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Density, excess volumes and partial volumes of the systems of *p*-xylene + ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K

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Abstract

Densities of the binary systems of *p*-xylene 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 densimeter. 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 binaries of *p*-xylene with methyl methacrylate and styrene and negative for the binary with butyl methacrylate. The excess volumes for the system *p*-xylene + ethyl acrylate are positive for *p*-xylene concentrations less than 0.7 mole fraction and negative afterwards. The values of the excess volume for the systems of *p*-xylene with ethyl acrylate and styrene are small enough to assume that they behave ideally.

Keywords: Acrylates; Densities; Excess volumes; Monomers; *p*-Xylene; Styrene

1. Introduction

The mixing of different compounds gives rise to solutions that generally do not behave ideally. The deviation from ideality is 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. In general, positive excess volumes may be due to the compensation between strong like interactions (such as those present in alcohols) and equally strong unlike H-bond interactions (such as those present between alcohols and ether). Negative excess volumes will occur when the unlike interactions prevail over self-association. Binary mixtures are an important class of solvents and the behavior of some of their physical properties is still not clear. For example, when a solution presents positive excess volumes the excess dynamic viscosity is negative, and vice versa.

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 systems under consideration. So far we have determined the excess volumes of monomers such as ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene with aromatic solvents such as benzene, diethyl benzene, toluene, *o*- and *m*-xylene, cyclic solvents such as cyclohexane, and ethers such as tetrahydrofuran and 2,2′-oxybis[propane] [1–10]. In general, our results show that styrene presents the largest negative excess volumes of all the monomers studied.

p-Xylene is an excellent solvent and may be useful in polymerization and other chemical reactions, 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

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also interesting because they contain both a double bond and an ester group.

Sastry and Dave [11,12] measured the excess volume, isentropic compressibility, and dielectric behavior of 15 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–π types). Sastry and Valand [13] 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 components. Sastry et al. [14] 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 exhibited positive excess volumes. The excess volumes for the system methyl methacrylate + *p*-xylene showed a sigmoid behavior, they were positive for mole fractions of *p*-xylene below 0.55 and then negative.

No literature data are available for the excess volumes of the systems of *p*-xylene with ethyl acrylate, butyl acrylate, and styrene.

2. Experimental

2.1. Materials

p-Xylene (99.7 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 1).

Table 1
Purity and densities of pure components at 298.15 K

Component	Purity (mass%)	Density ($g\,cm^{-3}$)	
		Measured	Literature
p-Xylene (1)	99.7	0.856670	0.8564 [21] 0.8563 [23]
Butyl acrylate (2)	99.9	0.893735	0.8941 [13]
Ethyl acrylate (3)	99.8	0.915930	0.9163 [13]
Methyl methacrylate (4)	99.9	0.937593	0.93766 [22] 0.93766 [24]
Styrene (5)	99.9	0.901941	0.9016 [14] 0.9011 [21]

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(1 0 0) platinum thermometers (DKD traceable), and a stated accuracy of $5 \times 10^{-6}\,g\,cm^{-3}$. The temperature in the cell was regulated to a precision (i.e. repeatability standard deviation) of ±0.001 K with a solid-state thermostat. The works calibration of the in-cell thermometer is done with an uncertainty of 0.01 K. 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 cm^3 rubber-stoppered vial to prevent 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 5.8×10^{-5}; precision of the density (duplicate) measurement $\pm 2 \times 10^{-6}\,g\,cm^{-3}$, and of the temperature ±0.002 K. Total uncertainty in the density measurement, as reported by the equipment manufacturer, was $5 \times 10^{-6}\,g\,cm^{-3}$.

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 ($0 \le x \le 1$).

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:

$$V^E = \left[\frac{xM_1 + (1-x)M_2}{\rho}\right] - \left[\frac{xM_1}{\rho_1} + \frac{(1-x)M_2}{\rho_2}\right] \qquad (1)$$

