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By
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EXPERIMENTAL AND PREDICTED VOLUMETRIC AND OPTICAL PROPERTIES OF MULTI-COMPONENT MIXTURES CONTAINING FLUORINATED HYDROCARBONS, ETHERS, AND ALCOHOLS AT A TEMPERATURE OF 298.15 K

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CONTENTS

EXPERIMENTAL AND PREDICTED VOLUMETRIC AND OPTICAL PROPERTIES OF MULTI-COMPONENT MIXTURES CONTAINING FLUORINATED HYDROCARBONS, ETHERS, AND ALCOHOLS AT A TEMPERATURE OF 298.15 K

Abstract:

The oxygenated hydrocarbons such as ethers are non-toxic and non- polluting materials. They are involved in the gasoline production processes, improving combustion and reducing emissions. The fluorohydrocarbons (HFCs) are also non-toxic, non-flammable, and have no potential for the destruction of the ozone layer, and so are suitable replacements for chlorofluorohydrocarbons (CFCs).

In this work, new data are reported of the volumetric and optical properties for binary and ternary systems containing: diisopropyl ether, tert-butyl methyl ether, tert-amyl methyl ether, fluorobenzene, α,α,α-trifluorotoluene, 2,2,2-trifluoroethanol, toluene, benzene, acetone, and ethanol at 298.15 K and 101 kPa .

The experimental excess properties of fourteen binary and four ternary systems are well fitted to and predicted by various empirical equations.

The examined thermodynamic properties help to compute and correlate the molecular packing and energetic effects among the mixture components and to develop and test models and theories of associated systems in the liquid state.

No data are available in literature for most of the studied systems despite their great theoretical and technical importance.

MESURE ET CORRELATION DES PROPRIÉTÉS VOLUMIQUES ET OPTIQUES DES MELANGES MULTI-COMPOSANT DES HYDROFLUOCARBONES, ETHERS, ET ALCOOLS A TEMPERATURE 298.15 K

Résumé:

Les hydrocarbones oxygénés tels que les éthers sont des composants non-toxiques et non-polluants. Ils sont impliqués dans les procédés de production des combustibles et carburants, pour améliorer la combustion et réduire émission de monoxyde de carbone. Les fluorohydrocarbones (HFCs) sont aussi non toxiques, inflammables, et ont un potentiel minime en vers la destruction de la couche d'ozone, et donc ils sont des remplaçant convenables pour chlorofluoro-hydrocarbones (CFCs).

Dans ce travail, nous reportons des nouvelles données expérimental des propriétés volumiques et optiques pour les systèmes binaires et ternaire contenant: diisopropyl ether, tert-butyl methyl ether, tert-amyl methyl ether, fluorobenzene, α,α,α-trifluorotoluene, 2,2,2-trifluoroethanol, toluene, benzene, acetone, et ethanol à 298.15 K et 101 kPa .

Les propriétés thermodynamiques d'excès des systèmes étudiés sont lissées et corrélées par plusieurs équations empiriques.

Les propriétés thermodynamiques examinées aident à mieux comprendre l'empilement moléculaire et les effets énergétiques parmi les composants des mélanges, enfin de développer et tester les modèles et les théories des solutions associés à l'état liquide.

La plupart des systèmes de ce travail sont très peu étudiés ailleurs.

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Finally, I thank my parents and my family for their continuous encouragement through this work.

Kenza LOURDANI,

4th October 2006

Glossary

List of symbols :

A, B, C densimeter constants

A_P, B_P, C_P polynomial coefficients

C number of components.

F variance (degree of freedom)

G Gibbs function

H enthalpy

M molecular mass

N number of data points

N_P number of fitting parameters

S entropy

T temperature

V volume

X thermodynamic function

X mixing property

c velocity of the light in vacuum

m mass

n amount of substance, refractive index

n degree of fitting parameters

p pressure

v velocity of light in solvent

x mole fraction

x' estimated composition

Abbreviations :

cal. calculated

const. constant

eq. equation

exp. experimental

id. ideal

max. maximum

min. minimum

mix. mixing

OF objective function

Greek letters:

ϕ number of phases

ρ density

τ oscillation period

σ_s standard deviation

Δ change

Δ_{ijk} ternary contribution

Δ_{ijk} difference between calculated and experimental value

Lower scripts:

A, B, C, component

T temperature

i, j, k components

m molar

m,i partial molar property

n polynomial degree

p pressure

x mole fraction

Upper scripts

E excess property

n polynomial degree

r real

* pure component

∞ infinite dilution

List of tables:

Table in the text:

List of figures:

Figures in the text:

CHAPTER 1

INTRODUCTION

Environmental protection rules has led to the use of green chemicals; such as tertiary ethers and light alcohols as oxygenating agents in gasoline technology in order to improve combustion and reduce emissions; since ethers and alcohols are non-toxic and non-polluting materials,[1-5] therefore; they are of great industrial interest.

Ethers are aprotic molecules; so they do not associate in the pure state through hydrogen bonding, whereas alcohols are strongly self-associated.[6,7] Mixtures of alcohols and ethers form complex systems, yet they are of great importance due to their wide use in applied chemical industries. The complexity of these mixtures is a consequence of the presence of various modes of formation/breaking of specific intermolecular interactions due to mixing.[8-13]

The fluoro-hydrocarbons (HFC's) are safe green chemicals, and do not have any potential for the destruction of ozone layer, and so are suitable replacements for CFC's with an acceptable short enviromental life time and find applications in refrigeration, fuels, and medicine.[14]

The HFC's and their mixtures show very characteristic thermodynamic properties, due to their highly polar C─ F bonds.

2,2,2-trifluoroethanol (TFE) and tetraethylene glycol dimethyl ether (TEGDME) have been proposed as a working pair in absorption heat pumps and heat transformers.[15-17] The thermal properties of the alcohols and their mixtures with other compounds are mainly influenced by the hydrogen bonding properties of the former. The better fluid absorbent is found to be an electron donor, which can form strong hydrogen bonds with atoms of high electron density.[18,19] In bioengineering TFE is used to generate and stabilize some configurational states of proteins.[20,21] Also TFE is important solvent for palladium catalyzed polymerization reactions.[22]

Water and 2,2,2-Trifluoroethanol have high chemical, dynamic, and thermal stabilities, and their mixtures have been identified and proposed for use in Rankine engines for terrestrial and space applications.[11,23]

Tert-butyl methyl ether (TBME) is easily dissolved in water, and is very resistant to microbial decomposition. Therefore cause severe pollution to water streams and reservoirs, whereas diisopropyl ether (DIPE) is partially miscible in water and can replace TBME in fuel treatments and production.[24] While di-n-butyl ether (DBE) find application in extractive distillation of azeotropic mixtures.[25]

Density is related to volume, and is an important thermodynamic property in all equations of state of pure components and mixtures. Liquid densities are required in many process design in industry. The design of condensers and reboilers, the sizing of storage vessels, the calculation of distillation columns efficiency, material and energy balances including liquids, and phase equilibria.[26]

Excess molar volumes reflect the differences in molecular size, shape of its molecules, and the various types of intermolecular interactions upon mixing, in which stronger or weaker specific interactions, mainly due to the different strengths of interactions between unlike molecules and this can be explained by symmetry and sign, and values of mixing.[27-31]

Refractive indices are indirectly related to dispersion forces between molecules which are due to instantaneous dipole formation as a result of oscillations of electron clouds around the cores of the molecules.[32]

The present work is dealing with the measurement and prediction of binary excess molar volumes V^E_m and change in refractive indices $\Delta_{mix}n$ and ternary excess molar volumes at pressure 101 kPa and temperature 298.15 K. The chemical components investigated in this study are: diisopropyl ether, tert-butyl methyl ether, tert-amyl methyl ether, fluorobenzene, α,α,α-trifluorotoluene, 2,2,2-trifluoroethanol, toluene, benzene, acetone, and ethanol. These chemicals all have important technological applications; such as combustion engine fuels, pharmaceutical and agriculture, and food industries, and separation processes.

The examined thermodynamics properties help to compute and correlate the molecular packing and energetic effects among the mixture components and to develop and test models and theories of associated systems in the liquid state.

No literature data are available to us for most of the studied systems despite their great theoretical and technical importance.

CHAPTER 2

FUNDAMENTAL THERMODYNAMICS
OF LIQUID MIXTURES

Introduction:

Mixtures are treated using several types of concentrations such as mole fraction or composition x: $x_i = n_i / \sum_i n_i$, and fulfil: $\sum_i x_i = 1$, where n_i is the amount of substance of component i in the mixture. The molar thermodynamic functions X_m are dependent on temperature T, pressure p, and composition x_i: X_m = f (T, p, x_i, …), and so the change in a molar thermodynamic function are:

$$dX_m = (\partial X_m / \partial T)_{P,xi}\, dT + (\partial X_m / \partial p)_{T,xi}\, dp + \sum (\partial X_m / \partial x_i)_{T,p,xj \neq xi} dxi \ , \qquad (2.\ 1)$$

where $(\partial X_m/\partial x_i)_{T,\ p,\ xj \neq xi}$ is the partial molar function $X_{m,i}$ with: X = Gibbs function G, enthalpy H, entropy S or volume V.

At constant temperature and pressure, the change in X_m is:

$$dX_m = \sum_i (\partial X_m / \partial x_i)_{T,p,xj \neq xi}\, dx_i$$
$$dX_m = \sum_i X_{m,i}\, dx_i \qquad (2.\ 2)$$

It follows that the molar function of a mixture is defined as:

$$X_m = \sum_i x_i X_{m,i} . (T, p, const.) \qquad (2.\ 3)$$

Differentiating equation (2. 3) gives:

$$dX_m = \sum_i X_{m,i}\, dx_i + \sum_i x_i\, dX_{m,i} \qquad (2.\ 4)$$

Equations (2. 2) and (2. 4) give the Gibbs-Duhem relation:

$$\sum_i x_i\, dX_{m,i} = 0 \text{ , (T, p, const.)} \qquad (2.\ 5)$$

The Gibbs-Duhem equation (2. 5), valid for any molar thermodynamic property X_m in a homogeneous phase.

The Gibbs phase rule gives the variance (degree of freedom F) of multi-component C, multi phase ϕ of mixtures as: F = C + 2 - ϕ.

The change of the molar function of mixing $\Delta_{mix}X_m$ due to mixing of several component is given by the following expression:

$$\Delta_{mix} X_m(T,p,x) = X_m(T,p,x) - \sum_i x_i X^*_{m,i}(T,p,x), \qquad (2.\ 6)$$

where X_m is the molar function of mixture, and $X^*_{m,i}$ is the molar function of pure component i. The property changes of mixing for the ideal mixtures are:

$$\Delta_{mix} G^{id}_m = RT\sum_i x_i \ln x_i \qquad (2.\ 7)$$

$$\Delta_{mix} S^{id}_m = -R\sum_i x_i \ln x_i \qquad (2.\ 7)$$

$$\Delta_{mix} H^{id}_m = 0, \qquad \Delta_{mix} V^{id}_m = 0 \qquad (2.\ 7)$$

The partial molar function of mixing $X_{m,i}$ is given by:

$$X_{m,i} = \Delta_{mix} X^r_m + \left\{\frac{\partial\left(\Delta_{mix} X^r_m\right)}{\partial x_i}\right\}_{T,P,xj} - \sum x_k \left\{\frac{\partial\left(\Delta_{mix} X^r_m\right)}{\partial x_k}\right\}_{T,p,xj} \qquad (2.\ 8)$$

Most multi-component mixtures do not generally behave ideally and have real behaviour

In real mixtures, the deviation from ideal behaviour is expressed by many thermodynamic quantities, particularly by excess properties.

The excess thermodynamic property of a mixture is defined as to the difference between the real property and the property when the system behaves ideally at the same conditions of (T, p, x):

$$X^E_m(T,p,x) = \Delta X^r_{mix}(T,p,x) - \Delta_{mix} X^{id}_m(T,p,x) \qquad (2.\ 9)$$

The fundamental excess molar functions are:

$$G^E_m = \Delta_{mix} G^r_m - RT\sum_i x_i \ln x_i \qquad (2.\ 10)$$

$$S^E_m = \Delta_{mix} S^r_m + R\sum_i x_i \ln x_i \qquad (2.\ 10)$$

$$H^E_m = \Delta_{mix} H^r_m \qquad (2.\ 10)$$

$$V^E_m = \Delta_{mix} V^r_m \qquad (2.\ 10)$$

The partial excess molar function $X^E_{m,i}$ of a component in a multi-component mixture is defined as:[33]

$$X^E_{m,i} = X^E_m + \left(\frac{\partial X^E_m}{\partial x_i}\right)_{T,P,x_j} - \sum x_k \left(\frac{\partial X^E_m}{\partial x_k}\right)_{T,p,xj} \qquad (2.\ 11)$$

For multi-component mixtures the partial excess molar volumes at infinite dilution $V^{E^\infty}_i$ is:

$$X^{E\infty}_{m,i} = \lim x_{i\to 0}\left(X^E_m + \left(\frac{\partial X^E_m}{\partial x_i}\right)_{T,P,x_j} - \sum x_k \left(\frac{\partial X^E_m}{\partial x_k}\right)_{T,p,xj}\right) \qquad (2.\ 12)$$

Excess functions of binary mixtures:

A single phase binary liquid mixtures at conditions of (T, p) constant has one degree of freedom, so the composition *x* is the only variable in the analytical expressions of the excess molar functions X^{E}_{m}. The excess molar functions of binary mixtures are well fitted using several types of the empirical equations, however the Redlich-Kister equation is still the most efficient expression to correlate excess molar functions of binary mixtures. The Redlich-Kister equation is:[34]

$$X^{E}_{m,ij} = x_i\, x_j \sum_{p=0}^{n} B_p\, (x_j - x_i)^p , \qquad (2.\ 13)$$

with the component j is added to component i and B_P are fitting parameters.

For binary mixtures, the expressions for the partial excess molar quantities and partial excess molar quantities at infinite dilution can be determined from equations (2. 11) to (2. 13).

Excess function of ternary mixtures:

The ternary liquid mixtures (x_AA + x_BB + x_CC) in thermodynamic study are more complicated than the binary liquid mixtures from the theoretical and experimental aspects.

The variance of a ternary mixture according to the equation (2. 8) is: $F = 5 - \phi$. For a homogeneous ternary mixture the variance becomes: F = 4, that is to say, in graphical representation this is in four dimensional system with independent variables such as:

(T, p, x_A, x_B), this is impractical graphical representation. In the case of constant pressure the ternary liquid mixture has tri-variant with independent variable such as: (T, x_A, x_B), this is possible three dimensional graphical representations.

The representation of graph in three and four dimensional are not discussed in this work.

At constant pressure and temperature, with a single phase the composition x_A, x_B, x_C of the ternary liquid mixture are represented in equilateral triangular coordinates which, each side of the equilateral triangular diagram represents a binary mixtures. This is a simple graphical representation.

The difference between experimental and predicted results of excess function of a ternary mixture are:

$$\Delta_{ijk} X^{E}_{m} = X^{E}_{m,ijk}\ (\text{exp.}) - X^{E}_{m,ijk}\,(\text{cal.}) \qquad (2.\ 14)$$

And can be written $\Delta_{ijk} X^{E}_{m}$ according to the following expression:

$$\Delta_{ijk} X^{E}_{m} = x_i x_j x_k \Delta_{ijk} \qquad (2.\ 15)$$

The experimental excess properties of ternary mixtures $X^{E}_{m,ijk}$ are well represented by binary mixing data (eq. 2. 13) and ternary contribution term $\Delta_{ijk}(x_i, x_j)$:

$$X^{E}_{m,ijk} = \sum_{j>i} X^{E}_{m,ij}(x_i, x_j) + x_i x_j x_k \Delta_{ijk}, \quad (2.\ 16)$$

where $X^{E}_{m,ij}(x_i, x_j)$ is the excess function of a binary mixture.

There are various types of empirical equations to estimate ternary contribution term Δ_{ijk} and are summarized in the following:

Polynomial series:[35]

$$\Delta_{ijk} = \sum_{n} \sum_{j>i} C_{P,ij} (x_i - x_j)^n, \quad (2.\ 17)$$

Nagata-Tamura polynomial:[36-38]

$$\Delta_{ijk} = \sum_{n} \sum_{j>i} C_{P,ij} x_i^n x_j^{n-1}, \quad (2.\ 18)$$

and :

$$\Delta_{ijk} = \sum_{n} C_{P,ij} (1 - 2x_i)^{n-1}, \quad (2.\ 19)$$

Lopez *et al.*:[39]

$$\Delta_{ijk} = \sum_{n} \sum_{j>i} C_{P,ij} x_i^n x_j, \quad (2.\ 20)$$

Cibulka:[40]

$$\Delta_{ijk} = c_0 + c_i x_i + c_j x_j, \quad (2.\ 21)$$

where $C_{P,ij}$ are fitting parameters.

The Cibulka equation is extensively used by researchers, because in mathematics is simple to solve.

For ternary mixtures, the expressions for the partial excess molar quantities and partial excess molar quantities at infinite dilution can be determined from equations (2. 11), (2. 12), and (2. 16).

Prediction of ternary properties from experimental binary data:

Assuming no ternary contribution effects $\Delta_{ijk} = 0$, the excess properties of ternary mixtures are well predicted from binary solution data with the expression:[41]

$$X^{E}_{m,ijk} = \sum_{i<j} \frac{x_i x_j}{x'_i x'_j} X^{E}_{m,ij}(x'_i, x'_j), \quad (2.\ 22)$$

where $X^{E}_{m,ij}(x'_i, x'_j)$ is the excess function of the binary mixture at (x'_i , x'_j); in which ($x'_i + x'_j$) = 1. For a ternary mixture, x'_i and x'_j may be obtained from a triangular diagram by projecting the point representing the ternary mixture onto the corresponding binary axis, using two different forms symmetric or asymmetric criteria of binary contribution to the ternary value.

In these rules, symmetry is understood to be the contribution of the three binaries to the ternary excess, all three of which contribute equally. Asymmetry is understood to indicate the different individual contribution of one of the binaries, the latter being normally attributed to polar components.[42-44]

The empirical equations of excess thermodynamic function are summarised in the following:

Redlich-Kister:[34]
$$X^{E}_{m,ijk} = \sum_{j>i} X^{E}_{m,ij}(x_i', x_j') \ , \qquad (2.\ 23)$$
$$x_i' = x_i$$

Scatchard *et al.* modified equation (2.23) for the mixtures of a polar substance with two non-polar liquids, obtaining another asymmetric equation (2. 24):

Scatchard *et al.*:[45]
$$X^{E}_{m,ijk} = \left\{ \sum_{j>i} \frac{x_j}{x_i'} X^{E}_{m,ij}(x_i, x_i') \right\} + X^{E}_{m,jk}(x_j, x_k), \qquad (2.\ 24)$$
$$x_i' = (1 - x_i)$$

Tsao and Smith proposed an unsymmetrical equation (2. 25):

Tsao-smith:[46]
$$X^{E}_{m,ijk} = \left\{ \sum_{j>i} \frac{x_j}{x_i'} X^{E}_{m,ij}(x_i, x_i') \right\} + x_i' X^{E}_{m,jk}(x_j', x_k'), \qquad (2.\ 25)$$

in which:
$$x_i' = (1 - x_i), \quad x_j' = \left\{ x_j / (x_j + x_k) \right\}, \quad x_k' = \left\{ x_k / (x_K + x_j) \right\}$$

According to the Kohler expression, the excess molar volume for a ternary mixture is given by:

Kohler:[47]
$$X^{E}_{m,ijk} = \sum_{i<j} (x_i + x_j)^2 X^{E}_{m,ij} \left\{ x_i', x_j' \right\}, \qquad (2.\ 26)$$

where:
$$x_i' = \frac{x_i}{x_i + x_j}, \qquad x_j' = \frac{x_j}{x_i + x_j},$$

Toop proposed an unsymmetrical equation which is very similar to that of Tsao and Smith:

Toop:[48]
$$X^{E}_{m,ijk} = \left\{ \sum_{j>i} \frac{x_j}{x_i'} X^{E}_{m,ij}(x_i, x_i') \right\} + (x_i')^2 X^{E}_{m,jk}(x_j', x_k'), \qquad (2.\ 27)$$
$$x_i' = (1 - x_i), \quad x_j' = \frac{x_j}{x_j + x_k}, \quad x_k' = \frac{x_k}{x_k + x_j}$$

Colinet suggested an equation to predict the excess molar property in which six different binary compositions appear:

Colinet:[49]
$$X^{E}_{m,ijk} = 1/2\sum_{j>i}\left(\frac{x_j}{x'_i}\left\{X^{E}_{m,ij}(x_i, x'_i)\right\} + \frac{x_i}{x'_j}\left\{X^{E}_{m,ij}(x'_j, x_j\right\}\right), \quad (2.28)$$

$$x'_i = 1 - x_i$$

Hillert also changed the third term of the above equations for the two last terms of the Colinet equation:

Hillert:[50]
$$X^{E}_{m,ijk} = \left\{\sum_{j>i}\frac{x_j}{x'_i}X^{E}_{m,ij}(x_i, x'_i)\right\} + \left\{\frac{x_k}{x'_j}X^{E}_{m,jk}(x_j, x'_j) + \frac{x_j}{x'_k}X^{E}_{m,jk}(x'_k, x_k)\right\}, \quad (2.29)$$

$$x'_i = (1 - x_i)$$

Muggianu *et al*. suggested the equation:

Mggianu.*al*:[51]
$$X^{E}_{m,ijk} = \left\{\sum_{j>i}\left(\frac{x_i x_j}{x'_i x'_j}\right)X^{E}_{m,ij}(x'_i, x'_j)\right\}, \quad (2.30)$$

where: $x'_i = \left\{(1 + x_i - x_j)/2\right\}$

Jacob-Fitzner suggested the equation:

Jacob-Fitzner:[52]
$$X^{E}_{m,ijk} = \left\{\sum_{j>i}\left(\frac{x_i x_j}{x'_i x'_j}\right)X^{E}_{m,ij}(x'_i, x'_j)\right\}, \quad (2.31)$$

where: $x'_i = \left\{x_i + (x_k/2)\right\}$

Finally the unsymmetrical method suggested by Hillert that introduces a last term similar to that of Muggianu *et al*. is:

Hillert:[53]
$$X^{E}_{m,ijk} = \left\{\sum_{j>i}\frac{x_j}{x'_i}X^{E}_{m,ij}(x_i, x'_i)\right\} + \frac{x_k x_j}{x'_j x'_k}X^{E}_{m,jk}(x'_j, x'_k), \quad (2.32)$$

$$x'_i = 1 - x_i, \quad x'_j = \left\{(1 + x_j - x_k)/2\right\}, \quad x'_k = \left\{(1 + x_k - x_j)/2\right\}$$

CHAPTER 3

EXPERIMENTAL TECHNIQUES

Electronic Densimetry:

The vibrating tube densimeters are largely used recently for measurements density of fluids, particularly liquids. Because of their simple operation, and high precision.

