

Densities, Viscosities, and Related Properties of Some (Methyl Ester + Alkane) Binary Mixtures in the Temperature Range from 283.15 to 313.15 K

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Densities, kinematic and dynamic viscosities, excess molar volumes, and viscosity deviations of binary mixtures of a methyl ester (pentanoate, hexanoate, or heptanoate) and an alkane (octane, decane, or dodecane) were determined at (283.15, 293.15, 303.15, and 313.15) K and atmospheric pressure for the whole composition range. Excess molar volumes were compared to those predicted by the group-contribution model of Nitta et al. employing three different parameter sets available in the literature. The best predictions were obtained using the primary parameter set. The experimental kinematic viscosities were used to test the group-contribution models UNIVAC and UNIFAC–VISCO, and the best predictions were obtained by means of the UNIFAC–VISCO model. Also, several empirical and semiempirical relationships were employed to correlate the composition–viscosity data.

Introduction

Thermodynamic and transport properties provide important information for the design of industrial processes, to improve our understanding of the molecular interactions existing in liquid mixtures, and to test the predictive capability of the models and methods developed to predict these properties. While there are several models to predict the mixture viscosities in the literature,¹ the models capable of predicting mixing volumes are very scarce.

In this work, which is a part of our research^{2,3} on the physical properties of ternary mixtures and their constituent binary mixtures, we present the densities, viscosities, excess molar volumes, and viscosity deviations of the binary systems (methyl pentanoate + octane, decane, or dodecane), (methyl hexanoate + octane, decane, or dodecane), and (methyl heptanoate + octane, decane, or dodecane) at the temperatures (283.15, 293.15, 303.15, and 313.15) K and atmospheric pressure. These results will be subsequently used to analyze the properties of several ternary systems in which the binary systems herein studied are involved.

The experimental excess molar volumes obtained in this work were compared to those predicted by the group-contribution model of Nitta et al.⁴ In the application of the model, we have employed three parameter sets, available in the literature, proposed by Navarro,^{5,6} Ortega and Legido,⁶ and Carballo et al.⁷ for the systems (an aliphatic ester + an *n*-alkane).

The experimental (kinematic or dynamic) viscosities were used to test the applicability of the equations proposed by Grunberg and Nissan,⁸ McAllister (assuming three-body and four-body interactions),⁹ Hind et al.,¹⁰ Heric,¹¹ and Lobe.¹² Also, the kinematic viscosities were compared to those predicted by the group-contribution models UNIVAC¹³ and UNIFAC–VISCO,¹⁴ both of which are based on the reaction rate theory¹⁵ and the basic principles of the UNIFAC model.¹⁶

Experimental Section

Materials. All of the chemicals employed in this work were provided by Fluka except for dodecane, which was provided by Aldrich. Their purities (expressed in percent, %), checked by gas chromatography, were as follows: methyl pentanoate (99.0); methyl hexanoate (99.5); methyl heptanoate (99.1); octane (99.8); decane (99); dodecane (99.2). The liquids were degassed by ultrasound and dried over molecular sieves (Union Carbide type 0.4 nm, from Fluka) and otherwise used as supplied. Table 1 shows the densities ρ , kinematic viscosities ν , and dynamic viscosities η ($=\rho\nu$) at the working temperatures. Values of these properties at 298.15 K are also included.

Apparatus and Procedures. Liquid mixtures were prepared by mass using a Mettler balance with an accuracy of $\pm 2 \times 10^{-5}$ g. The uncertainty of the mole fraction was estimated to be lower than $\pm 4 \times 10^{-5}$.

Density measurements were carried out with a mechanical-oscillation (Anton Paar model DMA 60/602) densimeter operating in static mode. The densimeter was calibrated

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Table 1. Physical Properties of the Pure Liquids at Several Temperatures

liquid	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$v/\text{mm}^2\cdot\text{s}^{-1}$		$\eta/\text{mPa}\cdot\text{s}$	
		exptl	lit.	exptl	lit.	exptl	lit.
octane	283.15	0.710 58	0.710 7 ^a	0.864		0.614	0.618 ^b
	293.15	0.702 54	0.702 56 ^c	0.771		0.542	0.541 ^b
	298.15	0.698 50	0.698 49 ^d	0.727	0.7251 ^e	0.508	0.5094 ^g
			0.698 54 ^c		0.7352 ^f		0.506 ^h
	303.15	0.694 35	0.694 32 ⁱ	0.696		0.483	0.4830 ^k
decane			0.694 49 ^j				
	313.15	0.686 12	0.686 29 ^j	0.627		0.430	0.428 ^b
	283.15	0.737 66	0.737 55 ^b	1.458		1.076	1.101 ^b
	293.15	0.730 15	0.730 12 ^c	1.254		0.916	0.9115 ^l
	298.15	0.726 36	0.726 35 ^m	1.168	1.161 ^e 1.183 ⁿ	0.848	0.8459 ^g 0.859 ⁿ
dodecane	303.15	0.722 47	0.722 45 ^d	1.096		0.792	0.7917 ^l
	313.15	0.714 81	0.714 76 ^o	0.967		0.691	0.6940 ^l
	283.15	0.756 75	0.755 9 ^a	2.407		1.821	1.856 ^b
	293.15	0.749 47	0.748 75 ^m	1.982		1.485	1.508 ^m
	298.15	0.745 84	0.745 45 ^e	1.818	1.804 ^e 1.824 ^q	1.356	1.324 ^p 1.378 ^m
methyl pentanoate	303.15	0.742 10	0.741 63 ^b	1.682		1.248	1.291 ^b
	313.15	0.734 78	0.744 60 ^b	1.444		1.061	1.098 ^b
	283.15	0.899 78		0.907		0.816	
	293.15	0.889 75		0.800		0.712	
	298.15	0.884 69	0.884 66 ^r	0.747	0.748 ^s	0.661	
methyl hexanoate	303.15	0.879 51		0.708		0.623	
	313.15	0.869 32		0.634		0.551	
	283.15	0.893 71		1.171		1.047	
	293.15	0.884 29		1.012		0.895	
	298.15	0.879 52	0.879 44 ^t 0.879 86 ^u	0.943	0.942 ^s	0.829	
methyl heptanoate	303.15	0.874 65		0.888		0.777	
	313.15	0.865 06		0.785		0.679	
	283.15	0.888 97		1.485		1.320	
	293.15	0.879 96		1.264		1.112	
	298.15	0.875 42	0.875 405 ^v	0.943		0.829	
	303.15	0.870 73		1.091		0.950	
	313.15	0.861 65		0.955		0.823	

^a Reference 17. ^b Reference 18. ^c Reference 19. ^d Reference 20. ^e Reference 21. ^f Reference 22. ^g Reference 23. ^h Reference 24. ⁱ Reference 25. ^j Reference 26. ^k Reference 27. ^l Reference 28. ^m Reference 29. ⁿ Reference 30. ^o Reference 31. ^p Reference 32. ^q Reference 33. ^r Reference 34. ^s Reference 35. ^t Reference 36. ^u Reference 37. ^v Reference 38.

with both deionized doubly distilled water and dry air as standard fluids. The temperature of the cell was kept constant within ± 0.01 K by means of a Polyscience 9010 thermostat, and the control of the temperature was carried out with an Anton Paar digital thermometer (DT 100-10, DT 100-20, DT 100-30, or DT 100-40, depending on the temperature). The accuracy of the density was estimated to better than $\pm 2 \times 10^{-5}$ g cm⁻³. The excess molar volumes were calculated from density-composition data as mentioned below, and their uncertainties were estimated to better than ± 0.003 cm³ mol⁻¹.

