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Thermochimica Acta 402 (2003) 247–252

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Volumetric properties of 1,2-dimethylbenzene + ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K

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Received 22 August 2002; received in revised form 25 November 2002; accepted 27 November 2002

Abstract

Densities of the binary systems of 1,2-dimethylbenzene with ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), 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 (V^E) were correlated with the Redlich–Kister equation. The excess volumes are positive for the binaries of *o*-xylene with MMA and styrene, and negative for *o*-xylene + butyl acrylate. All systems present small deviations from ideality; the system *o*-xylene + ethyl acrylate is closest to ideality.

Keywords: Densities; Excess volumes; Monomers; 1,2-Dimethylbenzene; Acrylates; 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 the so-called excess properties, which corresponds to the difference between the actual property and the property if the system behaves ideally.

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.

Sastry and Dave [1,2] measured the excess volumes (V^E), isentropic compressibilities, 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 [3] 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. [4] measured the excess volumes of methyl methacrylate (MMA) with ethylbenzene and other aromatic

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doi:10.1016/S0040-6031(02)00605-6

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 MMA + *o*-xylene showed almost ideal behavior with a maximum at about $V^E \approx 0.07\,\mathrm{cm^3\,mol^{-1}}$.

No literature data are available for the excess volumes of the systems of *o*-xylene with ethyl acrylate (EA), butyl acrylate (BA), and styrene.

2. Experimental section

2.1. Materials

1,2-Dimethylbenzene (*o*-xylene, 99.3 mass%), EA (>99 mass%), BA (>99 mass%), MMA (>99 mass%), and styrene (99 mass%) were purchased from Aldrich. The supplier certified the purity of all the reagents. 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).

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 $5 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$.

Table 1
Purity and densities of pure components at 298.15 K

Component	Purity (mass%)	Density ($\mathrm{g\,cm^{-3}}$)	
		Measured	Literature
o-Xylene (1)	99.3	0.875772	0.87563 [8]
Butyl acrylate (2)	>99	0.893958	0.8941 [3]
Ethyl acrylate (3)	99	0.915930	0.9163 [3]
Methyl methacrylate (4)	99	0.937669	0.93766 [9]
Styrene (5)	99	0.901972	0.9016 [10]

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 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. Accuracy in the mole fraction is $\pm 5 \times 10^{-5}$, of the density (duplicate) measurement $\pm 2 \times 10^{-6}\,\mathrm{g\,cm^{-3}}$, and of the temperature ±0.002 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 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:

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

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 2–5 and Fig. 1.

The values of V^E were correlated with composition using the Redlich–Kister expression [6]

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

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

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

$$\mathrm{OF} = \sum_{1}^{N} (V^E_{i,\,\mathrm{exp}\,t} - V^E_{i,\,\mathrm{calc}})^2 \tag{3}$$

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

x	ρ (g cm^{-3})	V (cm^3 mol^{-1})	$V^E \times 10^3$ (cm^3 mol^{-1})
0	0.893958	143.374	0
0.0249	0.893645	142.812	−11.3
0.0561	0.893232	142.108	−23.0
0.1000	0.892615	141.124	−34.7
0.1507	0.891889	139.989	−47.6
0.2003	0.891147	138.882	−57.2
0.2509	0.890371	137.751	−66.1
0.3006	0.889583	136.645	−72.6
0.3505	0.888766	135.534	−77.3
0.4009	0.887917	134.415	−80.5
0.4501	0.887078	133.323	−83.9
0.5002	0.886197	132.212	−85.7
0.5501	0.885295	131.108	−86.0
0.6002	0.884357	129.999	−84.0
0.6506	0.883389	128.886	−80.7
0.6995	0.882431	127.806	−77.3
0.7513	0.881371	126.668	−69.4
0.8001	0.880346	125.597	−60.7
0.8499	0.879277	124.502	−51.5
0.9000	0.878144	123.408	−36.6
0.9499	0.876984	122.320	−20.0
0.9749	0.876390	121.775	−11.2
1	0.875772	121.230	0

Table 3
Experimental densities, volumes, and calculated excess volumes for the system *o*-xylene (1) + ethyl acrylate (3) at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	$V^E \times 10^3$ (cm^3 mol^{-1})
0	0.915930	109.310	0
0.0250	0.914832	109.606	−1.71
0.0501	0.913746	109.903	−4.21
0.1000	0.911570	110.496	−5.33
0.1509	0.909382	111.100	−7.58
0.2010	0.907221	111.699	−6.12
0.2503	0.905118	112.288	−4.65
0.3015	0.902955	112.900	−3.14
0.3501	0.900902	113.484	1.33
0.3999	0.898877	114.075	−1.67
0.4504	0.896826	114.677	−2.24
0.4996	0.894851	115.262	−2.91
0.5514	0.892785	115.880	−2.57
0.6001	0.890821	116.466	3.03
0.6503	0.888895	117.061	−1.48
0.7011	0.886950	117.663	−3.45
0.7495	0.885082	118.243	−1.50
0.8002	0.883158	118.848	−1.01
0.8498	0.881294	119.440	−0.284
0.8996	0.879470	120.030	−3.58
0.9499	0.877619	120.630	−3.30
0.9745	0.876714	120.924	−2.41
1	0.875772	121.230	0

where N is the number of observations. The standard deviation s was calculated as

$$s = \left[\sum \frac{(V^{E}_{i,\,\exp t} - V^{E}_{i,\,\mathrm{calc}})^2}{N-k}\right]^{1/2} \tag{4}$$