The principle of the vibrating tube-densimeters is based on mechanical oscillations of a U shaped glass tube. The oscillations are related to the density of a fluid in the tube. The theoretical model based on the assumption of harmonic oscillations of the tube. The oscillation period τ of the vibrating tube is determined according to the following relation:[54]

$$\tau^2 = 4\pi^2\{V.\rho + m\}/C, \qquad (3.\ 1)$$

where V, ρ, are volume and density of the fluid in the tube; respectively.

The liquid density is estimated from equation (3. 2):

$$\rho = (\tau^2 - B)/A\ , \qquad (3.\ 2)$$

with: $$A = 4\pi^2\, V/C, \quad B = 4\pi^2 m/C, \qquad (3.\ 3)$$

where A , B and C are constants of densimeter and are determined by calibrated of apparatus using water and dry air:

$$A = (\tau^2_{water} - \tau^2_{air})/(\rho_{water} - \rho_{air}) \qquad (3.\ 4)$$

$$B = \tau^2_{air} - A\,\rho_{air,} \qquad (3.\ 5)$$

where, τ_i, ρ_i are oscillation period and density of fluid i at temperature T; respectively.

The refractive index *n* of a solvent is defined as the ratio of the velocity of light in vacuum to that in the solvent, and it depends on the nature of the substance: $n = \frac{c}{v}$

where *c, v* are velocity of the light in vacuum, and in solvent; respectively.

Chemical materials and experimental procedures:

The chemical products employed for this investigation have relatively simple chemical structures. The pure components are supplied by (Fluka Chemica, Riedel-de Haën, Prolabo).

The purity of the substances are checked by gas chromatography; Perkin-Elmer model: Clarus 500. These substances are used without further purification.

Chemical substances, suppliers and stated purities are given in table (3. 1)

Mixtures are prepared by mass in a glass vial with stopper, using a precision Balance: OHAUS balance to $\pm 2 \cdot 10^{-4}$g in the mole fraction determination.

In this investigation the refractive indices for pure components and mixtures are measured with a precision of $\pm 5 \cdot 10^{-4}$ using an Abbe-type refractometer (Phywe, No.990646), which temperature is kept constant within ± 0.03 K, using a LAUDA thermostat, RC6CP edition 2000. The refractometer is checked by substances with known values of refractive index.

The densities of the samples are measured with an Anton Paar Model DMA 5000 oscillating U-tube densimeter, provided with automatic viscosity correction, and a stated precision of $\pm 5 \cdot 10^{-6}$ g $\cdot cm^{-3}$, with thermostated bath at 298.15 K, controlled to within ± 0.005 K. Temperatures are read from calibrated precision thermometer.

The liquid mixtures are introduced into densimeter U-tube using hypodermic syringe, this latter should be degassed before the measurement, with ensure that there are no gas bubbles in the measuring cell.

The densimeter are checked by measuring the densities of the standard system $(x_1[(CH_3)_2CH]_2O + x_2C_2H_5OH)$, at 298.15 K, over the whole range of composition x.

The experimental densities and refractive indices for pure compounds are compared with litterature values in table (3. 2) at 298.15 K.

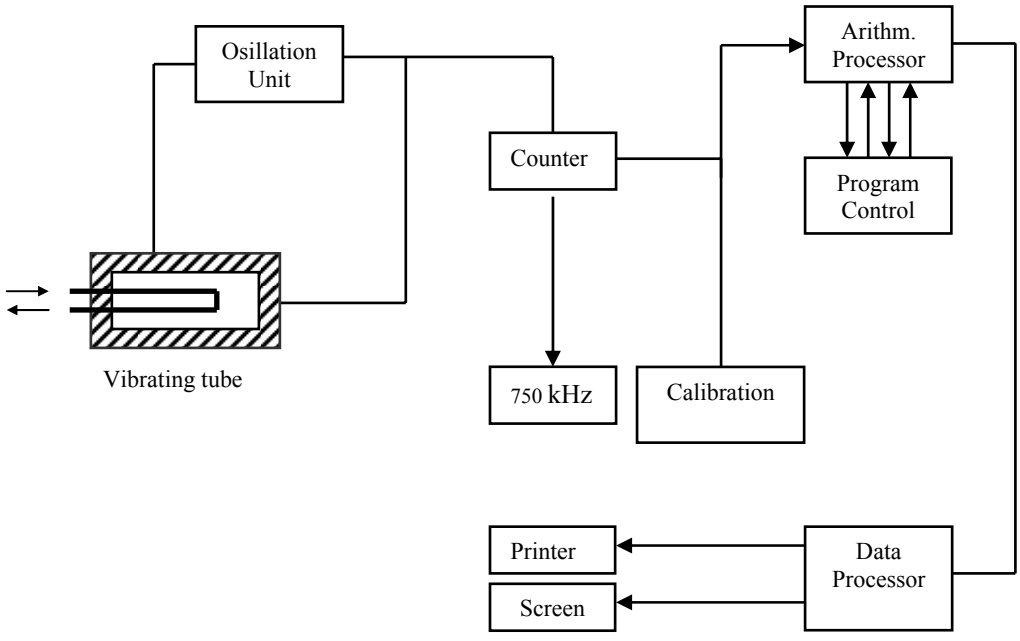


Figure (3. 1): Shematic diagram of a vibrating-tube densimeter.

Table (3. 1): Chemical substances, suppliers and stated purities.

Name	Symbol	Formula	Purity: mol %
Fluka Chemica			
Benzene	BE	C_6H_6	> 99.5
Toluene	TO	C_7H_8	> 99.5
Fluorobenzene	FB	C_6H_5F	≥ 99.5
α,α,α-Trifluorotoluene	TFT	$C_7H_5F_3$	≥ 99.5
Tert-amyl methyl ether	TAME	$C_2H_5C(CH_3)_2OCH_3$	≈ 97
2,2,2-Trifluoroethanol	TFE	CF_3CH_2OH	≥ 99
Riedel-de Haën			
Tert-butyl methyl ether	TBME	$C(CH_3)_3OCH_3$	> 99
Ethanol	ETOH	C_2H_5OH	> 99.8
Acetone	AC	$(CH_3)_2CO$	> 99.8
Prolabo			
Diisopropylether	DIPE	$[(CH_3)_2CH]_2O$	99

Table (3. 2): Densities and refractive indices of pure substances at 298.15 K

Substance	ρ/g·cm^{-3}		n	
	Exp.	Lit.	Exp.	Lit.
Benzene	0.873143	0.87360[55]	1.4982	1.49792[55]
Toluene	0.862083	0.86219[55]	1.4920	1.49413[55]
Acetone	0.784613	0.78440[55]	1.3570	1.35596[55]
Ethanol	0.785599	0.78510[56]	1.3593	1.35941[55]
Diisopropyl ether	0.719174	0.71870[7]	1.3661	1.36550[55]
α,α,α-Trifluorotoluene	1.182178	1.18129[55]	1.4124	1.41225[55]
2,2,2-Trifluoroethanol	1.382398	1.38180[55]	---	---
Tert-amyl methyl ether	0.766215	0.76601[57]	1.3860	---
Fluorobenzene	1.019076	1.01893[58]	1.4633	---
Tert-butyl methyl ether	0.735774	0.73530[59]	1.3665	1.36630[59]

CHAPTER 4

EXPERIMENTAL RESULTS

The present work deals with the measurement and correlation of excess molar volumes V_m^E and the change in refractive indices $\Delta_{mix}n$ for the binary and ternary mixtures.
The systems investigated are reported and numbered in the following:

Binary mixtures

ρ (x), $V_{m,ij}^E$, n(x), $\Delta_{mix}n$ at 298.15 K and 101 kPa

2- (x_1DIPE + x_2BE)
3- (x_1DIPE + x_2AC)
4- (x_1TO + x_2DIPE)
5- (x_1FB + x_2DIPE)
6- (x_1FB + x_2TBME)
7- (x_1TFT + x_2DIPE)
8- (x_1TFT + x_2TBME)
9- (x_1FB + x_2TAME)
10- (x_1TFT + x_2ETOH)
11- (x_1FB + x_2ETOH)

ρ (x), $V_{m,ij}^E$ at 298.15 K and 101 kPa

1- (x_1DIPE + x_2ETOH)
12- (x_1TFE + x_2ETOH)
13- (x_1DIPE + x_2TFE)
14- (x_1TFT + x_2TFE)

Ternary mixtures

ρ (x), $V_{m,ijk}^E$ at 298.15 K and 101 kPa

15- (x_1TFT + x_2DIPE + x_3ETOH);
16- (x_1FB + x_2DIPE + x_3ETOH)
17- (x_1DIPE + x_2TFE + x_3ETOH);
18- (x_1TFT + x_2TFE + x_3ETOH)

The density of pure components and mixtures are measured over the whole composition range at (T, p, const.) using Anton paar densimeter DMA 5000 with an accuracy of $\pm 5 \cdot 10^{-6}$ g· cm^{-3}, and temperature controlled of $\delta T = \pm 5 \cdot 10^{-3}$ K. The refractive indices of pure components and mixtures are measured over the entire range of composition at (T, p, const.) using Abbe-type refractometer with a precision of: $\pm 2 \cdot 10^{-4}$, with $\delta T = \pm 0.03$ K.

The densities and refractive indices of mixtures are fitted:

$$Y_i = Y_i^* + \sum_{P=1}^{n} A_P x_i^P \ , \qquad (4.\ 1)$$

where Y_i^* are density ρ_i^*, refractive indices n_i^* of pure component, and Y_i are density $(\rho(x)$ / g·cm^{-3}) and refractive indices $n(x)$ of mixtures.

The coefficients A_p of equation (4. 1) are determined by a least square procedure.

The excess molar volumes V_m^E of multi-component mixtures are obtained from molar mass M_i of the components, mole fractions x_i, and the density ρ_i^* of the pure liquids and the density ρ of the mixtures according to the relation:

$$V_m^E = \sum_{i=1}^{n} x_i M_i \left(\rho^{-1}(x) - \rho_i^{*-1}\right), \qquad (4.\ 2)$$

where n stands for the number of components in the mixtures.

The change in refractive indices of multi-component mixtures are determined from refractive indices measurements and compositions of mixtures:

$$\Delta_{mix} n = n(x_i) - \sum_{i=1}^{n} n_i^* x_i \ , \qquad (4.\ 3)$$

with n_i^* is the refractive indices of pure component i.

The mixing property of the studied binary mixtures are smoothed by the least squares method to the Redlich-Kister equation:

$$V_{m,ij}^E \ or \ \Delta_{mix} n = x_i \ x_j \sum_{P=0}^{n} B_P \ (x_j - x_i)^P \ , \qquad (4.\ 4)$$

where the component j is added to component i.

The adjustable parameters B_p are determined by least squares method and degree of the polynomials P, is optimized by standard deviations and applying the student statistic test t.

The densimeter is checked by measuring the excess molar volumes of binary system: {(1-x)[$(CH_3)_2CH]_2O$ + xC_2H_5OH} at atmospheric pressure and temperature T = 298.15 K, over the entire range of composition with good agreement with literature:

V_m^E (x = 0.5) /cm^3.mol^{-1} = (-0.841 ± 0.002); literature value, (-0.846 ± 0.004)[60].

The limiting excess partial properties for the binary mixtures $X_{m,i}^{E\infty}$: $V_i^{E\infty}$, $\Delta_{mix} n$ are estimated by equation (4. 4) as:

$$X_{m,i}^{E\infty} = \lim_{xi \to 0} \left(\frac{X_m^E (\text{eq. } 4.4)}{x_i x_j} \right), \qquad (4.\ 5)$$

The compositions of a three-component system x_A, x_B, x_C are conveniently represented by an equilateral triangle. The three apexes represent the pure component, and the three edges refer to the three binary mixtures: (A + B), (B + C), (A + C). The mole fractions of any ternary mixture is represented by a point within the triangle; with $\sum x_i = 1$.

The excess properties of the ternary mixtures can be predicted using equation (2. 26), with x'_i and x'_j may be obtained from a triangular diagram by projecting the point representing the ternary mixture on to the corresponding binary axis.

Various kinds of projection can be used:[41,61,62]

1- The normal projection: figure (4. 1), projection of the ternary mixture P from any apex of the triangle diagram, we obtain the relation: $x'_i = (x_i /(x_i + x_j))$, where: $i \neq j$, and, (i = A, B, C). This projection is similar to the direct one, and is used in Redlich-Kister**,** and Kohler equations, (2. 27) and (2. 30); respectively.

2- Parallel projection: figure (4. 2), projection of the ternary mixture P is parallel to each side of the triangle diagram, the binaries excess properties can be written as the arithmetic mean of excess properties at the point of composition $x'_i = 1 - x_i$. This type of projection is used in colinet's equation (2. 32).

3- Rectilinear projection: figure (4. 3), the projection of the ternary mixture P is perpendicular to each side of the triangle, we get: $x'_i = \{x_i + (x_k/2)\}$. This type of projection is used in Jacob-Fitzner's equation (2. 35)

4- Mixed projection: figure (4. 4), when the combine parallel and direct projection are obtained mixed projection: $x'_i = 1 - x_i$, $x'_j = x_j/(x_j + x_k)$, $x'_k = x_k/(x_k + x_j)$. This type of projection is used in Tsao-smith and Toop equations (2. 29) and (2. 31); respectively.

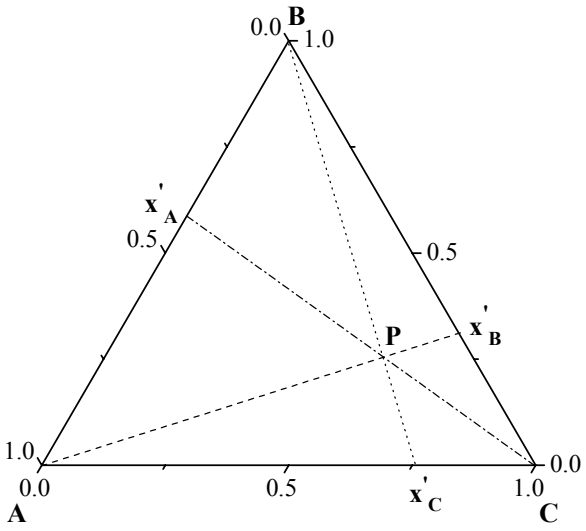


Figure (4. 1) : Schematic diagram of a normal projection

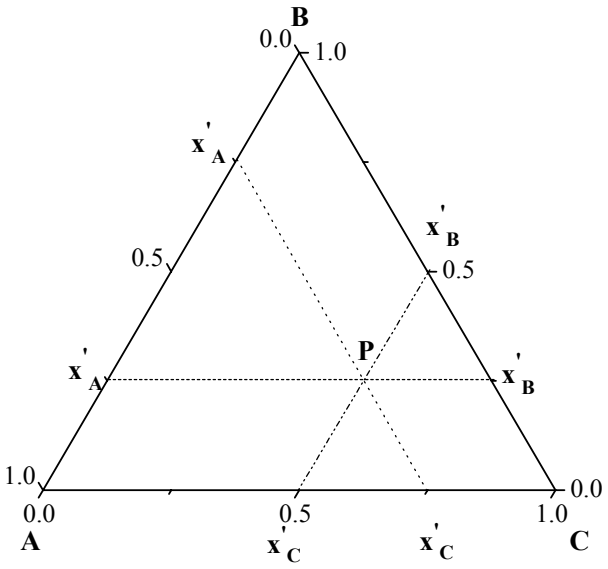


Figure (4. 2): Schematic diagram of a parallel projection.

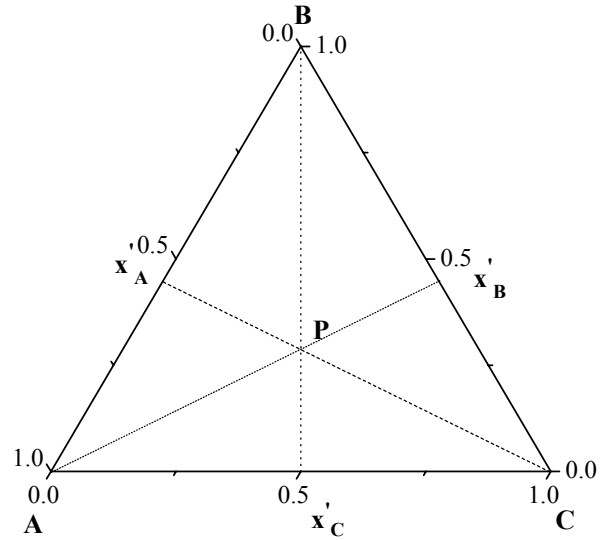


Figure (4. 3): Schematic diagram of a rectilinear projection.

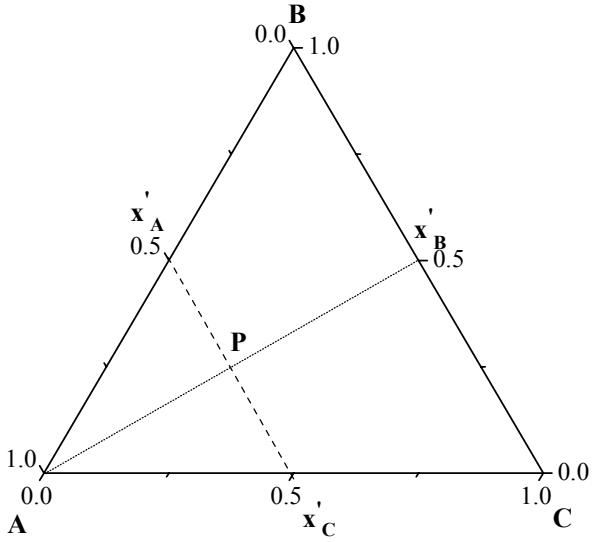


Figure (4. 4): Schematic diagram of a mixed projection

The experimental excess molar volumes of the ternary mixtures are correlated using Redlich-Kister and Cibulka equations(2. 27), and (2. 25); respectively.

$$V^{E}_{m,ijk} = \sum_{j>i} V^{E}_{m,ij} + x_i x_j x_k \Delta_{ijk}, \qquad (4.\ 6)$$

where: $$\Delta_{ijk} V^{E}_{m} = x_i x_j x_k \Delta_{ijk}, \qquad (4.\ 7)$$

with Δ_{ijk} is the ternary contribution represented by the Cibulka equation:

$$\Delta_{ijk} = C_0 + C_i x_i + C_j x_j, \qquad (4.\ 8)$$

The fitting parameters C_P are determined using a linear multiple regression, by minimizing the objective function:

$$OF = \sum_{n} \left\{ \Delta_{ijk}(\text{exp.}) - (C_0 + C_i x_i + C_j x_j) \right\}^2 \equiv \min \qquad (4.\ 9)$$

For ternary mixtures the partial excess molar volumes at infinite dilution $V^{E\infty}_{i}$ depends on the composition of the mixed solvents ij, and for more practical calculation:

$$V^{E\infty}_{i} = \lim_{xi \to 0} (V^{E}_{m,ijk}\ (\text{eq. 4. 6}) / x_i);\ with\ (x_j = x_K = 0.5) \qquad (4.\ 10)$$

Minimum and maximum values of excess molar volumes are calculated from equation (4. 6). The experimental values of the ternary mixtures give a good agreement with the predicted values when calculated from their binary contribution data using equation (2. 23) to equation (2. 32).

