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

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Densities of the binary systems of ethylbenzene 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 positive for the systems ethylbenzene + (methyl methacrylate, ethyl acrylate) and negative for the systems ethylbenzene + (butyl acrylate, styrene).

*Keywords:* Densities; Excess volumes; Monomers; Ethylbenzene

## 1. INTRODUCTION

The mixing of different compounds gives rise to properties such as volumes, enthalpies and entropies of mixing, which reflect the extent of the deviations from non-ideality. Excess thermodynamic properties

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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.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and commercially important monomers, in particular the influence of the chemical structure of the solute in the system under consideration.

Sastry and Dave measured the excess volumes, isentropic compressibilities, and dielectric behaviour of fifteen binary mixtures of alkyl (methyl, ethyl and butyl) methacrylate with hexane, heptane, carbon tetrachloride, chlorobenzene and *o*-dichlorobenzene at 308.15 K and found that with aliphatic hydrocarbons the results were controlled by dispersing interactions, with chlorinated solvents the controlling factors were specific interactions (O–Cl and  $n$ - $\pi$  types) [1,2]. Sastry and Valand also measured the excess volumes of mixtures of alkyl (methyl, ethyl and butyl) acrylates in several alkanols at 298.15 and 308.15 K and found that they were always positive. These results were explained on the basis of non-specific interactions between the compounds [3]. Sastry *et al.* [4] measured the excess volumes of methyl methacrylate with ethylbenzene and other aromatic hydrocarbons such as benzene, toluene and (*o*, *m*, *p*)-xylene, at 298.15 and 303.15 K and found that except for toluene all presented positive excess volumes. The excess volumes for the system MMA + ethylbenzene showed a non-symmetric behavior with a maximum at about  $V^E \approx 0.125 \text{ cm}^3/\text{mol}$  and  $x = 0.35$ .

No literature data are available on the excess volumes of the systems of alkyl acrylates analyzed in this work.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials

Ethylbenzene (99 mass%), ethyl acrylate, EA, (99 + mass%), butyl acrylate, BA, (99 + mass%), methyl methacrylate, MMA, (99 + mass%), and styrene (99 mass%), were purchased from Aldrich. EA, BA and MMA were vacuum distilled previous to use to eliminate the stabilizer (about 0.002% mass of hydroquinone monomethyl

TABLE I Purity and densities of pure components at 298.15 K

<i>Component</i>	<i>Purity (mass %)</i>	<i>Density (g cm<sup>-3</sup>)</i>	
		<i>Measured</i>	<i>Lit.</i>
Ethylbenzene (1)	99	0.862583	0.8626 [9]
Butyl acrylate (2)	99+	0.893666	0.8941 [3]
Ethyl acrylate (3)	99	0.925930	0.9163 [3]
Methyl methacrylate (4)	99	0.937669	0.93766 [10]
Styrene (5)	99	0.901972	0.9016 [9]

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. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with the 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 densitometer, provided with automatic viscosity correction, two integrated Pt 100 platinum thermometers (DKD traceable), and a stated accuracy of  $5 \times 10^{-6} \text{ g cm}^{-3}$ . The temperature in the cell was regulated to  $\pm 0.001 \text{ K}$  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  $10 \text{ cm}^3$  rubber-stoppered vial to prevent evaporation, using a Mettler AG 204 balance accurate to  $\pm 10^{-4} \text{ g}$ . To minimize the errors in composition, the heavier component was charged first and the sample kept in ice water. Accuracy in the mole fraction is  $5 \times 10^{-5}$ , of the density (duplicate) measurement  $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$ , and of the temperature  $\pm 0.002 \text{ K}$ . 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, in the full concentration range ( $0 \leq x \leq 1$ ).

