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MACROSCOPIC BEHAVIOUR OF HALOGENATED MULTICOMPONENT SOLUTIONS FROM THERMODYNAMIC EXCESS MOLAR PROPERTIES

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Abstract

The fluoro-alcohols such as 2,2,2-Trifluoroethanol are non-toxic, non-flammable and have an acceptable short environmental life time.

The volumetric properties of multi-component mixtures are needed for understanding their molecular interaction in order to improve equations of state, and recovery of the constituent compounds in separation processes.

In this work, new data are reported of the mixing volumetric properties for binary, ternary, and quaternary systems containing water, acetone, alcohol, hydrocarbons, and 2,2,2-trifluoroethanol.

The mixing volumetric properties were evaluated from density data.

Densities of pure components and mixtures were measured at 298.15K using an Anton-paar vibrating-tube densimeter DMA5000 with a temperature control of ± 2.10^{-3}K and an accuracy of ± 5.10^{-5} $g.cm^{-3}$.

The change of the mixing molar volumes with composition (V_m^E, x) of the multi-component systems were satisfactorily fitted and predicted by various empirical equations. The limiting partial mixing volumes $V_{m,i}^{E,\infty}$ for component of all mixtures were estimated.

The extent of chemical associations among the molecules forming the mixtures is discussed.

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Khalil GUELIFET,

Glossary

Symbols :

A, B, C	densimeter constants
A_P, B_P, C_P	polynomial coefficients
C	number of components.
F	variance (degree of freedom)
T	temperature
V	volume
m	mass
n	degree of fitting parameters
p	pressure
x	mole fraction
x'	estimated composition

Abbreviations :

cal.	calculated
const.	constant
eq.	equation
expt.	experimental
id.	ideal
max.	maximum
min.	minimum
mix.	mixing

Greek letters:

ϕ	number of phases
ρ	density
τ	oscillation period
σ_s	standard deviation
Δ	change
Δ_{ijk}	ternary contribution

Lower scripts:

A, B, C,	component
i, j, k	components
b	binary system
m	molar
m,i	partial molar property
n	polynomial degree
t	ternary system
q	quaternary system

Upper scripts

E	excess property
n	polynomial degree
r	real
*	pure component
∞	infinite dilution

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Appendix A.: Figures of experimental results.

CHAPTER 1

INTRODUCTION

The fluoro-alcohols are used in the field of the cleaning technology of electronic industry, because of a little risk in the destruction of the natural environment. [1]

The fluoro-alcohols are self-associated in the liquid state through hydrogen bonding.

2,2,2-trifluoroethanol (TFE) is miscible with water, alcohols, ketones, and toluene, non-toxic, non-flammable.[2-5]

It is used in pharmaceutical and agricultural chemical syntheses

Studies of volumetric properties of alcohol-water mixtures help to understand the molecular behaviour of the component mixture.

Alcohols are strongly self-associated and for binary solution rich in alcohol a three dimensional net work of hydrogen bonded alcohol molecules is believed to be present.[7-8]

Alcohols have advantage of being blending agents which can be obtained from natural regenerative resources. However, serious problems are connected with the use of pure alcohols, for example, the increase of the vapor pressure resulting from the formation of azeotropes with the light constituents of gasoline and (liquid + liquid) phase separation in the presence of water at low temperatures. To avoid these problems parts of the alcohol can be transformed into co-solvents.

Mixtures of alcohols and fluoro-alcohols form complex systems through cross associations via formation/breaking of specific intermolecular interactions due to mixing.[9]

Mixing thermodynamic properties are tools to investigate specific interactions and hydrogen bond effects in solutions properties containing different types of molecules.

The molecular packing in liquids and liquid solutions is revealed in mixing volumes, and is influenced by the molecular size, intermolecular interactions, and the chemical nature of component molecules.

The chemicals used in this work were chosen because of their use in the petroleum, perfume, and pharmaceutical industries.[10-12]

Application of the volumetric properties of these systems is to improve their industrial usage separation processes, and to reduce their production costs.

Measurements of these thermomechanical quantities for various multicomponent liquid systems have suggested that significant intermolecular interactions occur among components, the resulting geometrical effects markedly affecting the macroscopic behavior of the mixtures.[13-18]

The density is a basic physico-chemical property of pure components and mixtures and is necessary parameter in unit-process designs.

A knowledge of the densities of new working fluids and fluid mixtures is essential to understand the molecular interactions between the molecules and to develop new theoretical models, and also in the engineering applications of absorption heat pumps and heat transformers. The variation of these properties with temperature and composition of the mixtures containing polar and hydrogen-bonded complexes is due to an increase in hydrogen –bonding interaction.[19-35]

The present work reports precise data on excess molar volumes of binary, ternary, and quaternary systems containing water, methanol, ethanol, 2-propanol, 1-hexanol, acetone, toluene, and 2,2,2-trifluoroethanol at pressure 101 kPa and temperature 298.15 K.

CHAPTER 2

FUNDAMENTAL THERMODYNAMICS OF LIQUID MIXTURES

Introduction:

A mixture (or a solution) is defined by its composition (mole fraction) x_i of the component *i* from which it is composed. The state intensive variables of a multi-component mixture are temperature T, pressure p and mole fractions (x_i, x_j, ….).

The total change in the volume of a mixture $V\left(T, p, n_i, n_j, ...\right)$ with its variables is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial V}{\partial p}\right)_{T,n_i} dp + \sum \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j \neq n_i} dn_i \qquad (2.\ 1)$$

where n_i is the amount of substance of component *i*, (T , p) is temperature, and pressure of the system, respectively.

The partial molar volume $V_{m,i}$ of a component *i* is defined as:

$$V_{m,i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_i \neq n_j} \qquad (2.\ 2)$$

At constant temperature and pressure the change in the volume of a mixture $dV\left(T, p, n_i, n_j, ...\right)$ is:

$$dV = \sum_i V_{m,i} dn_i\ , \quad (T, p, \text{const.}) \qquad (2.\ 3)$$

Integrating equation (2. 3) gives:

$$V = \sum_i n_i V_{m,i}\ , \quad (T, p, \text{const.}) \qquad (2.\ 4)$$

By differentiating equation (2. 4) we get:

$$dV = \sum_i V_{m,i} dn_i + \sum_i n_i dV_{m,i} \qquad (2.\ 5)$$

Equations (2. 3) and (2. 5) give the Gibbs-Duhem relation:

$$\sum_i x_i dV_{m,i} = 0\ , \quad (T, p, \text{const.}), \qquad (2.\ 6)$$

where $x_i = \dfrac{n_i}{\sum_i n_i}$

The change of a molar volume on mixing of multi-component system $\Delta_{\mathrm{mix}}V_{\mathrm{m}}$ (T, p, x) is defined as :

$$\Delta_{\mathrm{mix}}V_m(\mathrm{T}, p, x) = V_{\mathrm{m}} - \sum_{\mathrm{i}} x_{\mathrm{i}} V^*_{\mathrm{m,i}}\,, \tag{2. 7}$$

where $V^*_{m,i}$, is molar volumes of pure component i, x_i mole fraction of component i, and V_m is molar volume of mixture.

The change of molar volumes of mixing of a real mixture is $\Delta_{\mathrm{mix}}V^r_m(T, p, x)$ and that of an ideal mixture is $\Delta_{\mathrm{mix}}V^{id}_m(T, P, x)$.

The excess molar volume V^E_m is related to the volume deviation of a real molar mixture from that of an ideal mixture:

$$V^E_m(T, p, x) = \Delta_{\mathrm{mix}}V^r_m(T, p, x) - \Delta_{\mathrm{mix}}V^{id}_m(T, p, x)\,, \tag{2. 8}$$

And, $$\Delta_{\mathrm{mix}}V^{id}_m(T, p, x) = 0 \tag{2. 9}$$

So, $$V^{\mathrm{E}}_{\mathrm{m}} = \Delta_{\mathrm{mix}}V^{\mathrm{r}}_{\mathrm{m}}\ , \text{ where } V^{\mathrm{E}}_{\mathrm{m}} \neq 0\,. \tag{2.10}$$

The partial excess molar volume $V^{\mathrm{E}}_{\mathrm{m,i}}$ is defined by equation:

$$V^{\mathrm{E}}_{\mathrm{m,i}} = V^{\mathrm{E}}_{\mathrm{m}} + \left\{\frac{\partial V^{\mathrm{E}}_{\mathrm{m}}}{\partial x_{\mathrm{i}}}\right\}_{\mathrm{T,P,xj}} - \sum x_{\mathrm{k}} \left\{\frac{\partial V^{\mathrm{E}}_{\mathrm{m}}}{\partial x_{\mathrm{k}}}\right\}_{\mathrm{T,p,xj}} \tag{2.11}$$

For component i, as $x_i \to 0$: the excess molar volume at infinite dilution $V^{\mathrm{E}\infty}_{\mathrm{m,i}}$ is obtained from:

$$V^{\mathrm{E}\infty}_{\mathrm{m,i}} = \lim_{x_{\mathrm{i}}\to 0} \left\{ V^{\mathrm{E}}_{\mathrm{m}} + \left(\frac{\partial V^{\mathrm{E}}_{\mathrm{m}}}{\partial x_{\mathrm{i}}}\right)_{\mathrm{T,P,x_j}} - \sum x_{\mathrm{k}} \left(\frac{\partial V^{\mathrm{E}}_{\mathrm{m}}}{\partial x_{\mathrm{k}}}\right)_{\mathrm{T,p,xj}} \right\} \tag{2.12}$$

Temperature dependence of molar excess volume, $\left(\frac{\partial V^E_m}{\partial T}\right)_p$ and the excess thermal expansion coefficient, α^E_p of liquid mixture is very important quantities in consideration of the differences in the (P, V, T) relation and in the behavior of component molecules between the solution state and the ideal state.[39-41]

The thermal excess expansion coefficients for the liquid mixtures are calculated at each temperature by equation:

$$\alpha^E_p = \frac{1}{V^E_m}\left(\frac{\partial V^E_m}{\partial T}\right)_p\,, \tag{2.13}$$

The degree of freedom *F*:

The degree of freedom, or the variance, of a system containing C components and ϕ phases is given by: $F = C + 2 - \phi$. F determine the minimum number of variables that must be defined in order to perfectly define a particular condition of the system from a knowledge of the number of system components and phases.

The experimental study of a multi-component mixture can be simplified using dilution composition ratios $\left(x_i / x_k\right)$ to form pseudo-binary systems.

Ternary mixtures (*ijk*):

The ternary mixtures are experimentally prepared by two ways:

- The mixtures are obtained by mixing known masses of components *i*, *j*, and *k* , having different mole fractions throughout the composition range, giving a map of compositions on a triangular plane representation: $\left\{x_i A + x_j B + (1 - x_i - x_j) C\right\}$

- Pseudo binary mixtures (*ij*+*k*): here, the ternary mixtures are obtained by mixing two components (*i* + *j*), having a constant composition ratio $k = \left(x_i / x_j\right)$, that is to say a starting binary mixture (x_i^0, x_k^0) : $\left\{x_i^0 A + (1 - x_i^0) B\right\}$, with known mass of component k , giving a section of compositions on a triangular plane representation: $\left[(1 - x_k)\left\{x_i^0 A + (1 - x_i^0) B\right\} + x_k C\right]$

The extent of the coverage of the ternary diagram by experimental measurements is shown in figure (2. 1)

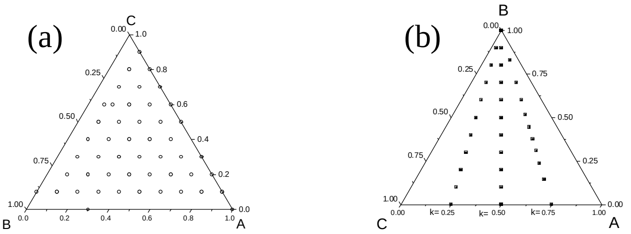

Figure (2.1): triangular plane representation of ternary mixtures: (a), map of compositions, (b), sections of compositions.

Correlation and Data Analysis of Excess Volumes:

1) binary mixtures (*ij*) :

The excess molar volumes of binary mixtures are fitted using the Redlich-Kister equation. The adjustable parameters A_P are determined by least squares method and degree of the polynomials P, is optimized by standard deviations and applying a Fortran program (home made).

The measured mixing volumes of multi-component mixtures are fitted to the equations [42]:

$$V_{\mathrm{m,ij}}^{\mathrm{E}} = x_{\mathrm{i}} x_j \sum_{P=0}^{n} A_P \left(x_{\mathrm{i}} - x_j\right)^n \quad , \tag{2.15}$$

with component i is added to component *j*, the adjustable parameters A_P obtained by fitting the equations to the experimental values with a least-squares algorithm.

The partial excess molar volumes of a binary mixture are derived from equation (2.15)

$$V_{\mathrm{m,i}}^{\mathrm{E}} = x_{\mathrm{j}}^2 \left\{ \sum_n A_n (x_i - x_j)^n + 2x_i \sum_n nA_n (x_i - x_j)^{n-1} \right\} \tag{2.16}$$

And the partial excess molar volumes at infinite dilution $V_{\mathrm{m,i}}^{\mathrm{E}\infty}$ of component *i* of a binary mixture is:

$$V_{\mathrm{m,i}}^{\mathrm{E}\infty} = \lim_{x_i \to 0} \left(\frac{V_{\mathrm{m}}^{\mathrm{E}}}{x_{\mathrm{i}} x_j} \right) \tag{2.17}$$

The graphical representation of equation (2. 15) justifies the conditions: $(T, p, const.)$, with F = 1: $V_{\mathrm{m,ij}}^{\mathrm{E}}(x_i)$.

2) ternary mixtures (*ijk*)

The excess molar volumes of ternary mixtures $V_{\mathrm{m,ik+j}}^{\mathrm{E}}$ are represented using pseudo-binary compositions along a dilution line k[43]:

$$V_{m,ik+j}^{\mathrm{E}} = V_{m,ijk}^{E} - (1 - x_j) V_{m,ik}^{E} , \tag{2. 18}$$

where $V_{m,ijk}^{E}$ is the total excess molar volume of ternary mixture.

The correlation of the excess molar volume of ternary systems $V_{m,t}^{\mathrm{E}}$ is obtained from binary and ternary contributions and fitted to two types of equations[44] :

1)

$$V_{m,t}^{\mathrm{E}} = C_{1t} x_1 x_2 + C_{2t} x_2 x_3 + C_{3t} x_1 x_3 + C_{4t} x_1 x_2 (x_2 - x_1) + C_{5t} x_2 x_3 (x_3 - x_2) + C_{6t} x_1 x_3 (x_1 - x_3) + C_{7t} x_1 x_2 x_3 \tag{2.19}$$

2) The excess molar volumes of a ternary system is fitted using the equation:

$$V_{m,ikj}^{\mathrm{E}} = \sum_{j \rangle i} V_{m,ij}^{E} + x_i x_j x_k \Delta_{ijk} \tag{2.20}$$

where Δ_{ijk} is the ternary contribution represented by the Cibulka equation[45]:

$$\Delta_{ijk} = C_0 + C_1 x_i + C_2 x_j \tag{2.21}$$

The partial excess molar volumes at infinite dilution $V_{\mathrm{m,i}}^{\mathrm{E}\infty}$ where obtained from equation (2.19) with: $\left(x_j = x_k = 0.5\right)$.

For ternary mixture, the graphical representation of a pseudo-binary section justifies: $\left\{T, p, \left(\frac{x_i}{x_k}\right), const.\right\}$, F = 1: $V_{\mathrm{m,ij+k}}^{\mathrm{E}}\left(x_k\right)$

3) Quaternary mixtures (*ijkl*):

The experimental excess molar volumes of the quaternary mixtures are fitted to the equation:

$$V_{m,q}^{\mathrm{E}} = C_{1q} x_1 x_2 + C_{2q} x_1 x_3 + C_{3q} x_1 x_4 + C_{4q} x_2 x_3 + C_{5q} x_2 x_4 + C_{6q} x_3 x_4 + C_{7q} x_1 x_2 x_3 x_4 \tag{2. 22}$$

The partial excess molar volumes at infinite dilution $V_{\mathrm{m,i}}^{\mathrm{E}\infty}$ where obtained from equation (2.22) with: $\left(x_j = 0.5, x_k = x_l = 0.25\right)$.

For a quaternary mixture, the graphical representation of a pseudo-binary section justifies:

$\left\{T, p, \left(\frac{x_i}{x_j}\right), \left(\frac{x_k}{x_l}\right), const.\right\}$, F =1: $V^{\mathrm{E}}_{\mathrm{m,ijk}+l}\left(x_l\right)$.

