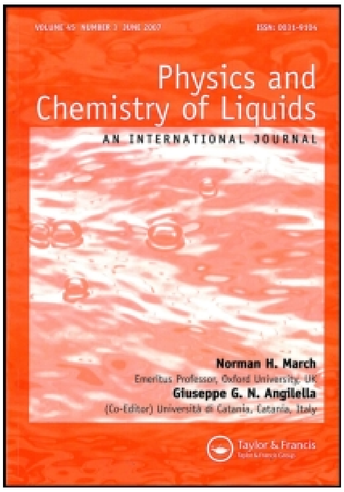

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Volumetric properties of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 k

René D. Peralta[a]; Ramiro Infante[a]; Gladis Cortez[a]; Jaime Wisniak[b]
[a] Centro de Investigación en Química Aplicada, Saltillo 25000, Coahuila, México; [b] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

To cite this Article Peralta, René D. , Infante, Ramiro , Cortez, Gladis and Wisniak, Jaime(2004) 'Volumetric properties of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 k', Physics and Chemistry of Liquids, 42: 4, 391 — 401

To link to this Article: DOI: 10.1080/00319100410001684499

URL: http://dx.doi.org/10.1080/00319100410001684499

Physics and Chemistry of Liquids
Vol. 42, No. 4, August 2004, pp. 391–401

VOLUMETRIC PROPERTIES OF ETHYL ETHANOATE WITH ETHYL ACRYLATE, BUTYL ACRYLATE, METHYL METHACRYLATE, AND STYRENE AT 298.15 K

RENÉ D. PERALTA[a,*], RAMIRO INFANTE[a],
GLADIS CORTEZ[a] and JAIME WISNIAK[b]

[a]*Centro de Investigación en Química Aplicada, Saltillo 25000, Coahuila, México;*
[b]*Department of Chemical Engineering, Ben-Gurion University of the Negev,*
Beer-Sheva 84105, Israel

(Received 25 June 2003)

Densities of the binary systems of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene have been measured as a function of the composition, at 298.15 K and atmospheric pressure, using an Anton Paar DMA 5000 oscillating U-tube densitometer. The calculated excess volumes were correlated with the Redlich-Kister equation and with a series of Legendre polynomials. The excess volumes are negative for systems ethyl ethanoate + (ethyl acrylate, methyl methacrylate, and styrene) and positive for the system with butyl acrylate.

Keywords: Acrylates; Ethyl ethanoate; Excess volumes; Styrene

1. INTRODUCTION

The mixing of different compounds gives rise to solutions that generally do not behave ideally. The deviation from ideality may be expressed by many thermodynamic variables, particularly by excess properties. Excess thermodynamic properties of mixtures correspond to the difference between the actual property and the property if the system behaves ideally, and thus are useful in the study of molecular interactions and arrangements. In particular, they reflect the interactions that take place between solute–solute, solute–solvent, and solvent–solvent species. Excess volumes represent the first derivative of the excess Gibbs function with respect to the pressure, $V^E = (\partial G^E/\partial P)_{T,n}$, the pertinent partial excess volume corresponds to the variation of the chemical potential with pressure, $\bar{V}_i^E = (\partial \mu_i/\partial P)_{T,n}$.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and commercially important monomers,

---

[*] Corresponding author. E-mail: rene@polimex.ciqa.mx

ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100410001684499

in particular the influence of the chemical structure of the solute in the systems under consideration. So far we have studied the volumetric behavior of the monomers with cyclic hydrocarbons [1], aromatic solvents [2–4], and aliphatic and cyclic ethers [5–7]. Ethyl ethanoate is an excellent solvent and may be useful in polymerization and other chemical reactions such as hydrogenation, in the cleaning of polymer surfaces, electronic materials, etc. Acrylic esters and styrene are important industrial chemicals used in the large-scale preparation of useful polymers. The esters are also interesting because they contain both a double bond and an ester group.

To the best of our knowledge no literature data are available for the excess volumes of the systems of ethyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene.

