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# Volumetric Properties of 3-Methylbutyl Ethanoate with Ethyl Acrylate, Butyl Acrylate, Methyl Methacrylate, and Styrene at 25°C

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Densities of the binary systems of 3-methylbutyl ethanoate (*iso*amyl acetate) with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene have been measured as a function of composition at 25°C 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 binary systems of 3-methylbutyl ethanoate with each of the three acrylate monomers and negative for the system with styrene. The 3-methylbutyl ethanoate + butyl acrylate system exhibits near-ideal behavior.

**KEY WORDS:** acrylates; densities; 3-methylbutyl ethanoate; excess volumes; monomers; 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

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pressure, $V^{\mathrm{E}} = (\partial G^{\mathrm{E}}/\partial P)_{T,n}$, and the pertinent partial excess volume corresponds to the variation of the chemical potential with pressure, $\bar{V}_i^{\mathrm{E}} = (\partial \mu_i/\partial P)_{T,n}$.

This work is part of our program to provide data for the characterization of the molecular interactions between solvents and commercially important monomers, 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]. 3-Methylbutyl ethanoate (banana oil) 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 3-methylbutyl ethanoate with ethyl acrylate, butyl acrylate, methyl methacrylate, and styrene.

## 2. EXPERIMENTAL

### 2.1. Materials

3-Methylbutyl ethanoate, (*iso*amyl acetate, 99.34 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 prior 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 substantiated by comparing their densities at 25°C 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 with a stated uncertainty of $5 \times 10^{-6}\,\mathrm{g \cdot cm^{-3}}$. The temperature

**Table I.** Purities and Densities of Pure Components at 25°C

| | | Density (g·cm$^{-3}$) | |
|---|---|---|---|
| Component | Purity (mass%) | Meas. | Lit. |
| 3-Methyl butyl ethanoate (1) | 99.34 | 0.867356 | 0.86843[13] |
| Butyl acrylate (2) | 99.9 | 0.893947 | 0.8941[14] |
| Ethyl acrylate (3) | 99.8 | 0.916124 | 0.9163[14] |
| Methyl methacrylate (4) | 99.9 | 0.937628 | 0.93766[15] |
| Styrene (5) | 99.9 | 0.901941 | 0.9016 [16] |

in the cell was regulated to ±0.001 K with a solid-state thermostat. The apparatus was calibrated daily 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 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. The total uncertainty (ISO 9001) in the mole fraction is $7.98 \times 10^{-5}$; the precision of the density (duplicate) measurements is $\pm 2 \times 10^{-6}$ g·cm$^{-3}$, and that of the temperature is ±0.002 K. The total uncertainty in the density measurement, as reported by the equipment manufacturer, is $5 \times 10^{-6}$g·cm$^{-3}$ and includes the calibration procedure.

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 $\rho, \rho_1$, and $\rho_2$ 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 $\rho$ and $V^E$ are reported in Tables II to V and Fig. 1.

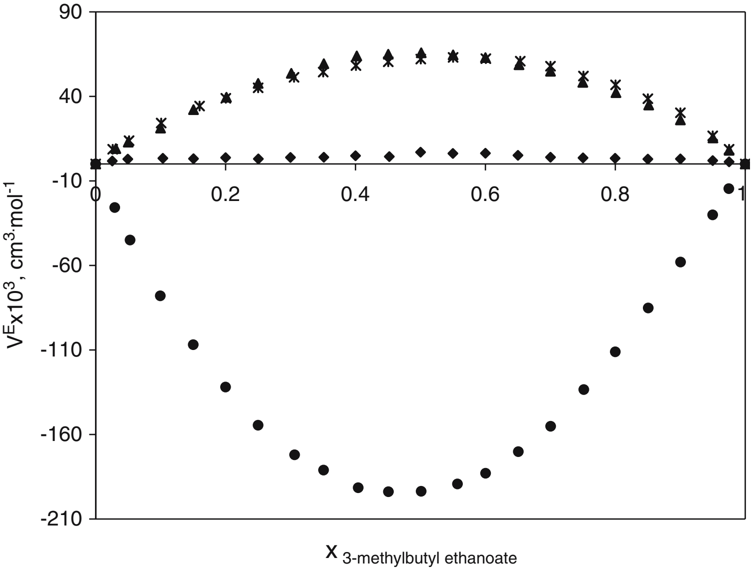

**Fig. 1.** Excess volumes at 298.15 K: *3-methylbutyl ethanoate + MMA; ▲3-methylbutyl ethanoate + EA; ◆ 3-methylbutyl ethanoate + BA; • 3-methylbutyl ethanoate + styrene.