Prediction of excess molar volumesV^{E}

The excess molar volumes of ternary or quaternary mixtures are predicted from[46]:

$$V^{\mathrm{E}}_{\mathrm{m,ijk}} = \sum_{\mathrm{i<j}} \frac{x_{\mathrm{i}} x_{\mathrm{j}}}{x'_{\mathrm{i}} x'_{\mathrm{j}}} V^{\mathrm{E}}_{\mathrm{m,ij}}\left(x'_{\mathrm{i}}, x'_{\mathrm{j}}\right) \quad , \tag{2.23}$$

where $V^{E}_{m,ij}\left(x'_i, x'_j\right)$ is the excess molar volumes of the binary mixtures for compositions $\left(x'_i, x'_j\right)$ according to the ternary/quaternary studied systems; with $\left(x'_i, x'_j\right)$ =1.

For this work, the following predictive equations are used:

1) Redlich-Kister equation[42] :

$$V^{\mathrm{E}}_{\mathrm{m,ijk}} = V^{\mathrm{E}}_{\mathrm{m,ij}}\left(x_i, x_j\right) + V^{\mathrm{E}}_{\mathrm{m,ik}}\left(x_i, x_k\right) + V^{\mathrm{E}}_{\mathrm{m,jk}}\left(x_j, x_k\right) , \tag{2.24}$$

where : $x_i = \left(1 - x_j - x_k\right)$,

2) Kohler equation [47]:

$$\begin{aligned} V^{\mathrm{E}}_{\mathrm{m,ijk}} = &\left(x_{\mathrm{i}} + x_{\mathrm{j}}\right)^2 V^{\mathrm{E}}_{\mathrm{m,ij}}\left(x'_{\mathrm{i}}, x'_{\mathrm{j}}\right) + \left(x_{\mathrm{i}} + x_{\mathrm{k}}\right)^2 V^{\mathrm{E}}_{\mathrm{m,ik}}\left(x'_{\mathrm{i}}, x'_{\mathrm{k}}\right) + \\ &\left(x_{\mathrm{j}} + x_{\mathrm{k}}\right)^2 V^{\mathrm{E}}_{\mathrm{m,ij}}\left(x'_{\mathrm{j}}, x'_{\mathrm{k}}\right) \end{aligned} , \tag{2.25}$$

where : $x'_{\mathrm{i}} = \dfrac{x_{\mathrm{i}}}{x_{\mathrm{i}} + x_{\mathrm{j}}} = 1 - x'_j$

3) Colinet equation[48]:

$$\begin{aligned} V^{\mathrm{E}}_{\mathrm{m,ijk}} = \frac{1}{2} &\frac{x_{\mathrm{j}}}{x'_{\mathrm{i}}} \left\{V^{\mathrm{E}}_{\mathrm{m,ij}}(x_{\mathrm{i}}, x'_{\mathrm{i}})\right\} + \frac{x_{\mathrm{i}}}{x'_{\mathrm{j}}} \left\{V^{\mathrm{E}}_{\mathrm{m,ij}}(x'_{\mathrm{j}}, x_{\mathrm{j}}\right\} + \\ &\frac{x_{\mathrm{k}}}{x'_{\mathrm{i}}} \left\{V^{\mathrm{E}}_{\mathrm{m,ik}}(x_{\mathrm{i}}, x'_{\mathrm{i}})\right\} + \frac{x_{\mathrm{i}}}{x'_{\mathrm{k}}} \left\{V^{\mathrm{E}}_{\mathrm{m,ik}}(x'_{\mathrm{k}}, x_{\mathrm{k}}\right\} + \\ &\frac{x_{\mathrm{k}}}{x'_{\mathrm{j}}} \left\{V^{\mathrm{E}}_{\mathrm{m,jk}}(x_{\mathrm{j}}, x'_{\mathrm{j}})\right\} + \frac{x_{\mathrm{j}}}{x'_{\mathrm{k}}} \left\{V^{\mathrm{E}}_{\mathrm{m,ij}}(x'_{\mathrm{k}}, x_{\mathrm{k}}\right\} + \end{aligned} , \tag{2.26}$$

where: $x'_{\mathrm{i}} = 1 - x_{\mathrm{i}}$

4) Muggianu et *al*. equation:[49]

$$\begin{aligned} V_{\mathrm{m,ijk}}^{\mathrm{E}} = {} & \left(\frac{x_{\mathrm{i}} x_{\mathrm{j}}}{v_{ij} v_{ji}}\right) V_{\mathrm{m,ij}}^{\mathrm{E}}\left(v_{ij}, v_{ji}\right) + \left(\frac{x_{\mathrm{i}} x_{\mathrm{k}}}{v_{ik} v_{ki}}\right) V_{\mathrm{m,ik}}^{\mathrm{E}}\left(v_{ik}, v_{ki}\right) + \\ & \left(\frac{x_{\mathrm{i}} x_{\mathrm{j}}}{v_{jk} v_{kj}}\right) V_{\mathrm{m,ij}}^{\mathrm{E}}\left(v_{jk}, v_{kj}\right) \end{aligned} , \qquad (2.27)$$

where : $v_{ij} = \left(\frac{1 + x_{\mathrm{i}} - x_{\mathrm{j}}}{2}\right)$

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-densimeter 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 oscillation period τ of the vibrating tube is determined according to the following relation:

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

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

The liquid density is obtained from equation (10):

$$\rho = (\tau^2 - B)/A\ , \qquad (3.2)$$

with:

$$A = 4\pi^2\, V/C,$$

$$B = 4\pi^2 m/C, \qquad (3.3)$$

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 .

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).

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

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 ± $5{\cdot}10^{-5}$ g $\cdot$cm^{-3}, with temperature at 298.15 K, controlled to within ± 0.002 K.

The liquid mixture are introduced into densimeter U-tube using syringe and degassed before the measuring , with ensure that there are no gas bubbles in the measuring cell.

The densities and refractive indices of mixtures are fitted:

$$Y_{\mathrm{i}} = Y_{\mathrm{i}}^{*} + \sum_{P=1}^{n} A_{\mathrm{P}} x_{\mathrm{i}}^{\mathrm{P}} \ , \tag{3.6}$$

where Y_{i}^{*} are density ρ_{i}^{*} , refractive indices n_{i}^{*} of pure component, and Y_{i} are density ($\rho(x)/\ g{\cdot}\mathrm{cm}^{-3}$) 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 $V_{\mathrm{m}}^{\mathrm{E}}$ 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:

$$V_{\mathrm{m}}^{\mathrm{E}} = \sum_{i=1}^{n} x_{\mathrm{i}} M_{\mathrm{i}} \left(\rho^{-1}(x) - \rho_{\mathrm{i}}^{*-1} \right), \tag{3.7}$$

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

Table (3.1): Densities pure substances at 298.15 K

Substance	$\rho\ /\ g.cm^{-3}$	
	Expt.	Lit
Water	0.99704	0,99705[50]
Acetone	0.78473	0,78440[50]
Methanol	0.78659	0,78637[50]
Ethanol	0.78573	0,78493[50]
2-Propanol	0.78095	0,78126[50]
2,2,2-Trifluoroethanol	1.38196	1,38180[50]
1-Hexanol	0.81526	0,81534[50]
Toluene	0.86219	0,86219[50]

CHAPTER 4

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

The systems investigated are reported and numbered in the following:
Binary liquid mixtures: $\rho(x), V_m^E$

T = 298.15 K

1. $(x_1CH_3OH + x_2H_2O)$
2. $(x_1C_2H_5OH + x_2H_2O)$
3. $(x_1 2\text{-}C_3H_7OH + x_2H_2O)$
4. $\{x_1(CH_3)_2CO + x_2H_2O\}$
5. $\{x_1(CH_3)_2CO + x_2CH_3OH\}$
6. $\{x_1(CH_3)_2CO + x_2\ C_2H_5OH\}$
7. $(x_1CH_3OH + x_2C_2H_5OH)$
8. $(x_1C_2H_5OH + x_2 2\text{-}C_3H_7OH)$
9. $\{x_1(CH_3)_2CO + x_2 2\text{-}C_3H_7OH\}$

T = 288.15 K, 298.15 K, 303.15 K

10. $(x_1C_7H_8 + x_2C_6H_{13}OH)$
11. $(x_1C_7H_8 + x_2CF_3CH_2OH)$
12. $(x_1C_6H_{13}OH + x_2CF_3CH_2OH)$

Ternary liquid mixtures: $\rho(x), V_m^E$
T = 298.15 K

13. $(x_1CH_3OH + x_2H_2O + x_3C_2H_5OH)$
14. $\{x_1(CH_3)_2CO + x_2CH_3OH + x_3H_2O\}$

T = 288.15 K, 298.15 K, 303.15 K

15. $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$

Quaternary liquid mixtures: $\rho(x), V_m^E$
T = 298.15 K

16. $\{(x_1C_2H_5OH + x_2H_2O + x_3 2\text{-}C_3H_7OH) + x_4(CH_3)_2CO\}$
17. $\{(x_1C_2H_5OH + x_2H_2O + x_3(CH_3)_2CO) + x_4CH_3OH\}$
18. $\{(x_1H_2O + x_2 2\text{-}C_3H_7OH + x_3\ CF_3CH_2OH) + x_4C_2H_5OH\}$
19. $\{(x_1H_2O + x_2(CH_3)_2CO) + x_3\ CF_3CH_2OH) + x_4C_2H_5OH\}$

Experimental uncertainty analysis:

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

$$\delta X^{2} = \left(\frac{\partial X}{\partial x}\right)^{2} (\delta x)^{2} + \left(\frac{\partial X}{\partial y}\right)^{2} (\delta y)^{2} + \ldots \tag{4.1}$$

So, the experimental uncertainties are:

Error in excess molar volumes:

$$\delta V_{\mathrm{m}}^{\mathrm{E}} = \left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial \rho(x)}\right)^{2}_{\mathrm{T,P,x_i}} \left(\delta \rho(x_{\mathrm{i}})\right)^{2} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x_{\mathrm{i}}}\right)^{2}_{\mathrm{T,p,x_{j\neq i}}} (\delta x_{\mathrm{i}})^{2} \right) + \sum \left(\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial \rho_{\mathrm{i}}^{*}}\right)^{2}_{\mathrm{T,p,x_i}} \delta(\rho_{\mathrm{i}}^{*})^{2} \right) \tag{4.2}$$

Error in composition x_i:

The liquid composition x_i is calculated from:

$$x_{\mathrm{i}} = (m_{\mathrm{i}} / M_{\mathrm{i}}) / \left(\sum_{\mathrm{i=1}}^{\mathrm{n}} (m_{\mathrm{i}} / M_{\mathrm{i}})\right)$$

The uncertainty in liquid composition is:

$$(\delta x_{\mathrm{i}})^{2} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\left(\frac{\partial x_{\mathrm{i}}}{\partial m_{\mathrm{i}}}\right)^{2} (\delta m_{\mathrm{i}})^{2} \right), \tag{4.3}$$

where: $$\frac{\partial x_{\mathrm{i}}}{\partial m_{\mathrm{i}}} = \frac{\left(\frac{1}{M_{\mathrm{i}}} \sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\frac{m_{\mathrm{i}}}{M_{\mathrm{i}}}\right) - \frac{m_{\mathrm{i}}}{M_{\mathrm{i}}^{2}} \right)}{\left(\sum_{\mathrm{i=1}}^{\mathrm{n}} \left(\frac{m_{\mathrm{i}}}{M_{\mathrm{i}}}\right) \right)^{2}}$$

Error contribution of composition:

$$\left(\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial x_{\mathrm{i}}}\right)_{\mathrm{T,\ p,\ x_{j\neq i}}} = \left(\frac{M_{\mathrm{i}}}{\rho(x)} - \frac{M_{\mathrm{i}}}{\rho_{\mathrm{i}}^{*}} \right) - \frac{\partial \rho(x)}{\partial x_{\mathrm{i}}} \sum_{\mathrm{i=1}} \frac{x_{\mathrm{i}} M_{\mathrm{i}}}{\rho(x)^{2}} \tag{4.4}$$

Error contribution of density:

$$\frac{\partial V_{\mathrm{m}}^{\mathrm{E}}}{\partial \rho(x)} = -\frac{\sum_{\mathrm{i=1}}^{\mathrm{n}} x_{\mathrm{i}} M_{\mathrm{i}}}{(\rho(x))^{2}} \tag{4.5}$$

The experimental uncertainties of our equipments are:

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

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

The standard deviation σ_s of the fit for excess molar volumes V_m^E is calculated from:

$$\sigma_s = \left(\frac{\sum_i \left(V_{m,\exp t}^E - V_{m,cal}^E \right)^2}{N - N_P} \right)^{0.5}, \tag{4.6}$$

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:

$$V_{m,ij}^E / \mathrm{cm^3{\cdot}mol^{-1}}:\ 0.0001 < \sigma_s < 0.003\ ,$$

For ternary contribution:

$$\Delta_{ijk} V_m^E / \mathrm{cm^3{\cdot}\ mol^{-1}}:\ 0.02 < \sigma_s < 0.04\ ,$$

For ternary by equ.(2.19) :

$$V_{m,ijk}^E / \mathrm{cm^3{\cdot}mol^{-1}}:\ 0.007 < \sigma_s < 0.02$$

For quaternary by equ.(2.22) :

$$V_{m,ijkl}^E / \mathrm{cm^3{\cdot}mol^{-1}}:\ 0.01 < \sigma_s < 0.025$$

Table (4.1.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^{E}}{cm^3.mol^{-1}}$
0.102	1.299	0.502
0.199	1.230	0.800
0.301	1.166	0.976
0.402	1.110	1.052
0.452	1.083	1.066
0.501	1.059	1.063
0.550	1.036	1.048
0.600	1.013	1.016
0.652	0.990	0.969
0.703	0.969	0.906
0.801	0.930	0.726
0.900	0.895	0.439

Table (4.1.b): Effect of temperature on smoothing coefficients for $V_{m,b}^{E}$ at T and 101kPa, the mean standard deviation of fit is σ_s = 0.001.

T/K	($x_1C_7H_8$ + $x_2C_6H_{13}OH$)			($x_1C_7H_8$ + $x_2CF_3CH_2OH$)			($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$)		
	A_0	A_1	A_2	A_0	A_1	A_2	A_0	A_1	A_2
288,15	0,498	0,429	0,351	3,816	0,018	1,293	5,485	-2,209	-0,112
298,15	0,537	0,450	0,402	4,254	-0,384	1,447	5,964	-2,338	0,135
303,15	0,554	0,460	0,433	4,354	-0,665	1,719	6,071	-2,428	0,443

$$A_0(T) = A_{01} + A_{02}T \ ; A_1(T) = A_{11} + A_{12}T \ ; \ A_2(T) = A_{21} + A_{22}T$$

Mixtures	A_{01}	A_{02}	A_{11}	A_{12}	A_{21}	A_{22}
To + 1-HexOH	-0.584	0.004	-0.384	0.003	-1.210	0.005
To + TFE	-6.829	0.037	12.930	-0.045	-6.340	0.026
1-HexOH + TFE	-6.117	0.040	1.932	-0.014	-10.294	0.035

Table (4.2): Summary of standard deviation σ_s; $V_{m,b}^{E}(x = 0.5)$; and infinite dilution calculated from eq. (2.12) at 298.15 K and 101kPa

Mixtures	σ_s	$V_{m,b}^{E}\ (x=0{,}5)$	$V_{m,1}^{E\infty}$	$V_{m,2}^{E\infty}$
	$cm^3.mol^{-1}$			
$x_1CH_3OH + x_2H_2O$	0.001	-1.005	-4.201	-3.839
$x_1C_2H_5OH + x_2H_2O$	0.001	-1.048	-8.555	-4.727
$x_1$2-$C_3H_7OH + x_2H_2O$	0.001	-0.945	-10.568	-5.909
$x_1(CH_3)_2CO + x_2H_2O$	0.003	-1.485	-7.214	-4.664
$x_1(CH_3)_2CO + x_2CH_3OH$	0.002	-0.353	-1.544	-1.279
$x_1(CH_3)_2CO + x_2C_2H_5OH$	0.001	-0.073	-0.574	-0.240
$x_1CH_3OH + x_2C_2H_5OH$	0.0001	0.009	0.034	0.034
$x_1C_2H_5OH + x_2$2-C_3H_7OH	0.002	-0.007	-0.028	-0.028
$x_1(CH_3)_2CO + x_2$2-C_3H_7OH	0.003	0.285	1.084	1.198
$x_1C_7H_8 + x_2C_6H_{13}OH$	0.001	0.134	0.488	1.389
$x_1C_7H8 + x_2CF_3CH_2OH$	0.001	1.064	6.085	5.318
$x_1C_6H_{13}OH + x_2CF_3CH_2OH$	0.001	1.491	8.437	3.761

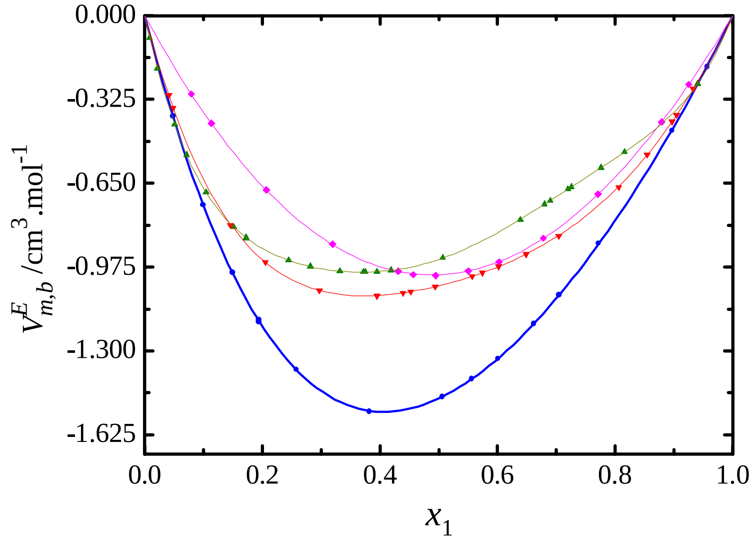

Figure (4.1): Excess molar volumes $V_{m,b}^{E}$ at 298.15 K for binary mixtures: ▲,($x_1$2-C_3H_7OH + x_2 H_2O); ●,{ $x_1(CH_3)_2CO$ + x_2H_2O}; ♦,(x_1CH_3OH + x_2H_2O); ▼,($x_1C_2H_5OH$ + x_2H_2O).