2. EXPERIMENTAL SECTION

2.1 Materials

Ethyl ethanoate, EE (ethyl acetate, 99.96 mass %), ethyl acrylate, EA (99.8 mass %), butyl acrylate, BA (99.9 mass %), methyl methacrylate, MMA (99.9 mass %), and styrene (99.9 mass %) were purchased from Aldrich. The supplier certified the purity of all the reagents by gas chromatography analysis. EA, BA, and MMA were vacuum distilled previous to use to eliminate the stabilizer (about 0.002% mass of hydroquinone monomethyl ether). Styrene, containing 10–15 ppm of 4-*tert*-butylcatechol as stabilizer, was not distilled to avoid polymerization but was degassed by freezing and heating. After purification all reagents were stored under molecular sieves. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with values reported in the literature (Table I).

2.2 Density Measurements

The density of the samples was measured with an Anton Paar model DMA 5000 oscillating U-tube densimeter, provided with automatic viscosity correction, two integrated Pt 100 platinum thermometers (DKD traceable), and a stated accuracy of $5 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$. The temperature in the cell was regulated to ±0.001 K with a solid-state thermostat. The apparatus was calibrated once a day with dry air and bi-distilled freshly degassed water.

All liquids were boiled or heated to remove dissolved air. Solutions of different compositions were prepared by mass in a $10\,\mathrm{cm^3}$ rubber-stoppered vial to prevent

TABLE I Purity and densities of pure components at 298.15 K

Component	*Purity (mass %)*	*Density* $(\mathrm{g\,cm})^{-3}$	
		Measured	*Literature*
Ethyl acetate (1)	99.96	0.894387	0.8940 [13]
Butyl acrylate (2)	99.9	0.893780	0.8941 [14]
Ethyl acrylate (3)	99.8	0.915930	0.9163 [14]
Methyl methacrylate (4)	99.9	0.937628	0.93766 [15]
Styrene (5)	99.9	0.901941	0.9016 [13]

evaporation, using a Mettler AG 204 balance accurate to $\pm 10^{-4}$ g. To minimize the errors in composition, the heavier component was charged first and the sample kept in ice water. Total uncertainty (ISO 9001) in the mole fraction is 7.7×10^{-6}; precision of the density (duplicate) measurement $\pm 2 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$, and of the temperature ±0.002 K. Total uncertainty in the density measurement, as reported by the equipment manufacturer, was $5 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$.

Proper safety measures were taken when handling all the materials.

3. RESULTS AND DISCUSSION

At least 21 density measurements were performed (with repetition) for each binary system over the full concentration range ($0 \leq x \leq 1$).

The excess volumes V^E of the solutions of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = [xM_1 + (1-x)M_2]/\rho - [xM_1/\rho_1 + (1-x)M_2/\rho_2] \tag{1}$$

where ρ, ρ_1, and ρ_2 are the densities of the solution and pure components 1 and 2, respectively, and M_1 and M_2 are the molar masses of the pure components. The corresponding values of ρ and V^E are reported in Tables II–V and Fig. 1.

The first term in Eq. (1) represents the actual volume of the solution, and the second, the volume it would occupy if the mixture behaved ideally. In general, while these two

TABLE II Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system ethyl acetate (1) + butyl acrylate (2) at 298.15 K

x_1	ρ (g cm^{-3})	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
		(cm^3 × mol^{-1})		
0	0.893780	143.4022	0	0
0.0252	0.893753	142.2785	5.982	0.72
0.0564	0.893738	140.8787	10.40	−0.65
0.1003	0.893706	138.9186	18.21	0.15
0.1500	0.893685	136.6952	24.56	−0.30
0.2002	0.893667	134.4448	30.39	−0.47
0.2504	0.893649	132.1983	36.13	−0.082
0.3003	0.893629	129.9633	42.05	1.0
0.3508	0.893622	127.7026	46.04	0.68
0.4011	0.893621	125.4472	49.15	0.027
0.4505	0.893626	123.2306	51.38	−0.75
0.4999	0.893627	121.0187	54.16	−0.11
0.5508	0.893642	118.7337	55.18	−0.20
0.6001	0.893669	116.5197	54.62	−0.59
0.6502	0.893706	114.2704	52.96	−0.64
0.7001	0.893747	112.0280	50.98	0.57
0.7493	0.893806	109.8154	46.94	1.3
0.8001	0.893896	107.5270	39.58	0.57
0.8499	0.894007	105.2807	30.13	−0.80
0.9002	0.894119	103.0142	21.16	−0.24
0.9499	0.894247	100.7744	10.90	−0.095
0.9748	0.894323	99.65126	4.676	−0.88
1	0.894387	98.51440	0	0

$\delta V^E = V^E_{\mathrm{exptl}} - V^E_{\mathrm{calc}}$.

