ORTJ0964

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Excess volumes of nine binary liquid mixtures of methyl n-alkanoates (C3 - C5) + propan-2-ol, + butan-2-ol, or + 2-methylpropan-1-ol at 298.15 K

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Excess molar volumes V^E for 9 binary mixtures formed by three methyl n-alkanoates (ethanoate, propanoate, and butanoate) with three alkanols (propan-2-ol, butan-2-ol, and 2-methylpropan-1-ol) have been determined from density measurements at 298.15 K . *All the V^E values are positive and decrease with the chain length of the n-alkanoate. For a given n-alkanoate, V^E increases in the order: 2-methylpropan-1-ol < propan-2-ol < butan-2-ol.*

1. INTRODUCTION

In continuation of our systematic experimental studies on the excess molar enthalpies H^E of mixtures containing alkanoates (esters) and alkanols (alcohols) [LOPM0860; ORTJ0954; ORTJ0956; SARF0880], we present here excess molar volume V^E measurements at 298.15 K for 9 binary mixtures formed by three methyl n-alkanoates (ethanoate, propanoate, and butanoate) with two alkan-2-ols (propan-2-ol and butan-2-ol) and an isoalkanol (2-methylpropan-1-ol). The excess molar enthalpies H^E of the same mixtures at 298.15 K have been reported previously [ORTJ0960].

The purpose of these investigations is to examine the effect of the molecular structure of isomeric alkanols on the properties of mixtures with n-alkanoates.

No V^E data are found in the literature for the systems of this work, except our preliminary measurements with butan-2-ol [ORTJ0965].

2. EXPERIMENTAL SECTION

2.1. Apparatus and Procedure

A vibrating tube densimeter, Model DMA 60 equipped with a cell model 602 (Anton Paar, Graz, Austria) was used. Temperature T was controlled to within 0.01 K with a Heto ultrathermostat and was measured by means of a calibrated Pt resistance thermometer against ITS-90 to within $\sigma(T)/K = 0.01$.

Density, ρ, was calculated from period of vibration, τ:

$$\rho = a + b\tau^2 \qquad (1)$$

Constants a and b were determined by calibrating the apparatus with doubly distilled and degassed H_2O, ρ(298.15 K)/kg m^{-3} = 997.043 [RIDJ0860], and nonane, from Fluka AG (Buchs, Switzerland) "purum" grade material, lot no. 74252, of stated purity > 99 mole %, ρ(298.15 K)/kg m^{-3} = 713.855, see [ORTJ0852]. Density measurements were taken with an accuracy of better than 0.01 kg m^{-3}.

Mixtures were prepared by mass. V^E was calculated from ρ of the mixtures and the densities ρ_i and molar masses M_i of the pure components i:

$$V^E = V - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (2)$$

$$V = (x_1M_1 + x_2M_2)/\rho \qquad (3)$$

The experimental uncertainties are $\sigma(x_1) = 0.0001$ and $\sigma(V^E)/10^{-9}m^3mol^{-1} < 3$.

2.2. Materials

$C_3H_6O_2$, Methyl ethanoate (Methyl acetate). Fluka AG (Buchs, Switzerland) "puriss" grade material of stated purity > 99 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D, 298.15 K) = 1.3589 (1.3589 [RIDJ0860]); ρ_i(298.15 K)/kg m^{-3} = 927.07 (927.9 [RIDJ0860]).

C_3H_8O, Propan-2-ol (Isopropanol) Fluka AG (Buchs, Switzerland) "puriss p.a." grade material of stated purity > 99.5 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D, 298.15 K) = 1.3751 (1.3752 [RIDJ0860]); ρ_i(298.15 K)/kg m^{-3} = 781.19 (781.26 [RIDJ0860]).

$C_4H_8O_2$, Methyl propanoate (Methyl propionate). Fluka AG (Buchs, Switzerland) "puriss" grade material of stated purity > 99 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D, 298.15 K) = 1.3745 (1.3775 at 293.15

K [LIDD1960]); ρ_i(298.15 K)/kg m^{-3} = 908.86 (909.0 [LIDD1940]).

