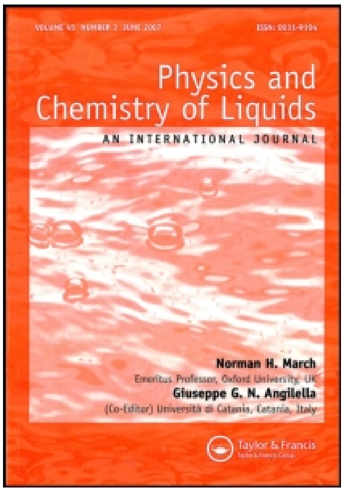

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# Density and other thermodynamic properties of the binary systems of tetrahydrofuran + ethenyl ethanoate, methacrylic acid, butyl methacrylate, and allyl methacrylate at 298.15 K

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# Density and other thermodynamic properties of the binary systems of tetrahydrofuran + ethenyl ethanoate, methacrylic acid, butyl methacrylate, and allyl methacrylate at 298.15 K

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Densities of the binary systems of tetrahydrofuran (THF) with ethenyl ethanoate (vinyl acetate), methacrylic acid, butyl methacrylate, and allyl methacrylate 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 negative for the three binaries methacrylic acid + tetrahydrofuran, butyl methacrylate + tetrahydrofuran, and allyl methacrylate + tetrahydrofuran, and become smaller as the solute becomes more branched or longer. Methacrylic acid exhibits substantially larger negative excess volumes probably due to hydrogen bonding with the solvent. The system tetrahydrofuran + vinyl acetate presents near ideal behavior.

*Keywords*: Densities; Excess volumes; Methacrylates; Tetrahydrofuran; Vinyl acetate

## 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 or residual extensive 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 pressure, $V^E = (\partial G^E/\partial P)_{T,n}$, the pertinent partial excess volume corresponds to

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the variation of the chemical potential with pressure, $\bar{V}_i^E = (\partial \mu_i / \partial P)_{T,n}$. Changes in temperature and solvent cause conformational changes in polymeric systems that have side groups like the methacrylates studied here.

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 acrylic monomers with cyclic hydrocarbons [1], aromatic solvents [2–4], and aliphatic and cyclic ethers [5–7]. Tetrahydrofuran (THF) is an excellent aprotic solvent, soluble in all proportions with water, alcohols, ethers, and all common solvents; it dissolves practically all plastics except certain polyamides, and may be useful in polymerization and other chemical reactions, in the cleaning of polymer surfaces, electronic materials, etc. Structurally THF may be considered the homomorph of cyclopentane, aprotic, and almost nonpolar. Interactions between a polar component and such ether are considered to occur via complex formation between the two species, or n–$\pi$ interaction [8]. The monomers considered in this study are important industrial chemicals used in the large-scale preparation of useful polymers and are also interesting because they contain both a double bond and an ester group. Methacrylic acid is a weak acid ($pK_s = 4.43$ at 298.15 K), similar to acetic acid ($pK_s = 4.76$ at 298.15 K), capable of acting as an acceptor or donor in hydrogen bonding. As reported by Eck and Maurer [9], in the liquid state the acid is assumed to exist only as a dimer.

Peralta *et al.* [7] determined the excess volumes of the system of THF with ethyl acrylate, butyl acrylate, and methyl methacrylate at 298.15 K and atmospheric pressure, and found that they are negative for all the systems studied. The system THF + methyl methacrylate behaved almost ideally. The values of the observed molar excess volumes increased as the length of the ester chain increased from methyl to butyl, signaling an increase of the contribution of the interstitial accommodation.

To the best of our knowledge no literature data are available for the excess volumes of the systems reported here.

## 2. Experimental

### 2.1. *Materials*

Tetrahydrofuran, THF (HPLC grade, mass fraction 0.9999), butyl methacrylate, BM (0.995 mass fraction, stabilized with 10 ppm of monomethyl ether of hydroquinone), methacrylic acid, MA (0.999 mass fraction, stabilized with 100–250 ppm of hydroquinone), allyl methacrylate, AMA (0.9989 mass fraction, stabilized with 50–185 ppm of monomethyl ether of hydroquinone), and vinyl acetate, VA (0.999 mass fraction, stabilized with 3–5 ppm of hydroquinone), were purchased from Aldrich. The supplier certified the purity of all the reagents by GC analysis. BM, AMA, MA, and VA were vacuum distilled prior to use to eliminate the stabilizer. 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.

