Excess Molar Volumes of Binary Mixtures Containing a Methyl Ester (Ethanoate to Tetradecanoate) with Odd *n*-Alkanes at 298.15 K

Miguel A. Postigo and Pablo H. Garcia

Cátedra de Fisicoquímica, Departamento de Química, Facultad de Ingeniería, Universidad Nacional de Comahue, Neuquén, Argentina

Juan Ortega* and Gloria Tardajos†

Laboratorio de Termodinámica y Fisicoquímica, Escuela Superior de Ingenieros Industriales, Universidad de Las Palmas de Gran Canaria, Canary Islands, Spain

Molar excess volumes of several methyl esters (from ethanoate to tetradecanoate) with five odd *n*-alkanes (from pentane to tridecane) were determined at 298.15 K and atmospheric pressure from the experimental densities and correlated by a suitable equation. The results for V^E are compared with those found in the literature and discussed in terms of the interactions between the groups intervening in the mixtures using the Flory and Nitta–Chao models. Only the Nitta–Chao model gives acceptable agreement with experiment when $V^E > 0$.

Introduction

Our laboratory has in recent years produced a series of papers presenting V^E and/or H^E values for binary mixtures of methyl esters + *n*-alkanes. This paper is intended to expand the systematic study in progress by presenting V^E values at 298.15 K for 40 such binary mixtures {$CH_3(CH_2)_{u-1}CO_2CH_3$ (1) (u = 1, 2, 3, 5, 7, 9, 11, 13) + $CH_3(CH_2)_{2v+1}CH_3$ (2) (v = 1–5)}. The V^E values have been published for the mixture methyl ethanoate + pentane (De Soria et al., 1988) and for mixtures of heptane and certain methyl esters, such as ethanoate (Grolier et al., 1974; Dusart et al., 1976; Pintos et al., 1988), propanoate and butanoate (Dusart et al., 1976; Pintos et al., 1988), hexanoate (Dusart et al., 1976), and octanoate (Pintos et al., 1988). Molecular interaction effects affecting the experimental V^E values are discussed in terms of the theory underlying the Flory (1965) and Nitta et al. (1977) models.

Experimental Section

All the liquids employed in this study were partially degassed by ultrasound and then dried on molecular sieves (type 4A from Fluka). All components were from Fluka with a purity of >99 mol % except the pentane and heptane, which were from J. T. Baker with a purity of >99.5 mol %. The molar volume of each component at 298.15 K is given in Table 3.

Solutions were prepared by mass using a Sartorius balance (precision $\pm 1 \times 10^{-4}$ g), taking precautions to prevent evaporation. The possible error in the calculation of the mole fraction was estimated to be less than $\pm 2 \times 10^{-4}$. V^E values were calculated from the densities of the pure components and binary mixtures measured with a vibrating-tube densimeter similar to that described by Corti et al. (1990) thermostated at 298.15 ± 0.01 K. This type of densimeter operates on the basis of a linear relationship between the density, ϱ, and the square of the resonance period, τ, of the vibrating tube:

$$\varrho = A + B\tau^2 \quad (1)$$

The constants A and B were calculated by calibrating the densimeter using four reference fluids and computing the coefficients of eq 1 by a method of least squares. The reference fluids were tetrachloroethylene, 1,2-dichloroethane, water, and 2-propanol, and density measurements were taken according to Riddick et al. (1986). The calibrations were monitored periodically by measuring the period of some of the above-mentioned reference fluids; fluctuations did not exceed ±0.01 μs. The precision in the V^E values was estimated to be ±0.002 $cm^3 \cdot mol^{-1}$.

Results

Table 1 presents the experimental V^E values at 298.15 K for the 40 binary mixtures considered. The results were fitted by the following polynomial equation, discussed in Ortega and Alcalde (1992), which yielded comparatively better fits than those obtained with the more widely used Redlich–Kister equation:

$$V^E/(cm^3 \cdot mol^{-1}) = x(1-x)\sum_{i=0}^{n} A_i[x/[x + k(1-x)]]^i \quad (2)$$

The values of the parameter A_i for a given value of k were calculated by a method of least squares. Table 2 lists the values for each mixture together with the corresponding standard deviations. A statistical criterion [F-test; see Bevington (1969)] was used to establish the degree of the polynomial.

Figure 1 plots the V^E values calculated using the coefficient values from Table 2 in eq 2 vs the mole fraction of the ester; literature values are also shown. For a given *n*-alkane the V^E values for the mixtures considered here decreased with methyl ester chain length. In the plots of the equimolar volumes, $V^E(x_1=0.5)$, vs ester chain length, the decrease was quasi-exponential. In contrast, those equimolar values increased linearly with *n*-alkane chain length (see Figure 2). For esters with a low number of carbon atoms, expansion effects predominated, but as R_1

† Present address: Departamento de Química-Física, Universidad Complutense, 28040 Madrid, Spain.

