# Densities, Refractive Indices, and Derived Excess Properties of the Binary Systems Toluene + Isooctane and Methylcyclohexane + Isooctane and the Ternary Systems *tert*-Butyl Alcohol + Toluene + Isooctane and *tert*-Butyl Alcohol + Methylcyclohexane + Isooctane at 298.15 K

**Juan B. Montón,* M. Pilar Peña, and V. Martínez-Soria**

Departamento de Ingenieria Quimica, Facultad de Quimica, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

This paper reports mesurements of the densities and refractive indices of the binary systems toluene + isooctane and methylcyclohexane + isooctane and the ternary systems *tert*-butyl alcohol (TBA) + toluene + isooctane and *tert*-butyl alcohol (TBA) + methylcyclohexane + isooctane over the entire range of composition at 298.15 K. Excess molar volumes and changes of refractive indices were evaluated from the experimental data obtained. These derived properties were fitted to variable-degree polynomials. The experimental values of physical properties were compared with the values estimated by different methods.

## 1. Introduction

The present work is part of our systematic studies on thermodynamic properties for mixtures of great interest in industry. Knowledge of these mixing properties has relevance in both theoretical and applied areas of research because such results are useful in design and simulation processes. In this sense, there has been an increasing interest in the thermodynamic behavior of liquid mixtures of the oxygenated compounds included in reformulated gasoline: methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether (TAME), and alcohols—methanol, ethanol, *tert*-butyl alcohol (TBA), and isobutyl alcohol (IBA).

In a previous paper (Peña et al., 1999), we have studied the densities and refractive indices for the binary systems TBA + isooctane, TBA + toluene, TBA + methylcyclohexane, and methylcyclohexane + toluene and the ternary system TBA + toluene + methylcyclohexane. The present work is the continuation of this work and reports densities and refractive indices for the toluene + isooctane and methylcyclohexane + isooctane binary system and for the TBA + toluene + isooctane and TBA + methylcyclohexane + isooctane ternary systems at 298.15 K, and the corresponding excess molar volumes and changes of refractive indices. Comparison has been made between the measured values and those predicted by different methods.

## 2. Experimental Section

The chemicals *tert*-butyl alcohol (2-methyl-2-propanol) (>99.5%), methylcyclohexane (>99%), toluene (>99.8%), and isooctane (2,2,4-trimethylpentane) (>99.7%) were supplied by Aldrich. The purity of all chemicals was checked by gas chromatography (GC), and the results of these analyses showed that the impurities did not exceed 0.2 mass %. The pure components were degassed ultrasonically. These reagents were used without further purification. The *tert*-butyl alcohol was dehydrated using zeolite A (4 Å).

The samples were prepared using a Mettler AE 200 balance with an accuracy of ±0.0001 g, covering the whole composition range of the binary and ternary mixtures. Precautions were taken such as using freshly prepared samples and reducing the vapor space in the vessels to a minimum, to avoid preferential evaporation during manipulation and subsequent composition errors. The estimated uncertainity in the mole fraction of the samples used was ±0.0001.

The densities of pure components and their mixtures were measured with an Anton Paar DMA 55 densimeter, and the refractive indices with an Abbe refractometer (Type 3T), with reproducibilities of ±0.01 kg·m$^{-3}$ and ±0.0002, respectively. Each apparatus was matched to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at 298.15 K with an uncertainity of ±0.01 K. The densimeter was calibrated with air-dried and distilled water.

## 3. Results and Discussion

Densities, $\rho$, refractive indices, $n_D$, excess molar volumes, $V^E$, and changes in refractive indices, $\delta n_D$, of binary and ternary mixtures are shown in Tables 1−4. In these tables, $x_i$ is the molar fraction of component $i$ in the mixture. No values of the entitled mixtures have been published, as far as we known, in the open literature. The density and refractive index for each component were measured at 298.15 K and compiled in a previous work (Martínez-Soria et al., 1999). Measurements of density and refractive index for pure components were realized by ascertaining the constancies of the values of these mentioned properties for every component at 298.15 K, which were reasonably in accordance with values found in the literature (*TRC Thermodynamic Tables*, 1996).

* To whom correspondence should be addressed. E-mail: Juan.B.Monton@uv.es. Telephone: 346 3864325. Fax: 346 3864898.

