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Volumetric properties of cyclohexane with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene at 298.15 K

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Abstract

Densities of the binary systems of cyclohexane 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 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 reported here. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Densities; Excess volumes; Monomers; Cyclohexane

1. Introduction

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

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 measured the excess volumes, isentropic compressibilities, and dielectric behavior 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–π 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 components [3]. Sastry et al. [4] measured the excess volumes of methyl methacrylate (MMA) with cyclohexane and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and (*o*, *m*, *p*)-xylene, at 298.15 and

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303.15 K and found that except for toluene all presented positive excess volumes. The excess volumes for the system MMA + cyclohexane showed a non-symmetric behavior with a maximum at about $V^E \approx 1.05$ cm^3/mol and $x = 0.45$.

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

2. Experimental

2.1. Materials

Cyclohexane (HPLC grade, >99.9 mass%); ethyl acrylate (EA, >99 mass%); butyl acrylate (BA, >99 mass%); MMA, (>99 mass%); and styrene (99 mass%), were purchased from Aldrich. EA, BA, and MMA were vacuum distilled previously 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. The purity of the solvents was further ascertained by comparing their densities at 298.15 K with the 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 densitometer, provided with automatic viscosity correction, two integrated Pt 100 platinum thermometers (DKD traceable), and a stated accuracy of 5×10^{-6} 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.

Table 1
Purity and densities of pure components at 298.15 K

Component	Purity (mass%)	Density (g cm^{-3})	
		Measured	Literature
Cyclohexane	>99.9	0.773780	0.77389 [8]
Butyl acrylate	>99	0.893666	0.8941 [3]
Ethyl acrylate	99	0.925930	0.9163 [3]
Methyl methacrylate	99	0.937669	0.93766 [9]
Styrene	99	0.901972	0.9016 [10]

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 was kept in ice water. Accuracy in the mole fraction is 5×10^{-5}, of the density (duplicate) measurement $\pm 2 \times 10^{-6}$ 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 twenty-one density measurements were performed (with repetition) for each binary system, in 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 the following equation:

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

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 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 two procedures:

(a) The Redlich–Kister expression [5]

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

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

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.

Table 2
Experimental densities, volumes, calculated excess volumes, and deviations δV^{E} for the system cyclohexane + butyl acrylate at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times10^{-2}$) (cm^3 mol^{-1})	V^{E} ($\times10$) (cm^3 mol^{-1})	δV^{E} ($\times10^3$) (cm^3 mol^{-1})
0.0000	0.893666	1.4342	0.0000	0
0.0247	0.891134	1.4261	0.4377	−6
0.0518	0.888304	1.4172	0.9446	−8
0.0997	0.883140	1.4016	1.9612	5
0.1503	0.877682	1.3850	2.8407	5
0.2075	0.871441	1.3660	3.6972	−1
0.2615	0.865395	1.3481	4.4869	−3
0.2999	0.861013	1.3353	5.0254	−3
0.3506	0.855152	1.3183	5.6543	−5
0.4018	0.849044	1.3013	6.3513	6
0.4506	0.843193	1.2849	6.8186	5
0.5024	0.836884	1.2673	7.2157	4
0.5504	0.831000	1.2509	7.4027	−4
0.5998	0.824805	1.2339	7.5541	−3
0.6503	0.818412	1.2164	7.5451	−2
0.6999	0.812067	1.1990	7.3514	0
0.7501	0.805627	1.1812	6.9161	0
0.8001	0.799219	1.1631	6.1867	−3
0.8500	0.792762	1.1449	5.2478	2
0.8999	0.786387	1.1262	3.8857	0
0.9500	0.779984	1.1072	2.2359	7
0.9747	0.776948	1.0976	1.1321	−2
1.0000	0.773780	1.0876	0.0000	0