Experimental uncertainty analysis:

For a thermodynamic function: X = F(x, y, ...) the uncertainty δX are evaluated from:

$$\delta X^2 = \left(\frac{\partial X}{\partial x}\right)^2 (\delta x)^2 + \left(\frac{\partial X}{\partial y}\right)^2 (\delta y)^2 + \ldots \qquad (4.\ 11)$$

So, the experimental uncertainties are:

error in excess molar volumes:

$$\delta V^{E}_{m} = \left(\frac{\partial V^{E}_{m}}{\partial \rho(x)}\right)^2_{T,P,x_i} (\delta\rho(x_i))^2 + \sum_{i=1}^{n} \left(\left(\frac{\partial V^{E}_{m}}{\partial x_i}\right)^2_{T,p,x_{j\neq i}} (\delta x_i)^2 \right) + \sum \left(\left(\frac{\partial V^{E}_{m}}{\partial \rho^{*}_{i}}\right)^2_{T,p,x_i} \delta(\rho^{*}_{i})^2 \right) \qquad (4.\ 12)$$

error in composition x_i:

the liquid composition x_i is calculated from:

$$x_i = (m_i / M_i) / (\sum_{i=1}^{n} (m_i / M_i))$$

the uncertainty in liquid composition is:

$$(\delta x_i)^2 = \sum_{i=1}^{n} \left(\left(\frac{\partial x_i}{\partial m_i} \right)^2 (\delta m_i)^2 \right), \tag{4. 13}$$

where:

$$\frac{\partial x_i}{\partial m_i} = \frac{\left(\frac{1}{M_i} \sum_{i=1}^{n} \left(\frac{m_i}{M_i} \right) - \frac{m_i}{M_i^2} \right)}{\left(\sum_{i=1}^{n} \left(\frac{m_i}{M_i} \right) \right)^2}$$

error contribution of composition:

$$\left(\frac{\partial V_m^E}{\partial x_i} \right)_{T,p,x_{j\neq i}} = \left(\frac{M_i}{\rho(x)} - \frac{M_i}{\rho_i^*} \right) - \frac{\partial \rho(x)}{\partial x_i} \sum_{i=1} \frac{x_i M_i}{\rho(x)^2} \tag{4. 14}$$

error contribution of density:

$$\frac{\partial V_m^E}{\partial \rho(x)} = -\frac{\sum_{i=1}^{n} x_i M_i}{(\rho(x))^2} \tag{4. 15}$$

The experimental uncertainties of our equipement are:

$\delta p = \pm 2$ kPa, $\delta T = \pm 5 \cdot 10^{-3}$ K, $\delta m_i = \pm 2 \cdot 10^{-4}$ g,

so: $\delta x = \pm 2 \cdot 10^{-4}$, $\delta \rho = \pm 5 \cdot 10^{-5}$ g·cm^{-3}.

The standard deviation σ_s of the fit for the properties $\rho(x)$, $n(x)$, V_m^E and $\Delta_{mix} n$, is calculated

from:

$$\sigma_s = \left(\frac{\sum_i \left(X_{exp} - X_{cal} \right)^2}{N - N_P} \right)^{0.5}, \tag{4. 16}$$

where N is the number of data points, and N_P is the number of adjustable parameters.

In this work, the standard deviation of measurements are:

For binary mixtures:

$(\rho(x)$ / g·cm$^{-3})$: $10^{-5} < \sigma_s < 4 \cdot 10^{-4}$,

$V_{m,ij}^E$ / cm^3·mol^{-1}: $5 \cdot 10^{-4} < \sigma_s < 2 \cdot 10^{-3}$,

and

$n(x)$: $3 \cdot 10^{-5} < \sigma_s < 7 \cdot 10^{-4}$,

$\Delta_{mix} n_{ij}$: $3 \cdot 10^{-4} < \sigma_s < 5 \cdot 10^{-4}$.

For ternary contribution:

$\Delta_{ijk}V_m^E$: $\sigma_s \approx 0.03$ cm$^3\cdot$ mol^{-1}.

In this chapter, the experimental results for three binary mixtures: (x_1TFT + x_2DIPE), (x_1TFT + x_2ETOH), (x_1DIPE + x_2ETOH) are give in tables (4. 1) to (4. 3), and a ternary mixture: (x_1TFT + x_2DIPE + x_3ETOH); is set in table (4. 6) and are shown in figure (4. 5), and figure (4. 6). Summaries of all the studied system are listed in tables (4. 4) and (4. 5) for binary mixtures, and in tables (4. 7) to (4. 9) for ternary mixtures. Experimental and predicted ternary properties are given in tables (4. 7) to (4. 9).

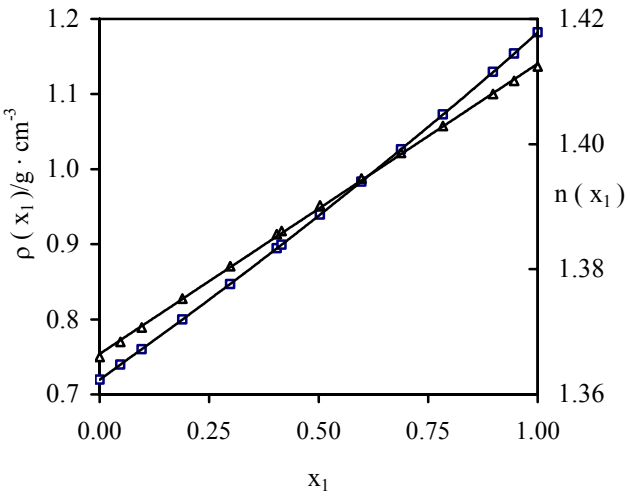
Appendix A contains total the experimental and fitting results: tables (A.1.S) for binary mixtures and tables (A.2.S) for ternary mixtures, where S stands for a number the studied systems.

Table(4. 1). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component:	1. Trifluorotoluene	$C_7H_5F_3$
	2. Diisopropyl ether	$[(CH_3)_2CH]_2O$

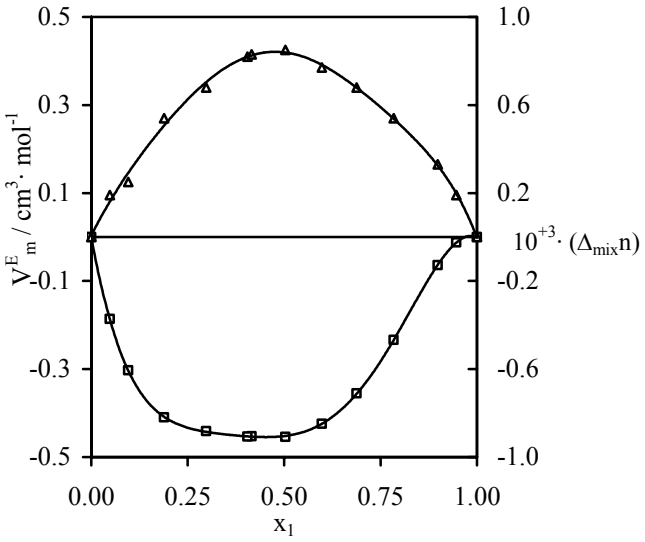
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3660	0.7195
0.0476	1.3684	0.7397
0.0959	1.3707	0.7602
0.1887	1.3753	0.7997
0.2979	1.3805	0.8469
0.4046	1.3856	0.8944
0.4154	1.3861	0.8993
0.5032	1.3902	0.9394
0.5975	1.3945	0.9835
0.6879	1.3986	1.0264
0.7836	1.4029	1.0727
0.8982	1.4080	1.1294
0.9463	1.4101	1.1540
1.0000	1.4124	1.1822

□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3660	0.0496	-0.0032	---	---	0.00003
$\rho(x_1)$ / g·cm^{-3}	0.7197	0.4169	0.0329	0.0135	-0.0011	0.0002

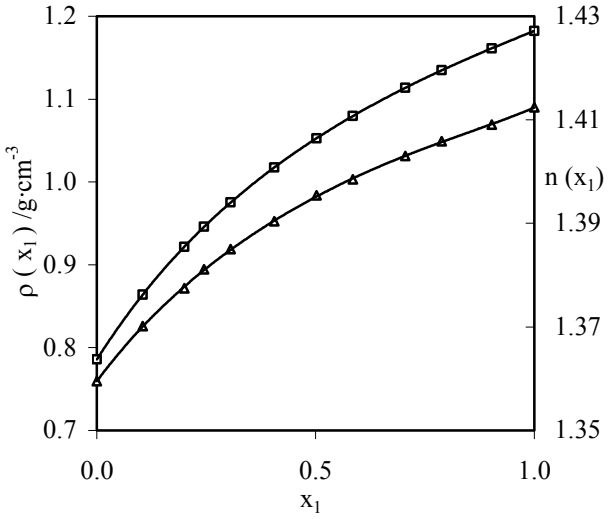
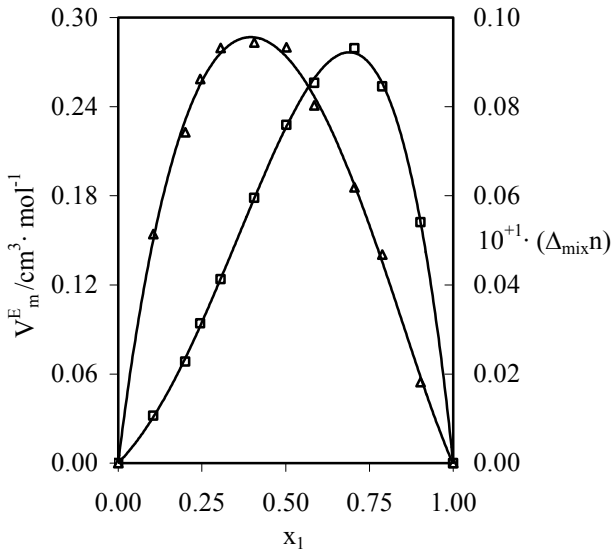
x_1	$10^{+3}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$
0.0000	0.00	0.000
0.0476	0.19	-0.186
0.0959	0.25	-0.302
0.1887	0.54	-0.410
0.2979	0.68	-0.441
0.4046	0.82	-0.453
0.4154	0.83	-0.453
0.5032	0.85	-0.454
0.5975	0.77	-0.425
0.6879	0.68	-0.355
0.7836	0.54	-0.234
0.8982	0.33	-0.064
0.9463	0.19	-0.013
1.0000	0.00	0.000



Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0033	---	---	---	---	0.00003
$V^E_{m,12}/cm^3\cdot mol^{-1}$	-1.809	-0.212	-0.398	-2.379	---	0.001

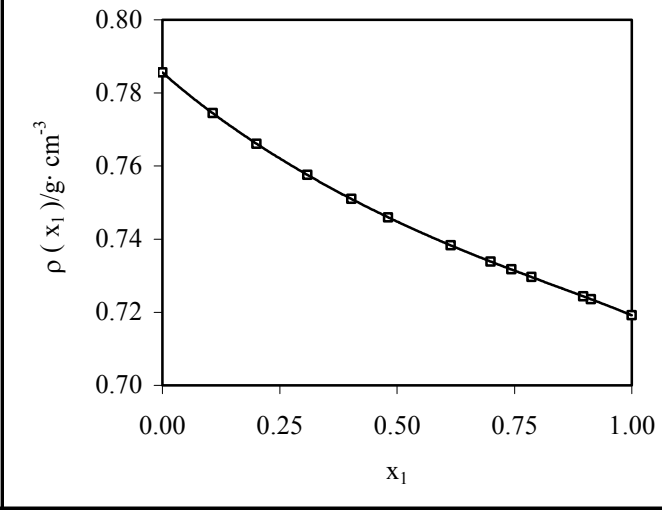
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	0.0008	-0.452	0.0033	0.0033	-4.797	0.384

Table(4. 2). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component:	1. Trifluorotoluene		$C_7H_5F_3$			
	2. Ethanol		C_2H_5OH			
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$		Δ; $n(x_1)$, $\Delta_{mix}n$	
0.0000	1.3595	0.7857				
0.1051	1.3702	0.8640				
0.1999	1.3775	0.9217				
0.2454	1.3811	0.9458				
0.3059	1.3850	0.9752				
0.4057	1.3904	1.0175				
0.5022	1.3954	1.0528				
0.5855	1.3985	1.0797				
0.7052	1.4030	1.1137				
0.7886	1.4059	1.1349				
0.9032	1.4091	1.1615				
1.0000	1.4124	1.1823				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3596	0.1087	-0.0993	0.0523	-0.0090	0.0002
$\rho(x_1)$ / g·cm^{-3}	0.7859	0.8182	-0.7957	0.5220	-0.1482	0.00002
x_1	$10^{+1}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$				
0.0000	0.000	0.000				
0.1051	0.051	0.032				
0.1999	0.074	0.068				
0.2454	0.086	0.094				
0.3059	0.093	0.124				
0.4057	0.094	0.179				
0.5022	0.093	0.228				
0.5855	0.080	0.256				
0.7052	0.062	0.279				
0.7886	0.047	0.254				
0.9032	0.018	0.162				
1.0000	0.000	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0368	0.0176	---	---	---	0.0002
$V^E_{m,12}/cm^3\cdot mol^{-1}$	0.902	-0.933	0.279	---	---	0.002
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	0.0092	0.225	0.0544	0.0192	0.248	2.114

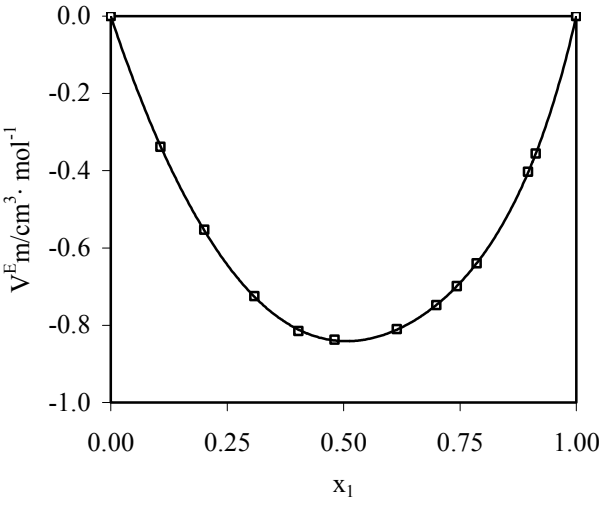
Table(4. 3). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component:	1. Diisopropyl ether	$[(CH_3)_2CH]_2O$			
	2. Ethanol	C_2H_5OH			

x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$
0.0000	---	0.7856	
0.1072	---	0.7745	
0.2007	---	0.7661	
0.3086	---	0.7576	
0.4030	---	0.7510	
0.4811	---	0.7460	
0.6142	---	0.7383	
0.6993	---	0.7338	
0.7432	---	0.7317	
0.7863	---	0.7296	
0.8965	---	0.7244	
0.9129	---	0.7236	
1.0000	---	0.7192	

Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	---	---	---	---	---	---
$\rho(x_1)$ / g·cm^{-3}	0.7856	-0.1100	0.0703	-0.0266	---	0.00007

x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$
0.0000	---	0.000
0.1072	---	-0.338
0.2007	---	-0.553
0.3086	---	-0.725
0.4030	---	-0.815
0.4811	---	-0.837
0.6142	---	-0.810
0.6993	---	-0.748
0.7432	---	-0.699
0.7863	---	-0.640
0.8965	---	-0.403
0.9129	---	-0.356
1.0000	---	0.000



Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	---	---	---	---	---	---
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	-3.364	0.067	-0.673	0.725	-0.389	0.002

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3 \cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3 \cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3 \cdot mol^{-1})$
0.500	---	-0.841	---	---	-3.631	-5.221

Table (4. 4). Equimolar and infinite dilution values of excess molar volumes and change in refractive indices for binary mixtures at 298.15 K and 101 kPa

System	$V_{m,12}^{E}$ / $cm^3 \cdot mol^{-1}$	$\Delta_{mix}n$	$V_1^{E\infty}$ / $cm^3 \cdot mol^{-1}$	$V_2^{E\infty}$ / $cm^3 \cdot mol^{-1}$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$
2	-0.485	-0.0168	-1.148	-2.036	-0.0804	-0.0541
3	0.048	0.0019	-0.157	0.049	0.0150	0.0088
4	-0.699	-0.0092	-2.994	-2.404	-0.0366	-0.0366
5	-0.867	-0.0069	-3.467	-3.467	-0.0274	-0.0274
6	-0.554	-0.0032	-4.623	-1.237	-0.0050	-0.0208
7	-0.452	0.0008	-4.797	0.384	0.0033	0.0033
8	-0.356	0.0033	-2.368	-0.479	0.0200	0.0062
9	-0.312	-0.0064	-1.617	-0.881	-0.0099	-0.0410
10	0.225	0.0092	0.248	2.114	0.0544	0.0192
11	-0.104	0.0139	-1.403	0.569	0.0680	0.0434
1	-0.841	---	-3.631	-5.221	---	---
12	0.828	---	2.876	3.747	---	---
13	-1.050	---	-0.489	-7.909	---	---
14	0.592	---	3.015	3.670	---	---

Table (4. 5). Error analysis for experimental properties of binary mixtures at 298.15 K and 101 kPa

Systems	x_1	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	Contrib.x_1	Contrib.ρ (x_1) / $g \cdot cm^{-3}$	$\delta V^E_{m,12}$ (Eq.(4.8)) / $cm^3 \cdot mol^{-1}$	$\frac{\delta V^E_{m,12}}{V^E_{m,12}}$	$\sigma V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$
1	0.481	-0.837	0.0002	0.007	0.0008	0.0020	0.0015
2	0.469	-0.472	0.0002	0.007	0.0009	0.0020	0.0011
3	0.49	0.046	0.0002	0.007	0.0009	0.0190	0.0011
4	0.502	-0.697	0.0002	0.008	0.0010	0.0010	0.0013
5	0.502	-0.87	0.0002	0.007	0.0009	0.0010	0.0010
6	0.503	-0.554	0.0003	0.006	0.0008	0.0010	0.0010
7	0.503	-0.454	0.0003	0.007	0.0009	0.0020	0.0012
8	0.497	-0.356	0.0003	0.006	0.0008	0.0020	0.0010
9	0.501	-0.314	0.0003	0.006	0.0008	0.0030	0.0010
10	0.502	0.228	0.0003	0.004	0.0006	0.0030	0.0007
11	0.506	-0.102	0.0003	0.004	0.0006	0.0050	0.0006
12	0.493	0.824	0.0003	0.003	0.0005	0.0006	0.0006
13	0.493	-1.039	0.0003	0.005	0.0008	0.0008	0.0009
14	0.496	0.594	0.0004	0.004	0.0006	0.0010	0.0007

Table (4. 6). Volumetric properties of ternary mixtures at 298.15 K and 101 kPa

Component:	1. α,α,α-Trifluorotoluene	$C_7H_5F_3$				
	2. Diisopropyl ether	$[(CH_3)_2CH]_2O$				
	3. Ethanol	CH_3CH_2OH				
x_1	x_2	ρ	$V^E_{m,123}$(exp .)	$V^E_{m,123}$ (eq. 2. 29)	$V^E_{m,123}$ (eq. 2. 30)	$V^E_{m,123}$ (eq. 2. 32)
		g·cm^{-3}	cm^3 · mol^{-1}			
0.0420	0.0467	0.8122	-0.144	-0.114	-0.144	-0.143
0.0447	0.8995	0.7416	-0.376	-0.332	-0.377	-0.377
0.0623	0.6861	0.7617	-0.721	-0.730	-0.736	-0.723
0.0631	0.4394	0.7812	-0.777	-0.806	-0.795	-0.775
0.0777	0.5997	0.7746	-0.761	-0.793	-0.780	-0.761
0.0783	0.2210	0.8124	-0.542	-0.521	-0.551	-0.539
0.0864	0.8030	0.7634	-0.562	-0.537	-0.569	-0.564
0.1133	0.4459	0.8044	-0.734	-0.764	-0.758	-0.732
0.1660	0.3402	0.8414	-0.627	-0.630	-0.642	-0.620
0.1784	0.2115	0.8670	-0.457	-0.426	-0.457	-0.448
0.1969	0.5993	0.8229	-0.647	-0.668	-0.668	-0.647
0.1991	0.7197	0.8116	-0.551	-0.548	-0.561	-0.552
0.2225	0.4327	0.8530	-0.630	-0.654	-0.650	-0.625
0.2694	0.2337	0.9047	-0.425	-0.412	-0.415	-0.412
0.2738	0.0527	0.9461	-0.048	0.021	-0.035	-0.042
0.3155	0.6116	0.8636	-0.521	-0.526	-0.532	-0.520
0.3251	0.4684	0.8867	-0.553	-0.578	-0.567	-0.547
0.3324	0.3440	0.9096	-0.495	-0.519	-0.495	-0.484
0.4027	0.1809	0.9686	-0.249	-0.253	-0.221	-0.233
0.4207	0.5216	0.9103	-0.484	-0.494	-0.492	-0.481
0.4297	0.3371	0.9451	-0.428	-0.465	-0.424	-0.415
0.4473	0.2445	0.9700	-0.320	-0.351	-0.299	-0.303
0.4655	0.0537	1.0240	0.062	0.085	0.083	0.070
0.5388	0.4022	0.9667	-0.429	-0.449	-0.435	-0.424
0.5516	0.1524	1.0256	-0.116	-0.147	-0.088	-0.100
0.5732	0.2283	1.0135	-0.240	-0.286	-0.227	-0.226
0.6357	0.2994	1.0152	-0.333	-0.359	-0.335	-0.326
0.7349	0.0578	1.1034	0.130	0.069	0.141	0.137
0.7558	0.2000	1.0699	-0.190	-0.211	-0.191	-0.186
0.8865	0.0692	1.1363	0.024	-0.004	0.025	0.027

Equation (4. 8):	C_0	C_1	C_2	σ_s
$\Delta_{123}V_m^E / cm^3 \cdot mol^{-1}$	-0.452	-0.567	0.906	0.041

Table (4. 7). The extreme of the ternary contribution values $\Delta_{123}V_m^E$ of the ternary mixtures at 298.15 K and 101 kPa

Systems	x_1 (ex)	x_2 (ex)	$\Delta_{123}V_m^E(ex)$
			$cm^3 \cdot mol^{-1}$
15	0.081	0.743	0.002
	0.455	0.210	-0.017
16	0.285	0.539	0.043
	0.200	0.146	-0.023
17	0.092	0.599	0.006
	0.542	0.217	-0.023
18	0.162	0.296	0.043
	0.630	0.216	-0.024

Table (4. 8). The extreme and infinite dilution values of excess molar volumes at 298.15 K and 101 kPa

Systems	x_1 (ex)	x_2 (ex)	$V_{m,123}^E(ex)$	$V_1^{E\infty}$	$V_2^{E\infty}$	$V_3^{E\infty}$
			$cm^3 \cdot mol^{-1}$			
15	0.655	0.008	0.254	-0.903	-2.653	-1.193
	0.008	0.505	-0.835			
16	0.873	0.002	0.028	-2.126	-3.680	-1.258
	0.125	0.467	-0.868			
17	0.012	0.529	0.782	-2.772	-1.687	-0.215
	0.654	0.345	-1.208			
18	0.081	0.505	0.848	2.022	2.983	2.234
	0.000	1.000	0.000			

Table (4. 9). Standard deviations of experimental and predicted excess molar volumes of the ternary mixtures at 298.15 K and 101 kPa

	$\sigma(V^{E}_{m,123} / cm^{3} \cdot mol^{-1})$			
Systems $\rightarrow$	M_1	M_2	M_3	M_4
Redlich-Kister	0.008	0.020	0.009	0.019
Scatchard *et al.*	0.035[a]	0.016[b]	0.031[a]	0.027[c]
Tsao-Smith	0.062[b]	0.026[b]	0.079[c]	0.027[b]
Kohler	0.029	0.024	0.026	0.026
Toop	0.031[a]	0.012[b]	0.023[a]	0.028[c]
Colinet	0.014	0.027	0.008	0.014
Hillert (1)	0.047	0.042	0.079	0.027
Muggianu *et al.*	0.008	0.020	0.009	0.019
Jacob-Fitzner	0.046	0.033	0.084	0.027
Hillert (2)	0.035[a]	0.016[b]	0.031[a]	0.027[c]

[a] component 3 asymmetric; [b] component 2 asymmetric; [c] component 1 asymmetric.