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**Table 1. Densities, $\rho$, Refractive Indices, $n_D$, Excess Molar Volumes, $V^E$, and Changes of Refractive Indices on Mixing, $\delta n_D$, for the Binary System Toluene (2) + Isooctane (4) at 298.15 K**

| $x_2$ | $\rho$/kg·m$^{-3}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ |
|---|---|---|---|---|
| 0.0000 | 687.67 | 1.3890 | 0.000 | 0.0000 |
| 0.0490 | 693.18 | 1.3927 | 0.018 | −0.0014 |
| 0.1098 | 700.27 | 1.3964 | 0.047 | −0.0042 |
| 0.1882 | 709.99 | 1.4023 | 0.063 | −0.0065 |
| 0.2418 | 716.97 | 1.4064 | 0.075 | −0.0080 |
| 0.3067 | 725.85 | 1.4113 | 0.087 | −0.0099 |
| 0.3691 | 734.88 | 1.4170 | 0.085 | −0.0108 |
| 0.4454 | 746.57 | 1.4240 | 0.084 | −0.0118 |
| 0.5035 | 756.03 | 1.4298 | 0.079 | −0.0121 |
| 0.5738 | 768.11 | 1.4372 | 0.072 | −0.0120 |
| 0.6183 | 776.19 | 1.4422 | 0.066 | −0.0117 |
| 0.6849 | 788.91 | 1.4497 | 0.055 | −0.0113 |
| 0.7644 | 805.13 | 1.4598 | 0.048 | −0.0095 |
| 0.8241 | 818.26 | 1.4674 | 0.030 | −0.0081 |
| 0.9020 | 836.63 | 1.4789 | 0.012 | −0.0048 |
| 0.9617 | 851.68 | 1.4871 | 0.004 | −0.0029 |
| 1.0000 | 861.87 | 1.4940 | 0.000 | 0.0000 |

**Table 2. Densities, $\rho$, Refractive Indices, $n_D$, Excess Molar Volumes, $V^E$, and Changes of Refractive Indices on Mixing, $\delta n_D$, for the Binary System Methylcyclohexane (3) + Isooctane (4) at 298.15 K**

| $x_3$ | $\rho$/kg·m$^{-3}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ |
|---|---|---|---|---|
| 0.0000 | 687.67 | 1.3890 | 0.000 | 0.0000 |
| 0.0708 | 692.08 | 1.3912 | −0.028 | −0.0001 |
| 0.1502 | 697.20 | 1.3930 | −0.057 | −0.0008 |
| 0.2326 | 702.70 | 1.3955 | −0.085 | −0.0008 |
| 0.3345 | 709.76 | 1.3984 | −0.108 | −0.0011 |
| 0.3928 | 713.95 | 1.3999 | −0.117 | −0.0015 |
| 0.5196 | 723.43 | 1.4040 | −0.124 | −0.0014 |
| 0.5556 | 726.22 | 1.4050 | −0.122 | −0.0015 |
| 0.6333 | 732.39 | 1.4076 | −0.114 | −0.0013 |
| 0.6875 | 736.83 | 1.4093 | −0.105 | −0.0013 |
| 0.7372 | 741.02 | 1.4110 | −0.097 | −0.0011 |
| 0.7545 | 742.48 | 1.4118 | −0.089 | −0.0009 |
| 0.7674 | 743.56 | 1.4120 | −0.080 | −0.0011 |
| 0.8756 | 753.16 | 1.4162 | −0.050 | −0.0003 |
| 0.9478 | 759.86 | 1.4187 | −0.022 | −0.0001 |
| 1.0000 | 764.87 | 1.4204 | 0.000 | 0.0000 |

The excess molar volumes and the changes in refractive indices on mixing for binary and ternary mixtures were calculated from eqs 1 and 2, respectively,

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

$$\delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di} \quad (2)$$

where $M_i$ is the molecular weight of component $i$ in the mixture, $\rho_i$ and $n_{Di}$ are the properties of the pure components, and $N$ is the number of components in the mixture.

Curves of excess molar volumes and changes in refractive index for binary mixtures are plotted in Figure 1. As can be seen, the toluene + isooctane system shows positive deviations of $V_m^E$ over the whole composition range with a maximum at nearly equimolecular composition, while the methylcyclohexane + isooctane system shows a negative deviation of this excess property. The binary systems studied show negative deviations for $\delta n_D$ in the whole range of composition, with the largest values for the toluene + isooctane mixture.

