

Density and Viscosity of Binary Mixtures of Ethyl-2-methylbutyrate and Ethyl Hexanoate with Methanol, Ethanol, and 1-Propanol at (293.15, 303.15, and 313.15) K

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The density and viscosity of binary mixtures of ethyl-2-methylbutyrate and ethyl hexanoate with methanol, ethanol, and 1-propanol over the whole composition range have been measured at three different temperatures (293.15, 303.15, and 313.15) K and atmospheric pressure. A Redlich–Kister-type polynomial equation was fitted to the calculated excess molar volumes and viscosity deviations.

Introduction

Fragrance and flavor substances are comparatively strong-smelling organic compounds with characteristic pleasant odors. These compounds are usually used for flavoring in foods and beverages as well as fragrance in perfumes and perfumed products. Physical properties such as the density and viscosity of binary mixtures of these compounds and other solvents are important from practical and theoretical points of view to the understanding of liquid theories. Several studies^{1–12} have been conducted to measure the density and viscosity of flavor substances in their mixtures; however, reliable density and viscosity data over a wide range of composition and temperature for different flavor systems are still needed.

Ethyl-2-methylbutyrate and ethyl hexanoate are important esters in process manufacturing in the flavor and fragrance industries. To our knowledge, the density and viscosity of these esters in binary mixtures with methanol, ethanol, and propanol at different temperatures and compositions have not been studied.

This article reports the experimental density and viscosity data of the binary mixtures of the above compounds at (293.15, 303.15, and 313.15) K. From these data, the excess molar volumes and the viscosity deviations were also calculated.

Experimental Section

Materials. High-purity and AR-grade samples of methanol, ethanol, propanol, ethyl-2-methylbutyrate, and ethyl hexanoate were purchased from Sigma-Aldrich Singapore. The purity of these chemicals was analyzed by gas chromatography (Shimadzu, GC-17A) using a flame ionization detector with a DB-5 column. Helium (high purity) was used as the carrier gas. Because the purity of all of the compounds was >99.0% (by weight), these compounds were used without any further purification.

The binary mixture samples were prepared by mass in airtight-stoppered glass bottles using a Mettler Toledo AE 240 balance with an uncertainty of $\pm 10^{-5}$ g. The uncertainty of the mole fraction for each binary mixture is less than 0.0001.

Table 1. Comparison of the Experimental Density and Viscosity of Ethyl-2-methylbutyrate, Ethyl Hexanoate, Methanol, Ethanol, and 1-Propanol with Literature Values at 293.15 K, 303.15 K, and 313.15 K

compound	T/K	$\rho_l/\text{g}\cdot\text{cm}^{-3}$		$\eta_l/\text{mPa}\cdot\text{s}$	
		expt	lit	expt	lit
ethyl 2-methylbutyrate	293.15	0.86973		0.831	
	303.15	0.86148		0.723	
	313.15	0.85341		0.635	
ethyl hexanoate	293.15	0.87901	0.87100 ¹³	0.816	
	303.15	0.86931		0.704	
	313.15	0.86328		0.614	
methanol	293.15	0.79108		0.577	
	303.15	0.78195	0.78199 ¹⁴	0.512	0.516 ¹⁴
	313.15	0.77201	0.77221 ¹⁵	0.447	
ethanol	293.15	0.78824		1.160	
	303.15	0.78073	0.78080 ¹⁶	0.968	0.995 ¹⁶
	313.15	0.77198	0.78068 ¹⁵ 0.77213 ¹⁵	0.810	0.987 ¹⁵ 0.814 ¹⁵
1-propanol	293.15	0.80364		2.188	
	303.15	0.79548	0.79540 ¹⁵	1.713	1.705 ¹⁵
	313.15	0.78702	0.78710 ¹⁵	1.378	

Density Measurements. The measurements of the densities of the pure components and the binary mixtures were carried out using a Mettler Toledo density meter type DE50 with an uncertainty of about 10^{-5} g·cm⁻³. Prior to measurement, the instrument was calibrated with double-distilled water at 293.15 K, 303.15 K, and 313.15 K. The temperature of the measuring cell was maintained at 293.15 K, 303.15 K, and 313.15 K using Julabo refrigerated and heating circulators, model F12-MD, with an uncertainty of 0.1 K.