| Components | Purity (mass fraction) | Density/g cm$^{-3}$ |  |
|---|---|---|---|
|  |  | Measured | Literature |
| Tetrahydrofuran (**1**) | 0.9999 | 0.882042 | 0.88193 [16] |
| Butyl methacrylate (**2**) | 0.995 | 0.890438 | 0.891 [17]<br>0.8909 [18] |
| Allyl methacrylate (**3**) | 0.9989 | 0.927997 | 0.9287 [19] |
| Methacrylic acid (**4**) | 0.999 | 1.00913 | 1.012 [18] |
| Ethenyl ethanoate (**5**) | 0.999 | 0.925775 | 0.92567 [19] |

### 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 a stated accuracy of $5 \times 10^{-6}$ g cm$^{-3}$. The temperature in the cell was regulated to $\pm 0.001$ 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 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 $9.86 \times 10^{-5}$; precision of the density (duplicate) measurement $\pm 2 \times 10^{-6}$ g cm$^{-3}$, and of the temperature $\pm 0.002$ 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 twenty-one density measurements were performed (with repetition) for each binary system over the full concentration range ($0 \leq x \leq 1$).

The excess molar volumes $V^E$ of the solutions of molar composition $x_i$ were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = [x_1 M_1 + (1 - x_1) M_2]/\rho - [x_1 M_1/\rho_1 + (1 - x_1) M_2/\rho_2] \tag{1}$$

where $\rho$, $\rho_1$, and $\rho_2$ are the densities of the solution and pure components 1 and 2 in g cm$^{-3}$, respectively, and $M_1$ and $M_2$ are the molar masses of the pure components in g mol$^{-1}$. The corresponding values of $\rho$, $\rho_1$, $\rho_2$, and $V^E$ are reported in tables 2 to 5 and figure 1.

The first term in equation (1) represents the actual molar volume of the solution and the second, the molar volume it would occupy if the mixture behaved ideally. In general, while these two molar volumes are similar in size (usually larger

Table 2. Experimental densities, molar volumes, calculated excess molar volumes, and deviations $\delta V^E$ for the system tetrahydrofuran (**1**) + butyl methacrylate (**2**) at 298.15 K.

| $x_1$ | $\rho/\mathrm{g\,cm^{-3}}$ | $V/^{\mathrm{a}}$ | $10^3/V^{E\,\mathrm{a}}$ | $10^3/\delta V^{E\,\mathrm{b}}$ |
|---|---|---|---|---|
| 0 | 0.890438 | 159.697 | 0 | 0 |
| 0.0255 | 0.890356 | 157.700 | −5.16957 | 0.02 |
| 0.0498 | 0.890280 | 155.806 | −10.7231 | −1 |
| 0.1005 | 0.890090 | 151.842 | −18.1641 | 1 |
| 0.1497 | 0.889908 | 147.997 | −27.3458 | 0.04 |
| 0.2013 | 0.889695 | 143.968 | −35.0812 | 0.4 |
| 0.2521 | 0.889480 | 140.004 | −43.7049 | −1 |
| 0.3004 | 0.889247 | 136.234 | −49.3345 | −0.3 |
| 0.3497 | 0.888993 | 132.383 | −54.7590 | −0.2 |
| 0.4007 | 0.888706 | 128.405 | −59.1342 | 0.3 |
| 0.4500 | 0.888402 | 124.564 | −62.0354 | 1 |
| 0.5013 | 0.888068 | 120.562 | −65.5090 | 0.3 |
| 0.5506 | 0.887717 | 116.716 | −67.7466 | −0.5 |
| 0.6003 | 0.887322 | 112.841 | −67.8519 | −0.3 |
| 0.6502 | 0.886890 | 108.949 | −67.1207 | −1 |
| 0.7000 | 0.886408 | 105.072 | −64.0580 | 0.1 |
| 0.7503 | 0.885874 | 101.157 | −59.8731 | 0.3 |
| 0.8000 | 0.885293 | 97.2887 | −54.5363 | −0.2 |
| 0.8502 | 0.884623 | 93.3864 | −45.5002 | 1 |
| 0.8999 | 0.883886 | 89.5225 | −34.9561 | 0.2 |
| 0.9499 | 0.883040 | 85.6389 | −20.7161 | −0.5 |
| 0.9752 | 0.882563 | 83.6737 | −11.7449 | −1 |
| 1 | 0.882042 | 81.7535 | 0 | 0 |

[a] Units: $\mathrm{cm^3\,mol^{-1}}$.
[b] $\delta V^E = V^E_{\mathrm{expt}} - V^E_{\mathrm{calc}}$.