The derived binary excess properties were correlated with the Redlich−Kister (Redlich and Kister, 1948) equation, according to the expression

**Table 3. Densities, $\rho$, Refractive Indices, $n_D$, Excess Molar Volumes, $V^E$, and Changes of Refractive Indices on Mixing, $\delta n_D$, for the Ternary System TBA (1) + Toluene (2) + Isooctane (4) at 298.15 K**

| $x_1$ | $x_2$ | $\rho$/kg·m$^{-3}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ |
|---|---|---|---|---|---|
| 0.9006 | 0.0549 | 775.97 | 1.3902 | 0.307 | −0.0009 |
| 0.7987 | 0.0969 | 768.91 | 1.3939 | 0.564 | −0.0020 |
| 0.6888 | 0.1099 | 755.84 | 1.3948 | 0.768 | −0.0029 |
| 0.7046 | 0.1923 | 776.51 | 1.4040 | 0.644 | −0.0023 |
| 0.5899 | 0.1105 | 743.80 | 1.3944 | 0.884 | −0.0038 |
| 0.6017 | 0.2071 | 764.86 | 1.4046 | 0.770 | −0.0037 |
| 0.6011 | 0.2904 | 783.60 | 1.4145 | 0.670 | −0.0026 |
| 0.5046 | 0.0984 | 732.83 | 1.3933 | 0.906 | −0.0040 |
| 0.4908 | 0.2160 | 753.07 | 1.4046 | 0.805 | −0.0051 |
| 0.4982 | 0.2945 | 769.79 | 1.4133 | 0.750 | −0.0046 |
| 0.4996 | 0.3963 | 792.88 | 1.4256 | 0.653 | −0.0030 |
| 0.3929 | 0.1022 | 723.76 | 1.3940 | 0.827 | −0.0041 |
| 0.4166 | 0.1870 | 739.94 | 1.4016 | 0.813 | −0.0053 |
| 0.4031 | 0.2943 | 757.83 | 1.4123 | 0.809 | −0.0059 |
| 0.3979 | 0.4002 | 778.86 | 1.4242 | 0.714 | −0.0052 |
| 0.3991 | 0.4974 | 801.38 | 1.4363 | 0.588 | −0.0033 |
| 0.2910 | 0.1086 | 716.94 | 1.3947 | 0.723 | −0.0045 |
| 0.3278 | 0.1829 | 730.99 | 1.4009 | 0.791 | −0.0060 |
| 0.2949 | 0.3126 | 750.09 | 1.4131 | 0.690 | −0.0075 |
| 0.2961 | 0.4024 | 766.99 | 1.4225 | 0.638 | −0.0076 |
| 0.3010 | 0.5042 | 788.49 | 1.4345 | 0.587 | −0.0062 |
| 0.3167 | 0.5818 | 808.58 | 1.4452 | 0.532 | −0.0036 |
| 0.2203 | 0.1201 | 713.65 | 1.3961 | 0.638 | −0.0046 |
| 0.2068 | 0.2068 | 725.22 | 1.4032 | 0.619 | −0.0067 |
| 0.2029 | 0.3049 | 740.26 | 1.4121 | 0.595 | −0.0081 |
| 0.1933 | 0.4108 | 757.46 | 1.4223 | 0.553 | −0.0091 |
| 0.2144 | 0.4981 | 776.22 | 1.4322 | 0.540 | −0.0083 |
| 0.2111 | 0.5872 | 794.32 | 1.4428 | 0.493 | −0.0070 |
| 0.2047 | 0.6842 | 815.49 | 1.4556 | 0.434 | −0.0044 |
| 0.1087 | 0.0909 | 702.99 | 1.3944 | 0.435 | −0.0037 |
| 0.1017 | 0.1845 | 714.91 | 1.4014 | 0.421 | −0.0066 |
| 0.1065 | 0.2984 | 731.50 | 1.4107 | 0.440 | −0.0092 |
| 0.1136 | 0.3973 | 747.70 | 1.4199 | 0.435 | −0.0103 |
| 0.1118 | 0.4932 | 764.07 | 1.4298 | 0.417 | −0.0106 |
| 0.1089 | 0.6913 | 802.90 | 1.4531 | 0.376 | −0.0081 |
| 0.1000 | 0.6081 | 784.47 | 1.4425 | 0.383 | −0.0099 |
| 0.0965 | 0.8055 | 827.78 | 1.4686 | 0.268 | −0.0046 |
| 0.0434 | 0.0655 | 696.63 | 1.3929 | 0.253 | −0.0028 |
| 0.0417 | 0.0629 | 696.25 | 1.3926 | 0.245 | −0.0028 |
| 0.0806 | 0.0878 | 701.12 | 1.3941 | 0.367 | −0.0038 |
| 0.0772 | 0.2000 | 715.67 | 1.4030 | 0.335 | −0.0067 |
| 0.0703 | 0.2920 | 728.03 | 1.4103 | 0.346 | −0.0091 |
| 0.0675 | 0.3973 | 743.78 | 1.4197 | 0.353 | −0.0107 |
| 0.0747 | 0.4825 | 758.60 | 1.4283 | 0.350 | −0.0111 |
| 0.0634 | 0.5882 | 776.59 | 1.4397 | 0.310 | −0.0109 |
| 0.0668 | 0.6906 | 797.43 | 1.4520 | 0.284 | −0.0093 |
| 0.0660 | 0.7805 | 817.24 | 1.4639 | 0.234 | −0.0068 |
| 0.0578 | 0.8890 | 842.40 | 1.4794 | 0.171 | −0.0027 |

