Study on Properties Derived from Densities and Viscosities for the Ternary Systems (Methyl Pentanoate or Methyl Heptanoate) + Octane + 1-Hexanol and Their Binary Subsystems at Various Temperatures

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The density and kinematic viscosity of the binary systems (methyl pentanoate or methyl heptanoate) + 1-hexanol and octane + 1-hexanol were determined at (293.15, 303.15, and 313.15) K and atmospheric pressure over the whole concentration range. Moreover, the same properties were determined for the ternary systems (methyl pentanoate or methyl heptanoate) + octane + 1-hexanol at the same experimental conditions. The experimental binary and ternary viscosities were used to evaluate the applicability of several empirical and semiempirical correlation models available in the literature. The excess volumes of the binary and ternary mixtures were compared to those predicted by the group-contribution model proposed by Nitta et al. using structural and energetic parameter sets previously reported in the literature. Also, viscosities were used to test the predictive capability of two group-contribution models (UNIVAC and UNIFAC-VISCO).

Introduction

Densities and viscosities of multicomponent liquid mixtures are required for the design of processes involving heat transfer and mass transfer. Besides, the derived properties (excess molar volumes and viscosity deviations), in combination with other mixing properties, provide valuable information as much for qualitatively analyzing the molecular interactions and for understanding structural effects which occur in the chosen mixtures as for evaluating the efficiency and the predictive capability of the solution models.

In this work, which is a contribution to the study of ternary systems composed by an aliphatic ester, an *n*-alkane, and a 1-alcohol, we have determined densities, kinematic viscosities, and related properties for the binary systems (methyl pentanoate or methyl heptanoate) + 1-hexanol and octane + 1-hexanol at (293.15, 303.15, and 313.15) K and atmospheric pressure over the entire composition range. We also measured, at the same experimental conditions, the same properties for the ternary systems (methyl pentanoate or methyl heptanoate) + octane + 1-hexanol. The corresponding properties for the binary systems (methyl pentanoate or methyl heptanoate) + octane have been previously reported by us.[1]

The experimental viscosities of the binary mixtures studied in this work were used to test several specific correlation equations.[2−6] Also, the viscosities for the ternary systems were correlated to composition using two different equations[6,7] making use of the binary parameters optimized earlier.

The excess molar volumes of both binary and ternary systems were compared with those predicted by the multiproperty group-contribution model proposed by Nitta et al.[8] using structural and energetic parameter sets available in the literature.[8−12] In addition, the binary and ternary viscosities were also used to compare with those predicted by the group-contribution models UNIFAC-VISCO[13] and UNIVAC[14] using the parameter sets proposed by the authors of both the models.

Experimental Section

Materials. 1-Hexanol (99.5% pure, checked by gas chromatography) was supplied by Fluka, and its physical properties compared with those found in the literature at the working temperatures are gathered in Table 1, which also includes its properties at 298.15 K. The remaining chemicals employed in this work were the same as those employed in a previous work[1] in which their physical properties were reported. All the liquids were stored over molecular sieves (Union Carbide type 4 nm, from Fluka) and partially degassed by ultrasound prior to their experimental use.

Apparatus and Procedure. The compositions (mole fraction) of both binary and ternary mixtures were determined by mass (Mettler AE240 balance, ±0.01 mg) with an average uncertainty of less than ±0.0001. The densities of the pure liquids and their mixtures were measured with an Anton Paar DMA-60/602 vibrating-tube densimeter thermostated to within ±0.01 K by means of a Polyscience 9010 bath. The temperature of the densimeter measurement cell was checked with several thermometers (DT100-20, 30, and 40) from Anton Paar. The densimeter was calibrated with deionized doubly distilled water and dry air as standard calibration fluids. The calibrations were verified with dodecane whose densities, obtained by the National Physical Laboratory of the U.K. and certified by the National Measurement Accreditation Service (NAMAS), were known with an uncertainty of ±0.000 01 g·cm^{-3} from (283.15 to 323.15) K, within the 95% confidence intervals. The average uncertainty of the density

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Table 1. Physical Properties of 1-Hexanol at Several Temperatures

	ρ/g·cm^{-3}		η/mPa·s	
T/K	this work	lit	this work	lit
293.15	0.81884	0.81875[a]	5.412	5.18[f]
		0.8196[b]		
298.15	0.81527	0.81515[c]	4.596	4.592[a]
		0.8153[d]		
303.15	0.81156	0.8114[e]	3.964	3.861[g]
		0.8118[d]		3.90[h]
313.15	0.80428	0.8041[e]	2.966	2.936[g]
		0.8046[b]		

[a] Reference 15. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19. [f] Reference 20. [g] Reference 21. [h] Reference 22.

values was less than ±0.000 02 g·cm^{-3}. The excess molar volumes, calculated from composition−density data, were obtained with an average uncertainty of less than ±0.002 cm^3·mol^{-1}.

The kinematic viscosities, ν, of both the pure liquids and mixtures were obtained by using several Ubbelohde capillary viscosimeters, previously calibrated, and a Schott-Geräte apparatus formed by a CT 1450/2 thermostat controlled to ±0.01 K and a stand which contains two optoelectronic sensors fixed transversally to the capillary viscometer to measure the running time of the meniscus between two fixed positions. The flow time t of a liquid between two given positions was measured with a Schott-Geräte stopwatch AVS 350 which measures the flow time with an accuracy of ±0.01 s. The control of the capillary temperature was carried out by means of the same digital thermometers mentioned above. The kinematic viscosities were calculated through the equation $\nu = K(t - \vartheta)$ where K is the viscosimeter constant and ϑ is the Hagenbach correction whose value is given by the manufacturer and depends on t. The experimental viscosities were obtained by averaging six to eight measures of flow times. The average uncertainty of the viscosity values was less than 0.3%.

Experimental Results and Correlations

In Table 2, we show values of densities and kinematic viscosities for binary systems as well as the molar excess volumes, V^E, and viscosity deviations, $\Delta\eta$, computed through the following equations:

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

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

which are valid for ternary systems, as well. In the above equations, ρ and η (=$\rho\nu$) are the density and dynamic viscosity of the mixture, respectively, and ρ_i and η_i are the corresponding properties of the pure components; n represents the number of components in the mixture, and M_i and x_i are the molecular weight and the mole fraction of the ith pure component, respectively.

As has been stated in the Introduction, several equations proposed in the literature to correlate (x,ν or η) data were employed to evaluate their utility to describe the viscometric behavior of the binary systems of the present study. The equations selected in this work were those due to McAllister[2] (for three- and four-body interactions), Grunberg and Nissan,[3] Lobe,[4] Hind et al.,[5] and Heric.[6] These equations are widely known, and we do not show them herein for briefness. The values of the corresponding adjustable parameters, obtained by the least-squares method combined with the nonlinear optimization algorithm by Marquardt,[23] are given in Table 3 along with the standard deviations.

The binary V^E and $\Delta\eta$ values were correlated with composition x (mole fraction of the first mentioned component) using the Redlich−Kister polynomial equation

$$Y = x(1 - x)\sum_{i=0}^{p} A_i(2x - 1)^i \quad (3)$$

where $Y \equiv (V^E$ or $\Delta\eta)$, with the exception of the V^E for the system (x) octane + (1−x) 1-hexanol, for which the following function was used:

$$V^E = x(1 - x)\sum_{i=0}^{p} A_i \left[\frac{2x - 1}{1 - c(2x - 1)}\right]^i \quad (4)$$

The last equation is an empirical modification of that by Myers and Scott,[24] in which the term $[1 \pm c(2x - 1)]$ has been introduced into the polynomial. In eq 4, c is a dimensionless adjustable parameter (when $c = 0$ in eq 4, eq 3 is obtained). We have tested this equation with high asymmetry curves and established it to be very suitable for them and, in particular, for correlating thermodynamic properties with composition of the n-alkane + 1-alkanol systems. The A_i and c coefficients and standard deviations σ, listed in Table 4, were calculated by the unweighted least-squares method. The optimum number of coefficients p was determined, in both cases, using the F-test[25] as the statistical criterion.

For the binary systems (x) methyl pentanoate + (1 − x) 1-hexanol and (x) methyl heptanoate + (1 − x) 1-hexanol, $V^E(x)$ data have been obtained at 298.15 K by Chaar.[26] As can be seen in Figure 1a, for both of the binary systems, the published results are reasonably consistent at any composition with those obtained in this work. There are no literature $\Delta\eta(x)$ data of these systems for comparison. Figure 1b provides a graphical representation of our $\Delta\eta$ data.