Table 3. Experimental densities, molar volumes, calculated excess molar volumes, and deviations $\delta V^E$ for the system tetrahydrofuran (**1**) + allyl methacrylate (**3**) at 298.15 K.

| $x_1$ | $\rho/\mathrm{g\,cm^{-3}}$ | $V/^{\mathrm{a}}$ | $10^3/V^{E\,\mathrm{a}}$ | $10^3/\delta V^{E\,\mathrm{b}}$ |
|---|---|---|---|---|
| 0 | 0.927997 | 135.949 | 0 | 0 |
| 0.0250 | 0.927376 | 134.583 | −11.111 | 1 |
| 0.0501 | 0.926735 | 133.211 | −21.741 | 1 |
| 0.0997 | 0.925421 | 130.503 | −41.415 | 1 |
| 0.1501 | 0.924020 | 127.751 | −60.354 | −0.1 |
| 0.1999 | 0.922573 | 125.035 | −78.602 | −2 |
| 0.2499 | 930129.0 | 122.310 | −94.709 | −3 |
| 0.2999 | 0.919371 | 119.593 | −102.49 | 3 |
| 0.3500 | 0.917670 | 116.863 | −116.54 | 1 |
| 0.3999 | 0.915866 | 114.152 | −126.56 | 1 |
| 0.4494 | 0.913964 | 111.458 | −134.01 | 1 |
| 0.4999 | 0.911926 | 108.714 | −141.21 | −1 |
| 0.5502 | 0.909743 | 105.989 | −142.57 | 0.1 |
| 0.5988 | 0.907524 | 103.351 | −144.28 | −2 |
| 0.6493 | 0.905043 | 100.621 | −139.79 | −0.4 |
| 0.6999 | 0.902395 | 97.8855 | −132.95 | 1 |
| 0.7501 | 0.899609 | 95.1709 | −125.47 | −1 |
| 0.7999 | 0.896624 | 92.4878 | −111.52 | 1 |
| 0.8500 | 0.893441 | 89.7854 | −97.824 | −1 |
| 0.8999 | 0.889939 | 87.1103 | −70.578 | 4 |
| 0.9492 | 0.886252 | 84.4643 | −43.216 | 1 |
| 0.9748 | 0.884270 | 83.0858 | −31.612 | −8 |
| 1 | 0.882042 | 81.7535 | 0 | 0 |

[a] Units: $\mathrm{cm^3\,mol^{-1}}$.
[b] $\delta V^E = V^E_{\mathrm{expt}} - V^E_{\mathrm{calc}}$.

Table 4. Experimental densities, molar volumes, calculated excess molar volumes, and deviations $\delta V^E$ for the system tetrahydrofuran (**1**) + methacrylic acid (**4**) at 298.15 K.

| $x_1$ | $\rho/\mathrm{g\,cm^{-3}}$ | $V/^{\mathrm{a}}$ | $10^3/V^{E\,\mathrm{a}}$ | $10^3/\delta V^{E\,\mathrm{b}}$ |
|---|---|---|---|---|
| 0 | 1.009127 | 85.3114 | 0 | 0 |
| 0.0259 | 1.006701 | 85.1573 | −61.9170 | −2 |
| 0.0521 | 1.004145 | 85.0095 | −116.541 | 3 |
| 0.0995 | 0.999620 | 84.7314 | −225.995 | −3 |
| 0.1501 | 0.994623 | 84.4463 | −331.203 | −1 |
| 0.2003 | 0.989553 | 84.1688 | −429.802 | 1 |
| 0.2505 | 0.984402 | 83.8961 | −523.891 | 1 |
| 0.3006 | 0.979146 | 83.6310 | −610.721 | 1 |
| 0.3605 | 0.972643 | 83.3299 | −698.822 | 2 |
| 0.4006 | 0.968202 | 83.1331 | −753.009 | −2 |
| 0.4501 | 0.962457 | 82.9103 | −799.621 | 0.3 |
| 0.5005 | 0.956417 | 82.6974 | −833.312 | −0.3 |
| 0.5503 | 0.950212 | 82.5050 | −848.574 | −2 |
| 0.6003 | 0.943682 | 82.3347 | −840.879 | −1 |
| 0.6500 | 0.936926 | 82.1864 | −812.264 | −0.5 |
| 0.7002 | 0.929798 | 82.0614 | −758.571 | 1 |
| 0.7502 | 0.922454 | 81.9584 | −684.007 | 0.4 |
| 0.7999 | 0.914839 | 81.8798 | −585.477 | 1 |
| 0.8503 | 0.906868 | 81.8229 | −463.094 | 2 |
| 0.8999 | 0.898835 | 81.7832 | −326.510 | −1 |
| 0.9499 | 0.890539 | 81.7606 | −171.271 | −2 |
| 0.9750 | 0.886321 | 81.7531 | −89.3507 | −4 |
| 1 | 0.882042 | 81.7535 | 0 | 0 |