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{m} A_p (x_i - x_j)^p \quad (3)$$

In this equation $\Delta Q_{ij}$ is the excess property, $A_p$ is a parameter, and $m$ is the degree of the polynomial expansion.

The excess molar volumes for the ternary mixtures were correlated with the Cibulka equation (Cibulka, 1982):

$$\Delta Q_{123} = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1 x_2 x_3 (C_1 + C_2 x_1 + C_3 x_2) \quad (4)$$

where $\Delta Q_{12}$, $\Delta Q_{13}$, and $\Delta Q_{23}$ are the binary contributions expressed by the Redlich−Kister equation described above, and $C_1$, $C_2$, and $C_3$ are adjustable ternary parameters.

The unweighted least-squares method was used to fit the polynomials to the data. The F-test method was used to evaluate the number of adjustable parameters in correla-

**Table 4. Densities, $\rho$, Refractive Indices, $n_D$, Excess Molar Volumes, $V^E$, and Changes of Refractive Indices on Mixing, $\delta n_D$, for the Ternary System TBA (1) + Methylcyclohexane (3) + Isooctane (4) at 298.15 K**

| $x_1$ | $x_3$ | $\rho$/kg·m$^{-3}$ | $n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ |
|---|---|---|---|---|---|
| 0.9077 | 0.0442 | 769.76 | 1.3859 | 0.315 | −0.0008 |
| 0.7953 | 0.1012 | 759.20 | 1.3873 | 0.598 | −0.0016 |
| 0.6958 | 0.2008 | 757.24 | 1.3911 | 0.712 | −0.0014 |
| 0.6942 | 0.1048 | 746.00 | 1.3873 | 0.778 | −0.0021 |
| 0.6005 | 0.3009 | 756.51 | 1.3949 | 0.746 | −0.0011 |
| 0.6059 | 0.1998 | 745.93 | 1.3910 | 0.797 | −0.0018 |
| 0.6078 | 0.0925 | 734.95 | 1.3871 | 0.858 | −0.0024 |
| 0.5163 | 0.3834 | 755.53 | 1.3980 | 0.733 | −0.0010 |
| 0.5044 | 0.2957 | 744.99 | 1.3948 | 0.742 | −0.0014 |
| 0.5036 | 0.1977 | 734.99 | 1.3913 | 0.799 | −0.0019 |
| 0.5002 | 0.1025 | 725.69 | 1.3880 | 0.841 | −0.0022 |
| 0.4067 | 0.4954 | 755.17 | 1.4021 | 0.659 | −0.0008 |
| 0.3842 | 0.4048 | 743.67 | 1.3989 | 0.649 | −0.0012 |
| 0.4057 | 0.2886 | 734.55 | 1.3946 | 0.699 | −0.0018 |
| 0.4062 | 0.2021 | 726.63 | 1.3918 | 0.738 | −0.0019 |