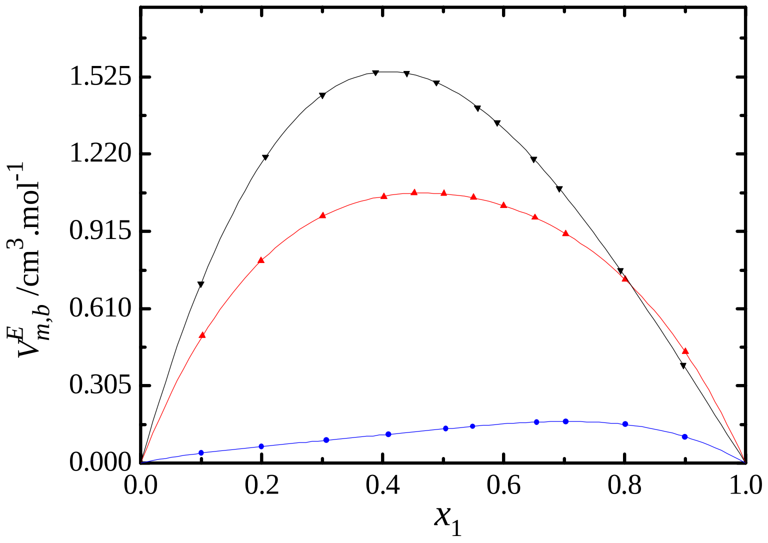

Figure (4.2): Excess molar volumes $V_{m,b}^{E}$ at 298.15 K for binary mixtures: ▲, (x_1 C_7H_8+ $x_2CF_3CH_2OH$); ●,($x_1C_7H_8$ + x_2 $C_6H_{13}OH$); ▼,(x_1 $C_6H_{13}OH$ + x_2 CF_3CH_2OH).

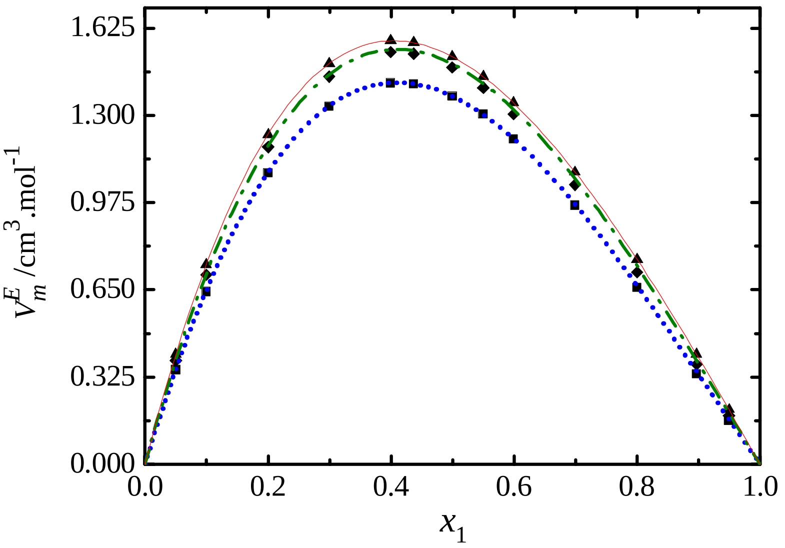

Figure (4.3): Effect of temperature on excess molar volumes $V_{m,b}^{E}$ at T for binary mixtures (x_1 $C_6H_{13}OH$ + x_2 CF_3CH_2OH): …; 288.15K ;-·-·- , 298.15K ; __; 303.15K

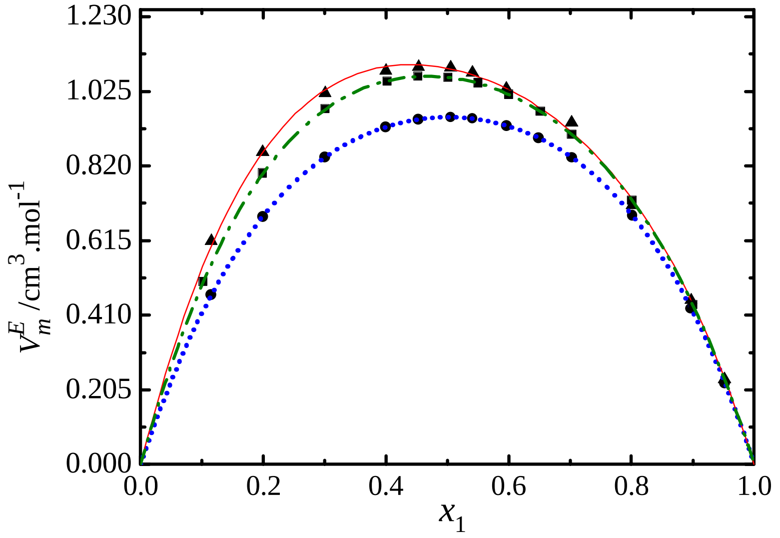

Figure (4.4): Effect of temperature on excess molar volumes $V_{m,b}^{E}$ at for binary mixtures (x_1 C_7H_8 + x_2 CF_3CH_2OH): …; 288.15K; -·-·-·-·- ; 298.15K; ___ ;303.15K

Table (4.3.a): Densities ρ and excess molar volumes $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 298.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^E_{m,(13+2)}}{cm^3.mol^{-1}}$
Section 1 : $x°_1 = 0.25$, $x°_3 = 0.75$				
0.250	0.000	0.750	1.197	0.901
0.224	0.103	0.673	1.135	1.237
0.200	0.200	0.600	1.083	1.403
0.175	0.300	0.525	1.037	1.452
0.150	0.400	0.450	0.996	1.398
0.137	0.451	0.412	0.976	1.340
0.125	0.500	0.375	0.959	1.266
0.100	0.600	0.300	0.925	1.074
0.074	0.705	0.221	0.893	0.826
0.025	0.900	0.075	0.840	0.290
0.012	0.951	0.037	0.827	0.145
0.045	0.821	0.134	0.860	0.514
Section 2 : $x°_1 = 0.5$, $x°_3 = 0.5$				
0.500	0.000	0.500	1.059	1.063
0.450	0.100	0.450	1.024	1.196
0.399	0.202	0.399	0.992	1.228
0.349	0.302	0.349	0.964	1.183
0.300	0.400	0.300	0.938	1.085
0.275	0.451	0.274	0.926	1.017
0.250	0.500	0.250	0.914	0.937
0.225	0.550	0.225	0.903	0.865
0.200	0.600	0.200	0.892	0.781
0.175	0.650	0.175	0.881	0.690
0.150	0.700	0.150	0.871	0.598
0.099	0.802	0.099	0.851	0.401
0.049	0.902	0.049	0.832	0.204

x_i^0, x_j^0 : initial binary mixture

Table (4.3): contd.

x_1	x_2	x_3	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^E_{m,(13+2)}}{\mathrm{cm^3.mol^{-1}}}$
Section 3 : $x°_1 = 0.75$, $x°_3 = 0.25$				
0.750	0.000	0.250	0.826	0.826
0.674	0.101	0.225	0.859	0.859
0.601	0.199	0.200	0.831	0.831
0.524	0.301	0.175	0.762	0.762
0.450	0.400	0.150	0.672	0.672
0.412	0.450	0.138	0.620	0.620
0.337	0.550	0.113	0.512	0.512
0.300	0.600	0.100	0.457	0.457
0.262	0.651	0.087	0.402	0.402
0.225	0.700	0.075	0.347	0.347
0.160	0.787	0.053	0.251	0.251
0.075	0.900	0.025	0.123	0.123

x_i^0, x_j^0 : initial binary mixture

Table (4.3.b): Effect of temperature on smoothing coefficients and standard deviations of $V^E_{m,(13+2)}$ for {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 101kPa

T/K	eq. (2.20);(2.21) eq. (2.19)	C_0 C_{1t}	C_1 C_{2t}	C_2 C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	σ_s
288.15		-2.115	0.623	2.861					0.029
		0.765	5.640	4.023	-0.534	2.153	-0.167	-2.831	0.019
298.15		1.018	-1.802	-4.368					0.043
		0.762	6.270	4.494	-0.658	2.695	-0.385	-3.470	0.018
303.15		1.206	-1.839	-2.821					0.022
		0.793	6.477	4.588	-0.519	2.782	-0.489	-3.027	0.020

Table (4.4): Summary of standard deviation σ_s ,extreme and infinite dilution for V^E_{123} of ternary systems calculated at 298.15 K and 101kPa

Mixture		σ_s	$x_1(ex.)$	$x_2(ex.)$	$V^E_{m,t}(ex.)$	$V^{E\infty}_{m,1}$	$V^{E\infty}_{m,2}$	$V^{E\infty}_{m,3}$
		cm^3mol^{-1}			cm^3mol^{-1}			
{$x_1(CH_3)_2CO$ + x_2CH_3OH + x_3H_2O}	eq.(2.20)	0.039	0.406	0.001	-1.536			
	eq.(2.19)	0.008				-4.877	-3.880	-4.297
(x_1CH_3OH + x_2H_2O + $x_3C_2H_5OH$)	eq.(2.20)	0.021	0.141	0.591	-1.110			
	eq.(2.19)	0.024				-2.788	-3.039	-2.670
{($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$}	eq.(2.20)	0.043	0.001	0.409	1.545			
	eq.(2.19)	0.018				3.260	4.610	3.935

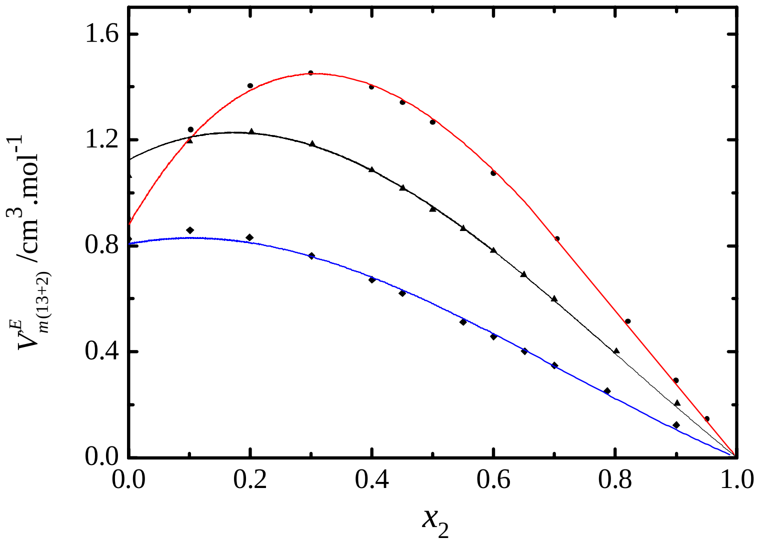

Figure (4.5): Excess molar volumes $V^E_{m,(13+2)}$ of {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 298.15 K and 101kPa for sections: ●,S1; ▲,S2; ▼,S3.

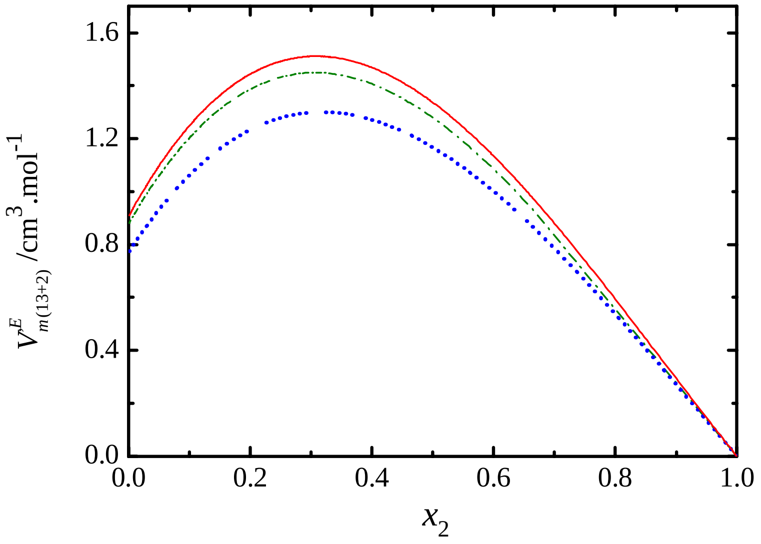

Figure (4.6): Effect of temperature on excess molar volumes $V^E_{m,(13+2)}$ of {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 101kPa for S1: …, 288.15K; -.-.-.-.-.- ; 298.15K;____;303.15K

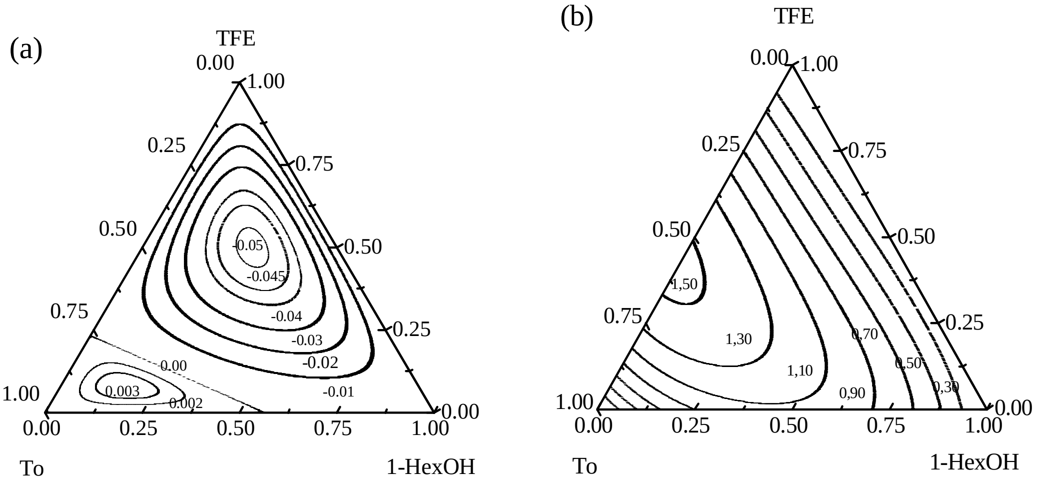

Figure (4.7): Excess molar volumes (cm^3.mol^{-1}) of {(x_1C$_7$H$_8$ + x_3CF$_3$CH$_2$OH) + x_2C$_6$H$_{13}$OH} at 298.15 K and 101kPa: (a) $\Delta V^E_{m,(13+2)}$; (b) $V^E_{m,(13+2)}$