[a] Units: $\mathrm{cm^3\,mol^{-1}}$.
[b] $\delta V^E = V^E_{\mathrm{expt}} - V^E_{\mathrm{calc}}$.

Table 5. Experimental densities, molar volumes, calculated excess molar volumes, and deviations $\delta V^E$ for the system tetrahydrofuran (**1**) + vinyl acetate (**5**)* at 298.15 K.

| $x_1$ | $\rho/\mathrm{g\,cm^{-3}}$ | $V/^{\mathrm{a}}$ | $10^3/V^{E\,\mathrm{a}}$ | $10^3\delta V^{E\,\mathrm{b}}$ |
|---|---|---|---|---|
| 0 | 0.925775 | 92.99236 | 0 | 0 |
| 0.0255 | 0.924783 | 92.70693 | 0.93750 | −0.2 |
| 0.0576 | 0.923515 | 92.34730 | 2.8125 | 0.1 |
| 0.0999 | 0.921834 | 91.87461 | 5.2249 | 0.3 |
| 0.1499 | 0.919835 | 91.31448 | 6.9466 | −0.4 |
| 0.2007 | 0.917772 | 90.74647 | 9.4690 | 0.1 |
| 0.2497 | 0.915769 | 90.19676 | 10.589 | −0.2 |
| 0.3013 | 0.913631 | 89.61821 | 12.006 | 0.5 |
| 0.3506 | 0.911581 | 89.06372 | 11.568 | −0.1 |
| 0.4004 | 0.909487 | 88.50292 | 10.734 | −0.3 |
| 0.4526 | 0.907266 | 87.91569 | 9.8371 | −0.1 |
| 0.5001 | 0.905222 | 87.37975 | 8.3824 | 0.1 |
| 0.5507 | 0.903027 | 86.81000 | 6.4435 | 0.3 |
| 0.6002 | 0.900852 | 86.25011 | 3.8272 | 0.2 |
| 0.6502 | 0.898638 | 85.68613 | 0.80393 | 0.1 |
| 0.7009 | 0.896369 | 85.11189 | −3.3295 | −0.9 |
| 0.7501 | 0.894122 | 84.55681 | −5.6670 | −0.2 |
| 0.8002 | 0.891799 | 83.99175 | −7.7018 | 0.4 |
| 0.8500 | 0.889454 | 83.43057 | −9.2635 | 0.6 |
| 0.9005 | 0.887030 | 82.86209 | −9.7753 | 0.05 |
| 0.9502 | 0.884584 | 82.30493 | −7.7768 | −0.8 |
| 0.9749 | 0.883328 | 82.03100 | −4.0756 | 0.1 |
| 1 | 0.882042 | 81.75348 | 0 | 0 |

[a] Units: $\mathrm{cm^3\,mol^{-1}}$.
[b] $\delta V^E = V^E_{\mathrm{expt}} - V^E_{\mathrm{calc}}$.
*This system is considered ideal.