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, tested by the Durbin–Watson statistic, as suggested by Wisniak and Polishuk [7]. It was not deemed necessary to perform a step-wise regression. The optimal values of the different adjustable parameters, A_k are reported in Table 6 together with the pertinent statistics.

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, $\bar{V}_i^{E,\infty}$, which can also be calculated from the adjustable parameters as follows [5]:

$$\bar{V}_1^{E,\infty} = A_0 - A_1 + A_2 - \cdots = \bar{V}_1^{\infty} - V_1^0 \tag{5}$$

$$\bar{V}_2^{E,\infty} = A_0 + A_1 + A_2 + \cdots = \bar{V}_2^{\infty} - V_2^0 \tag{6}$$

where V_i^0 is the molar volume of pure component i. The pertinent values of $\bar{V}_i^{E,\infty}$ are given in Table 6.

Fig. 2 compares the results of this work with those of Sastry et al. [4] for the system *o*-xylene + methyl methacrylate. It is seen that the results of the latter are somewhat bigger than those reported here and show a large degree of dispersion near the middle range of concentrations. Anyhow, the results of Sastry et al. may also be interpreted as showing near ideal behavior. The difference between the two sets of measurements may be explained by considering the numerical value of the two terms that compose the RHS of Eq. (1). Consider for example the point $x = 0.5508$ in Table 4. For this concentration the molar volumes of the solution and of the equivalent ideal solution (rounded) are 114.796 and 114.737 cm^3 mol^{-1}, respectively. Hence,

Table 4
Experimental densities, volumes, and calculated excess volumes for the system *o*-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})
0	0.937669	106.775	0
0.0258	0.935825	107.152	4.40
0.0505	0.934081	107.513	7.15
0.1008	0.930548	108.248	15.0
0.1503	0.927122	108.971	23.0
0.1928	0.924219	109.591	29.5
0.2504	0.920329	110.433	38.2
0.2998	0.917043	111.155	45.9
0.3507	0.913730	111.895	50.4
0.4006	0.910532	112.619	53.8
0.4503	0.907386	113.341	56.9
0.5006	0.904253	114.071	59.0
0.5508	0.901183	114.796	58.8
0.6001	0.898212	115.508	58.5
0.6502	0.895236	116.231	56.4
0.7000	0.892338	116.945	52.2
0.7501	0.889461	117.665	46.7
0.8004	0.886623	118.385	39.2
0.8504	0.883843	119.099	31.2
0.9000	0.881140	119.805	20.2
0.9503	0.878414	120.523	11.2
0.9742	0.877135	120.864	6.47
1	0.875772	121.230	0

Table 5
Experimental densities, volumes, and calculated excess volumes for the system *o*-xylene (1) + styrene (5) at 298.15 K

x_1	ρ (g cm^{-3})	V (cm^3 mol^{-1})	$V^E \times 10^3$ (cm^3 mol^{-1})
0	0.901972	115.469	0
0.0261	0.901191	115.628	8.17
0.0504	0.900472	115.775	15.0
0.1003	0.899014	116.075	27.4
0.1511	0.897580	116.374	34.6
0.2005	0.896196	116.665	41.1
0.2512	0.894792	116.963	46.3
0.3006	0.893443	117.251	50.3
0.3506	0.892098	117.541	52.2
0.4005	0.890767	117.830	53.6
0.4502	0.889451	118.117	54.4
0.5012	0.888114	118.411	54.5
0.5502	0.886841	118.693	53.5
0.6002	0.885553	118.979	52.1
0.6500	0.884289	119.263	49.2
0.6996	0.883038	119.545	46.0
0.7504	0.881772	119.834	41.1
0.8003	0.880545	120.115	35.2
0.8502	0.879329	120.396	28.6
0.9004	0.878111	120.678	21.7
0.9501	0.876934	120.955	11.9
0.9749	0.876351	121.092	6.52
1	0.875772	121.230	0

calculation of the excess volumes will normally involve taking the difference between two very large numbers of about the same size and yielding, for the specific concentration, $V^E = -0.059\,\text{cm}^3\,\text{mol}^{-1}$. This *very* small figure (relative to *V*) is a consequence of the solution being almost ideal. 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