For the system (x) octane + (1 − x) 1-hexanol, there were, in the literature, four data sets (x,V^E) at 298.15 K due to Treszczanowicz and Benson,[27] Iglesias et al.,[28] Kaur et al.,[29] and Franjo et al.[30] As can be observed in Figure 2a, there is no good agreement among the results of the different authors. However, the results obtained by averaging the published data are in good agreement with our experimental values. Also, excess molar volumes of this system have been reported by Gupta et al.[31] at 303.15 K, which deviate from the present measurements with an average absolute deviation of 0.031 cm^3·mol^{-1}. For the system (x) octane + (1 − x) 1-hexanol, no published data $\Delta\eta(x)$ were found for the temperatures considered in this work; nevertheless, Franjo et al.[30] studied the mixture at 298.15 K. It can be observed from Figure 2b that the data of Franjo et al.[30] agree with the present work in the n-alkane rich region, while their values are more negative than expected at mole fractions of octane lower than 0.4.

In Table 5, we show the densities and kinematic viscosities as well as the excess molar volumes V^E_{123} and viscosity deviations $\Delta\eta_{123}$ for the systems (methyl pentanoate or methyl heptanoate) + octane + 1-hexanol at the different temperatures.

Table 2. Densities, ρ, Kinematic Viscosities, ν, Excess Molar Volumes, V^E, and Viscosity Deviations, $\Delta\eta$, for the Binary Mixtures at Several Temperatures

x	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	x	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s	x	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E / cm^3·mol^{-1}	$\Delta\eta$ / mPa·s
					(x) Methyl Pentanoate + (1 − x) 1-Hexanol									
					T = 293.15 K									
0.0000	0.818 84	6.609			0.4123	0.847 40	1.870	0.218	−1.8892	0.9071	0.882 86	0.857	0.084	−0.3916
0.0850	0.824 62	4.728	0.076	−1.1135	0.5087	0.854 22	1.533	0.223	−1.7111	0.9274	0.884 35	0.842	0.068	−0.3082
0.1145	0.826 65	4.250	0.097	−1.3608	0.6157	0.861 84	1.256	0.211	−1.4362	1.0000	0.889 75	0.800		
0.1854	0.831 55	3.367	0.140	−1.7406	0.6835	0.866 67	1.129	0.197	−1.2216					
0.2862	0.838 56	2.527	0.186	−1.9479	0.7846	0.873 96	0.982	0.155	−0.8664					
					T = 303.15 K									
0.0000	0.811 56	4.885			0.4502	0.841 37	1.436	0.243	−1.2519	0.7873	0.864 46	0.855	0.172	−0.5946
0.0771	0.816 54	3.701	0.077	−0.6844	0.4593	0.841 99	1.412	0.243	−1.2405	0.8796	0.870 90	0.775	0.116	−0.3503
0.1183	0.819 23	3.251	0.110	−0.9058	0.5089	0.845 34	1.285	0.246	−1.1778	0.9346	0.874 80	0.739	0.069	−0.1955
0.1920	0.824 09	2.619	0.159	−1.1645	0.6130	0.852 44	1.085	0.234	−0.9910	1.0000	0.879 51	0.708		
0.2983	0.831 16	1.994	0.209	−1.3104	0.6910	0.857 80	0.967	0.213	−0.8264					
					T = 313.15 K									
0.0000	0.804 28	3.688			0.3995	0.829 39	1.321	0.260	−0.9052	0.7876	0.854 78	0.752	0.196	−0.4209
0.0802	0.809 21	2.858	0.084	−0.4593	0.5141	0.836 80	1.083	0.271	−0.8184	0.9035	0.862 60	0.675	0.112	−0.2020
0.1168	0.811 47	2.580	0.118	−0.5899	0.5480	0.838 99	1.028	0.271	−0.7806	0.9358	0.864 80	0.658	0.083	−0.1370
0.1965	0.816 46	2.082	0.177	−0.7915	0.5971	0.842 20	0.961	0.265	−0.7150	1.0000	0.869 32	0.634		
0.2939	0.822 62	1.644	0.230	−0.9042	0.6912	0.848 37	0.844	0.242	−0.5808					
					(x) Methyl Heptanoate + (1 − x) 1-Hexanol									
					T = 293.15 K									
0.0000	0.818 84	6.609			0.3966	0.846 13	2.309	0.170	−1.7526	0.8937	0.874 45	1.321	0.079	−0.4141
0.0702	0.824 02	5.107	0.052	−0.9021	0.4898	0.851 87	1.992	0.178	−1.6089	0.9370	0.876 69	1.293	0.054	−0.2489
0.1168	0.827 40	4.398	0.076	−1.2708	0.5940	0.858 04	1.736	0.172	−1.3678	1.0000	0.879 96	1.264		
0.1890	0.832 46	3.588	0.112	−1.6123	0.7085	0.864 51	1.520	0.154	−1.0514					
0.3018	0.840 04	2.760	0.152	−1.7953	0.7917	0.869 04	1.415	0.129	−0.7777					
					T = 303.15 K									
0.0000	0.811 56	4.885			0.4003	0.838 05	1.874	0.199	−1.1865	0.8676	0.864 00	1.151	0.108	−0.3551
0.0753	0.816 90	3.812	0.061	−0.6230	0.4934	0.843 60	1.642	0.206	−1.0919	0.9415	0.867 77	1.114	0.055	−0.1593
0.1200	0.819 99	3.350	0.091	−0.8553	0.5979	0.849 60	1.449	0.196	−0.9309	1.0000	0.870 73	1.091		
0.1919	0.824 84	2.794	0.130	−1.0806	0.6849	0.854 38	1.321	0.183	−0.7707					
0.2963	0.831 61	2.244	0.172	−1.2050	0.8004	0.860 53	1.203	0.141	−0.5166					
					T = 313.15 K									
0.0000	0.804 28	3.688			0.3995	0.829 76	1.556	0.227	−0.8189	0.8720	0.855 24	0.999	0.125	−0.2433
0.0640	0.808 63	3.046	0.063	−0.3658	0.5299	0.837 23	1.322	0.236	−0.7234	0.9368	0.858 50	0.978	0.068	−0.1184
0.1198	0.812 36	2.623	0.104	−0.5783	0.6009	0.841 13	1.218	0.232	−0.6543	1.0000	0.861 65	0.955		
0.1968	0.817 35	2.213	0.154	−0.7353	0.6925	0.846 03	1.123	0.212	−0.5320					
0.2986	0.823 70	1.826	0.202	−0.8221	0.8022	0.851 72	1.038	0.166	−0.3629					
					(x) Octane + (1 − x) 1-Hexanol									
					T = 293.15 K									
0.0000	0.818 84	6.609			0.3022	0.776 82	2.746	0.011	−1.8073	0.8381	0.717 02		0.117	
0.0618	0.809 74	5.495	−0.015	−0.6610	0.4039	0.764 07	2.085	0.043	−1.8520	0.8767	0.713 37		0.111	
0.0860	0.806 25		−0.018		0.4950	0.753 22	1.670	0.074	−1.7434	0.9078	0.710 50	0.843	0.101	−0.3920
0.1114	0.802 62	4.744	−0.018	−1.0615	0.4994	0.752 71		0.076		0.9272	0.708 75		0.090	
0.1597	0.795 86		−0.017		0.6088	0.740 42	1.307	0.106	−1.4791	0.9458	0.707 09	0.803	0.079	−0.2380
0.1891	0.791 83		−0.016		0.7150	0.729 21	1.085	0.119	−1.1390	1.0000	0.702 54	0.771		
0.1928	0.791 32	3.740	−0.014	−1.5131	0.7991	0.720 79		0.120						
0.2346	0.785 68		−0.006		0.8086	0.719 86	0.947	0.121	−0.7921					
					T = 303.15 K									
0.0000	0.811 56	4.885			0.3080	0.768 33	2.154	0.023	−1.2369	0.7143	0.721 15		0.142	
0.0233	0.808 05		−0.005		0.3690	0.760 56		0.042		0.7740	0.715 10		0.143	
0.0510	0.803 93		−0.010		0.3936	0.757 47	1.749	0.056	−1.2689	0.7909	0.713 42		0.143	
0.0860	0.798 81	3.850	−0.013	−0.5896	0.4152	0.754 82		0.062		0.8042	0.712 11	0.842	0.143	−0.5646
0.1189	0.794 07		−0.013		0.4508	0.750 49		0.079		0.8532	0.707 39		0.134	
0.1308	0.792 38	3.415	−0.013	−0.8027	0.4994	0.744 75	1.382	0.094	−1.1966	0.8767	0.705 17	0.773	0.129	−0.3672
0.1581	0.788 53		−0.011		0.5249	0.741 79		0.103		0.9009	0.702 91		0.124	
0.1880	0.784 37	2.938	−0.006	−1.0056	0.5780	0.735 78		0.118		0.9272	0.700 52	0.736	0.109	−0.2204
0.1922	0.783 80		−0.007		0.5852	0.734 98	1.170	0.119	−1.0669	0.9470	0.698 76		0.094	
0.2352	0.777 94		0.004		0.6255	0.730 55		0.129		1.0000	0.694 35	0.696		
0.2632	0.774 20		0.011		0.7026	0.722 36	0.966	0.142	−0.8202					
					T = 313.15 K									
0.0000	0.804 28	3.688			0.3132	0.759 85		0.042		0.7108	0.713 30	0.836	0.177	−0.5674
0.0229	0.800 79		−0.005		0.3441	0.755 84		0.056		0.7570	0.708 56		0.179	
0.0502	0.796 68		−0.009		0.3882	0.750 23	1.457	0.077	−0.8885	0.7619	0.708 06		0.180	
0.0646	0.794 53	3.132	−0.009	−0.3142	0.3938	0.749 53		0.079		0.7893	0.705 32	0.756	0.178	−0.4313
0.0825	0.791 88		−0.009		0.4703	0.740 16		0.113		0.8428	0.700 08		0.174	
0.1067	0.788 35	2.812	−0.010	−0.4784	0.4916	0.737 63	1.180	0.121	−0.8493	0.8748	0.697 03		0.168	
0.1205	0.786 35		−0.009		0.4949	0.737 24		0.122		0.9109	0.693 67	0.667	0.154	−0.1930
0.1569	0.781 14		−0.005		0.5873	0.726 62	1.000	0.154	−0.7496	0.9297	0.691 97		0.141	
0.2007	0.774 99	2.236	0.006	−0.7240	0.6023	0.724 95		0.158		0.9599	0.689 33	0.641	0.105	−0.0897
0.2441	0.769 04		0.019		0.6746	0.717 11		0.171		1.0000	0.686 12	0.627		
0.2976	0.761 89	1.783	0.037	−0.8533	0.6964	0.714 81		0.174						