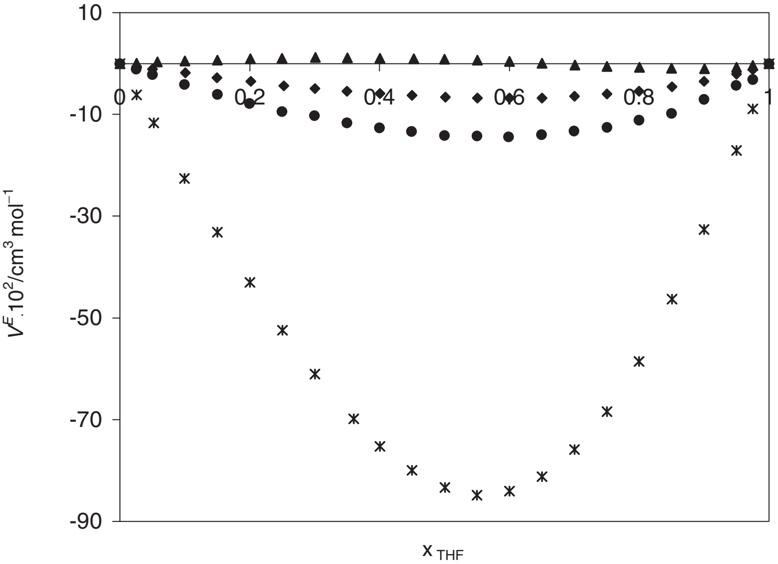

Figure 1. Excess molar volumes at 298.15 K: × THF + methacrylic acid; ▲ THF + vinyl acetate; ◆ THF + butyl methacrylate; ● THF + allyl methacrylate.

than 100 cm$^3$ mol$^{-1}$) their difference is usually smaller by two to three orders of magnitude and thus may carry a significantly larger error.

Partial molar volumes were calculated using the relations [10]:

$$\bar{V}_1 = V + x_2 \frac{dV}{dx_1} \tag{2}$$

$$\bar{V}_2 = V - x_1 \frac{dV}{dx_1} \tag{3}$$

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

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

(a) The Redlich–Kister expression [11]

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

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

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 molar volumes and excess enthalpies of mixing. Notwithstanding, it suffers from the important drawback that the values of

Table 6. Partial molar volumes $\bar{V}_i$, cm$^{-3}$mol$^{-1}$.

| | THF (**1**) + MB (**2**) | | THF (**1**) + MA (**3**) | | THF (**1**) + AM (**4**) | | THF (**1**) + VA (**5**)[a] | |
|---|---|---|---|---|---|---|---|---|
| $x_1$ | $\bar{V}_1$ | $\bar{V}_2$ | $\bar{V}_1$ | $\bar{V}_3$ | $\bar{V}_1$ | $\bar{V}_4$ | $\bar{V}_1$ | $\bar{V}_5$ |
| 0 | 81.56458 | 159.6967 | 81.26334 | 135.9487 | 79.41190 | 85.31136 | 81.79203 | 92.99236 |
| 0.05 | 81.56551 | 159.6966 | 81.31814 | 135.9473 | 79.50773 | 85.30898 | 81.80430 | 92.99210 |
| 0.10 | 81.57214 | 159.6961 | 81.36310 | 135.9437 | 79.58990 | 85.30233 | 81.80495 | 92.99195 |
| 0.15 | 81.58238 | 159.6946 | 81.40029 | 135.9384 | 79.67251 | 85.29047 | 81.79869 | 92.99229 |
| 0.20 | 81.59464 | 159.6920 | 81.43150 | 135.9318 | 79.76543 | 85.27063 | 81.78854 | 92.99297 |
| 0.25 | 81.60775 | 159.6882 | 81.45836 | 135.9241 | 79.87482 | 85.23870 | 81.77634 | 92.99355 |
| 0.30 | 81.62089 | 159.6832 | 81.48223 | 135.9150 | 80.00355 | 85.18964 | 81.76304 | 92.99353 |
| 0.35 | 81.63357 | 159.6771 | 81.50428 | 135.9044 | 80.15171 | 85.11803 | 81.74915 | 92.99257 |
| 0.40 | 81.64554 | 159.6699 | 81.52545 | 135.8917 | 80.31708 | 85.01850 | 81.73496 | 92.99052 |
| 0.45 | 81.65674 | 159.6616 | 81.54647 | 135.8761 | 80.49561 | 84.88622 | 81.72077 | 92.98757 |
| 0.50 | 81.66730 | 159.6520 | 81.56783 | 135.8567 | 80.68187 | 84.71736 | 81.70710 | 92.98416 |
| 0.55 | 81.67739 | 159.6409 | 81.58982 | 135.8324 | 80.86955 | 84.50959 | 81.69471 | 92.98094 |
| 0.60 | 81.68724 | 159.6275 | 81.61250 | 135.8016 | 81.05194 | 84.26254 | 81.68465 | 92.97860 |
| 0.65 | 81.69706 | 159.6111 | 81.63571 | 135.7628 | 81.22236 | 83.97828 | 81.67817 | 92.97761 |
| 0.70 | 81.70700 | 159.5904 | 81.65907 | 135.7142 | 81.37471 | 83.66177 | 81.67655 | 92.97786 |
| 0.75 | 81.71705 | 159.5638 | 81.68199 | 135.6536 | 81.50385 | 83.32139 | 81.68082 | 92.97826 |
| 0.80 | 81.72705 | 159.5292 | 81.70363 | 135.5788 | 81.60619 | 82.96936 | 81.69139 | 92.97619 |
| 0.85 | 81.73657 | 159.4840 | 81.72297 | 135.4872 | 81.68004 | 82.62224 | 81.70759 | 92.96682 |
| 0.90 | 81.74492 | 159.4251 | 81.73875 | 135.3762 | 81.72618 | 82.30140 | 81.72706 | 92.94237 |
| 0.95 | 81.75104 | 159.3487 | 81.74948 | 135.2428 | 81.74830 | 82.03351 | 81.74503 | 92.89119 |
| 1 | 81.75348 | 159.2503 | 81.75348 | 135.0839 | 81.75348 | 81.85098 | 81.75348 | 92.79681 |