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

Table 3
Experimental densities, volumes, calculated excess volumes, and deviations δV^{E} for the system cyclohexane + ethyl acrylate at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times10^{-2}$) (cm^3 mol^{-1})	V^{E} ($\times10$) (cm^3 mol^{-1})	δV^{E} ($\times10^3$) (cm^3 mol^{-1})
0.0000	0.915930	1.0931	0.0000	0
0.0346	0.910184	1.0939	1.0244	−15
0.0495	0.907569	1.0945	1.6435	−1
0.1011	0.899009	1.0957	3.1733	−3
0.1508	0.890976	1.0967	4.4183	−13
0.2010	0.882780	1.0978	5.7999	4
0.2510	0.874837	1.0986	6.9198	9
0.3007	0.867066	1.0994	7.8957	13
0.3511	0.859435	1.0997	8.5644	−2
0.4002	0.851990	1.1002	9.2506	1
0.4503	0.844589	1.1003	9.6937	−8
0.5013	0.837016	1.1006	10.1979	5
0.5499	0.830060	1.1004	10.3482	1
0.6004	0.822978	1.1001	10.2982	−5
0.6502	0.816124	1.0996	10.0663	−7
0.7001	0.809366	1.0990	9.6865	0
0.7502	0.802826	1.0980	8.9492	−2
0.8003	0.796443	1.0967	7.9819	4
0.8501	0.790408	1.0950	6.5705	−1
0.9002	0.784531	1.0931	4.8600	3
0.9501	0.778977	1.0906	2.6956	4
0.9745	0.776337	1.0893	1.5213	10
1.0000	0.773780	1.0876	0.0000	0

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

Table 4

Experimental densities, volumes, calculated excess volumes, and deviations δV^{E} for the system cyclohexane + methyl methacrylate at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$) (cm^3 mol^{-1})	V^{E} ($\times 10$) (cm^3 mol^{-1})	δV^{E} ($\times 10^3$) (cm^3 mol^{-1})
0.0000	0.937669	1.0678	0.0000	0
0.0256	0.932648	1.0691	0.0863	−8
0.0509	0.927635	1.0705	0.1776	−5
0.1016	0.917823	1.0732	0.3394	−8
0.1516	0.908268	1.0757	0.4913	−3
0.2014	0.898880	1.0781	0.6314	5
0.2511	0.889746	1.0802	0.7465	4
0.3006	0.880810	1.0822	0.8483	4
0.3505	0.871973	1.0840	0.9322	0
0.4003	0.863235	1.0858	1.0093	4
0.4505	0.854675	1.0873	1.0603	−1
0.5007	0.846194	1.0888	1.1038	4
0.5508	0.837993	1.0899	1.1144	−5
0.6005	0.829950	1.0909	1.1160	−1
0.6505	0.822075	1.0916	1.0908	−1
0.7004	0.814458	1.0920	1.0356	−5
0.7501	0.807040	1.0922	0.9570	−3
0.8001	0.799801	1.0921	0.8471	0
0.8504	0.792788	1.0917	0.7022	4
0.9002	0.786154	1.0908	0.5135	2
0.9511	0.779634	1.0895	0.2827	8
0.9746	0.776781	1.0887	0.1533	4
1.0000	0.773780	1.0876	0.0000	0

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

Table 5

Experimental densities, volumes, calculated excess volumes, and deviations δV^{E} for the system cyclohexane + styrene at 298.15 K

x_1	ρ (g cm^{-3})	V ($\times 10^{-2}$) (cm^3 mol^{-1})	V^{E} ($\times 10$) (cm^3 mol^{-1})	δV^{E} ($\times 10^3$) (cm^3 mol^{-1})
0.0000	0.901972	1.1547	0.0000	0
0.0263	0.898485	1.1533	0.3989	−5
0.0519	0.895001	1.1521	0.8864	1
0.1012	0.888418	1.1495	1.6343	−2
0.1513	0.881684	1.1470	2.4147	1
0.2016	0.874964	1.1443	3.1075	−1
0.2507	0.868389	1.1416	3.7448	−1
0.3009	0.861678	1.1389	4.3650	2
0.3511	0.855010	1.1360	4.8786	0
0.4004	0.848465	1.1332	5.3341	1
0.4502	0.841850	1.1303	5.7499	6
0.5000	0.835362	1.1271	5.9538	−2
0.5502	0.828796	1.1239	6.1249	−1
0.5998	0.822387	1.1206	6.1589	−3
0.6503	0.815883	1.1172	6.1014	1
0.6995	0.809669	1.1136	5.8339	−2
0.7499	0.803364	1.1098	5.4095	−2
0.8001	0.797167	1.1059	4.8219	0
0.8500	0.791114	1.1017	4.0154	2
0.8998	0.785216	1.0973	2.9581	2
0.9499	0.779403	1.0926	1.6385	3
0.9752	0.776561	1.0901	0.8324	0
1.0000	0.773780	1.0876	0.0000	0