Table 3. Values of Parameters and Standard Deviations, σ, Obtained with Several Specific Correlative Models Proposed in the Literature To Correlate Composition−Viscosity Data of Binary Systems

		methyl pentanoate + 1-hexanol			methyl heptanoate + 1-hexanol			octane + 1-hexanol		
		T = 293.15	T = 303.15	T = 313.15	T = 293.15	T = 303.15	T = 313.15	T = 293.15	T = 303.15	T = 313.15
McAllister[a] (for three-body interactions)	ν_{12} [f]	1.0967	0.9417	0.8024	1.5570	1.3147	1.1122	0.9296	0.8319	0.7393
	ν_{21} [f]	1.6643	1.4233	1.2306	1.8769	1.5724	1.3405	2.4225	1.9273	1.5576
	σ	0.019	0.013	0.006	0.027	0.020	0.015	0.011	0.008	0.006
McAllister[a] (for four-body interactions)	ν_{1112} [f]	0.9203	0.8104	0.7371	1.3377	1.1528	0.9959	0.9318	0.8248	0.7341
	ν_{1122} [f]	1.5052	1.2623	1.0234	1.9333	1.6021	1.3452	1.4263	1.2154	1.0324
	ν_{2221} [f]	2.2770	1.8857	1.6034	2.4629	2.0066	1.6631	3.1592	2.4626	1.9564
	σ	0.003	0.004	0.005	0.003	0.002	0.005	0.006	0.005	0.004
Grunberg and Nissan[b]	d	−1.7558	−1.5250	−1.3594	−1.7354	−1.5483	−1.3813	−1.1207	−1.0561	−1.0047
	σ	0.054	0.035	0.020	0.083	0.059	0.040	0.042	0.028	0.018
Lobe[c]	α_{12}	0.9155	0.9177	0.8712	0.8577	0.8584	0.8168	−0.1151	−0.1023	−0.1020
	α_{21}	−1.7439	−1.7049	−1.6183	−1.6160	−1.6058	−1.5527	−0.6695	−0.6539	−0.6371
	σ [f]	0.032	0.022	0.011	0.028	0.020	0.016	0.014	0.009	0.006
Hind et al.[d]	η_{12} [g]	−0.6695	−0.2066	0.0251	−0.1868	0.1233	0.2960	−0.6047	−0.2420	−0.0363
	σ [g]	0.418	0.249	0.160	0.375	0.245	0.157	0.276	0.188	0.119
Heric[e]	β_{12}	−1.5897	−1.4163	−1.2877	−1.5358	−1.3810	−1.2500	−1.2207	−1.1235	−1.0416
	β'_{12}	0.4299	0.3460	0.2388	0.5453	0.4795	0.3940	−0.3625	−0.2864	−0.2320

[a] Reference 2. [b] Reference 3. [c] Reference 4. [d] Reference 5. [e] Reference 6. [f] Units: $mm^2 \cdot s^{-1}$. [g] Units: mPa·s; the remaining parameters and standard deviations are dimensionless.

Table 4. Coefficients of Equations 3 and 4 and Standard Deviations, σ, for Excess Molar Volumes, V^E, and Viscosity Deviations, $\Delta\eta$, of the Binary Systems at Different Temperatures

T/K	property	eq	A_0	A_1	A_2	A_3	A_4	A_5	σ
			(x) Methyl Pentanoate + (1 − x) 1-Hexanol						
293.15	V^E/cm^3·mol^{-1}	3	0.8900	0.0045	0.1224				0.001
	$\Delta\eta$/mPa·s	3	−6.9299	4.3357	−2.9562	2.1608	−1.0604	0.0464	0.002
303.15	V^E/cm^3·mol^{-1}	3	0.9783	0.0120	0.1540				0.001
	$\Delta\eta$/mPa·s	3	−4.7564	2.8769	−1.5805	0.7025	−0.9915	0.7510	0.002
313.15	V^E/cm^3·mol^{-1}	3	1.0847	0.0623	0.2048				0.002
	$\Delta\eta$/mPa·s	3	−3.3188	1.9378	−1.2298	0.4777			0.005
			(x) Methyl Heptanoate + (1 − x) 1-Hexanol						
293.15	V^E/cm^3·mol^{-1}	3	0.7084	0.0432	0.1444				0.002
	$\Delta\eta$/mPa·s	3	−6.3534	4.0539	−2.7694	1.3116	−1.1207	1.0027	0.003
303.15	V^E/cm^3·mol^{-1}	3	0.8181	0.0384	0.1366				0.002
	$\Delta\eta$/mPa·s	3	−4.3336	2.6444	−1.7548	0.8157	−0.6731	0.5920	0.002
313.15	V^E/cm^3·mol^{-1}	3	0.9475	0.0619	0.1883				0.002
	$\Delta\eta$/mPa·s	3	−2.9998	1.6368	−1.3524	0.9244			0.005
			(x) Octane + (1 − x) 1-Hexanol						
293.15	V^E/cm^3·mol^{-1}	4	0.3034	0.6314	−0.3470	0.2442		c = 0.5234	0.001
	$\Delta\eta$/mPa·s	3	−6.9443	3.6066	−1.1363	0.3525	−0.3311		0.002
303.15	V^E/cm^3·mol^{-1}	4	0.3751	0.6980	−0.3630	0.2273		c = 0.5798	0.001
	$\Delta\eta$/mPa·s	3	−4.7838	2.3491	−0.5958	0.2370	−0.4265		0.002
313.15	V^E/cm^3·mol^{-1}	4	0.4950	0.7830	−0.4019	0.3234		c = 0.5595	0.001
	$\Delta\eta$/mPa·s	3	−3.3552	1.6255	−0.5424				0.003

The ternary kinematic viscosities were correlated with composition through two specific equations proposed by Heric[6] and by Kalidas and Laddha,[7] which utilize the binary parameters listed in Table 3, and include only a ternary parameter. These equations have been previously compiled,[32] and we do not show them herein for brevity. The values of the ternary parameters together with the goodness-of-fit statistics are listed in Table 6.