Viscosity Measurements. For the viscosity measurement, an automatic microviscosimeter (Anton Paar type AMV_n) equipped with an automatic timer (± 0.01 s) was used. This instrument uses the rolling ball principle according to DIN 53015 and ISO/DIS 12058, where gold-covered steel balls roll down inside an inclined, sample-filled glass capillary. The uncertainty of time in the range of (0 to 250) s is less than 0.02 s with a precision of ± 0.01 s. The temperature range of this viscosimeter is from (283.15 to 343.15) K with an uncertainty of less than 0.05 K. The calibration of the instrument was performed periodically with double-distilled water. The uncertainty

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Table 2. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl-2-methylbutyrate (1) + Methanol (2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K											
0.0000	0.79108	0.577	0.000	0.4001	0.82255	0.667	2.507	0.8028	0.85422	0.773	1.592
0.1084	0.79961	0.600	1.038	0.4982	0.83026	0.692	2.587	0.9144	0.86300	0.805	0.779
0.2031	0.80705	0.621	1.723	0.6152	0.83947	0.722	2.422	1.0000	0.86973	0.831	0.000
0.3197	0.81622	0.648	2.289	0.7045	0.84649	0.746	2.113				
303.15 K											
0.0000	0.78195	0.512	0.000	0.4001	0.81377	0.588	2.585	0.8028	0.84580	0.675	1.640
0.1084	0.79057	0.531	1.071	0.4982	0.82157	0.608	2.667	0.9144	0.85467	0.702	0.803
0.2031	0.79810	0.549	1.777	0.6152	0.83088	0.633	2.497	1.0000	0.86148	0.723	0.000
0.3197	0.80738	0.572	2.361	0.7045	0.83798	0.653	2.177				
313.15 K											
0.0000	0.77201	0.447	0.000	0.4001	0.80458	0.514	2.698	0.8028	0.83736	0.593	1.710
0.1084	0.78083	0.464	1.119	0.4982	0.81256	0.532	2.782	0.9144	0.84644	0.616	0.836
0.2031	0.78854	0.480	1.856	0.6152	0.82209	0.555	2.604	1.0000	0.85341	0.635	0.000
0.3197	0.79803	0.500	2.465	0.7045	0.82936	0.572	2.270				

Table 3. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl Hexanoate (1) + Methanol(2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K											
0.0000	0.79108	0.577	0.000	0.4008	0.82632	0.663	3.159	0.8074	0.86207	0.763	1.961
0.0902	0.79901	0.595	1.116	0.5031	0.83532	0.687	3.253	0.9105	0.87114	0.791	1.017
0.2147	0.80996	0.622	2.263	0.6098	0.84470	0.713	3.062	1.0000	0.87901	0.816	0.000
0.3046	0.81786	0.641	2.815	0.7106	0.85356	0.738	2.619				
303.15 K											
0.0000	0.78195	0.512	0.000	0.4008	0.81696	0.582	3.209	0.8074	0.85248	0.662	1.991
0.0902	0.78983	0.527	1.134	0.5031	0.82590	0.601	3.304	0.9105	0.86149	0.684	1.033
0.2147	0.80071	0.548	2.299	0.6098	0.83522	0.622	3.110	1.0000	0.86931	0.704	0.000
0.3046	0.80856	0.564	2.860	0.7106	0.84403	0.642	2.660				
313.15 K											
0.0000	0.77201	0.447	0.000	0.4008	0.80859	0.508	3.405	0.8074	0.84570	0.578	2.108
0.0902	0.78024	0.460	1.206	0.5031	0.81793	0.524	3.504	0.9105	0.85511	0.597	1.092
0.2147	0.79161	0.479	2.442	0.6098	0.82767	0.543	3.296	1.0000	0.86328	0.614	0.000
0.3046	0.79981	0.492	3.036	0.7106	0.83687	0.560	2.817				