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 the molar masses of the pure components. The corresponding values of ρ and V^E are reported in Tables 2–5 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 volumes are similar in size (usually larger than 100 $cm^3\,mol^{-1}$) 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 [15]:

$$\overline{V}_1 = V + x_2 \frac{dV}{dx_1} \qquad (2)$$

Table 2
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system *p*-xylene (1) + butyl acrylate (2) at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	V^E ($\times 10^3$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})
0	0.893735	143.4094	0	0
0.0253	0.892963	142.9105	−6.507	−1.0
0.0508	0.892162	142.4084	−10.70	0.45
0.0996	0.890647	141.4475	−22.96	−1.1
0.1504	0.889030	140.4473	−33.49	−0.57
0.2046	0.887278	139.3804	−44.52	−0.25
0.2497	0.885790	138.4934	−52.36	0.87
0.3005	0.884092	137.4959	−60.98	1.6
0.3505	0.882405	136.5131	−70.71	0.11
0.4003	0.880687	135.5343	−78.75	−0.86
0.4500	0.878932	134.5609	−84.19	−0.57
0.4997	0.877138	133.5900	−87.45	0.36
0.5498	0.875296	132.6118	−89.84	0.45
0.6001	0.873410	131.6309	−90.89	−0.083
0.6499	0.871504	130.6618	−90.20	−1.0
0.7000	0.869534	129.6899	−86.09	−0.92
0.7497	0.867524	128.7291	−78.22	0.42
0.7997	0.865456	127.7668	−67.57	1.8
0.8501	0.863345	126.7957	−57.69	−0.78
0.9001	0.861170	125.8386	−40.98	0.42
0.9501	0.858951	124.8834	−22.64	−0.15
0.9750	0.857821	124.4077	−12.17	−0.46
1	0.856670	123.9334	0	0

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

Table 3
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system *p*-xylene (1) + ethyl acrylate (3)[a] at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	V^E ($\times 10^3$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})
0	0.915930	109.3097	0	0
0.0256	0.914184	109.6876	4.110	0
0.0501	0.912541	110.0477	5.548	0
0.0996	0.909260	110.7745	7.789	0
0.1506	0.905937	111.5209	9.481	0
0.1999	0.902764	112.2433	10.75	0
0.2507	0.899538	112.9878	11.77	0
0.3005	0.896422	113.7167	12.34	0
0.3501	0.893364	114.4419	12.12	0
0.3998	0.890344	115.1679	11.01	0
0.4503	0.887317	115.9050	9.859	0
0.4999	0.884392	116.6273	7.617	0
0.5505	0.881430	117.3670	6.388	0
0.5999	0.878589	118.0862	4.134	0
0.6501	0.875727	118.8192	2.518	0
0.7002	0.872912	119.5494	0.4587	0
0.7503	0.870130	120.2800	−1.590	0
0.8001	0.867417	121.0036	−6.409	0
0.8502	0.864698	121.7347	−8.087	0
0.9002	0.862000	122.4666	−7.362	0
0.9502	0.859294	123.2041	−0.5861	0
0.9747	0.857999	123.5628	−0.1360	0
1.0000	0.856670	123.9334	0	0

[a] This system is considered ideal.

$$\overline{V}_2 = V - x_1 \frac{\mathrm{d}V}{\mathrm{d}x_1} \tag{3}$$

The pertinent values are reported in Table 6 and are necessarily consistent.

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

(a) The Redlich–Kister expression [16]:

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

where the A_k's are the adjustable parameters of the model.

Table 4
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system *p*-xylene (1) + methyl methacrylate (4) at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	V^E ($\times 10^3$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})
0	0.937593	106.7841	0	0
0.0254	0.935160	107.2263	6.361	0.073
0.0500	0.932829	107.6538	12.05	−0.22
0.1001	0.928137	108.5245	23.82	0.0042
0.1501	0.923543	109.3916	34.22	0.15
0.2002	0.919018	110.2604	42.75	0.0070
0.2504	0.914572	111.1286	49.83	0.24
0.3001	0.910266	111.9841	54.26	−0.22
0.3502	0.905997	112.8463	57.33	−0.21
0.4001	0.901822	113.7035	58.76	−0.057
0.4500	0.897722	114.5591	58.56	0.056
0.5003	0.893662	115.4202	56.80	−0.00060
0.5502	0.889698	116.2740	54.24	0.28
0.6003	0.885794	117.1283	50.23	0.041
0.6501	0.881968	117.9783	45.55	−0.20
0.6999	0.878200	118.8275	40.82	0.0049
0.7501	0.874460	119.6828	35.85	0.41
0.7997	0.870821	120.5280	29.28	−0.48
0.8506	0.867141	121.3944	23.33	−0.19
0.8999	0.863626	122.2341	16.93	0.084
0.9497	0.860135	123.0803	9.629	0.44
0.9746	0.858414	123.5025	4.840	−0.022
1	0.856670	123.9334	0	0