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Table 1. Experimental Molar Volumes V^E for the Binaries Methyl Ester + *n*-Alkane at 298.15 K (∂V^E Represents the Difference between Experimental and Correlated Values)

x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)
					CH_3COOCH_3 (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0532	0.360	0	0.3315	1.078	−1	0.6072	0.867	0	0.8417	0.377	0
0.0854	0.530	−1	0.3846	1.082	−1	0.6473	0.797	−1	0.9073	0.217	−0
0.1537	0.801	1	0.4527	1.053	1	0.7115	0.674	2	0.9385	0.143	1
0.2378	0.992	−1	0.5133	0.997	0	0.7483	0.593	−0			
0.3061	1.068	2	0.5408	0.963	−1	0.8236	0.418	−2			
					CH_3COOCH_3 (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0372	0.253	0	0.2933	1.287	1	0.5538	1.442	2	0.7906	0.979	−2
0.0873	0.546	−0	0.3413	1.370	−1	0.6086	1.386	1	0.8471	0.778	−0
0.1518	0.853	1	0.4211	1.453	1	0.6432	1.337	3	0.8816	0.635	1
0.2173	1.090	−0	0.4573	1.465	−2	0.6885	1.247	−4	0.9308	0.399	1
0.2406	1.158	−1	0.5127	1.462	−1	0.7327	1.148	0			
					CH_3COOCH_3 (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0396	0.266	−2	0.2939	1.339	2	0.5391	1.586	−0	0.8417	0.941	2
0.0874	0.551	1	0.3416	1.438	1	0.5907	1.558	1	0.9011	0.650	2
0.1432	0.826	−0	0.3826	1.504	2	0.6339	1.509	−0	0.9338	0.453	−5
0.2071	1.080	−1	0.4312	1.555	−2	0.7341	1.311	0			
0.2418	1.194	−1	0.4873	1.585	−2	0.8074	1.078	0			
					CH_3COOCH_3 (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.0931	0.573	3	0.3041	1.371	−2	0.4949	1.654	0	0.6982	1.507	−0
0.1438	0.820	1	0.3385	1.453	1	0.5316	1.665	1	0.7315	1.428	−2
0.2117	1.091	−2	0.3961	1.557	1	0.5786	1.653	−2	0.8385	1.053	1
0.2432	1.199	−1	0.4522	1.625	1	0.6437	1.599	1	0.8883	0.799	1
					CH_3COOCH_3 (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.0480	0.322	2	0.3073	1.405	1	0.5417	1.711	2	0.7891	1.320	1
0.0837	0.529	−1	0.3509	1.502	−1	0.5887	1.700	−1	0.8383	1.115	0
0.1327	0.782	1	0.4036	1.597	−0	0.6327	1.667	−1	0.9337	0.551	0
0.1879	1.020	−1	0.4385	1.644	0	0.6883	1.589	−0			
0.2461	1.228	−1	0.4924	1.693	1	0.7429	1.464	−1			
					$CH_3CH_2COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0707	0.260	0	0.3686	0.520	−2	0.6692	0.283	−1	0.8989	0.060	−1
0.1088	0.352	−3	0.4193	0.501	2	0.7108	0.239	−1	0.9139	0.051	2
0.1612	0.450	4	0.4952	0.447	−1	0.7404	0.211	1	0.9304	0.037	−1
0.1950	0.484	−1	0.5451	0.406	0	0.7968	0.150	−2			
0.2634	0.527	0	0.5937	0.361	1	0.8323	0.118	−0			
0.3324	0.531	−0	0.6340	0.321	1	0.8531	0.101	2			
					$CH_3CH_2COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0478	0.223	−0	0.3307	0.931	0	0.5433	0.992	3	0.8579	0.495	0