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

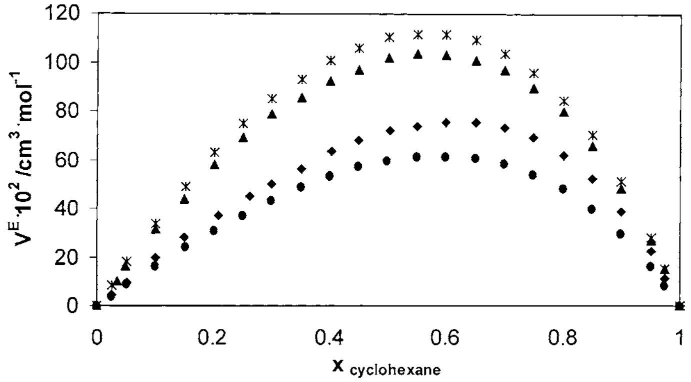

Fig. 1. Excess volumes at 298.15 K: (∗) cyclohexane + MMA; (▲) cyclohexane + EA; (◆) cyclohexane + BA; (●) cyclohexane + styrene.

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

$$V^{\mathrm{E}} = x_1x_2\sum_{k=0}^{n} a_kL_k(x_1) \tag{3}$$

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

$$V^{\mathrm{E}} = x_1x_2[a_0 + a_1(2x_1 - 1) + a_2(6x_1^2 - 6x_1 + 1)] \tag{4}$$

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

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

$$\mathrm{OF} = \sum_{1}^{N}(V_{i,\mathrm{exptl}}^{\mathrm{E}} - V_{i,\mathrm{calc}}^{\mathrm{E}})^2 \tag{5}$$

where N is the number of observations. The values of the different adjustable parameters, A_k and a_k, are reported in Tables 6 and 7 for different values of k, together with the pertinent statistics. The standard deviation s was calculated as:

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

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,

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

System	A_0	A_1	A_2	A_3	s ($\times 10^3$)	d[a]	$(\bar{V}^{\mathrm{E}})_{x=0.5}$ (cm^3 mol^{-1})	$\bar{V}_1^{\mathrm{E},\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{\mathrm{E},\infty}$ (cm^3 mol^{-1})
1 + 2	2.8635	1.3683	0.5620	–	4.4	1.73	0.7159	2.057	4.794
1 + 3	4.0555	1.1519	0.6155	–	7.2	1.66	1.014	3.519	5.823
1 + 4	4.399	1.088	0.5423	0.2501	3.0	2.29	1.100	3.603	6.280
1 + 5	2.388	0.8988	0.2372	–	2.3	2.04	0.597	1.726	3.524

[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})^2/\sum_{u=2}^{N}e_u^2$; where $e_u = V_{u,\mathrm{calc}}^{\mathrm{E}} - V_{u,\mathrm{exptl}}^{\mathrm{E}}$.

Table 7
Coefficients A_k (Eq. (3)), standard deviation s (Eq. (6)), Durbin–Watson statistic d, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K

System	a_0	a_1	a_2	a_3	s (10^3)	d^a	$(\bar{V}^E)_{x=0.5}$ (cm^3 mol^{-1})	$\bar{V}_1^{E,\infty}$ (cm^3 mol^{-1})	$\bar{V}_2^{E,\infty}$ (cm^3 mol^{-1})
1 + 2	3.051	1.3683	0.3746	–	4.6	1.73	0.7159	2.057	4.794
1 + 3	4.261	1.152	0.4103	–	7.4	1.66	1.01	3.5191	5.8228
1 + 4	5.580	2.439	0.3615	−0.1000	3.1	2.29	1.100	3.6030	6.2810
1 + 5	2.4670	0.8989	0.1581	–	2.4	2.04	0.597	1.7262	3.5239

[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})^2/\sum_{u=2}^{N}e_u^2$; where $e_u = V^E_{u,\mathrm{calc}} - V^E_{u,\mathrm{exptl}}$.