M_1; (x_1TFT + x_2DIPE + x_3ETOH), M_2 ; (x_1FB + x_2DIPE + x_3ETOH),

M_3; (x_1DIPE + x_2TFE + x_3ETOH), M_4; (x_1TFT + x_2TFE + x_3ETOH).

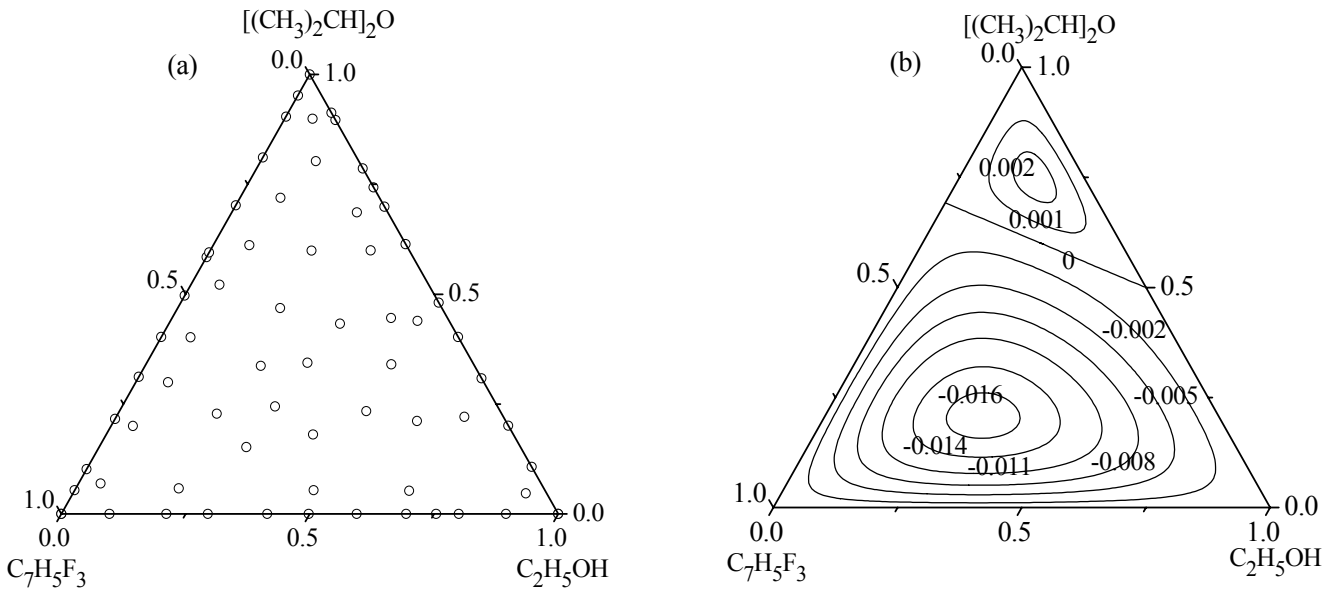


Figure (4. 5): Excess molar volumes of the mixtures ($x_1C_7H_5F_3 + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), experimental compositions; (b), $\Delta_{123}V_m^E$ isolines. $\Delta_{123}V_m^E$ /$cm^3.mol^{-1}$

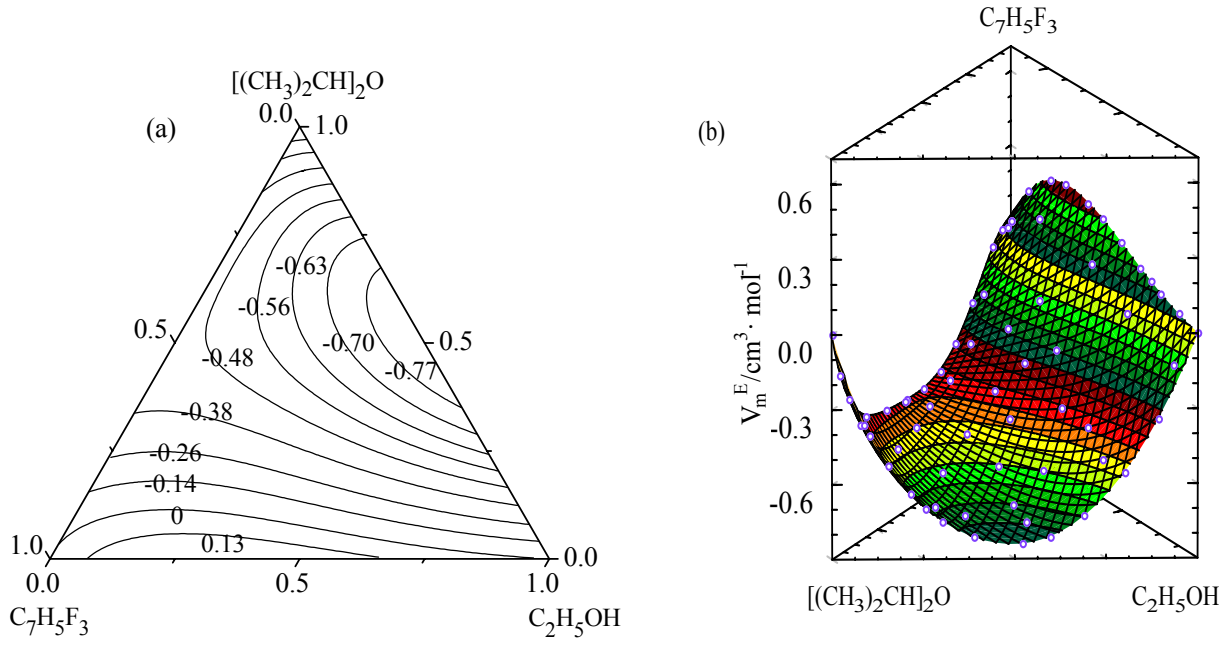


Figure (4. 6): Excess molar volumes of the ternary mixtures ($x_1C_7H_5F_3 + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), $V_{m,123}^E$ isolines; (b), surfaces. $V_{m,123}^E$ /$cm^3.mol^{-1}$

CHAPTER 5

DISCUSSION

Thermodynamic properties of mixtures reflect the physico-chemical interactions between like and unlike molecules, in particular specific interactions such as hydrogen bonding.[63-66]

Mixing of different components leads in general to changes in the thermodynamic properties of the formed solutions. Accordingly, the deviation from the ideal behaviour is described particularly by excess properties.[67-69] In general, positive excess properties indicate presence of repulsive intermolecular interactions among mixture components, while negative excess property values point out that cross-molecular interactions are dominating in the system.[70-74]

Volumes of mixing of multi-component mixtures reflect the differences in molecular size and shape of its molecules and the various types of intermolecular interactions upon mixing between like and unlike molecules.[75-77]

Polar substances interact often among each others and produce energetic effect of different magnitudes.[78] Ethers are aprotic polar molecules, and do not form hydrogen bonds among each other in the pure state. The intermolecular energies in systems consisting of ethers and fluorohydrocarbons involve dipole-dipole and dipole-induced dipole interactions, in addition to hydrogen and halogen bonding among solute-solvent molecules.[79]

In the present binary mixtures, interactions between the three ether solutions of (ether + ethanol), (ether + 2,2,2-trifluoroethanol), (ether + fluorobenzene), (ether + α,α,α-trifluorotoluene), are believed to occur via complex bonding formation between the mixture species.[80] Branched ethers are more likely to participate in cross association effects with the aromatic delocalized π-electrons causing the system to shrink and show small and negative excess molar volumes[81-84] within the range:

$-0.47 < V^{E}_{m,ij}/cm^3.mol^{-1} < -0.38$. From comparison of different mixtures of (fluorobenzene + ethers) and (α,α,α-trifluorotoluene + ethers) it can be concluded that the $V^{E}_{m,ij}$ increases in the order: TAME >TBME > DIPE. This trend seems to indicate a more organised packing effect in mixtures containing the shortest branched ethers.[85,86]

The excess molar volumes for the binary systems of (diisopropyl ether + benzene), (diisopropyl ether + toluene), (diisopropyl ether + fluorobenzene), are small and negative around: -0.87< $V^{E}_{m,ij}$/cm^3.mol^{-1}< -0.32, with the $V^{E}_{m,ij}$ are as follows: BE >TO >FB, indicating stronger specific interactions for system containing fluorobenzene, in which the inductive effect of the fluorine group results in an enhanced repulsion between the electron pairs on the oxygen atom of an ether molecule and an aromatic π- ring electrons.[30,76,87,88]

2,2,2-Trifluoroethanol is a better proton donnor than Ethanol, because of the strong electronegative inductive effects of the three fluorine atoms[89], and both are strongly self-self associated through hydrogen bondings. The addition of diisopropyl ether to ethanol or to trifluoroethanol would disturb the associative structure in alcohols in favour of unlike associations, in which the $-\ddot{\underset{\ddot{}}{O}}-$ group in the ether molecule may act as an electron donor to the proton of the hydroxyl group in an alcohol, via dipole-dipole interactions with Diisopropyl ether molecules [90-97], and gives small and negative $V^{E}_{m,ij}$ within the range:

–1.20< $V^{E}_{m,ij}$/cm^3.mol^{-1}<-0.83, consequently the systems (diisopropyl ether + 2,2,2-trifluoroethanol) is more compacted than for the systems (diisopropyl ether + ethanol). $V^{E}_{m,ij}$ results for the binary system (diisopropyl ether + acetone) exhibit sign change within the range:

-0.006 < $V^{E}_{m,ij}$/cm^3.mol^{-1}< 0.05, this can be explained by the weak interaction between ether and acetone molecules.

In the ternary systems, the hydrogen bonding and the dipole-dipole interaction are combined in the measured mixing volumes of ternary contribution terms. Therefore; the studied ternary mixtures reveal change of packing modes caused mainly by breaking and forming hydrogen bonding.

The ternary system of (α,α,α–trifluorotoluene + diisopropyl ether + ethanol) shows negative values of mixing volumes $V^{E}_{m,ijk}$ in wide range of compositions of component diisopropyl ether, while mixtures rich in α,α,α-trifluorotoluene are mainly slightly larger with positive values: -0.84< $V^{E}_{m,ijk}$ (ex.)/cm^3.mol^{-1}<0.25. Similar behaviour is observed for the system (fluorobenzene + diisopropyl ether + ethanol): (-0.87< $V^{E}_{m,ijk}$ (ex.)/cm^3.mol^{-1} < 0.03), and the system (diisopropyl ether + 2,2,2-trifluoroethanol + ethanol):

(–1.21< $V^{E}_{m,ijk}$ (ex.)/cm^3.mol^{-1}< 0.79); whereas the ternary system of (α,α,α-trifluorotoluene + 2,2,2-trifluoroethanol + ethanol) shows expands in the whole range of compositions: $V^{E}_{m,ijk}$ (max.) = 0.848 cm^3.mol^{-1}.

The ternary systems are well predicted using binary data alone by the empirical equations: Redlich-Kister, Scatchard *et al*., Tsao-smith, Kohler, Toop, Colinet, Hillert, Muggianu *et al*., and Jacob-Fitzner equations. The mean value of standard deviations of prediction is 0.029 cm^3.mol^{-1}.

The change in refractive indices of most binary mixtures studied are small and negative and are around zero for (α,α,α-trifluorotoluene + diisopropyl ether). These $\Delta_{mix}n$ values indicate that the light is slightly better refracted when passing through the studied mixtures caused by small mixing dispersion energies.

Conclusion:

- New data of excess molar volumes V^E_m and change in refractive indices of mixing $\Delta_{mix}n$ have been obtained at 298.15 K for binary and ternary mixtures composed of alcohols, aromatic hydrocarbons, ethers, and fluorinated hydrocarbons.
- The mixtures studied show deviations from ideality with weak mixing properties.
- The ternary excess molar volumes are predicted from binary values using several empirical equations.
- The experimental data are discussed in terms intermolecular interations.

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APPENDIX A.
EXPERIMENTAL RESULTS

Table (A. 1. 1). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

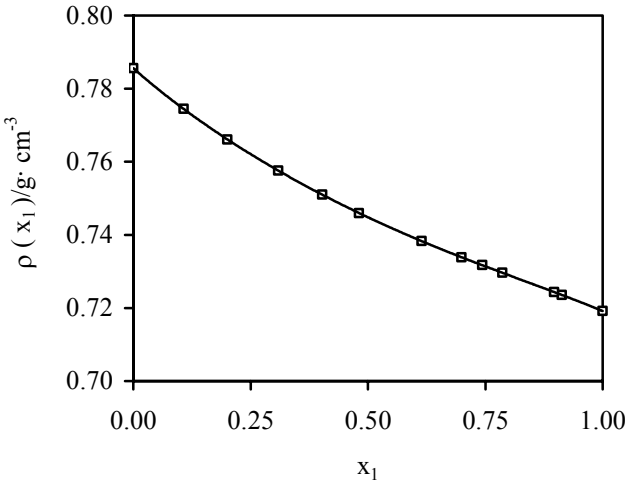
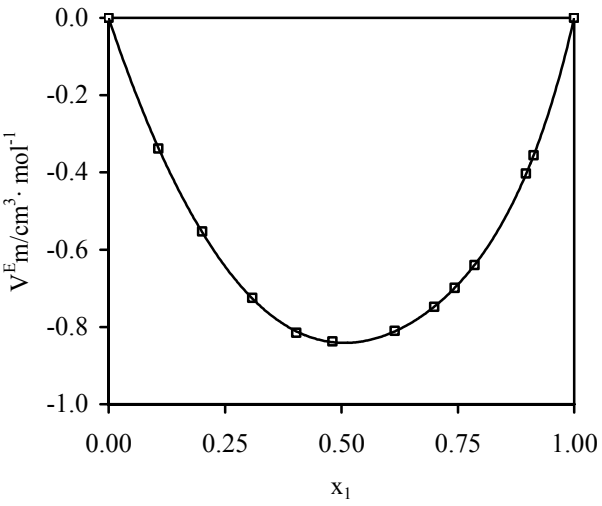
Component:	1. Diisopropyl ether		$[(CH_3)_2CH]_2O$			
	2. Ethanol		C_2H_5OH			
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$			
0.0000	---	0.7856				
0.1072	---	0.7745				
0.2007	---	0.7661				
0.3086	---	0.7576				
0.4030	---	0.7510				
0.4811	---	0.7460				
0.6142	---	0.7383				
0.6993	---	0.7338				
0.7432	---	0.7317				
0.7863	---	0.7296				
0.8965	---	0.7244				
0.9129	---	0.7236				
1.0000	---	0.7192				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	---	---	---	---	---	---
$\rho(x_1)$ / g·cm^{-3}	0.7856	-0.1100	0.0703	-0.0266	---	0.00007
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$				
0.0000	---	0.000				
0.1072	---	-0.338				
0.2007	---	-0.553				
0.3086	---	-0.725				
0.4030	---	-0.815				
0.4811	---	-0.837				
0.6142	---	-0.810				
0.6993	---	-0.748				
0.7432	---	-0.699				
0.7863	---	-0.640				
0.8965	---	-0.403				
0.9129	---	-0.356				
1.0000	---	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	---	---	---	---	---	---
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	-3.364	0.067	-0.673	0.725	-0.389	0.002
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3 \cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3 \cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3 \cdot mol^{-1})$
0.500	---	-0.841	---	---	-3.631	-5.221

Table (A. 1. 2). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

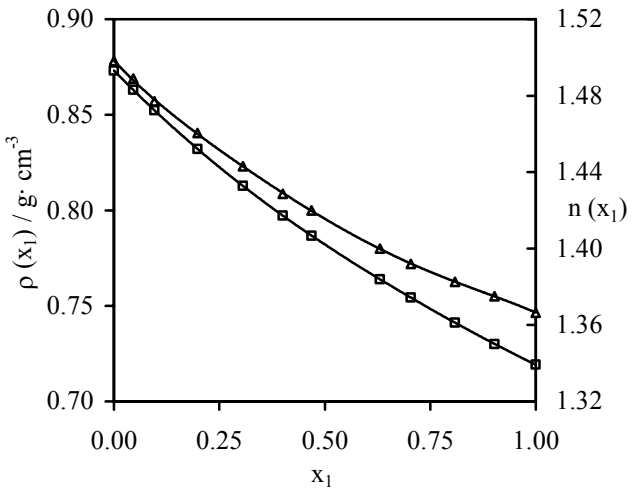
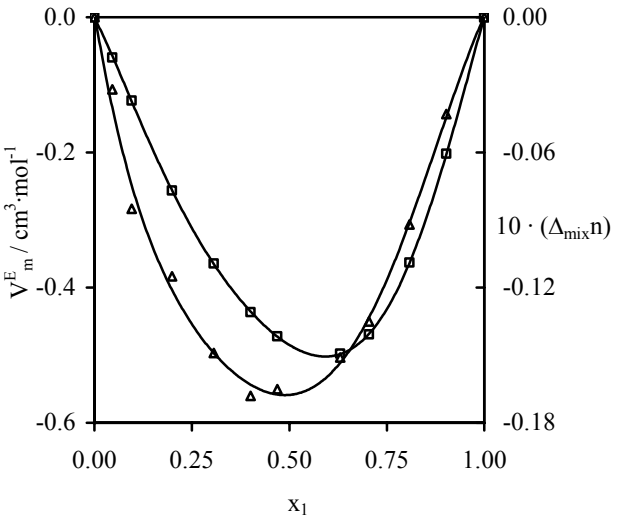
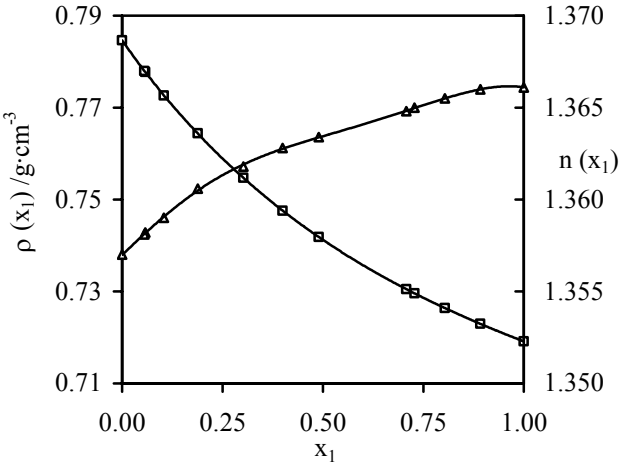
Component	1. Diisopropyl ether		$[(CH_3)_2CH]_2O$			
	2. Benzene		C_6H_6			
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$		Δ; $n(x_1)$, $\Delta_{mix}n$	
0.0000	1.4982	0.8731				
0.0458	1.4890	0.8632				
0.0962	1.4770	0.8524				
0.1987	1.4605	0.8321				
0.3060	1.4430	0.8128				
0.4008	1.4286	0.7972				
0.4689	1.4199	0.7867				
0.6306	1.4000	0.7639				
0.7041	1.3920	0.7543				
0.8087	1.3825	0.7413				
0.9027	1.3750	0.7301				
1.0000	1.3665	0.7192				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.4978	-0.2091	0.1000	-0.0220	---	0.0007
$\rho(x_1)$ / g·cm^{-3}	0.8732	-0.2255	0.1017	-0.0302	---	0.00009
x_1	$10\cdot(\Delta_{mix}n)$	$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$				
0.0000	0.000	0.000				
0.0458	-0.032	-0.060				
0.0962	-0.085	-0.123				
0.1987	-0.115	-0.256				
0.3060	-0.149	-0.365				
0.4008	-0.168	-0.437				
0.4689	-0.165	-0.472				
0.6306	-0.151	-0.497				
0.7041	-0.135	-0.469				
0.8087	-0.092	-0.363				
0.9027	-0.043	-0.202				
1.0000	0.000	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	-0.0672	-0.0131	---	---	---	0.0007
$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$	-1.939	0.705	-0.353	-0.261	0.700	0.002
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	-0.0168	-0.485	-0.0804	-0.0541	-1.148	-2.036