0.1167	0.483	0	0.3812	0.974	−0	0.5883	0.962	0	0.8925	0.391	−1
0.1593	0.612	1	0.4281	0.995	−2	0.6758	0.868	−1	0.9327	0.262	3
0.2131	0.742	−1	0.4825	1.005	0	0.7534	0.741	0	0.9567	0.173	1
0.2837	0.871	0	0.5162	0.999	−0	0.8180	0.598	−1	0.9794	0.084	−0
					$CH_3CH_2COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.1689	0.685	0	0.6175	1.148	2	0.6826	1.062	2	0.8809	0.531	−1
0.2706	0.952	−1	0.5732	1.183	0	0.7113	1.010	1	0.8854	0.516	1
0.3130	1.035	−0	0.5942	1.165	−3	0.7599	0.905	2	0.9224	0.366	−0
0.3970	1.150	0	0.6497	1.105	−4	0.7902	0.822	−3			
0.4475	1.187	−1	0.5145	1.204	1	0.8151	0.755	2			
0.4802	1.201	1	0.6596	1.094	−1	0.8518	0.635	−1			
					$CH_3CH_2COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.1879	0.777	1	0.5218	1.291	3	0.7164	1.131	1	0.8726	0.674	−3
0.2997	1.055	−1	0.5772	1.282	1	0.7439	1.074	−1	0.8947	0.584	2
0.3502	1.146	1	0.6400	1.237	−1	0.7615	1.034	−1	0.9113	0.505	−0
0.4224	1.233	−2	0.6824	1.186	−0	0.8365	0.816	2	0.9455	0.332	2
0.4692	1.270	−1	0.6771	1.195	1	0.8475	0.773	−1			
					$CH_3CH_2COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.2074	0.849	1	0.5027	1.332	0	0.7112	1.205	−2	0.8615	0.778	0
0.2174	0.877	0	0.5449	1.344	3	0.7701	1.080	−0	0.8993	0.607	−1
0.3089	1.095	−3	0.6134	1.320	−1	0.7827	1.046	−1	0.8970	0.619	−0
0.4057	1.253	−0	0.6370	1.302	−1	0.8175	0.944	3			
0.4622	1.309	1	0.6749	1.262	−0	0.8320	0.892	1			
					$CH_3(CH_2)_2COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0450	0.077	−1	0.2973	0.177	−1	0.4929	0.103	1	0.8229	−0.052	0
0.1134	0.147	−1	0.3576	0.159	−2	0.6091	0.038	0	0.8425	−0.056	−2
0.1567	0.172	1	0.3878	0.149	−1	0.6706	0.005	1	0.8902	−0.052	1
0.2715	0.184	2	0.4712	0.114	1	0.7438	−0.031	−2	0.9657	−0.023	2
					$CH_3(CH_2)_2COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0624	0.217	1	0.3618	0.727	−0	0.5452	0.726	0	0.7928	0.442	−2
0.0912	0.302	2	0.4126	0.747	0	0.5939	0.694	−0	0.8416	0.359	3
0.1609	0.468	−2	0.4436	0.750	−1	0.6411	0.652	0	0.9135	0.208	1
0.2362	0.602	−1	0.4861	0.750	0	0.7082	0.570	−3	0.9618	0.097	2
0.3044	0.685	0	0.5327	0.734	2	0.7391	0.528	−2			
					$CH_3(CH_2)_2COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0618	0.237	−0	0.2927	0.813	2	0.5436	0.939	−1	0.7837	0.652	−3
0.1076	0.387	−3	0.3433	0.876	0	0.6081	0.900	−1	0.8346	0.543	1
0.1318	0.461	−1	0.3936	0.920	0	0.6437	0.872	4	0.8912	0.393	2
0.2114	0.661	−2	0.4526	0.946	−1	0.7106	0.781	−2	0.9471	0.208	−2
0.2436	0.733	5	0.4946	0.949	−2	0.7381	0.741	2			