$C_4H_{10}O$, Butan-2-ol (sec-Butanol). Fluka AG (Buchs, Switzerland) "puriss p. a." grade material of stated purity > 99.5 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification; n(D, 298.15 K) = 1.3953 (1.3939 [RIDJ0860]); ρ_i(298.15 K)/kg m^{-3} = 802.36 (802.41 [RIDJ0860]).

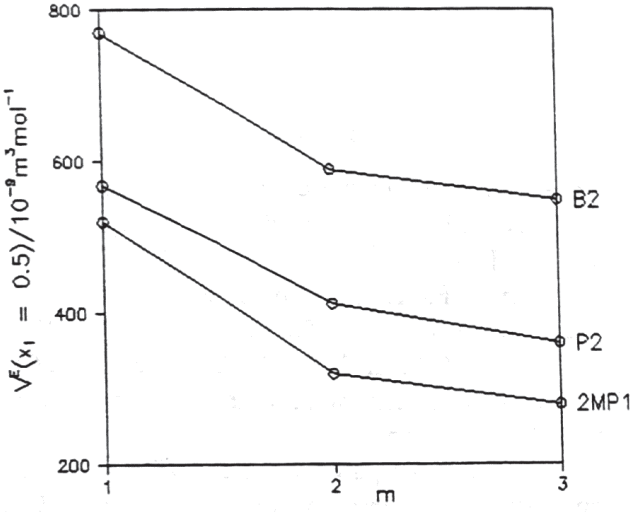

Figure 1. Equimolar excess volumes V^E at 298.15 K of propan-2-ol (P2), butan-2-ol (B2), and 2-methylpropan-1-ol (2MP1) + methyl ethanoate (m = 1), methyl propanoate (m = 2), or methyl butanoate (m = 3) (this work)

$C_4H_{10}O$, 2-Methylpropan-1-ol (Isobutanol). Fluka AG (Buchs, Switzerland) "puriss p. a." grade material of stated purity > 99.5 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification; n(D, 298.15 K) = 1.3939 (1.3939 [RIDJ0860]); ρ_i(298.15 K)/kg m^{-3} = 797.83 (797.8 [RIDJ0860]).

$C_5H_{10}O_2$, Methyl butanoate (Methyl butyrate). Fluka AG (Buchs, Switzerland) "puriss" grade material of stated purity > 99 mole % was degassed ultrasonically and dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification; n(D, 298.15 K) = 1.3849 (1.3878 at 293.15 K [LIDD1960]); ρ_i(298.15 K)/kg m^{-3} = 892.61 (892.6 [LIDD1940]).

3. RESULTS

The experimental V^E values of the 9 systems are tabulated and graphed in the Appendix and saved on disk as Standard ELDATA Files **ORTJ0964.001** through **ORTJ0964.009**.

The data were fitted to Eq. (4):

$$V^E_{calc}/\ m^3mol^{-1} = x_1x_2\Sigma A_i[x_1/(x_1 + kx_2)]^{i-1} \quad (4)$$

all points weighted equally. With an adjusted coefficient k and n = 3 coefficients A_i the standard deviations $\sigma(V^E)$, defined by Eq.(5):

$$\sigma(V^E) = [\Sigma(V^E_{calc} - V^E)^2/(N-n)]^{1/2} \quad (5)$$

where N is the number of experimental values, are less

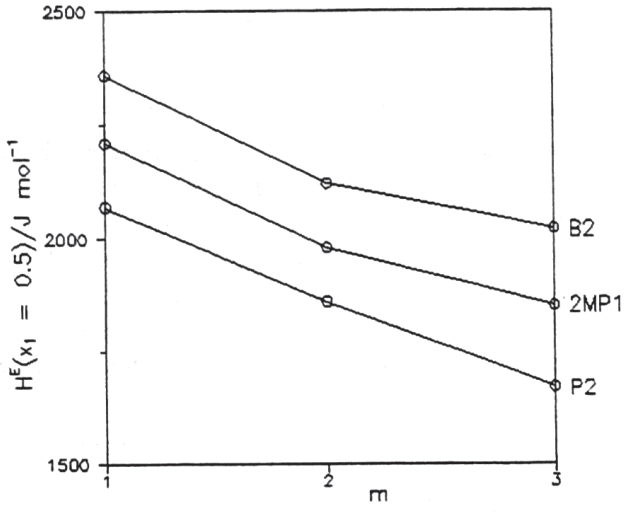

Figure 2. Equimolar excess enthalpies H^E at 298.15 K of propan-2-ol (P2), butan-2-ol (B2), and 2-methylpropan-1-ol (2MP1) + methyl ethanoate (m = 1), methyl propanoate (m = 2), or methyl butanoate (m = 3) [ORTJ0960]