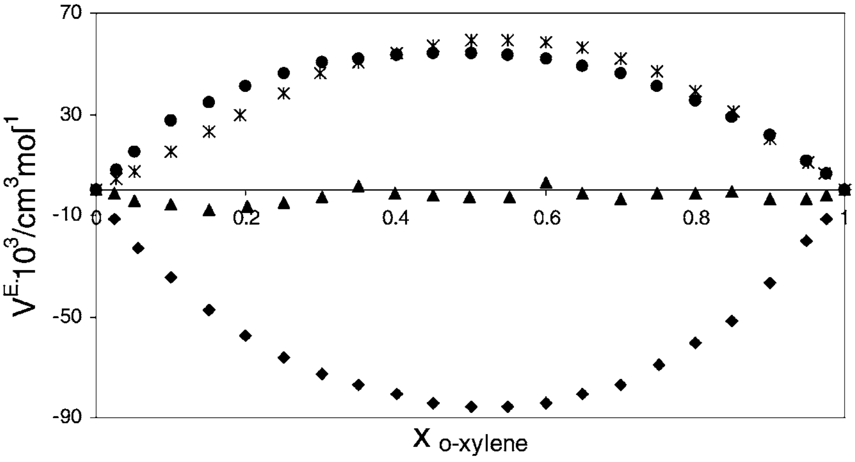

Fig. 1. Excess volumes at 298.15 K: (✱) *o*-xylene + MMA; (▲) *o*-xylene + EA; (◆) *o*-xylene + BA; (●) *o*-xylene + styrene.

Table 6
Coefficients A_k (Eq. (2)), standard deviation s (Eq. (4)), Durbin–Watson statistic d $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System[a]	$A_0 \times 10^2$	$A_1 \times 10^2$	$A_2 \times 10^2$	$A_3 \times 10^2$	$s \times 10^4$	d[b]	$(V^E)_{x=0.5} \times 10^2$ (cm^3 mol^{-1})	$\bar{V}_1^{E,\infty} \times 10^2$ (cm^3 mol^{-1})	$\bar{V}_2^{E,\infty} \times 10^2$ (cm^3 mol^{-1})
(1) + (2)	−34.05	−3.58	−9.05	4.82	7.31	1.70	−8.513	−44.35	−41.86
(1) + (4)	23.71	4.36	−5.02		6.32	1.65	5.928	14.32	23.05
(1) + (5)	21.69	−2.04	7.06	−2.47	5.06	1.51	5.422	33.27	24.24

[a] The system (1) + (3) is considered ideal.
[b] $d = \sum_{u=2}^{N}(e_u - e_{u-1})^2/\sum_{u=1}^{N}e_u^2$; $e_u = V^E_{u,\text{calc}} - V^E_{u,\text{exp}\,tl}$.

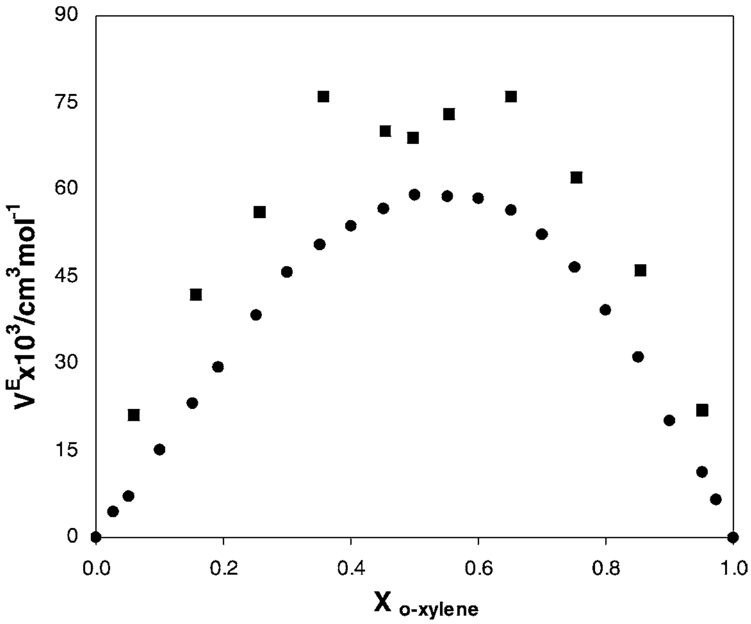

Fig. 2. Comparison of the density measurements for the system o-xylene + MMA: (●) this work; (■) Sastry et al. [4].

the particular system and concentration the overall uncertainty is about ±6 × 10^{-4}. Hence the importance of making the measurements very carefully and using equipment that will provide enough significant figures. This is the same problem present in the calculation of heats of reaction; they can be calculated from heats of formation or from heats of combustion. The second case is usually in large error for the same reason; we are taking the difference between large numbers to obtain a number smaller in one order of magnitude (at least) of the original figures.

Inspection of the results of Tables 2–5 and Fig. 1 show that the excess volumes are very small (relative to V) for all systems and positive for the binaries of o-xylene with MMA and styrene, negative for the binary o-xylene + butyl acrylate, and that the system o-xylene + ethyl acrylate is the closest to ideality. The function $V^E(x)$ is almost symmetric for all the systems, suggesting that the maximum specific interaction occurs near the equimolar composition and lack of self-association of the solute or solvent.

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