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

Table 5
Experimental densities, volumes, calculated excess volumes, and deviations δV^E for the system *p*-xylene (1) + styrene (5)[a] at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	V^E ($\times 10^3$ cm^3 mol^{-1})	δV^E ($\times 10^3$ cm^3 mol^{-1})
0	0.901941	115.4732	0	0
0.0252	0.900718	115.6865	0.09151	0
0.0544	0.899310	115.9331	0.08252	0
0.1005	0.897092	116.3236	0.3009	0
0.1505	0.894704	116.7470	0.6155	0
0.2007	0.892322	117.1723	1.067	0
0.2503	0.889986	117.5925	1.415	0
0.3000	0.887662	118.0135	1.885	0
0.3506	0.885312	118.4422	2.467	0
0.4001	0.883035	118.8606	2.939	0
0.4501	0.880746	119.2843	3.406	0
0.4999	0.878482	119.7063	3.720	0
0.5500	0.876223	120.1303	4.189	0
0.6002	0.873973	120.5557	4.655	0
0.6505	0.871738	120.9812	5.064	0
0.6999	0.869554	121.3999	5.579	0
0.7499	0.867360	121.8235	5.964	0
0.8000	0.865181	122.2471	6.190	0
0.8500	0.863018	122.6708	6.068	0
0.9000	0.860880	123.0926	5.393	0
0.9499	0.858766	123.5131	3.416	0
0.9749	0.857715	123.7233	2.077	0
1	0.856670	123.9334	0	0

[a] This system is considered ideal.

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 6
Partial volumes $\overline{V}_i$[a] ($cm^3\,mol^{-1}$)

x_1	*p*-Xylene (1) + BA (2)		*p*-Xylene (1) + AE (3)		*p*-Xylene (1) + MMA (4)		*p*-Xylene (1) + St (5)	
	$\overline{V}_2$	$\overline{V}_1$	$\overline{V}_3$	$\overline{V}_1$	$\overline{V}_4$	$\overline{V}_1$	$\overline{V}_5$	$\overline{V}_1$
0	143.409	123.713	109.310	132.507	106.784	124.182	115.473	123.935
0.05	143.409	123.712	109.462	125.900	106.784	124.174	115.473	123.936
0.10	143.409	123.714	109.713	123.092	106.786	124.155	115.473	123.938
0.15	143.408	123.719	109.937	122.528	106.790	124.129	115.473	123.940
0.20	143.407	123.727	110.187	123.184	106.796	124.100	115.473	123.942
0.25	143.404	123.737	110.604	124.447	106.804	124.071	115.474	123.943
0.30	143.399	123.749	111.352	125.994	106.815	124.044	115.475	123.945
0.35	143.392	123.763	112.557	127.690	106.827	124.019	115.477	123.947
0.40	143.383	123.779	114.260	129.496	106.839	123.998	115.480	123.949
0.45	143.371	123.795	116.397	131.401	106.852	123.980	115.483	123.951
0.50	143.355	123.812	118.782	133.365	106.864	123.967	115.486	123.954
0.55	143.336	123.830	121.118	135.284	106.875	123.957	115.489	123.957
0.60	143.313	123.847	123.032	136.973	106.884	123.951	115.491	123.960
0.65	143.285	123.864	124.124	138.177	106.891	123.946	115.492	123.962
0.70	143.252	123.880	124.043	138.602	106.897	123.943	115.493	123.962
0.75	143.213	123.894	122.596	137.973	106.903	123.941	115.493	123.960
0.80	143.168	123.907	119.870	136.120	106.908	123.939	115.494	123.956
0.85	143.117	123.918	116.399	133.089	106.917	123.938	115.498	123.950
0.90	143.059	123.926	113.348	129.291	106.930	123.936	115.507	123.943
0.95	142.994	123.932	112.736	125.673	106.951	123.934	115.527	123.937
1	142.920	123.933	117.693	123.933	106.985	123.933	115.565	123.933

[a] Systems 1 + 3 and 1 + 5 are considered ideal.

