , ethyl acetoacetate + ethanol;  $\square$ , ethyl isovalerate + ethanol;  $\triangle$ , methyl benzoate + ethanol;  $\times$ , benzyl acetate + ethanol;  $*$ , ethyl salicylate + ethanol;  $\circ$ , benzyl propionate + ethanol.

where  $n$  is the number of experimental points and  $p$  is the number of adjustable parameters. The  $\sigma$  values lie between  $0.0006\text{ cm}^3\cdot\text{mol}^{-1}$  and  $0.0055\text{ cm}^3\cdot\text{mol}^{-1}$  and between  $0.0014\text{ mPa}\cdot\text{s}$  for  $V^E$  and  $\Delta\eta$ , respectively.

McAllister's multibody interaction model<sup>21</sup> is widely used for correlating the kinematic viscosity of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln \left( x_1 + \frac{x_2 M_2}{M_1} \right) + 3x_1^2 x_2 \ln \left( \frac{2 + M_2/M_1}{3} \right) + 3x_1 x_2^2 \ln \left( \frac{1 + 2M_2/M_1}{3} \right) + x_2^3 \ln \left( \frac{M_2}{M_1} \right) \quad (6)$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln \nu_{1112} + 6x_1^2 x_2^2 \ln \nu_{1122} + 4x_1 x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln \left( x_1 + \frac{x_2 M_2}{M_1} \right) + 4x_1^3 x_2 \ln \left( \frac{3 + M_2/M_1}{4} \right) + 6x_1^2 x_2^2 \ln \left( \frac{1 + M_2/M_1}{2} \right) + 4x_1 x_2^3 \ln \left( \frac{1 + 3M_2/M_1}{4} \right) + x_2^4 \ln \left( \frac{M_2}{M_1} \right) \quad (7)$$

where  $\nu$ ,  $\nu_1$ , and  $\nu_2$  are the kinematic viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. The  $\nu_{12}$ ,  $\nu_{21}$ ,  $\nu_{1112}$ ,  $\nu_{1122}$ , and  $\nu_{2221}$  are the model parameters. Table 10 records the calculated results with the standard deviation ( $\sigma$ ) defined as eq 5. It is shown that McAllister's four-body equation generally gave a better result for those three systems. The  $\sigma/\text{mm}^2\cdot\text{s}^{-1}$  values for the four-body model lie between 0.0013 and 0.0090, and the largest value corresponds to the benzyl acetate + ethanol system at  $T = 298.15\text{ K}$ .

## Conclusion

Experimental determinations of densities and viscosities were carried out at the temperatures 288.15 to 318.15 K and at atmospheric pressure over entire composition range for six binary mixtures ethyl acetoacetate, ethyl isovalerate, methyl

benzoate, benzyl acetate, ethyl salicylate, or benzyl propionate + ethanol. Excess molar volumes ( $V^E$ ) and deviations in the viscosity from mole fraction average ( $\Delta\eta$ ) for the binary mixtures were derived from experimental data. The values of  $V^E$  and  $\Delta\eta$  increase with a rise in temperature for all of the mixtures. The binary data of  $V^E$  and  $\Delta\eta$  were correlated by using the Redlich–Kister equation. The binary kinematic viscosities were correlated by the McAllister three- and four-body interaction equations. Both the Redlich–Kister equation and the McAllister equation can represent data very well.