TABLE III Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system ethyl acetate (1) + ethyl acrylate (3) at 298.15 K

x_1	ρ (g cm^{-3})	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
		(cm^3 × mol^{-1})		
0	0.915930	109.3097	0	0
0.0251	0.915468	109.0350	−3.256	1.1
0.0498	0.915021	108.7641	−7.538	0.81
0.1002	0.914096	108.2128	−15.44	0.34
0.1605	0.912960	107.5543	−23.07	0.26
0.2010	0.912187	107.1124	−27.90	−0.35
0.2502	0.911224	106.5759	−32.27	−0.46
0.3005	0.910220	106.0304	−35.29	−0.15
0.3509	0.909201	105.4841	−38.01	−0.53
0.3997	0.908191	104.9550	−39.42	−0.62
0.4501	0.907121	104.4123	−38.68	0.55
0.4996	0.906061	103.8785	−38.25	0.52
0.5498	0.904968	103.3376	−37.11	0.36
0.6001	0.903855	102.7960	−35.32	0.045
0.6498	0.902732	102.2626	−32.14	0.44
0.7001	0.901589	101.7222	−29.54	−0.44
0.7498	0.900433	101.1895	−25.40	−0.29
0.7998	0.899250	100.6551	−20.23	0.40
0.8502	0.898056	100.1146	−16.41	−0.69
0.8997	0.896850	99.58664	−10.23	0.41
0.9498	0.895635	99.05066	−5.966	−0.62
0.9752	0.894997	98.77955	−2.172	0.46
1	0.894387	98.51440	0	0

$\delta V^E = V^E_{\text{exptl}} - V^E_{\text{calc}}$.

TABLE IV Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system ethyl acetate (1) + methyl methacrylate (4) at 298.15 K

x_1	ρ (g cm^{-3})	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
		(cm^3 × mol^{-1})		
0	0.937628	106.7801	0	0
0.0260	0.936603	106.5638	−1.536	0.11
0.0496	0.935668	106.3670	−3.031	0.16
0.1003	0.933655	105.9448	−6.578	0.0094
0.1503	0.931650	105.5275	−10.12	−0.20
0.2004	0.929624	105.1106	−13.15	−0.073
0.2499	0.927599	104.6984	−15.70	0.23
0.3007	0.925511	104.2755	−18.79	−0.29
0.3504	0.923439	103.8630	−20.42	0.18
0.4005	0.921338	103.4476	−22.22	0.027
0.4499	0.919241	103.0381	−23.34	0.051
0.5004	0.917075	102.6203	−23.86	0.18
0.5501	0.914923	102.2089	−24.22	−0.053
0.6005	0.912718	101.7926	−23.90	−0.13
0.6498	0.910538	101.3860	−22.99	−0.14
0.6999	0.908300	100.9729	−21.68	−0.30
0.7499	0.906040	100.5621	−19.26	0.11
0.8003	0.903742	100.1492	−16.32	0.45
0.8500	0.901450	99.74043	−13.49	0.12
0.8999	0.899130	99.33179	−10.00	−0.19
0.9497	0.896782	98.92446	−5.412	−0.10
0.9748	0.895592	98.71933	−3.085	−0.32
1	0.894387	98.51440	0	0

$\delta V^E = V^E_{\text{exptl}} - V^E_{\text{calc}}$.

TABLE V Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system ethyl acetate (1) + styrene (5) at 298.15 K

x_1	ρ (g cm^{-3})	V	$V^E \times 10^3$	$\delta V^E \times 10^3$
		(cm^3 × mol^{-1})		
0	0.901941	115.4732	0	0
0.0252	0.901989	115.0189	–26.91	1.3
0.0516	0.902028	114.5442	–53.64	0.77
0.1005	0.902046	113.6731	–96.13	–0.14
0.1499	0.902014	112.7986	–132.8	–1.6
0.2007	0.901908	111.9089	–161.5	0.44
0.2498	0.901785	111.0499	–186.9	0.34
0.3001	0.901626	110.1743	–209.2	–0.21
0.3498	0.901418	109.3161	–225.2	0.78
0.4004	0.901187	108.4435	–239.7	–1.1
0.4500	0.900880	107.5977	–244.7	1.2
0.5002	0.900545	106.7436	–247.5	0.48
0.5503	0.900163	105.8959	–245.3	–0.70
0.6002	0.899721	105.0578	–236.6	–0.71
0.6500	0.899228	104.2266	–222.8	–0.52
0.7001	0.898673	103.3969	–203.0	0.98
0.7499	0.898106	102.5724	–182.6	–1.0
0.8001	0.897454	101.7506	–154.0	1.2
0.8499	0.896781	100.9353	–123.8	1.1
0.8998	0.896081	100.1218	–91.91	–1.7
0.9499	0.895279	99.31410	–50.17	–0.78
0.9751	0.894827	98.91169	–24.41	1.4
1	0.894387	98.51440	0	0