than 3.1 10^{-9}m^{3}mol^{-1} (less than 1 % at x_1 = 0.5).

4. DISCUSSION AND CONCLUSIONS

All the V^E values are positive with fairly symmetrical V^E vs. x_1 curves. The change of the equimolar V^E with the chain-length of the n-alkanoate, for a given alkanol (Figure 1), is similar to the change of H^E (Figure 2) [ORTJ0960]. For a given alkanol, V^E decreases from methyl ethanoate to methyl propanoate. For a given n-alkanoate, V^E increases in the order: 2-methylpropan-1-ol < propan-2-ol < butan-2-ol and H^E increases in the order: propan-2-ol < 2-methylpropan-1-ol < butan-2-ol.

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Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.001**

State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid

Parameters: [P1] T/K, Temperature

Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume

Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_3H_6O_2$, Methyl ethanoate**
2. C_3H_8O , Propan-2-ol

[P1] = .298150E+03

[X1]	[Y1]
.613000E–01	.155100E–06
.156500E+00	.327100E–06
.221900E+00	.424100E–06
.271200E+00	.473400E–06
.308100E+00	.500700E–06
.405600E+00	.553100E–06
.468600E+00	.562700E–06
.504700E+00	.568100E–06
.552500E+00	.553700E–06
.630300E+00	.518500E–06
.707300E+00	.468900E–06
.746100E+00	.432000E–06
.849500E+00	.293700E–06
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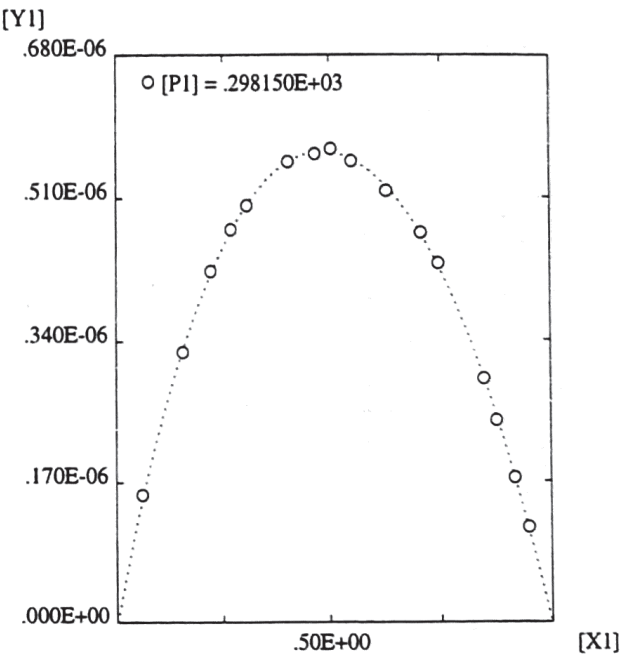
.949300E+00	.115600E–06



Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.002**

State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid

Parameters: [P1] T/K, Temperature

Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume

Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_3H_6O_2$, Methyl ethanoate**
2. $C_4H_{10}O$, Butan-2-ol

