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# Surface Tension Deviations and Excess Molar Volumes on the Ternary System Propyl Propanoate + Hexane + *p*-Xylene at 298.15 K

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This paper reports experimental densities and surface tensions of the ternary system propyl propanoate + hexane + *p*-xylene at a temperature of 298.15 K and atmospheric pressure, over the whole composition range. We present here the experimental densities and surface tensions of the binary system hexane + *p*-xylene and the ternary system propyl propanoate + hexane + *p*-xylene. The excess molar volumes and the surface tension deviations of these mixtures have been calculated. Finally, we will compare the experimental data of the surface tension deviations with different theoretical and empirical approximations.

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## Introduction

This work continues our studies concerning the excess thermodynamic properties for ternary mixtures containing propyl propanoate, hexane, and aromatic hydrocarbons.[1−3] We present here the experimental measurements of densities and surface tension for the ternary system propyl propanoate + hexane + *p*-xylene and the corresponding binary mixture hexane + *p*-xylene at a temperature of 298.15 K and atmospheric pressure, over the whole composition range. The binary mixtures propyl propanoate + hexane and propyl propanoate + *p*-xylene were published previously by us in refs 2 and 4, respectively. The importance of the xylenes is that these compounds are used as raw materials in the plastic industry to produce synthetic fibers, a soft plastic for aircrafts and other vehicles. From a theoretical point of view, these compounds are very interesting to test some theories published to predict the surface tension deviations in mixtures. Therefore, we will compare the experimental data with the theories of Hildebrand and Scott, which are extensions of the classical Guggenheim's ideal solution theory, one of them for ideal solutions containing molecules of similar size (HSIS) and the other one for mixtures of molecules with different size (HSEG), which were presented together in a paper.[5]

From the measured data we will extract the excess molar volumes and surface tension deviations. These results will be fitted with a Redlich−Kister type equation[6] and a new one developed by us[7] for the binary mixtures, while for the ternary mixture we used Cibulka's equation.[8] Finally, the data for the calculated excess property in the ternary system will be compared with those obtained from several empirical equations based on the experimental data obtained for the corresponding binary mixtures. Among the many empirical equations published we have checked five, those of Kohler, Colinet, Toop, Scatchard et al., and Hillert, compiled in a previous paper.[2] The two first approximations are symmetrical, and the three last are asymmetrical, which means that the order of the components is relevant in the results obtained.

## Experimental Section

The chemicals employed were supplied by Fluka and Sigma-Aldrich. The mass purities of the substances were >99 % for propyl propanoate (Sigma-Aldrich), ≥99.5 % for hexane (Fluka), and ≥99 % for *p*-xylene (Fluka). The substances were degassed by ultrasound, dried over molecular sieves (Sigma type 0.4 nm), and otherwise used as supplied.

**Table 1. Density and Surface Tension of the Pure Components at 298.15 K**

| | $\rho$/(g·cm$^{-3}$) | | $\sigma$/(mN·m$^{-1}$) | |
|---|---|---|---|---|
| component | expt | lit. | expt | lit. |
| propyl propanoate | 0.87553 | 0.87553[10] | 24.10 | 24.21[13] |
| hexane | 0.65470 | 0.65471[11] | 17.91 | 17.90[11] |
| *p*-xylene | 0.85651 | 0.85661[12] | 27.70 | 27.76[11] |

All of the mixtures were prepared by mass using a Mettler AT 201 balance. The uncertainty of the molar fraction is estimated to be about $\pm 1 \cdot 10^{-4}$. Densities ($\rho$) of pure liquids and their corresponding mixtures were measured using an Anton Paar digital densimeter (model 60/602) thermostatted with a Schott-Gërate CT 1450 circulating-water bath, with a precision in the temperature control of 0.01 K. The uncertainties of the densities are about $\pm 1 \cdot 10^{-5}$ g·cm$^{-3}$. Calibration is performed daily with Milli-Q water and heptane (Sigma, >99 %). Surface tension ($\sigma$) was determined using a Lauda TVT1 automated tensiometer which employs the principle of the drop volume. This technique consists in measuring the volume of a drop detaching from a capillary with a known circular cross section. The uncertainty of the surface tension measured with this method is $\pm 1 \cdot 10^{-2}$ mN·m$^{-1}$. A Lauda RC6CP thermostatic bath controlled the temperature to better than 0.1 K. A detailed description of the tensiometer used and the experimental procedure has been described previously.[9]

## Results

The measured densities and surface tensions for the pure liquids are compared with the published results at 298.15 K in Table 1. The agreement, within the experimental uncertainties, between both sets of data indicates the high quality of our compounds and that our experimental equipment has good accuracy.