Table (4.5.a): Densities ρ and excess molar volumes $V^E_{m,(123+4)}$ of {(x_1H_2O + $x_2(CH_3)_2CO$ + $x_3CF_3CH_2OH$) + C_2H_5OH} at 298.15 K and 101kPa

x_1	x_2	x_3	x_4	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^E_{m,(123+4)}}{cm^3.mol^{-1}}$
Section 1: ($x°_1$= 0.15 , $x°_2$= 0.75 , $x°_3$= 0.10)					
0.150	0.750	0.100	0.000	0.864	-0.356
0.135	0.675	0.090	0.100	0.858	-0.366
0.120	0.599	0.080	0.201	0.850	-0.338
0.105	0.526	0.070	0.299	0.843	-0.305
0.090	0.450	0.060	0.400	0.836	-0.267
0.083	0.412	0.055	0.450	0.832	-0.248
0.075	0.375	0.050	0.500	0.828	-0.234
0.068	0.337	0.045	0.550	0.824	-0.218
0.060	0.300	0.040	0.600	0.820	-0.199
0.053	0.262	0.035	0.650	0.816	-0.177
0.038	0.188	0.025	0.749	0.808	-0.146
0.015	0.075	0.010	0.900	0.795	-0.074
Section 2: ($x°_1$= 0.20 , $x°_2$= 0.50 , $x°_3$= 0.30)					
0.200	0.500	0.300	0.000	1.009	-0.260
0.180	0.450	0.270	0.100	0.987	-0.184
0.160	0.400	0.240	0.200	0.965	-0.136
0.140	0.350	0.210	0.300	0.943	-0.084
0.117	0.292	0.175	0.416	0.918	-0.063
0.100	0.250	0.150	0.500	0.900	-0.054
0.090	0.225	0.135	0.550	0.888	-0.048
0.080	0.200	0.120	0.600	0.877	-0.046
0.070	0.175	0.105	0.650	0.866	-0.039
0.060	0.150	0.090	0.700	0.855	-0.037
0.040	0.099	0.060	0.801	0.832	-0.037
0.030	0.074	0.045	0.851	0.821	-0.039
0.020	0.050	0.030	0.900	0.809	-0.031
0.010	0.025	0.015	0.950	0.798	-0.026

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (4.5.a): contd.

x_1	x_2	x_3	x_4	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,(123+4)}}{\text{cm}^3.\text{mol}^{-1}}$
Section 3: ($x°_1$= 0.35 , $x°_2$= 0.60 , $x°_3$= 0.05)					
0.350	0.600	0.050	0.000	0.866	-1.033
0.315	0.540	0.045	0.100	0.858	-1.013
0.280	0.480	0.040	0.200	0.851	-0.953
0.245	0.420	0.035	0.300	0.842	-0.839
0.210	0.361	0.030	0.399	0.834	-0.740
0.193	0.330	0.028	0.449	0.830	-0.683
0.182	0.311	0.026	0.481	0.827	-0.649
0.158	0.270	0.023	0.549	0.822	-0.587
0.141	0.241	0.020	0.598	0.818	-0.534
0.124	0.212	0.018	0.646	0.814	-0.480
0.106	0.182	0.015	0.697	0.810	-0.431
0.053	0.090	0.008	0.849	0.798	-0.245

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (4.5.b): Smoothing coefficients C_{iq} of equation (2.22) with standard deviation σ_s for $V^E_{m,(123+4)}$ at 298.15 K and 101kPa

System n°	C_{1q}	C_{2q}	C_{3q}	C_{4q}	C_{5q}	C_{6q}	C_{7q}	σ_s
16	-5.098	2.956	-0.371	-5.001	-5.126	1.939	-39.040	0.024
17	-5.439	6.232	-17.838	-11.212	13.309	-1.342	7.986	0.024
18	-4.212	4.580	-3.946	2.895	-0.283	3.280	2.303	0.010
19	-5.200	-5.023	-4.209	3.773	-0.407	3.125	16.620	0.016

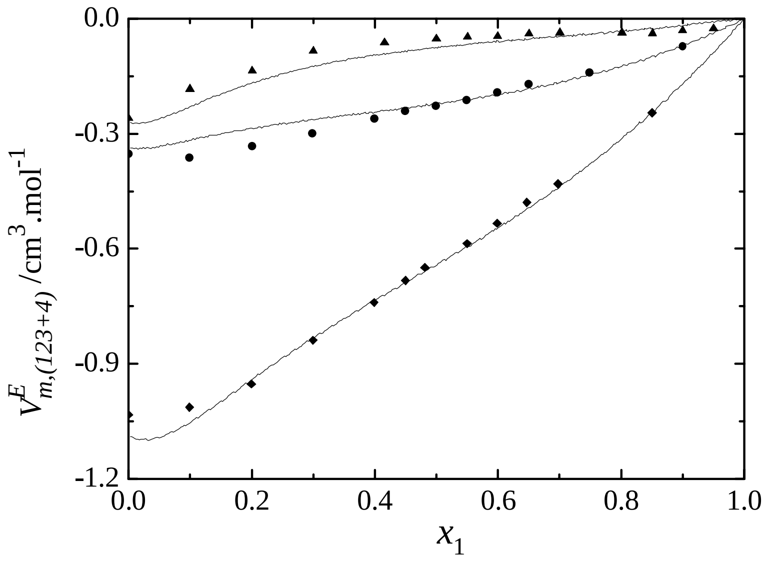

Figure (4.8): Excess molar volumes $V^E_{m,(123+4)}$ of {(x_1H_2O + $x_2(CH_3)_2CO$ + $x_3CF_3CH_2OH$) + C_2H_5OH} at 298.15 K and 101kPa for sections: ●, S1; ▲, S2; ♦, S3; —, Kohler

Table (4.6): Summary of standard deviation σ_s; infinite dilution for $V^E_{(123+4)}$ of quaternary systems calculated from eq. (2.22) at 298.15 K and 101kPa

Mixtures	σ_s	$V^{E\infty}_{m,1}$	$V^{E\infty}_{m,2}$	$V^{E\infty}_{m,3}$	$V^{E\infty}_{m,4}$
	cm^3.mol^{-1}				
($x_1C_2H_5OH$ + x_2H_2O + $x_3$2-C_3H_7OH) + $x_4(CH_3)_2CO$	0.024	-4.267	-5.856	-1.512	-2.783
{$x_1C_2H_5OH$ + x_2H_2O + $x_3(CH_3)_2CO$} + x_4CH_3OH	0.024	-5.193	-3.480	-1.851	-6.279
(x_1H_2O + $x_2$2-C_3H_7OH + $x_3CF_3CH_2OH$) + $x_4C_2H_5OH$	0.010	-106.321	-35.245	32.700	-54.093
{x_1H_2O + $x_2(CH_3)CO$ + $x_3CF_3CH_2OH$} + $x_4C_2H_5OH$	0.016	-3.773	-2.198	-1.469	-1.948

Table (4.7): Standard deviations $\sigma(V_\mathrm{m}^\mathrm{E}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$ of predicted V_m^E for ternary and quaternary systems at 298.15 K and 101kPa.

$\sigma(V_\mathrm{m}^\mathrm{E}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$							
	Ternary Mixture			Quaternary Mixture			
System n°	13	14	15	16	17	18	19
Redlich-Kister, eq (2.24)	0.014	0.024	0.030	0.030	0.040	0.038	0.027
Kohler, eq (2.25)	0.036	0.028	0.030	0.088	0.032	0.024	0.024
Colinet, eq (2.26)	0.033	0.029	0.046	0.081	0.038	0.030	0.035
Mggianu:, eq (2.27)	0.014	0.024	0.030	0.032	0.039	0.032	0.025
$\overline{\sigma}(V_\mathrm{m}^\mathrm{E}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1})$	0.024	0.026	0.034	0.058	0.037	0.031	0.028

CHAPTER 5

DISCUSSION

Excess molar volumes can be explained in terms of positive contributions due to breaking of like interactions of the pure liquids and negative contributions due to the formation of unlike interaction and to the packing effect.[51-53]

The chemical interactions between the molecules in particular hydrogen bonding contribute directly to excess thermodynamic properties. The investigated substances are all polar molecules and have strong self –and cross – associative behaviour.[54-57]

Polar substances interact often among each others and produce energetic effect of different magnitudes.[58-59]

In the present binary an ternary mixtures, interactions between ($x_1C_7H_8$ + $x_2CF_3CH_2OH$), ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$), ($x_1C_7H_8$ + $x_2C_6H_{13}OH$), {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$}at 288.15K to 303.15K. Alcohol in mixtures may exhibit amphoteric behaviour due the homo-molecular and hetro-molecular hydrogen bonds, and the molecular interaction in their aqueous systems are complex and show some competition between like and unlike molecules.[60-63] Trifluoroethanol is abetter proton donor than the other alcohols. Because the strong electronegative inductive effects of the fluorine atoms reduces the ability of the oxygen atom to act as a potential acceptor for hydrogen bonding with other solvents, and makes the hydrolytic hydrogen atom considerably more aciditic than the corresponding hydrogen atom in the hydrocarbon alcohols. [64-65]

$V_{m,b}^{E}(x = 0.5)/\mathrm{cm^3.mol^{-1}} = 1.064$ for (x_1 C_7H_8 + $x_2CF_3CH_2OH$) and $V_{m,b}^{E}(x = 0.5)/\mathrm{cm^3.mol^{-1}} = 1.491$ for ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) and $V_{m,b}^{E}(x = 0.5)/\mathrm{cm^3.mol^{-1}} = 0.134$ for ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 298.15K

The positive $V_{m,b}^{E}$ values arise due to the breaking of hydrogen bonds in self-associated alcohols and physical dipole-dipole interaction between alcohols and the presence of π −electrons in toluene resulting in the formation of weak intermolecular complexes. The results show that the positive values increase with increase in chain length. [66-67]

The mixing behavior of (trifluoroethanol + 1-alcohol) is mainly attributed to disruption or weakening of the self-association in both trifluoroethanol and 1-alcohol through hydrogen bonding revealing a combination of asymmetry and new weak association effecs. [68]

The ternary system of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ shows positive values of mixing volumes $V_{\mathrm{m,t}}^{\mathrm{E}}$ were obtained for all mole fraction of ternary mixture investigate.

The ternary system of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ increase their $V_{\mathrm{m,t}}^{\mathrm{E}}$ values with increasing temperature for the same mole fraction.

The excess molar volumes of the quaternary agree with the values to be expected from binary results. [69-70]

The ternary and quaternary systems are well predicted using binary data alone by the empirical equations: Redlich-Kister, Kohler, Colinet,and Muggianu *et al.* equations. The mean value of standard deviations of prediction is 0.034 $cm^3.mol^{-1}$ for ternary system and $(0.030 < \sigma(V_{\mathrm{m,q}}^{\mathrm{E}}/cm^3.mol^{-1}) < 0.060)$ for quaternary system.

Conclusion:

- New data of excess molar volumes V^E_m have been obtained at 288.15 to 303K for binary, ternary and quaternary mixtures composed of alcohols, aromatic hydrocarbons, acetone, water, and fluorinated hydrocarbons.
- The mixtures studied show deviations from ideality with weak mixing properties.
- The ternary and quaternary excess molar volumes are predicted from binary values using several empirical equations.
- The experimental data are discussed in terms intermolecular interactions.

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APPENDIX A.

EXPERIMENTAL RESULTS

Table (A.1.1.a): Densities ρ and excess molar volumes $V^E_{m,b}$ of ($x_1CH_3OH + x_2H_2O$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,b}}{\text{cm}^3.\text{mol}^{-1}}$
0.079	0.978	-0.303
0.113	0.970	-0.417
0.207	0.947	-0.676
0.319	0.921	-0.886
0.431	0.896	-0.991
0.457	0.891	-1.004
0.495	0.883	-1.008
0.55	0.871	-0.99
0.602	0.861	-0.954
0.678	0.845	-0.863
0.771	0.828	-0.692
0.879	0.808	-0.412
0.925	0.800	-0.267

Table (A.1.1.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,b}$ of ($x_1CH_3OH + x_2H_2O$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2 .15)	-4.020	0.181				0.001

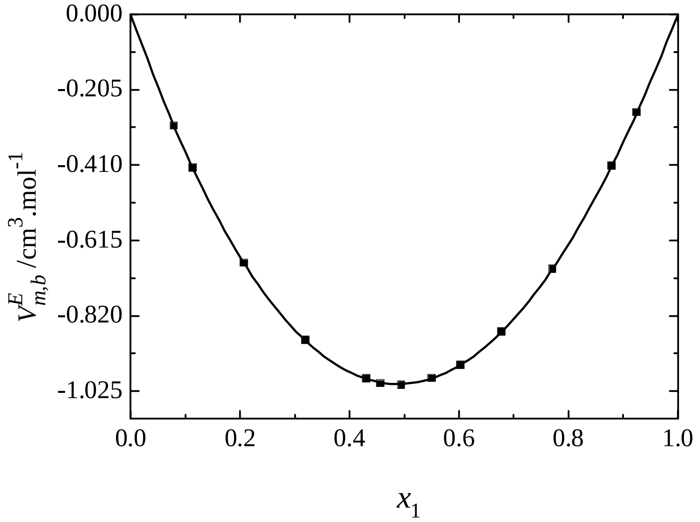

Figure (A.1): Excess molar volumes of ($x_1CH_3OH + x_2H_2O$) at 298.15 K and 101kPa

Table (A.1.2.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_2H_5OH + x_2H_2O$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V_{m,b}^{E}}{\mathrm{cm^3.mol^{-1}}}$
0.041	0.987	-0.306
0.048	0.985	-0.357
0.146	0.954	-0.811
0.205	0.935	-0.956
0.297	0.907	-1.065
0.395	0.882	-1.086
0.452	0.869	-1.070
0.494	0.861	-1.050
0.557	0.849	-1.010
0.602	0.841	-0.972
0.649	0.834	-0.925
0.704	0.826	-0.853
0.806	0.812	-0.665
0.855	0.805	-0.539
0.905	0.799	-0.383
0.933	0.795	-0.284

Table (A.1.2.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_2H_5OH + x_2H_2O$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	-4.191	1.113	-2.45	0.801		0.001

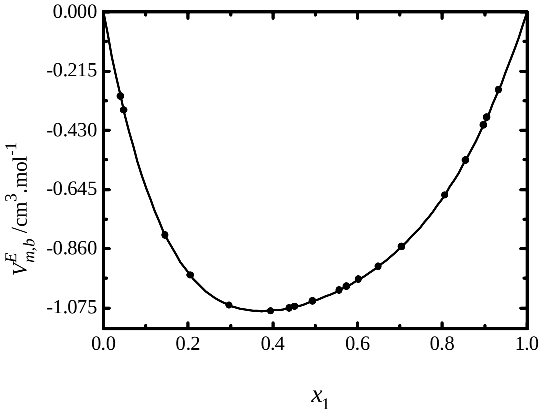

Figure (A.2): Excess molar volumes of ($x_1C_2H_5OH + x_2H_2O$) at 298.15 K and 101kPa

Table (A.1.3.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1$2-C_3H_7OH + x_2H_2O) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3.\text{mol}^{-1}}$
0.051	0.976	-0.421
0.104	0.953	-0.684
0.151	0.932	-0.819
0.173	0.923	-0.863
0.245	0.898	-0.949
0.282	0.887	-0.973
0.332	0.874	-0.991
0.375	0.863	-0.994
0.395	0.859	-0.993
0.507	0.838	-0.939
0.639	0.818	-0.791
0.680	0.813	-0.731
0.726	0.808	-0.663
0.776	0.802	-0.589
0.816	0.798	-0.528
0.941	0.787	-0.263

Table (A.1.3.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1$2-C_3H_7OH + x_2H_2O) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	-3.780	1.534	-0.832	0.796	-3.626	0.001

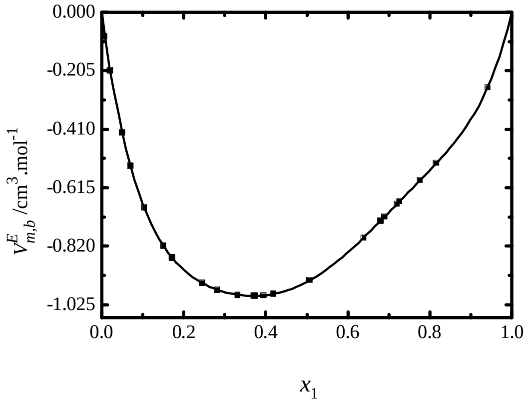

Figure (A.3): Excess molar volumes of ($x_1$2-C_3H_7 OH + x_2H_2O) at 298.15 K and 101kPa