Kinematic viscosities were determined using a Schott-Geräte apparatus consisting of a CT 1450/2 thermostatic bath and a stand which contains two thermal conductance (TC) sensors located transversally to the capillary viscometer to measure the running time of the meniscus between two fixed positions. Also, several Schott KPG Ubbelohde capillary viscometers, previously calibrated by Schott Geräte, were used. However, the viscometer constants were periodically checked using water, benzene, and other liquids with known viscosities.²⁹ The control of the capillary temperature was carried out to an uncertainty of ± 0.01 K by means of the digital thermometers mentioned above. The kinematic viscosities were calculated by

$$\nu = K(t - \vartheta) \quad (1)$$

where K is the viscometer constant, ϑ the Hagenbach

correction, and t the flow time, which was measured employing an automatic stopwatch AVS 350 with a precision of ± 0.01 s. The ϑ values were provided by Schott-Geräte. The experimental viscosities were obtained by averaging six to eight measures of flow time. The uncertainty of the kinematic viscosity was estimated to be lower than $\pm 0.4\%$.

Results and Discussion

The densities of the pure components and their mixtures were used to calculate the excess molar volumes V^E , as the following equation indicates

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

where x_i , M_i , and ρ_i are the mole fraction, molecular weight, and density of component i , respectively, and ρ is the density of the mixture.

The viscosity deviations $\Delta\eta$ were obtained from dynamic viscosity-composition data through

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where η , η_1 , and η_2 are the dynamic viscosities of the

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	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$	x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$
(x)Methyl Pentanoate + (1 - x)Octane									
$T = 283.15 \text{ K}$									
0.0388	0.716 08	0.854	0.098	-0.0098	0.5948	0.809 92	0.831	0.530	-0.0611
0.1003	0.725 02	0.842	0.241	-0.0243	0.7027	0.831 83	0.842	0.444	-0.0559
0.1940	0.739 33	0.830	0.397	-0.0392	0.7858	0.849 62	0.856	0.354	-0.0457
0.3055	0.757 40	0.823	0.512	-0.0527	0.8918	0.873 63	0.877	0.200	-0.0281
0.3990	0.773 43	0.821	0.564	-0.0596	0.9477	0.886 93	0.891	0.101	-0.0154
0.4870	0.789 37	0.823	0.562	-0.0624					
$T = 293.15 \text{ K}$									
0.0697	0.712 15	0.759	0.194	-0.0128	0.5974	0.801 17	0.740	0.556	-0.0506
0.1170	0.719 04	0.751	0.300	-0.0219	0.7015	0.822 09	0.749	0.476	-0.0453
0.2087	0.732 99	0.741	0.455	-0.0345	0.7919	0.841 38	0.761	0.360	-0.0366
0.3076	0.748 92	0.735	0.557	-0.0443	0.8595	0.856 43	0.771	0.264	-0.0281
0.3914	0.763 15	0.733	0.599	-0.0495	0.9362	0.874 30	0.785	0.129	-0.0152
0.4903	0.780 83	0.734	0.606	-0.0524					
$T = 303.15 \text{ K}$									
0.0683	0.703 63	0.685	0.197	-0.0106	0.4546	0.765 22	0.659	0.646	-0.0426
0.1015	0.708 38	0.681	0.277	-0.0152	0.5178	0.776 71	0.659	0.633	-0.0435
0.1172	0.710 66	0.678	0.312	-0.0174	0.6046	0.793 15	0.663	0.590	-0.0416
0.2116	0.724 84	0.668	0.481	-0.0286	0.6977	0.811 75	0.669	0.504	-0.0377
0.3065	0.739 89	0.662	0.596	-0.0359	0.8708	0.849 10	0.688	0.261	-0.0209
0.4074	0.756 89	0.659	0.647	-0.0410	0.9451	0.866 41	0.699	0.114	-0.0093
$T = 313.15 \text{ K}$									
0.0571	0.693 86	0.619	0.170	-0.0079	0.6021	0.783 28	0.598	0.628	-0.0349
0.0934	0.698 93	0.615	0.269	-0.0113	0.6942	0.801 46	0.602	0.538	-0.0320
0.2019	0.714 85	0.604	0.486	-0.0224	0.7940	0.822 28	0.610	0.404	-0.0241
0.2986	0.729 94	0.598	0.608	-0.0291	0.9044	0.846 82	0.621	0.208	-0.0134
0.3957	0.746 00	0.595	0.667	-0.0339	0.9335	0.853 58	0.625	0.146	-0.0100
0.5021	0.764 65	0.595	0.676	-0.0358					
(x)Methyl Pentanoate + (1 - x)Decane									
$T = 283.15 \text{ K}$									
0.0703	0.744 70	1.387	0.195	-0.0247	0.5925	0.814 02	1.049	0.685	-0.0680
0.1150	0.749 40	1.347	0.305	-0.0371	0.7037	0.833 79	1.002	0.601	-0.0580
0.1975	0.758 61	1.281	0.470	-0.0526	0.8070	0.854 38	0.963	0.450	-0.0432
0.2969	0.770 70	1.212	0.606	-0.0648	0.8911	0.872 91	0.935	0.287	-0.0283
0.3879	0.782 77	1.156	0.682	-0.0701	0.9405	0.884 67	0.921	0.167	-0.0165
0.4992	0.799 00	1.095	0.713	-0.0712					
$T = 293.15 \text{ K}$									
0.0611	0.736 10	1.205	0.186	-0.0165	0.5993	0.806 27	0.918	0.729	-0.0537
0.1258	0.742 78	1.160	0.353	-0.0283	0.6913	0.822 38	0.885	0.647	-0.0470
0.1860	0.749 37	1.120	0.481	-0.0391	0.7943	0.842 30	0.852	0.505	-0.0360
0.3009	0.763 05	1.053	0.649	-0.0516	0.8678	0.857 96	0.831	0.360	-0.0260
0.3948	0.775 34	1.006	0.732	-0.0555	0.9327	0.872 93	0.815	0.201	-0.0147
0.5028	0.790 91	0.957	0.760	-0.0564					
$T = 303.15 \text{ K}$									
0.0964	0.731 82	1.034	0.296	-0.0187	0.5980	0.797 06	0.813	0.761	-0.0429
0.1217	0.734 44	1.020	0.356	-0.0224	0.7105	0.816 61	0.778	0.655	-0.0369
0.2007	0.742 96	0.976	0.530	-0.0331	0.7884	0.831 57	0.756	0.535	-0.0298
0.2978	0.754 35	0.929	0.681	-0.0407	0.8626	0.847 06	0.737	0.384	-0.0222
0.3885	0.766 00	0.890	0.760	-0.0443	0.9267	0.861 58	0.723	0.216	-0.0124
0.4974	0.781 35	0.848	0.794	-0.0449					
$T = 313.15 \text{ K}$									
0.0988	0.724 22	0.914	0.314	-0.0152	0.5868	0.786 25	0.730	0.811	-0.0348
0.1124	0.725 59	0.908	0.350	-0.0163	0.7123	0.807 67	0.696	0.681	-0.0293
0.2039	0.735 26	0.865	0.560	-0.0265	0.7932	0.823 03	0.676	0.549	-0.0240
0.2949	0.745 76	0.828	0.704	-0.0327	0.8738	0.839 76	0.658	0.372	-0.0157
0.3850	0.757 07	0.794	0.794	-0.0361	0.9298	0.852 34	0.647	0.220	-0.0098
0.4996	0.772 94	0.756	0.833	-0.0371					
(x)Methyl Pentanoate + (1 - x)Dodecane									
$T = 283.15 \text{ K}$									
0.0780	0.762 58	2.213	0.225	-0.0546	0.5566	0.812 83	1.388	0.801	-0.1336
0.1136	0.765 41	2.133	0.317	-0.0738	0.5870	0.817 14	1.348	0.794	-0.1291
0.2042	0.773 16	1.947	0.515	-0.1108	0.7102	0.836 63	1.197	0.692	-0.1062
0.2960	0.781 91	1.780	0.661	-0.1315	0.7992	0.853 00	1.098	0.558	-0.0808
0.4088	0.794 08	1.599	0.769	-0.1402	0.9033	0.875 23	0.993	0.324	-0.0442
0.4987	0.805 05	1.467	0.806	-0.1388	0.9468	0.885 74	0.953	0.194	-0.0255
$T = 293.15 \text{ K}$									
0.0785	0.755 19	1.836	0.240	-0.0373	0.6001	0.810 47	1.147	0.823	-0.0911
0.1268	0.758 96	1.754	0.371	-0.0560	0.7199	0.829 37	1.030	0.709	-0.0745
0.1866	0.763 96	1.660	0.505	-0.0728	0.8043	0.844 80	0.954	0.568	-0.0573
0.3015	0.774 60	1.496	0.701	-0.0929	0.8741	0.859 17	0.895	0.408	-0.0403
0.4108	0.786 19	1.357	0.810	-0.1005	0.9360	0.873 36	0.847	0.230	-0.0215
0.4938	0.796 11	1.261	0.843	-0.0993	0.9776	0.883 79	0.816	0.087	-0.0083
$T = 303.15 \text{ K}$									
0.0770	0.747 56	1.569	0.248	-0.0269	0.5941	0.800 92	1.008	0.857	-0.0697
0.1372	0.752 19	1.486	0.411	-0.0443	0.7077	0.818 23	0.914	0.758	-0.0577
0.1926	0.756 76	1.416	0.536	-0.0556	0.7933	0.833 31	0.849	0.616	-0.0452
0.3017	0.766 67	1.290	0.728	-0.0704	0.9001	0.855 14	0.772	0.357	-0.0254
0.3916	0.775 88	1.196	0.828	-0.0753	0.9350	0.863 17	0.749	0.245	-0.0166
0.4954	0.787 91	1.095	0.872	-0.0754					