Table 4. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl 2-Methylbutyrate (1) + Ethanol (2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_L/\text{g}\cdot\text{cm}^{-3}$	$\eta_L/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K											
0.0000	0.78824	1.160	0.000	0.4058	0.82131	1.013	2.185	0.8056	0.85389	0.886	1.365
0.1148	0.79760	1.116	0.948	0.5096	0.82977	0.978	2.242	0.9049	0.86198	0.857	0.743
0.2087	0.80525	1.082	1.526	0.6143	0.83830	0.945	2.104	1.0000	0.86973	0.831	0.000
0.3049	0.81309	1.047	1.940	0.7033	0.84555	0.917	1.837				
303.15 K											
0.0000	0.78073	0.968	0.000	0.4058	0.81350	0.859	2.207	0.8056	0.84578	0.765	1.379
0.1148	0.79000	0.936	0.958	0.5096	0.82188	0.834	2.264	0.9049	0.85380	0.743	0.750
0.2087	0.79758	0.910	1.542	0.6143	0.83033	0.809	2.125	1.0000	0.86148	0.723	0.000
0.3049	0.80535	0.885	1.960	0.7033	0.83752	0.788	1.855				
313.15 K											
0.0000	0.77198	0.810	0.000	0.4058	0.80502	0.733	2.267	0.8056	0.83758	0.665	1.415
0.1148	0.78133	0.787	0.985	0.5096	0.81348	0.715	2.326	0.9049	0.84567	0.649	0.770
0.2087	0.78897	0.769	1.585	0.6143	0.82200	0.697	2.182	1.0000	0.85341	0.635	0.000
0.3049	0.79681	0.752	2.014	0.7033	0.82925	0.682	1.905				

in the viscosity measurement was estimated to be less than 0.004 mPa·s. The measuring temperature was kept at 293.15 K, 303.15 K, and 313.15 K by placing the sample-filled glass capillary in a block controlled by a Julabo refrigerated and heating circulator.

All measurements described above were performed at least three times, and the results were averaged to give the final values. A comparison between the experimental results of the density and viscosity of pure liquids and those from the literature is given in Table 1. From this Table, it is clear that the experimental values of the density and viscosity of pure liquids are generally in agreement with those from the literature.^{13–16} The experimental and literature values for the density of ethyl hexanoate are different because of the different purities of ethyl hexanoate used.

Results and Discussion

The density and viscosity data of binary mixtures of ethyl-2-methylbutyrate (1) + methanol (2), ethyl hexanoate (1) + methanol (2), ethyl-2-methylbutyrate (1) + ethanol (2), ethyl hexanoate (1) + ethanol (2), ethyl-2-methylbutyrate (1) + 1-propanol (2), and ethyl hexanoate (1) + 1-propanol (2) at (293.15, 303.15, and 313.15) K are given in Tables 2–7. The excess molar volume, V^E , was calculated from the density data according to the following equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_L} - (x_1 V_1 + x_2 V_2) \quad (1)$$

where ρ_L is the density of the mixture and x_1 , V_1 , M_1 , x_2 , V_2 , and M_2 are the mole fraction, molar volume, and