Table (A.1.4.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of $\{x_1(CH_3)_2CO + x_2H_2O\}$ at 298.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^{E}}{cm^3.mol^{-1}}$
0.048	0.979	-0.389
0.099	0.961	-0.734
0.149	0.944	-0.996
0.194	0.93	-1.179
0.194	0.93	-1.187
0.258	0.911	-1.373
0.382	0.879	-1.535
0.506	0.853	-1.478
0.556	0.843	-1.409
0.601	0.836	-1.331
0.662	0.826	-1.194
0.705	0.82	-1.082
0.772	0.811	-0.882
0.897	0.796	-0.445
0.957	0.789	-0.198

Table (A.1.4.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of $\{x_1(CH_3)_2CO + x_2H_2O\}$ at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	-5.939	2.136	-0.861			0.003

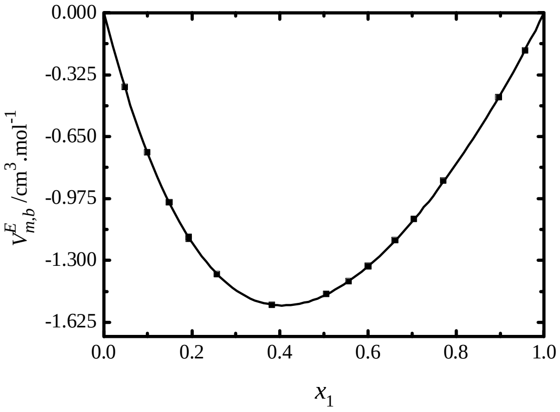

Figure (A.4): Excess molar volumes of $\{x_1(CH_3)_2CO + x_2H_2O\}$at 298.15 K and 101kPa

Table (A.1.5.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of $\{x_1(CH_3)_2CO + x_2CH_3OH\}$ at 298.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^{E}}{cm^{3}.mol^{-1}}$
0.101	0.789	-0.141
0.200	0.791	-0.241
0.300	0.791	-0.306
0.400	0.791	-0.345
0.450	0.791	-0.353
0.499	0.791	-0.352
0.550	0.790	-0.347
0.597	0.790	-0.332
0.651	0.790	-0.313
0.676	0.789	-0.292
0.800	0.788	-0.220
0.858	0.787	-0.162
0.951	0.786	-0.061

Table (A.1.5.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of $\{x_1(CH_3)_2CO + x_2CH_3OH\}$ at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	-1.412	0.132				0.002

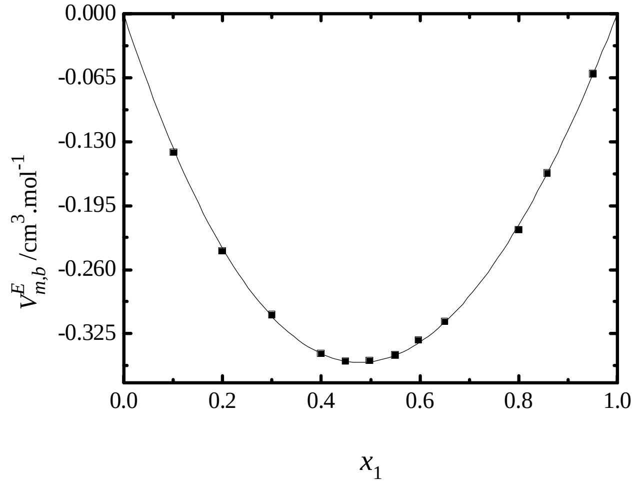

Figure (A.5): Excess molar volumes of $\{x_1(CH_3)_2CO + x_2CH_3OH\}$ at 298.15K and101kPa

Table (A.1.6.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of (x_1CH_3OH + $x_2C_2H_5OH$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^{E}}{cm^3.mol^{-1}}$
0.046	0.786	0.002
0.093	0.786	0.003
0.186	0.786	0.006
0.279	0.786	0.007
0.380	0.786	0.008
0.427	0.786	0.008
0.480	0.786	0.008
0.527	0.786	0.008
0.578	0.786	0.008
0.629	0.786	0.008
0.680	0.786	0.007
0.784	0.787	0.006
0.891	0.787	0.003
0.942	0.787	0.002

Table (A.1.6.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of (x_1CH_3OH + $x_2C_2H_5OH$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	0.034					0.0001

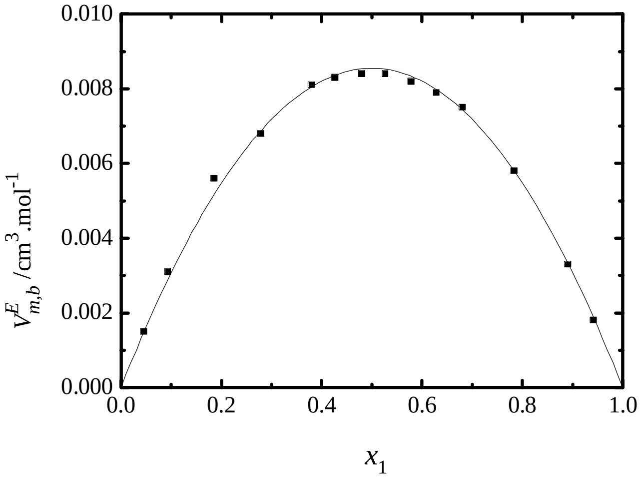

Figure (A.6): Excess molar volumes of (x_1CH_3OH + $x_2C_2H_5OH$) at 298.15K and 101kPa

Table (A.1.7.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_2H_5OH$ + x_2 2-C_3H_7OH) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V_{m,b}^{E}}{\mathrm{cm^3.mol^{-1}}}$
0.053	0.781	-0.002
0.099	0.781	-0.002
0.196	0.782	-0.004
0.301	0.782	-0.005
0.399	0.783	-0.006
0.450	0.783	-0.006
0.501	0.783	-0.006
0.601	0.784	-0.006
0.645	0.784	-0.006
0.699	0.784	-0.008
0.750	0.784	-0.007
0.948	0.786	-0.007

Table (A.1.7.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_2H_5OH$ + $x_2$2-C_3H_7OH) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	-0.028					0.002

Table (A.1.8.a): Densities ρ and excess molar volumes $V_{m,b}^E$ of$\{x_1(CH_3)_2CO + x_2 2\text{-}C_3H_7OH\}$ at 298.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^E}{\text{cm}^3.\text{mol}^{-1}}$
0.050	0.781	0.052
0.101	0.780	0.098
0.201	0.780	0.175
0.299	0.780	0.236
0.393	0.780	0.269
0.437	0.780	0.281
0.550	0.780	0.283
0.593	0.780	0.280
0.648	0.781	0.264
0.697	0.781	0.241
0.749	0.781	0.221
0.772	0.782	0.210
0.898	0.783	0.104
0.949	0.784	0.058

Table (A.1.8.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^E$ of $\{x_1(CH_3)_2CO + x_2 2\text{-}C_3H_7OH\}$ at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	1.141	0.057				0.003

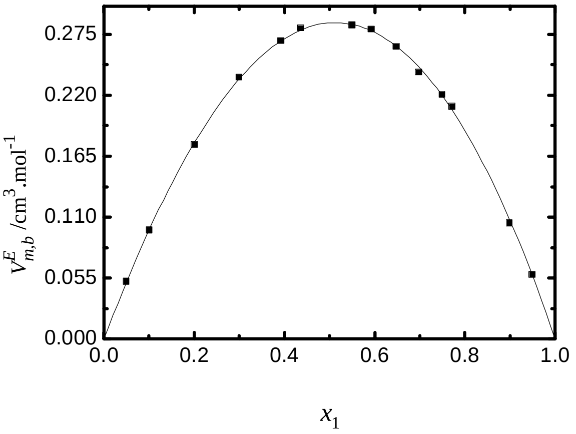

Figure (A.7): Excess molar volumes of $\{x_1(CH_3)_2CO + x_2 2\text{-}C_3H_7OH\}$ at 298.15 K and 101kPa

Table (A.1.9.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{12}^{E}}{cm^3.mol^{-1}}$
0.100	0.819	0.040
0.200	0.823	0.065
0.307	0.827	0.091
0.409	0.832	0.114
0.505	0.836	0.136
0.549	0.838	0.145
0.655	0.843	0.161
0.703	0.845	0.164
0.802	0.850	0.153
0.900	0.856	0.103

Table (A.1.9.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	0.537	0.450	0.402			0.001

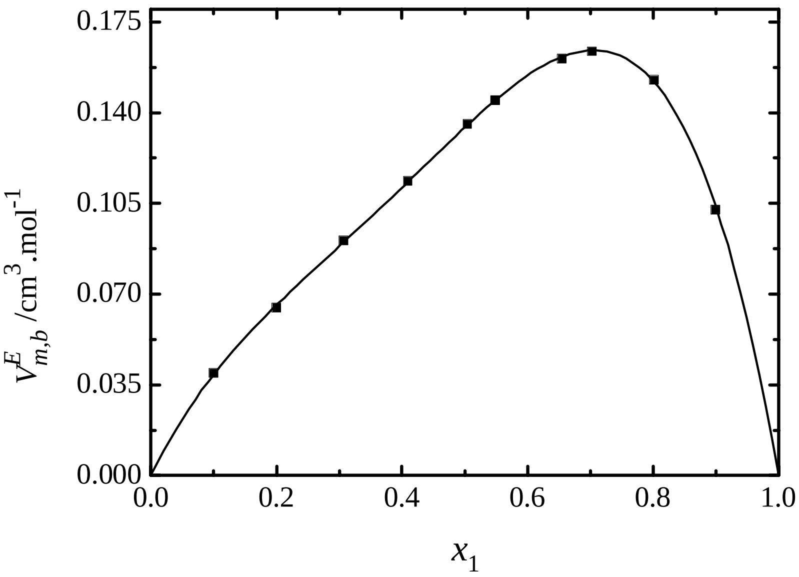

Figure (A.8): Excess molar volumes of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 298.15K and 101kPa

Table (A.1.10.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V_{m,b}^{E}}{\mathrm{cm^3.mol^{-1}}}$
0.102	1.299	0.502
0.199	1.230	0.800
0.301	1.166	0.976
0.402	1.110	1.052
0.452	1.083	1.066
0.501	1.059	1.063
0.550	1.036	1.048
0.600	1.013	1.016
0.652	0.990	0.969
0.703	0.969	0.906
0.801	0.930	0.726
0.900	0.895	0.439

Table (A.1.10.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	4.254	-0.384	1.447			0.001

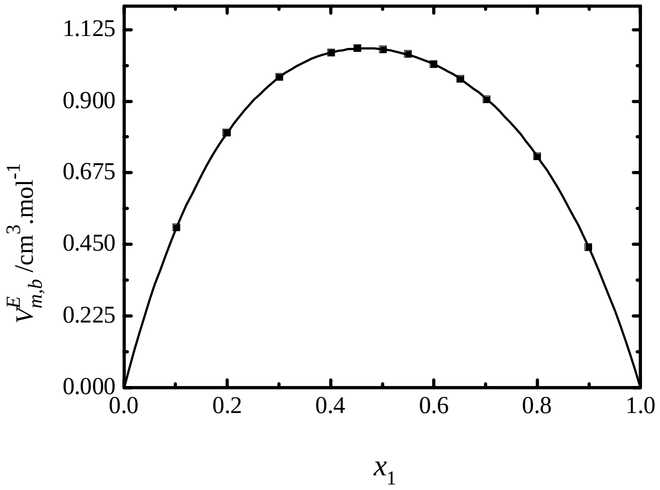

Figure (A.9): Excess molar volumes of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 298.15K and 101kPa

Table (A.1.11.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3.\text{mol}^{-1}}$
0.099	1.280	0.709
0.207	1.189	1.209
0.300	1.122	1.453
0.388	1.067	1.543
0.440	1.039	1.540
0.489	1.013	1.503
0.557	0.980	1.404
0.589	0.965	1.344
0.650	0.939	1.201
0.692	0.922	1.085
0.793	0.884	0.761
0.897	0.848	0.388

Table (4.11.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	5.964	-2.338	0.135			0.001

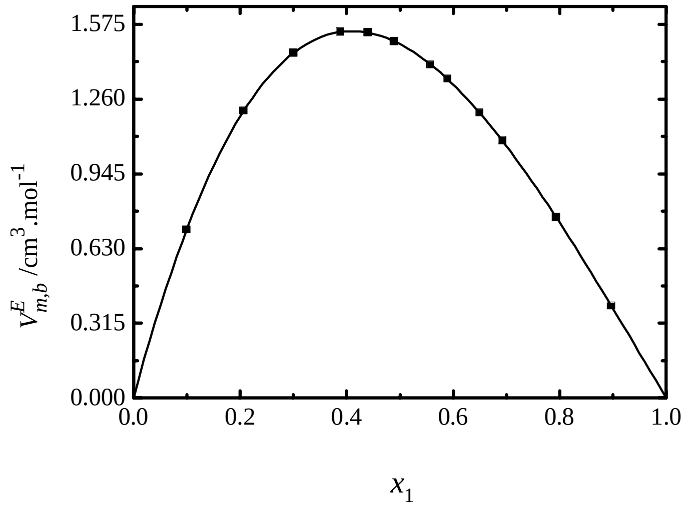

Figure (A.10): Excess molar volumes of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 298.15 K and 101kPa

Table (A.1.12.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 288.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3.\text{mol}^{-1}}$
0.050	0.824	0.019
0.100	0.826	0.034
0.200	0.831	0.059
0.299	0.835	0.080
0.400	0.839	0.102
0.450	0.842	0.113
0.500	0.844	0.124
0.529	0.845	0.130
0.579	0.848	0.140
0.700	0.854	0.153
0.799	0.859	0.142
0.901	0.865	0.096
0.950	0.868	0.054

Table (A.1.12.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 288.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	0.498	0.429	0.351			0.001

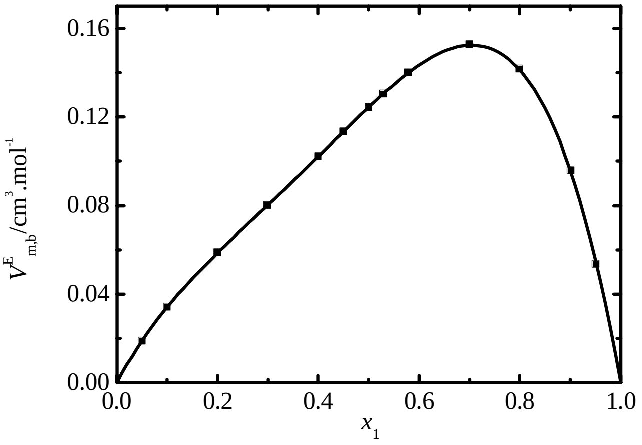

Figure (A.11): Excess molar volumes of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 288.15K and 101kPa

Table (A.1.13.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 303.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^{E}}{cm^3.mol^{-1}}$
0.050	0.814	0.023
0.100	0.815	0.041
0.200	0.819	0.068
0.299	0.823	0.091
0.400	0.827	0.114
0.450	0.830	0.126
0.500	0.832	0.139
0.529	0.833	0.146
0.579	0.835	0.155
0.700	0.841	0.171
0.799	0.846	0.159
0.901	0.851	0.108
0.950	0.854	0.063

Table (A.1.13.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 303.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	0.554	0.473	0.433			0.001

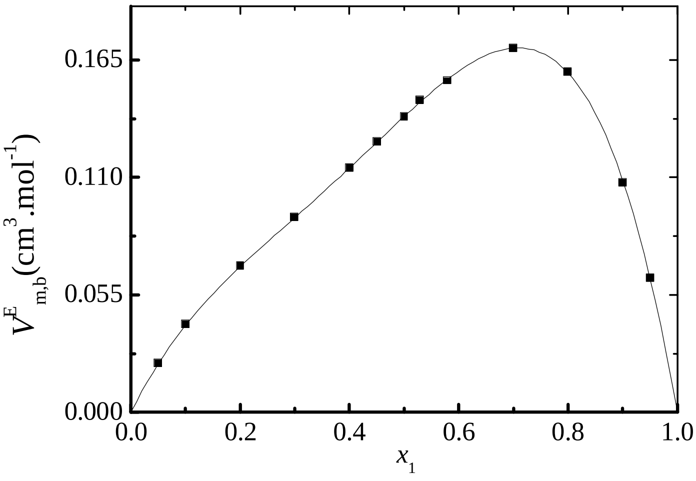

Figure (A.12): Excess molar volumes of ($x_1C_7H_8$ + $x_2C_6H_{13}OH$) at 303.15K and 101kPa

Table (A.1.14.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 288.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3.\text{mol}^{-1}}$
0.115	1.306	0.465
0.199	1.247	0.681
0.300	1.182	0.844
0.400	1.125	0.927
0.453	1.097	0.948
0.505	1.070	0.954
0.541	1.053	0.950
0.596	1.027	0.931
0.649	1.003	0.897
0.703	0.980	0.843
0.801	0.941	0.684
0.897	0.906	0.428
0.952	0.887	0.223