Table (A. 1. 3). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component: 1. Diisopropyl ether $[(CH_3)_2CH]_2O$ 2. Acetone $(CH_3)_2CO$						
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$		Δ; $n(x_1)$, $\Delta_{mix}n$	
0.0000	1.3570	0.7846				
0.0560	1.3581	0.7780				
0.0580	1.3582	0.7777				
0.1039	1.3590	0.7727				
0.1883	1.3606	0.7644				
0.3021	1.3618	0.7547				
0.4001	1.3628	0.7476				
0.4898	1.3634	0.7418				
0.7075	1.3648	0.7305				
0.7285	1.3650	0.7296				
0.8039	1.3655	0.7264				
0.8915	1.3660	0.7230				
1.0000	1.3661	0.7191				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3569	0.0259	-0.0427	0.0438	-0.0177	0.0001
$\rho(x_1)$ / g·cm^{-3}	0.7846	-0.1233	0.0934	-0.0453	0.0098	0.00003
x_1	$10\cdot(\Delta_{mix}n)$	$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$				
0.0000	0.000	0.000				
0.0560	0.006	-0.006				
0.0580	0.007	-0.005				
0.1039	0.010	0.001				
0.1883	0.019	0.005				
0.3021	0.020	0.019				
0.4001	0.022	0.039				
0.4898	0.019	0.046				
0.7075	0.014	0.038				
0.7285	0.014	0.036				
0.8039	0.012	0.023				
0.8915	0.009	0.013				
1.0000	0.000	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0077	0.0031	0.0042	---	---	0.0001
$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$	0.193	-0.103	-0.247	---	---	0.003
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ /($cm^3\cdot mol^{-1}$)	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}$ /($cm^3\cdot mol^{-1}$)	$V^{E\infty}_{m,2}$ /($cm^3\cdot mol^{-1}$)
0.500	0.0019	0.048	0.0150	0.0088	-0.157	0.049



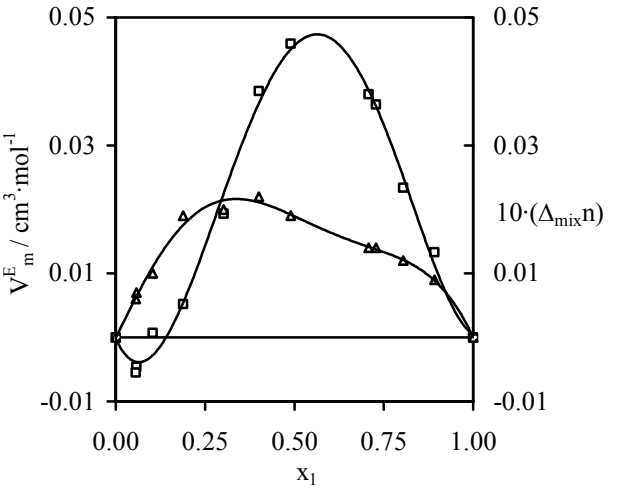
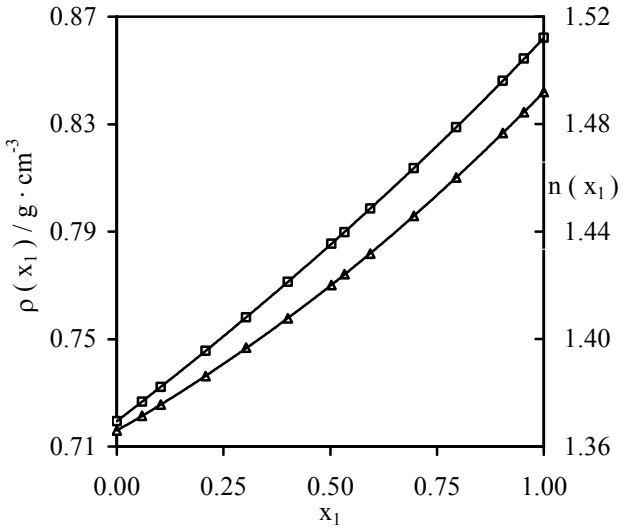


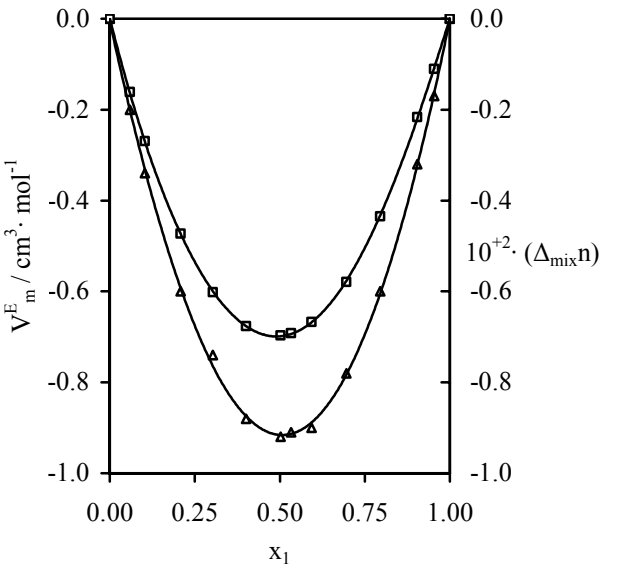
Table (A. 1. 4). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component: 1. Toluene C_7H_8						
	2. Diisopropyl ether $[(CH_3)_2CH]_2O$					
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$		Δ; $n(x_1)$, $\Delta_{mix}n$	



x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3660	0.7194
0.0589	1.3714	0.7267
0.1029	1.3756	0.7322
0.2080	1.3862	0.7456
0.3031	1.3968	0.7581
0.4010	1.4077	0.7713
0.5024	1.4201	0.7854
0.5331	1.4241	0.7898
0.5938	1.4318	0.7986
0.6955	1.4458	0.8136
0.7952	1.4602	0.8289
0.9040	1.4767	0.8461
0.9539	1.4845	0.8543
1.0000	1.4920	0.8621

Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3660	0.0907	0.0329	0.0024	---	0.0001
$\rho(x_1)$ / g·cm^{-3}	0.7194	0.1227	0.0146	0.0530	---	0.00004



x_1	$10^{+2}\cdot(\Delta_{mix}n)$	$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$
0.0000	0.00	0.000
0.0589	-0.20	-0.161
0.1029	-0.34	-0.269
0.2080	-0.60	-0.473
0.3031	-0.74	-0.602
0.4010	-0.88	-0.677
0.5024	-0.92	-0.697
0.5331	-0.91	-0.692
0.5938	-0.90	-0.667
0.6955	-0.78	-0.580
0.7952	-0.60	-0.435
0.9040	-0.32	-0.216
0.9539	-0.17	-0.110
1.0000	0.00	0.000

Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	-0.0366	---	---	---	---	0.0001
$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$	-2.796	-0.119	0.097	-0.176	---	0.002

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	-0.0092	-0.699	-0.0366	-0.0366	-2.994	-2.404

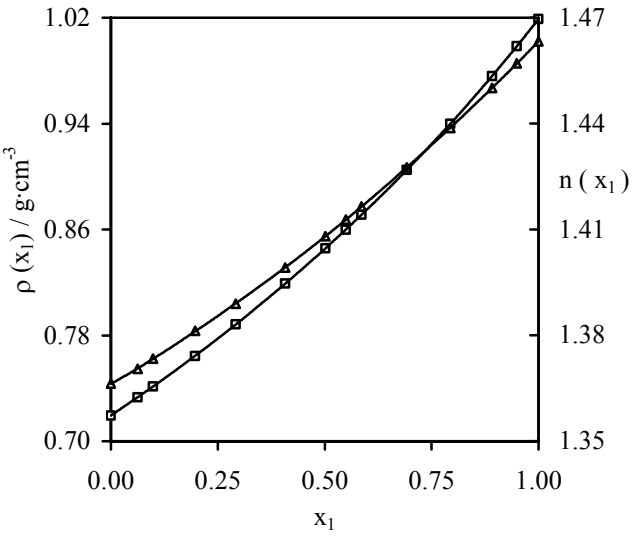
Table (A. 1. 5). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component: 1. Fluorobenzene C_6H_5F

2. Diisopropyl ether $[(CH_3)_2CH]_2O$

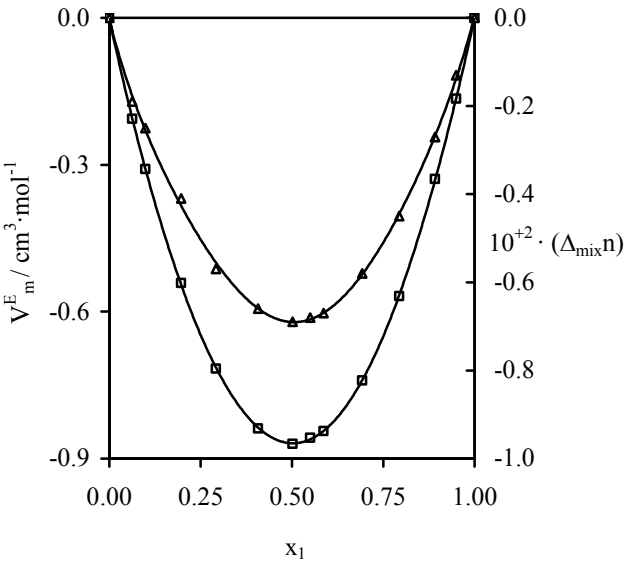
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3663	0.7194
0.0625	1.3705	0.7332
0.0989	1.3734	0.7415
0.1968	1.3813	0.7645
0.2921	1.3889	0.7883
0.4077	1.3992	0.8190
0.5021	1.4081	0.8458
0.5494	1.4128	0.8599
0.5862	1.4165	0.8711
0.6923	1.4276	0.9051
0.7937	1.4388	0.9399
0.8914	1.4501	0.9758
0.9495	1.4571	0.9986
1.0000	1.4633	1.0191

□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3662	0.0697	0.0273	---	---	0.0001
$\rho(x_1)$ / g·cm^{-3}	0.7194	0.2157	0.0650	0.0074	0.0114	0.00002

x_1	$10^{+2}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$
0.0000	0.00	0.000
0.0625	-0.19	-0.206
0.0989	-0.25	-0.309
0.1968	-0.41	-0.542
0.2921	-0.57	-0.716
0.4077	-0.66	-0.838
0.5021	-0.69	-0.870
0.5494	-0.68	-0.858
0.5862	-0.67	-0.844
0.6923	-0.58	-0.740
0.7937	-0.45	-0.569
0.8914	-0.27	-0.329
0.9495	-0.13	-0.165
1.0000	0.00	0.000



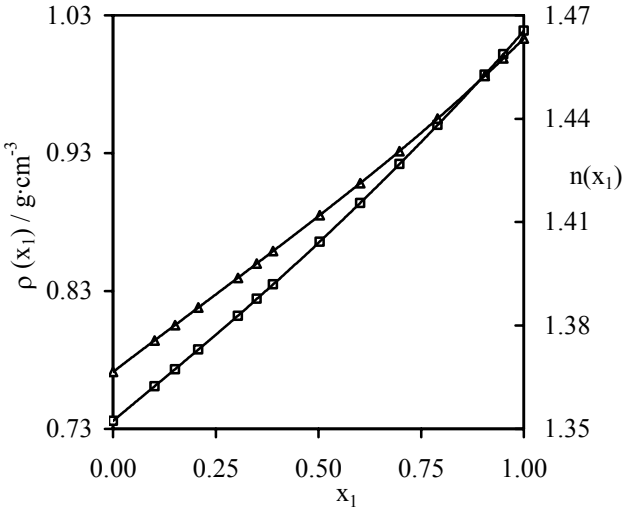
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	-0.0274	---	---	---	---	0.0001
$V^E_{m,12}/cm^3\cdot mol^{-1}$	-3.467	---	---	---	---	0.003

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	-0.0069	-0.867	-0.0274	-0.0274	-3.467	-3.467

Table (A. 1. 6). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

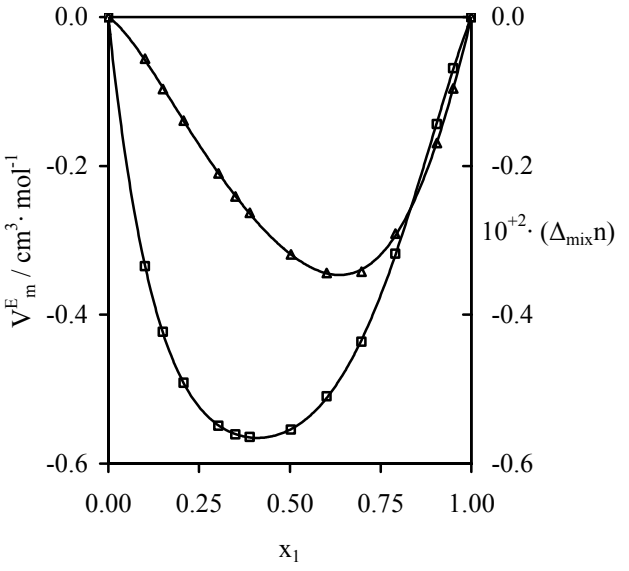
Component:	1. Fluorobenzene		C_6H_5F			
	2. Tert-butyl methyl ether		$C(CH_3)_3OCH_3$			

x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$
0.0000	1.3665	0.7358	
0.1008	1.3757	0.7609	
0.1506	1.3801	0.7733	
0.2076	1.3852	0.7875	
0.3037	1.3938	0.8121	
0.3503	1.3980	0.8243	
0.3897	1.4016	0.8348	
0.5030	1.4120	0.8658	
0.6016	1.4213	0.8939	
0.6975	1.4306	0.9222	
0.7904	1.4401	0.9505	
0.9049	1.4524	0.9869	
0.9500	1.4575	1.0018	
1.0000	1.4633	1.0188	



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3665	0.0918	-0.0107	0.0157	---	0.00003
$\rho(x_1)$ / g·cm^{-3}	0.7359	0.2462	0.0036	0.0479	-0.0150	0.0001

x_1	$10^{+2}\cdot(\Delta_{mix}n)$	$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$
0.0000	0.000	0.000
0.1008	-0.056	-0.335
0.1506	-0.097	-0.423
0.2076	-0.139	-0.492
0.3037	-0.210	-0.549
0.3503	-0.241	-0.561
0.3897	-0.263	-0.564
0.5030	-0.319	-0.554
0.6016	-0.344	-0.510
0.6975	-0.342	-0.437
0.7904	-0.291	-0.318
0.9049	-0.169	-0.144
0.9500	-0.096	-0.069
1.0000	0.000	0.000



Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	-0.0129	0.0079	---	---	---	0.00003
$V^E_{m,12}$ / $cm^3\cdot mol^{-1}$	-2.217	-0.500	-0.713	-1.193	---	0.002

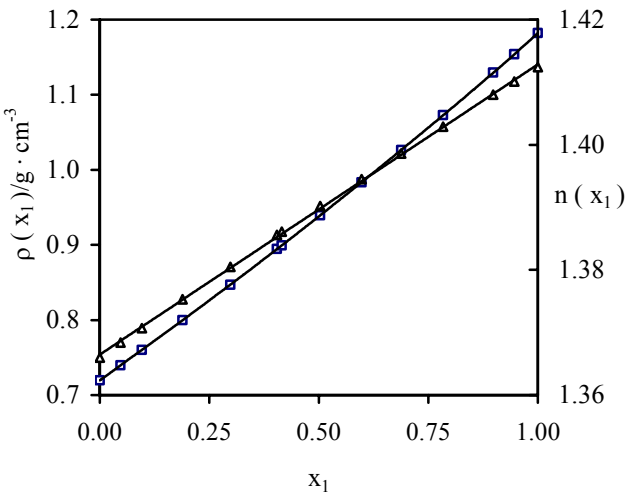
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	-0.0032	-0.554	-0.0050	-0.0208	-4.623	-1.237

Table (A. 1. 7). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component:	1. Trifluorotoluene	$C_7 H_5 F_3$
	2. Diisopropyl ether	$[(CH_3)_2 CH]_2 O$

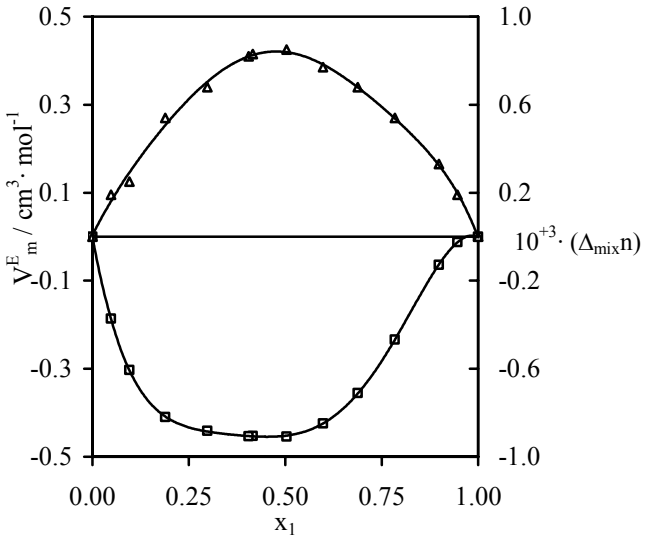
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3660	0.7195
0.0476	1.3684	0.7397
0.0959	1.3707	0.7602
0.1887	1.3753	0.7997
0.2979	1.3805	0.8469
0.4046	1.3856	0.8944
0.4154	1.3861	0.8993
0.5032	1.3902	0.9394
0.5975	1.3945	0.9835
0.6879	1.3986	1.0264
0.7836	1.4029	1.0727
0.8982	1.4080	1.1294
0.9463	1.4101	1.1540
1.0000	1.4124	1.1822

□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3660	0.0496	-0.0032	---	---	0.00003
$\rho(x_1)$ / g·cm^{-3}	0.7197	0.4169	0.0329	0.0135	-0.0011	0.0002

x_1	$10^{+3}\cdot(\Delta_{mix}n)$	$V^E_{m,12} / cm^3 \cdot mol^{-1}$
0.0000	0.00	0.000
0.0476	0.19	-0.186
0.0959	0.25	-0.302
0.1887	0.54	-0.410
0.2979	0.68	-0.441
0.4046	0.82	-0.453
0.4154	0.83	-0.453
0.5032	0.85	-0.454
0.5975	0.77	-0.425
0.6879	0.68	-0.355
0.7836	0.54	-0.234
0.8982	0.33	-0.064
0.9463	0.19	-0.013
1.0000	0.00	0.000



Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0033	---	---	---	---	0.00003
$V^E_{m,12} / cm^3 \cdot mol^{-1}$	-1.809	-0.212	-0.398	-2.379	---	0.001

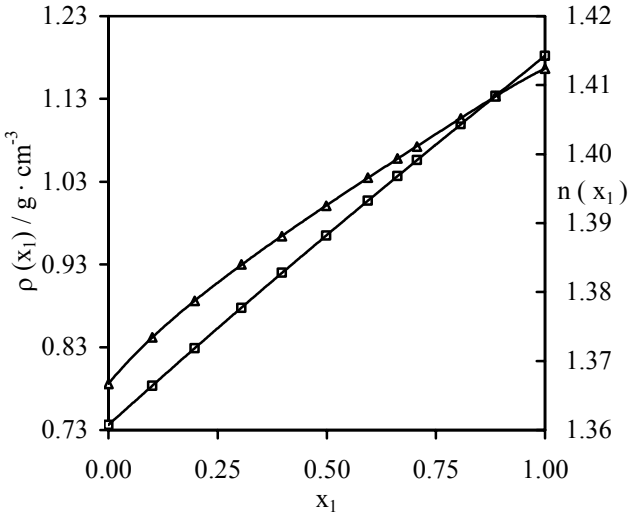
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3 \cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3 \cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3 \cdot mol^{-1})$
0.500	0.0008	-0.452	0.0033	0.0033	-4.797	0.384

Table (A. 1. 8). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component:	1. Trifluorotoluene	$C_7H_5F_3$			
	2. Tert-butyl methyl ether	$C(CH_3)_3OCH_3$			

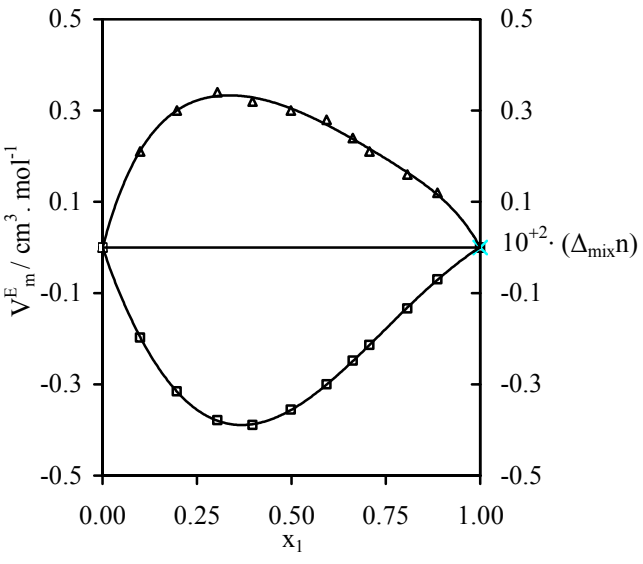
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3667	0.7363
0.0999	1.3734	0.7834
0.1972	1.3787	0.8286
0.3041	1.3840	0.8776
0.3974	1.3881	0.9198
0.4986	1.3925	0.9649
0.5938	1.3966	1.0069
0.6623	1.3994	1.0369
0.7068	1.4011	1.0562
0.8070	1.4052	1.0995
0.8865	1.4084	1.1336
1.0000	1.4124	1.1822