[a] The system THF (**1**) + vinyl acetate (**5**) is considered ideal.

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 $L_k(x_1)$

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

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

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

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 its coefficients, its value remains constant. For the case of discrete measurements, such as determination of molar 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 has 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 [12,13] 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

Table 7. Coefficients $A_k$ (equation (2)), standard deviation $s$ (equation (5)), Durbin–Watson statistic $d$, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K.

| System* | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $s10^4$ | $d^a$ | $10^2\,(V^E)_{x=0.5}{}^b$ | $10^2\bar{V}_1^{E,\infty b}$ | $10^2\bar{V}_2^{E,\infty b}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 + 2 | −0.263 | −0.0830 | −0.0320 | −0.0457 | −0.043 | 6.302 | 1.87 | −6.575 | −20.89 | −46.65 |
| 1 + 3 | −0.561 | −0.1508 | −0.0229 | −0.107 | −0.18 | 26.03 | 2.12 | −14.02 | −50.23 | −101.9 |
| 1 + 4 | −3.33 | −0.9552 | 0.430 | 0.396 |  | 17.93 | 2.04 | −83.28 | −234.1 | −346.0 |
| 1 + 5 | 0.0332 | −0.07636 | −0.0643 | −0.041 | −0.047 | 4.018 | 1.97 | 0.8314 | 3.856 | −19.55 |

*System (**1**) + (**5**) is considered ideal.
[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})/\sum_{u=1}^{N} e_u^2;\ e_u = V_{m,u,\mathrm{calc}}^E - V_{m,u,\mathrm{expt}}^E$.
[b] Units: $\mathrm{cm^3\,mol^{-1}}$.

Table 8. Coefficients $a_k$ (equation (3)), standard deviation $s$ (equation (5)), Durbin–Watson statistic $d$, $(V^E)_{x=0.5}$, and $\bar{V}_i^{E,\infty}$ at 298.15 K.

| System* | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $s10^4$ | $d^a$ | $10^2(\bar{V}^E)_{x=0.5}.b$ | $10^2\bar{V}_1^{E,\infty b}$ | $10^2\bar{V}_2^{E,\infty b}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 + 2 | −0.2822 | −0.11048 | −0.04571 | −0.01829 | −0.0098 | 6.49 | 1.87 | −6.580 | −20.89 | −46.64 |
| 1 + 3 | −0.6038 | −0.21523 | −0.11623 | −0.04292 | −0.040 | 26.83 | 2.12 | −14.02 | −50.23 | −101.9 |
| 1 + 4 | −3.188 | −0.71772 | 0.28682 | 0.1583 |  | 18.45 | 2.04 | −83.30 | −234.2 | −346.4 |
| 1 + 5 | 0.002336 | −0.10077 | −0.069981 | −0.01627 | −0.010 | 4.14 | 1.97 | 0.8309 | 3.856 | −19.55 |

*System (**1**) + (**5**) is considered ideal.
[a] $d = \sum_{u=2}^{N}(e_u - e_{u-1})/\sum_{u=1}^{N} e_u^2;\ e_u = V_{m,u,\mathrm{calc}}^E - V_{m,u,\mathrm{expt}}^E$.
[b] Units: $\mathrm{cm^3\,mol^{-1}}$.