| 0.3958 | 0.0981 | 716.79 | 1.3885 | 0.770 | −0.0020 |
| 0.3074 | 0.5883 | 754.23 | 1.4056 | 0.552 | −0.0007 |
| 0.2989 | 0.4978 | 744.54 | 1.4023 | 0.538 | −0.0011 |
| 0.3060 | 0.3995 | 736.01 | 1.3986 | 0.554 | −0.0017 |
| 0.3117 | 0.2896 | 726.78 | 1.3950 | 0.573 | −0.0018 |
| 0.2925 | 0.2002 | 717.58 | 1.3922 | 0.616 | −0.0019 |
| 0.3029 | 0.1094 | 711.04 | 1.3894 | 0.665 | −0.0018 |
| 0.2055 | 0.6929 | 754.32 | 1.4092 | 0.430 | −0.0007 |
| 0.1993 | 0.5936 | 744.25 | 1.4056 | 0.417 | −0.0012 |
| 0.2071 | 0.4954 | 735.99 | 1.4022 | 0.442 | −0.0016 |
| 0.1975 | 0.4972 | 735.36 | 1.4022 | 0.423 | −0.0016 |
| 0.2090 | 0.4020 | 728.15 | 1.3991 | 0.437 | −0.0017 |
| 0.2064 | 0.2933 | 719.02 | 1.3956 | 0.453 | −0.0018 |
| 0.2135 | 0.1987 | 712.06 | 1.3924 | 0.495 | −0.0020 |
| 0.1956 | 0.1020 | 703.75 | 1.3898 | 0.496 | −0.0016 |
| 0.1943 | 0.0940 | 702.98 | 1.3896 | 0.521 | −0.0016 |
| 0.1155 | 0.7922 | 755.28 | 1.4128 | 0.286 | −0.0006 |
| 0.1123 | 0.6833 | 744.77 | 1.4088 | 0.275 | −0.0012 |
| 0.1076 | 0.5949 | 736.60 | 1.4057 | 0.257 | −0.0015 |
| 0.0913 | 0.4989 | 727.34 | 1.4024 | 0.225 | −0.0019 |
| 0.0962 | 0.4022 | 720.05 | 1.3995 | 0.234 | −0.0017 |
| 0.0968 | 0.3041 | 712.65 | 1.3964 | 0.246 | −0.0018 |
| 0.1065 | 0.1974 | 705.35 | 1.3932 | 0.317 | −0.0016 |
| 0.0948 | 0.1009 | 698.00 | 1.3907 | 0.327 | −0.0011 |
| 0.0641 | 0.8903 | 759.75 | 1.4162 | 0.217 | −0.0005 |
| 0.0658 | 0.8425 | 755.34 | 1.4144 | 0.208 | −0.0008 |
| 0.0646 | 0.7454 | 746.34 | 1.4110 | 0.177 | −0.0012 |
| 0.0554 | 0.6478 | 737.05 | 1.4075 | 0.146 | −0.0016 |
| 0.0606 | 0.5482 | 729.24 | 1.4040 | 0.138 | −0.0020 |
| 0.0613 | 0.4456 | 721.21 | 1.4010 | 0.132 | −0.0017 |
| 0.0695 | 0.3430 | 714.04 | 1.3976 | 0.145 | −0.0019 |
| 0.0770 | 0.2312 | 706.13 | 1.3944 | 0.235 | −0.0015 |
| 0.0778 | 0.2313 | 706.28 | 1.3943 | 0.215 | −0.0016 |
| 0.0671 | 0.1485 | 699.96 | 1.3922 | 0.213 | −0.0012 |
| 0.0379 | 0.0505 | 692.14 | 1.3898 | 0.162 | −0.0007 |
| 0.0532 | 0.0494 | 692.75 | 1.3894 | 0.205 | −0.0009 |