TABLE II Experimental densities, volumes, calculated excess volumes, and deviations  $\delta V^E$  for the system ethylbenzene (1) + butyl acrylate (2) at 298.15 K

$x_1$	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm <sup>3</sup> mol <sup>-1</sup> )	$V^E \times 10^3$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\delta V^E \times 10^5$ (cm <sup>3</sup> mol <sup>-1</sup> )
0	0.893666	143.420	0	0
0.0272	0.892986	142.861	-7.557	-18.2
0.0508	0.892382	142.373	-13.115	-42.0
0.1009	0.891067	141.347	-21.024	41.0
0.1502	0.889747	140.338	-27.599	20.5
0.2025	0.888315	139.270	-32.874	27.5
0.2500	0.886992	138.298	-37.585	-32.1
0.3000	0.885575	137.278	-41.480	-40.3
0.3504	0.884122	136.251	-44.795	-33.9
0.4067	0.882466	135.102	-47.778	-15.8
0.4497	0.881175	134.226	-49.120	38.8
0.5004	0.879632	133.194	-50.540	48.0
0.5498	0.878100	132.189	-51.116	53.5
0.5999	0.876515	131.168	-51.053	30.5
0.6498	0.874909	130.155	-50.055	2.2
0.7002	0.873255	129.133	-48.096	-35.7
0.7502	0.871567	128.120	-43.542	76.7
0.8001	0.869858	127.109	-39.132	53.0
0.8487	0.868157	126.128	-32.990	73.5
0.8994	0.866352	125.104	-26.542	-97.0
0.9494	0.864505	124.099	-14.866	-4.8
0.9752	0.863534	123.580	-8.032	-18.2
1	0.862583	123.084	0	0

$$\delta V^E = V_{\text{expt}}^E - V_{\text{calc}}^E.$$

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 the following equation:

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

where  $\rho$ ,  $\rho_1$  and  $\rho_2$  are the densities of the solutions and pure components 1 and 2, respectively, and  $M_1$  and  $M_2$  the molar masses of the pure components. The corresponding values of  $\rho$  and  $V^E$  are reported in Tables II–V and Fig. 1. The values of  $V^E$  were correlated with composition using the procedure:

(a) The Redlich–Kister expression [5]

$$V^E = x_1x_2 \sum_{k=0}^n A_k(x_1 - x_2)^k, \quad (2)$$

where the  $A_k$ s are the adjustable parameter of the model.

TABLE III Experimental densities, volumes, calculated excess volumes, and deviations  $\delta V^E$  for the system ethylbenzene (1) + ethyl acrylate (3) at 298.15 K

$x_1$	$\rho$ ( $\text{g cm}^{-3}$ )	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$V^E \times 10^3$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\delta V^E \times 10^5$ ( $\text{cm}^3 \text{mol}^{-1}$ )
0	0.915390	109.310	0	0
0.0256	0.914371	109.665	3.140	8.0
0.0521	0.912766	110.034	6.776	51.1
0.1008	0.909854	110.710	12.089	-6.0
0.1506	0.906908	111.402	17.428	-56.8
0.2006	0.903985	112.097	23.806	31.7
0.2498	0.901151	112.780	28.675	29.3
0.3003	0.898289	113.479	32.503	-22.2
0.3504	0.895490	114.172	35.994	-24.3
0.4001	0.892747	114.860	38.677	-17.6
0.4500	0.890035	115.549	40.798	26.6
0.5000	0.887362	116.238	41.231	1.2
0.5511	0.884668	116.941	40.948	7.7
0.6002	0.882113	117.617	39.616	8.4
0.6505	0.879537	118.307	37.471	30.0
0.7000	0.877037	118.986	33.984	7.6
0.7500	0.874553	119.670	29.359	-39.1
0.8000	0.872097	120.354	24.292	-51.5
0.8503	0.869657	121.041	19.323	14.6
0.9000	0.867281	121.719	13.179	8.0
0.9503	0.864904	122.406	6.903	30.7
0.9751	0.863738	122.745	3.812	50.6
1	0.862583	123.084	0	0

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

The Redlich–Kister regressor is very powerful and frequently used to correlate vapor–liquid equilibrium data and excess properties. Notwithstanding, it suffers from the important drawback that the values of the adjustable parameters change as the number of terms in the series is increased.