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

Partial molar 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 $V^{\mathrm{E}}$ were correlated with composition using two methods.

(a) The Redlich–Kister expression [9],

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

**Table II.** Experimental Densities, Molar Volumes, Calculated Excess Volumes, and Deviations $\delta V^{\mathrm{E}}(\delta V^{\mathrm{E}} = V^{\mathrm{E}}_{\mathrm{expt}} - V^{\mathrm{E}}_{\mathrm{calc}})$ for the 3-Methylbutyl Ethanoate (1) + Butyl Acrylate (2) System at 25°C

| $x_1$ | $\rho$(g.cm$^3$) | $V$ (cm$^3$·mol$^{-1}$) | $10^3 V^{\mathrm{E}}$ (cm$^3$·mol$^{-1}$) | $10^3 \delta V^{\mathrm{E}}$ (cm$^3$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0.893947 | 143.3754 | 0 | 0 |
| 0.0257 | 0.893222 | 143.5498 | 1.7980 | −0.07 |
| 0.0496 | 0.892552 | 143.7117 | 2.8609 | −0.01 |
| 0.1035 | 0.891059 | 144.0747 | 3.4107 | −0.2 |
| 0.1504 | 0.889769 | 144.3902 | 3.1018 | −0.3 |
| 0.2000 | 0.888407 | 144.7243 | 3.7951 | 0.7 |
| 0.2504 | 0.887040 | 145.0619 | 2.9886 | −0.2 |
| 0.2999 | 0.885689 | 145.3963 | 3.9056 | 0.4 |
| 0.3512 | 0.884304 | 145.7411 | 4.0588 | −0.2 |
| 0.4001 | 0.882985 | 146.0706 | 4.8667 | −0.1 |
| 0.4521 | 0.881596 | 146.4200 | 4.3701 | −1 |
| 0.5000 | 0.880304 | 146.7448 | 7.0043 | 1 |
| 0.5500 | 0.878984 | 147.0800 | 6.2586 | 0.2 |
| 0.6000 | 0.877664 | 147.4163 | 6.3475 | 0.5 |
| 0.6500 | 0.876356 | 147.7517 | 5.1423 | −0.07 |
| 0.7003 | 0.875048 | 148.0886 | 4.0557 | −0.4 |
| 0.7502 | 0.873751 | 148.4238 | 3.6748 | −0.1 |
| 0.7998 | 0.872467 | 148.7571 | 3.3661 | 0.07 |
| 0.8500 | 0.871176 | 149.0938 | 2.8609 | −0.1 |
| 0.9000 | 0.869889 | 149.4306 | 3.0344 | 0.3 |
| 0.9500 | 0.868618 | 149.7654 | 1.9960 | −0.04 |
| 0.9752 | 0.867980 | 149.9342 | 1.2457 | −0.01 |
| 1 | 0.867356 | 150.0998 | 0 | 0 |

where the $A_k$'s 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 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. Nevertheless, 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.

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

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

**Table III.** Experimental Densities, Molar Volumes, Calculated Excess Volumes, and Deviations $\delta V^{\mathrm{E}} (\delta V^{\mathrm{E}} = V^{\mathrm{E}}_{\mathrm{expt}} - V^{\mathrm{E}}_{\mathrm{calc}})$ for the 3-Methylbutyl Ethanoate (1) + Ethyl Acrylate (3) System at 25°C