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 function 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], and can be calculated from the adjustable parameters as follows:

(a) Redlich–Kister

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

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

(b) Legendre

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

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

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 6 and 7. Eqs. (7) and (8) or Eqs. (9) and (10) yield the same values of $\bar{V}_i^{E,\infty}$.

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

Inspection of the results of Tables 2–5 and Fig. 1 indicates that the excess volumes for the binaries cyclohexane + (ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene) are positive for the whole composition range. As shown in Fig. 3, the results for the system cyclohexane + MMA obtained in this work are in excellent agreement with those of Sastri et al. [4]. The small difference may be attributed to the fact that Sastri 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 equipment used (pyknometer 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 asymmetric for the four binaries; the maximum specific interaction

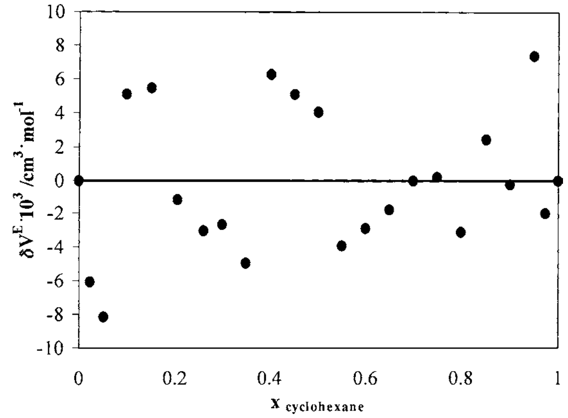

Fig. 2. Residual distribution plot for the system cyclohexane + BA according to the fit given in Table 6.

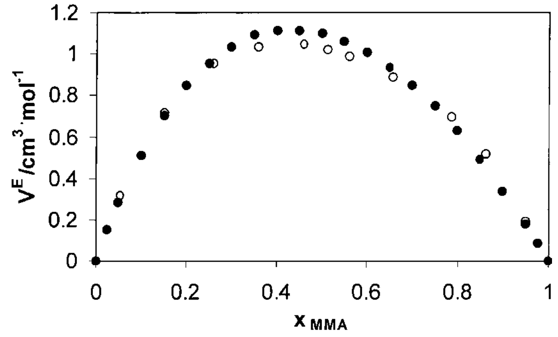

Fig. 3. Comparison of results for MMA + cyclohexane: (●) this work; (○) Sastry et al. [4].

deviating to the right of $x = 0.5$, indicating the presence of a very small amount of self association of the solute.

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 (originating from non-chemical or chemical interactions such as hydrogen bonding or complex forming interactions such as self-association) and (b) a negative one due to physical interactions (e.g. hetero-association) 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 sphericicity of the solute molecule and higher molar volume of the solvent.

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 maximum value of V^{E} ranging from about $+0.60$ to $+1.15$ cm^3/mol. As said, the V^{E} curves are positive, their relative intensity depending on the nature of the solute (monomer) and the solvent. In the case of the esters, the overall positive magnitude of V^{E} results from an intercalation effect of cyclohexane that breaks dipole–dipole associations. The n–π interactions between an aromatic hydrocarbon (such as benzene and styrene) and an ester are much stronger than those between a cyclic hydrocarbon (such as cyclohexane) and an aromatic. As shown in Fig. 1, the system cyclohexane + 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 cyclohexane.

Anyhow, it is clear that there is a substantial difference in cyclohexane dislocation between the esters and styrene. The value of $(V^{\mathrm{E}})_{x=0.5}$ for the latter is about one-half that of MMA.

The observed molar excess volumes exhibit an interesting dependence with respect to the structure of the unsaturated ester: their value increases as the length of the ester chain increases from methyl to butyl, signaling an increase of dislocation effect.

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