tion polynomials. The fitting parameters of eqs 3 and 4 and the corresponding standard deviations obtained are given in Table 5 for the excess molar volumes and in Table 6 for the changes in refractive index. The standard deviations were calculated using the following expression:

$$\sigma = \left( \frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{calc})^2}{n_{DAT} - n_{PAR}} \right)^{1/2} \quad (5)$$

In this equation $z$ is the value of the property, $n_{DAT}$ is the number of experimental data, and $n_{PAR}$ is the number of parameters.

As can be expected, taking into account the behavior of binary mixtures, the ternary systems exhibit positive values of $V^E$ over most of the diagram (Figures 2a and 3a),

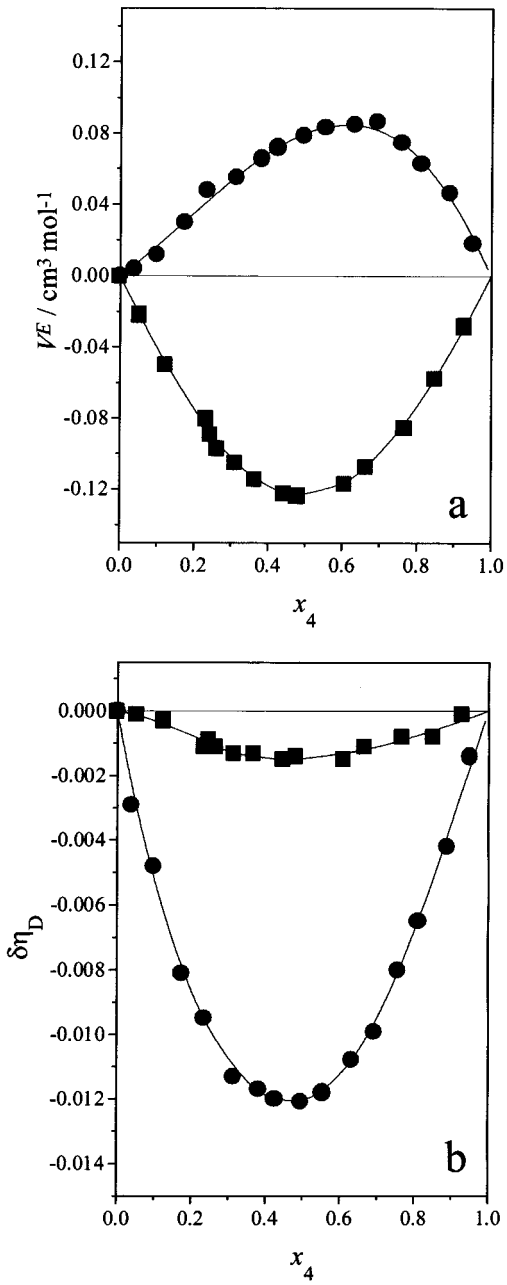


**Figure 1.** Excess molar properties at 298.15 K, as a function of composition, for (●) toluene (2) + isooctane (4) and (■) methylcyclohexane (3) + isooctane (4) systems: (—) Redlich−Kister equation; (a) $V^E$; (b) $\delta n_D$.

**Table 5. Parameters of Estimation of Eqs 3 and 4, and Standard Deviations at 298.15 K for $V^E$/cm$^3$·mol$^{-1}$**

| binary system | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $\sigma$ |
|---|---|---|---|---|---|---|
| MCH[a] + isooctane[b] | −0.496 | 0.005 | 0.078 | | | 0.002 |
| toluene + isooctane[b] | 0.323 | 0.171 | | | | 0.003 |
| TBA + toluene[c] | 2.146 | −0.451 | 0.731 | 0.704 | | 0.005 |
| TBA + MCH[a,c] | 2.695 | −1.075 | 0.711 | 1.812 | | 0.003 |
| TBA + isooctane[c] | 3.459 | −1.099 | 0.559 | 1.957 | 0.645 | 0.006 |

| ternary system | $C_1$ | $C_2$ | $C_3$ | $\sigma$ |
|---|---|---|---|---|
| TBA + toluene + isooctane[b] | 6.732 | −10.029 | −3.475 | 0.025 |
| TBA + MCH[a] + isooctane[b] | 3.727 | −9.653 | 0.174 | 0.027 |

[a] MCH: methylcyclohexane. [b] This paper. [c] Peña et al. (1999).

except for the ternary system TBA + methylcyclohexane + isooctane, where a change in sign occurs at compositions close to the binary system methylcyclohexane + isooctane.

**Table 6. Parameters of Estimation of Eqs 3 and 4, and Standard Deviations at 298.15 K for $\delta n_D$**

| system | $10^4A_0$ | $10^4A_1$ | $10^4A_2$ | $10^4A_3$ | $10^4A_4$ | $10^4\sigma$ |
|---|---|---|---|---|---|---|
| MCH[a] + isooctane[b] | −60 | 13 | 34 | −30 | | 1 |
| toluene + isooctane[b] | −483 | 59 | −14 | 98 | | 3 |
| TBA + toluene[c] | 7 | 35 | | | | 0.23 |
| TBA + MCH[a,c] | −5 | 44 | −14 | | | 0.6 |
| TBA + isooctane[c] | −81 | 33 | −35 | | | 0.4 |

| system | $C_1$ | $C_2$ | $C_3$ | $10^4\sigma$ |
|---|---|---|---|---|
| TBA + toluene + isooctane[b] | −0.0098 | 0.0748 | −0.0566 | <1 |
| TBA + MCH[a] + isooctaneb | −0.0187 | 0.0398 | −0.0037 | 2 |

[a] MCH: methylcyclohexane. [b] This paper. [c] Peña et al. (1999).