| $x_1$ | $\rho(\mathrm{g.cm}^3)$ | $V$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ | $10^3 V^{\mathrm{E}}$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ | $10^3 \delta V^{\mathrm{E}}$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ |
|---|---|---|---|---|
| 0 | 0.916124 | 109.2865 | 0 | 0 |
| 0.0310 | 0.913999 | 110.5591 | 9.0815 | 1 |
| 0.0501 | 0.912721 | 111.3458 | 12.982 | 0.6 |
| 0.0999 | 0.909503 | 113.3850 | 21.227 | −1 |
| 0.1505 | 0.906326 | 115.4620 | 32.155 | 0.4 |
| 0.2012 | 0.903286 | 117.5372 | 39.544 | −0.5 |
| 0.2501 | 0.900442 | 119.5430 | 47.669 | 0.4 |
| 0.3010 | 0.897604 | 121.6253 | 53.588 | −0.3 |
| 0.3512 | 0.894897 | 123.6805 | 59.359 | 0.2 |
| 0.4020 | 0.892257 | 125.7586 | 63.971 | 0.8 |
| 0.4505 | 0.889840 | 127.7396 | 64.963 | −0.4 |
| 0.5010 | 0.887406 | 129.7993 | 65.849 | −0.2 |
| 0.5502 | 0.885117 | 131.8082 | 64.610 | −0.5 |
| 0.6002 | 0.882870 | 133.8436 | 62.978 | 0.3 |
| 0.6518 | 0.880634 | 135.9458 | 58.693 | −0.2 |
| 0.7001 | 0.878602 | 137.9132 | 54.887 | 0.7 |
| 0.7499 | 0.876582 | 139.9402 | 48.348 | −0.3 |
| 0.8008 | 0.874573 | 142.0131 | 42.223 | 0.06 |
| 0.8514 | 0.872644 | 144.0689 | 34.915 | 0.1 |
| 0.9001 | 0.870846 | 146.0495 | 26.073 | −0.3 |
| 0.9503 | 0.869055 | 148.0862 | 15.408 | 0.2 |
| 0.9752 | 0.868197 | 149.0941 | 8.0672 | −0.2 |
| 1.0000 | 0.867356 | 150.0998 | 0 | 0 |

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

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

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 the 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

**Table IV.** Experimental Densities, Molar Volumes, Calculated Excess Volumes, and Deviations $\delta V^{\mathrm{E}}(\delta V^{\mathrm{E}} = V^{\mathrm{E}}_{\mathrm{expt}} - V^{\mathrm{E}}_{\mathrm{calc}})$ for the 3-Methylbutyl Ethanoate (1) + Methyl Methacrylate (3) System at 25°C

| $x_1$ | $\rho(\mathrm{g.cm}^3)$ | $V$ $(\mathrm{cm}^3{\cdot}\mathrm{mol}^{-1})$ | $10^3 V^{\mathrm{E}}$ $(\mathrm{cm}^3{\cdot}\mathrm{mol}^{-1})$ | $10^3 \delta V^{\mathrm{E}}$ $(\mathrm{cm}^3{\cdot}\mathrm{mol}^{-1})$ |
|---|---|---|---|---|
| 0 | 0.937628 | 106.7801 | 0 | 0 |
| 0.0263 | 0.934984 | 107.9270 | 8.7730 | 0.9 |
| 0.0515 | 0.932526 | 109.0251 | 13.848 | −0.4 |
| 0.1007 | 0.927871 | 111.1658 | 24.184 | −0.3 |
| 0.1599 | 0.922520 | 113.7398 | 34.245 | 0.3 |
| 0.2002 | 0.919025 | 115.4930 | 38.933 | −0.4 |
| 0.2500 | 0.914860 | 117.6532 | 45.038 | −0.05 |
| 0.3053 | 0.910408 | 120.0550 | 51.323 | 0.7 |
| 0.3502 | 0.906930 | 122.0072 | 54.399 | −0.2 |
| 0.4005 | 0.903170 | 124.1889 | 58.299 | 0.1 |
| 0.4504 | 0.899578 | 126.3530 | 60.478 | −0.4 |
| 0.5005 | 0.896102 | 128.5221 | 62.088 | −0.4 |
| 0.5502 | 0.892767 | 130.6765 | 63.107 | 0.1 |
| 0.6005 | 0.889513 | 132.8559 | 62.282 | −0.06 |
| 0.6538 | 0.886188 | 135.1613 | 60.822 | 0.6 |
| 0.7003 | 0.883384 | 137.1751 | 57.807 | 0.5 |
| 0.7508 | 0.880451 | 139.3563 | 51.983 | −0.7 |
| 0.8003 | 0.877660 | 141.4951 | 46.823 | −0.02 |
| 0.8500 | 0.874956 | 143.6425 | 38.641 | −0.6 |
| 0.9002 | 0.872311 | 145.8074 | 30.313 | 0.9 |
| 0.9499 | 0.869798 | 147.9472 | 16.689 | −0.1 |
| 0.9751 | 0.868558 | 149.0308 | 8.7091 | −0.2 |
| 1 | 0.867356 | 150.0998 | 0 | 0 |