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

$$V^E = x_1 x_2 \sum_{k=0}^n a_k L_k(x_1) \quad (3)$$

which for the three first terms ( $k=0, 1, 2$ ) is

$$V^E = x_1 x_2 [a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1)] \quad (4)$$

Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, and Chebyshev, which have the important

TABLE IV Experimental densities, volumes, calculated excess volumes, and deviations  $\delta V^E$  for the system ethylbenzene (1) + methyl methacrylate (4) at 298.15 K

$x_1$	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm <sup>3</sup> mol <sup>-1</sup> )	$V^E \times 10^2$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\delta V^E \times 10^4$ (cm <sup>3</sup> mol <sup>-1</sup> )
0	0.937669	106.775	0	0
0.0259	0.935284	107.215	1.786	-0.6
0.0505	0.933018	107.635	3.603	24.6
0.1023	0.928410	108.507	6.321	11.3
0.1500	0.924264	109.306	8.460	11.1
0.2001	0.920032	110.138	9.981	-16.2
0.2505	0.915842	110.975	11.399	-11.9
0.3020	0.911664	111.825	12.519	0.5
0.3503	0.907838	112.619	12.983	-12.8
0.4003	0.903953	113.437	13.341	-7.3
0.4502	0.900151	114.252	13.432	0.6
0.5003	0.896403	115.068	13.271	9.6
0.5501	0.892766	115.873	12.739	5.2
0.6001	0.889173	116.682	12.018	4.0
0.6504	0.885630	117.493	10.992	-7.0
0.6995	0.882223	118.283	9.992	0.4
0.7500	0.878777	119.095	8.758	5.1
0.8004	0.875414	119.900	7.161	-10.3
0.8499	0.872151	120.692	5.646	-4.5
0.9001	0.868887	121.495	4.102	16.0
0.9499	0.865726	122.287	1.981	-7.1
0.9750	0.864157	122.685	0.838	-20.6
1	0.862583	123.084	0	0

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

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 physical explanation 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 slightly. In addition, the series of Legendre polynomials have the important characteristic that the structure of the first three terms is the same as the first three terms of the Redlich–Kister expression.

Equations (2) and (3) were fitted using a least-squares optimization procedure, with all points weighted equally and minimizing the following objective function (OF):

$$\text{OF} = \sum_1^N (V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E)^2 \quad (5)$$

TABLE V Experimental densities, volumes, calculated excess volumes, and deviations  $\delta V^E$  for the system ethylbenzene (1)+styrene (5) at 298.15 K

$x_1$	$\rho$ ( $\text{g cm}^{-3}$ )	$V$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$V^E \times 10^2$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\delta V^E \times 10^4$ ( $\text{cm}^3 \text{mol}^{-1}$ )
0	0.901778	115.494	0	0
0.0259	0.900720	115.688	-0.270	-2.9
0.0500	0.899735	115.869	-0.491	-2.4
0.1009	0.897664	116.250	-0.941	-0.7
0.1507	0.895651	116.624	-1.383	-1.4
0.2004	0.893649	116.998	-1.749	1.7
0.2499	0.891669	117.370	-2.113	0.3
0.3047	0.889484	117.782	-2.438	-0.1
0.3507	0.887655	118.130	-2.615	3.1
0.4000	0.885707	118.502	-2.811	-0.6
0.4507	0.883711	118.885	-2.906	-1.2
0.5005	0.881753	119.263	-2.890	1.5
0.5509	0.879779	119.647	-2.844	-0.2
0.6010	0.877828	120.028	-2.722	-1.5
0.6497	0.875932	120.400	-2.502	0.7
0.6998	0.873994	120.783	-2.264	-1.8
0.7525	0.871965	121.186	-1.929	-1.7
0.8000	0.870143	121.550	-1.570	0.2
0.8501	0.868231	121.934	-1.174	1.0
0.9002	0.866329	122.319	-0.754	2.7
0.9501	0.864451	122.701	-0.394	-1.4
0.9753	0.863502	122.895	-0.147	3.7
1	0.862583	123.084	0	0