[P1] = .298150E+03

[X1]	[Y1]
.878000E–01	.275000E–06
.132500E+00	.385200E–06
.172100E+00	.474000E–06
.225400E+00	.574100E–06
.270100E+00	.634400E–06
.312500E+00	.689800E–06
.408700E+00	.757000E–06
.472800E+00	.768500E–06
.514500E+00	.772600E–06
.590900E+00	.740600E–06
.626900E+00	.717600E–06
.687500E+00	.667500E–06
.707400E+00	.638200E–06
.742200E+00	.595100E–06
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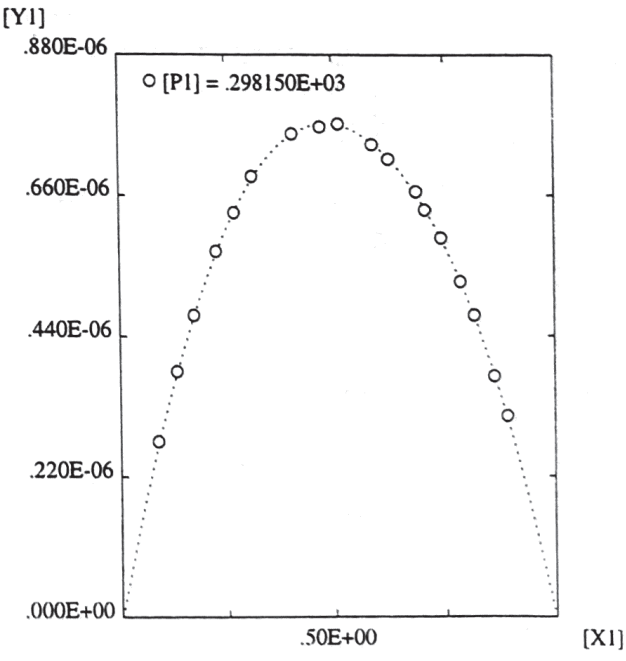

Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.003**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_3H_6O_2$, Methyl ethanoate**
2. $C_4H_{10}O$, 2-Methylpropan-1-ol

[P1] = .298150E+03

[X1]	[Y1]
.557000E–01	.136200E–06
.167500E+00	.326500E–06
.263600E+00	.423300E–06
.346800E+00	.484900E–06
.397300E+00	.507100E–06
.439100E+00	.514100E–06
.470400E+00	.522800E–06
.507100E+00	.520200E–06
.559900E+00	.518800E–06
.632000E+00	.496900E–06
.677100E+00	.464200E–06
.714200E+00	.436100E–06
.742400E+00	.412800E–06
.769800E+00	.386700E–06
.807600E+00	.345200E–06
.860100E+00	.271500E–06
.889000E+00	.221400E–06
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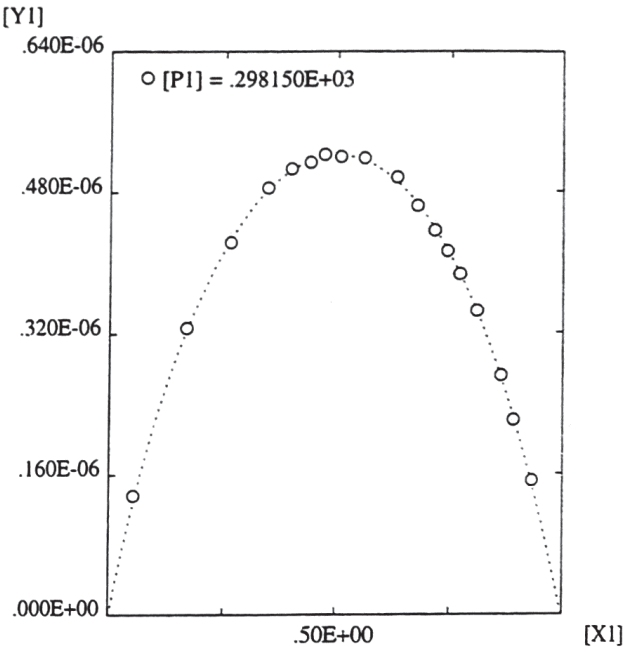
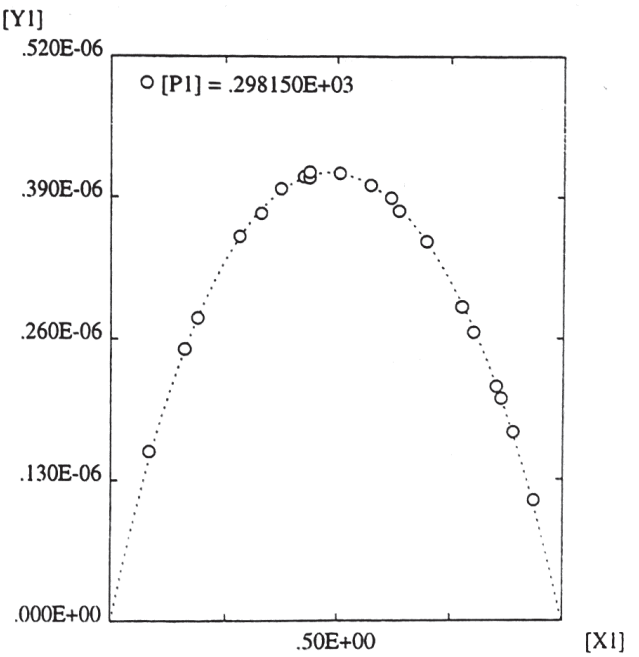


Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.004**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. C_3H_8O , Propan-2-ol**
2. $C_4H_8O_2$, Methyl propanoate

[P1] = .298150E+03

[X1]	[Y1]
.844000E–01	.156700E–06
.162300E+00	.251100E–06
.189300E+00	.279500E–06
.281800E+00	.354200E–06
.330400E+00	.375600E–06
.374100E+00	.398200E–06
.425600E+00	.409400E–06
.438300E+00	.408500E–06
.438300E+00	.414000E–06
.505600E+00	.412700E–06
.574700E+00	.401300E–06
.620100E+00	.389600E–06
.636600E+00	.378200E–06
.697400E+00	.349700E–06
.773500E+00	.289800E–06
.799700E+00	.266400E–06
.849500E+00	.217100E–06
.859700E+00	.205800E–06
.886800E+00	.174500E–06
.933700E+00	.111600E–06



Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.005**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. C_3H_8O , Propan-2-ol**
2. $C_5H_{10}O_2$, Methyl butanoate

[P1] = .298150E+03

[X1]	[Y1]
.534000E-01	.917000E-07
.122200E+00	.177000E-06
.173200E+00	.230700E-06
.219300E+00	.274000E-06
.299300E+00	.316500E-06
.366100E+00	.347300E-06
.407200E+00	.357300E-06
.454900E+00	.360200E-06
.492400E+00	.361900E-06
.522500E+00	.359700E-06
.582000E+00	.345200E-06
.604200E+00	.336000E-06
.649900E+00	.323800E-06
.692800E+00	.299000E-06
.754700E+00	.260800E-06
.796800E+00	.231300E-06
.821300E+00	.209600E-06
.852300E+00	.182800E-06
.880400E+00	.156600E-06
.916200E+00	.118100E-06
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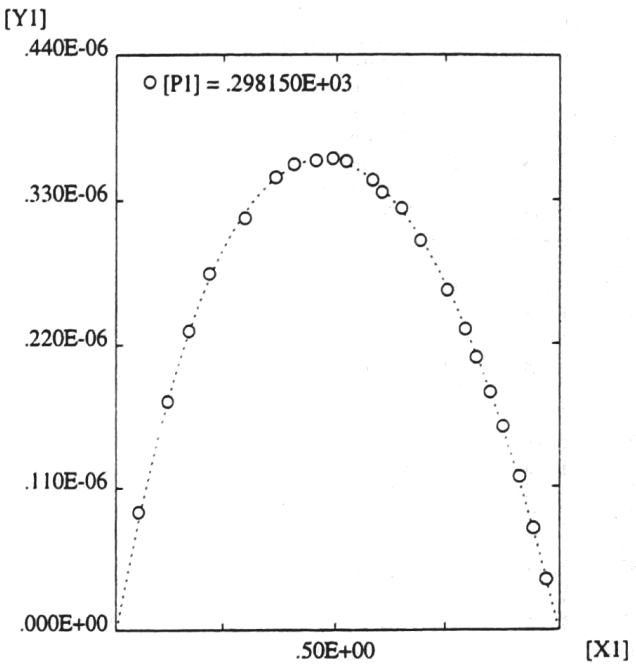

Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.006**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_4H_8O_2$, Methyl propanoate**
2. $C_4H_{10}O$, Butan-2-ol