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

$$V^E = x_1x_2\sum_{k=0}^{n} a_k L_k(x_1) \tag{5}$$

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

$$V^E = x_1x_2[a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1) + a_3(20x_1^3 - 30x_1^2 + 12x_1 - 1)] \tag{6}$$

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 [17,18] has de-

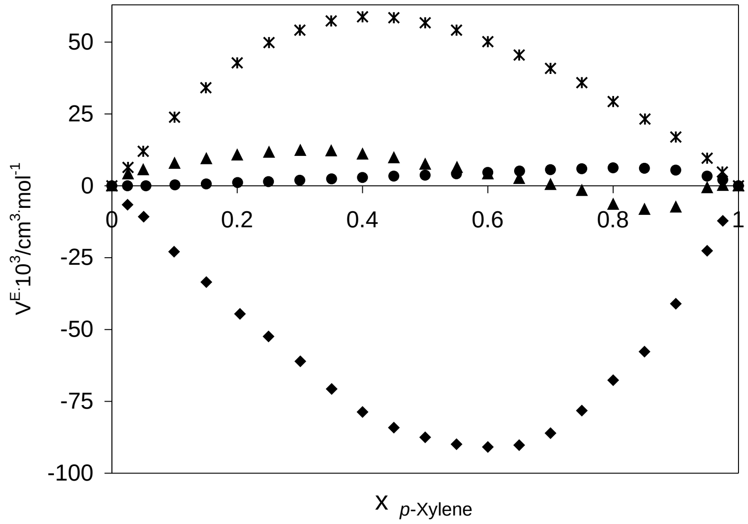


Fig. 1. Excess volumes at 298.15 K: (✱) *p*-xylene + MMA; (▲) *p*-xylene + EA; (◆) *p*-xylene + BA; (●) *p*-xylene + styrene.

scribed 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 formulae 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.

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

$$\mathrm{OF} = \sum_{1}^{N} \left(V^{\mathrm{E}}_{i,\mathrm{exptl}} - V^{\mathrm{E}}_{i,\mathrm{calc}} \right)^2 \tag{7}$$

where N is the number of observations. The values of the different adjustable parameters (A_k and a_k) are reported in Tables 7 and 8 for different values of k, together with the pertinent statistics. The standard deviation s was calculated as:

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

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 [19]. It was not deemed necessary to perform a step-wise regression.

A plot of the function $V^{\mathrm{E}}/x_i x_j$ 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, $\overline{V}_1^{\mathrm{E},\infty}$, which can be also calculated from the adjustable parameters as follows [15]:

(a) Redlich–Kister

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

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

(b) Legendre

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

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

where V_i^0 is the molar volume of pure component i. The pertinent values of $\overline{V}_i^{E,\infty}$ are also shown in Tables 7 and 8. 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. Eqs. (9) and (10) or (11) and (12) yield the same values of $\overline{V}_2^{E,\infty}$.

Fig. 2 shows a typical distribution of the residuals, which is random as shown by the Durbin–Watson statistic. The same behavior is observed for all the systems studied.

Inspection of the results of Tables 2–5 and Fig. 1 indicates that the excess volumes are positive for the binaries of *p*-xylene with methyl methacrylate and styrene and negative for the binary with butyl methacrylate, while for the system *p*-xylene + ethyl acrylate they present a sigmoid behavior: positive for solvent concentrations less than 0.7 M and negative afterwards. The values of the excess volumes for the systems of *p*-xylene with ethyl acrylate and styrene are small enough to allow assuming that both systems behave ideally.

Figs. 3 and 4 compare the results of this work with those of Sastry et al. [14] for the density and excess volumes of the system *p*-xylene + methyl methacrylate. Although, there

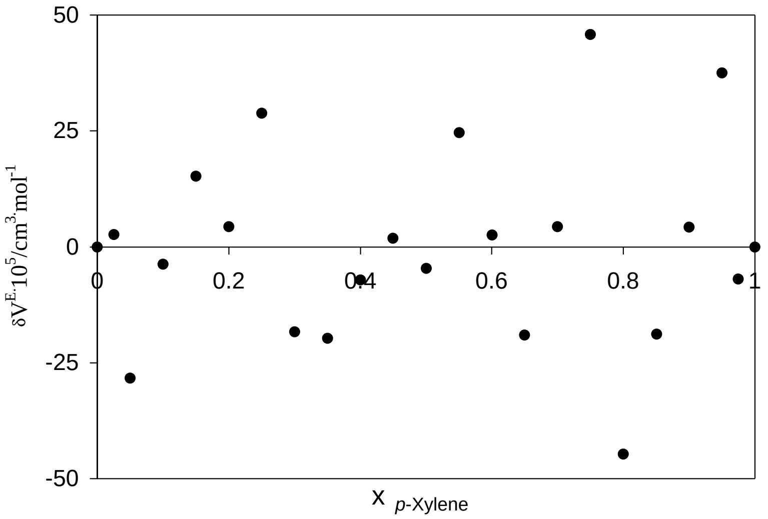


Fig. 2. Residual distribution plot for the system *p*-xylene + MMA, according to the fit given in Table 6.