Table (A.1.14.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 288.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	3.816	0.018	1.293			0.0002

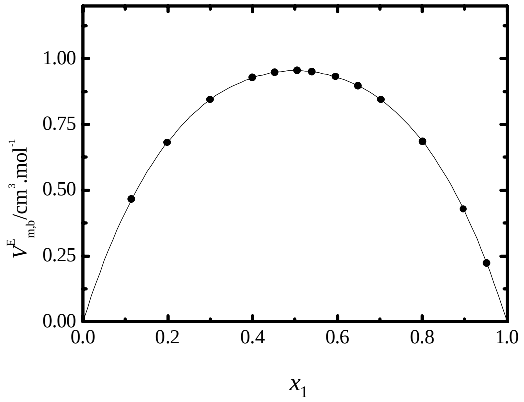

Figure (A.13): Excess molar volumes of ($x_1C_7H_8$+$x_2CF_3CH_2OH$) at 288.15K and 101kPa

Table (A.1.15.a): Densities ρ and excess molar volumes $V_{m,b}^E$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 303.15 K and 101kPa

x_1	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,b}^E}{cm^3.mol^{-1}}$
0.115	1.280	0.599
0.199	1.222	0.857
0.300	1.159	1.028
0.400	1.104	1.093
0.453	1.076	1.098
0.505	1.051	1.087
0.541	1.034	1.071
0.596	1.009	1.033
0.703	0.963	0.910
0.801	0.925	0.731
0.897	0.891	0.455
0.952	0.873	0.233

Table (A.1.15.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^E$ of ($x_1C_7H_8$ + $x_2CF_3CH_2OH$) at 303.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	4.354	-0.665	1.719			0.001

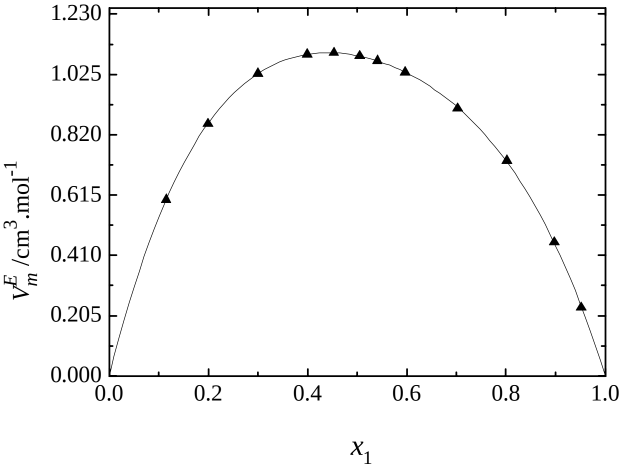

Figure (A.14): Excess molar volumes of ($x_1C_7H_8$+$x_2CF_3CH_2OH$) at 303.15K and 101kPa

Table (A.1.16.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 288.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3.\text{mol}^{-1}}$
0.050	1.345	0.352
0.099	1.296	0.643
0.200	1.209	1.084
0.300	1.136	1.334
0.400	1.074	1.420
0.437	1.052	1.416
0.500	1.019	1.372
0.550	0.994	1.304
0.599	0.971	1.211
0.699	0.929	0.965
0.800	0.890	0.658
0.897	0.856	0.336
0.949	0.838	0.165

Table (A.1.16.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 288.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	5.485	-2.209	-0.112			0.001

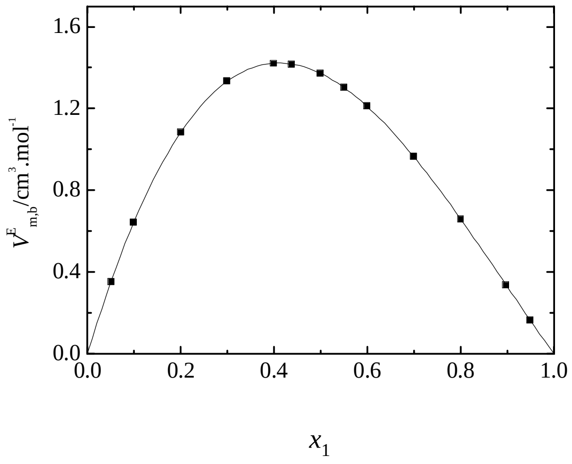

Figure (A.15): Excess molar volumes of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 288.15 K and 101kPa

Table (A.1.17.a): Densities ρ and excess molar volumes $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 303.15 K and 101kPa

x_1	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V_{m,b}^{E}}{\text{cm}^3\text{.mol}^{-1}}$
0.050	1.320	0.410
0.099	1.271	0.743
0.200	1.187	1.228
0.300	1.116	1.493
0.400	1.055	1.578
0.437	1.035	1.571
0.500	1.003	1.519
0.550	0.978	1.444
0.599	0.956	1.347
0.699	0.915	1.088
0.800	0.877	0.763
0.897	0.844	0.410
0.949	0.827	0.205

Table (A.1.17.b): Smoothing coefficients and standard deviation σ_s for $V_{m,b}^{E}$ of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 303.15 K and 101kPa

	A_0	A_1	A_2	A_3	A_4	σ_s
eq. (2.15)	6.071	-2.428	0.443			0.001

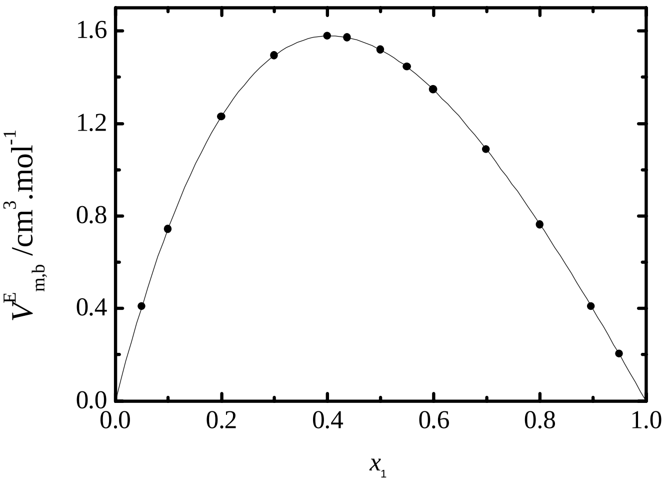

Figure (A.16): Excess molar volumes of ($x_1C_6H_{13}OH$ + $x_2CF_3CH_2OH$) at 303.15 K and 101kPa

Table (A.1.17. c): Effect of temperature on smoothing coefficients for $V_{m,b}^{E}$ at 101kPa , the mean standard deviation of fit is $\sigma_s = 0.001$.

T/K	($x_1C_7H_8 + x_2C_6H_{13}OH$)			($x_1C_7H_8 + x_2CF_3CH_2OH$)			($x_1C_6H_{13}OH + x_2CF_3CH_2OH$)		
	A_0	A_1	A_2	A_0	A_1	A_2	A_0	A_1	A_2
288,15	0,498	0,429	0,351	3,816	0,018	1,293	5,485	-2,209	-0,112
298,15	0,537	0,450	0,402	4,254	-0,384	1,447	5,964	-2,338	0,135
303,15	0,554	0,460	0,433	4,354	-0,665	1,719	6,071	-2,428	0,443

$A_0(T) = A_{01} + A_{02}T$; $A_1(T) = A_{11} + A_{12}T$; $A_2(T) = A_{21} + A_{22}T$

Mixtures	A_{01}	A_{02}	A_{11}	A_{12}	A_{21}	A_{22}
To + 1-HexOH	-0.584	0.004	-0.384	0.003	-1.210	0.005
To + TFE	-6.829	0.037	12.930	-0.045	-6.340	0.026
1-HexOH + TFE	-6.117	0.040	1.932	-0.014	-10.294	0.035

Table (A.1.18): Summary of standard deviation σ_s; $V_{m,b}^{E}(x = 0.5)$; and infinite dilution calculated from eq. (2.12) at 298.15 K and 101kPa

Mixtures	σ_s	$V_{m,b}^{E}$ ($x = 0,5$)	$V_{m,1}^{E\infty}$	$V_{m,2}^{E\infty}$
	$cm^3.mol^{-1}$			
$x_1CH_3OH + x_2H_2O$	0.001	-1.005	-4.201	-3.839
$x_1C_2H_5OH + x_2H_2O$	0.001	-1.048	-8.555	-4.727
$x_1$2-$C_3H_7OH + x_2H_2O$	0.001	-0.945	-10.568	-5.909
$x_1(CH_3)_2CO + x_2H_2O$	0.003	-1.485	-7.214	-4.664
$x_1(CH_3)_2CO + x_2CH_3OH$	0.002	-0.353	-1.544	-1.279
$x_1(CH_3)_2CO + x_2C_2H_5OH$	0.001	-0.073	-0.574	-0.240
$x_1CH_3OH + x_2C_2H_5OH$	0.0001	0.009	0.034	0.034
$x_1C_2H_5OH + x_2$2-C_3H_7OH	0.002	-0.007	-0.028	-0.028
$x_1(CH_3)_2CO + x_2$2-C_3H_7OH	0.003	0.285	1.084	1.198
$x_1C_7H_8 + x_2C_6H_{13}OH$	0.001	0.134	0.488	1.389
$x_1C_7H8 + x_2CF_3CH_2OH$	0.001	1.064	6.085	5.318
$x_1C_6H_{13}OH + x_2CF_3CH_2OH$	0.001	1.491	8.437	3.761

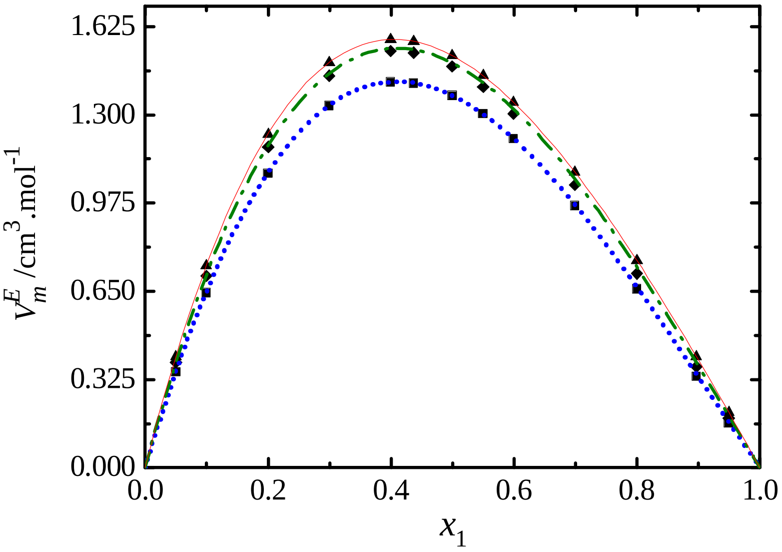

Figure (A.17): Effect of temperature on excess molar volumes $V_{m,b}^E$ for binary mixtures (x_1 $C_6H_{13}OH$ + x_2 CF_3CH_2OH) at: …;288.15K; -.-.- ; 298.15K; _, 303.15K

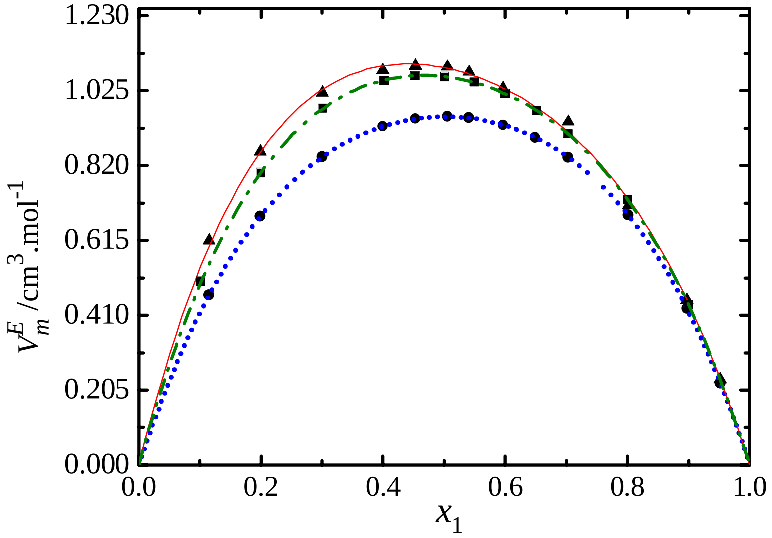

Figure (A.18): Effect of temperature on excess molar volumes $V_{m,b}^E$ for binary mixtures (x_1 C_7H_8 + x_2 CF_3CH_2OH) at: …;288.15K; -.-.- ; 298.15K; _; 303.15K

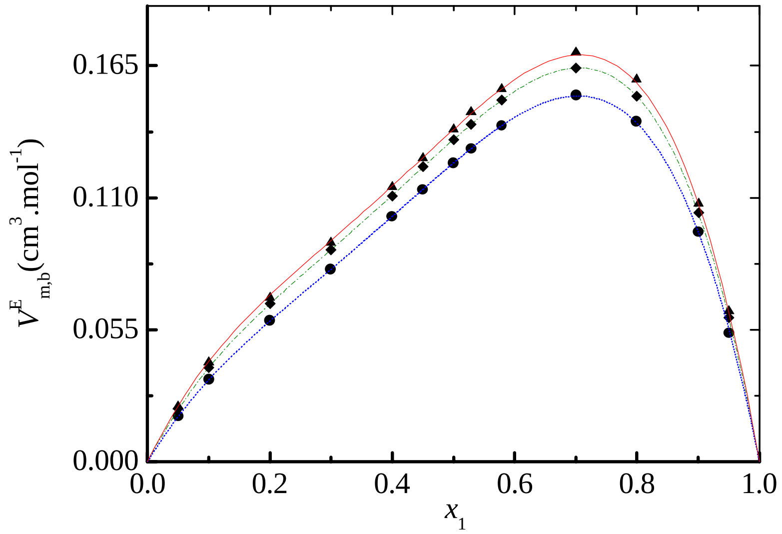

Figure (A.19): Effect of temperature on excess molar volumes $V^E_{m,b}$ for binary mixtures (x_1 C_7H_8 + x_2 $C_6H_{13}OH$) at: …;288.15K; -·-·- ; 298.15K; __; 303.15K

Table (A.2.1.a): Densities ρ and excess molar volumes $V_{m,t}^{E}$ of ($x_1CH_3OH + x_2H_2O + x_3C_2H_5OH$) at 298.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{g.cm^{-3}}$	$\frac{V_{m,t}^{E}}{cm^3.mol^{-1}}$
0.085	0.806	0.109	0.945	-0.845
0.089	0.247	0.664	0.820	-0.763
0.099	0.529	0.372	0.870	-1.082
0.113	0.116	0.771	0.802	-0.437
0.115	0.623	0.262	0.894	-1.093
0.123	0.513	0.365	0.868	-1.076
0.123	0.426	0.451	0.850	-1.011
0.130	0.339	0.531	0.835	-0.910
0.167	0.177	0.656	0.811	-0.600
0.175	0.678	0.146	0.913	-1.033
0.196	0.519	0.285	0.872	-1.081
0.251	0.615	0.134	0.900	-1.057
0.261	0.451	0.288	0.860	-1.034
0.263	0.318	0.419	0.834	-0.871
0.331	0.101	0.568	0.801	-0.361
0.344	0.194	0.462	0.815	-0.615
0.345	0.406	0.249	0.853	-0.986
0.380	0.350	0.271	0.843	-0.911
0.387	0.512	0.101	0.880	-1.044
0.393	0.462	0.144	0.868	-1.029
0.402	0.242	0.356	0.823	-0.717
0.486	0.090	0.425	0.800	-0.309
0.534	0.087	0.379	0.799	-0.297
0.589	0.308	0.103	0.840	-0.838
0.671	0.121	0.208	0.806	-0.398
0.716	0.121	0.163	0.806	-0.399
0.772	0.103	0.124	0.804	-0.347

Table (A.2.1.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,t}$ of ($x_1CH_3OH + x_2H_2O + x_3C_2H_5OH$) at 298.15 K and 101kPa

eq. (2.20);(2.21)	C_0	C_1	C_2					σ_s
	0.685	1.289	-1.772					0.021
eq. (2.19)	C_{1t}	C_{2t}	C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	
	-4.397	-4.529	-0.368	-0.887	1.018	0.368	4.161	0.024