□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3667	0.0724	-0.0718	0.0764	-0.0313	0.00007
$\rho(x_1)$ / g·cm^{-3}	0.7363	0.4750	-0.0332	-0.0024	0.0065	0.00001

x_1	$10^{+2}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$
0.0000	0.00	0.000
0.0999	0.21	-0.197
0.1972	0.30	-0.315
0.3041	0.34	-0.379
0.3974	0.32	-0.389
0.4986	0.30	-0.356
0.5938	0.28	-0.300
0.6623	0.24	-0.248
0.7068	0.21	-0.214
0.8070	0.16	-0.134
0.8865	0.12	-0.070
1.0000	0.00	0.000



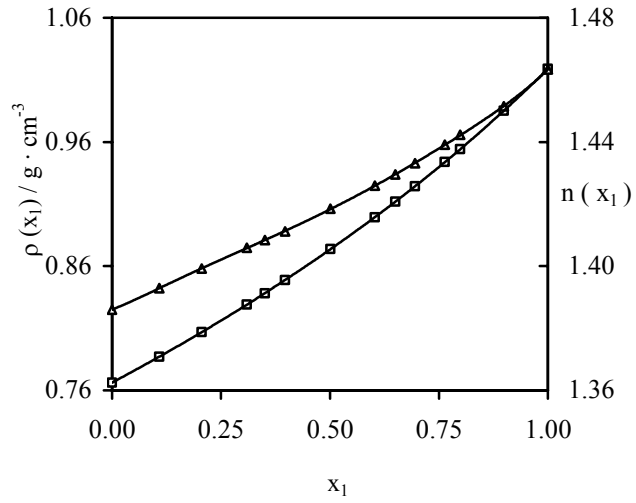
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0131	0.0069	---	---	---	0.0002
$V^E_{m,12}/cm^3\cdot mol^{-1}$	-1.423	-0.945	---	---	---	0.001

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	0.0033	-0.356	0.0200	0.0062	-2.368	-0.479

Table (A. 1. 9). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

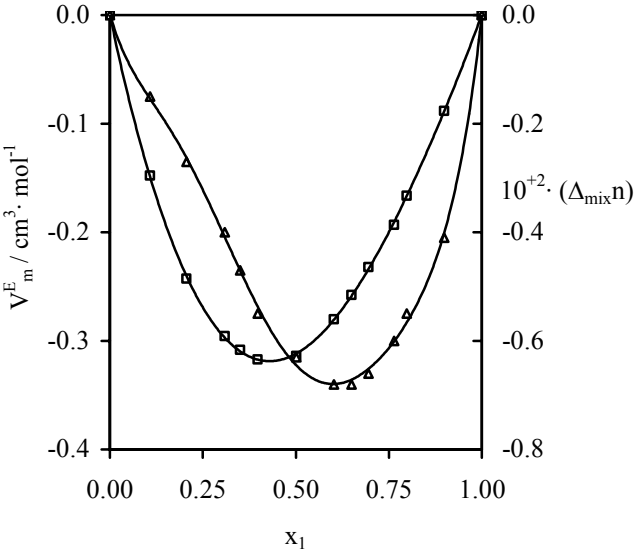
Component:	1. Fluorobenzene	C_6H_5F				
	2. Tert-amyl methyl ether	$C_2H_5\ C(CH_3)_2OCH_3$				

x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}
0.0000	1.3860	0.7662
0.1081	1.3929	0.7871
0.2059	1.3992	0.8070
0.3092	1.4059	0.8290
0.3506	1.4084	0.8382
0.3971	1.4112	0.8488
0.5013	1.4185	0.8737
0.6029	1.4259	0.8994
0.6500	1.4295	0.9119
0.6950	1.4332	0.9243
0.7636	1.4391	0.9438
0.7986	1.4423	0.9541
0.8986	1.4515	0.9852
1.0000	1.4634	1.0191



Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3860	0.0644	-0.0051	0.0061	0.0118	0.0002
$\rho(x_1)$ / g·cm^{-3}	0.7662	0.1879	0.0456	0.0089	0.0104	0.00001

x_1	$10^{+2}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$
0.0000	0.00	0.000
0.1081	-0.15	-0.148
0.2059	-0.27	-0.243
0.3092	-0.40	-0.296
0.3506	-0.47	-0.308
0.3971	-0.55	-0.317
0.5013	-0.63	-0.314
0.6029	-0.68	-0.280
0.6500	-0.68	-0.258
0.6950	-0.66	-0.232
0.7636	-0.60	-0.193
0.7986	-0.55	-0.166
0.8986	-0.41	-0.088
1.0000	0.00	0.000



Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	-0.0255	0.0155	---	---	---	0.0002
$V^E_{m,12}/cm^3\cdot mol^{-1}$	-1.250	-0.368	---	---	---	0.002

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	-0.0064	-0.312	-0.0099	-0.0410	-1.617	-0.881

Table (A. 1. 10). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

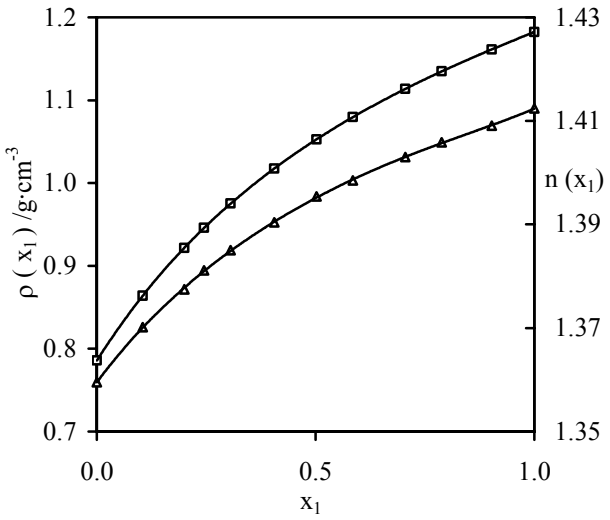
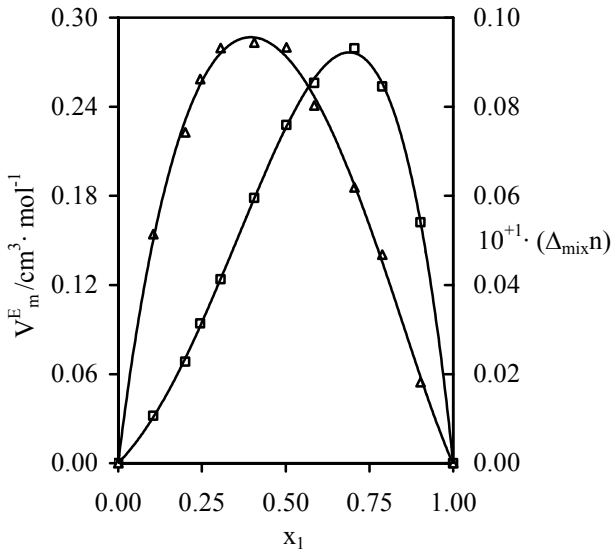
Component: 1. Trifluorotoluene $C_7H_5F_3$						
2. Ethanol C_2H_5OH						
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$ Δ; $n(x_1)$, $\Delta_{mix}n$			
0.0000	1.3595	0.7857				
0.1051	1.3702	0.8640				
0.1999	1.3775	0.9217				
0.2454	1.3811	0.9458				
0.3059	1.3850	0.9752				
0.4057	1.3904	1.0175				
0.5022	1.3954	1.0528				
0.5855	1.3985	1.0797				
0.7052	1.4030	1.1137				
0.7886	1.4059	1.1349				
0.9032	1.4091	1.1615				
1.0000	1.4124	1.1823				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3596	0.1087	-0.0993	0.0523	-0.0090	0.0002
$\rho(x_1)$ / g·cm^{-3}	0.7859	0.8182	-0.7957	0.5220	-0.1482	0.00002
x_1	$10^{+1}\cdot(\Delta_{mix}n)$	$V^E_{m,12}/cm^3\cdot mol^{-1}$				
0.0000	0.000	0.000				
0.1051	0.051	0.032				
0.1999	0.074	0.068				
0.2454	0.086	0.094				
0.3059	0.093	0.124				
0.4057	0.094	0.179				
0.5022	0.093	0.228				
0.5855	0.080	0.256				
0.7052	0.062	0.279				
0.7886	0.047	0.254				
0.9032	0.018	0.162				
1.0000	0.000	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0368	0.0176	---	---	---	0.0002
$V^E_{m,12}/cm^3\cdot mol^{-1}$	0.902	-0.933	0.279	---	---	0.002
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3\cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3\cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3\cdot mol^{-1})$
0.500	0.0092	0.225	0.0544	0.0192	0.248	2.114

Table (A. 1. 11). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

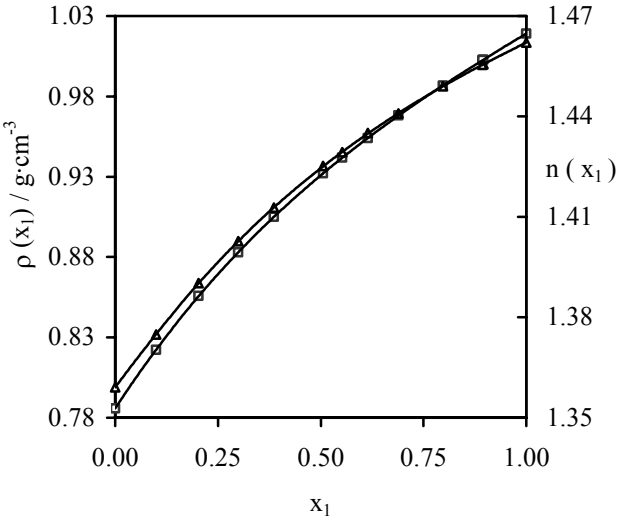
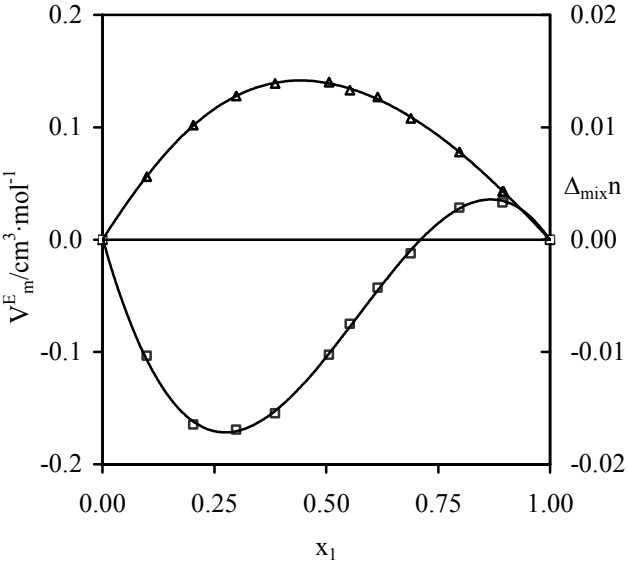
Component: 1. Fluorobenzene C_6H_5F						
2. Ethanol C_2H_5OH						
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$	Δ; $n(x_1)$, $\Delta_{mix}n$		
0.0000	1.3591	0.7858				
0.0991	1.3749	0.8222				
0.2031	1.3902	0.8557				
0.2992	1.4027	0.8829				
0.3862	1.4128	0.9050				
0.5062	1.4252	0.9322				
0.5525	1.4293	0.9418				
0.6147	1.4351	0.9541				
0.6892	1.4409	0.9681				
0.7971	1.4490	0.9868				
0.8937	1.4555	1.0026				
0.8956	1.4556	1.0028				
1.0000	1.4621	1.0190				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	1.3590	0.1702	-0.0865	0.0136	0.0058	0.0001
$\rho(x_1)$ / g·cm^{-3}	0.7858	0.3927	-0.2652	0.1344	-0.0288	0.00003
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$				
0.0000	0.0000	0.000				
0.0991	0.0056	-0.103				
0.2031	0.0102	-0.165				
0.2992	0.0128	-0.169				
0.3862	0.0139	-0.155				
0.5062	0.0140	-0.102				
0.5525	0.0133	-0.075				
0.6147	0.0127	-0.043				
0.6892	0.0108	-0.013				
0.7971	0.0078	0.029				
0.8937	0.0043	0.033				
0.8956	0.0043	0.035				
1.0000	0.0000	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	0.0557	0.0123	---	---	---	0.0001
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	-0.417	-0.986	---	---	---	0.003
x_1	$\Delta_{mix}n$	$V^E_{m,12}$/($cm^3 \cdot mol^{-1}$)	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}$/($cm^3 \cdot mol^{-1}$)	$V^{E\infty}_{m,2}$/($cm^3 \cdot mol^{-1}$)
0.500	0.0139	-0.104	0.0680	0.0434	-1.403	0.569

Table (A. 1. 12). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

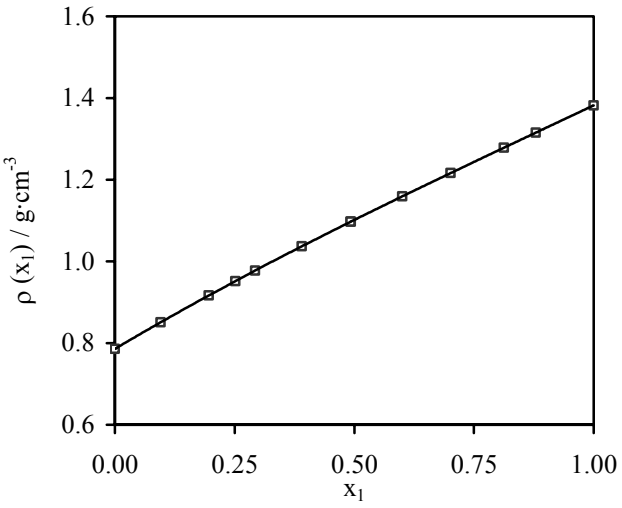
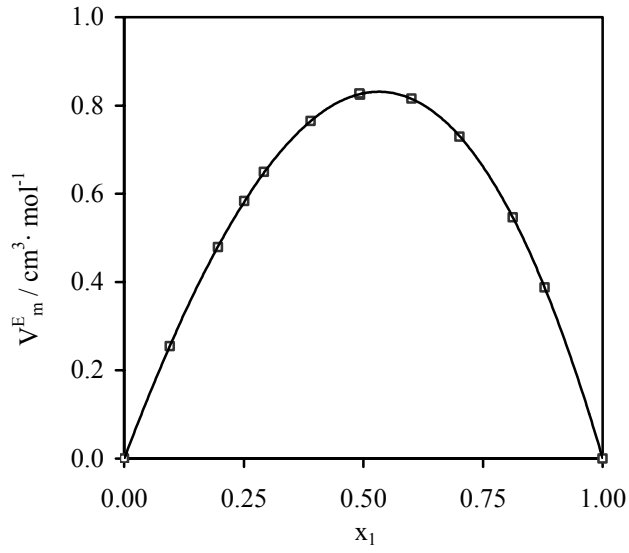
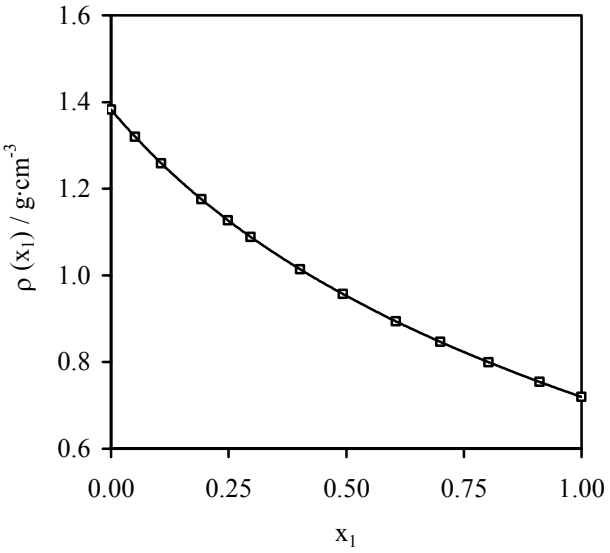
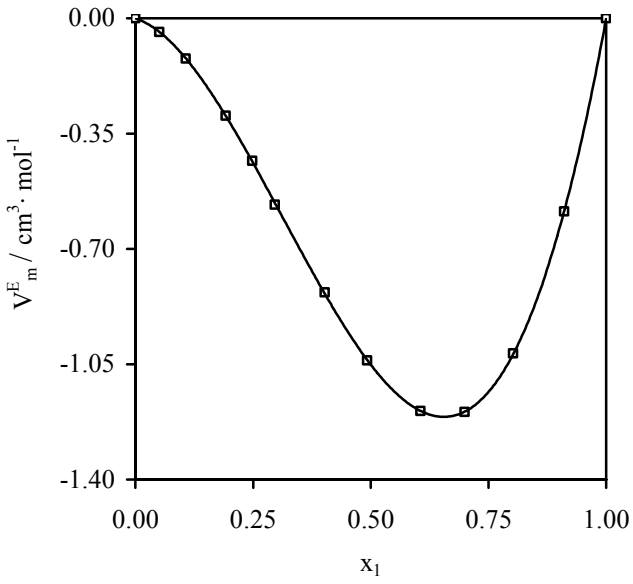
Component:	1. 2,2,2-Trifluoroethanol CF_3CH_2OH					
	2. Ethanol C_2H_5OH					
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$			
0.0000	---	0.7859				
0.0957	---	0.8512				
0.1960	---	0.9167				
0.2512	---	0.9517				
0.2927	---	0.9775				
0.3900	---	1.0366				
0.4922	---	1.0969				
0.4930	---	1.0975				
0.6007	---	1.1595				
0.7012	---	1.2163				
0.8123	---	1.2783				
0.8794	---	1.3155				
1.0000	---	1.3823				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	---	---	---	---	---	---
$\rho(x_1)$ / g·cm^{-3}	0.7860	0.6972	-0.1675	0.0744	-0.0078	0.00002
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$				
0.0000	---	0.000				
0.0957	---	0.255				
0.1960	---	0.479				
0.2512	---	0.584				
0.2927	---	0.649				
0.3900	---	0.765				
0.4922	---	0.827				
0.4930	---	0.824				
0.6007	---	0.816				
0.7012	---	0.729				
0.8123	---	0.546				
0.8794	---	0.388				
1.0000	---	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	---	---	---	---	---	---
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	3.312	-0.435	---	---	---	0.001
x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3 \cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3 \cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3 \cdot mol^{-1})$
0.500	---	0.828	---	---	2.876	3.747

Table (A. 1. 13). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

Component: 1. Diisopropyl ether $[(CH_3)_2CH]_2O$ 2. Trifluoroethanol CF_3CH_2OH			
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$
0.0000	---	1.3826	
0.0511	---	1.3200	
0.1069	---	1.2585	
0.1922	---	1.1757	
0.2483	---	1.1273	
0.2968	---	1.0889	
0.4021	---	1.0138	
0.4927	---	0.9571	
0.6059	---	0.8940	
0.6997	---	0.8469	
0.8024	---	0.7998	
0.9113	---	0.7542	
1.0000	---	0.7196	

Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	---	---	---	---	---	---
$\rho(x_1)$ / g·cm^{-3}	1.3822	-1.2693	1.1550	-0.7879	0.2398	0.0004

x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	
0.0000	---	0.000	
0.0511	---	-0.042	
0.1069	---	-0.122	
0.1922	---	-0.295	
0.2483	---	-0.433	
0.2968	---	-0.565	
0.4021	---	-0.832	
0.4927	---	-1.039	
0.6059	---	-1.192	
0.6997	---	-1.195	
0.8024	---	-1.017	
0.9113	---	-0.586	
1.0000	---	0.000	

Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	---	---	---	---	---	---
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	-4.199	3.710	---	---	---	0.003

x_1	$\Delta_{mix}n$	$V^E_{m,12}/(cm^3 \cdot mol^{-1})$	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}/(cm^3 \cdot mol^{-1})$	$V^{E\infty}_{m,2}/(cm^3 \cdot mol^{-1})$
0.500	---	-1.050	---	---	-0.489	-7.909

Table (A. 1. 14). Volumetric and refractive indices properties of binary mixtures at 298.15 K and 101 kPa