Table 2 (Continued)

x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$	x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$
(x)Methyl Pentanoate + (1 - x)Dodecane (Continued)									
$T = 313.15 \text{ K}$									
0.0790	0.740 26	1.352	0.260	-0.0197	0.5920	0.791 96	0.892	0.898	-0.0531
0.1304	0.744 11	1.295	0.404	-0.0305	0.7022	0.808 34	0.814	0.796	-0.0449
0.1899	0.748 87	1.235	0.548	-0.0392	0.8004	0.825 30	0.750	0.629	-0.0338
0.3024	0.758 83	1.127	0.758	-0.0518	0.8909	0.843 41	0.695	0.400	-0.0206
0.3995	0.768 61	1.042	0.867	-0.0563	0.9370	0.853 73	0.669	0.251	-0.0121
0.4928	0.779 20	0.966	0.913	-0.0567					
(x)Methyl Hexanoate + (1 - x)Octane									
$T = 283.15 \text{ K}$									
0.0441	0.717 55	0.862	0.084	-0.0141	0.5977	0.813 62	0.971	0.380	-0.0828
0.1038	0.727 10	0.864	0.191	-0.0309	0.6907	0.831 35	1.007	0.324	-0.0761
0.1941	0.741 93	0.872	0.310	-0.0510	0.7971	0.852 21	1.055	0.234	-0.0601
0.2981	0.759 59	0.888	0.387	-0.0681	0.9104	0.875 09	1.116	0.114	-0.0312
0.4015	0.777 69	0.911	0.423	-0.0798	0.9342	0.879 98	1.130	0.087	-0.0245
0.5034	0.796 11	0.939	0.413	-0.0840					
$T = 293.15 \text{ K}$									
0.0606	0.712 00	0.770	0.129	-0.0154	0.6020	0.805 53	0.855	0.392	-0.0655
0.1113	0.720 08	0.772	0.217	-0.0253	0.7081	0.825 66	0.889	0.325	-0.0580
0.1973	0.734 09	0.778	0.334	-0.0406	0.7914	0.841 92	0.921	0.248	-0.0464
0.3010	0.751 57	0.790	0.411	-0.0543	0.8688	0.857 39	0.951	0.160	-0.0337
0.3965	0.768 17	0.807	0.440	-0.0620	0.9244	0.868 63	0.975	0.103	-0.0213
0.4970	0.786 15	0.828	0.436	-0.0664					
$T = 303.15 \text{ K}$									
0.0996	0.709 85	0.696	0.207	-0.0183	0.5947	0.795 09	0.761	0.409	-0.0528
0.2132	0.728 22	0.702	0.361	-0.0347	0.6431	0.804 12	0.772	0.381	-0.0511
0.2914	0.741 28	0.709	0.423	-0.0427	0.6942	0.813 79	0.785	0.344	-0.0481
0.3987	0.759 75	0.723	0.460	-0.0512	0.7924	0.832 77	0.814	0.255	-0.0380
0.5497	0.786 78	0.750	0.435	-0.0546	0.9033	0.854 82	0.851	0.133	-0.0216
$T = 313.15 \text{ K}$									
0.0915	0.700 19	0.627	0.203	-0.0138	0.5794	0.783 20	0.677	0.434	-0.0443
0.1966	0.716 97	0.630	0.356	-0.0270	0.6378	0.793 99	0.688	0.399	-0.0428
0.2783	0.730 46	0.636	0.424	-0.0343	0.6768	0.801 30	0.696	0.370	-0.0405
0.3882	0.749 14	0.647	0.471	-0.0417	0.7998	0.824 87	0.726	0.258	-0.0302
0.4834	0.765 84	0.661	0.472	-0.0444	0.8860	0.841 90	0.749	0.156	-0.0196
(x)Methyl Hexanoate + (1 - x)Decane									
$T = 283.15 \text{ K}$									
0.0564	0.743 87	1.417	0.135	-0.0204	0.6092	0.819 34	1.207	0.540	-0.0693
0.1037	0.749 25	1.388	0.238	-0.0330	0.7041	0.835 46	1.190	0.470	-0.0616
0.2048	0.761 39	1.334	0.404	-0.0541	0.8053	0.853 91	1.178	0.355	-0.0466
0.2895	0.772 24	1.297	0.497	-0.0656	0.8990	0.872 31	1.171	0.206	-0.0289
0.4063	0.788 27	1.257	0.564	-0.0732	0.9583	0.884 65	1.170	0.093	-0.0132
0.5118	0.803 89	1.228	0.572	-0.0742					
$T = 293.15 \text{ K}$									
0.0884	0.739 83	1.206	0.217	-0.0221	0.6004	0.809 34	1.048	0.566	-0.0554
0.1398	0.745 77	1.182	0.312	-0.0311	0.7031	0.826 52	1.032	0.489	-0.0482
0.2166	0.755 00	1.149	0.436	-0.0445	0.7888	0.841 87	1.022	0.390	-0.0394
0.2890	0.764 19	1.123	0.515	-0.0519	0.8690	0.857 18	1.015	0.263	-0.0278
0.4058	0.779 99	1.089	0.590	-0.0585	0.9179	0.866 96	1.013	0.177	-0.0187
0.4911	0.792 37	1.069	0.600	-0.0587					
$T = 303.15 \text{ K}$									
0.0867	0.731 82	1.056	0.221	-0.0177	0.6115	0.802 33	0.919	0.589	-0.0458
0.1240	0.736 03	1.041	0.298	-0.0241	0.7016	0.817 27	0.907	0.515	-0.0405
0.2050	0.745 55	1.012	0.437	-0.0349	0.7488	0.825 50	0.902	0.461	-0.0358
0.2900	0.756 14	0.986	0.539	-0.0416	0.7895	0.832 87	0.898	0.400	-0.0322
0.4081	0.771 93	0.957	0.614	-0.0469	0.8820	0.850 38	0.891	0.251	-0.0208
0.4934	0.784 16	0.939	0.626	-0.0486	0.9213	0.858 23	0.889	0.172	-0.0152
$T = 313.15 \text{ K}$									
0.0811	0.723 39	0.935	0.221	-0.0140	0.6127	0.793 76	0.815	0.615	-0.0366
0.1281	0.728 60	0.919	0.326	-0.0195	0.7048	0.808 89	0.803	0.531	-0.0325
0.1866	0.735 31	0.901	0.441	-0.0258	0.7930	0.824 36	0.794	0.417	-0.0265
0.2994	0.749 15	0.871	0.579	-0.0344	0.8698	0.838 69	0.789	0.288	-0.0186
0.3991	0.762 31	0.849	0.643	-0.0392	0.9212	0.848 77	0.787	0.185	-0.0119
0.4884	0.774 90	0.834	0.655	-0.0391					
(x)Methyl Hexanoate + (1 - x)Dodecane									
$T = 283.15 \text{ K}$									
0.0692	0.762 43	2.262	0.175	-0.0424	0.5995	0.821 16	1.514	0.644	-0.1140
0.0916	0.764 34	2.220	0.228	-0.0531	0.7005	0.836 40	1.414	0.572	-0.0958
0.1968	0.773 90	2.036	0.432	-0.0927	0.8011	0.853 38	1.323	0.445	-0.0719
0.3152	0.785 90	1.858	0.581	-0.1170	0.8996	0.872 09	1.243	0.260	-0.0407
0.4160	0.797 26	1.726	0.652	-0.1230	0.9455	0.881 62	1.209	0.151	-0.0232
0.5032	0.808 06	1.620	0.669	-0.1225					
$T = 293.15 \text{ K}$									
0.0666	0.754 82	1.879	0.178	-0.0277	0.5830	0.810 49	1.305	0.680	-0.0830
0.1182	0.759 21	1.804	0.296	-0.0453	0.6946	0.826 89	1.216	0.600	-0.0702
0.1903	0.765 71	1.710	0.436	-0.0637	0.7974	0.843 90	1.141	0.466	-0.0515
0.3035	0.776 88	1.575	0.592	-0.0819	0.8605	0.855 40	1.098	0.352	-0.0383
0.4010	0.787 55	1.473	0.669	-0.0884	0.9342	0.870 02	1.051	0.184	-0.0198
0.5027	0.799 85	1.375	0.694	-0.0884					