Densities and surface tensions of the binary system hexane + *p*-xylene obtained in this work are shown in Tables 2 and 3, respectively. In Tables 4 and 5 we include the same properties for the ternary system.

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**Table 2. Densities, $\rho$, and Excess Molar Volumes, $V_m^E$, for the Binary Mixture Hexane (1) + *p*-Xylene (2) at 298.15 K**

| $x_1$ | $\rho$ / $g \cdot cm^{-3}$ | $V_m^E$ / $cm^3 \cdot mol^{-1}$ | $x_1$ | $\rho$ / $g \cdot cm^{-3}$ | $V_m^E$ / $cm^3 \cdot mol^{-1}$ |
|---|---|---|---|---|---|
| 0.0393 | 0.84842 | −0.049 | 0.5404 | 0.74602 | −0.266 |
| 0.0869 | 0.83863 | −0.097 | 0.5836 | 0.73732 | −0.259 |
| 0.1535 | 0.82496 | −0.157 | 0.6380 | 0.72641 | −0.245 |
| 0.2080 | 0.81378 | −0.195 | 0.6903 | 0.71594 | −0.226 |
| 0.3063 | 0.79359 | −0.238 | 0.7872 | 0.69669 | −0.180 |
| 0.3524 | 0.78421 | −0.256 | 0.8297 | 0.68825 | −0.150 |
| 0.4333 | 0.76775 | −0.273 | 0.8952 | 0.67528 | −0.095 |
| 0.4867 | 0.75693 | −0.273 | 0.9417 | 0.66619 | −0.056 |

**Table 3. Surface Tensions, $\sigma$, and Surface Tension Deviations, $\delta\sigma$, for the Binary Mixture Hexane (1) + *p*-Xylene (2) at 298.15 K**

| $x_1$ | $\sigma$ / $mN \cdot m^{-1}$ | $\delta\sigma$ / $mN \cdot m^{-1}$ | $x_1$ | $\sigma$ / $mN \cdot m^{-1}$ | $\delta\sigma$ / $mN \cdot m^{-1}$ |
|---|---|---|---|---|---|
| 0.0535 | 26.84 | −0.33 | 0.4920 | 21.59 | −1.30 |
| 0.0718 | 26.58 | −0.41 | 0.5267 | 21.29 | −1.25 |
| 0.1265 | 25.76 | −0.70 | 0.6034 | 20.67 | −1.12 |
| 0.1341 | 25.66 | −0.73 | 0.6394 | 20.39 | −1.05 |
| 0.3083 | 23.45 | −1.23 | 0.6877 | 20.07 | −0.90 |
| 0.3397 | 23.10 | −1.27 | 0.7826 | 19.41 | −0.62 |
| 0.3990 | 22.47 | −1.33 | 0.8126 | 19.22 | −0.52 |
| 0.4670 | 21.81 | −1.32 | 0.8798 | 18.79 | −0.29 |

**Table 4. Densities, $\rho$, and Excess Molar Volumes, $V_m^E$, for the Ternary Mixture Propyl Propanoate (1) + Hexane (2) + *p*-Xylene (3) at 298.15 K**