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

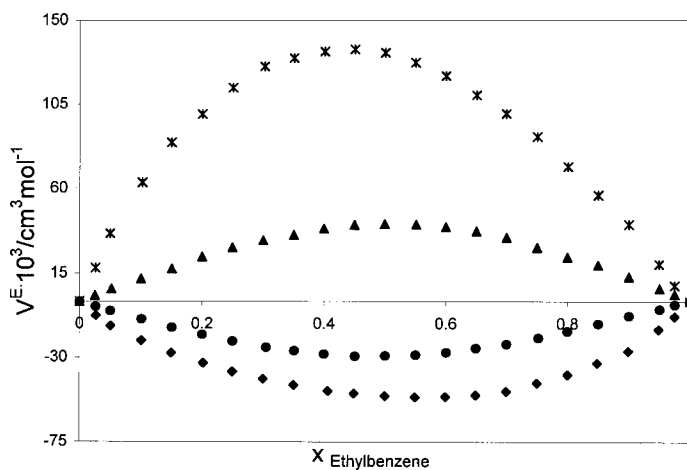
FIGURE 1 Excess volumes at 298.15 K: \* ethylbenzene + MMA;  $\blacktriangle$  ethylbenzene + EA;  $\blacklozenge$  ethylbenzene + BA;  $\bullet$  ethylbenzene + styrene.



TABLE VI Coefficient  $A_k$  (Eq. (2)), standard deviation (Eq. (5)), Durbin–Watson statistic  $d$  ( $V^E$ )<sub>x=0.5</sub>, and  $V_i^{E,\infty}$  at 298.15 K

System	$A_0 \times 10^2$	$A_1 \times 10^2$	$A_2 \times 10^2$	$A_3 \times 10^2$	$A_4 \times 10^2$	$s \times 10^4$	$d^a$	$(V^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
								(cm <sup>3</sup> mol <sup>-1</sup> )	(cm <sup>3</sup> mol <sup>-1</sup> )	(cm <sup>3</sup> mol <sup>-1</sup> )
1+2	-20.40	-4.33	-3.30	2.26	-8.43	4.95	1.67	-5.101	-30.07	-34.21
1+3	16.49	0.72	-3.93			3.16	1.70	4.122	11.84	13.28
1+4	52.71	-14.93	4.78			11.57	1.62	13.180	72.41	42.56
1+5	-11.62	1.00	3.33			1.87	2.05	-2.906	-9.29	-7.29

$$d = \sum_{u=2}^N (e_u - e_{u-1})^2 / \sum_{u=1}^N e_u^2; \quad e_u = V_{u,\text{calc}}^E - V_{u,\text{exptl}}^E.$$

TABLE VII Coefficient  $a_k$  (Eq. (3)), standard deviation (Eq. (5)), ( $\bar{V}^E$ )<sub>x=0.5</sub>, and  $\bar{V}_i^{E,\infty}$  at 298.15 K

System	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^2$	$s \times 10^4$	$d^a$	$(V^E)_{x=0.5} \times 10^2$	$\bar{V}_1^{E,\infty} \times 10^2$	$\bar{V}_2^{E,\infty} \times 10^2$
								(cm <sup>3</sup> mol <sup>-1</sup> )	(cm <sup>3</sup> mol <sup>-1</sup> )	(cm <sup>3</sup> mol <sup>-1</sup> )
1+2	-23.19	-2.978	-7.02	0.904	-1.927	5.1	1.67	-5.10	-30.06	-34.21
1+3	15.18	0.722	-2.62			3.2	1.70	4.12	11.84	13.28
1+4	54.30	-14.895	3.33			11.8	1.63	13.2	72.52	42.73
1+5	-10.52	0.997	2.22			1.9	2.05	0.01	-9.28	-7.29