Table 1 (Continued)

x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)
					$CH_3(CH_2)_2COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.0426	0.173	−0	0.3561	0.947	−0	0.6121	1.017	0	0.8781	0.503	1
0.1035	0.393	4	0.3920	0.986	−1	0.6552	0.977	−1	0.9291	0.317	1
0.1427	0.508	−3	0.4383	1.025	2	0.6948	0.930	1			
0.2428	0.759	−1	0.4876	1.045	0	0.8084	0.705	−1			
0.2875	0.846	0	0.5543	1.044	−1	0.8316	0.643	−1			
					$CH_3(CH_2)_2COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.0368	0.154	3	0.2869	0.860	0	0.5893	1.093	−1	0.8437	0.679	−2
0.0973	0.373	2	0.3433	0.953	−0	0.6416	1.061	−2	0.9061	0.461	3
0.1562	0.553	−1	0.4128	1.038	1	0.6932	1.008	0	0.9475	0.276	0
0.2047	0.681	−2	0.4943	1.093	1	0.7386	0.937	−0			
0.2386	0.760	−2	0.5368	1.104	2	0.7914	0.826	0			
					$CH_3(CH_2)_4COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0638	−0.105	−0	0.3118	−0.387	2	0.5607	−0.460	2	0.8068	−0.302	1
0.0962	−0.154	−1	0.3463	−0.411	1	0.6039	−0.452	−1	0.9106	−0.160	1
0.1362	−0.210	−1	0.3881	−0.435	−0	0.6436	−0.437	−2	0.9417	−0.108	1
0.2134	−0.299	1	0.4365	−0.452	1	0.6819	−0.414	−0			
0.2591	−0.348	−3	0.5083	−0.465	−0	0.7362	−0.374	−1			
					$CH_3(CH_2)_4COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0438	0.076	−2	0.2923	0.285	2	0.5416	0.264	−2	0.8066	0.137	2
0.1074	0.161	−2	0.3594	0.294	0	0.5883	0.247	−3	0.8407	0.116	3
0.1425	0.197	−2	0.4137	0.296	3	0.6385	0.225	−3	0.9121	0.066	2
0.1906	0.237	0	0.4583	0.288	1	0.6931	0.200	−1	0.9308	0.054	3
0.2367	0.265	2	0.4909	0.279	−2	0.7416	0.174	−0			
					$CH_3(CH_2)_4COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0308	0.082	−2	0.2873	0.485	3	0.5384	0.530	2	0.8135	0.296	−3
0.0916	0.222	1	0.3412	0.513	−2	0.5839	0.515	5	0.8424	0.257	−3
0.1537	0.329	−2	0.3883	0.528	−5	0.6408	0.476	2	0.8876	0.192	−2
0.1961	0.393	3	0.4324	0.540	−1	0.6933	0.434	3	0.9375	0.112	−1
0.2391	0.439	0	0.4837	0.537	−3	0.7417	0.384	0			
					$CH_3(CH_2)_4COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.0408	0.116	−2	0.2904	0.573	2	0.5319	0.666	−1	0.8447	0.344	1
0.0896	0.241	1	0.3389	0.615	−1	0.5944	0.640	−2	0.8051	0.227	3
0.1516	0.375	−3	0.3873	0.647	−0	0.6409	0.611	0	0.9608	0.101	3
0.1843	0.430	2	0.4421	0.667	−1	0.7122	0.540	−1			
0.2417	0.514	0	0.5037	0.673	1	0.7936	0.430	0			
					$CH_3(CH_2)_4COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.0471	0.136	−0	0.2936	0.623	−1	0.4887	0.752	−2	0.6921	0.646	0
0.1121	0.301	−0	0.3374	0.673	0	0.5427	0.750	−1	0.7538	0.579	2
0.1936	0.473	2	0.3906	0.717	1	0.5936	0.739	6	0.8144	0.472	−4
0.2361	0.543	−1	0.4359	0.741	0	0.6385	0.702	−3	0.8816	0.338	3
					$CH_3(CH_2)_6COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0384	−0.149	1	0.2349	−0.667	−2	0.5117	−0.824	−2	0.8166	−0.440	−1
0.0935	−0.337	−2	0.3116	−0.767	0	0.5558	−0.800	−2	0.8438	−0.379	3
0.1148	−0.400	−2	0.3587	−0.803	3	0.6273	−0.739	−4	0.9390	−0.163	−2
0.1463	−0.477	4	0.3864	−0.820	1	0.6839	−0.663	2			
0.2075	−0.618	−2	0.4479	−0.832	3	0.7427	−0.573	2			
					$CH_3(CH_2)_6COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0417	0.024	3	0.2861	0.049	−1	0.5908	−0.048	0	0.8932	−0.026	1
0.1051	0.045	−2	0.3619	0.028	1	0.6413	−0.055	1	0.9423	−0.015	−2
0.1589	0.057	−1	0.4038	0.013	1	0.7317	−0.059	−1			
0.1921	0.061	0	0.4839	−0.020	−2	0.7924	−0.050	0			
0.2413	0.059	1	0.5381	−0.035	0	0.8566	−0.036	0			
					$CH_3(CH_2)_6COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0438	0.075	−2	0.2891	0.298	3	0.5426	0.298	−1	0.8929	0.099	1
0.1132	0.167	−3	0.3374	0.309	0	0.6037	0.279	−0	0.9364	0.062	2
0.1724	0.227	−0	0.3921	0.315	−1	0.6452	0.261	−1			
0.2081	0.256	2	0.4265	0.315	−2	0.7345	0.215	1			
0.2417	0.276	2	0.4876	0.309	−2	0.8396	0.143	2			
					$CH_3(CH_2)_6COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.0583	0.121	−1	0.3573	0.439	−1	0.5872	0.435	−2	0.9126	0.138	2
0.1127	0.212	−2	0.4137	0.456	−0	0.6428	0.409	−0	0.9385	0.102	4
0.1889	0.315	1	0.4416	0.460	−0	0.7117	0.358	−3			
0.2407	0.366	0	0.4937	0.460	−0	0.7913	0.289	2			
0.2929	0.410	4	0.5381	0.452	−1	0.8409	0.232	1			
					$CH_3(CH_2)_6COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.0638	0.149	1	0.2917	0.477	1	0.5126	0.555	−2	0.8891	0.222	−1
0.0913	0.201	−2	0.3362	0.509	0	0.5408	0.552	−1	0.9463	0.116	0
0.1386	0.288	0	0.3887	0.537	0	0.5921	0.539	2			
0.1941	0.370	0	0.4426	0.553	−0	0.6448	0.510	1			
0.2368	0.422	0	0.4873	0.556	−2	0.7936	0.367	0			
					$CH_3(CH_2)_8COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0636	−0.323	−4	0.2836	−1.012	−2	0.5375	−1.034	3	0.8409	−0.467	−4
0.0987	−0.480	0	0.3413	−1.080	−5	0.5824	−0.981	4	0.9317	−0.221	−12
0.1663	−0.732	5	0.4119	−1.105	−3	0.6422	−0.888	7			
0.2087	−0.857	3	0.4585	−1.096	−3	0.7083	−0.768	4			
0.2312	−0.913	1	0.4912	−1.078	−2	0.7869	−0.600	−2			