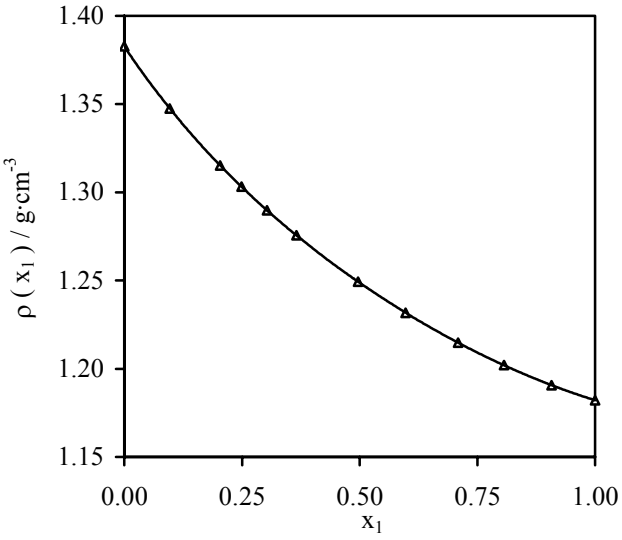
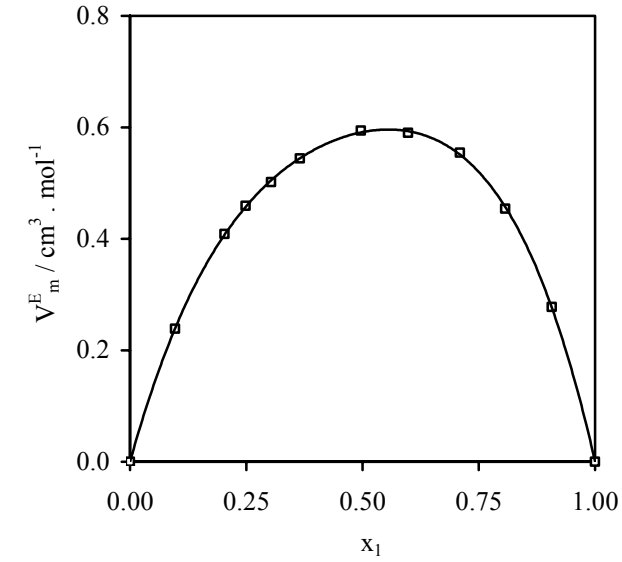
Component:	1. α,α,α-Trifluorotoluene $C_7H_5F_3$					
	2. 2,2,2-Trifluoroethanol CF_3CH_2OH					
x_1	$n(x_1)$	$\rho(x_1)$ / g·cm^{-3}	□; $\rho(x_1)$, $V^E_{m,12}$			
0.0000	---	1.3827				
0.0965	---	1.3476				
0.2036	---	1.3153				
0.2488	---	1.3032				
0.3034	---	1.2898				
0.3657	---	1.2756				
0.4964	---	1.2493				
0.5979	---	1.2318				
0.7092	---	1.2148				
0.8068	---	1.2020				
0.9076	---	1.1907				
1.0000	---	1.1822				
Equation (4. 1):	A_0	A_1	A_2	A_3	A_4	σ_s
$n(x_1)$	---	---	---	---	---	---
$\rho(x_1)$ / g·cm^{-3}	1.3826	-0.3928	0.3525	-0.2500	0.0900	0.0001
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$				
0.0000	---	0.000				
0.0965	---	0.238				
0.2036	---	0.408				
0.2488	---	0.459				
0.3034	---	0.502				
0.3657	---	0.544				
0.4964	---	0.594				
0.5979	---	0.590				
0.7092	---	0.554				
0.8068	---	0.454				
0.9076	---	0.278				
1.0000	---	0.000				
Equation (4. 4):	B_0	B_1	B_2	B_3	B_4	σ_s
$\Delta_{mix}n$	---	---	---	---	---	---
$V^E_{m,12}$ / $cm^3 \cdot mol^{-1}$	2.366	-0.328	0.976	---	---	0.003
x_1	$\Delta_{mix}n$	$V^E_{m,12}$ /($cm^3 \cdot mol^{-1}$)	$\Delta_{mix}n_1^{\infty}$	$\Delta_{mix}n_2^{\infty}$	$V^{E\infty}_{m,1}$ /($cm^3 \cdot mol^{-1}$)	$V^{E\infty}_{m,2}$ /($cm^3 \cdot mol^{-1}$)
0.500	---	0.592	---	---	3.015	3.670

Table (A. 2. 1). Volumetric properties of ternary mixtures at 298.15 K and 101 kPa

Component:	1. α,α,α-Trifluorotoluene	$C_7H_5F_3$				
	2. Diisopropyl ether	$[(CH_3)_2CH]_2O$				
	3. Ethanol	CH_3CH_2OH				
x_1	x_2	ρ	$V^E_{m,123}$(exp .)	$V^E_{m,123}$ (eq. 2. 27)	$V^E_{m,123}$ (eq. 2. 28)	$V^E_{m,123}$ (eq. 2. 30)
		$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$			
0.0420	0.0467	0.8122	-0.144	-0.114	-0.144	-0.143
0.0447	0.8995	0.7416	-0.376	-0.332	-0.377	-0.377
0.0623	0.6861	0.7617	-0.721	-0.730	-0.736	-0.723
0.0631	0.4394	0.7812	-0.777	-0.806	-0.795	-0.775
0.0777	0.5997	0.7746	-0.761	-0.793	-0.780	-0.761
0.0783	0.2210	0.8124	-0.542	-0.521	-0.551	-0.539
0.0864	0.8030	0.7634	-0.562	-0.537	-0.569	-0.564
0.1133	0.4459	0.8044	-0.734	-0.764	-0.758	-0.732
0.1660	0.3402	0.8414	-0.627	-0.630	-0.642	-0.620
0.1784	0.2115	0.8670	-0.457	-0.426	-0.457	-0.448
0.1969	0.5993	0.8229	-0.647	-0.668	-0.668	-0.647
0.1991	0.7197	0.8116	-0.551	-0.548	-0.561	-0.552
0.2225	0.4327	0.8530	-0.630	-0.654	-0.650	-0.625
0.2694	0.2337	0.9047	-0.425	-0.412	-0.415	-0.412
0.2738	0.0527	0.9461	-0.048	0.021	-0.035	-0.042
0.3155	0.6116	0.8636	-0.521	-0.526	-0.532	-0.520
0.3251	0.4684	0.8867	-0.553	-0.578	-0.567	-0.547
0.3324	0.3440	0.9096	-0.495	-0.519	-0.495	-0.484
0.4027	0.1809	0.9686	-0.249	-0.253	-0.221	-0.233
0.4207	0.5216	0.9103	-0.484	-0.494	-0.492	-0.481
0.4297	0.3371	0.9451	-0.428	-0.465	-0.424	-0.415
0.4473	0.2445	0.9700	-0.320	-0.351	-0.299	-0.303
0.4655	0.0537	1.0240	0.062	0.085	0.083	0.070
0.5388	0.4022	0.9667	-0.429	-0.449	-0.435	-0.424
0.5516	0.1524	1.0256	-0.116	-0.147	-0.088	-0.100
0.5732	0.2283	1.0135	-0.240	-0.286	-0.227	-0.226
0.6357	0.2994	1.0152	-0.333	-0.359	-0.335	-0.326
0.7349	0.0578	1.1034	0.130	0.069	0.141	0.137
0.7558	0.2000	1.0699	-0.190	-0.211	-0.191	-0.186
0.8865	0.0692	1.1363	0.024	-0.004	0.025	0.027

Equation (4. 8):	C_0	C_1	C_2	σ_s
$\Delta_{123}V_m^E / cm^3 \cdot mol^{-1}$	-0.452	-0.567	0.906	0.041

Table (A. 2. 2). Volumetric properties of ternary mixtures at 298.15 K and 101 kPa

Component:	1. Fluorobenzene	C_6H_5F				
	2. Diisopropyl ether (DIPE)	$[(CH_3)_2CH]_2O$				
	3. Ethanol	CH_3CH_2OH				
x_1	x_2	ρ	$V^E_{m,123}$(exp .)	$V^E_{m,123}$ (eq. 2. 27)	$V^E_{m,123}$ (eq. 2. 28)	$V^E_{m,123}$ (eq. 2. 30)
		$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$			
0.0286	0.3362	0.7635	-0.779	-0.782	-0.775	-0.775
0.0408	0.5806	0.7493	-0.835	-0.847	-0.844	-0.844
0.0421	0.1851	0.7807	-0.568	-0.565	-0.558	-0.558
0.0505	0.7212	0.7430	-0.722	-0.732	-0.739	-0.738
0.0516	0.0601	0.7976	-0.263	-0.260	-0.257	-0.257
0.0637	0.4353	0.7646	-0.856	-0.868	-0.857	-0.857
0.0649	0.8791	0.7368	-0.410	-0.408	-0.420	-0.419
0.1178	0.2809	0.7921	-0.764	-0.768	-0.751	-0.751
0.1440	0.1152	0.8195	-0.480	-0.473	-0.461	-0.460
0.1472	0.6477	0.7665	-0.790	-0.808	-0.830	-0.824
0.1483	0.1939	0.8102	-0.646	-0.643	-0.626	-0.626
0.1583	0.7555	0.7610	-0.655	-0.657	-0.686	-0.681
0.1842	0.4835	0.7873	-0.864	-0.892	-0.894	-0.888
0.2240	0.0563	0.8515	-0.345	-0.339	-0.331	-0.331
0.2337	0.5708	0.7893	-0.831	-0.856	-0.885	-0.874
0.2377	0.2836	0.8209	-0.773	-0.783	-0.769	-0.766
0.3029	0.1390	0.8576	-0.545	-0.537	-0.525	-0.524
0.3039	0.3562	0.8260	-0.811	-0.834	-0.838	-0.830
0.3184	0.6072	0.8017	-0.812	-0.820	-0.855	-0.843
0.3345	0.0347	0.8848	-0.275	-0.271	-0.266	-0.266
0.3783	0.4483	0.8294	-0.831	-0.853	-0.887	-0.871
0.4151	0.2595	0.8623	-0.691	-0.703	-0.711	-0.702
0.4289	0.1372	0.8862	-0.494	-0.491	-0.488	-0.484
0.4424	0.4510	0.8408	-0.829	-0.845	-0.881	-0.864
0.4483	0.3700	0.8525	-0.782	-0.802	-0.834	-0.817
0.5440	0.1514	0.9067	-0.468	-0.470	-0.478	-0.471
0.5693	0.2363	0.8956	-0.604	-0.617	-0.640	-0.627
0.5696	0.0256	0.9390	-0.148	-0.146	-0.146	-0.145
0.6313	0.2838	0.8985	-0.676	-0.686	-0.710	-0.697
0.6524	0.0594	0.9467	-0.203	-0.202	-0.207	-0.203
0.6742	0.1402	0.9328	-0.396	-0.401	-0.416	-0.407
0.7379	0.1654	0.9386	-0.450	-0.455	-0.471	-0.462
0.8342	0.0252	0.9865	-0.052	-0.052	-0.055	-0.054
0.8638	0.0809	0.9778	-0.235	-0.237	-0.243	-0.239

Equation (4. 8):	C_0	C_1	C_2	σ_s
$\Delta_{123} V_m^E / cm^3 \cdot mol^{-1}$	-2.854	3.856	6.210	0.041

Table (A. 2. 3). Volumetric properties of ternary mixtures at 298.15 K and 101 kPa

Component: 1. Diisopropyl ether		$[(CH_3)_2CH]_2O$				
2. 2,2,2-Trifluoroethanol		CF_3CH_2OH				
3. Ethanol		CH_3CH_2OH				
x_1	x_2	ρ	$V^E_{m,123}$(exp .)	$V^E_{m,123}$ (eq. 2. 27)	$V^E_{m,123}$ (eq. 2. 28)	$V^E_{m,123}$ (eq. 2. 30)
		$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$			
0.0183	0.5871	1.1427	0.742	0.733	0.739	0.739
0.0206	0.3651	1.0141	0.654	0.691	0.652	0.653
0.0310	0.7088	1.2033	0.586	0.563	0.581	0.583
0.0327	0.0461	0.8130	0.011	0.033	0.011	0.011
0.0415	0.8259	1.2605	0.336	0.312	0.330	0.333
0.0641	0.4285	1.0344	0.527	0.563	0.522	0.523
0.1145	0.1119	0.8410	-0.100	-0.070	-0.100	-0.100
0.1150	0.6014	1.1066	0.319	0.327	0.307	0.313
0.1216	0.2044	0.8926	0.050	0.092	0.048	0.049
0.1246	0.7550	1.1801	0.105	0.099	0.093	0.101
0.1303	0.7010	1.1506	0.160	0.158	0.147	0.155
0.1356	0.8189	1.2066	-0.068	-0.072	-0.075	-0.070
0.1635	0.4026	0.9880	0.120	0.151	0.114	0.118
0.1789	0.2391	0.8993	-0.086	-0.058	-0.086	-0.085
0.1930	0.4987	1.0271	0.029	0.046	0.018	0.027
0.2245	0.6320	1.0805	-0.169	-0.165	-0.183	-0.170
0.2362	0.6791	1.0983	-0.272	-0.271	-0.284	-0.273
0.2389	0.0486	0.7893	-0.537	-0.539	-0.535	-0.535
0.2820	0.3896	0.9510	-0.309	-0.304	-0.311	-0.302
0.2978	0.0671	0.7927	-0.617	-0.631	-0.613	-0.612
0.3051	0.5030	0.9972	-0.401	-0.399	-0.413	-0.397
0.3060	0.2144	0.8637	-0.474	-0.487	-0.466	-0.464
0.3290	0.5814	1.0256	-0.544	-0.543	-0.556	-0.541
0.3428	0.2722	0.8846	-0.531	-0.547	-0.524	-0.518
0.4079	0.3917	0.9257	-0.706	-0.715	-0.709	-0.693
0.4286	0.0234	0.7603	-0.811	-0.825	-0.808	-0.808
0.4475	0.1760	0.8267	-0.784	-0.819	-0.769	-0.765
0.4500	0.4831	0.9556	-0.887	-0.887	-0.893	-0.880
0.5045	0.0728	0.7763	-0.848	-0.878	-0.836	-0.836
0.5177	0.2629	0.8545	-0.923	-0.942	-0.914	-0.902
0.5855	0.3429	0.8771	-1.107	-1.105	-1.107	-1.095
0.6661	0.1410	0.7906	-0.976	-0.971	-0.962	-0.956
0.7193	0.2098	0.8116	-1.083	-1.068	-1.078	-1.071
0.7328	0.0523	0.7521	-0.816	-0.780	-0.807	-0.806
0.7677	0.1117	0.7718	-0.904	-0.869	-0.894	-0.891
0.8658	0.0504	0.7436	-0.621	-0.559	-0.616	-0.615

Equation (4. 8):	C_0	C_1	C_2	σ_s
$\Delta_{123}V_m^E / cm^3 \cdot mol^{-1}$	0.182	-2.036	0.563	0.017

Table (A. 2. 4). Volumetric properties of ternary mixtures at 298.15 K and 101 kPa

Component:	1. α,α,α -Trifluorotoluene	$C_7H_5F_3$				
	2. 2,2,2-Trifluoroethanol	CF_3CH_2OH				
	3. Ethanol	CH_3CH_2OH				
x_1	x_2	ρ	$V^E_{m,123}$(exp .)	$V^E_{m,123}$ (eq. 2. 27)	$V^E_{m,123}$ (eq. 2. 28)	$V^E_{m,123}$ (eq. 2. 30)
		g·cm^{-3}	cm^3 · mol^{-1}			
0.0062	0.3993	1.0455	0.777	0.774	0.775	0.774
0.0128	0.5347	1.1270	0.836	0.832	0.832	0.830
0.0169	0.3169	1.0017	0.693	0.685	0.687	0.684
0.0176	0.9352	1.3500	0.212	0.212	0.212	0.211
0.0200	0.4229	1.0658	0.803	0.794	0.795	0.792
0.0203	0.1454	0.8980	0.385	0.378	0.380	0.378
0.0254	0.0488	0.8392	0.146	0.142	0.143	0.142
0.0393	0.7316	1.2447	0.682	0.679	0.676	0.673
0.0686	0.5684	1.1659	0.836	0.820	0.821	0.813
0.0689	0.1713	0.9440	0.469	0.444	0.453	0.446
0.0879	0.7991	1.2923	0.527	0.526	0.522	0.519
0.1026	0.2955	1.0321	0.704	0.666	0.680	0.667
0.1450	0.0602	0.9239	0.228	0.207	0.217	0.212
0.1533	0.6705	1.2434	0.708	0.700	0.700	0.693
0.1764	0.4225	1.1281	0.825	0.784	0.803	0.788
0.1801	0.2037	1.0189	0.580	0.529	0.555	0.541
0.1828	0.2975	1.0679	0.726	0.673	0.700	0.683
0.1870	0.7332	1.2818	0.570	0.569	0.568	0.565
0.1978	0.5545	1.1991	0.797	0.776	0.786	0.776
0.2212	0.0365	0.9525	0.193	0.176	0.186	0.182
0.2707	0.1322	1.0231	0.462	0.412	0.447	0.434
0.2921	0.1398	1.0356	0.486	0.433	0.472	0.458
0.3149	0.2675	1.1027	0.696	0.638	0.687	0.670
0.3546	0.3370	1.1460	0.745	0.699	0.747	0.732
0.3812	0.0600	1.0345	0.332	0.301	0.329	0.321
0.3965	0.1415	1.0753	0.516	0.465	0.515	0.503
0.3966	0.5440	1.2444	0.643	0.640	0.651	0.648
0.4090	0.4209	1.1964	0.724	0.705	0.739	0.731
0.4666	0.0214	1.0494	0.269	0.256	0.269	0.267
0.4962	0.3056	1.1720	0.680	0.653	0.704	0.696
0.5038	0.1836	1.1262	0.589	0.546	0.607	0.596
0.5895	0.3403	1.2073	0.629	0.623	0.648	0.646
0.6227	0.1861	1.1586	0.569	0.545	0.597	0.592
0.6450	0.0312	1.1085	0.343	0.331	0.350	0.348
0.7621	0.0587	1.1479	0.370	0.359	0.384	0.383
0.7701	0.1558	1.1821	0.470	0.464	0.488	0.487
0.8257	0.0537	1.1610	0.322	0.315	0.333	0.332
0.8694	0.0612	1.1730	0.289	0.286	0.299	0.298

Equation (4. 8):	C_0	C_1	C_2	σ_s
$\Delta_{123}V_m^E / cm^3 \cdot mol^{-1}$	3.378	-6.367	-2.385	0.021

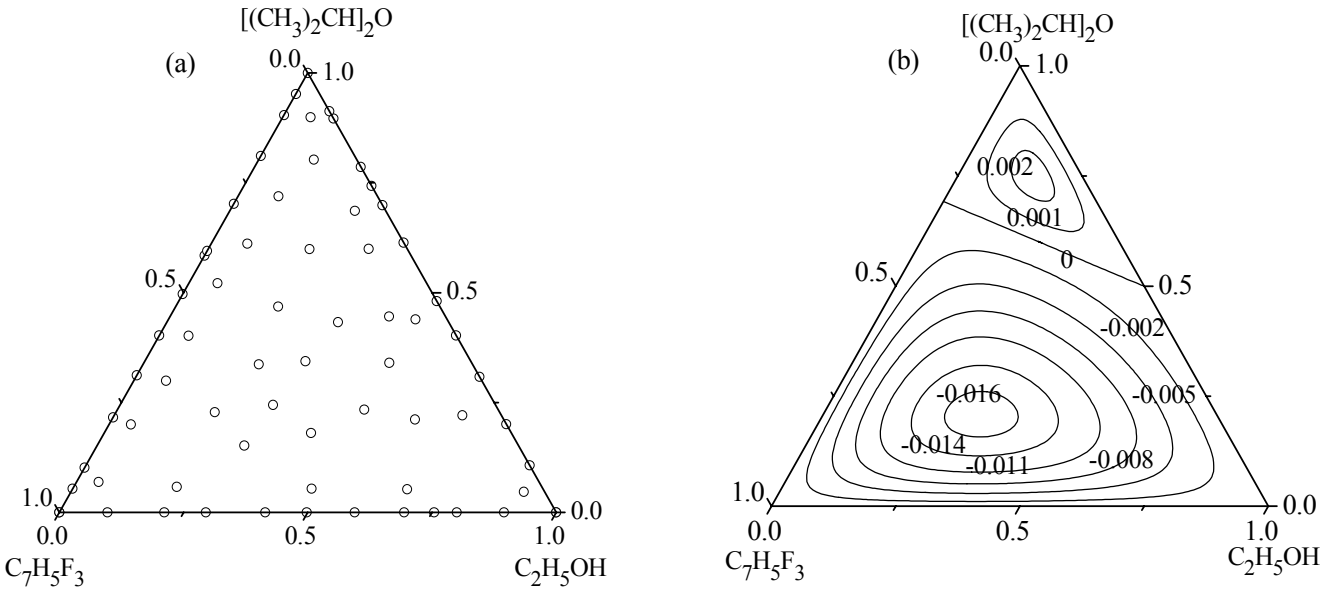


Figure (A. 1). Excess molar volumes of the mixtures ($x_1C_7H_5F_3 + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), experimental compositions; (b), $\Delta_{123}V_m^E$ isolines. $\Delta_{123}V_m^E$ /$cm^3.mol^{-1}$