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

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

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

$$s = \left[ \sum \left( V_{i,\text{exptl}}^E - V_{i,\text{calc}}^E \right)^2 / (N - k) \right]^{1/2}, \quad (6)$$

where  $k$  is the number of adjustable parameters. The statistical significance of adding one or more terms after the third, was examined using  $\chi^2$ -based test, coupled to the requirement that the residues be randomly distributed, as suggested by Wisniak and Polishuk [6]. It was not deemed necessary to perform a step-wise regression.

The values of the functions  $V^E/x_1x_2$  at infinite dilution represent the values of the partial excess volume at infinite dilution,  $\bar{V}_i^{E,\infty}$  [7], an can be calculated from the adjustable parameters as follows:

(a) *Redlich–Kister*

$$\bar{V}_i^{E,\infty} = A_0 - A_1 + A_2 - \dots = \bar{V}_1 - V_1^0 \quad (7)$$

$$V_2^{E,\infty} = A_0 + A_1 + A_2 + \dots = \bar{V}_2 - V_2^0 \quad (8)$$

(b) *Legendre*

$$\bar{V}_1^{E,\infty} = a_0 - a_1 + a_2 - \dots = \bar{V}_1 - V_1^0 \quad (9)$$

$$\bar{V}_2^{E,\infty} = a_0 + a_1 + a_2 + \dots = \bar{V}_2 - V_2^0, \quad (10)$$

where  $V_i^0$  is the molar volume of pure component  $i$ . The pertinent values of  $\bar{V}_i^{E,\infty}$  are also shown in Tables VI and VII. Equations (7) and (8) or (9) and (10) yield the same values  $\bar{V}_i^{E,\infty}$ .

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

Inspection of the results of Tables II–V and Fig. 1 indicates that the excess volumes are positive for the systems ethylbenzene + (methyl methacrylate, ethyl acrylate) and negative for the systems ethylbenzene + (butyl acrylate, styrene). As shown in Fig. 3, the results for the system ethylbenzene + MMA obtained in this work are in very good agreement with those of Sastry *et al.* [4]. The small difference may be attributed to the fact that Sastry *et al.* used MMA as purchased, with the stabilizer, and here the monomer was freshly distilled before the measurements. An additional reason may be the different experimental

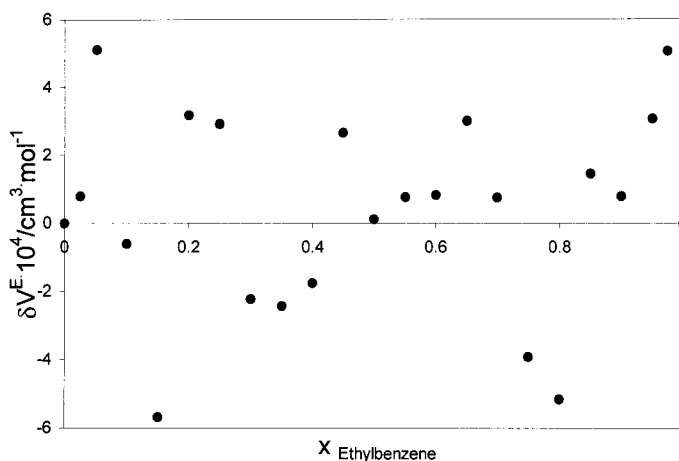


FIGURE 2 Residual distribution plot for the system ethylbenzene + EA, according to the fit given in Table VI.