Table 1 (Continued)

x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)	x_1	V^E/ ($cm^3 \cdot mol^{-1}$)	$\partial V^E \times 10^3$/ ($cm^3 \cdot mol^{-1}$)
					$CH_3(CH_2)_8COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0583	−0.029	0	0.2832	−0.151	0	0.5381	−0.209	1	0.8741	−0.087	1
0.0918	−0.049	−1	0.3506	−0.181	−2	0.6136	−0.201	0	0.9467	−0.039	−0
0.1325	−0.071	−0	0.3873	−0.192	−2	0.7039	−0.176	−0			
0.1834	−0.099	1	0.4435	−0.202	1	0.7414	−0.161	−1			
0.2327	−0.124	2	0.4929	−0.208	1	0.8326	−0.113	0			
					$CH_3(CH_2)_8COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0408	0.041	−2	0.3461	0.158	2	0.6124	0.119	−2	0.9068	0.038	6
0.1071	0.090	−4	0.3835	0.156	0	0.6433	0.110	−3	0.9426	0.023	3
0.2074	0.139	1	0.4596	0.148	−1	0.7385	0.085	−2			
0.2582	0.151	2	0.4918	0.144	−1	0.8109	0.069	5			
0.2906	0.156	3	0.5535	0.132	−2	0.8426	0.053	−1			
					$CH_3(CH_2)_8COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.0345	0.055	3	0.3463	0.297	3	0.6375	0.259	1	0.8829	0.102	−1
0.0869	0.119	−0	0.3908	0.303	1	0.6891	0.235	1	0.9375	0.059	2
0.1273	0.163	−0	0.4924	0.300	−1	0.7468	0.202	2			
0.1932	0.218	−2	0.5535	0.287	−1	0.8136	0.155	−1			
0.2836	0.273	−0	0.6046	0.270	−2	0.8408	0.134	−2			
					$CH_3(CH_2)_8COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.0593	0.099	−2	0.2474	0.320	−0	0.4469	0.404	−1	0.7312	0.301	1
0.0878	0.142	−1	0.3068	0.363	2	0.4837	0.405	−1	0.8536	0.186	1
0.1367	0.211	2	0.3558	0.383	−1	0.5436	0.398	1	0.9133	0.114	−1
0.1826	0.261	−0	0.4136	0.400	−1	0.6837	0.334	−0	0.9571	0.058	−1
					$CH_3(CH_2)_{10}COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0979	−0.674	1	0.2870	−1.248	2	0.5013	−1.250	0	0.6918	−0.926	0
0.1921	−1.057	−2	0.4028	−1.311	−1	0.5833	−1.141	−1	0.7982	−0.654	1
					$CH_3(CH_2)_{10}COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.1088	−0.134	3	0.3050	−0.289	0	0.4783	−0.326	1	0.6997	−0.255	0
0.1628	−0.194	−3	0.3866	−0.317	1	0.5785	−0.311	−1			
					$CH_3(CH_2)_{10}COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.0810	0.017	−1	0.3826	0.027	0	0.6982	−0.021	−1			
0.1903	0.031	−0	0.4973	0.013	1	0.7988	−0.029	1			
0.3000	0.033	1	0.5940	−0.005	−1	0.9113	−0.024	0			
					$CH_3(CH_2)_{10}COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.3939	0.192	2	0.8265	0.078	3	0.5015	0.180	1	0.2625	0.170	−2
0.5188	0.177	2	0.7205	0.112	−4	0.4304	0.193	5	0.2030	0.145	−2
0.5835	0.158	−2	0.6665	0.131	−4	0.3496	0.189	0	0.1382	0.106	2
0.9075	0.052	11	0.6177	0.146	−4	0.2948	0.180	−1			
					$CH_3(CH_2)_{10}COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.9076	0.075	−3	0.7302	0.202	5	0.4175	0.284	−1	0.1817	0.193	2
0.8543	0.177	−2	0.6785	0.233	5	0.3570	0.273	−3			
0.8156	0.146	−1	0.5804	0.267	0	0.2921	0.253	−2			
0.7887	0.166	1	0.4845	0.284	−1	0.2221	0.221	3			
					$CH_3(CH_2)_{12}COOCH_3$ (1) + $CH_3(CH_2)_3CH_3$ (2)						
0.0899	−0.799	0	0.2861	−1.470	−1	0.5804	−1.333	−1			
0.1064	−0.904	−0	0.3834	−1.521	0	0.6916	−1.094	−4			
0.1722	−1.212	0	0.4865	−1.462	2	0.7950	−0.787	4			
					$CH_3(CH_2)_{12}COOCH_3$ (1) + $CH_3(CH_2)_5CH_3$ (2)						
0.0908	−0.188	1	0.2807	−0.408	0	0.4902	−0.469	−0	0.7136	−0.327	1
0.1905	−0.327	−1	0.3847	−0.460	1	0.5874	−0.434	−1	0.7859	−0.246	−1
					$CH_3(CH_2)_{12}COOCH_3$ (1) + $CH_3(CH_2)_7CH_3$ (2)						
0.1168	−0.022	0	0.3153	−0.071	−1	0.4754	−0.097	−2	0.6871	−0.083	0
0.1934	−0.041	−0	0.3867	−0.082	2	0.6011	−0.095	0	0.7904	−0.057	−0
					$CH_3(CH_2)_{12}COOCH_3$ (1) + $CH_3(CH_2)_9CH_3$ (2)						
0.3915	0.108	1	0.1886	0.090	0	0.6716	0.063	−1	0.4468	0.101	−2
0.3007	0.106	−1	0.9118	0.014	−0	0.6051	0.077	−1			
0.4633	0.100	−1	0.7993	0.036	−0	0.5479	0.089	1			
0.0899	0.055	1	0.7272	0.053	1	0.5149	0.096	2			
					$CH_3(CH_2)_{12}COOCH_3$ (1) + $CH_3(CH_2)_{11}CH_3$ (2)						
0.9731	0.018	3	0.3890	0.195	1	0.2108	0.150	−1	0.5507	0.182	−1
0.8570	0.072	−2	0.3618	0.192	1	0.1734	0.132	−1	0.4569	0.193	−1
0.6435	0.161	1	0.3147	0.187	3	0.9302	0.038	1	0.9302	0.038	1
0.4825	0.191	−1	0.2810	0.176	0	0.8458	0.078	−2	0.8458	0.078	−2
0.4257	0.193	−2	0.2401	0.163	0	0.7034	0.143	3	0.7034	0.143	3

in R_1COOCH_3 increased in chain length, the polarity of the ester decreased, allowing greater accommodation of the *n*-alkane molecules, thus resulting in $V^E < 0$, as was the case for pentane, heptane, and nonane. The effects of the *n*-alkane on mixing volume were wholly steric. Similar findings were documented in previous work (Ortega and Alcalde, 1992; Ortega and Legido, 1994).

The V^E values published by De Soria et al. (1988) for methyl ethanoate + pentane, also plotted in Figure 1a, were appreciably lower than our values, with an average difference of 38%. Figure 1b compares the (x_1,V^E) values for the mixtures containing heptane; the percent differences with respect to the results for mixtures with methyl ethanoate, propanoate, and butanoate published by Dusart et al. (1976) and Pintos et al. (1988) were acceptable at less than 5% in all cases. The difference between our values and those by Grolier et al. (1974) for the mixture with methyl ethanoate were less than 7%. Our results for