The calculated ternary properties were correlated with ternary mole fractions (x_1,x_2,$x_3 = 1 - x_1 - x_2$) using the following equation:

$$Y_{123} = Y_{12} + Y_{13} + Y_{23} + x_1x_2x_3\sum_{m=0}^{3}\sum_{n=0}^{m} B_{mn}x_1^{(m-n)}x_2^{n} \quad (5)$$

where Y ($\equiv V^E$ or $\Delta\eta$), being the fourth term proposed by Morris et al.[33] In eq 5, the sum of the three first terms $Y_{bin} = \sum_{i<j} Y_{ij}$ is known as the binary contribution to the excess ternary properties, Y_{ij} being obtained according to

$$Y_{ij} = x_ix_j\sum_{k=0}^{N_{ij}} A_{k,ij}(x_i - x_j)^k \quad (6)$$

for the binary subsystems 1 + 2 and 1 + 3 and according to

$$Y_{ij} = x_ix_j\sum_{k=0}^{N_{ij}} A_{k,ij}\left[\frac{(x_i - x_j)}{1 - c_{ij}(x_i - x_j)}\right]^k \quad (7)$$

for the binary constituent 2 + 3 using the $A_{k,ij}$, $B_{k,ij}$, and c_{ij} binary parameters shown in Table 4. In Table 7, we show the B_{mn} parameters optimized through the least-squares method combined with the algorithm by Marquardt together with their corresponding standard deviations. Figures 3 and 4 show lines of constant V^E_{123} and $\Delta\eta_{123}$, respectively, for the referred ternary systems at (293.15, 303.15, and 313.15) K.

Discussion

As expected, from all the specific equations we selected to correlate the binary composition−viscosity data, the best results were obtained with the three-parameter equation proposed by McAllister, which correlates the experimental results with an overall percent deviation (estimated for all temperatures and compositions) of 0.2% for both the system octane + 1-hexanol and the two systems methyl ester +

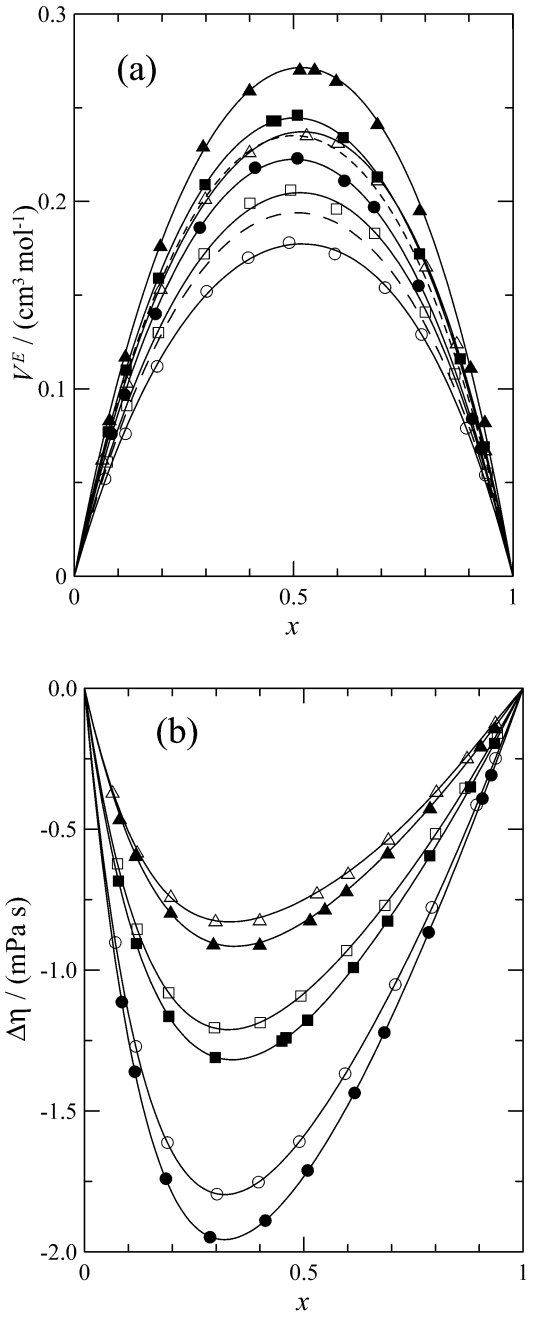

Figure 1. (a) Excess molar volumes, V^E, and (b) viscosity deviations, $\Delta\eta$, for the binary mixtures (x) methyl pentanoate + (1 − x) 1-hexanol (filled symbols) and (x) methyl heptanoate + (1 − x) 1-hexanol (open symbols): (●, ○), at 293.15 K; (■, □), at 303.15 K; (▲, △), at 313.15 K; —, calculated from eq 3 with coefficients from Table 3; - - -, Chaar (ref 26) at 298.15 K for the system containing methyl pentanoate; — — —, Chaar (ref 26) at 298.15 K for the system containing methyl heptanoate.

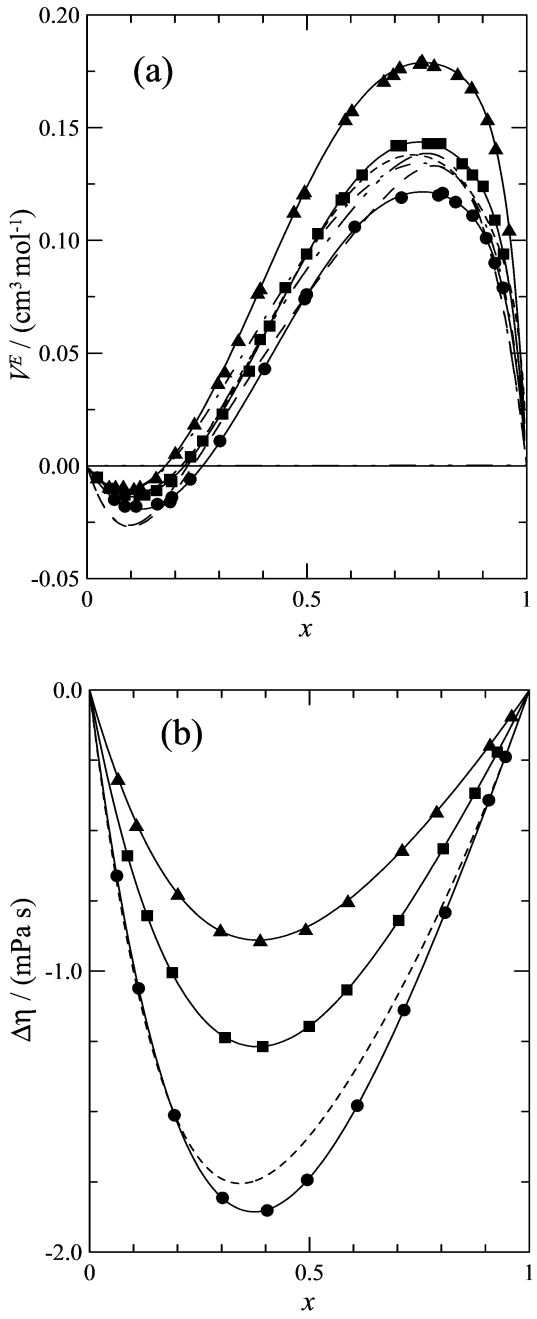

Figure 2. (a) Excess molar volumes, V^E, for the binary mixture (x) octane + (1 − x) 1-hexanol: —, calculated from eq 4 with coefficients from Table 3; - - -, Treszczanowicz and Benson (ref 27) at 298.15 K; — — —, Iglesias et al. (ref 28) at 298.15 K; — - — - —, Kaur et al. (ref 29) at 298.15 K; — - - — - - —, Franjo et al. (ref 30) at 298.15 K. (b) Viscosity deviations, $\Delta\eta$, for the binary mixture (x) octane + (1 − x) 1-hexanol: —, calculated from eq 3 with coefficients from Table 3; - - -, Franjo et al. (ref 30) at 298.15 K. Experimental points: ●, at 293.15 K; ■, at 303.15 K; ▲, at 313.15 K.

1-hexanol. As regards the two-parameter models, the equations proposed by McAllister and by Heric produce the same results (0.5% for the system containing octane and 0.9% for the systems containing methyl ester), while the Lobe equation gives deviations of 0.5 and 1.2%, respectively. The one-parameter equations were less adequate, giving the deviations as follows: Grunberg and Nissan equation, 2.1 and 2.8%, respectively; and Hind et al. equation, 16.2 and 15.7%, respectively. These latter results should be due to the fact that these equations are unsuitable for systems containing an associated component.

The equations employed to correlate the ternary composition−viscosity data were adequate, since both equations present overall percent deviations of ≤1.0%. However, it must be pointed out that these equations give deviations oscillating between 0.2% and 0.3% when they are fitted to the experimental data not employing the binary parameters listed in Table 3.