Table 2 (Continued)

x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$	x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$
(x)Methyl Hexanoate + (1 - x)Dodecane (Continued)									
$T = 303.15 \text{ K}$									
0.0626	0.747 03	1.604	0.172	-0.0205	0.5884	0.802 76	1.130	0.704	-0.0639
0.1092	0.750 89	1.550	0.285	-0.0326	0.6980	0.818 69	1.058	0.616	-0.0532
0.2035	0.759 27	1.450	0.469	-0.0512	0.7961	0.834 67	0.998	0.485	-0.0400
0.3017	0.768 82	1.357	0.611	-0.0629	0.8605	0.846 23	0.961	0.361	-0.0297
0.3949	0.778 80	1.276	0.689	-0.0680	0.9284	0.859 44	0.924	0.202	-0.0167
0.5073	0.792 14	1.188	0.721	-0.0681					
$T = 313.15 \text{ K}$									
0.0722	0.740 38	1.371	0.203	-0.0184	0.5889	0.794 41	0.990	0.728	-0.0500
0.1051	0.743 07	1.340	0.282	-0.0249	0.6982	0.810 01	0.929	0.643	-0.0423
0.1977	0.751 09	1.260	0.476	-0.0395	0.7963	0.825 74	0.878	0.505	-0.0318
0.3001	0.760 84	1.180	0.629	-0.0484	0.8590	0.836 79	0.848	0.383	-0.0229
0.4056	0.771 98	1.105	0.720	-0.0531	0.9306	0.850 51	0.815	0.207	-0.0125
0.5066	0.783 79	1.040	0.753	-0.0525					
(x)Methyl Heptanoate + (1 - x)Octane									
$T = 283.15 \text{ K}$									
0.0363	0.716 87	0.871	0.054	-0.0156	0.5975	0.816 24	1.128	0.261	-0.1148
0.1029	0.728 42	0.887	0.147	-0.0406	0.6969	0.834 13	1.200	0.216	-0.1050
0.2101	0.747 21	0.922	0.241	-0.0733	0.8014	0.852 99	1.286	0.154	-0.0828
0.3033	0.763 66	0.961	0.289	-0.0941	0.9061	0.871 94	1.383	0.077	-0.0477
0.4005	0.780 94	1.009	0.305	-0.1088	0.9585	0.881 46	1.437	0.031	-0.0237
0.4928	0.797 43	1.061	0.297	-0.1159					
$T = 293.15 \text{ K}$									
0.0743	0.715 31	0.784	0.116	-0.0234	0.6020	0.808 37	0.986	0.265	-0.0881
0.0950	0.718 88	0.787	0.144	-0.0301	0.6686	0.820 29	1.023	0.236	-0.0841
0.1926	0.735 85	0.813	0.239	-0.0538	0.8001	0.843 91	1.107	0.157	-0.0641
0.2930	0.753 45	0.846	0.295	-0.0720	0.8905	0.860 20	1.172	0.089	-0.0416
0.3972	0.771 87	0.886	0.312	-0.0844	0.9373	0.868 64	1.210	0.052	-0.0253
0.4998	0.790 11	0.933	0.301	-0.0899					
$T = 303.15 \text{ K}$									
0.0656	0.705 53	0.705	0.108	-0.0166	0.5967	0.798 56	0.867	0.273	-0.0697
0.0962	0.710 76	0.711	0.153	-0.0229	0.6970	0.816 43	0.914	0.224	-0.0625
0.2005	0.728 77	0.733	0.256	-0.0426	0.8064	0.835 98	0.970	0.156	-0.0486
0.2930	0.744 90	0.757	0.304	-0.0558	0.9107	0.854 68	1.032	0.077	-0.0263
0.4016	0.763 98	0.791	0.322	-0.0665	0.9413	0.860 18	1.051	0.050	-0.0186
0.4987	0.781 16	0.827	0.306	-0.0699					
$T = 313.15 \text{ K}$									
0.0614	0.696 49	0.635	0.110	-0.0121	0.6002	0.790 38	0.772	0.278	-0.0559
0.0995	0.702 99	0.640	0.161	-0.0191	0.7068	0.809 30	0.813	0.222	-0.0498
0.1999	0.720 24	0.659	0.258	-0.0336	0.8053	0.826 84	0.856	0.158	-0.0385
0.3125	0.739 78	0.684	0.314	-0.0468	0.9022	0.844 13	0.903	0.086	-0.0226
0.4029	0.755 59	0.708	0.325	-0.0533	0.9389	0.850 71	0.922	0.053	-0.0150
0.5031	0.773 21	0.738	0.313	-0.0567					
(x)Methyl Heptanoate + (1 - x)Decane									
$T = 283.15 \text{ K}$									
0.0470	0.743 36	1.438	0.084	-0.0185	0.5975	0.819 64	1.388	0.434	-0.0838
0.0866	0.748 20	1.426	0.161	-0.0301	0.7008	0.836 22	1.403	0.369	-0.0740
0.2036	0.763 10	1.398	0.327	-0.0587	0.8108	0.854 74	1.427	0.269	-0.0538
0.3008	0.776 14	1.384	0.407	-0.0754	0.8892	0.868 53	1.449	0.175	-0.0350
0.3894	0.788 50	1.378	0.455	-0.0840	0.9466	0.878 99	1.465	0.087	-0.0190
0.5056	0.805 53	1.380	0.461	-0.0874					
$T = 293.15 \text{ K}$									
0.0795	0.739 66	1.231	0.165	-0.0206	0.5980	0.811 32	1.192	0.454	-0.0662
0.1137	0.743 86	1.222	0.226	-0.0293	0.6888	0.825 73	1.201	0.394	-0.0590
0.2052	0.755 46	1.205	0.353	-0.0462	0.8133	0.846 49	1.221	0.270	-0.0414
0.3017	0.768 26	1.192	0.439	-0.0591	0.8595	0.854 49	1.229	0.215	-0.0345
0.3908	0.780 60	1.187	0.480	-0.0656	0.9375	0.868 38	1.247	0.110	-0.0168
0.5062	0.797 36	1.186	0.483	-0.0692					
$T = 303.15 \text{ K}$									
0.0674	0.730 39	1.078	0.153	-0.0156	0.6002	0.803 05	1.038	0.477	-0.0528
0.1095	0.735 49	1.069	0.230	-0.0233	0.6931	0.817 67	1.044	0.412	-0.0475
0.2049	0.747 43	1.052	0.369	-0.0384	0.7949	0.834 45	1.055	0.303	-0.0376
0.2913	0.758 74	1.043	0.449	-0.0470	0.8963	0.851 94	1.071	0.170	-0.0216
0.3982	0.773 35	1.036	0.507	-0.0539	0.9315	0.858 18	1.077	0.123	-0.0152
0.5107	0.789 55	1.035	0.510	-0.0557					
$T = 313.15 \text{ K}$									
0.0778	0.723 86	0.949	0.184	-0.0143	0.6030	0.794 98	0.914	0.495	-0.0436
0.1133	0.728 12	0.942	0.251	-0.0200	0.6976	0.809 75	0.919	0.426	-0.0391
0.1989	0.738 71	0.930	0.381	-0.0303	0.8122	0.828 55	0.928	0.299	-0.0292
0.2944	0.751 05	0.920	0.479	-0.0389	0.8549	0.835 81	0.933	0.242	-0.0238
0.4056	0.766 16	0.914	0.531	-0.0445	0.9315	0.849 23	0.944	0.122	-0.0120
0.4898	0.778 13	0.913	0.535	-0.0457					