| $x_1$ | $x_2$ | $\rho$ / $g \cdot cm^{-3}$ | $V_{m,123}^E$ / $cm^3 \cdot mol^{-1}$ | $x_1$ | $x_2$ | $\rho$ / $g \cdot cm^{-3}$ | $V_{m,123}^E$ / $cm^3 \cdot mol^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.8516 | 0.0662 | 0.85948 | 0.026 | 0.2534 | 0.0638 | 0.84911 | −0.132 |
| 0.7688 | 0.0655 | 0.85834 | −0.021 | 0.2484 | 0.1537 | 0.83034 | −0.142 |
| 0.7501 | 0.1656 | 0.83707 | 0.092 | 0.2590 | 0.2361 | 0.81347 | −0.128 |
| 0.6754 | 0.0635 | 0.85718 | −0.059 | 0.2530 | 0.3318 | 0.79357 | −0.091 |
| 0.6781 | 0.1614 | 0.83673 | 0.043 | 0.2570 | 0.4851 | 0.76226 | 0.012 |
| 0.6785 | 0.2403 | 0.82032 | 0.139 | 0.2508 | 0.5838 | 0.74205 | 0.103 |
| 0.5960 | 0.0597 | 0.85661 | −0.090 | 0.2549 | 0.6637 | 0.72608 | 0.185 |
| 0.5999 | 0.1389 | 0.84017 | −0.038 | 0.1691 | 0.0637 | 0.84729 | −0.119 |
| 0.6021 | 0.2343 | 0.82026 | 0.076 | 0.1752 | 0.1587 | 0.82773 | −0.149 |
| 0.6089 | 0.3109 | 0.80451 | 0.172 | 0.1744 | 0.2361 | 0.81171 | −0.155 |
| 0.5193 | 0.0669 | 0.85368 | −0.101 | 0.1808 | 0.3311 | 0.79229 | −0.143 |
| 0.4949 | 0.1687 | 0.83181 | −0.021 | 0.1783 | 0.4002 | 0.77804 | −0.118 |
| 0.4999 | 0.2376 | 0.81770 | 0.018 | 0.1771 | 0.4818 | 0.76146 | −0.078 |
| 0.5050 | 0.4112 | 0.78191 | 0.223 | 0.1718 | 0.5707 | 0.74331 | −0.020 |
| 0.4217 | 0.0643 | 0.85252 | −0.143 | 0.1794 | 0.6685 | 0.72367 | 0.091 |
| 0.4254 | 0.1528 | 0.83399 | −0.090 | 0.1786 | 0.7422 | 0.70888 | 0.169 |
| 0.4254 | 0.2329 | 0.81742 | −0.053 | 0.0933 | 0.0651 | 0.84527 | −0.099 |
| 0.4342 | 0.2959 | 0.80451 | 0.009 | 0.0985 | 0.1421 | 0.82946 | −0.141 |
| 0.4345 | 0.4053 | 0.78193 | 0.127 | 0.0739 | 0.2243 | 0.81220 | −0.208 |
| 0.3434 | 0.0621 | 0.85133 | −0.133 | 0.0782 | 0.3248 | 0.79169 | −0.232 |
| 0.3493 | 0.1565 | 0.83186 | −0.130 | 0.0728 | 0.4186 | 0.77223 | −0.203 |
| 0.3507 | 0.2352 | 0.81544 | −0.079 | 0.0777 | 0.5841 | 0.73871 | −0.137 |
| 0.3384 | 0.3217 | 0.79736 | −0.038 | 0.0774 | 0.6601 | 0.72340 | −0.086 |
| 0.3415 | 0.3970 | 0.78206 | −0.001 | 0.0773 | 0.7502 | 0.70544 | −0.032 |
| 0.3394 | 0.5793 | 0.74463 | 0.229 | 0.0799 | 0.8352 | 0.68848 | 0.076 |

The excess molar volumes ($V_m^E$) and the surface tension deviations were computed using eqs 1 to 2, respectively:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{1}$$

$$\delta\sigma = \sigma - \sum_{i=1}^{N} x_i \sigma_i \tag{2}$$

**Table 5. Surface Tensions, $\sigma$, and Surface Tension Deviations, $\delta\sigma$, for the Ternary Mixture Propyl Propanoate (1) + Hexane (2) + *p*-Xylene (3) at 298.15 K**