The V^E values of the systems (methyl pentanoate or heptanoate) + 1-hexanol are positive over the whole range of compositions and increase with temperature (Figure 1).

Table 5. Densities, ρ, Kinematic Viscosities, ν, Excess Molar Volumes, V^E_{123}, and Viscosity Deviations, $\Delta\eta_{123}$, for the Ternary Mixtures at Several Temperatures

x_1	x_2	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E_{123} / cm^3·mol^{-1}	$\Delta\eta_{123}$ / mPa·s	x_1	x_2	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E_{123} / cm^3·mol^{-1}	$\Delta\eta_{123}$ / mPa·s
(x_1) Methyl Pentanoate + (x_2) Octane + (1 − x_1 − x_2) 1-Hexanol											
T = 293.15 K											
0.0773	0.1203	0.806 36	3.455	0.075	−1.6768	0.2779	0.4211	0.778 66	1.070	0.420	−1.2220
0.0812	0.3271	0.778 53	1.968	0.147	−1.9052	0.3038	0.2020	0.809 49	1.519	0.304	−1.7704
0.1057	0.3954	0.771 39	1.582	0.209	−1.7700	0.3095	0.4853	0.772 73	0.925	0.479	−0.8789
0.1189	0.0861	0.813 99	3.279	0.118	−1.7649	0.3109	0.0877	0.826 69	1.927	0.241	−1.9309
0.1218	0.4854	0.761 43	1.275	0.270	−1.5041	0.3637	0.5450	0.768 92	0.798	0.552	−0.4346
0.1235	0.1851	0.800 14	2.490	0.151	−1.9383	0.3652	0.2364	0.808 67	1.261	0.362	−1.5244
0.1387	0.5645	0.753 29	1.078	0.319	−1.1991	0.4042	0.0973	0.831 57	1.531	0.286	−1.7655
0.1562	0.6451	0.745 37	0.929	0.367	−0.8447	0.4195	0.2884	0.805 01	1.054	0.423	−1.1880
0.1626	0.2369	0.795 50	1.966	0.212	−1.9302	0.4747	0.3210	0.804 12	0.926	0.472	−0.8728
0.1730	0.7261	0.737 74	0.818	0.406	−0.4599	0.4835	0.1250	0.832 79	1.252	0.321	−1.4881
0.1770	0.1313	0.811 27	2.445	0.180	−1.9570	0.5452	0.3532	0.804 35	0.812	0.517	−0.4766
0.1985	0.3029	0.788 92	1.551	0.279	−1.7797	0.5521	0.1462	0.834 30	1.080	0.339	−1.2045
0.2303	0.1615	0.810 46	1.972	0.230	−1.9450	0.6329	0.1608	0.837 55	0.942	0.361	−0.8657
0.2384	0.3613	0.783 81	1.275	0.348	−1.5330	0.7118	0.1821	0.839 76	0.833	0.365	−0.4801
T = 303.15 K											
0.0781	0.3244	0.770 64	1.638	0.169	−1.3119	0.2883	0.4141	0.771 51	0.924	0.462	−0.8464
0.0883	0.1252	0.798 50	2.563	0.117	−1.1864	0.3008	0.1996	0.801 09	1.294	0.335	−1.2270
0.1099	0.1843	0.791 44	2.084	0.155	−1.3065	0.3137	0.4858	0.764 12	0.808	0.527	−0.6082
0.1183	0.0871	0.805 97	2.578	0.136	−1.1876	0.3218	0.0837	0.819 53	1.555	0.279	−1.3237
0.1232	0.4833	0.753 45	1.094	0.306	−1.0461	0.3589	0.2466	0.798 07	1.072	0.403	−1.0505
0.1417	0.5651	0.744 98	0.932	0.362	−0.8296	0.3637	0.5305	0.761 65	0.720	0.594	−0.3545
0.1550	0.6419	0.737 13	0.824	0.408	−0.6049	0.4049	0.0943	0.823 33	1.292	0.317	−1.2188
0.1675	0.2403	0.787 15	1.580	0.247	−1.3239	0.4142	0.2851	0.796 16	0.925	0.461	−0.8515
0.1824	0.7178	0.730 51	0.726	0.462	−0.3260	0.4773	0.1279	0.822 91	1.076	0.362	−1.0390
0.1834	0.1218	0.804 98	1.984	0.203	−1.3303	0.5501	0.3581	0.794 67	0.712	0.565	−0.3138
0.1970	0.3052	0.780 18	1.303	0.309	−1.2265	0.5574	0.1448	0.825 57	0.929	0.388	−0.8306
0.2353	0.1726	0.800 87	1.561	0.269	−1.3268	0.6355	0.1621	0.828 05	0.822	0.401	−0.5955
0.2381	0.3717	0.773 92	1.072	0.393	−1.0446	0.7025	0.1876	0.828 62	0.738	0.413	−0.3520
T = 313.15 K											
0.0889	0.1216	0.791 36	2.066	0.116	−0.8080	0.2800	0.4186	0.761 85	0.816	0.484	−0.6063
0.0907	0.3159	0.764 49	1.349	0.195	−0.9149	0.3049	0.2031	0.792 40	1.089	0.357	−0.8516
0.1049	0.4013	0.754 28	1.119	0.259	−0.8512	0.3180	0.0871	0.810 44	1.308	0.289	−0.9172
0.1182	0.0836	0.798 74	2.089	0.137	−0.7995	0.3265	0.4769	0.757 18	0.713	0.564	−0.4282
0.1251	0.1856	0.784 26	1.624	0.181	−0.9190	0.3640	0.5361	0.752 13	0.641	0.625	−0.2455
0.1274	0.4813	0.745 67	0.943	0.331	−0.7347	0.3672	0.2381	0.791 12	0.930	0.424	−0.7395
0.1438	0.5584	0.737 47	0.823	0.390	−0.5958	0.4064	0.0977	0.814 30	1.097	0.334	−0.8439
0.1618	0.6350	0.729 81	0.728	0.439	−0.4339	0.4171	0.2846	0.787 54	0.809	0.490	−0.5999
0.1630	0.2436	0.778 33	1.328	0.254	−0.9207	0.4795	0.3194	0.786 46	0.716	0.544	−0.4351
0.1794	0.7207	0.721 48	0.649	0.488	−0.2372	0.4826	0.1224	0.815 25	0.932	0.373	−0.7300
0.1871	0.1274	0.796 37	1.589	0.218	−0.9262	0.5492	0.3528	0.786 08	0.642	0.591	−0.2402
0.2051	0.2979	0.773 34	1.108	0.333	−0.8582	0.5589	0.1411	0.817 16	0.818	0.400	−0.5907
0.2413	0.1613	0.794 64	1.323	0.282	−0.9232	0.6413	0.1600	0.819 44	0.723	0.415	−0.4197
0.2448	0.3588	0.767 54	0.937	0.412	−0.7460	0.7128	0.1886	0.819 61	0.653	0.428	−0.2314
(x_1) Methyl Heptanoate + (x_2) Octane + (1 − x_1 − x_2) 1-Hexanol											
T = 293.15 K											
0.0816	0.3217	0.780 68	2.071	0.106	−1.8776	0.2729	0.4232	0.782 66	1.232	0.269	−1.2140
0.0819	0.1244	0.806 92	3.448	0.061	−1.6719	0.3008	0.1996	0.812 41	1.780	0.203	−1.7006
0.1102	0.3968	0.773 63	1.640	0.150	−1.7367	0.3197	0.0824	0.829 48	2.207	0.181	−1.8048
0.1185	0.4778	0.764 66	1.378	0.186	−1.5217	0.3214	0.4768	0.780 01	1.077	0.302	−0.8680
0.1193	0.0866	0.814 99	3.435	0.083	−1.6782	0.3580	0.2405	0.811 05	1.508	0.234	−1.4781
0.1231	0.1818	0.802 09	2.644	0.102	−1.8765	0.3632	0.5357	0.776 49	0.963	0.324	−0.4935
0.1419	0.5535	0.757 92	1.170	0.224	−1.2195	0.4039	0.1085	0.831 45	1.822	0.204	−1.6317
0.1586	0.2451	0.796 28	2.089	0.148	−1.8734	0.4235	0.2822	0.810 25	1.299	0.260	−1.1635
0.1609	0.6407	0.749 98	1.005	0.253	−0.8460	0.4729	0.1289	0.833 11	1.598	0.223	−1.4199
0.1713	0.1250	0.813 36	2.748	0.121	−1.8318	0.4808	0.3197	0.809 51	1.162	0.277	−0.8466
0.1829	0.7058	0.745 02	0.904	0.261	−0.5153	0.5380	0.3596	0.808 55	1.056	0.285	−0.4935
0.2031	0.2972	0.792 88	1.705	0.191	−1.7390	0.5582	0.1368	0.837 41	1.421	0.222	−1.1556
0.2393	0.1666	0.812 50	2.124	0.168	−1.8453	0.6266	0.1686	0.837 47	1.272	0.225	−0.8317
0.2437	0.3648	0.787 48	1.409	0.238	−1.4779	0.7128	0.1830	0.840 81	1.171	0.206	−0.4708