Table 2. Parameters A_i and Standard Deviations $s(V^E)$ Obtained for Eq 2

mixture	k	A_0	A_1	A_2	A_3	$10^3 s(V^E)/(cm^3 \cdot mol^{-1})$
CH_3COOCH_3 (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.947	7.768	−11.784	11.588	−5.376	1.1
$CH_3(CH_2)_5CH_3$ (2)	1.011	7.223	−4.577	3.714		1.5
$CH_3(CH_2)_7CH_3$ (2)	1.017	7.188	−3.843	4.378		2.0
$CH_3(CH_2)_9CH_3$ (2)	1.025	7.009	−3.229	4.960		1.6
$CH_3(CH_2)_{11}CH_3$ (2)	1.047	7.162	−3.682	5.961		1.1
$CH_3CH_2COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.787	4.588	−7.733	6.500	−2.967	1.8
$CH_3(CH_2)_5CH_3$ (2)	0.865	5.077	−3.286	2.424		1.3
$CH_3(CH_2)_7CH_3$ (2)	0.975	5.018	−1.033	1.233		1.7
$CH_3(CH_2)_9CH_3$ (2)	1.056	5.359	−2.127	3.128		1.6
$CH_3(CH_2)_{11}CH_3$ (2)	1.100	5.411	−2.087	3.991		1.5
$CH_3(CH_2)_2COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.699	2.096	−4.777	5.181	−3.374	1.6
$CH_3(CH_2)_5CH_3$ (2)	0.477	3.849	−1.288			1.7
$CH_3(CH_2)_7CH_3$ (2)	2.030	4.146	−1.669	1.913		2.3
$CH_3(CH_2)_9CH_3$ (2)	1.055	4.280	−1.019	1.706		1.5
$CH_3(CH_2)_{11}CH_3$ (2)	1.093	4.295	−1.010	2.175		1.7
$CH_3(CH_2)_4COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	1.277	−1.744	−0.260			1.3
$CH_3(CH_2)_5CH_3$ (2)	0.419	1.972	−1.218			2.2
$CH_3(CH_2)_7CH_3$ (2)	0.345	2.881	−0.983			2.7
$CH_3(CH_2)_9CH_3$ (2)	0.225	3.091	−0.493			1.7
$CH_3(CH_2)_{11}CH_3$ (2)	1.707	3.044	−0.296	0.619		2.5
$CH_3(CH_2)_6COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.664	−4.140	1.391			2.6
$CH_3(CH_2)_5CH_3$ (2)	0.762	0.542	0.120	−3.925	3.071	1.4
$CH_3(CH_2)_7CH_3$ (2)	0.345	1.959	−0.971			2.0
$CH_3(CH_2)_9CH_3$ (2)	0.303	2.329	−0.639			2.0
$CH_3(CH_2)_{11}CH_3$ (2)	0.799	2.554	−0.994	0.742		1.3
$CH_3(CH_2)_8COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.251	−4.953	−2.884	4.662		5.0
$CH_3(CH_2)_5CH_3$ (2)	0.840	−0.451	−1.216	0.929		1.2
$CH_3(CH_2)_7CH_3$ (2)	0.359	1.189	−0.835			2.8
$CH_3(CH_2)_9CH_3$ (2)	0.670	1.584	−0.643			1.7
$CH_3(CH_2)_{11}CH_3$ (2)	0.903	1.828	−0.402			1.3
$CH_3(CH_2)_{10}COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.231	−8.610	2.135	2.834		1.5
$CH_3(CH_2)_5CH_3$ (2)	2.168	−1.435	0.424			2.1
$CH_3(CH_2)_7CH_3$ (2)	1.989	0.277	−0.692			1.0
$CH_3(CH_2)_9CH_3$ (2)	0.161	−0.163	3.549	−2.936		4.4
$CH_3(CH_2)_{11}CH_3$ (2)	1.111	1.362	−0.482			2.4
$CH_3(CH_2)_{12}COOCH_3$ (1) +						
$CH_3(CH_2)_3CH_3$ (2)	0.086	−8.375	−10.067	13.972		2.4
$CH_3(CH_2)_5CH_3$ (2)	0.878	−2.528	2.901	−5.386	4.257	1.1
$CH_3(CH_2)_7CH_3$ (2)	1.559	−0.138	−1.068	1.101		1.3
$CH_3(CH_2)_9CH_3$ (2)	0.687	0.740	−0.601			1.1
$CH_3(CH_2)_{11}CH_3$ (2)	0.811	1.025	−0.476			1.8

Table 3. Molar Volumes and Characteristic Properties of Pure Liquids Used in This Work

substance	$V/(cm^3 \cdot mol^{-1})$	$V^*/(cm^3 \cdot mol^{-1})$	$p^*/(J \cdot cm^{-3})$	T^*/K	$\alpha \times 10^3/K^{-1}$	κ_T/TPa^{-1}
CH_3COOCH_3	79.892	60.16	653.67	4387.7	1.42[a]	1143[a]
$CH_3CH_2COOCH_3$	96.923	74.10	620.28	4555.1	1.31[a]	1077[a]
$CH_3(CH_2)_2COOCH_3$	114.421	88.63	588.14	4714.8	1.22[a]	1031[a]
$CH_3(CH_2)_4COOCH_3$	148.052	117.13	544.99	5018.1	1.08[a]	944[a]
$CH_3(CH_2)_6COOCH_3$	181.414	145.48	531.83	5241.0	0.997[b]	869[b]
$CH_3(CH_2)_8COOCH_3$	214.557	173.73	524.63	5418.8	0.939[b]	814[b]
$CH_3(CH_2)_{10}COOCH_3$	247.811	202.13	531.04	5570.6	0.895[b]	755[b]
$CH_3(CH_2)_{12}COOCH_3$	280.905	230.25	542.47	5675.4	0.867[b]	709[b]
$CH_3(CH_2)_3CH_3$	116.083	84.98	431.25	4123.8	1.643[c]	2120[c]
$CH_3(CH_2)_5CH_3$	147.511	113.82	433.48	4668.0	1.245[c]	1438[c]
$CH_3(CH_2)_7CH_3$	179.743	141.98	443.96	4993.7	1.090[d]	1173[d]
$CH_3(CH_2)_9CH_3$	212.292	169.97	453.19	5216.8	1.005[d]	1031[d]
$CH_3(CH_2)_{11}CH_3$	245.053	199.23	434.13	5506.7	0.913[d]	948[d]