| $x_1$ | $x_2$ | $\sigma$ / $mN \cdot m^{-1}$ | $\delta\sigma$ / $mN \cdot m^{-1}$ | $x_1$ | $x_2$ | $\sigma$ / $mN \cdot m^{-1}$ | $\delta\sigma$ / $mN \cdot m^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.8630 | 0.0593 | 23.83 | −0.18 | 0.2649 | 0.1434 | 24.49 | −0.85 |
| 0.7445 | 0.0791 | 23.89 | −0.36 | 0.2781 | 0.1690 | 24.13 | −0.91 |
| 0.7684 | 0.1453 | 23.12 | −0.39 | 0.2760 | 0.2959 | 22.80 | −1.00 |
| 0.6602 | 0.0854 | 23.95 | −0.54 | 0.2536 | 0.3942 | 22.09 | −0.84 |
| 0.6786 | 0.1353 | 23.33 | −0.60 | 0.2686 | 0.4825 | 21.38 | −0.63 |
| 0.6970 | 0.2136 | 22.51 | −0.59 | 0.2727 | 0.5609 | 20.89 | −0.34 |
| 0.6055 | 0.1445 | 23.44 | −0.67 | 0.2670 | 0.6557 | 20.19 | −0.13 |
| 0.6056 | 0.2122 | 22.67 | −0.77 | 0.1582 | 0.0773 | 25.82 | −0.55 |
| 0.5998 | 0.3209 | 21.70 | −0.70 | 0.1604 | 0.2418 | 23.66 | −1.09 |
| 0.5030 | 0.2445 | 22.65 | −0.84 | 0.1668 | 0.2897 | 23.18 | −1.08 |
| 0.5188 | 0.2898 | 22.15 | −0.85 | 0.1618 | 0.4112 | 22.18 | −0.92 |
| 0.5024 | 0.4186 | 21.10 | −0.69 | 0.1728 | 0.4492 | 21.88 | −0.80 |
| 0.4313 | 0.1469 | 23.78 | −0.93 | 0.1633 | 0.7601 | 19.75 | 0.07 |
| 0.4723 | 0.1344 | 23.84 | −0.85 | 0.0897 | 0.1593 | 24.98 | −0.84 |
| 0.4300 | 0.3140 | 22.17 | −0.91 | 0.0897 | 0.2358 | 23.98 | −1.09 |
| 0.4178 | 0.4000 | 21.55 | −0.73 | 0.0951 | 0.2854 | 23.43 | −1.14 |
| 0.3279 | 0.0784 | 25.02 | −0.73 | 0.0915 | 0.3987 | 22.39 | −1.08 |
| 0.3342 | 0.1370 | 24.27 | −0.88 | 0.0983 | 0.4590 | 21.90 | −0.95 |
| 0.3523 | 0.1989 | 23.51 | −0.98 | 0.0930 | 0.5469 | 21.26 | −0.75 |
| 0.3806 | 0.3369 | 22.14 | −0.89 | 0.0946 | 0.6493 | 20.57 | −0.43 |
| 0.3441 | 0.4761 | 21.21 | −0.59 | 0.0944 | 0.7218 | 20.08 | −0.21 |
| 0.3889 | 0.5210 | 20.69 | −0.51 | 0.0947 | 0.8147 | 19.50 | 0.11 |

**Table 6. Coefficients $A_K$ from Equation 3 and $K$, $n$, $K'$, and $n'$ from Equation 4 with Standard Deviations, $s$**

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $s$ |
|---|---|---|---|---|---|
| Propyl Propanoate + Hexane | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})^1$ | 1.366 | −0.652 | 0.300 | | 0.005 |
| $\delta\sigma/(mN \cdot m^{-1})^2$ | −2.58 | −1.92 | 4.88 | −1.31 | 0.010 |
| Propyl Propanoate + *p*-Xylene | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})^3$ | −0.543 | 0.077 | | −0.060 | 0.001 |
| $\delta\sigma/(mN \cdot m^{-1})^3$ | −0.48 | 0.24 | 0.64 | 0.16 | 0.002 |
| Hexane + *p*-Xylene | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})$ | −1.084 | 0.105 | −0.085 | | 0.002 |
| $\delta\sigma/(mN \cdot m^{-1})$ | −5.16 | 1.97 | 1.02 | 0.51 | 0.010 |
| | $K$ | $n$ | $K'$ | $n'$ | $s$ |
| Propyl Propanoate + Hexane | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})$ | 14.4 | 0.965 | −13.3 | 0.997 | 0.005 |
| $\delta\sigma/(mN \cdot m^{-1})$ | 111 | 0.968 | −117 | 1.02 | 0.035 |
| Propyl Propanoate + *p*-Xylene | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})$ | −0.508 | 0.916 | | | 0.002 |
| $\delta\sigma/(mN \cdot m^{-1})$ | −7.12 | 0.960 | 1.07 | −8.18 | 0.005 |
| Hexane + *p*-Xylene | | | | | |
| $V_m^E/(cm^3 \cdot mol^{-1})$ | −1.03 | 0.920 | | | 0.002 |
| $\delta\sigma/(mN \cdot m^{-1})$ | | | −6.71 | 1.39 | 0.012 |
| | $B_1$ | $B_2$ | $B_3$ | | $s$ |
| Propyl Propanoate + Hexane + *p*-Xylene | | | | | |
| $V_{m,123}^E/(cm^3 \cdot mol^{-1})$ | −2.096 | 4.177 | 1.348 | | 0.016 |
| $\delta\sigma_{123}/(mN \cdot m^{-1})$ | −19.59 | 1.37 | 55.25 | | 0.040 |