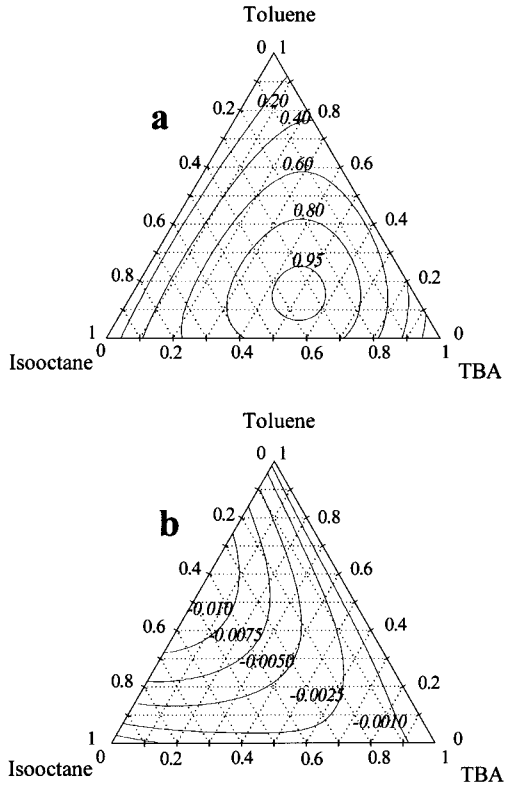


**Figure 2.** Curves of constant excess properties at 298.15 K for the ternary system TBA + toluene + isooctane: (a) $V^E$; (b) $\delta n_D$.

This ternary system also shows a maximum $V^E$ value corresponding to the binary system TBA + isooctane. Curves of constant $\delta n_D$ for ternary systems have been plotted in Figures 2b and 3b. All the experimental points measured present negative values of $\delta n_D$ (Tables 3 and 4). The TBA + toluene + isooctane mixture shows a minimum value for the binary system toluene + isooctane, while in the TBA + methylcyclohexane + isooctane ternary system the minimum is placed in the binary system TBA + isooctane, and moreover this ternary system shows a minimum valley for values of molar fraction of isooctane of 0.5.

Several methods to predict the physical properties of mixtures were applied to test their validities, which are compiled by Iglesias et at. (1996). The agreement between the experimental values of densities and refractive indices and the predicted ones is shown by standard deviation values, $\sigma$, calculated by eq 5 (in this case, $n_{PAR} = 0$) and given in Tables 7 and 8, respectively. The densities of

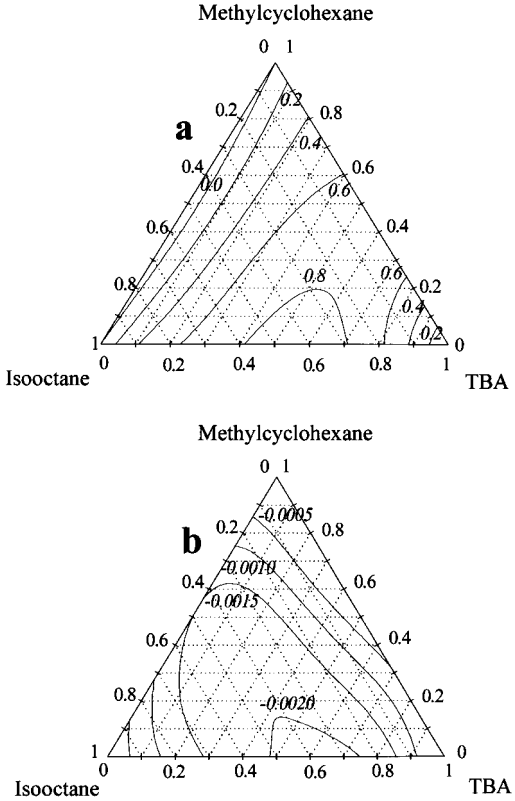


**Figure 3.** Curves of constant excess properties at 298.15 K for the ternary system TBA + methylcyclohexane + isooctane: (a) $V^E$; (b) $\delta n_D$.

**Table 7. Standard Deviations, $\sigma$, of the Experimental Results from Those Estimated for Density (kg·m$^{-3}$)[a]**

| | $\sigma$ | | | | | | |
|---|---|---|---|---|---|---|---|
| system | HBT | R | SDR | BT | Ri | N | YW |
| toluene + isooctane | 6.35 | 10.22 | 4.34 | 5.88 | 16.94 | 7.11 | 5.49 |
| MCH[b] + isooctane | 1.15 | 9.54 | 0.71 | 4.49 | 16.59 | 3.02 | 3.50 |
| TBA + toluene + isooctane | 2.90 | 7.95 | 6.52 | 6.12 | 26.16 | 6.24 | 4.69 |
| TBA + MCH[b] + isooctane | 4.00 | 10.60 | 8.35 | 51.8 | 29.5 | 1.48 | 0.42 |

[a] Methods: Hankinson−Brobst−Thomson (HBT), Rackett (R), Spencer and Danner modified Rackett (SDR), Bradford−Thodos (BT), Riedel (Ri), Narsinham (N), and Yen−Woods (YW). [b] MCH: Methylcyclohexane.