[a] González et al. (1993). [b] González et al. (1994b). [c] Letcher et al. (1989). [d] Diaz-Peña et al. (1978).

methyl hexanoate differed by 10% from the values published by Dusart et al. (1976), and quantitative comparison of our results for methyl octanoate with the values reported by Pintos et al. (1988) would not appear to be in order, since on a qualitative basis our values suggest behavior approaching ideality, yielding a sigmoidal curve over the range of concentrations considered.

Application of the Theoretical Models

Flory Model. The Flory model (Flory, 1965; Abe and Flory, 1965) has been considered valid only for nonpolar liquids, pure and in mixtures, consisting of molecules with different sizes and shapes. However, in order to generalize the Flory equation of state several modifications have been carried out in the original version, and therefore, some researchers have applied that theory to other kinds of substances (Deshpande and Prabu, 1978; Awwad and Jbara, 1981; De Soria et al., 1988) to evaluate the contribution of polar molecules present in the mixtures.

The parameters for pure component liquids required in the calculations of the volume of mixing, V^E, are listed in Table 3. The interactional parameter, χ_{12}, was determined

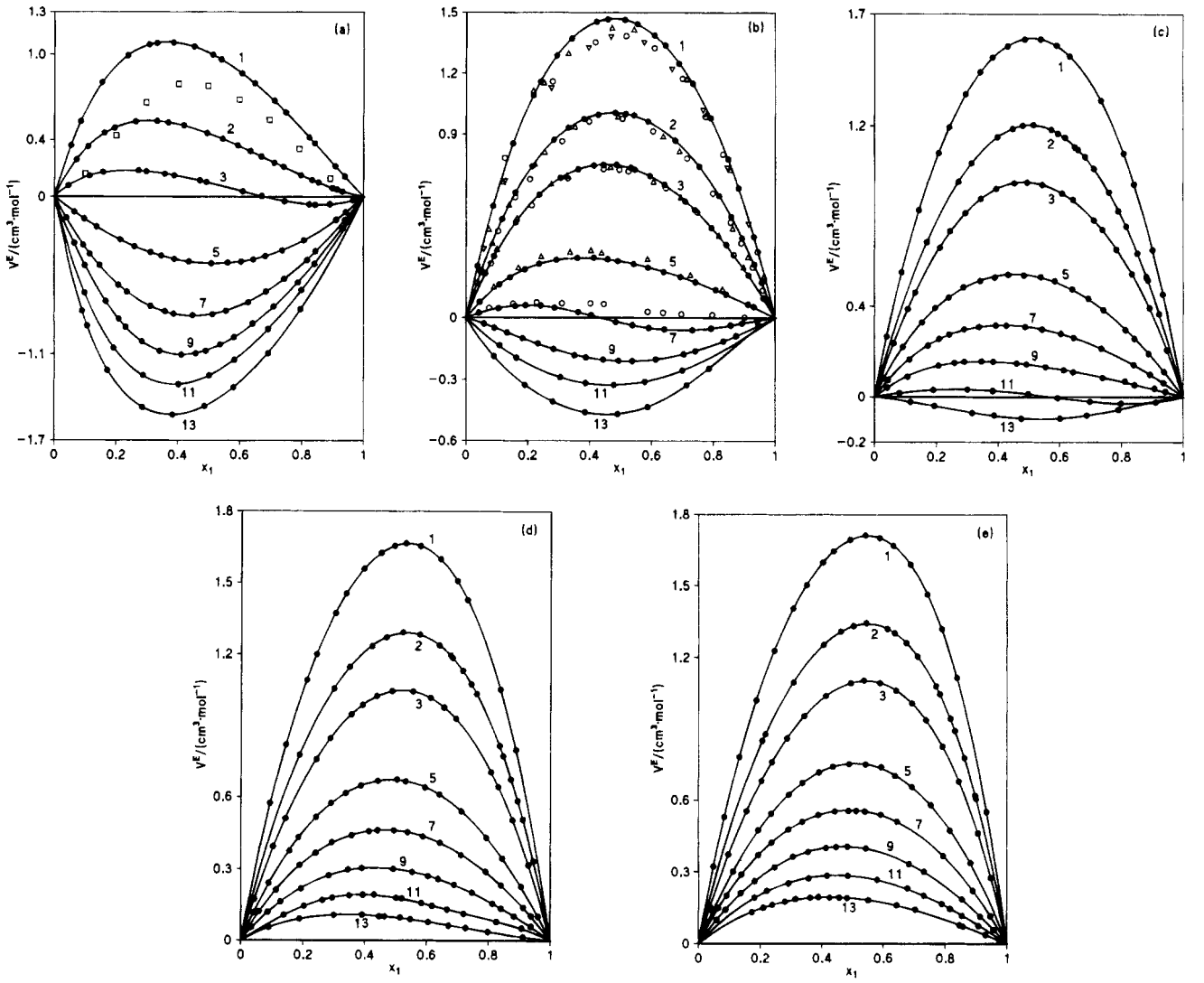

Figure 1. Excess molar volumes at 298.15 K, experimental values (●) and smoothing equation for the binary mixtures $CH_3(CH_2)_{u-1}CO_2CH_3$ (1) + $CH_3(CH_2)_{2v+1}$ (2): (a) $v = 1$, (□) De Soria et al. (1988); (b) $v = 2$, (▽) Grolier et al. (1974), (△) Dusart et al. (1976), (○) Pintos et al. (1988); (c) $v = 3$; (d) $v = 4$; (e) $v = 5$. Numbers in the plot indicate the u values.