In this equation, $\rho$ and $\sigma$ are respectively the density and the surface tension in the mixture; $\rho_i$ and $\sigma_i$ are the property of the pure components, and $N$ is the number of the components in the mixture ($N = 2$ in the case of a binary mixture and $N = 3$ for a ternary one). The calculated values of $V_m^E$ and $\delta\sigma$ appear respectively in Tables 2 and 3 for the binary system hexane + *p*-xylene and in Tables 4 and 5 for the ternary system studied. The derived excess function of the binary system can be represented by a Redlich−Kister equation[6]

$$Q_{ij}^E = x_i x_j \sum_{K=0}^{m} A_K (x_i - x_j)^K \tag{3}$$

where $Q_{ij}^E$ represents $V_m^E$ and $\delta\sigma$; $x_i$ and $x_j$ are the mole fractions of components $i$ and $j$, respectively, and $A_K$ denotes the polynomial coefficients. The degree ($m$) of the polynomial Redlich−Kister equation was optimized by applying the F-test.[14] The coefficients $A_K$ for eq 3 and the standard deviations, $s$, appear in Table 6, where we also include the parameters already published for some of the binary mixtures. Also, these results

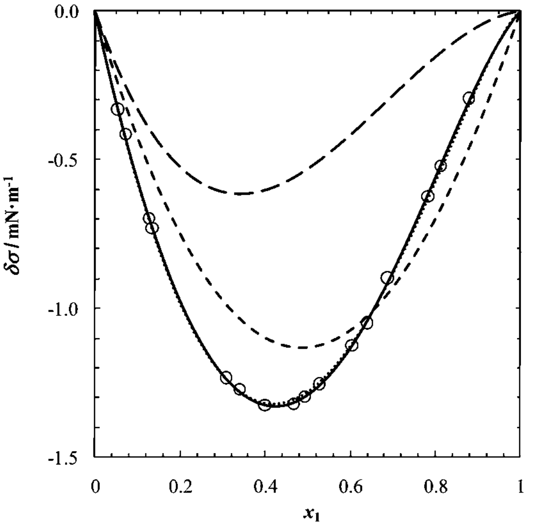

**Figure 1.** Surface tension deviations of hexane (1) + *p*-xylene (2) at 298.15 K vs the molar fraction of hexane. The different lines correspond to: solid line, Redlich−Kister eq 2; dotted line, our new eq 4; short dashed line, HSEG approximation; long dashed line, HSIS empirical model.

were fitted with a new equation developed by us,[7] which only has four parameters:

$$Q^{\mathrm{E}} = Kx_1^{n}x_2 + K'x_1x_2^{n'} \qquad (4)$$

where $K$, $n$, $K'$, and $n'$ are the fitting parameters. All of them are real numbers, but the exponents $n$ and $n'$ are always positive (if not eq 4 diverges for $x_1$ or $x_2 = 0$). The values of the fitting parameters with the corresponding standard deviations are included in Table 6.