Table 7
Coefficients A_k (Eq. (4)), standard deviation, s (Eq. (8)), Durbin–Watson statistic d, $(V^{\mathrm{E}})_{x=0.5}$, and $\overline{V}_i^{\mathrm{E},\infty}$ at 298.15 K

System[a]	$A_0 \times 10^2$	$A_1 \times 10^2$	$A_2 \times 10^2$	$A_3 \times 10^2$	$A_4 \times 10^2$	$A_5 \times 10^2$	$A_6 \times 10^2$	$s \times 10^4$	d[b]	$(V^{\mathrm{E}})_{x=0.5}$ ($\times 10^2$ cm^3 mol^{-1})	$\overline{V}_1^{\mathrm{E},\infty}$ ($\times 10^2$ cm^3 mol^{-1})	$\overline{V}_2^{\mathrm{E},\infty}$ ($\times 10^2$ cm^3 mol^{-1})
1 + 2	−35.13	−13.50	−0.15					8.4	1.8	−8.783	−21.78	−48.78
1 + 3	3.04	−5.59	8.04	−12.60	−56.74	9.95	60.28	7.2	2.2	0.761	22.87	6.38
1 + 4	22.72	−9.24	−0.23	6.89				2.3	2.2	5.68	24.83	20.14
1 + 5	1.51	1.69	1.43	2.81	1.72			0.5	2.8	0.377	0.15	9.17

[a] Systems 1 + 3 and 1 + 5 are considered ideal.

[b]
$$d = \frac{\sum_{u=2}^{N}(e_u - e_{u-1})^2}{\sum_{u=1}^{N} e_u^2}, \quad e_u = V^{\mathrm{E}}_{u,\mathrm{calc}} - V^{\mathrm{E}}_{u,\mathrm{exptl}}.$$

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

System[a]	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	$a_4 \times 10^2$	$a_5 \times 10^2$	$a_6 \times 10^2$	$s \times 10^4$	d[b]	$(V^{\mathrm{E}})_{x=0.5}$ ($\times 10^2$ cm^3 mol^{-1})	$\overline{V}_1^{\mathrm{E},\infty}$ ($\times 10^2$ cm^3 mol^{-1})	$\overline{V}_2^{\mathrm{E},\infty}$ ($\times 10^2$ cm^3 mol^{-1})
1 + 2	−35.08	−3.440						8.6	1.8	−8.77	−21.64	−48.52
1 + 3	131.63	−8.887	430.44	−0.62	286.48	1.26	4.16	7.4	2.2	0.76	860.95	844.47
1 + 4	22.64	−5.103	−0.16	−2.75				2.4	2.2	5.68	24.83	20.14
1 + 5	2.33	3.38	1.94	1.12	0.39			0.5	2.8	0.38	0.16	9.17

[a] Systems 1 + 3 and 1 + 5 are considered ideal.

[b]
$$d = \frac{\sum_{u=2}^{N}(e_u - e_{u-1})^2}{\sum_{u=1}^{N} e_u^2}, \quad e_u = V^{\mathrm{E}}_{u,\mathrm{calc}} - V^{\mathrm{E}}_{u,\mathrm{exptl}}.$$