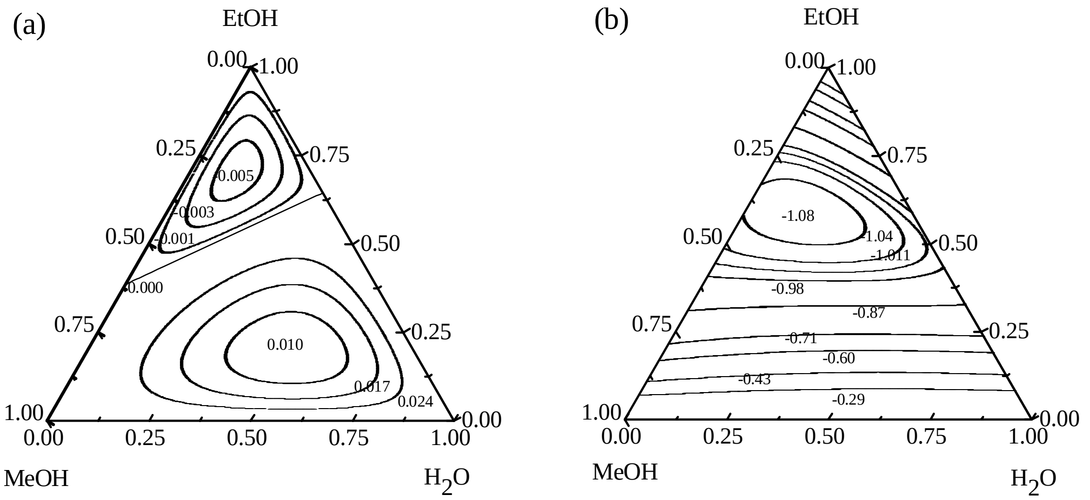

Figure (A.20): Excess molar volumes ($cm^3.mol^{-1}$) of ($x_1CH_3OH + x_2H_2O + x_3C_2H_5OH$) at 298.15 K and 101kPa : (a): $\Delta V^E_{m,t}$; (b): $V^E_{m,t}$, Table (A.2.2.a): Densities ρ and excess molar volumes $V_{m,t}^{E}$ of {$x_1(CH_3)_2CO$ + x_2CH_3OH + x_3H_2O} at 298.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V_{m,t}^{E}}{\mathrm{cm^3.mol^{-1}}}$
0.057	0.804	0.139	0.812	-0.557
0.078	0.727	0.195	0.821	-0.741
0.096	0.070	0.833	0.946	-0.891
0.124	0.822	0.054	0.798	-0.365
0.125	0.491	0.384	0.854	-1.157
0.127	0.281	0.592	0.893	-1.257
0.128	0.395	0.477	0.871	-1.243
0.128	0.619	0.253	0.831	-0.939
0.130	0.130	0.740	0.923	-1.141
0.138	0.651	0.211	0.824	-0.854
0.220	0.060	0.720	0.910	-1.332
0.221	0.695	0.084	0.803	-0.558
0.235	0.648	0.118	0.808	-0.676
0.243	0.262	0.494	0.868	-1.380
0.250	0.453	0.296	0.835	-1.131
0.253	0.127	0.620	0.889	-1.422
0.255	0.373	0.372	0.847	-1.260
0.259	0.497	0.244	0.827	-1.027
0.352	0.471	0.177	0.815	-0.893
0.368	0.251	0.381	0.843	-1.313
0.380	0.126	0.494	0.860	-1.452
0.382	0.372	0.245	0.823	-1.062
0.398	0.498	0.104	0.804	-0.691
0.447	0.279	0.274	0.825	-1.120
0.491	0.316	0.193	0.814	-0.927
0.494	0.383	0.123	0.805	-0.740
0.513	0.119	0.368	0.835	-1.288
0.623	0.261	0.116	0.802	-0.674
0.624	0.057	0.319	0.825	-1.164
0.640	0.130	0.230	0.814	-0.956
0.765	0.118	0.117	0.799	-0.585

Table (A.2.2.b): Smoothing coefficients and standard deviation σ_s for $V_{m,t}^E$ of $\{x_1(CH_3)_2CO + x_2CH_3OH + x_3H_2O\}$ at 298.15 K and 101kPa

eq. (2.20);(2.21)	C_0	C_1	C_2					σ_s
	0.265	3.300	-1.324					0.039
eq. (2.19)	C_{1t}	C_{2t}	C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	
	-1.544	-4.267	-5.997	-0.111	-0.287	2.321	2.275	0.008

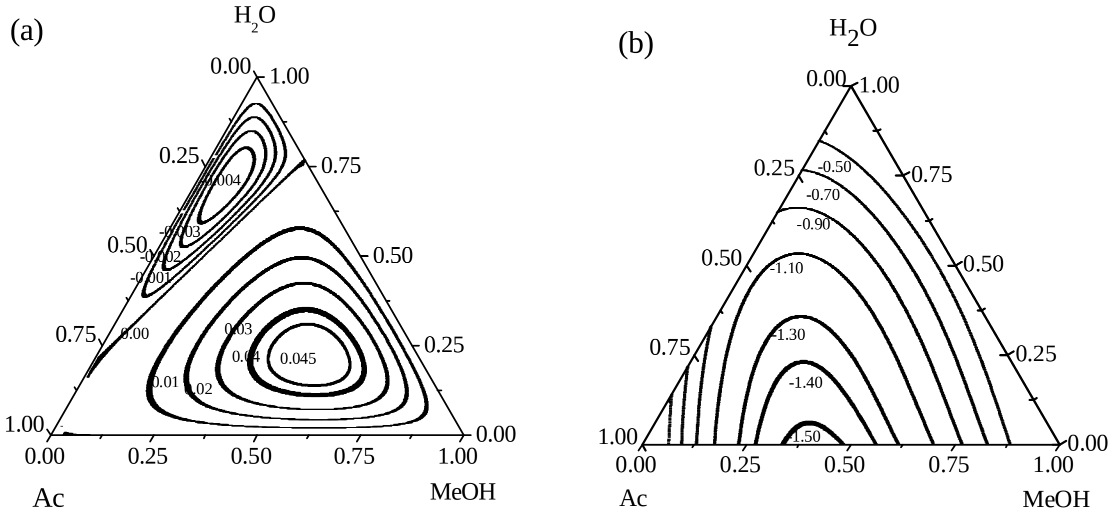

Figure (A.21): Excess molar volumes ($cm^3.mol^{-1}$) of $\{x_1(CH_3)_2CO + x_2CH_3OH + x_3H_2O\}$ at 298.15 K and 101kPa: (a): $\Delta V_{m,t}^E$; (b): $V_{m,t}^E$

Table (A.2.3.a): Densities ρ and excess molar volumes $V^E_{m,(13+2)}$of {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 298.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^E_{m,(13+2)}}{cm^3.mol^{-1}}$
Section 1 : $x°_1 = 0.25$, $x°_3 = 0.75$				
0.250	0.000	0.750	1.197	0.901
0.224	0.103	0.673	1.135	1.237
0.200	0.200	0.600	1.083	1.403
0.175	0.300	0.525	1.037	1.452
0.150	0.400	0.450	0.996	1.398
0.137	0.451	0.412	0.976	1.340
0.125	0.500	0.375	0.959	1.266
0.100	0.600	0.300	0.925	1.074
0.074	0.705	0.221	0.893	0.826
0.025	0.900	0.075	0.840	0.290
0.012	0.951	0.037	0.827	0.145
0.045	0.821	0.134	0.860	0.514
Section 2 : $x°_1 = 0.5$, $x°_3 = 0.5$				
0.500	0.000	0.500	1.059	1.063
0.450	0.100	0.450	1.024	1.196
0.399	0.202	0.399	0.992	1.228
0.349	0.302	0.349	0.964	1.183
0.300	0.400	0.300	0.938	1.085
0.275	0.451	0.274	0.926	1.017
0.250	0.500	0.250	0.914	0.937
0.225	0.550	0.225	0.903	0.865
0.200	0.600	0.200	0.892	0.781
0.175	0.650	0.175	0.881	0.690
0.150	0.700	0.150	0.871	0.598
0.099	0.802	0.099	0.851	0.401
0.049	0.902	0.049	0.832	0.204

x_i^0, x_k^0 : initial ternary mixture

Table (A.2.3.a): contd.

x_1	x_2	x_3	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,(13+2)}}{\text{cm}^3.\text{mol}^{-1}}$
Section 3 : $x°_1 = 0.75$, $x°_3 = 0.25$				
0.750	0.000	0.250	0.826	0.826
0.674	0.101	0.225	0.859	0.859
0.601	0.199	0.200	0.831	0.831
0.524	0.301	0.175	0.762	0.762
0.450	0.400	0.150	0.672	0.672
0.412	0.450	0.138	0.620	0.620
0.337	0.550	0.113	0.512	0.512
0.300	0.600	0.100	0.457	0.457
0.262	0.651	0.087	0.402	0.402
0.225	0.700	0.075	0.347	0.347
0.160	0.787	0.053	0.251	0.251
0.075	0.900	0.025	0.123	0.123

x_i^0, x_k^0 : initial ternary mixture

Table (A.2.3.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(13+2)}$of {($x_1$$C_7H_8$ + $x_3$$CF_3CH_2OH$) + $x_2$$C_6H_{13}OH$} at 298.15 K and 101kPa

eq. (2.20);(2.21)	C_0	C_1	C_2					σ_s
	1.018	-1.802	-4.368					0.043
eq. (2.19)	C_{1t}	C_{2t}	C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	
	0.762	6.270	4.494	-0.658	2.695	-0.385	-3.470	0.018

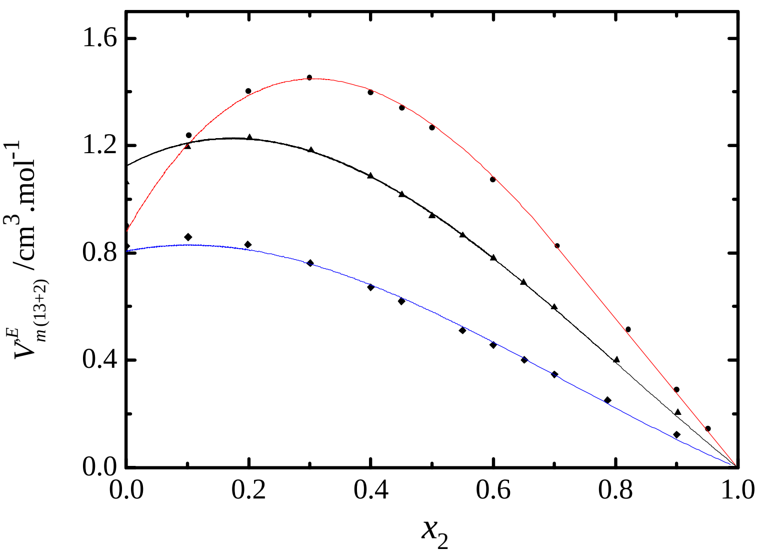

Figure (A.22): Excess molar volumes $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 298.15 K and 101kPa for sections: ●,S1; ▲,S2; ▼,S3.

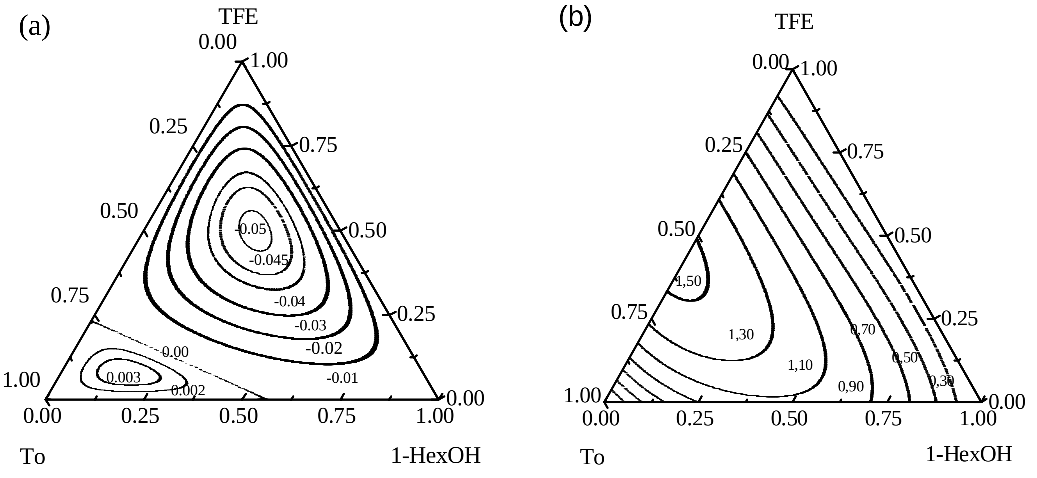

Figure (A.23): Excess molar volumes (cm^3.mol^{-1}) of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 298.15 K and 101kPa: (a) $V^E_{m,(13+2)}$;(b) $V^E_{m,(13+2)}$

Table (A.2.4.a): Densities ρ and excess molar volumes $V^E_{m,(13+2)}$ of {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 288.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,(13+2)}}{\text{cm}^3.\text{mol}^{-1}}$
Section 1 : $x°_1 = 0.25$, $x°_3 = 0.75$				
0,250	0,000	0,750	1,212	0,826
0,224	0,103	0,673	1,150	1,067
0,200	0,200	0,600	1,097	1,232
0,175	0,300	0,525	1,049	1,299
0,150	0,400	0,450	1,007	1,274
0,137	0,451	0,412	0,987	1,230
0,125	0,500	0,375	0,969	1,169
0,100	0,600	0,300	0,935	0,999
0,074	0,705	0,221	0,902	0,766
0,025	0,901	0,075	0,847	0,258
0,012	0,950	0,037	0,835	0,126
0,045	0,822	0,134	0,868	0,468
Section 2 : $x°_1 = 0.5$, $x°_3 = 0.5$				
0,500	0,000	0,500	1,073	0,954
0,450	0,100	0,450	1,037	1,054
0,399	0,203	0,399	1,004	1,091
0,349	0,303	0,349	0,975	1,070
0,300	0,400	0,300	0,949	1,002
0,275	0,451	0,274	0,936	0,949
0,250	0,501	0,250	0,923	0,888
0,225	0,550	0,225	0,912	0,819
0,200	0,599	0,200	0,901	0,743
0,175	0,650	0,175	0,890	0,657
0,150	0,700	0,150	0,879	0,569
0,099	0,803	0,099	0,859	0,376
0,049	0,901	0,049	0,840	0,184

x_i^0, x_k^0 : initial ternary mixture

Table (A.2.4.a): contd.

x_1	x_2	x_3	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^E_{m,(13+2)}}{\mathrm{cm^3.mol^{-1}}}$
Section 3 : $x°_1 = 0.75$, $x°_3 = 0.25$				
0,750	0,000	0,250	0,961	0,775
0,674	0,101	0,225	0,943	0,785
0,601	0,199	0,200	0,926	0,761
0,524	0,301	0,175	0,911	0,708
0,450	0,400	0,150	0,896	0,636
0,412	0,450	0,138	0,889	0,593
0,337	0,550	0,113	0,876	0,497
0,300	0,600	0,100	0,869	0,446
0,262	0,651	0,087	0,863	0,392
0,225	0,700	0,075	0,857	0,337
0,160	0,787	0,053	0,846	0,240
0,075	0,900	0,025	0,833	0,112

x_i^0, x_k^0 : initial ternary mixture

Table (A.2.4.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 288.15 K and 101kPa

eq. (2.20);(2.21)	C_0	C_1	C_2					σ_s
	-2.115	0.623	2.861					0.029
eq. (2.19)	C_{1t}	C_{2t}	C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	
	0.765	5.640	4.023	-0.534	2.153	-0.167	-2.831	0.019

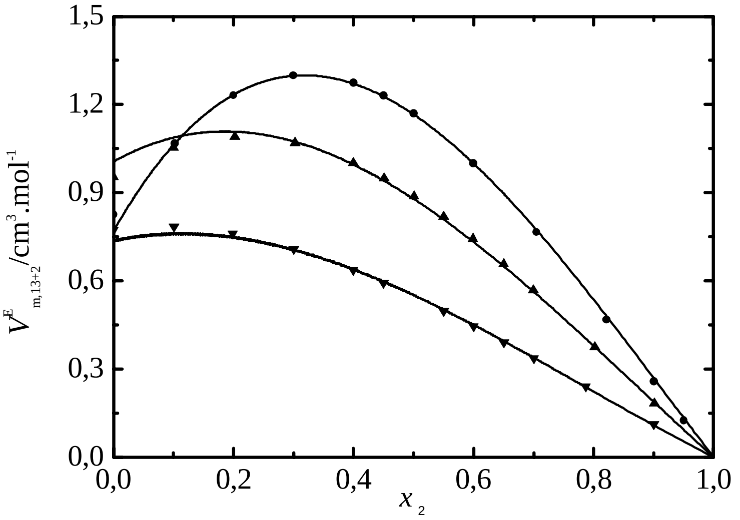

Figure (A.24): Excess molar volumes $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 288.15 K and 101kPa for sections: ●, S1; ▲,S2; ▼,S3.