To correlate the excess property of the ternary mixture we have employed as usual the following equation

$$Q_{123}^{\mathrm{E}} = Q_{\mathrm{bin}}^{\mathrm{E}} + x_1x_2(1 - x_1 - x_2)\Delta_{123} \qquad (5)$$

where

$$Q_{\mathrm{bin}}^{\mathrm{E}} = Q_{12}^{\mathrm{E}} + Q_{13}^{\mathrm{E}} + Q_{23}^{\mathrm{E}} \qquad (6)$$

Here the symbol $Q_{123}^{\mathrm{E}}$ represents $V_{\mathrm{m},123}^{\mathrm{E}}$, $\delta\sigma_{123}$, and $Q_{ij}^{\mathrm{E}}$ given by eq 3, and the term $x_1x_2x_3\Delta_{123}$ is the ternary contribution. The term $\Delta_{123}$ can be fitted to an expression given by Cibulka[8] that reads

$$\Delta_{123} = B_1 + B_2x_1 + B_3x_2 \qquad (7)$$

where $B_i$ are fitting parameters. The parameters $B_i$ for eq 7 with the corresponding standard deviations of the fit, $s$, are also given in Table 6.

## Discussion

The excess molar volume ($V_{\mathrm{m}}^{\mathrm{E}}$) for the binary system hexane + *p*-xylene shows negative values over the whole composition range, with a minimum at nearly equimolecular composition. These results are similar in sign and shape with those obtained for the binary mixtures hexane + ethylbenzene[2] and hexane + *m*-xylene.[3] This same mixture and property was published previously,[15,16] and our data match in sign and shape with those published before, but the absolute value of $V_{\mathrm{m}}^{\mathrm{E}}$ in our case is about 12 % higher than ref 15 and 2 % than ref 16 for the equimolar composition.

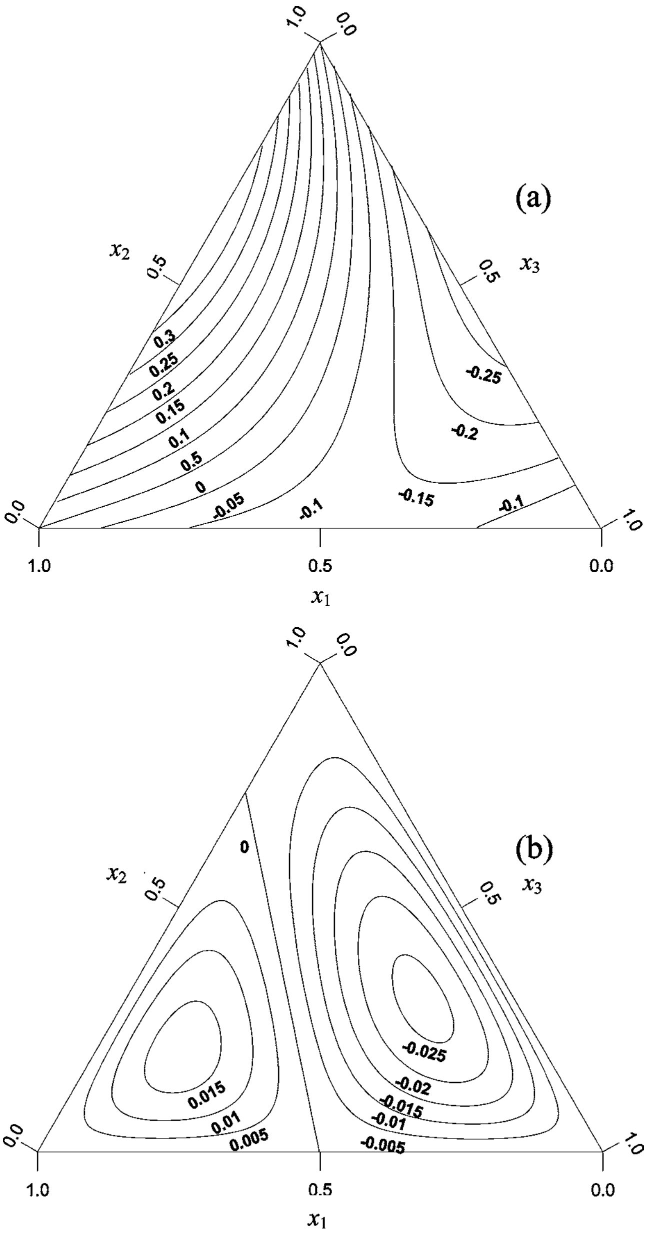

**Figure 2.** (a) Curves of constant $V_{\mathrm{m},123}^{\mathrm{E}}$/(cm$^3$·mol$^{-1}$) for the ternary system propyl propanoate (1) + hexane (2) + *p*-xylene (3) calculated from eq 4. (b) Ternary contribution, ($V_{\mathrm{m},123}^{\mathrm{E}} - V_{\mathrm{m,bin}}^{\mathrm{E}}$)/(cm$^3$·mol$^{-1}$), for the ternary system.