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 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):

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

**Table V.** Experimental Densities, Molar Volumes, Calculated Excess Volumes, and Deviations $\delta V^{\mathrm{E}}(\delta V^{\mathrm{E}} = V^{\mathrm{E}}_{\mathrm{expt}} - V^{\mathrm{E}}_{\mathrm{calc}})$ for the 3-Methylbutyl Ethanoate (1) + Styrene (5) System at 25°C

| $x_1$ | $\rho$(g.cm$^3$) | $V$ (cm$^3$·mol$^{-1}$) | $10^3 V^{\mathrm{E}}$ (cm$^3$·mol$^{-1}$) | $10^3 \delta V^{\mathrm{E}}$ (cm$^3$·mol$^{-1}$) |
|---|---|---|---|---|
| 0 | 0.901941 | 115.473 | 0 | 0 |
| 0.0293 | 0.900833 | 116.463 | −25.761 | −0.2 |
| 0.0529 | 0.899946 | 117.260 | −45.044 | −0.7 |
| 0.0997 | 0.898180 | 118.846 | −78.029 | −0.5 |
| 0.1502 | 0.896274 | 120.567 | −106.88 | 1 |
| 0.2000 | 0.894422 | 122.267 | −131.90 | 1 |
| 0.2502 | 0.892590 | 123.982 | −154.58 | −1 |
| 0.3064 | 0.890541 | 125.910 | −172.01 | −0.6 |
| 0.3509 | 0.888929 | 127.443 | −181.05 | 1 |
| 0.4042 | 0.887046 | 129.278 | −191.52 | −1 |
| 0.4508 | 0.885398 | 130.888 | −193.81 | 0.4 |
| 0.5011 | 0.883646 | 132.629 | −193.59 | 0.7 |
| 0.5571 | 0.881719 | 134.575 | −189.32 | 0.1 |
| 0.6002 | 0.880257 | 136.072 | −182.94 | −0.6 |
| 0.6507 | 0.878546 | 137.836 | −170.13 | −0.03 |
| 0.7003 | 0.876895 | 139.568 | −155.21 | −1 |
| 0.7514 | 0.875198 | 141.358 | −133.45 | 0.7 |
| 0.7999 | 0.873614 | 143.061 | −111.05 | 0.7 |
| 0.8507 | 0.871983 | 144.845 | −85.237 | 0.3 |
| 0.9005 | 0.870410 | 146.597 | −58.076 | −0.3 |
| 0.9499 | 0.868881 | 148.334 | −30.045 | −1 |
| 0.9747 | 0.868119 | 149.208 | −14.568 | 0.06 |
| 1 | 0.867356 | 150.100 | 0 | 0 |

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

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

where $k$ is the number of adjustable parameters. The statistical significance of adding one or more terms after the third was examined using a $\chi^2$-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