[P1] = .298150E+03

[X1]	[Y1]
.359000E-01	.926000E-07
.104000E+00	.242600E-06
.108300E+00	.252200E-06
.145500E+00	.317400E-06
.178300E+00	.365000E-06
.273600E+00	.486300E-06
.310400E+00	.520400E-06
.349800E+00	.541800E-06
.442400E+00	.582000E-06
.500500E+00	.589900E-06
.551700E+00	.575800E-06
.592600E+00	.567500E-06
.610300E+00	.553600E-06
.674200E+00	.511800E-06
.708200E+00	.487900E-06
.743600E+00	.449600E-06
.792600E+00	.393100E-06
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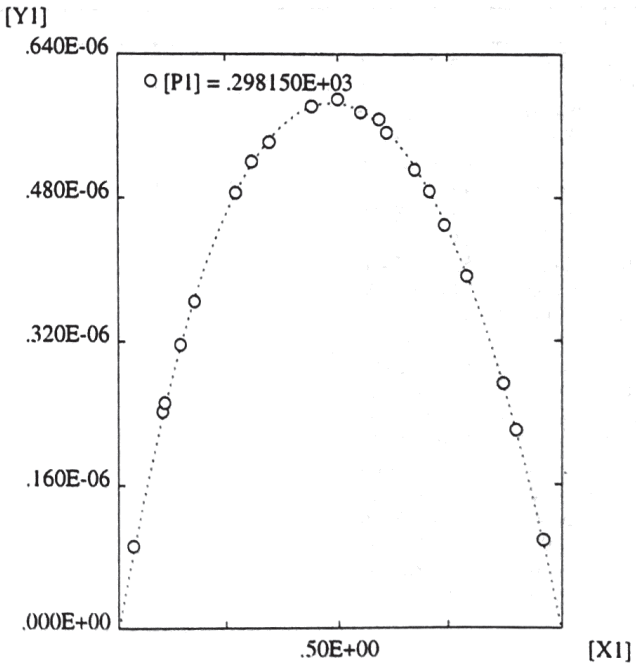
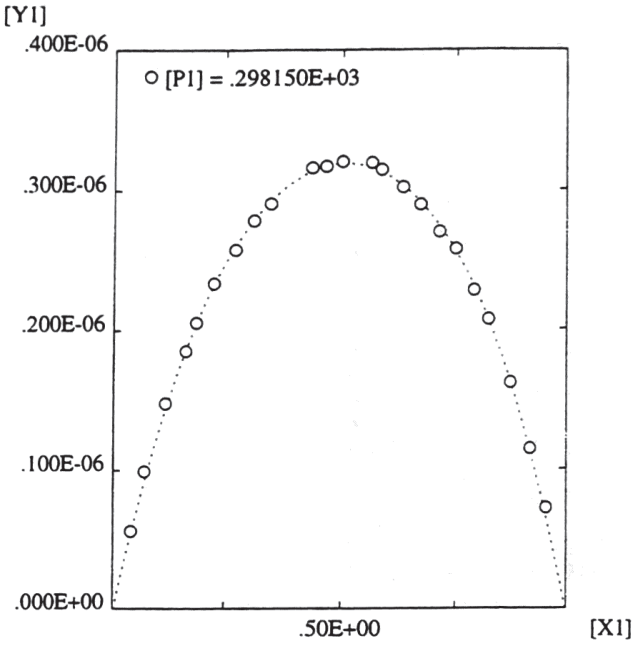


Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.007**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_4H_8O_2$, Methyl propanoate**
2. $C_4H_{10}O$, 2-Methylpropan-1-ol

[P1] = .298150E+03

[X1]	[Y1]
.413000E-01	.560000E-07
.716000E-01	.991000E-07
.117900E+00	.147800E-06
.163600E+00	.185400E-06
.186100E+00	.205600E-06
.225400E+00	.233500E-06
.272400E+00	.257900E-06
.311300E+00	.278800E-06
.347100E+00	.290700E-06
.434900E+00	.316000E-06
.465000E+00	.317200E-06
.500100E+00	.320600E-06
.565100E+00	.319600E-06
.586800E+00	.314700E-06
.633500E+00	.302200E-06
.671400E+00	.289700E-06
.712700E+00	.270300E-06
.748600E+00	.257700E-06
.789700E+00	.228400E-06
.822900E+00	.207100E-06
.873200E+00	.161800E-06
.917400E+00	.114500E-06
.955100E+00	.725000E-07