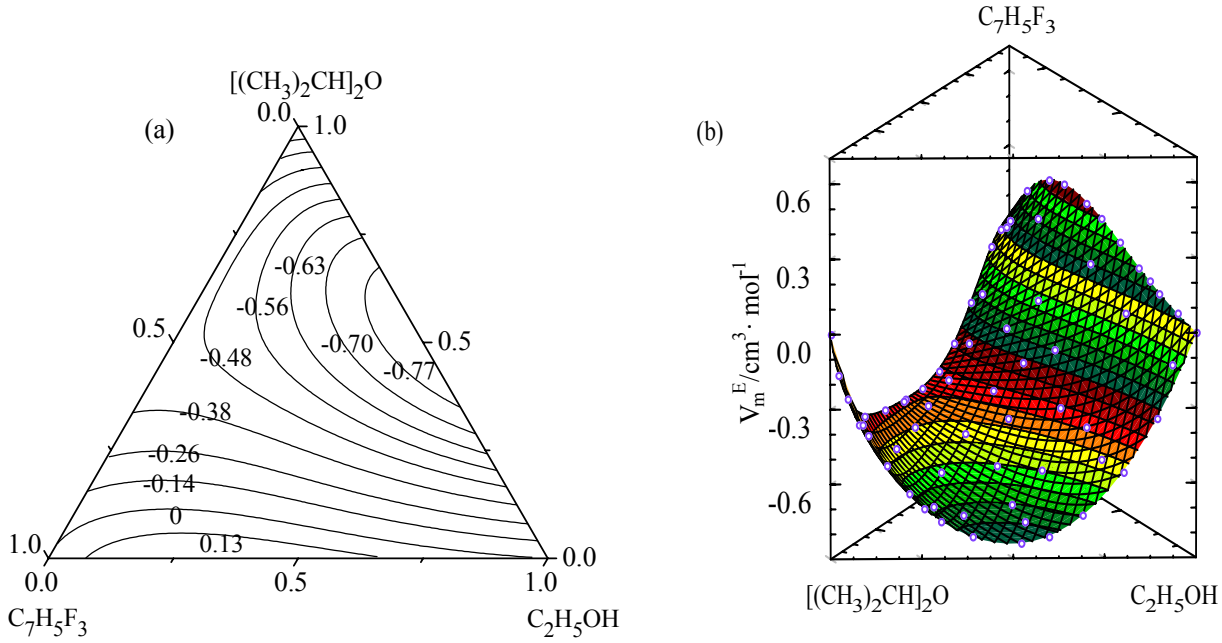


Figure (A. 2). Excess molar volumes of the ternary mixtures ($x_1C_7H_5F_3 + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), $V_{m,123}^E$ isolines; (b), surfaces. $V_{m,123}^E$ /$cm^3.mol^{-1}$

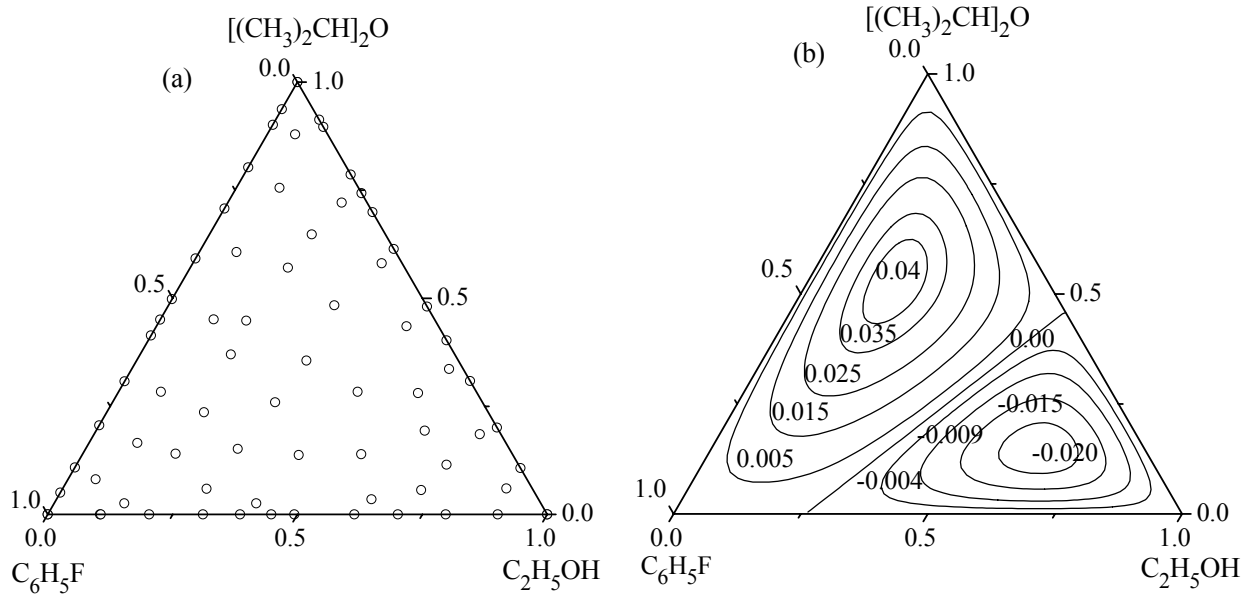


Figure (A. 3). Excess molar volumes of the mixtures ($x_1C_6H_5F + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), experimental compositions; (b), $\Delta_{123}V_m^E$ isolines. $\Delta_{123}V_m^E$ /$cm^3.mol^{-1}$

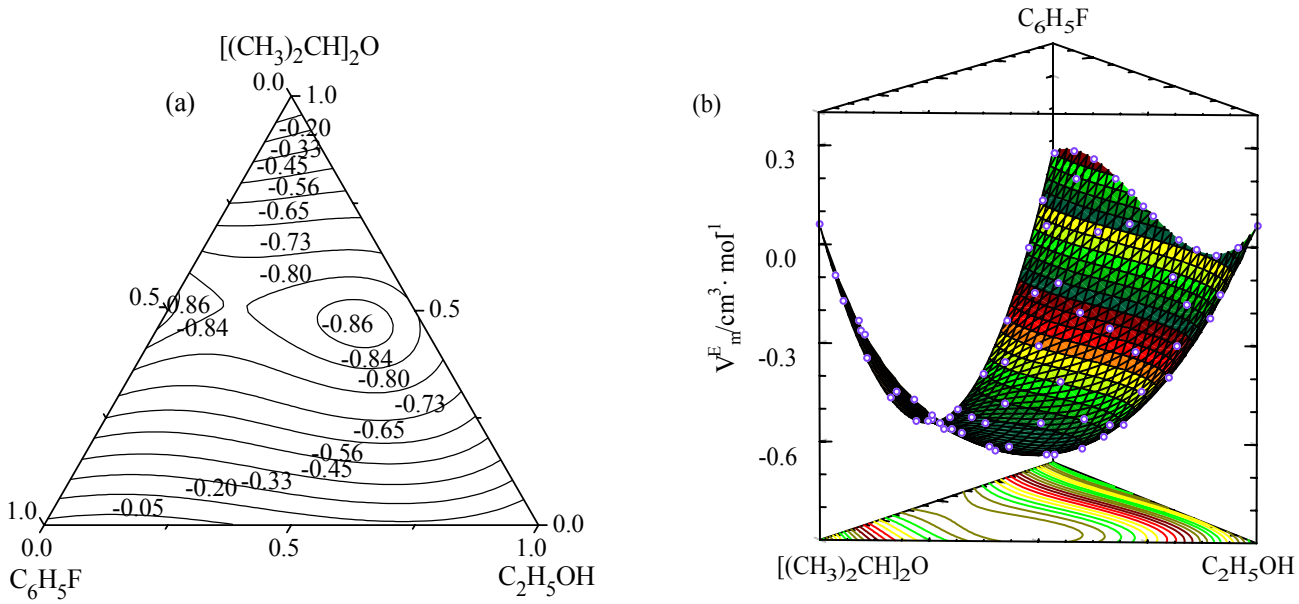


Figure (A. 4). Excess molar volumes of the ternary mixtures ($x_1C_6H_5F + x_2[(CH_3)_2CH]_2O + x_3C_2H_5OH$) at 298.15 K: (a), $V_{m,123}^E$ isolines; (b), surfaces. $V_{m,123}^E$ /$cm^3.mol^{-1}$

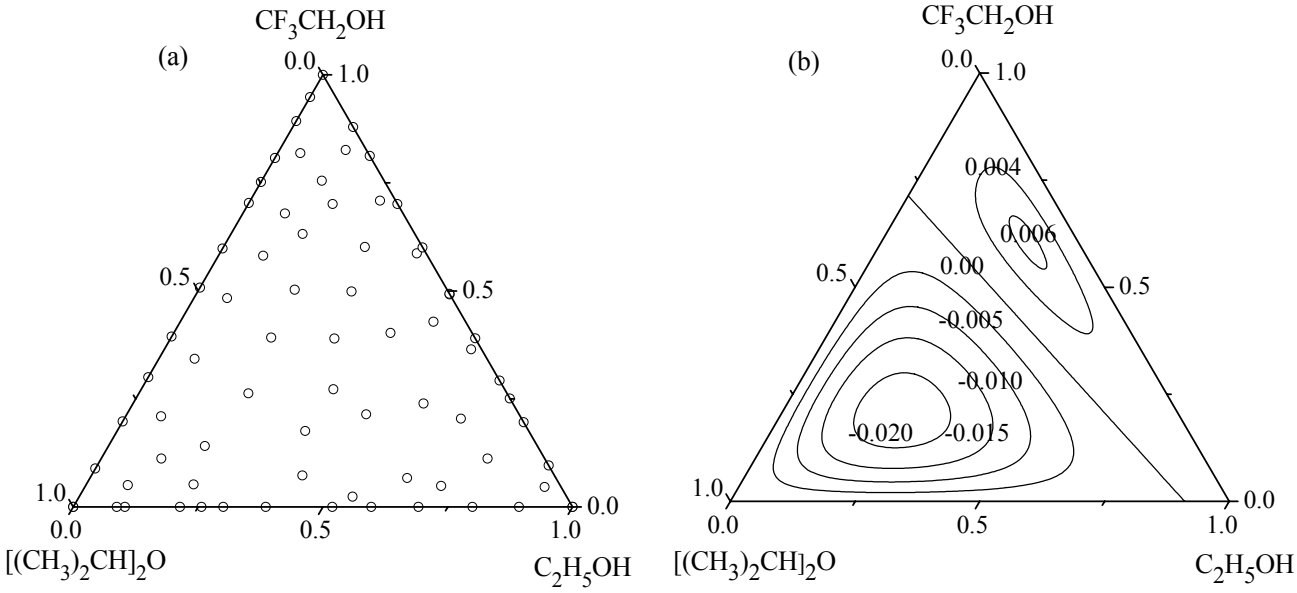


Figure (A. 5). Excess molar volumes of the mixtures ($x_1[(CH_3)_2CH]_2O + x_2CF_3CH_2OH + x_3C_2H_5OH$) at 298.15 K: (a), experimental compositions; (b), $\Delta_{123}V_m^E$ isolines. $\Delta_{123}V_m^E / cm^3.mol^{-1}$

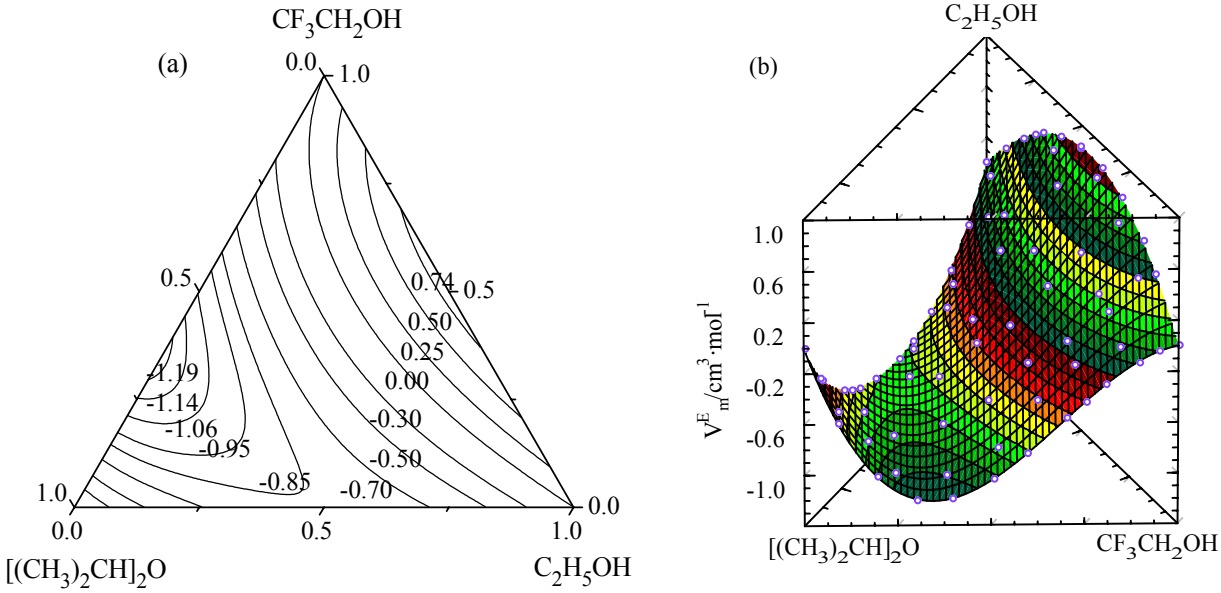


Figure (A. 6). Excess molar volumes of the ternary mixtures ($x_1[(CH_3)_2CH]_2O + x_2CF_3CH_2OH + x_3C_2H_5OH$) at 298.15 K: (a), $V_{m,123}^E$ isolines; (b), surfaces. $V_{m,123}^E / cm^3.mol^{-1}$

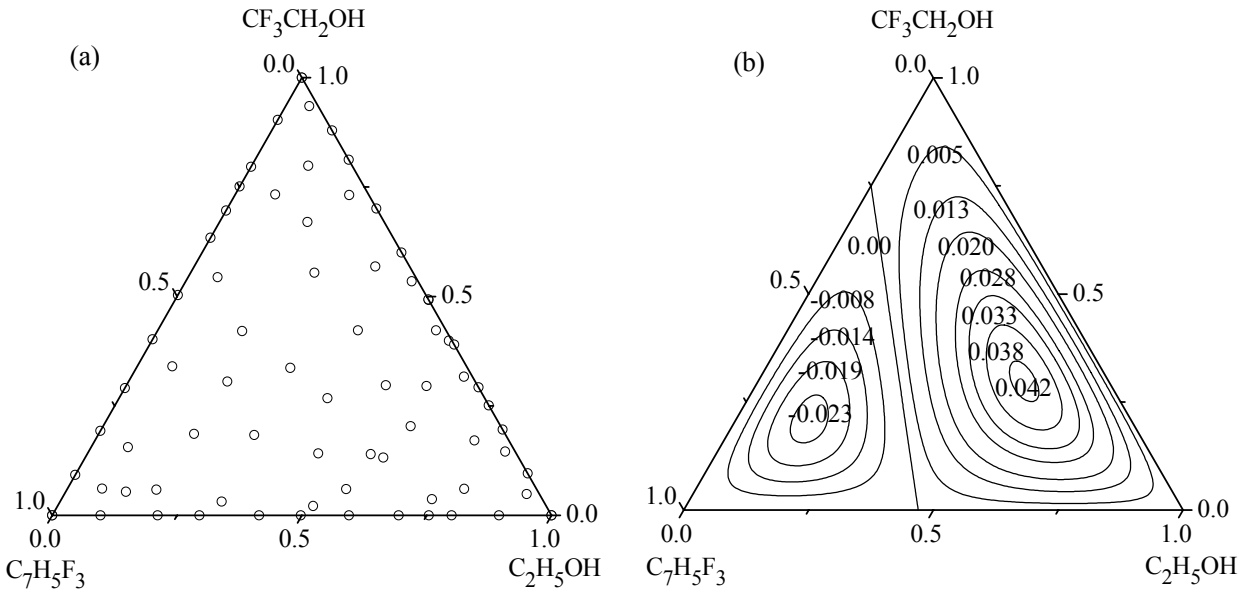


Figure (A. 7). Excess molar volumes of the mixtures ($x_1C_7H_5F_3 + x_2CF_3CH_2OH + x_3C_2H_5OH$) at 298.15 K: (a), experimental compositions; (b), $\Delta_{123}V_m^E$ isolines. $\Delta_{123}V_m^E / cm^3.mol^{-1}$

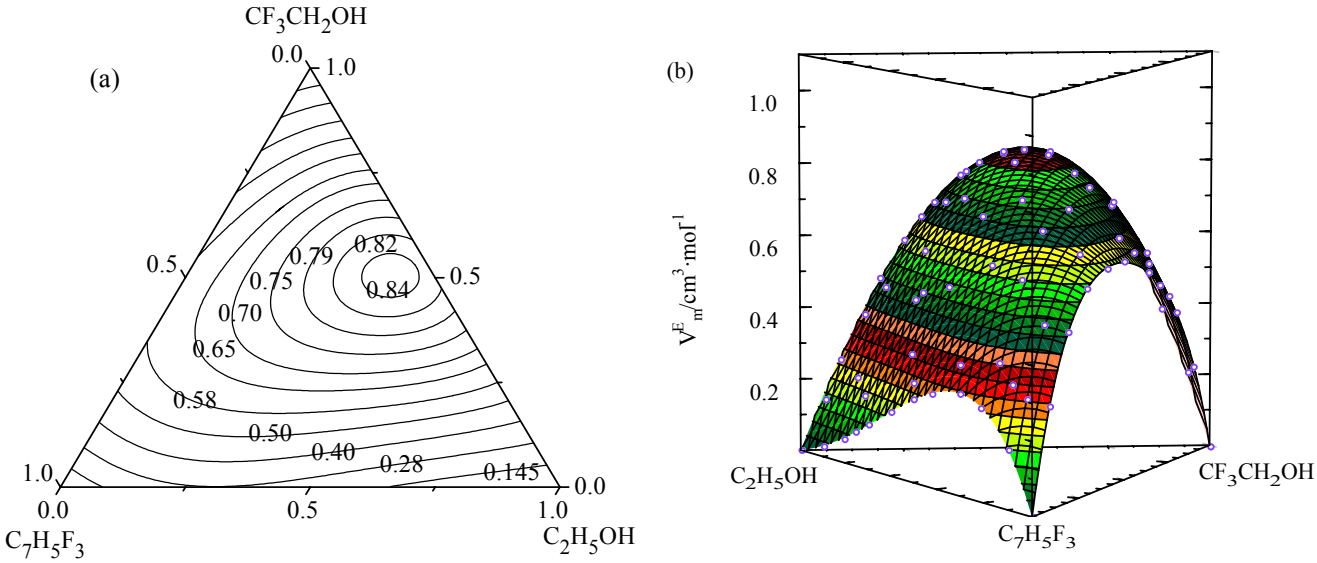


Figure (A. 8). Excess molar volumes of the ternary mixtures ($x_1C_7H_5F_3 + x_2CF_3CH_2OH + x_3C_2H_5OH$) at 298.15 K: (a), $V_{m,123}^E$ isolines; (b), surfaces. $V_{m,123}^E / cm^3.mol^{-1}$

قياسات و تقدير الخواص الحجمية والضوئية لمزج متعددة المكونات تحوي مركبات فلوروعضوية، إيثيرات، كحولات بدرجة حرارة 298.15 K

الملخص:

إن المركبات الهيدروكربونات الأكسجنية مثل الإيثيرات غير سامة و غير ملوثة للبيئة، حيث تستعمل في عملية إنتاج البنزين لتحسين و تخفيض انبعات غازات الإحتراق.

فلوروعضوية هي أيضا مركبات غير سامة،غير قابلة للا شتعال،آمنة على طبقة الأزون، وبالتالي فهي مناسبة كبدائل لمركبات كلوروفلوروعضوية CFC.

قيست حجوم المزج الجزيئية للزيادة و تغير قرائن الإنكسار لمزج متعددة المكونات،الثنائية و الثلاثية تحتوي على:

ثنائي إيزوبروبيل إيثر، ثلاثي بيوتيل مثيل إيثر، ثلا ثي أميل مثيل إيثر، فلورو بنزن، α، α، α- ثلا ثي فلورو تولوين،

2،2،2-ثلا ثي فلورو إيثانول، تولوين، بنزن، أسيتون، والإيثانول عند 298.15 K و 101 kPa

قيست الحجوم الجزيئية للزيادة بمكثاف إلكتروني Anton Paar

كما قيس تغير قرائن الإنكسار بمقياس قرينة الإنكسار Abbe

حللت حجوم المزج الجزيئية و تغير قرائن الإنكسار للمزج الثنائية المقاسة في مجال التركيب $0.0 < x < 1.0$

وفقا لمعاد لة Redlich-Kister.

حللت حجوم المزج الجزيئية للمزج الثلا ثية المقاسة وفقا لمعادلتين Redlich-Kister **و** Cibulka.

كما قدرت الحجوم الجزيئية للمزج الثلا ثية انطلاقا من حجومها الجزيئية الثنائية وفقا أنواع مختلفة من المعادلات التجريبية.

أنشئت لهذ ه المزج المدروسة البيانات التالية: (V^E_m, x_i) **و**$(\Delta_{mix}n, x_i)$.

لم نحصل على منشورات علمية تجريبية لمعظم الجمل المدروسة قصد مقارنة النتائج المحصل عليها.

تساعد الخواص المدروسة في هذا العمل على حساب و تحليل التعبئة الجزيئية و طاقة التأثير بين مكونات المزج و كذا في تطوير واختبار النماذج النظرية للمزج المتجمعة السائلة.

الجمهورية الجزائرية الديمقراطية الشعبية

وزارة التعليم العالي والبحث العلمي

مذكرة ماجستير

جامعة العلوم والتكنولوجيا هواري بومدين

لورداني كنزة

قياسات و تقدير الخواص الحجمية والضوئية لمزج متعددة المكونات تحوي مركبات فلوروعضوية، إيثيرات، و كحولات بدرجة حرارة 298.15 K

كلية الكيمياء

مخبر علم البلورات- الترمود يناميك

باب الزوار، الجزائر