Table 5. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl Hexanoate (1) + Ethanol (2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K											
0.0000	0.78824	1.160	0.000	0.4008	0.82462	1.007	2.794	0.8046	0.86127	0.874	1.751
0.1044	0.79772	1.118	1.125	0.5171	0.83518	0.967	2.869	0.9051	0.87040	0.843	0.947
0.2078	0.80710	1.078	1.957	0.5908	0.84187	0.942	2.755	1.0000	0.87901	0.816	0.000
0.3105	0.81642	1.039	2.516	0.7133	0.85299	0.902	2.300				
303.15 K											
0.0000	0.78073	0.968	0.000	0.4008	0.81623	0.852	2.788	0.8046	0.85200	0.749	1.749
0.1044	0.78998	0.936	1.122	0.5171	0.82653	0.821	2.863	0.9051	0.86090	0.725	0.945
0.2078	0.79914	0.906	1.952	0.5908	0.83306	0.801	2.750	1.0000	0.86931	0.704	0.000
0.3105	0.80823	0.876	2.510	0.7133	0.84391	0.771	2.296				
313.15 K											
0.0000	0.77198	0.810	0.000	0.4008	0.80857	0.724	2.914	0.8046	0.84544	0.648	1.825
0.1044	0.78151	0.786	1.174	0.5171	0.81919	0.701	2.997	0.9051	0.85462	0.630	0.986
0.2078	0.79095	0.764	2.042	0.5908	0.82592	0.687	2.872	1.0000	0.86328	0.614	0.000
0.3105	0.80033	0.743	2.625	0.7133	0.83710	0.664	2.397				

Table 6. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl-2-methylbutyrate (1) + 1-Propanol (2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K							
0.0000	0.80364	2.188	0.000	0.6051	0.84363	1.218	1.405
0.1132	0.81112	1.961	0.614	0.7244	0.85152	1.085	1.163
0.2146	0.81782	1.778	1.022	0.8134	0.85740	0.996	0.878
0.2937	0.82305	1.647	1.250	0.9057	0.86350	0.910	0.490
0.4056	0.83045	1.477	1.440	1.0000	0.86973	0.831	0.000
0.4903	0.83604	1.361	1.482				
303.15 K							
0.0000	0.79548	1.713	0.000	0.6051	0.83542	1.016	1.429
0.1132	0.80295	1.554	0.625	0.7244	0.84329	0.917	1.183
0.2146	0.80964	1.424	1.040	0.8134	0.84916	0.849	0.893
0.2937	0.81486	1.329	1.272	0.9057	0.85526	0.784	0.499
0.4056	0.82225	1.207	1.465	1.0000	0.86148	0.723	0.000
0.4903	0.82784	1.122	1.508				
313.15 K							
0.0000	0.78702	1.378	0.000	0.6051	0.82719	0.862	1.464
0.1132	0.79454	1.262	0.640	0.7244	0.83511	0.786	1.211
0.2146	0.80127	1.167	1.066	0.8134	0.84102	0.734	0.914
0.2937	0.80652	1.098	1.303	0.9057	0.84715	0.683	0.511
0.4056	0.81395	1.006	1.501	1.0000	0.85341	0.635	0.000
0.4903	0.81957	0.943	1.545				

Table 7. Experimental Density and Viscosity and Excess Molar Volume of Binary Mixtures of Ethyl Hexanoate (1) + 1-Propanol (2) at 293.15 K, 303.15 K, and 323.15 K

x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	x_1	$\rho_l/\text{g}\cdot\text{cm}^{-3}$	$\eta_l/\text{mPa}\cdot\text{s}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$
293.15 K							
0.0000	0.80364	2.188	0.000	0.6024	0.84904	1.208	1.901
0.1032	0.81142	1.976	0.769	0.7056	0.85682	1.091	1.634
0.2075	0.81928	1.783	1.352	0.8184	0.86532	0.976	1.157
0.3144	0.82734	1.605	1.756	0.9035	0.87174	0.898	0.674
0.4082	0.83441	1.463	1.951	1.0000	0.87901	0.816	0.000
0.5003	0.84135	1.336	2.002				
303.15 K							
0.0000	0.79548	1.713	0.000	0.6024	0.83996	1.003	1.905
0.1032	0.80310	1.563	0.770	0.7056	0.84757	0.915	1.637
0.2075	0.81080	1.424	1.355	0.8184	0.85590	0.827	1.160
0.3144	0.81869	1.295	1.759	0.9035	0.86219	0.767	0.675
0.4082	0.82562	1.192	1.954	1.0000	0.86931	0.704	0.000
0.5003	0.83242	1.098	2.006				
313.15 K							
0.0000	0.78702	1.378	0.000	0.6024	0.83296	0.847	1.991
0.1032	0.79489	1.268	0.806	0.7056	0.84083	0.779	1.711
0.2075	0.80284	1.165	1.418	0.8184	0.84943	0.711	1.212
0.3144	0.81100	1.069	1.841	0.9035	0.85592	0.664	0.705
0.4082	0.81815	0.991	2.045	1.0000	0.86328	0.614	0.000
0.5003	0.82517	0.919	2.098				