$\delta V^E = V^E_{\text{exptl}} - V^E_{\text{calc}}$.

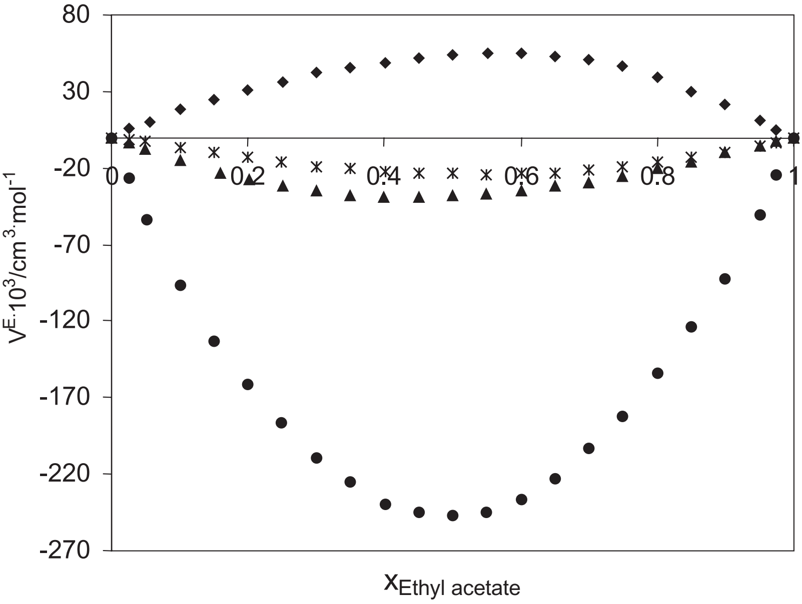

FIGURE 1 Excess volumes at 298.15 K: ⋇ ethyl acetate + MMA; ▲ ethyl acetate + EA; ◆ ethyl acetate + BA; ● ethyl acetate + styrene.

volumes are similar in size (usually larger than $100\,\mathrm{cm^3\,mol^{-1}}$) their difference is usually smaller by two to three orders of magnitude and thus carries a significantly larger error.

Partial volumes were calculated using the relations [8]

$$\bar{V}_1 = V + x_2 \frac{dV}{dx_1} \tag{2}$$

$$\bar{V}_2 = V - x_1 \frac{dV}{dx_1} \tag{3}$$

The pertinent values are reported in Table VI and are necessarily consistent.

The values of V^E were correlated with composition using two methods:

(a) The Redlich–Kister expression [9]

$$V^E = x_1 x_2 \sum_{k=0}^{n} A_k (x_1 - x_2)^k \tag{4}$$

where the A_ks are the adjustable parameters of the model.

The Redlich–Kister equation was originally developed to correlate the excess Gibbs function and calculate the values of the activity coefficients. It turned out to be such a powerful and versatile correlating tool that its use has been extended to other properties, particularly, excess volumes and excess enthalpies of mixing. Notwithstanding, it suffers from the important drawback that the values of its adjustable parameters change as the number of terms in the series is increased, so that no physical interpretation can be attached to them.