Table 2. (Continued)

x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$	x	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\nu/\text{mm}^2\cdot\text{s}^{-1}$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$	$\Delta\eta/\text{mPa}\cdot\text{s}$
(x)Methyl Heptanoate + (1 - x)Dodecane									
$T = 283.15 \text{ K}$									
0.0602	0.762 15	2.306	0.126	-0.0328	0.6049	0.823 76	1.718	0.534	-0.1029
0.1078	0.766 58	2.232	0.217	-0.0560	0.6947	0.836 70	1.655	0.474	-0.0880
0.2052	0.776 11	2.100	0.378	-0.0882	0.8018	0.853 46	1.586	0.357	-0.0653
0.2986	0.785 96	1.992	0.481	-0.1054	0.8938	0.869 14	1.536	0.217	-0.0382
0.3984	0.797 30	1.892	0.544	-0.1134	0.9488	0.879 16	1.509	0.113	-0.0187
0.5036	0.810 24	1.799	0.562	-0.1107					
$T = 293.15 \text{ K}$									
0.0678	0.755 43	1.898	0.160	-0.0257	0.5966	0.814 41	1.457	0.559	-0.0755
0.1104	0.759 33	1.852	0.249	-0.0378	0.6948	0.828 31	1.401	0.498	-0.0658
0.1927	0.767 27	1.765	0.382	-0.0591	0.7979	0.844 22	1.349	0.381	-0.0484
0.3191	0.780 44	1.652	0.528	-0.0770	0.8712	0.856 44	1.315	0.265	-0.0340
0.3907	0.788 51	1.595	0.570	-0.0813	0.9342	0.867 59	1.289	0.147	-0.0185
0.5124	0.803 31	1.509	0.585	-0.0819					
$T = 303.15 \text{ K}$									
0.0851	0.749 51	1.600	0.203	-0.0236	0.5950	0.805 83	1.255	0.585	-0.0597
0.1367	0.754 25	1.554	0.304	-0.0353	0.6945	0.819 75	1.208	0.511	-0.0510
0.2074	0.761 05	1.496	0.420	-0.0472	0.7927	0.834 66	1.166	0.397	-0.0388
0.3084	0.771 45	1.423	0.534	-0.0581	0.8780	0.848 69	1.132	0.259	-0.0254
0.3885	0.780 29	1.370	0.588	-0.0632	0.9257	0.857 00	1.115	0.170	-0.0161
0.4967	0.793 14	1.306	0.613	-0.0640					
$T = 313.15 \text{ K}$									
0.0806	0.741 66	1.382	0.205	-0.0168	0.6068	0.799 12	1.089	0.608	-0.0466
0.1248	0.745 63	1.349	0.298	-0.0253	0.6893	0.810 55	1.056	0.540	-0.0409
0.2126	0.753 94	1.291	0.445	-0.0374	0.7992	0.827 05	1.017	0.403	-0.0298
0.3042	0.763 23	1.236	0.553	-0.0456	0.8802	0.840 25	0.990	0.266	-0.0195
0.3902	0.772 58	1.190	0.613	-0.0491	0.9238	0.847 78	0.977	0.175	-0.0131
0.4999	0.785 44	1.136	0.641	-0.0500					

mixture and pure components 1 (methyl ester) and 2 (alkane), respectively.

Table 2 shows the experimental densities, kinematic viscosities, excess molar volumes, and viscosity deviations obtained for each binary mixture at working temperatures.

The V^E and $\Delta\eta$ values were correlated with composition x (mole fraction of methyl ester) using a variable-degree polynomial function of the form

$$Y = x(1 - x) \sum_{k=0}^N A_k (2x - 1)^k \quad (4)$$

where $Y \equiv (V^E \text{ or } \Delta\eta)$. The fitting parameters A_k were obtained by the unweighted least-squares method, and the optimum number of parameters N was determined using an F-test.³⁹ Table 3 shows the fitting parameters and the standard deviations for each of the binary mixtures at all the four temperatures.

(x, V^E , or $\Delta\eta$) data for the current systems and temperatures have not been found in the literature, while (x, V^E) data at 298.15 K were found for all of these systems.⁴⁰⁻⁴² The coherence among the previously published data and those expected (at the same temperature) from our experimental results is adequate in the main part of the cases, from both quantitative and qualitative (curves symmetry) points of view. The methyl heptanoate + octane system represents an exception with respect to the above-mentioned behavior because the V^E values published are slightly larger than those obtained in this work at 303.15 K; however, the difference between the maximum value of the reported $V^E(x)$ curve and that expected from our data, at 298.15 K, does not exceed 0.005 $\text{cm}^3 \text{mol}^{-1}$.

As noted from Table 2, the V^E values were positive over the entire composition range for all the studied systems and temperatures. In general, the shapes of the curves were nearly symmetrical except those from the binary mixtures containing octane which showed their maxima slightly skewed toward mole fractions lower in ester. Figure

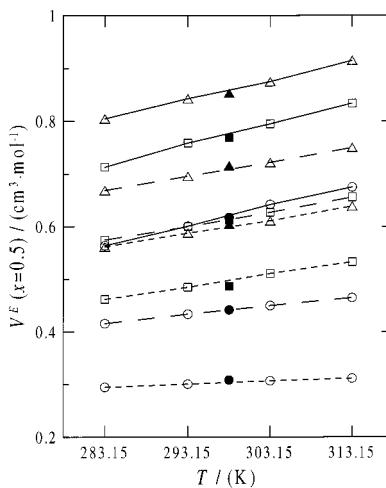


Figure 1. Plots of $V^E(x=0.5)$ as a function of T for the different methyl ester + alkane binary systems: ○, octane; □, decane; △, dodecane; ■, methyl pentanoate; ●, methyl hexanoate; ▲, methyl heptanoate; ●, Ortega et al.⁴⁰ for a mixture containing octane; ■, Ortega et al.⁴¹ for mixtures containing decane; ▲, Ortega et al.⁴² for mixtures containing dodecane.