Table 5. (Continued)

x_1	x_2	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E_{123} / cm^3·mol^{-1}	$\Delta\eta_{123}$ / mPa·s	x_1	x_2	ρ / g·cm^{-3}	ν / mm^2·s^{-1}	V^E_{123} / cm^3·mol^{-1}	$\Delta\eta_{123}$ / mPa·s
(x_1) Methyl Heptanoate + (x_2) Octane + (1 − x_1 − x_2) 1-Hexanol (Continued)											
T = 303.15 K											
0.0802	0.1221	0.799 33	2.733	0.087	−1.1123	0.2803	0.4167	0.775 48	1.060	0.305	−0.8464
0.0879	0.3145	0.774 02	1.701	0.143	−1.2873	0.3023	0.2057	0.803 33	1.454	0.245	−1.1691
0.1061	0.3955	0.765 26	1.392	0.190	−1.2025	0.3237	0.4736	0.771 97	0.940	0.333	−0.6139
0.1179	0.1841	0.793 41	2.134	0.132	−1.2748	0.3252	0.0807	0.821 79	1.789	0.219	−1.2329
0.1193	0.4840	0.755 74	1.168	0.226	−1.0367	0.3592	0.2393	0.802 77	1.273	0.273	−1.0264
0.1273	0.0861	0.807 79	2.635	0.116	−1.1516	0.3607	0.5327	0.767 97	0.861	0.354	−0.3614
0.1437	0.5678	0.748 13	0.989	0.267	−0.8144	0.4003	0.1053	0.823 16	1.518	0.242	−1.1409
0.1609	0.6368	0.741 97	0.884	0.290	−0.6066	0.4177	0.2854	0.800 81	1.113	0.300	−0.8208
0.1633	0.2376	0.789 47	1.726	0.184	−1.2816	0.4745	0.3181	0.800 51	1.012	0.315	−0.6166
0.1806	0.1230	0.806 27	2.137	0.158	−1.2686	0.4798	0.1297	0.824 81	1.322	0.258	−0.9764
0.1814	0.7100	0.735 94	0.795	0.307	−0.3606	0.5335	0.3586	0.799 50	0.923	0.318	−0.3697
0.2043	0.3055	0.783 63	1.402	0.234	−1.1856	0.5580	0.1464	0.827 37	1.191	0.259	−0.7874
0.2420	0.1734	0.803 55	1.708	0.208	−1.2590	0.6379	0.1647	0.829 72	1.087	0.257	−0.5658
0.2454	0.3699	0.778 59	1.186	0.277	−1.0140	0.7004	0.1854	0.830 79	1.018	0.235	−0.3616
T = 313.15 K											
0.0808	0.1273	0.790 79	2.144	0.124	−0.7752	0.2776	0.4116	0.767 29	0.932	0.368	−0.6123
0.0886	0.3214	0.765 04	1.389	0.196	−0.8981	0.3052	0.2060	0.795 10	1.230	0.291	−0.8116
0.1004	0.4067	0.755 20	1.167	0.245	−0.8385	0.3159	0.0914	0.811 43	1.476	0.258	−0.8592
0.1120	0.1824	0.785 23	1.771	0.167	−0.8724	0.3244	0.4760	0.763 01	0.825	0.406	−0.4348
0.1203	0.0845	0.799 66	2.159	0.147	−0.7680	0.3595	0.5350	0.758 83	0.755	0.420	−0.2659
0.1241	0.4869	0.747 37	0.993	0.297	−0.7233	0.3644	0.2396	0.794 56	1.089	0.322	−0.7124
0.1447	0.5626	0.740 25	0.871	0.338	−0.5841	0.4048	0.1058	0.814 94	1.279	0.286	−0.7882
0.1550	0.6445	0.732 09	0.779	0.364	−0.4294	0.4215	0.2785	0.793 28	0.975	0.345	−0.5836
0.1596	0.2395	0.780 78	1.435	0.230	−0.8965	0.4809	0.1179	0.817 89	1.153	0.295	−0.6933
0.1803	0.7130	0.726 84	0.708	0.392	−0.2565	0.4824	0.3180	0.792 28	0.882	0.361	−0.4268
0.1841	0.1221	0.798 56	1.748	0.203	−0.8657	0.5257	0.3616	0.789 79	0.818	0.366	−0.2765
0.2026	0.3044	0.775 32	1.197	0.285	−0.8318	0.5616	0.1432	0.819 29	1.033	0.299	−0.5534
0.2437	0.3618	0.770 97	1.038	0.334	−0.7264	0.6350	0.1708	0.819 97	0.944	0.290	−0.3981
0.2446	0.1576	0.797 66	1.458	0.246	−0.8793	0.7093	0.1852	0.822 41	0.891	0.259	−0.2433

Table 6. Ternary Parameters of Heric, γ_{123}, and Kalidas and Laddha, ν_{123}, Equations, Standard Deviations, σ, and Percent of Average Absolute Deviations, ϵ, for Representation of Kinematic Viscosity, ν, of Ternary Systems

	methyl pentanoate + octane + 1-hexanol						methyl heptanoate + octane + 1-hexanol					
T/K	γ_{123} [a]	σ [b]	ϵ (%)	ν_{123} [b]	σ [b]	ϵ (%)	γ_{123} [a]	σ [b]	ϵ (%)	ν_{123} [b]	σ [b]	ϵ (%)
293.15	−0.0133	0.011	0.7	0.8669	0.016	0.9	−0.0101	0.017	0.9	1.0584	0.021	1.0
303.15	−0.0164	0.009	0.7	0.7484	0.015	0.9	−0.0117	0.010	0.6	0.9079	0.015	0.8
313.15	−0.0123	0.008	0.6	0.6833	0.011	0.8	−0.0070	0.008	0.6	0.8231	0.010	0.6

[a] Units: mm^2·s^{-1}. [b] Dimensionless.

Table 7. Adjustable Parameters B_{mn} of Equation 5 and Standard Deviations, σ, for V^E_{123} and $\Delta\eta_{123}$ of the Ternary Systems at Different Temperatures

T/K	property	B_{00}	B_{10}	B_{11}	B_{20}	B_{21}	B_{22}	B_{30}	B_{31}	B_{32}	B_{33}	σ
(x_1) Methyl Pentanoate + (x_2) Octane + (x_3) 1-Hexanol												
293.15	V^E_{123} [a]	2.4669	−4.3593	−7.9418	0.2014	8.2605	12.0614	2.4788	−1.9182	−1.6092	−10.6545	0.003
	$\Delta\eta_{123}$ [b]	15.2546	−21.2997	−19.5804	11.9976	32.3020	16.2128	−1.6011	−17.9949	−24.1287	−8.6321	0.004
303.15	V^E_{123} [a]	3.8480	−11.8013	−9.0735	19.4661	6.8082	9.0406	−9.0114	−10.3034	9.9969	−5.2800	0.003
	$\Delta\eta_{123}$ [b]	4.3193	9.1636	5.9989	−27.2576	−21.5679	−11.4794	17.7500	14.7436	4.7726	2.9877	0.002
313.15	V^E_{123} [a]	1.3150	−3.6058	−1.9909	2.3668	5.5406	−5.7644	−0.5491	−2.1674	2.4796	6.8151	0.002
	$\Delta\eta_{123}$ [b]	1.1843	18.1811	13.5273	−38.8005	−58.3550	−21.9915	21.8601	48.0502	36.9384	8.2028	0.002
(x_1) Methyl Heptanoate + (x_2) Octane + (x_3) 1-Hexanol												
293.15	V^E_{123} [a]	1.9003	0.5720	−5.9076	−7.9706	−7.6615	9.1219	10.4726	−0.8233	27.1014	−10.4635	0.002
	$\Delta\eta_{123}$ [b]	13.6286	−3.0874	−23.7196	−30.4603	3.1252	35.8691	25.2370	28.1533	−22.3730	−23.5513	0.007
303.15	V^E_{123} [a]	3.8911	−8.0778	−2.2236	8.4428	−19.2866	−10.0743	−1.3021	20.2816	40.3153	10.4342	0.003
	$\Delta\eta_{123}$ [b]	6.1244	0.1301	0.4734	−14.0639	−17.3181	−3.5693	11.2567	15.1299	11.9142	−3.0873	0.003
313.15	V^E_{123} [a]	7.8452	−26.6158	−4.8891	40.9243	−10.5010	−24.4517	−18.6685	4.7160	71.9583	32.6012	0.006
	$\Delta\eta_{123}$ [b]	5.9540	−11.6039	−7.2608	11.4886	23.8296	5.0523	−3.8795	−18.2387	−20.3535	−1.9771	0.003

[a] Units: cm^3·mol^{-1}. [b] Units: mPa·s.