molecular weight of pure compounds 1 and 2, respectively. The average uncertainty for V^E is less than $0.001 \text{ cm}^3\cdot\text{mol}^{-1}$. The excess molar volume values calculated from eq 1 are also summarized in Tables 2–7. The excess molar volumes

for all mixtures are positive and increase with increasing temperature from 298.15 K to 313.15 K. The positive V^E values are due to several factors such as the declustering of alcohol in the presence of ester,^{1,4,15} repulsive forces due

Table 8. Parameters and Standard Deviations of the Redlich–Kister Polynomial Equation for Selected Ester + Ethanol Systems

T/K	A_0	A_1	A_2	A_3	σ	T/K	A_0	A_1	A_2	A_3	σ		
Ethyl-2-methylbutyrate (1) + Methanol (2)						Ethyl Hexanoate (1) + Ethanol (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	10.3463	-0.4900	0.0232	-0.0011	0.0014	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	11.5094	-0.6266	0.0342	-0.0019	0.0012
	303.15	10.6658	-0.5162	0.0250	-0.0012	0.0009		303.15	11.4852	-0.61666	0.0332	-0.0018	0.0010
	313.15	11.1279	-0.5573	0.0279	-0.0014	0.0011		313.15	11.9996	-0.6699	0.0375	-0.0021	0.0009
$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.0462	-0.0028	0.0001	-0.0001	0.0006	$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.0618	0.0076	-0.0035	-0.0112	0.0009
	303.15	-0.0363	-0.0021	-0.0001	-0.0003	0.0012		303.15	-0.0434	0.0019	-0.0029	-0.0011	0.0035
	313.15	-0.0329	-0.0019	-0.0001	0.0001	0.0003		313.15	-0.0299	-0.0013	-0.0025	0.0109	0.0030
Ethyl Hexanoate (1) + Methanol (2)						Ethyl-2-methylbutyrate (1) + 1-Propanol (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	13.0159	-0.6853	0.0361	-0.0019	0.0009	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	5.9266	-0.2341	0.0093	-0.0004	0.0018
	303.15	13.2228	-0.6996	0.0371	-0.0019	0.0007		303.15	6.0304	-0.2402	0.0096	-0.0004	0.0015
	313.15	14.0200	-0.7825	0.0438	-0.0024	0.0013		313.15	6.1772	-0.2500	0.0101	-0.0004	0.0016
$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.0413	-0.0024	-0.0001	-0.000015	0.0002	$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.6443	0.1032	-0.0125	0.0012	0.0004
	303.15	-0.0305	-0.0016	-0.00008	-0.000019	0.0001		303.15	-0.4205	0.0601	-0.0065	0.0006	0.0003
	313.15	-0.0265	-0.0014	-0.0005	0.000013	0.0003		313.15	-0.2843	0.0365	-0.0035	0.0003	0.0003
Ethyl-2-methylbutyrate (1) + Ethanol (2)						Ethyl Hexanoate (1) + 1-Propanol (2)							
$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	8.9781	-0.4413	0.0217	-0.0011	0.0012	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	293.15	8.0088	-0.3587	0.0161	-0.0007	0.0011
	303.15	9.0677	-0.4459	0.0220	-0.0011	0.0009		303.15	8.0238	-0.3558	0.0158	-0.0007	0.0015
	313.15	9.3149	-0.4667	0.0234	-0.0012	0.0008		313.15	8.3928	-0.3878	0.0179	-0.0008	0.0014
$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.0561	0.0050	-0.0057	-0.0096	0.0012	$\Delta\eta/\text{mPa}\cdot\text{s}$	293.15	-0.6632	0.1082	-0.0133	0.0013	0.0011
	303.15	-0.0375	0.0070	-0.0021	-0.0102	0.0011		303.15	-0.4414	0.0650	-0.0072	0.0007	0.0001
	313.15	-0.0230	0.0008	-0.0087	-0.0017	0.0057		313.15	-0.3047	0.0408	-0.0041	0.0004	0.0002