TABLE VI Partial volumes $\bar{V}_i$, $\mathrm{cm^3\,mol^{-1}}$

x_1	*EE (1) + BA (2)*		*EE (1) + EA (3)*		*EE (1) + MMA (4)*		*EE (1) + Styrene (5)*	
	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_3$	$\bar{V}_1$	$\bar{V}_4$	$\bar{V}_1$	$\bar{V}_5$	$\bar{V}_1$
0	143.402	98.7355	109.310	98.3370	106.780	98.4527	115.473	97.3273
0.05	143.403	98.6936	109.309	98.3563	106.780	98.4482	115.467	97.5649
0.10	143.405	98.6656	109.308	98.3749	106.780	98.4473	115.454	97.7198
0.15	143.408	98.6473	109.305	98.3927	106.780	98.4491	115.437	97.8233
0.20	143.411	98.6351	109.302	98.4096	106.779	98.4528	115.414	97.8960
0.25	143.413	98.6265	109.297	98.4253	106.778	98.4577	115.383	97.9506
0.30	143.416	98.6194	109.291	98.4398	106.776	98.4633	115.341	97.9939
0.35	143.419	98.6123	109.285	98.4531	106.773	98.4693	115.285	98.0289
0.40	143.424	98.6045	109.278	98.4649	106.769	98.4752	115.215	98.0565
0.45	143.430	98.5956	109.270	98.4754	106.765	98.4810	115.131	98.0771
0.50	143.440	98.5854	109.262	98.4846	106.760	98.4864	115.038	98.0915
0.55	143.452	98.5744	109.253	98.4923	106.754	98.4914	114.940	98.1018
0.60	143.468	98.5628	109.245	98.4987	106.748	98.4959	114.846	98.1114
0.65	143.487	98.5514	109.236	98.5038	106.742	98.4999	114.763	98.1252
0.70	143.509	98.5407	109.228	98.5078	106.734	98.5034	114.699	98.1487
0.75	143.533	98.5315	109.221	98.5106	106.726	98.5065	114.657	98.1873
0.80	143.559	98.5241	109.214	98.5126	106.717	98.5091	114.637	98.2442
0.85	143.583	98.5188	109.209	98.5137	106.707	98.5112	114.629	98.3187
0.90	143.605	98.5158	109.205	98.5143	106.696	98.5129	114.612	98.4029
0.95	143.619	98.5145	109.203	98.5144	106.682	98.5140	114.548	98.4789
1	143.622	98.5144	109.204	98.5144	106.666	98.5144	114.378	98.5144

(b) A series of Legendre polynomials $L_k(x_1)$

$$V^E = x_1 x_2 \sum_{k=0}^{n} a_k L_k(x_1) \tag{5}$$

which for the four first terms ($k = 0, 1, 2, 3$) becomes

$$V^E = x_1 x_2 [a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1) + a_3(20x_1^3 - 30x_1^2 + 12x_1 - 1)] \tag{6}$$

Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, and Chebyshev, which have the valuable characteristic that for a continuous series of observations (infinite) the values of the coefficients do not change as the number of terms in the series is increased. This is an important property because if a physical interpretation can be assigned to one of its coefficients, its value remains constant. For the case of discrete measurements, such as determination of volumes of mixing, the values of the coefficients will vary, but only slightly. In addition, it can be shown that the series of Legendre polynomials have the important characteristic that the structure of its first four terms is the same as that of the first four terms of the Redlich–Kister expression. Tomiska [10,11] has described the mathematical procedure to transform a power expansion, such as that of Redlich–Kister, into an orthogonal series. In addition, Tomiska has provided the iteration formulas for Legendre or Chebyshev's series of any order as well as the proof that the procedure is independent of the conversion coefficients from the actual excess property.

Equations (4) and (5) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$OF = \sum_{1}^{N} (V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E)^2 \tag{7}$$

where N is the number of observations. The values of the different adjustable parameters, A_k and a_k, are reported in Tables VII and VIII for different values of k, together with the pertinent statistics. The standard deviation s was calculated as

$$s = \left[\sum (V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E)^2 / (N - k)\right]^{1/2} \tag{8}$$

where k is the number of adjustable parameters. The statistical significance of adding one or more terms after the third was examined using a χ^2-based test, coupled to the requirement that the residues be randomly distributed, as suggested by Wisniak and Polishuk [12]. It was not deemed necessary to perform a step-wise regression.