1 shows the equimolar excess volumes against temperature for all the binary systems.

On one hand, the V^E values, for a given ester, increase with the chain length in the alkane. On the other hand, the V^E values decrease, for a given alkane, with the molecular size of the ester. This latter effect is shown in Figure 2 where we may observe that the influence of temperature is stronger as the number of carbon atoms in the ester decreases. The same behavior may be observed for the excess molar enthalpies H^E at 298.15 K for the systems herein studied which are, also, available in the literature.⁴⁰⁻⁴² These results suggest that the positive contribution to both of these properties, due to the net rupture of dipole-dipole interactions in the esters, prevails over the negative contributions associated both with the

Table 3. Parameters (A_k) of Eq 4 and Standard Deviations (s) for V^E ($\text{cm}^3 \cdot \text{mol}^{-1}$) and $\Delta\eta$ ($\text{mPa} \cdot \text{s}$) of the $\{(x)\text{CH}_3(\text{CH}_2)_{m-2}\text{COOCH}_3 + (1 - x)\text{C}_n\text{H}_{2n+2}\}$ Binary Systems

<i>m</i>	<i>n</i>	<i>T/K</i>		<i>A</i> ₀	<i>A</i> ₁	<i>A</i> ₂	<i>A</i> ₃	<i>A</i> ₄	<i>s</i>
5	8	283.15	V^E	2.255	-0.366	0.159			0.003
		293.15	$\Delta\eta$	-0.2497	-0.0194	-0.0434			0.0005
		293.15	V^E	2.406	-0.473	0.222			0.003
		303.15	$\Delta\eta$	-0.2081	-0.0152	-0.0224			0.0006
		303.15	V^E	2.568	-0.490	0.144			0.003
	10	313.15	$\Delta\eta$	-0.1733	-0.0111				0.0004
		313.15	V^E	2.701	-0.458	0.107			0.002
		313.15	$\Delta\eta$	-0.1439	-0.0117				0.0003
		283.15	V^E	2.851	-0.041	0.204			0.002
		293.15	$\Delta\eta$	-0.2856	0.0355	-0.0419	-0.0216	-0.0399	0.0004
5	12	293.15	V^E	3.034	-0.054	0.247			0.002
		303.15	$\Delta\eta$	-0.2263	0.0271	-0.0348			0.0005
		303.15	V^E	3.178	-0.081	0.205			0.003
		313.15	$\Delta\eta$	-0.1808	0.0191	-0.0316			0.0003
		313.15	V^E	3.334	-0.080	0.174			0.002
	12	283.15	$\Delta\eta$	-0.1476	0.0154	-0.0154			0.0003
		293.15	V^E	3.219	0.190	0.305	0.239		0.002
		293.15	$\Delta\eta$	-0.5542	0.1455	-0.1102			0.0005
		303.15	V^E	3.374	0.192	0.266	0.112		0.001
		313.15	$\Delta\eta$	-0.3960	0.0918	-0.0663			0.0003
6	8	303.15	V^E	3.498	0.219	0.337	0.133		0.002
		313.15	$\Delta\eta$	-0.3001	0.0662	-0.0442			0.0004
		283.15	V^E	3.660	0.245	0.199	0.179	0.163	0.001
		293.15	$\Delta\eta$	-0.2264	0.0375	-0.0209			0.0003
		303.15	V^E	1.663	-0.423	0.110			0.003
	10	313.15	$\Delta\eta$	-0.3364	-0.0367	-0.0346			0.0003
		283.15	V^E	1.737	-0.493	0.143			0.003
		293.15	$\Delta\eta$	-0.2653	-0.0253	-0.0192			0.0005
		303.15	V^E	1.801	-0.547	0.165	0.086		0.001
		313.15	$\Delta\eta$	-0.2176	-0.0223				0.0005
6	12	313.15	V^E	1.860	-0.530	0.177			0.002
		283.15	$\Delta\eta$	-0.1793	-0.0170				0.0002
		293.15	V^E	2.296	-0.181	0.192			0.002
		303.15	$\Delta\eta$	-0.2958	0.0285	-0.0624			0.0005
		313.15	V^E	2.398	-0.202	0.148			0.002
	12	303.15	$\Delta\eta$	-0.2354	0.0306	-0.0361	-0.0284		0.0004
		283.15	V^E	2.509	-0.170	0.120	-0.115		0.002
		293.15	$\Delta\eta$	-0.1926	0.0137	-0.0312			0.0004
		303.15	V^E	2.625	-0.262	0.211			0.003
		313.15	$\Delta\eta$	-0.1570	0.0096	-0.0235			0.0004
7	8	313.15	V^E	2.677	0.057	0.210			0.003
		283.15	$\Delta\eta$	-0.4895	0.1119	-0.0824			0.0006
		293.15	V^E	2.783	0.028	0.199	0.067		0.001
		303.15	$\Delta\eta$	-0.3528	0.0746	-0.0383			0.0003
		313.15	V^E	2.889	0.059	0.143			0.002
	10	313.15	$\Delta\eta$	-0.2719	0.0572	-0.0301			0.0003
		283.15	V^E	2.999	0.093	0.157			0.002
		293.15	$\Delta\eta$	-0.2115	0.0360	-0.0269	0.0195		0.0003
		303.15	V^E	1.178	-0.429	0.093			0.002
		313.15	$\Delta\eta$	-0.4644	-0.0604	-0.0337	-0.0204	-0.0341	0.0002
7	10	283.15	V^E	1.203	-0.466	0.135			0.001
		293.15	$\Delta\eta$	-0.3590	-0.0465	-0.0415			0.0004
		303.15	V^E	1.228	-0.500	0.185			0.001
		313.15	$\Delta\eta$	-0.2808	-0.0357	-0.0211			0.0003
		283.15	V^E	1.248	-0.509	0.198			0.002
	12	313.15	$\Delta\eta$	-0.2266	-0.0284	-0.0089			0.0002
		283.15	V^E	1.849	-0.265	0.058	0.173		0.004
		293.15	$\Delta\eta$	-0.3494	0.0107	-0.0303			0.0007
		303.15	V^E	1.939	-0.305	0.123			0.003
		313.15	$\Delta\eta$	-0.2778					0.0007
7	12	303.15	V^E	2.042	-0.321	0.095			0.003
		283.15	$\Delta\eta$	-0.2219	0.0052	-0.0266			0.0003
		293.15	V^E	2.134	-0.341	0.140	-0.045		0.001
		313.15	$\Delta\eta$	-0.1862					0.0008
		283.15	V^E	2.247	-0.115	0.144	0.203	-0.156	0.001
	12	293.15	$\Delta\eta$	-0.4477	0.1104	-0.0706			0.0008
		303.15	V^E	2.353	-0.100	0.165			0.003
		313.15	$\Delta\eta$	-0.3274	0.0607	-0.0317			0.0005
		283.15	V^E	2.445	-0.113	0.109			0.001
		293.15	$\Delta\eta$	-0.2548	0.0426	-0.0212			0.0002
	12	303.15	V^E	2.556	-0.089	0.100	-0.102		0.002
		313.15	$\Delta\eta$	-0.2004	0.0302	-0.0125			0.0003

molecular packing and the promotion of heteromolecular dipole-dipole induced interactions.