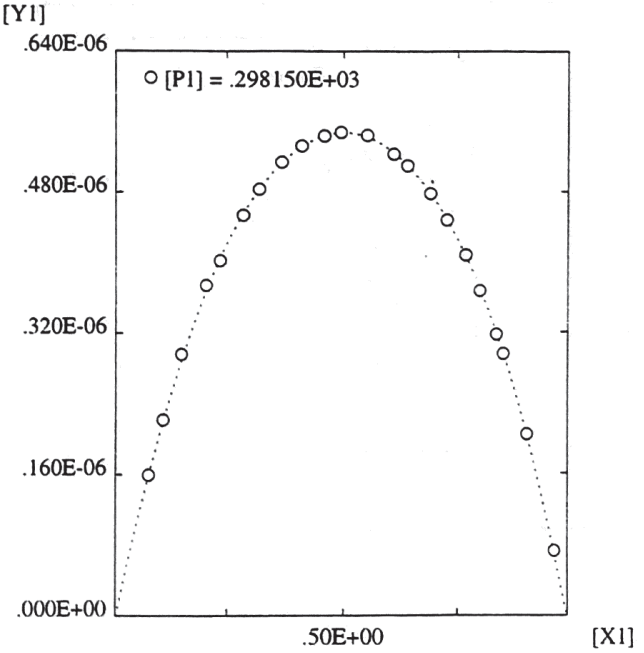


Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.008**
State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid
Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume
Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_4H_{10}O$, Butan-2-ol**
2. $C_5H_{10}O_2$, Methyl butanoate

[P1] = .298150E+03

[X1]	[Y1]
.744000E-01	.159500E-06
.107100E+00	.221900E-06
.147400E+00	.296600E-06
.203300E+00	.375100E-06
.234400E+00	.402600E-06
.285100E+00	.454200E-06
.320000E+00	.483700E-06
.368500E+00	.514600E-06
.410500E+00	.533200E-06
.459200E+00	.544700E-06
.494100E+00	.548200E-06
.551700E+00	.545200E-06
.609900E+00	.523400E-06
.640200E+00	.511100E-06
.689900E+00	.479100E-06
.726300E+00	.448600E-06
.767400E+00	.408800E-06
.798800E+00	.367300E-06
.837500E+00	.317700E-06
.852400E+00	.295700E-06
.907800E+00	.204100E-06
.971300E+00	.736000E-07



Property Code: [VMSL1000] VOLUMETRIC PROPERTIES OF LIQUID MIXTURES AND SOLUTIONS **ORTJ0964.009**

State: Two-component system, single-phase liquid
Pure component 1, liquid
Pure component 2, liquid

Parameters: [P1] T/K, Temperature
Variables: [X1] x_1/-, Mole fraction of component 1
[Y1] V^E/m^{3}mol^{-1}, Molar excess volume

Method: Calculation of V^E from low-pressure density measurements at variable x_1 and constant T

Components: **1. $C_4H_{10}O$, 2-Methylpropan-1-ol**
2. $C_5H_{10}O_2$, Methyl butanoate

[P1] = .298150E+03

[X1]	[Y1]
.534000E-01	.711000E-07
.101200E+00	.121900E-06
.164600E+00	.172700E-06
.202800E+00	.203100E-06
.241500E+00	.220000E-06
.285300E+00	.241900E-06
.324200E+00	.259600E-06
.449800E+00	.282400E-06
.492200E+00	.283800E-06
.535100E+00	.283400E-06
.573300E+00	.278900E-06
.610600E+00	.273100E-06
.699000E+00	.245400E-06
.723600E+00	.237000E-06
.766300E+00	.212800E-06
.796000E+00	.197100E-06
.833000E+00	.172800E-06
.864200E+00	.148500E-06
.903600E+00	.116300E-06
.940900E+00	.752000E-07
.969800E+00	.387000E-07