to the electronic charges of both components, and more domination of steric hindrance in the ester molecules. From Tables 2–7, it can be seen that the excess molar volume values of ester + alcohol systems decrease with increasing

alcohol molecular weight/size. This phenomenon indicates that interstitial accommodation becomes important with increasing alcohol size.¹⁷ Interstitial accommodation and orientation ordering lead to a more compact structure and tend to decrease V^E values. Figure 1 depicts the excess molar volumes for all systems at 303.15 K.

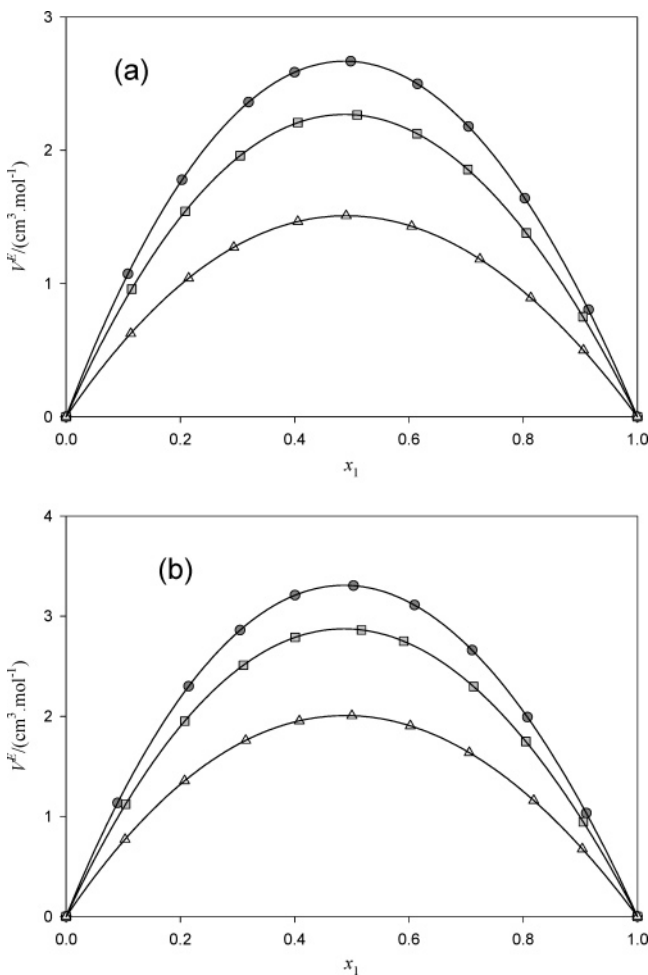


Figure 1. Excess molar volume, V^E , at 303.15 K for (a) ●, ethyl 2-methylbutyrate (1) + methanol (2); □, ethyl 2-methylbutyrate (1) + ethanol (2); and △, ethyl-2-methylbutyrate (1) + 1-propanol (2) and (b) ●, ethyl hexanoate (1) + methanol (2); □, ethyl hexanoate (1) + ethanol (2); and △, ethyl hexanoate (1) + 1-propanol (2).