Surface tension deviation ($\delta\sigma$) versus molar fraction of hexane, $x_1$, for the binary system hexane + *p*-xylene is shown in Figure 1. The values of the $\delta\sigma$ are negative, and the minimum is skewed toward the mixtures rich in the aromatic compound. This curve observed is very similar to that presented before for the mixtures hexane + ethylbenzene and hexane + *m*-xylene[2,3] even in absolute value. The continuous line corresponds to the fit of a Redlich−Kister eq 3 with the fitting parameters given in Table 6, while the dotted line corresponds to our new eq 3 with the free parameters also given in Table 6. The other lines that appear in Figure 1 correspond to the different theoretical approximations tested; thus, the short dashed line represents the HSEG approximation and the long dashed line to the HSIS empirical model. All of these equations have been compiled in ref 4. As observed, none of the empirical models give a reliable prediction of $\delta\sigma$, but the HSEG equation is the most accurate to predict this binary mixture because it is also skewed to the mixtures rich in *p*-xylene.

In Figures 2 to 3 we present the results obtained for the ternary mixture studied here. Thus, in Figures 2a and 3a we show lines of constant $V_{\mathrm{m},123}^{\mathrm{E}}$ and $\delta\sigma_{123}$, respectively. While in

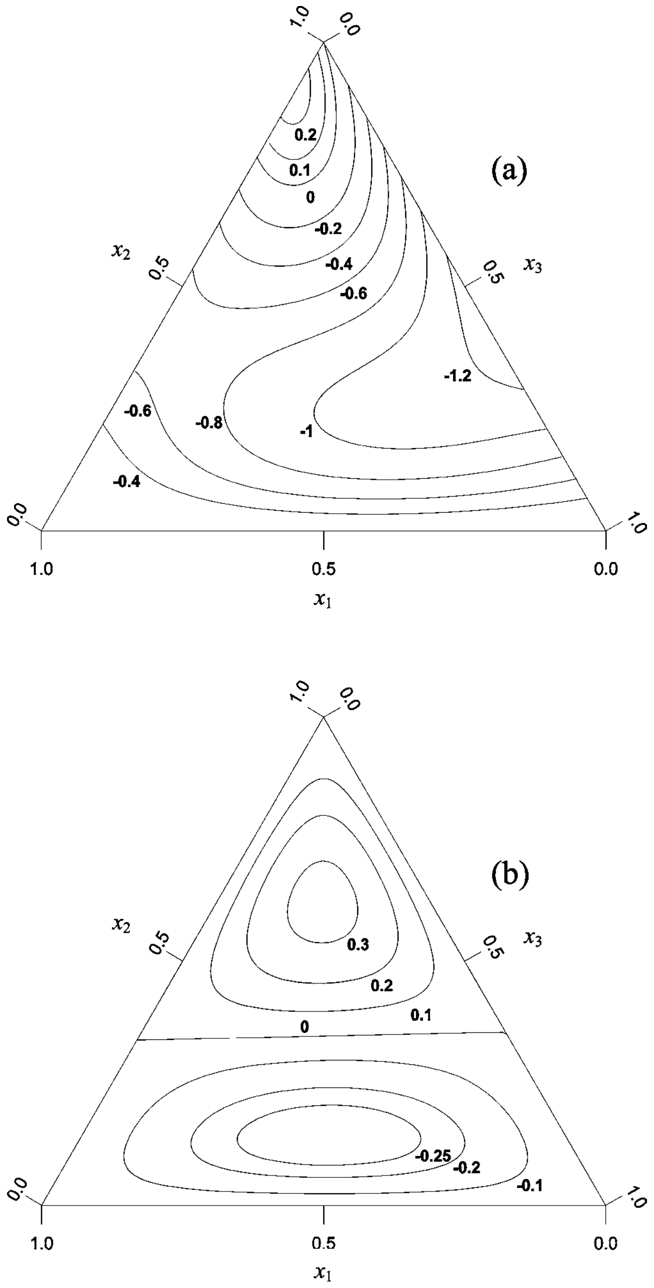

**Figure 3.** (a) Curves of constant $\delta\sigma_{123}$/mN·m$^{-1}$ for the ternary system propyl propanoate (1) + hexane (2) + *p*-xylene (3) calculated from eq 4. (b) Curves of the ternary contribution, $(\delta\sigma_{123} - \delta\sigma_{\mathrm{bin}})$/mN·m$^{-1}$, for the ternary system.