**Table VI.** Partial Molar Volumes $\bar{V}_i$, in $cm^3 \cdot mol^{-1}$

| | 3-Methylbutyl ethanoate (1)+ BA (2) | | 3-Methylbutyl ethanoate (1)+ EA (3) | | 3-Methylbutyl ethanoate (1)+ MMA (4) | | 3-Methylbutyl ethanoate (1)+ St (5) | |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | $\bar{V}_2$ | $\bar{V}_1$ | $\bar{V}_3$ | $\bar{V}_1$ | $\bar{V}_4$ | $\bar{V}_1$ | $\bar{V}_5$ | $\bar{V}_1$ |
| 0 | 143.375 | 150.192 | 109.287 | 150.376 | 106.780 | 150.425 | 115.473 | 149.187 |
| 0.05 | 143.377 | 150.131 | 109.288 | 150.323 | 106.782 | 150.340 | 115.470 | 149.322 |
| 0.10 | 143.379 | 150.105 | 109.290 | 150.295 | 106.786 | 150.289 | 115.461 | 149.433 |
| 0.15 | 143.381 | 150.099 | 109.294 | 150.279 | 106.792 | 150.259 | 115.448 | 149.525 |
| 0.20 | 143.383 | 150.104 | 109.300 | 150.269 | 106.798 | 150.242 | 115.431 | 149.603 |
| 0.25 | 143.386 | 150.115 | 109.309 | 150.262 | 106.805 | 150.234 | 115.412 | 149.671 |
| 0.30 | 143.392 | 150.128 | 109.324 | 150.257 | 106.815 | 150.230 | 115.389 | 149.731 |
| 0.35 | 143.402 | 150.142 | 109.346 | 150.252 | 106.829 | 150.229 | 115.362 | 149.786 |
| 0.40 | 143.416 | 150.156 | 109.374 | 150.250 | 106.847 | 150.229 | 115.332 | 149.836 |
| 0.45 | 143.434 | 150.170 | 109.407 | 150.251 | 106.868 | 150.232 | 115.298 | 149.882 |
| 0.50 | 143.455 | 150.184 | 109.444 | 150.255 | 106.893 | 150.235 | 115.260 | 149.925 |
| 0.55 | 143.476 | 150.198 | 109.481 | 150.260 | 106.919 | 150.237 | 115.217 | 149.963 |
| 0.60 | 143.494 | 150.209 | 109.514 | 150.265 | 106.944 | 150.239 | 115.170 | 149.998 |
| 0.65 | 143.506 | 150.217 | 109.540 | 150.267 | 106.967 | 150.237 | 115.121 | 150.028 |
| 0.70 | 143.509 | 150.219 | 109.555 | 150.264 | 106.987 | 150.230 | 115.069 | 150.053 |
| 0.75 | 143.501 | 150.213 | 109.558 | 150.251 | 107.001 | 150.217 | 115.018 | 150.072 |
| 0.80 | 143.481 | 150.197 | 109.550 | 150.228 | 107.011 | 150.197 | 114.970 | 150.086 |
| 0.85 | 143.453 | 150.172 | 109.538 | 150.195 | 107.022 | 150.170 | 114.929 | 150.095 |
| 0.90 | 143.425 | 150.142 | 109.534 | 150.155 | 107.042 | 150.140 | 114.900 | 150.099 |
| 0.95 | 143.413 | 150.114 | 109.561 | 150.118 | 107.083 | 150.112 | 114.888 | 150.100 |
| 1 | 143.438 | 150.100 | 109.650 | 150.100 | 107.167 | 150.100 | 114.902 | 150.100 |

**Table VII.** Coefficients $A_k$ (Eq. (4)), Standard Deviation $s$ (Eq.(8)), Durbin–Watson Statistic $d$, and $(V^{\mathrm{E}})_{x=0.5}$ and $\bar{V}_i^{\mathrm{E},\infty}$ at 25°C

| System | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $s \times 10^4$ | $d^a$ | $10^2(V^{\mathrm{E}})_{x=0.5}$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ | $10^2\bar{V}_1^{\mathrm{E},\infty}$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ | $10^2\bar{V}_2^{\mathrm{E},\infty}$ $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 + 2 | 0.024 | 0.0095 | −0.0479 | −0.024 | 0.101 | 4.85 | 2.62 | 0.60 | 9.20 | 6.31 |
| 1 + 3 | 0.264 | −0.0046 | −0.0646 | 0.481 | 0.120 | 6.04 | 2.60 | 6.60 | 27.60 | 36.31 |
| 1 + 4 | 0.250 | 0.0446 | 0.0244 | −0.014 | 0.081 | 5.13 | 2.58 | 6.25 | 32.51 | 38.65 |
| 1 + 5 | −0.777 | 0.0760 | 0.0354 | 0.095 |  | 7.59 | 2.16 | −19.43 | −91.25 | −57.10 |