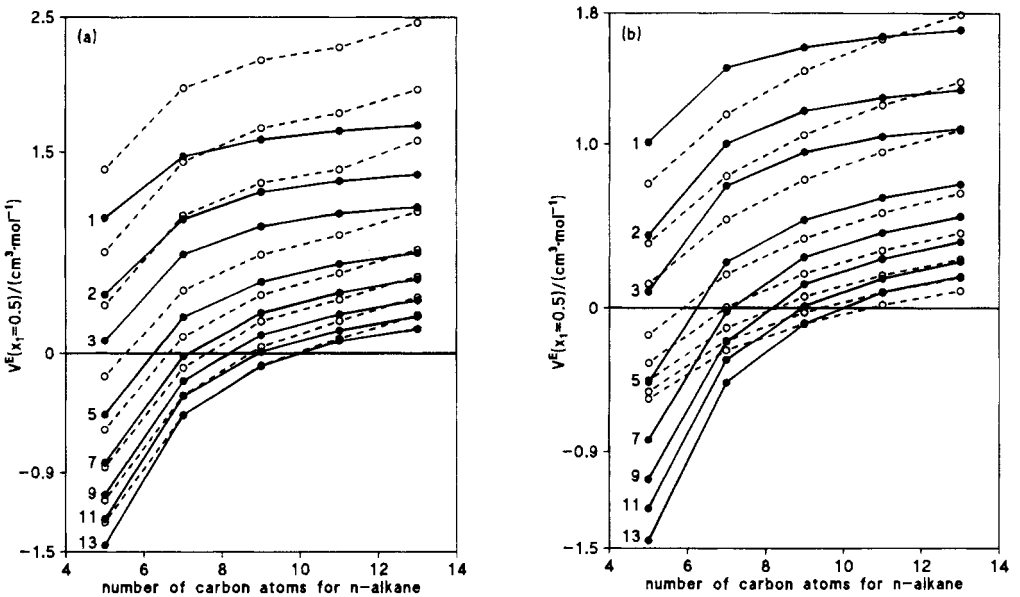

Figure 2. Comparison between the equimolar V^E values at 298.15 K obtained from eq 2 (●) and the theoretical values (○) from the (a) Flory model and (b) Nitta–Chao model for the binary mixtures $CH_3(CH_2)_{u-1}CO_2CH_3$ (1) + $CH_3(CH_2)_{2v+1}CH_3$ (2). Numbers in the plot indicate the u values.

using the excess molar enthalpies, H^E, published previously (Ortega, 1991a,b, 1992; Ortega et al., 1990a,b, 1991, 1992) and the V^E from Table 1. The ratio of the contact areas of the molecules of each mixture, S_1/S_2, was estimated on the

basis of the characteristic volumes of the components, simplified by considering the molecules to be spherical in shape. The estimation of the excess properties gave an overall mean error of 9% for H^E and of 51% for V^E. A comparison between the experimental and estimated values at equimolar concentration is shown in Figure 2a, demonstrating a major qualitative difference in the systems containing the short-chain esters.

Nitta–Chao Model. The model of Nitta et al. (1977) uses the CH_2/COO group interaction; the values of this interaction pair for the alkane/ester interaction were recently recalculated by Ortega and Legido (1994). Certain considerations can be made regarding estimation of the V^E values for the mixtures in Table 1 using these values. On the whole, quantitative evaluation of the model would not seem to be appropriate. The estimated values by this model were below the experimental curves for most mixtures, taking only the curves for which $V^E > 0$ yielded mean errors greater than 50%. The systems with V^E values close to 0 and sigmoidal distributions have been omitted from the evaluation, because the difficulty involved in reproducing such small values gave rise to relative errors that may exceed 100%. In Figure 2b a comparison, for V^E (at $x_1 = 0.5$), between the experimental and theoretical values is shown.

Conclusions

This paper presents the V^E values at 298.15 K for 40 binary mixtures of eight methyl alkanoates and five odd *n*-alkanes (from pentane to tridecane). Certain aspects of their behavior can be established on the basis of the results of this study and those published previously for this same series of mixtures. The excess volumes, along with other excess properties, increased progressively with *n*-alkane chain length, suggestive of steric effects. On the other hand, excess volumes decreased with ester chain length and eventually became negative. Hence, there are contraction effects for the mixtures containing the lightest hydrocarbons, indicative of interstitial accommodation enhanced by weakening of the polar effects of the ester molecules as the chain length of the R_1 group in R_1COOCH_3 increased.

Neither of the models employed in the theoretical modeling of the V^E values carried out in this study adequately described the volumetric behavior of the mixtures considered, although estimation using the model of Nitta et al. (1977) improved for mixtures containing the heaviest hydrocarbons, though it worsened for long-chain esters. This was reported earlier by González and Ortega (1994a) using older values for the CH_2/COO interaction pair. The higher errors with increasing ester chain length obtained using the model of Nitta et al. (1977) can be attributed to a shortage of excess values in the data base for mixtures of the heaviest components. The model of Flory (1965) yielded more uniform errors for the estimates of the volumes for the set of mixtures as a whole, but the errors were in all cases high.

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