## Literature Cited

- (1) Nikam, P. S.; Kharat, S. J. Density and viscosity studies of binary mixtures of *N,N*-dimethylformamide with toluene and methyl benzoate at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data* **2005**, *50*, 455–459.
- (2) Nayak, J. N.; Aralaguppi, M. I.; Aminabhavi, T. M. Density, viscosity, refractive index, and speed of sound in the binary mixtures of 1,4-dioxane + ethyl acetoacetate, + diethyl oxalate, + diethyl phthalate, or + dioctyl phthalate at 298.15, 303.15, and 308.15 K. *J. Chem. Eng. Data* **2003**, *48*, 1489–1494.
- (3) Garcia, B.; Alcalde, R.; Aparicio, S.; Leal, J. M. Thermophysical behavior of methylbenzoate + *n*-alkanes mixed solvents. Application of cubic equations of state and viscosity models. *Ind. Eng. Chem. Res.* **2002**, *41*, 4399–4408.
- (4) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Thermodynamic properties and ideal-gas enthalpies of formation for methyl benzoate, ethyl benzoate, (*R*)-(+)-limonene, *tert*-amyl methyl ether, *trans*-crotonaldehyde, and diethylene glycol. *J. Chem. Eng. Data* **2002**, *47*, 667–688.
- (5) Garcia, B.; Alcalde, R.; Aparicio, S.; Leal, J. M. Volumetric properties, viscosities, and refractive indices of binary mixed solvents containing methyl benzoate. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5833–5840.
- (6) Indraswati, N.; Mudjijati; Wicaksana, F.; Hindarso, H.; Ismadji, S. Measurements of density and viscosity of binary mixture of several flavor compounds with 1-butanol and 1-pentanol at 293.15 K, 303.15 K, 313.15 K, and 323.15 K. *J. Chem. Eng. Data* **2001**, *46*, 696–702.
- (7) Kauffman, G. W.; Jurs, P. C. Prediction of surface tension, viscosity, and thermal conductivity for common organic solvents using quantitative structure–property relationships. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 408–418.
- (8) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950; Vol. I.
- (9) Marcus, Y. *The Properties of Solvents*; John Wiley and Sons: West Sussex, U.K., 1998.
- (10) Djojoputro, H.; Ismadji, S. Density and viscosity correlation for several common fragrance and flavor esters. *J. Chem. Eng. Data* **2005**, *50*, 727–731.
- (11) Garcia, B.; Alcalde, R.; Aparicio, S.; Leal, J. M. Thermophysical behavior of methylbenzoate + *n*-alkanes mixed solvents. Application of cubic equations of state and viscosity models. *Ind. Eng. Chem. Res.* **2002**, *41*, 4399–4408.
- (12) Aminabhavi, T. M.; Phayde, H. T. S.; Khinnavar, R. S.; Gopalkrishna, B.; Hansen, K. C. 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. *J. Chem. Eng. Data* **1994**, *39*, 251–260.
- (13) Rodriguez, A.; Canosa, J.; Tojo, J. Dynamic viscosities of diethyl carbonate with linear and secondary alcohols at several temperatures. *J. Chem. Eng. Data* **2004**, *49*, 157–162.
- (14) Riddick, J. A.; Bunger, W. S.; Sakano, T. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.
- (15) Segade, L.; Jiménez de Liano, J.; Domínguez-Pérez, M.; Cabeza, O.; Cabanas, M.; Jiménez, E. Density, surface tension, and refractive index of octane + 1-alkanol mixtures at  $T = 298.15\text{ K}$ . *J. Chem. Eng. Data* **2003**, *48*, 1251–1255.
- (16) Azizian, S.; Hemmati, M. Surface tension of binary mixtures of ethanol + ethylene glycol from 20 to 50 °C. *J. Chem. Eng. Data* **2003**, *48*, 662–663.
- (17) Chen, S.; Fang, W.; Yao, J.; Zong, H. Density and refractive index at 298.15 K and vapor–liquid equilibria at 101.3 kPa for binary mixtures of ethanol + *N*-methylpiperazine. *J. Chem. Eng. Data* **2001**, *46*, 596–600.



- (18) Agarwal, D.; Singh, M. Densities and viscosities of binary liquid mixtures of trichloroethylene and tetrachloroethylene with some polar and nonpolar solvents. *J. Chem. Eng. Data* **2004**, *49*, 1218–1224.
- (19) Brocos, P.; Piñeiro, Á.; Bravo, R.; Amigo, A. Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. *Phys. Chem. Chem. Phys.* **2003**, *5*, 550–557.
- (20) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
- (21) McAllister, R. A. The viscosity of liquid mixtures. *AIChE J.* **1960**, *6*, 427–431.

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