A plot of the function $V^E/x_i x_j$ against composition was used in every case to test the quality of the data; this function is extremely sensitive to experimental errors, particularly in the dilute ranges and helps detecting outliers. In addition, its values at infinite dilution represent the values of the partial excess volume at infinite dilution, $\bar{V}_i^{E,\infty}$,

TABLE VII Coefficients A_k (Eq. 5), standard deviation s (Eq. 8), Durbin–Watson statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	$A_0 \times 10^2$	$A_1 \times 10^2$	$A_2 \times 10^2$	$A_3 \times 10^2$	$A_4 \times 10^2$	$s \times 10^4$	d	$(V^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
								$(\mathrm{cm}^3 \times \mathrm{mol}^{-1})$		
1 + 2	21.71	6.90	0.34	−6.74		6.67	1.57	5.43	22.10	22.00
1 + 3	−15.51	3.57	1.34			5.42	1.75	−3.88	−17.74	−10.59
1 + 4	−9.61	−1.56	0.82	−1.06		2.11	1.83	−2.40	−6.17	−11.43
1 + 5	−99.18	2.55	9.24	2.04	−24.2	10.85	2.38	−24.79	−118.70	−109.52

$d = \sum_{u=2}^{N} (e_u - e_{u-1})^2 \Big/ \sum_{u=1}^{N} e_u^2.$

$e_u = V_{u,\mathrm{calc}}^E - V_{u,\mathrm{exptl}}^E.$

TABLE VIII Coefficients a_k (Eq. 5), standard deviation s (Eq. 8), Durbin–Watson statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K.

System	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^2$	$s \times 10^4$	d[a]	$(\bar{V}^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
								(cm^3 × mol^{-1})		
1 + 2	21.83	2.653	0.24	−2.70		6.9	1.57	5.43	22.11	22.01
1 + 3	−15.06	3.571	0.89			5.6	1.75	−3.88	−17.74	−10.60
1 + 4	−9.34	−2.201	0.54	−0.42		2.2	1.83	−2.40	−6.17	−11.43
1 + 5	−100.93	3.777	−7.65	0.82	−5.52	11.19	2.38	−24.8	−118.71	−109.52

[a] $d = \sum_{u=2}^{N} (e_u - e_{u-1})^2 \Big/ \sum_{u=1}^{N} e_u^2$

$e_u = V^E_{u,\mathrm{calc}} - V^E_{u,\mathrm{exptl}}$.

which can be also calculated from the adjustable parameters as follows [8]:

(a) Redlich–Kister

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - \cdots = \bar{V}_1^{\infty} - V_1^0 \tag{9}$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + \cdots = \bar{V}_2^{\infty} - V_2^0 \tag{10}$$

(b) Legendre

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - \cdots = \bar{V}_1^{\infty} - V_1^0 \tag{11}$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + \cdots = \bar{V}_2^{\infty} - V_2^0 \tag{12}$$

where V_i^0 is the molar volume of pure component i. The pertinent values of $\bar{V}_2^{E,\infty}$ are also shown in Tables VII and VIII. In addition, it should be realized that in the absence of homo-association, the value of the partial excess volume at infinite dilution reflects the true solute–solvent interaction. Equations (9) and (10) or (11) and (12) yield the same values of $\bar{V}_2^{E,\infty}$.

Figure 2 shows a typical distribution of the residuals, which is random as shown by the Durbin–Watson statistic.

Inspection of the results of Tables II–V and Fig. 1 indicates that the excess volumes are negative for the binaries of ethyl ethanoate with methyl methacrylate, ethyl acrylate, and styrene, and positive for the binary with butyl methacrylate.

The magnitude and sign of V^E is a reflection of the type of interactions taking place in the mixture. This is very well exhibited by the mixtures studied here with the minimum

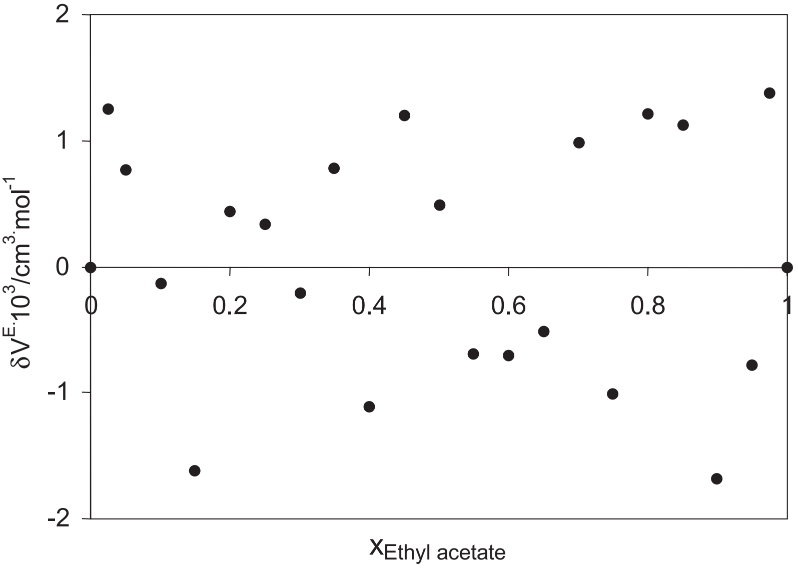

FIGURE 2 Residual distribution plot for the system ethyl acetate + styrene, according to the fit given in Table VI.