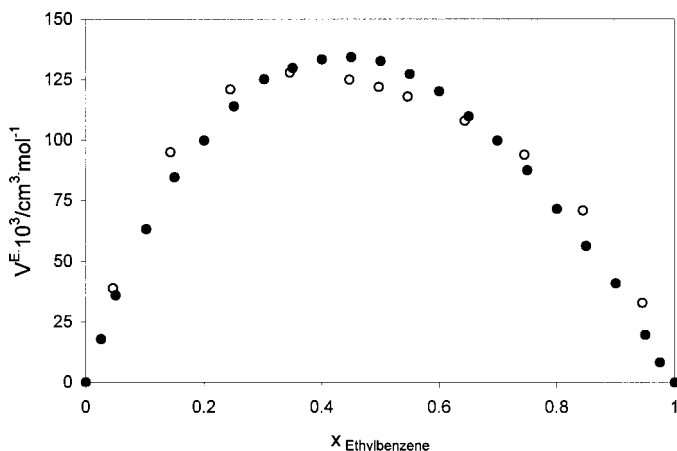


FIGURE 3 Comparison of the calculated excess volumes for the system ethylbenzene + MMA: ● this work; ○ Sastry *et al.* [4].

equipment used (pycnometer against oscillating U-tube densitometer), and the background error.

As regards to the symmetry of the excess function, Fig. 1 shows that the function  $V^E(x)$  is symmetric only for the system ethylbenzene + ethyl acrylate indicating that the maximum specific interaction occurs at about equimolar composition with  $(V^E)_{x=0.5} \approx 0.041 \text{ cm}^3 \text{ mol}^{-1}$ . For the other systems the maximum of the curve deviates to the right or to the left of  $x = 0.5$ , pointing to a small amount of self-association of the solute for methyl methacrylate, and of ethylbenzene for the case of styrene and butyl acrylate.

The sign and intensity of the volume changes that take place during mixing is the result of several effects that operate in the same or opposite directions. The most important ones are: (a) a positive effect caused by the break-up of the structure of one or both components (originated from non-chemical or chemical interaction such as hydrogen bonding or complex-forming interactions such as self-association) and (b) a negative one due to physical interactions (for example, heteroassociation) or geometric fitting of one component into the second, leading to a more compact packing (interstitial accommodation). The second contribution becomes more and more important with increasing sphericity of the solute molecule and higher molar volume of the solvent.

Structurally ethylbenzene may be considered the homomorph of ethyl cyclohexane, aprotic and almost apolar ( $\mu \approx 0$ ). Interactions between a polar compound and an aromatic compound such as ethylbenzene ( $\mu = 0.4$ ) is considered to occur via complex formation between the two species, or  $n-\pi$  interaction [8].

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 minimax value of  $V^E$  ranging from about  $+0.13$  to  $-0.051$  cm<sup>3</sup>/mol. The  $V^E$  curves are positive or negative, their relative intensity depending on the nature of the solute (monomer) and the solvent. In the case of the MMA and EA, the overall positive magnitude of  $V^E$  results from an intercalation effect of ethylbenzene that breaks dipole-dipole associations.  $n-\pi$  interactions between an aromatic hydrocarbon (such as ethylbenzene) and an ester are much stronger than those between a cyclic hydrocarbon (such as ethyl cyclohexane) and an aromatic. The very low negative values for the system ethylbenzene + styrene indicates that the disruption of the dipolar association of the ester is considerably less than the specific interaction between its pairs of electrons and the  $\pi$  electrons of the aromatic ring. In addition, the substitution of an ethyl group in the benzene ring constitutes an obstacle to  $n-\pi$  specific interactions because of its bulkiness. As shown in Fig. 1, the system ethylbenzene + styrene presents the smallest expansion effect. This fact is a result of the inductive effect of the vinyl group in styrene enhancing 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 net result is a smaller dislocation of the structure of ethylbenzene.

Anyhow, it is clear that there is a substantial difference in ethylbenzene dislocation between the MMA and styrene. The value of  $(V^E)_{x=0.5}$  for the latter is about one-quarter that of MMA. In addition, there is clear effect of the side of the alkyl group of the ester. The chain with the smallest size has the largest positive excess volumes, it then decreases and becomes negative as the alkyl group becomes longer.

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