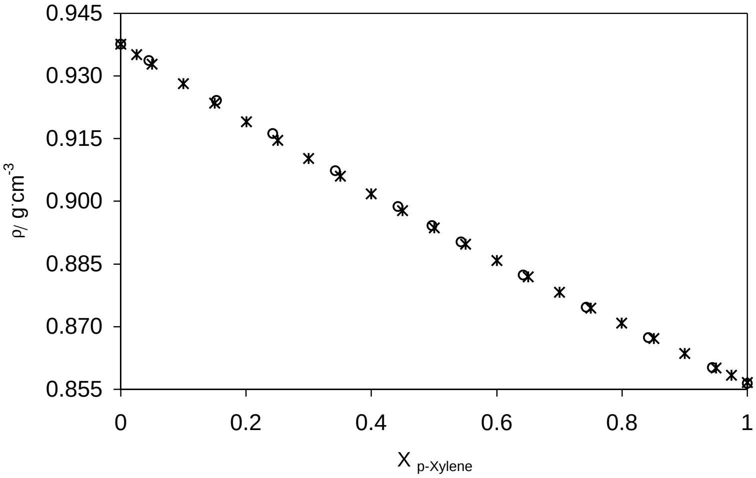


Fig. 3. Comparison of the density measurements for the system *p*-xylene + MMA: (✱) this work; (○) Sastry et al. [14].

seems to be an excellent agreement between the experimental values of the density reported in Table 4 and those calculated using Sastry's correlations (Fig. 3), this is not the case for the excess volumes (Fig. 4). Sastry et al. reported a sigmoidal behavior with negative values for mole fractions of *p*-xylene below 0.45 and positive afterwards, against the all positive values obtained in this work. The difference between the two sets of measurements may be due to the different experimental technique (Sastry used a picknometer), to a different degree in purity of the reagents, and particularly by considering the very similar numerical value of the two terms that compose the right-hand side of Eq. (1), as explained in Section 1. Consider for example the point $x_1 = 0.2002$ in Table 4. For this concentration the molar volumes (rounded) of the solution and of the equivalent ideal solution are 110.2604 and 110.2177 $\mathrm{cm^3\,mol^{-1}}$, respectively. Hence, calculation of the excess volumes involves taking the difference between two very large numbers of about the same size and yielding, for the specific concentration, $V^E = 0.0427\,\mathrm{cm^3\,mol^{-1}}$. It is clear that a small error in each of the two large volumes may reflect in a *very* large error in their difference. For the particular system and concentration the overall uncertainty is about $\pm 6 \times 10^{-4}$. Hence, the importance of making the measurements very carefully and using equipment that will provide enough significant figures.

The magnitude and sign of V^E is a reflection of the type of interactions taking place in the mixture [20]. This is very well exhibited by the mixtures studied here with the minimum and maximum values of V^E ranging from about −0.09 to 0.06 $\mathrm{cm^3\,mol^{-1}}$. The change from positive magnitude of V^E for the system *p*-xylene + MMA to negative values for the system *p*-xylene + BA indicates a change from a dislocation effect to a packing one, probably caused by the more branched structure of MMA.

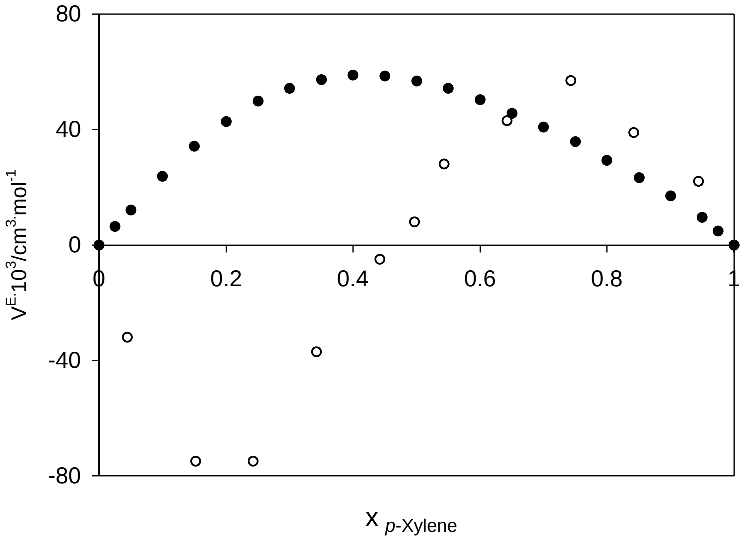


Fig. 4. Comparison of the excess volumes for the system *p*-xylene + MMA: (●) this work; (○) Sastry et al. [14].