Figures 2b and 3b we show lines of ternary contribution, $(V^{\mathrm{E}}_{\mathrm{m},123} - V^{\mathrm{E}}_{\mathrm{m,bin}})$ and $(\delta\sigma_{123} - \delta\sigma_{\mathrm{bin}})$, respectively. If we compare the results for the ternary mixture propyl propanoate + hexane + *p*-xylene with those published previously with ethylbenzene[2] and *m*-xylene,[3] it can be observed that the results for $V^{\mathrm{E}}_{\mathrm{m},123}$ are very similar for the three systems, both in shape and in absolute value, but for the ternary contribution the results differ among the three systems. Thus, while the system with ethylbenzene has all negative values, with a minimum of about −0.08, the system with *m*-xylene has positive and negative values with maximum and minimum values of about 0.025 and −0.01, respectively, and the system with *p*-xylene has positive and negative values with maximum values about 0.017 and minimum values about −0.027, as shown in Figure 2b. The curves for $\delta\sigma_{123}$ and $(\delta\sigma_{123} - \delta\sigma_{\mathrm{bin}})$ are very similar in shape for the three systems.

**Table 7. Standard Deviations, *s*, of Empirical Expressions for (a) Propyl Propanoate + Hexane + *p*-Xylene, (b) Hexane + *p*-Xylene + Propyl Propanoate, and (c) *p*-Xylene + Propyl Propanoate + Hexane, at 298.15 K**

| | a | b | c |
|---|---|---|---|
| | $V^{\mathrm{E}}_{\mathrm{m},123}$/(cm$^3$·mol$^{-1}$) | | |
| Kohler | 0.022 | | |
| Colinet | 0.016 | | |
| Toop | 0.026 | 0.024 | 0.023 |
| Scatchard et al. | 0.023 | 0.024 | 0.020 |
| Hillert | 0.024 | 0.024 | 0.021 |
| | $\delta\sigma_{123}$/(mN·m$^{-1}$) | | |
| Kohler | 0.16 | | |
| Colinet | 0.19 | | |
| Toop | 0.16 | 0.24 | 0.19 |
| Scatchard et al. | 0.17 | 0.24 | 0.19 |
| Hillert | 0.18 | 0.24 | 0.21 |

The data of the ternary mixture have been compared with five empirical models that predict the ternary excesses from the corresponding binary ones. These theories are those of Kohler,[17] Colinet, Toop,[18] Scatchard et al.,[19] and Hillert.[20] The two first approximations are symmetrical, and the three last are asymmetric, which means that the order of the components is relevant in the results obtained. In Table 7 we present the obtained standard deviations, *s*, from the calculated data using each theory and the experimental results. We can observe in Table 7 that the empirical approximation of Colinet presents the lower *s* among the symmetrical equations for the excess molar volumes and that of Kohler for the surface tension deviations. For the asymmetric equations the value of *s* depends on the order of the components taken to perform the calculations, and the model of Scatchard et al. presents the lowest *s* value for selected order of components in the case of the excess molar volumes and that of Toop, followed by the approximation given by Scatchard et al., for the surface tension deviations.

## Conclusions

From the measured density and surface tension data presented in this paper of the ternary system propyl propanoate + hexane + *p*-xylene and the hexane + *p*-xylene system at a temperature of 298.15 K and atmospheric pressure, we extract the corresponding excess molar volumes and surface tension deviations. For binary systems the new equation, eq 4, proposed in this work for correlation purposes has a performance similar to the widely used Redlich−Kister equation. After comparing the data of the excesses of the two properties for the ternary mixture we conclude that the best model to predict the ternary contribution among the five tested is that of Colinet for the excess molar volumes and Kohler for the surface tension deviations. In the case of the binary mixture, the surface tension deviations must be compared with different theoretical models. Neither of the two models tested predicts the property and shape of the data measured.

### Supporting Information Available:

Detailed description of the novel equation with figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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