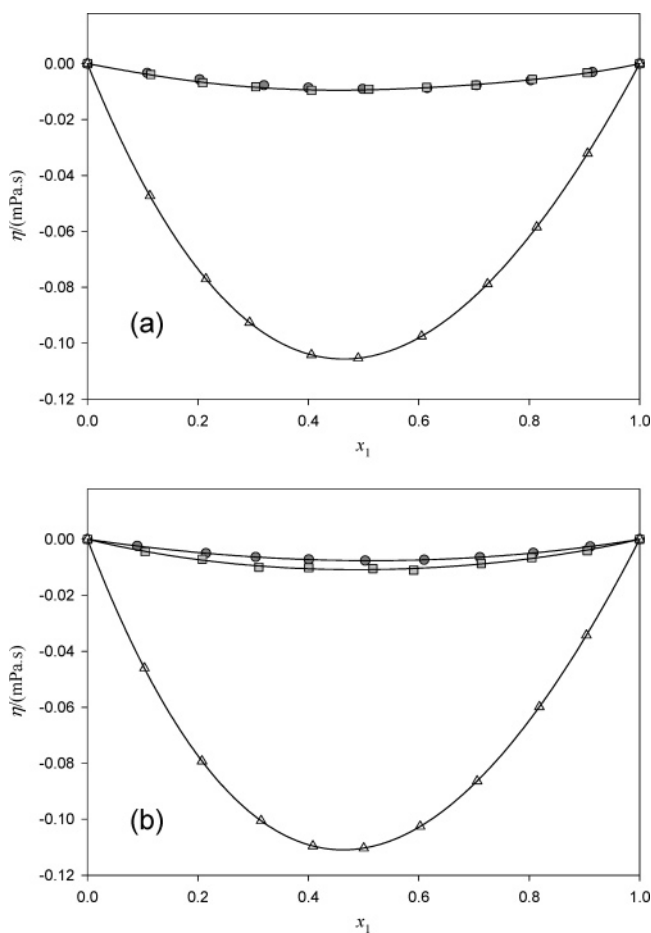


Figure 2. Viscosity deviation, η , at 303.15 K for (a) ●, ethyl 2-methylbutyrate (1) + methanol (2); □, ethyl 2-methylbutyrate (1) + ethanol (2); and △, ethyl 2-methylbutyrate (1) + 1-propanol (2) and (b) ●, ethyl hexanoate (1) + methanol (2); □, ethyl hexanoate (1) + ethanol (2); and △, ethyl hexanoate (1) + 1-propanol (2).

The viscosity deviations were also calculated using the experimental values of viscosity listed in Table 2–7. The following equation was used to obtain the viscosity deviations, $\Delta\eta$,

$$\Delta\eta = \eta_L - x_1\eta_{L1} - x_2\eta_{L2} \quad (2)$$

where η_L is the measured mixture viscosity and η_{L1} and η_{L2} represent the pure-component viscosities. The viscosity deviations of all systems at 303.15 K are given in Figure 2. The viscosity deviations for all systems are negative over the entire composition range and become more negative with increasing alcohol chain length, suggesting a decrease in the hetero-association of molecules with increasing alcohol molar mass.⁴

The well-known Redlich–Kister polynomial equation, which has the following form

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{i=0}^n A_i(x_1 - x_2)^i \quad (3)$$

or

$$\Delta\eta/\text{mPa}\cdot\text{s} = x_1x_2\sum_{i=0}^n A_i(x_1 - x_2)^i \quad (4)$$

was used to correlate the experimental data. The coefficients A_i were evaluated from a least-squares method, and the results together with the standard deviations, σ , are presented in Table 8. From this Table, it is clear that the Redlich–Kister polynomial equation can represent the excess molar volume and viscosity deviation very well, which is indicated by a low standard deviation.

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