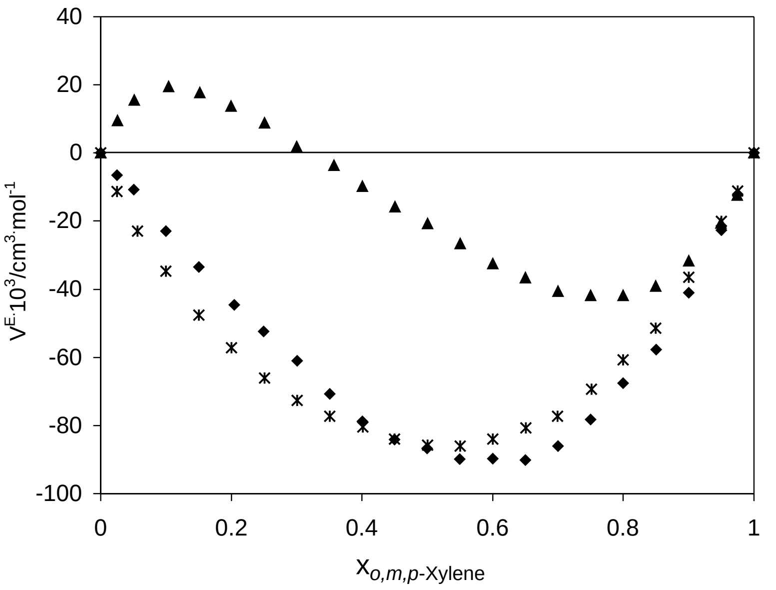
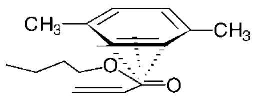


Fig. 5. Excess volumes at 298.15 K: (✱) *o*-xylene + BA [7]; (▲) *m*-xylene + BA [10]; (◆) *p*-xylene + BA (this work).

It is interesting to compare the effect of the nature of the xylene isomer on their excess volumes with butyl acrylate (as shown in Fig. 5). First of all, the non-ideality of the system increases in the order *para*- > *meta*- > *ortho*-xylene, with the system *o*-xylene + BA presenting a sigmoid behavior. Second, we can guess similar molecular interactions for the *ortho* and *para* isomers. The different behavior exhibited by the *meta* isomer can be explained by a play between repulsive and attractive interactions. The marked decrease of the excess volume of the solutions of butyl acrylate and *o*- and *p*-xylene at about an equimolar concentration is probably caused by a transient charge transfer complex between the electronic cloud of xylene, enriched by the positive hyperconjugation effect of the methyl group in these isomers with the electrophilic carbonyl group of butyl acrylate, as shown in the following figure:



It is probable that *m*-xylene-butyl acrylate solutions present two kinds of interactions, one of them at 10% mole concentration and the other at 80% mole fraction of *m*-xylene. The first one represents a pure steric repulsive effect without any electronic interaction and provoking an increase of the excess volume, and the second having the same attractive interaction shown in the *o*- and *p*-xylene mixtures. These molecular interactions will alter the spectroscopic properties of the mixtures. To verify these assumptions, we performed an FT-IR analysis coupled with an attenuated total reflectance device (ATR). The test was focused on the absorption of the carbonyl group, which is sensitive to the electronic interactions; if some charge complex is present it will displace the absorption band to a higher wave number value. The following mixtures (molar basis) were tested: (a) butyl acrylate, 100%; (b) butyl acrylate, 90% + *m*-xylene, 10%; (c) butyl acrylate, 50% + *m*-xylene, 50%; (d) butyl acrylate, 20% + *m*-xylene, 80%; (e) butyl acrylate, 50% + *o*-xylene, 50%. The first two solutions showed an absorption peak at 1724 cm^{-1}, which increased to 1727 cm^{-1} for the remaining solutions. These results indicate clearly that an interaction between the electronic cloud of *o*- and *p*-xylene and the carbonyl group of the butyl ester increases the electropositive character of the carbon and reflects in the 3 cm^{-1} increase in the absorption peak. The same situation is present when there is an excess of *m*-xylene concentration (80%). The solution containing 90 mol% butyl acrylate and 10 mol% of *m*-xylene does not show any shift of the absorption peak, indicating that the increase in excess volume is due to a simple steric effect.

For the effect of the nature of the xylene isomer on the V^E of the mixtures with each of the other three monomers, we found that for MMA and St, all V^E values are positive indicating the presence of repulsive interactions [7,10]. The system *p*-xylene with St was found to have almost ideal behavior as reported earlier [10]. In the case of the EA monomer, the *o*- [7] and *p*-xylene—EA systems present very small V^E values and were declared ideal. Finally, the *m*-xylene—EA system showed positive values of V^E in the full concentration range indicating again repulsive interactions between the molecules of the two components [10].

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