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.

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

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

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

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

where $k$ is the number of adjustable parameters. The residuals (the difference between the experimental and predicted value) were checked to be randomly distributed, as suggested by Wisniak and Polishuk [14]. It was not deemed necessary to perform a step-wise regression.

A plot of the function $V^E/x_ix_j$ 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 detect outliers. In addition, its values at infinite dilution represent the values of the partial excess molar volume at infinite dilution, $\bar{V}_i^{E,\infty}$, which can also be calculated from the adjustable parameters as follows [10]:

(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 $\bar{V}_i^{E,\infty}$ 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 molar volume at infinite dilution reflects the true solute–solvent interaction. Equations (9) and (10) or (11) and (12) yield the same values of $\bar{V}_i^{E,\infty}$.

Figure 2 shows the distribution of the residuals for the system THF + butyl methacrylate, which is random as shown by the Durbin–Watson statistic. This behavior is typical of the fit attained for the systems studied here.

Inspection of the results of tables 2 to 5 and figure 1 indicates that the excess molar volumes are negative for the four binaries (probably as a result of the relatively large

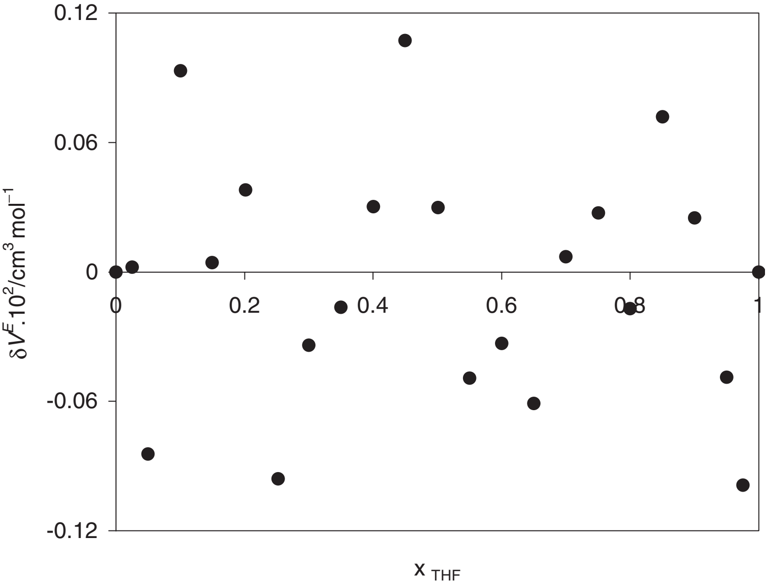

Figure 2. Residual distribution plot for the system THF + butyl methacrylate, according to the fit given in table 7.