The experimental excess molar volumes were compared to those predicted by the molecular group-contribution

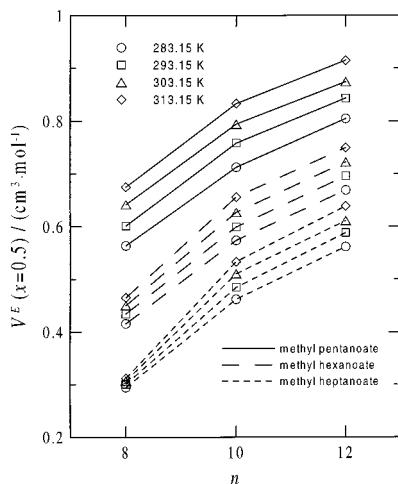


Figure 2. Excess molar volumes at equimolar composition against n , the number of carbon atoms in the alkane, at different temperatures.

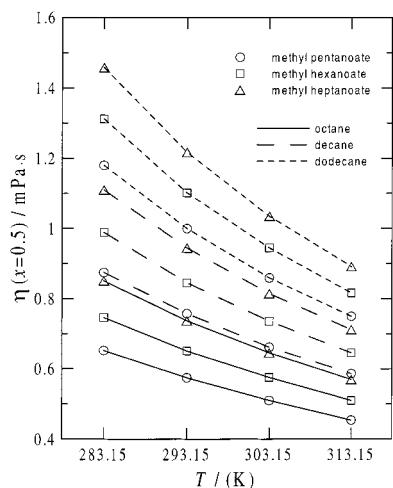


Figure 3. Temperature dependence of η at the equimolar fraction for all the binary mixtures studied.

model by Nitta et al.⁴ employing three parameter sets proposed by Navarro,^{5,6} by Ortega and Legido,⁶ and by Carballo et al.,⁷ henceforth referred as EA1, EA2, and EA3, respectively. Minimum and maximum differences between the experimental and theoretical V^E values were as follows: 8.6 and 24% using EA1, 7.7 and 30% using EA2; and 8.9 and 64% using EA3. These differences were calculated averaging, for each system, the results for all of the temperatures and compositions. The best agreement between the experimental and predict results, from a quantitative point of view, was obtained employing the EA1 parameters; nevertheless, the model in combination with EA2 predicts the shape of the curves with higher accuracy.

In Figure 3, the equimolar dynamic viscosities are plotted against temperature. As may be observed, the $\eta(x=0.5)$ values decrease both as the temperature increases and as the chain length in both the alkane and ester decreases. Viscosity deviations were negative over the entire composition range for all of the systems in this study, and they increased (values were less negative) as the temperature increased. Figure 4 shows the variation of $\Delta\eta(x=0.5)$ values against the number of carbon atoms in the ester. The sign of the viscosity deviations was strongly related to the predominance of the dispersion forces in these mixtures.⁴³ The solubility parameter components by

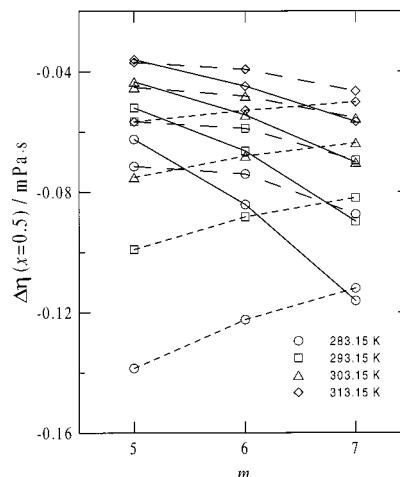


Figure 4. Viscosity Deviations, $\Delta\eta$, versus the number of carbon atoms in the ester for $\{0.5\text{CH}_3(\text{CH}_2)_{m-2}\text{COOCH}_3 + 0.5\text{C}_n\text{H}_{2n+2}\}$ at different temperatures: —, $n = 8$; ---, $n = 10$; - · -, $n = 12$.

Hansen (see ref 44) showed that the dispersive energy is dominant in all of the studied liquids.

As mentioned above, the equations proposed by Grunberg and Nissan, McAllister (assuming three-body and four-body interaction), Hind et al., Heric, and Lobe were used to test their applicability to correlate the composition-viscosity data of the mixtures analyzed in this work. These equations were described in an earlier paper,³ and the results obtained in the current work are shown in Tables 4 and 5. All of the tested models were capable of describing the experimental behavior. The overall mean errors obtained for each equation were the following: McAllister equation assuming four-body interactions (0.03%), McAllister equation assuming three-body interactions and Heric equation (0.08%), Lobe equation (0.15%), Grunberg–Nissan equation (0.17%), and Hind et al. equation (0.30%). As could be expected, the most accurate were due the McAllister model with three adjustable parameters.

We have used the group contribution models UNIFAC–VISCO¹³ and UNIVAC¹⁴ to predict the kinematic viscosities of the binary mixtures studied in this work and found that in all cases the agreement was good. For the UNIFAC–VISCO model the minimum and maximum differences between experimental and theoretical values were 0.40 and 1.2%, respectively, whereas for the UNIVAC model these differences were 0.46 and 1.9%, respectively. These percentual differences were calculated as an average for all of the temperatures and compositions.

Conclusions

Densities and kinematic viscosities of the binary systems $\{\text{CH}_3(\text{CH}_2)_{m-2}\text{COOCH}_3 + \text{C}_n\text{H}_{2n+2}\}$, for ($m = 5, 6$, and 7) and ($n = 8, 10$, and 12), have been experimentally determined at several temperatures (283.15, 293.15, 303.15, and 313.15) K and atmospheric pressure for the whole composition range. Also, the absolute viscosities, excess molar volumes, and viscosity deviations were computed.

The excess volumes were compared to those predicted by the multiproperty group-contribution model by Nitta et al., using three different parameter sets. The best predictions were obtained with the primary parameters with an overall absolute deviation of 14.2%.

All of the selected equations to correlate composition–viscosity data were capable of describing the experimental behavior, and the overall absolute deviations were lower than 0.35%. We remark that the Grunberg and Nissan

Table 4. Parameter Values and Standard Deviations (*s*) for the Binary Systems $\{(x)\text{CH}_3(\text{CH}_2)_{m-2}\text{COOCH}_3 + (1-x)\text{C}_n\text{H}_{2n+2}\}$ Using the McAllister Equations