Also, the molar excess enthalpies H^E for these systems determined by Ortega et al.[34] at 298.15 K are positive at any composition. On the other hand, it can be observed that both the V^E and H^E values decrease when the length of radical R in the methyl ester RCOOCH$_3$ is increased, for a given temperature.

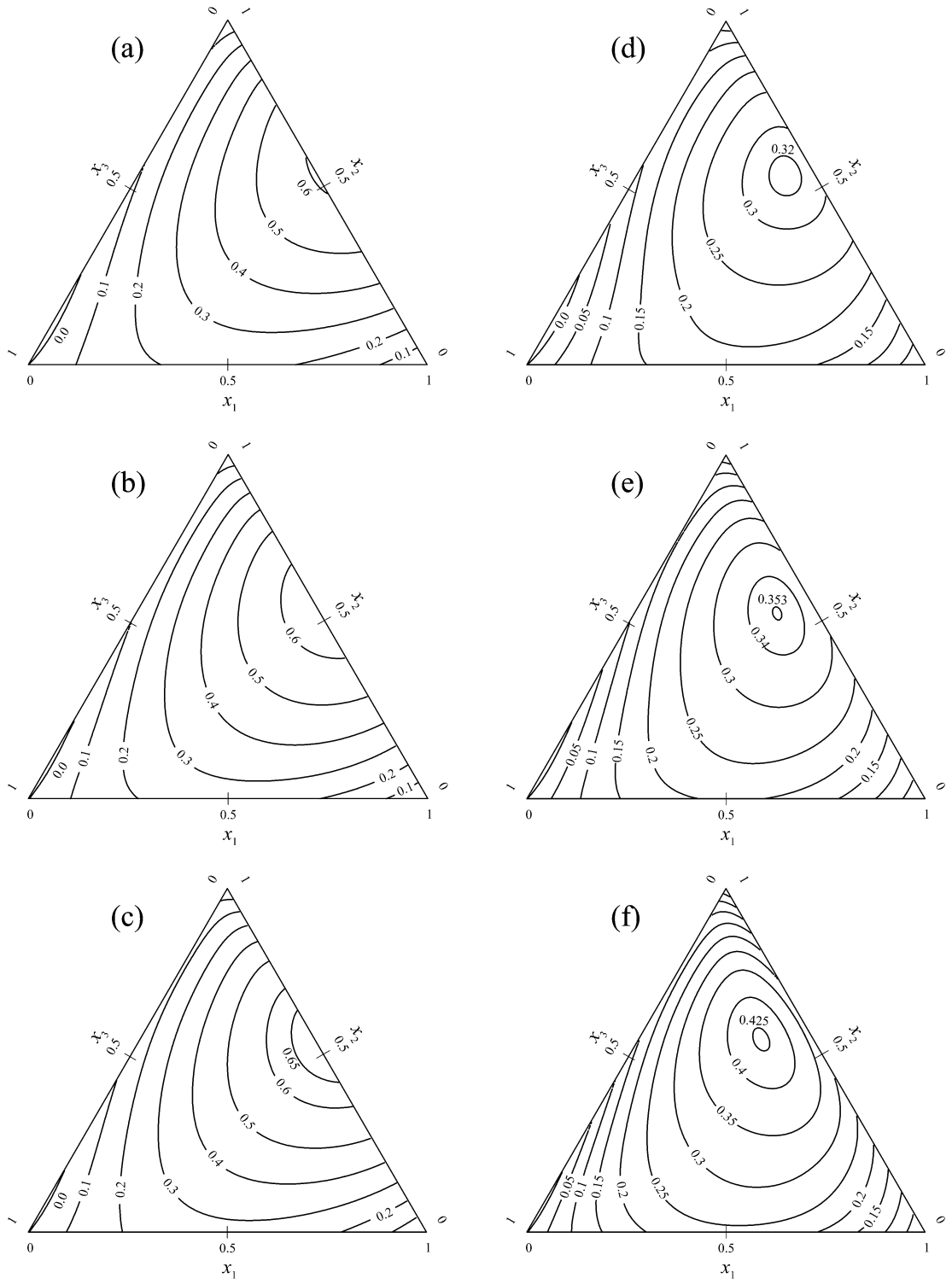

Figure 3. Isolines at constant V^E_{123} (cm^3·mol^{-1}) for the ternary system (x_1) methyl pentanoate + (x_2) octane + (x_3) 1-hexanol at 293.15 K (a), 303.15 K (b), and 313.15 K (c) and for the ternary system (x_1) methyl heptanoate + (x_2) octane + (x_3) 1-hexanol at 293.15 K (d), 303.15 K (e), and 313.15 K (f).

As Figure 2a shows, the V^E values of the system octane + 1-hexanol are small and negative in the region where the mole fraction of octane is very low, whereas for the remaining compositions the V^E values are positive and increase with temperature. As measured by Nguyen and Ratcliff[35] at 288.15 K, the excess molar enthalpies H^E of this system are quite small (H^E_{max} = 288.2 J·mol^{-1}) and positive over the whole range of compositions. A description of the volumetric behavior of this system at 298.15 K has been previously given by Treszczanowicz and Benson.[27]

The $\Delta\eta$ values for the three binary systems analyzed in this work are negative over the entire range of compositions and decrease in absolute value with temperature rise (Figures 1b and 2b). The sign of $\Delta\eta$ values is in agreement