and maximum values of V^E ranging from about -0.248 to $+0.056\,\mathrm{cm^3\,mol^{-1}}$. As regards to the symmetry of the excess function, Fig. 1 shows that the function $V^E(x)$ is essentially symmetric for all the systems, except for ethyl ethanoate + butyl methacrylate, indicating that the maximum specific interaction occurs at about equimolar composition. For the system ethyl ethanoate + butyl acrylate the maximum of the curve deviates to the right of $x = 0.5$, pointing to a small amount of self-association of the solute.

The V^E curves are either positive or negative, the relative intensity depending on the nature of the solute (monomer) and the solvent. While the overall magnitude of V^E is a result of the effect of breaking the ester's dipole–dipole association, the negative sign indicates a net packing effect contributed by structural effects arising from interstitial accommodation. n–π interactions between an aromatic hydrocarbon (such as styrene) and an ester are much stronger than those between a cyclic hydrocarbon (such as cyclohexane) and an ester. In addition, the observed molar excess volumes point to their dependence with respect to the structure of the unsaturated ester. Their value augments as the length and branching of the ester chain increases from ethyl to butyl, and signaling a decrease of the contribution of interstitial accommodation and an increase of steric interference. For butyl acrylate steric interference is large enough to make the excess volumes positive.

As shown in Fig. 1, the mixture of ethyl ethanoate and styrene presents a relative large contraction effect. This fact may be the result of an inductive effect of the vinyl group in styrene, which enhances the electron density of its ring and the electrostatic interaction with the benzene ring, and of the vinyl group introducing a steric effect that operates in the opposite direction. The electron cloud of styrene interacts well with the ester group of the solvent and results in a contraction of the mixture.

References

[1] R.D. Peralta, R. Infante, G. Cortez, L. Villarreal and J. Wisniak (2002). *Thermochimica Acta*, **390**, 47.

[2] R.D. Peralta, R. Infante, G. Cortez, J.R. Torres-Lubián and J. Wisniak (2003). *Thermochimica Acta*, **402**, 247.

[3] R.D. Peralta, R. Infante, G. Cortez, A. Cisneros and J. Wisniak (2002). *Thermochimica Acta*, **398**, 39.

[4] R.D. Peralta, R. Infante, G. Cortez, O. Rodríguez and J. Wisniak (2002). *J. Solution Chem.*, **31**, 175.

[5] R.D. Peralta, R. Infante, G. Cortez, R.G. López and J. Wisniak (2003). *International J. Thermophysics*, **24**, 173.

[6] R.D. Peralta, R. Infante, G. Cortez, R.R. Ramirez and J. Wisniak (2003). *J. Chem. Thermodynamics*, **35**, 239.

[7] R.D. Peralta, R. Infante, G. Cortez, L.F. Ramos and J. Wisniak (2003). *Phys. Chem. Liq.*, **41**, 361.

[8] H.C. van Ness and M.M. Abbott (1982). *Classical Thermodynamics of Nonelectrolyte Solutions*. McGraw-Hill, New York.

[9] O. Redlich and A.T. Kister (1948). *Ind. Eng. Chem.*, **40**, 345.

[10] J. Tomiska (1981). *CALPHAD*, **5**, 93.

[11] J. Tomiska (1984). *CALPHAD*, **8**, 283.

[12] J. Wisniak and A. Polishuk (1999). *Fluid Phase Equilibria*, **164**, 61.

[13] TRC Thermodynamic Tables, extant 2002. Hydrocarbons, Thermodynamics Research Center, The Texas A&M University System, College Station, Texas, TX, table a-5550, 1969, ethyl ethanoate; table a-4490, 1989, styrene.

[14] N.V. Sastry and M.K. Valand (2000). *Phys. Chem. Liq.*, **38**, 61.

[15] L. Beichen, S.E.M. Hamam and B.C.-Y. Lu (1986). *J. Chem. Thermodyn.*, **18**, 1043.