dipole moment of the solvent, 1.7 Debye) and become smaller as the solute becomes more branched or longer. Methacrylic acid exhibits substantially larger excess molar volumes probably due to hydrogen bonding with the solvent. The magnitude and sign of $V^E$ is a reflection of the type of interactions taking place in the mixture. For the three methacrylates, the excess molar volumes become smaller as the dipole moment increases from 1.66 Debye for methacrylic acid to 2.15 Debye for butyl methacrylate. Vinyl acetate with a dipole moment of 1.79 Debye packs better than allyl methacrylate ($\mu = 1.69$ Debye) because it lacks the steric hindrance caused by a lateral methyl group. All these effects reflect well in the minimum negative value of $V^E$ ranging from about $-0.07$ to $-0.85\,\mathrm{cm^3\,mol^{-1}}$. The $V^E$ are essentially symmetric, except for the system with methacrylic acid. Methacrylic acid presents the largest negative excess molar volumes and also the largest deviation from symmetry; the fact that the curve is biased to small concentrations of the acid attests that hydrogen bonding with the solvent is stronger than dimerization effects in the acid. This effect is remarkably strong because the maximum excess molar volume of the system is almost three times larger than that observed for the system tetrahydrofuran with styrene [8]. Another interesting aspect is a comparison between the excess molar volumes of the systems of tetrahydrofuran with different acrylic and methacrylic esters. For example, the systems of THF with butyl acrylate and butyl methacrylate behave almost ideally but addition of a methyl side branch in the latter decreases the minimum value of the excess molar volume from $-0.11$ to $-0.068\,\mathrm{cm^3\,mol^{-1}}$, probably because of steric hindrance of the dipole–dipole interaction between double bonds. Similarly, in the binary systems of THF with methacrylic acid, allyl methacrylate, and methyl methacrylate [7], the minimum values of the excess molar volume are $-0.85$, $-0.145$, and $-0.01\,\mathrm{cm^3\,mol^{-1}}$, respectively, reflecting the presence of an additional double bond (allyl against methyl), or the strong hydrogen bonding that results between the carbonyl group and the ethenyl bond. The methyl group present in the $\alpha$ position with respect to the carbonyl group is enough to disrupt the strongly packed structure of THF. In addition, freedom of rotation is higher in butyl methacrylate compared to allyl methacrylate, allowing a better accommodation in THF, in spite of the fact that the chain length in butyl acrylate is longer.

These conclusions are in accordance with the hypothesis of Brower *et al.* that organic molecules in any intensive cohesive solvent will experience a greatly increased barrier to internal rotation and that the mixing molar volume arises from the different space requirements of rotatable and frozen methylene groups. The two new methylene groups created by hydrogenation (of the allyl group) might conformationally freeze in some cases and not in others [15].

## References

[1] R.D. Peralta, R. Infante, G. Cortez, L. Villarreal, J. Wisniak, *Thermochim. Acta*, **390**, 47 (2002).
[2] R.D. Peralta, R. Infante, G. Cortez, J.R. Torres-Lubián, J. Wisniak, *Thermochim. Acta*, **402**, 247 (2003).
[3] R.D. Peralta, R. Infante, G. Cortez, A. Cisneros, J. Wisniak, *Thermochim. Acta*, **398**, 39 (2002).
[4] R.D. Peralta, R. Infante, G. Cortez, O. Rodríguez, J. Wisniak, *J. Solution Chem.*, **31**, 175 (2002).
[5] R.D. Peralta, R. Infante, G. Cortez, R. G. López, J. Wisniak, *Int. J. Thermophys.*, **24**, 173 (2003).
[6] R.D. Peralta, R. Infante, G. Cortez, R.R. Ramírez, J. Wisniak, *J. Chem. Thermodynamics*, **35**, 239 (2003).
[7] R.D. Peralta, R. Infante, G. Cortez, L.F. Ramos, J. Wisniak, *Phys. Chem. Liq.*, **41**, 361 (2003).
[8] S.C. Sharma, R. Kaur, J. Singh, *J. Chem. Thermodyn.*, **24**, 1171 (1992).
[9] B. Eck, G. Maurer, *Fluid Phase Equilibria*, **209**, 281 (2003).

[10] H.C. Van, M.M. Ness, M.M. Abbott, *Classical Thermodynamics of Nonelectrolyte Solutions*, McGraw-Hill, New York (1982).
[11] O. Redlich, A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948).
[12] J. Tomiska, *CALPHAD*, **5**, 93 (1981).
[13] J. Tomiska, *CALPHAD*, **8**, 283 (1984).
[14] J. Wisniak, A. Polishuk, *Fluid Phase Equilibria*, **164**, 61 (1999).
[15] K.R. Brower, J. Psiak, J. Elrod, *J. Phys. Chem.*, **73**, 207 (1969).
[16] H. Naorem, K. Suri, *Can. J. Chem.*, **67**, 1672 (1989).
[17] C. Yaws, *Chemical Properties Handbook*, McGraw-Hill, New York (1999).
[18] T.E. Daubert, R.P. Danner, H.M. Sibul, C.C. Stebbins, *Physical and Thermodynamic Properties of Pure Chemicals*, *Data Compilations*, Taylor & Francis, Bristol, PA (1989–2002).
[19] C. González, J.M. Resa, J. Lanz, A. Ruiz, *ELDATA: Int. Electron. J. Phys.-Chem. Data*, **2**, 185 (1996).