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

**Table VIII.** Coefficients $a_k$ (Eq. (5)), Standard Deviation $s$ (Eq. (8)), Durbin–Watson Statistic $d$, and $(V^{\mathrm{E}})_{x=0.5}$ and $\bar{V}_i^{\mathrm{E},\infty}$ at 25°C

| System | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $s \times 10^4$ | $d^a$ | $10^2(\bar{V}^{\mathrm{E}})_{x=0.5}$ ($\mathrm{cm^3 \cdot mol^{-1}}$) | $10^2\bar{V}_1^{\mathrm{E},\infty}$ ($\mathrm{cm^3 \cdot mol^{-1}}$) | $10^2\bar{V}_2^{\mathrm{E},\infty}$ ($\mathrm{cm^3 \cdot mol^{-1}}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 + 2 | 0.0285 | −0.00487 | 0.02590 | −0.00957 | 0.0231 | 5.00 | 2.62 | 0.60 | 9.196 | 6.307 |
| 1 + 3 | 0.2667 | 0.02427 | 0.02539 | 0.01926 | 0.0274 | 6.2 | 2.60 | 6.61 | 0.276 | 0.363 |
| 1 + 4 | 0.2743 | 0.03626 | 0.06283 | −0.00555 | 0.0186 | 5.29 | 2.58 | 6.25 | 0.325 | 0.386 |
| 1 + 5 | −0.7654 | 0.13284 | 0.02360 | 0.03789 |  | 7.81 | 2.16 | −19.40 | −0.912 | −0.571 |

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

to experimental errors, particularly in the dilute ranges and is helpful for detecting outliers. In addition, its values at infinite dilution represent the values of the partial excess volume at infinite dilution, $\bar{V}_i^{\mathrm{E},\infty}$, 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 $\bar{V}_i^{\mathrm{E},\infty}$ 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 $\bar{V}_i^{\mathrm{E},\infty}$. 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 to V and Fig. 1 indicates that the excess volumes are positive for the binaries of 3-methylbutyl ethanoate (1) with butyl acrylate (2), ethyl acrylate (3), and methyl methacrylate (4), and negative for the binary with styrene (5). The magnitude and sign of $V^{\mathrm{E}}$ 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 and maximum values of $V^E$ ranging from about $-0.194$ to $+0.066\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. With regard to the symmetry of the excess function, Fig. 1 shows that the function $V^{\mathrm{E}}(x)$ is essentially symmetric for all the systems, indicating that the maximum specific interaction occurs at about the equimolar composition.

As shown in Fig. 1, the mixture of 3-methylbutyl ethanoate and styrene presents a relative large contraction effect. This behavior 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. $n$–$\pi$ interactions between an aromatic hydrocarbon (such as styrene)

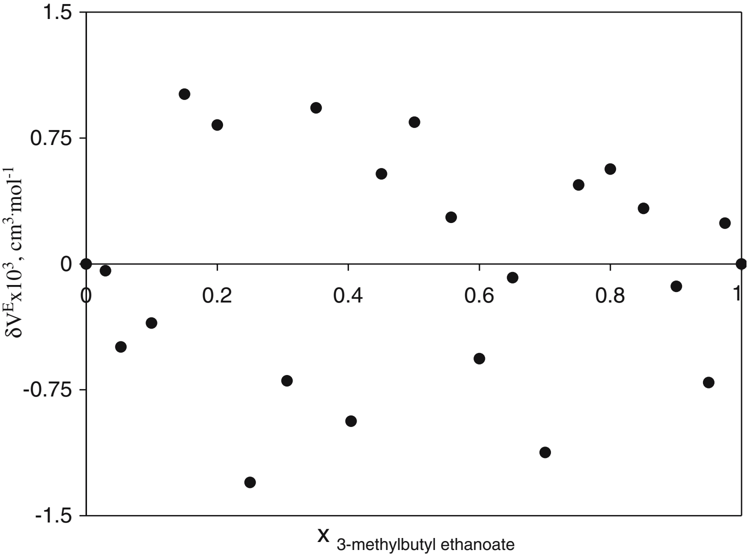

**Fig. 2.** Residual distribution plot for the 3-methylbutyl ethanoate + styrene system, according to the fit given in Table V.

and an ester are much stronger than those between a cyclic hydrocarbon (such as cyclohexane) and an ester. The negative sign indicates a net packing effect contributed by structural effects arising from interstitial accommodation.

The $V^E$ curves are either positive or negative, the relative intensity depending on the nature of the solute (monomer) and the solvent. The overall positive magnitude of $V^E$ for the systems with an acrylate monomer is the result of the breaking and dislocation of the ester's dipole–dipole association. In addition, the observed positive molar excess volumes point to their dependence with respect to the structure of the unsaturated ester: their values increase as the length of the ester chain decreases from ethyl to butyl, signaling a decrease of the contribution of interstitial accommodation and an increase of steric interference.

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