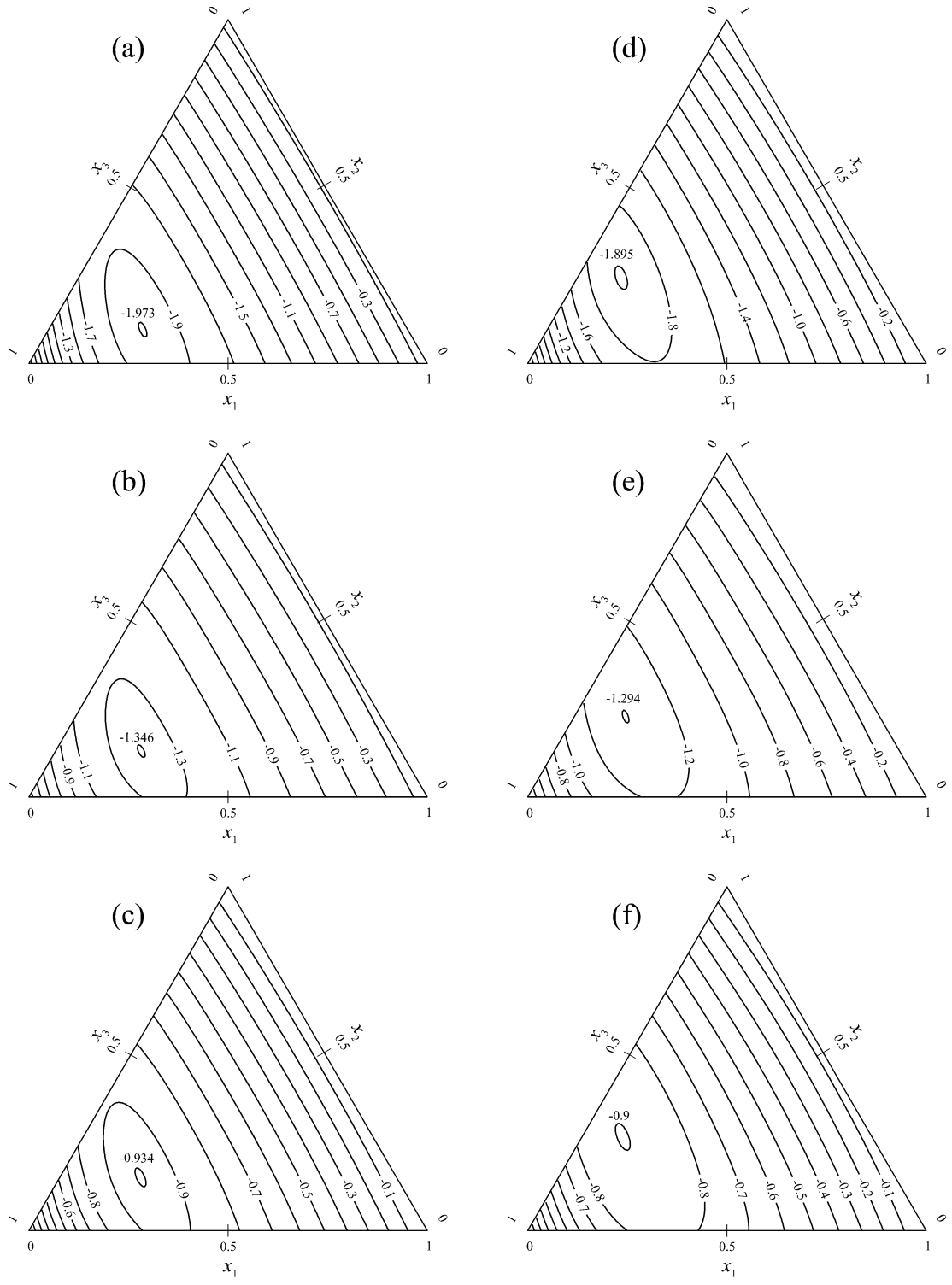

Figure 4. Isolines at constant $\Delta\eta_{123}$ (mPa·s) for the ternary system (x_1) methyl pentanoate + (x_2) octane + (x_3) 1-hexanol at 293.15 K (a), 303.15 K (b), and 313.15 K (c) and for the ternary system (x_1) methyl heptanoate + (x_2) octane + (x_3) 1-hexanol at 293.15 K (d), 303.15 K (e), and 313.15 K (f).

with the conclusions by Fort and Moore,[36] who proposed that this behavior is characteristic of systems where dispersion forces are predominant.

The V^E_{123} values for the ternary systems (x_1) (methyl pentanoate or heptanoate) + (x_2) octane + (x_3) 1-hexanol are positive over the whole composition area, except for those regions very rich in 1-hexanol. As can be observed in Figure 3, the surfaces $V^E_{123}(x_1,x_2)$ for the ternary system containing methyl pentanoate show neither maxima nor minima at the working temperatures. However, at any of the temperatures, the surfaces representing the V^E_{123} for the ternary system containing methyl heptanoate show maxima located in a region poor in 1-hexanol and where the mole fraction of octane is somewhat greater than 0.5. As can be seen in Figure 4, the $\Delta\eta_{123}$ values for the ternary systems addressed in this study are negative over the whole range of compositions and they increase as temperature rises. For both ternary systems, minima were

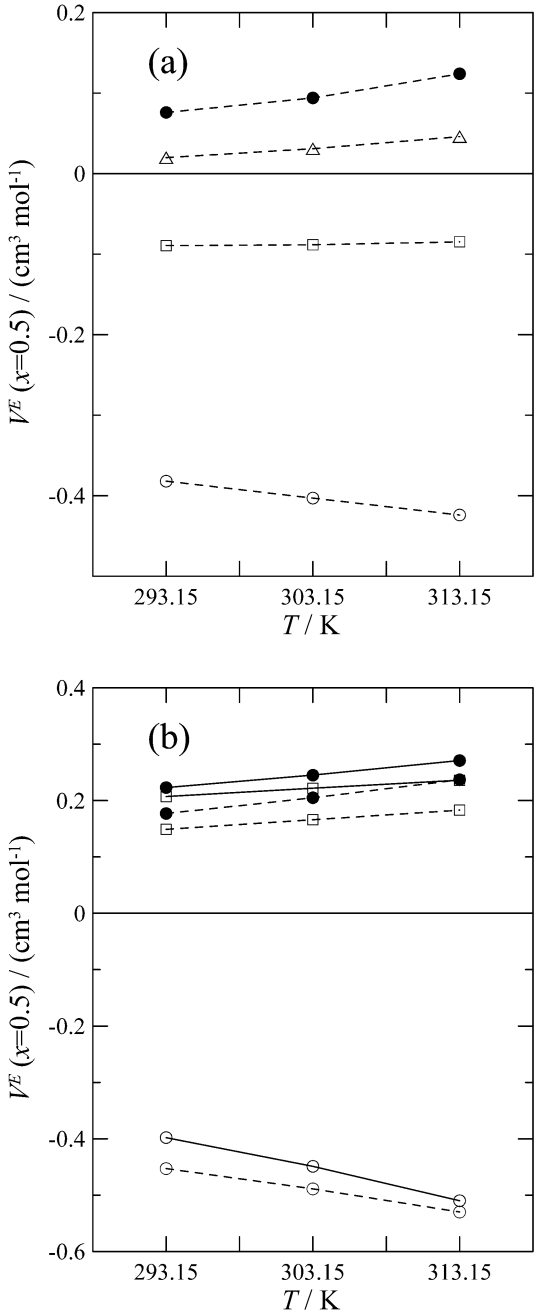

Figure 5. Experimental and predicted values from the Nitta et al. model for equimolar octane + 1-hexanol (a) and (methyl pentanoate or heptanoate) + 1-hexanol (b) mixtures against the temperature. For the system octane + 1-hexanol: ○, with AOL1 parameter set; □, with AOL2 parameter set; △, with AOL3 parameter set. For the systems methyl ester + 1-hexanol: —, mixture containing methyl pentanoate; - - -, mixture containing methyl heptanoate; ○, with EOL1 parameter set; □, with EOL2 parameter set. Experimental values (●).

observed on the mesh $\Delta\eta_{123}(x_1,x_2)$ located in a region rich in 1-hexanol ($x_3 \cong 0.75$) at all temperatures.

Predictions of the Nitta et al. Model. The group-contribution model proposed by Nitta et al. was applied to the system *n*-octane + 1-hexanol using three sets of parameters available in the literature proposed by Nitta et al.,[8] Fernández et al.,[11] and González et al.,[12] henceforth referred as AOL1, AOL2, and AOL3, respectively. The parameter sets AOL1 and AOL2 were obtained using the traditional group definition criterion, whereas for AOL3 a quantum mechanical criterion, based on the theory of atoms in molecules proposed by Bader,[37] was used to characterize functional groups. For this system, the V^E predictions improve, from both qualitative and quantitative points of view, using the revised parameter sets, the overall absolute deviations between the experimental and predicted results being as follows: 0.314 cm^3·mol^{-1} (with AOL1), 0.114 cm^3·mol^{-1} (with AOL2), and 0.036 cm^3·mol^{-1} (with AOL3). For the systems (methyl pentanoate or methyl heptanoate) + 1-hexanol, two parameter sets (Navarro[9] and Legido et al.,[10] henceforth referred as EOL1 and EOL2, respectively) were available in the literature. Like in the previous case, better predictions were obtained using the revised set of parameters, the overall absolute deviations between the experimental and predicted results being as follows: 0.475 cm^3·mol^{-1} with EOL1 and 0.025 cm^3·mol^{-1} with EOL2. Figure 5 shows the comparison, at equimolar composition, between the experimental results of V^E and those predicted by the model using the different parameter sets.

Since the structural and energetic parameter sets available in the literature for (an aliphatic ester + a 1-alcohol) systems are also suitable for the ternary systems herein studied, the application of the model by Nitta et al. to the systems (methyl pentanoate or methyl heptanoate) + octane + 1-hexanol was carried out using the parameter sets EOL1 and EOL2. The overall absolute deviations between the experimental and predicted results were 0.485 cm^3·mol^{-1} using EOL1 and 0.110 cm^3·mol^{-1} using EOL2, respectively.

Predictions of the UNIFAC-VISCO and UNIVAC Models. The group-contribution models UNIVAC and UNIFAC-VISCO have been applied with the aim of comparing their predictions with the experimental viscosities of this study. A remarkable aspect in the predictions of these models is that for both binary and ternary mixtures the average percent deviations decrease as temperature rises. Averaging over all the compositions and temperatures, the overall percent deviations obtained with UNIFAC-VISCO and with UNIVAC were as follows: 3.4% and 8.4%, respectively, for the system octane + 1-hexanol; 5.9% and 6.5%, respectively, for the systems aliphatic methyl ester + 1-hexanol; and 6.3% and 8.5%, respectively, for the two systems aliphatic methyl ester + octane + 1-hexanol.

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