**Table 8. Standard Deviations, $\sigma$, of the Experimental Results from Those Estimated for Refractive Index[a]**

| | $\sigma$ | | | | | |
|---|---|---|---|---|---|---|
| system | LL | DG | AB | E | Nw | O |
| toluene + isooctane | 0.0003 | 0.0005 | 0.0005 | 0.0011 | 0.0012 | 0.0015 |
| MCH[b] + isooctane | 0.0005 | 0.0005 | 0.0005 | 0.0006 | 0.0004 | 0.0007 |
| TBA + toluene + isooctane | 0.0024 | 0.0031 | 0.0031 | 0.0017 | 0.0037 | 0.0015 |
| TBA + MCH[b] + isooctane | 0.0022 | 0.0021 | 0.0021 | 0.0020 | 0.0022 | 0.0019 |

[a] Methods: Lorentz−Lorenz (LL), Dale−Gladstone (DG), Arago−Biot (AB), Eykman (E), Newton (Nw), and Oster (O). [b] MCH: methylcyclohexane.

binary and ternary systems were estimated using the following methods: Hankinson−Brobst−Thompson (HBT), Rackett (R), Spencer and Danner modified Rackett (SDR), Bradford−Thodos (BT), Riedel (Ri), Narsinham (N), and Yen−Woods (YW). The parameter values needed in the HBT and SDR methods can be found in Hankinson and Thomson (1979) and Muñoz et al. (1999). The SDR method

**Table 9. Standard Deviations, $\sigma$, of the Experimental Results from Those Estimated for Different Empirical Equations, Using Binary Mixture Data**

| empirical equation | TBA + toluene + isooctane ($\sigma$) | | TBA + MCH + isooctane ($\sigma$) | |
|---|---|---|---|---|
| | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ | $V^E$/cm$^3$·mol$^{-1}$ | $\delta n_D$ |
| Kohler | 0.050 | 0.0005 | 0.070 | 0.0007 |
| Jacob−Fitzner | 0.062 | 0.0005 | 0.076 | 0.0007 |
| Colinet | 0.046 | 0.0005 | 0.069 | 0.0007 |
| Tsao−Smith[a] | 0.042 | 0.0012 | 0.075 | 0.0007 |
| Tsao−Smith[b] | 0.097 | 0.0005 | 0.124 | 0.0008 |
| Tsao−Smith[c] | 0.053 | 0.0011 | 0.131 | 0.0007 |
| Toop[a] | 0.051 | 0.0006 | 0.065 | 0.0007 |
| Toop[b] | 0.051 | 0.0008 | 0.071 | 0.0008 |
| Toop[c] | 0.063 | 0.0011 | 0.086 | 0.0007 |
| Scatchard[a] | 0.052 | 0.0006 | 0.066 | 0.0007 |
| Scatchard[b] | 0.058 | 0.0008 | 0.076 | 0.0008 |
| Scatchard[c] | 0.066 | 0.0011 | 0.094 | 0.0008 |

[a] TBA is the asymmetric component in the equation. [b] Toluene or MCH is the asymmetric component in the equation. [c] Isooctane is the asymmetric component in the equation.

gives the best estimation in binary systems whereas in TBA + toluene + isooctane and TBA + methylcyclohexane + isooctane ternary systems the HBT and Y methods present the smallest deviations. In all the cases the Ri method is the poorest predictive method. Refractive index estimation was carried out using the mixing rules proposed by Lorentz−Lorenz (LL), Dale−Gladstone (DG), Arago−Biot (AB), Eykman (E), Newton (N), and Oster (O). Predictions for binary systems are significantly better than those for ternary systems, and differences of one order of magnitude can be found. The Oster equation shows the best estimation in the two ternary systems whereas the lowest deviation in the toluene + isooctane and methylcyclohexane + isooctane mixtures was obtained by the LL and N rules, respectively.

Several methods for the estimation of excess properties of ternary and multicomponent solutions have been developed using additive binary contributions. A compilation of the equations for the different methods has recently been summarized (Muñoz et al., 1999). The standard deviations between experimental and predicted methods are given in Table 9. With respect to $V^E$, the Tsao−Smith and Toop equations, both with TBA as the asymmetric component, give the best results for the TBA + toluene + isooctane and TBA + methylcyclohexane + isooctane systems, respectively. On the other hand, with respect to $\delta n_D$, there are not great differences between the different equations, although it is worth noting that the poorest correlation for the system TBA + toluene + isooctane is given by equations in which isooctane is the asymmetric component. It has to be noted that the correlation equations give deviations significantly lower than those of the estimation equations, especially in the case of $V^E$. This fact clearly shows that, if information about binary systems is available, the use of the correlation methods of excess properties is more convenient than the use of the methods for direct estimation of these properties, since the correlation methods fit better the experimental results for multicomponent systems.

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