<i>m</i>	<i>n</i>	<i>T/K</i>	McAllister (three-body interactions)			McAllister (four-body interactions)			
			<i>v</i> ₁₂	<i>v</i> ₂₁	<i>s</i>	<i>v</i> ₁₁₁₂	<i>v</i> ₁₁₂₂	<i>v</i> ₂₂₂₁	<i>s</i>
5	8	283.15	0.8158	0.7901	0.001	0.8299	0.8170	0.8000	0.001
		293.15	0.7272	0.7084	0.001	0.7421	0.7225	0.7210	0.001
		303.15	0.6519	0.6390	0.0003	0.6658	0.6450	0.6530	0.0004
		313.15	0.5879	0.5789	0.0003	0.5986	0.5844	0.5600	0.0003
5	10	283.15	1.0020	1.1563	0.002	0.9647	1.0981	1.2130	0.001
		293.15	0.8807	1.0138	0.001	0.8540	0.9541	1.0635	0.0004
		303.15	0.7816	0.8952	0.001	0.7575	0.8447	0.9367	0.0004
		313.15	0.7007	0.7986	0.001	0.6801	0.7531	0.8346	0.0003
5	12	283.15	1.2752	1.6933	0.003	1.1496	1.4993	1.8298	0.0003
		293.15	1.1011	1.4417	0.002	1.0048	1.2758	1.5497	0.0003
		303.15	0.9673	1.2479	0.001	0.8871	1.1071	1.3375	0.001
		313.15	0.8543	1.0996	0.001	0.7884	0.9726	1.1729	0.001
6	8	283.15	0.9787	0.8574	0.001	1.0163	0.9277	0.8526	0.001
		293.15	0.8602	0.7657	0.001	0.8939	0.8148	0.7650	0.001
		303.15	0.7644	0.6901	0.0003	0.7927	0.7274	0.6907	0.0003
		313.15	0.6827	0.6210	0.0004	0.7055	0.6532	0.6212	0.0004
6	10	283.15	1.1742	1.2358	0.002	1.1623	1.2241	1.2774	0.0004
		293.15	1.0181	1.0758	0.001	1.0105	1.0575	1.1119	0.001
		303.15	0.8956	0.9471	0.001	0.8878	0.9320	0.9763	0.0002
		313.15	0.7942	0.8411	0.001	0.7858	0.8284	0.8650	0.001
6	12	283.15	1.4429	1.7952	0.003	1.3533	1.6344	1.9162	0.001
		293.15	1.2361	1.5179	0.001	1.1704	1.3762	1.6174	0.001
		303.15	1.0788	1.3090	0.001	1.0232	1.1936	1.3893	0.0003
		313.15	0.903	1.1405	0.001	0.8986	1.0485	1.2040	0.0003
7	8	283.15	1.1605	0.9400	0.002	1.2215	1.0654	0.9078	0.001
		293.15	1.0093	0.8320	0.002	1.0577	0.9324	0.8068	0.001
		303.15	0.8885	0.7466	0.001	0.9301	0.8222	0.7285	0.0004
		313.15	0.7888	0.6707	0.0004	0.8258	0.7291	0.6579	0.0003
7	10	283.15	1.3714	1.3281	0.001	1.3949	1.3571	1.3552	0.001
		293.15	1.1757	1.1500	0.001	1.1959	1.1651	1.1739	0.001
		303.15	1.0239	1.0063	0.001	1.0367	1.0214	1.0246	0.0003
		313.15	0.9015	0.8899	0.001	0.9094	0.9052	0.9035	0.0004
7	12	283.15	1.6572	1.8947	0.002	1.5985	1.7952	1.9982	0.001
		293.15	1.3998	1.6022	0.001	1.3599	1.5047	1.6851	0.001
		303.15	1.2077	1.3770	0.001	1.1739	1.2949	1.4441	0.001
		313.15	1.0550	1.1989	0.0005	1.0272	1.1271	1.2541	0.0004

Table 5. Parameter Values and Standard Deviations (*s*) for $\{(x)\text{CH}_3(\text{CH}_2)_{m-2}\text{COOCH}_3 + (1-x)\text{C}_n\text{H}_{2n+2}\}$ Using Several Correlations

<i>m</i>	<i>n</i>	<i>T/K</i>	Grunberg and Nissan		Hind et al.		Heric			Lobe		
			<i>d</i>	<i>s</i>	<i>v</i> ₁₂	<i>s</i>	<i>v</i> ₁₂	<i>v</i> ₂₁	<i>s</i>	<i>v</i> ₁₂	<i>v</i> ₂₁	<i>s</i>
5	8	283.15	-0.3321	0.002	0.5868	0.002	-0.2929	0.0238	0.001	-0.59348	14.7029	0.002
		293.15	-0.3126	0.001	0.5211	0.002	-0.2700	0.0207	0.006	-8.1443	19.0295	0.001
		303.15	-0.2934	0.001	0.4666	0.001	-0.2518	0.0215	0.0003	-19.8352	42.9683	0.0004
		313.15	-0.2719	0.001	0.4185	0.001	-0.2328	0.0177	0.0003	-29.9555	62.5430	0.001
5	10	283.15	-0.2945	0.002	0.7983	0.004	-0.1846	0.0228	0.002	1.7685	-3.0419	0.004
		293.15	-0.2621	0.001	0.6981	0.002	-0.1611	0.0140	0.001	1.7841	-2.9998	0.002
		303.15	-0.2420	0.001	0.6143	0.002	-0.1416	0.0153	0.001	1.8270	-3.0146	0.002
		313.15	-0.2225	0.001	0.5458	0.001	-0.1233	0.0151	0.001	1.8681	-3.0257	0.001
5	12	283.15	-0.1417	0.004	1.0343	0.011	0.0327	0.0652	0.003	1.3806	-2.2804	0.008
		293.15	-0.1231	0.002	0.8950	0.007	0.0507	0.0518	0.002	1.3890	-2.2466	0.005
		303.15	-0.1054	0.002	0.7812	0.005	0.0691	0.0528	0.001	1.4285	2.2735	0.004
		313.15	-0.0934	0.001	0.6909	0.003	0.0873	0.0349	0.001	1.4037	-2.1763	0.002
6	8	283.15	-0.2883	0.003	0.6599	0.003	-0.2747	0.0464	0.001	-0.0818	1.3503	0.001
		293.15	-0.2625	0.002	0.5841	0.002	-0.2484	0.0384	0.001	-0.1613	1.4356	0.001
		303.15	-0.2445	0.001	0.5206	0.002	-0.2319	0.0317	0.0003	-0.2214	1.5264	0.0004
		313.15	-0.2300	0.001	0.4646	0.001	-0.2180	0.0296	0.0004	-0.3400	1.6939	0.001
6	10	283.15	-0.2966	0.003	0.9087	0.003	-0.2412	0.0329	0.002	2.7752	-5.0548	0.003
		293.15	-0.2743	0.002	0.7846	0.002	-0.2182	0.0245	0.001	2.7361	-4.8477	0.002
		303.15	-0.2585	0.001	0.6857	0.002	-0.2036	0.0214	0.001	2.7434	-4.7687	0.002
		313.15	-0.2410	0.001	0.6044	0.001	-0.1891	0.0182	0.001	2.7266	-4.6465	0.002
6	12	283.15	-0.2131	0.002	0.1833	0.009	-0.1027	0.0333	0.003	1.4818	-2.4086	0.006
		293.15	-0.1853	0.001	0.0107	0.006	-0.0761	0.0287	0.001	1.5258	2.4265	0.003
		303.15	-0.1706	0.001	0.8743	0.004	-0.0600	0.0299	0.001	1.5713	-2.4647	0.002
		313.15	-0.1564	0.001	0.7623	0.003	-0.0463	0.0286	0.001	1.6014	-2.4780	0.002
7	8	283.15	-0.2271	0.003	0.7316	0.005	-0.2253	0.0447	0.002	0.6556	-0.0698	0.002
		293.15	-0.2093	0.003	0.6443	0.004	-0.2052	0.0421	0.002	0.5835	0.0219	0.002
		303.15	-0.1885	0.002	0.5745	0.003	-0.1848	0.0358	0.001	0.5649	0.0349	0.001
		313.15	-0.1705	0.001	0.5124	0.002	-0.1675	0.0324	0.0004	0.5291	0.0626	0.0004
7	10	283.15	-0.2835	0.003	1.0209	0.001	-0.2592	0.0390	0.001	18.8636	41.3927	0.002
		293.15	-0.2629	0.002	0.8750	0.001	-0.2384	0.0291	0.001	-41.7804	88.4548	0.001
		303.15	-0.2501	0.002	0.7578	0.001	-0.2233	0.0283	0.001	76.7581	-155.0078	0.001
		313.15	-0.2367	0.002	0.6639	0.001	-0.2111	0.0256	0.001	28.3038	-55.5239	0.001
7	12	283.15	-0.2508	0.004	1.3410	0.008	-0.1852	0.0407	0.002	1.8039	-2.9843	0.004
		293.15	-0.2217	0.002	1.1325	0.005	-0.1568	0.0226	0.001	1.7785	-2.8532	0.002
		303.15	-0.2043	0.001	0.9695	0.003	-0.1384	0.0199	0.001	1.8076	-2.8479	0.002
		313.15	-0.1081	0.001	0.8405	0.002	0.1205	0.0151	0.001	1.8210	-2.8118	0.001

equation, despite the incorporation of a single parameter, presents an overall absolute deviation of 0.17%.

Both UNIFAC-VISCO and UNIVAC predicted with relatively high accuracy the kinematic viscosities obtained in this work, and the overall absolute deviations were 0.7 and 1.3%, respectively.

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