Table (A.2.5.a): Densities ρ and excess molar volumes $V^{E}_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 303.15 K and 101kPa

x_1	x_2	x_3	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^{E}_{m,(13+2)}}{\mathrm{cm^3.mol^{-1}}}$
Section 1 : $x°_1 = 0.25$, $x°_3 = 0.75$				
0.250	0.000	0.750	1.190	0.914
0.224	0.103	0.673	1.127	1.302
0.200	0.200	0.600	1.077	1.470
0.175	0.300	0.525	1.031	1.514
0.150	0.400	0.450	0.990	1.455
0.137	0.451	0.412	0.971	1.394
0.125	0.500	0.375	0.953	1.317
0.100	0.600	0.300	0.920	1.120
0.074	0.705	0.221	0.888	0.865
0.025	0.901	0.075	0.836	0.310
0.012	0.950	0.037	0.823	0.156
0.045	0.822	0.134	0.856	0.544
Section 2 : $x°_1 = 0.5$, $x°_3 = 0.5$				
0.500	0.000	0.500	1.053	1.088
0.450	0.100	0.450	1.018	1.233
0.399	0.203	0.399	0.986	1.273
0.349	0.303	0.349	0.958	1.232
0.300	0.400	0.300	0.933	1.136
0.275	0.451	0.274	0.921	1.069
0.250	0.501	0.250	0.909	0.995
0.225	0.550	0.225	0.898	0.914
0.200	0.599	0.200	0.887	0.828
0.175	0.650	0.175	0.877	0.733
0.150	0.700	0.150	0.867	0.638
0.099	0.803	0.099	0.847	0.430
0.049	0.901	0.049	0.829	0.221

Table (A.2.5.a): contd.

x_1	x_2	x_3	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^E_{m,(13+2)}}{\mathrm{cm^3.mol^{-1}}}$
Section 3 : $x°_1 = 0.75$, $x°_3 = 0.25$				
0.750	0.000	0.250	0.945	0.835
0.674	0.101	0.225	0.927	0.873
0.601	0.199	0.200	0.911	0.853
0.524	0.301	0.175	0.896	0.791
0.450	0.400	0.150	0.882	0.705
0.412	0.450	0.138	0.875	0.654
0.337	0.550	0.113	0.863	0.546
0.300	0.600	0.100	0.856	0.490
0.262	0.651	0.087	0.850	0.432
0.225	0.700	0.075	0.844	0.375
0.160	0.787	0.053	0.835	0.273
0.075	0.900	0.025	0.822	0.133

Table (A.2.5.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 303.15 K and 101kPa

eq. (2.20);(2.21)	C_0	C_1	C_2					σ_s
	1.206	-1.839	-2.821					0.022
eq. (2.19)	C_{1t}	C_{2t}	C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	
	0.793	6.477	4.588	-0.519	2.782	-0.489	-3.027	0.020

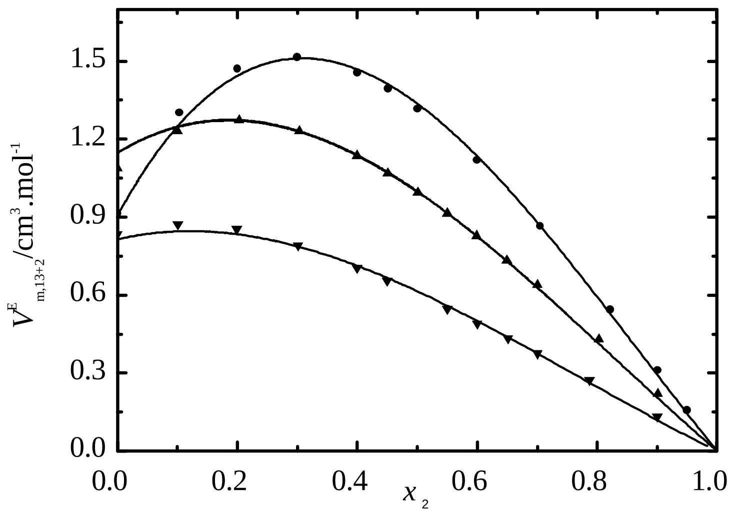

Figure (A.25): Excess molar volumes $V^E_{m,(13+2)}$ of $\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$ at 303.15 K and 101kPa for sections: ●, S1; ▲,S2; ▼,S3.

Table (A.2.5.c): Effect of temperature on smoothing coefficients and standard deviations of $V_{m,(13+2)}^{E}$ for {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at 101kPa

T/K	eq. (2.20);(2.21) eq. (2.19)	C_0 C_{1t}	C_1 C_{2t}	C_2 C_{3t}	C_{4t}	C_{5t}	C_{6t}	C_{7t}	σ_s
288.15		-2.115	0.623	2.861					0.029
		0.765	5.640	4.023	-0.534	2.153	-0.167	-2.831	0.019
298.15		1.018	-1.802	-4.368					0.043
		0.762	6.270	4.494	-0.658	2.695	-0.385	-3.470	0.018
303.15		1.206	-1.839	-2.821					0.022
		0.793	6.477	4.588	-0.519	2.782	-0.489	-3.027	0.020

Table (A.2.6): Standard deviations $\sigma(V_m^E/\mathrm{cm^3 \cdot mol^{-1}})$ of predicted V_m^E for {($x_1C_7H_8$ + $x_3CF_3CH_2OH$) + $x_2C_6H_{13}OH$} at T

T/K	288.15	298.15	303.15
Redlich-Kister, eq (2.24)	0.020	0.030	0.015
Kohler, eq (2.25)	0.033	0.030	0.023
Colinet, eq (2.26)	0.030	0.046	0.023
Mggianu:, eq (2.27)	0.020	0.030	0.015
$\overline{\sigma}(V_m^E/\mathrm{cm^3 \cdot mol^{-1}})$	0.035	0.045	0.025

Table (A.2.7): Summary of standard deviation σ_s ,extreme and infinite dilution for V_{123}^{E} of ternary systems calculated at 298.15 K and 101kPa

Mixture		σ_s	$x_1(ex.)$	$x_2(ex.)$	$V_{m,t}^{E}(ex.)$	$V_{m,1}^{E\infty}$	$V_{m,2}^{E\infty}$	$V_{m,3}^{E\infty}$
		cm^3mol^{-1}			cm^3mol^{-1}			
$\{x_1(CH_3)_2CO + x_2CH_3OH + x_3H_2O\}$	eq.(2.20)	0.039	0.406	0.001	-1.536			
	eq.(2.19)	0.008				-4.877	-3.880	-4.297
$(x_1CH_3OH + x_2H_2O + x_3C_2H_5OH)$	eq.(2.20)	0.021	0.141	0.591	-1.110			
	eq.(2.19)	0.024				-2.788	-3.039	-2.670
$\{(x_1C_7H_8 + x_3CF_3CH_2OH) + x_2C_6H_{13}OH\}$	eq.(2.20)	0.043	0.001	0.409	1.545			
	eq.(2.19)	0.018				3.260	4.610	3.935

Table (A.3.1.a): Densities ρ and excess molar volumes $V^E_{m,(123+4)}$ of {($x_1C_2H_5OH$ + x_2H_2O + $x_3$2-C_3H_7OH) + $(CH_3)_2CO$} at 298.15 K and 101kPa

x_1	x_2	x_3	x_4	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^E_{m,(123+4)}}{cm^3.mol^{-1}}$
Section 1: ($x°_1$= 0.15 , $x°_2$= 0.60 , $x°_3$= 0.25)					
0.151	0.602	0.247	0.000	0.866	-1.060
0.143	0.572	0.235	0.050	0.863	-1.202
0.135	0.542	0.223	0.100	0.857	-1.205
0.120	0.482	0.198	0.200	0.847	-1.247
0.106	0.423	0.174	0.297	0.838	-1.226
0.090	0.362	0.149	0.399	0.828	-1.137
0.078	0.313	0.129	0.480	0.821	-1.042
0.068	0.271	0.111	0.550	0.815	-0.912
0.060	0.241	0.099	0.600	0.811	-0.847
0.054	0.216	0.089	0.641	0.808	-0.753
0.045	0.182	0.075	0.698	0.804	-0.669
0.038	0.150	0.062	0.750	0.800	-0.552
0.030	0.121	0.050	0.799	0.797	-0.474
0.016	0.063	0.026	0.895	0.790	-0.208
0.007	0.029	0.012	0.952	0.788	-0.156
Section 2: ($x°_1$= 0.2 , $x°_2$= 0.4 , $x°_3$= 0.4)					
0.201	0.402	0.397	0.000	0.829	-0.940
0.192	0.385	0.380	0.043	0.828	-0.959
0.147	0.293	0.290	0.270	0.816	-0.872
0.128	0.255	0.252	0.365	0.811	-0.789
0.118	0.235	0.232	0.415	0.809	-0.758
0.108	0.215	0.213	0.464	0.806	-0.696
0.098	0.196	0.194	0.512	0.804	-0.631
0.087	0.175	0.173	0.565	0.802	-0.574
0.077	0.154	0.152	0.617	0.800	-0.536
0.066	0.133	0.131	0.670	0.797	-0.444
0.056	0.112	0.110	0.722	0.795	-0.374
0.045	0.091	0.090	0.774	0.793	-0.310
0.022	0.045	0.044	0.889	0.788	-0.149
0.012	0.023	0.023	0.942	0.787	-0.078

x^0_i, x^0_j, x^0_k : initial ternary mixture

Table (A.3.1.a): contd.

x_1	x_2	x_3	x_4	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^E_{m,(123+4)}}{\mathrm{cm^3.mol^{-1}}}$
Section 3: ($x°_1$= 0.24 , $x°_2$= 0.32 , $x°_3$= 0.44)					
0.239	0.319	0.442	0.000	0.818	-0.814
0.227	0.303	0.419	0.051	0.816	-0.824
0.215	0.287	0.398	0.100	0.815	-0.829
0.191	0.255	0.353	0.201	0.811	-0.770
0.167	0.223	0.309	0.301	0.807	-0.685
0.146	0.194	0.269	0.391	0.803	-0.603
0.132	0.175	0.243	0.450	0.801	-0.542
0.120	0.160	0.221	0.499	0.800	-0.513
0.108	0.144	0.200	0.548	0.798	-0.436
0.096	0.128	0.176	0.600	0.796	-0.396
0.084	0.111	0.154	0.651	0.795	-0.347
0.073	0.098	0.135	0.694	0.793	-0.291
0.060	0.080	0.111	0.749	0.791	-0.239
0.048	0.064	0.089	0.799	0.790	-0.187
0.024	0.031	0.044	0.901	0.787	-0.094
0.012	0.016	0.022	0.950	0.786	-0.086
Section 4: ($x°_1$= 0.3 , $x°_2$= 0.6 , $x°_3$= 0.1)					
0.300	0.600	0.100	0.000	0.875	-1.110
0.285	0.571	0.095	0.049	0.869	-1.187
0.270	0.540	0.090	0.100	0.863	-1.237
0.240	0.480	0.080	0.200	0.852	-1.278
0.210	0.421	0.070	0.299	0.841	-1.266
0.180	0.360	0.060	0.400	0.831	-1.205
0.150	0.300	0.050	0.500	0.821	-1.068
0.120	0.241	0.040	0.599	0.813	-0.936
0.090	0.181	0.030	0.699	0.805	-0.723
0.059	0.119	0.020	0.802	0.797	-0.497
0.031	0.062	0.010	0.897	0.791	-0.284
0.008	0.016	0.003	0.973	0.786	-0.098

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.1.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(123+4)}$ of $\{(x_1C_2H_5OH + x_2H_2O + x_32\text{-}C_3H_7OH) + (CH_3)_2CO\}$ at 298.15 K and 101kPa

	C_{1q}	C_{2q}	C_{3q}	C_{4q}	C_{5q}	C_{6q}	C_{7q}	σ_s
eq. (2.22)	-5.098	2.956	-0.371	-5.001	-5.126	1.939	-39.040	0.024

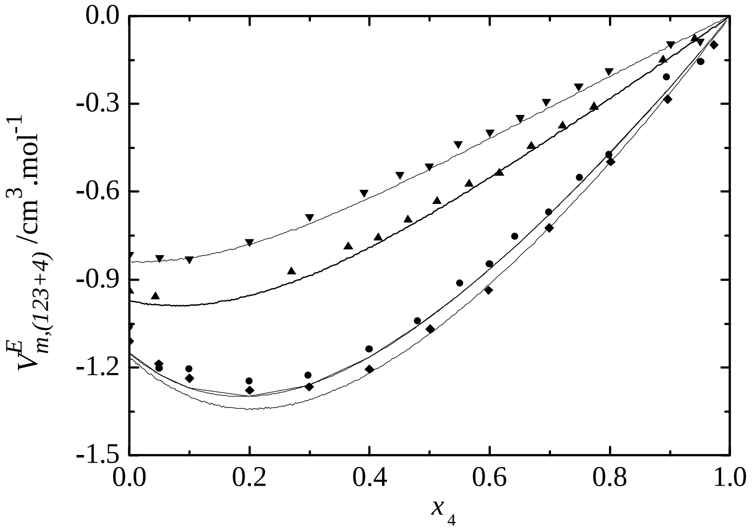

Figure (A.26): Excess molar volumes $V^E_{m,(123+4)}$of $\{(x_1C_2H_5OH + x_2H_2O + x_32\text{-}C_3H_7OH) + (CH_3)_2CO\}$ at 298.15 K and 101kPa for sections: ●, S1; ▲,S2; ▼, S3; ♦ , S4; —,Muggianu

Table (A.3.2.a): Densities ρ and excess molar volumes $V^{E}_{m,(123+4)}$ of {($x_1 C_2H_5OH$ + $x_2 H_2O$ + $x_3 (CH_3)_2CO$) + CH_3OH} at 298.15 K and 101kPa

x_1	x_2	x_3	x_4	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^{E}_{m,(123+4)}}{cm^3.mol^{-1}}$
Section 1: ($x°_1$= 0.1 , $x°_2$= 0.1 , $x°_3$= 0.8)					
0.100	0.101	0.799	0.000	0.796	-0.420
0.095	0.096	0.758	0.051	0.797	-0.577
0.090	0.091	0.721	0.098	0.796	-0.488
0.079	0.080	0.635	0.205	0.797	-0.512
0.070	0.071	0.560	0.299	0.797	-0.518
0.060	0.061	0.480	0.399	0.797	-0.519
0.054	0.055	0.435	0.455	0.796	-0.498
0.050	0.051	0.400	0.500	0.796	-0.485
0.045	0.045	0.358	0.552	0.796	-0.460
0.040	0.041	0.321	0.599	0.796	-0.442
0.035	0.036	0.281	0.649	0.795	-0.412
0.030	0.031	0.242	0.697	0.794	-0.378
0.006	0.006	0.044	0.945	0.789	-0.100
Section 2: ($x°_1$= 0.25 , $x°_2$= 0.25 , $x°_3$= 0.50)					
0.250	0.250	0.500	0.000	0.815	-0.931
0.238	0.237	0.476	0.049	0.816	-0.975
0.226	0.225	0.451	0.098	0.815	-0.921
0.200	0.200	0.400	0.200	0.813	-0.885
0.175	0.175	0.350	0.301	0.811	-0.828
0.150	0.149	0.299	0.402	0.809	-0.754
0.137	0.137	0.275	0.451	0.808	-0.713
0.125	0.125	0.250	0.500	0.807	-0.680
0.107	0.106	0.213	0.574	0.805	-0.597
0.098	0.098	0.196	0.608	0.804	-0.564
0.087	0.087	0.175	0.650	0.802	-0.517
0.075	0.074	0.149	0.702	0.800	-0.462
0.062	0.062	0.124	0.751	0.799	-0.402
0.031	0.031	0.062	0.877	0.793	-0.216

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.2.a): contd.

x_1	x_2	x_3	x_4	$\frac{\rho}{\mathrm{g.cm^{-3}}}$	$\frac{V^E_{m,(123+4)}}{\mathrm{cm^3.mol^{-1}}}$
Section 3: ($x°_1$= 0.4 , $x°_2$= 0.4 , $x°_3$= 0.2)					
0.400	0.400	0.200	0.000	0.842	-1.266
0.380	0.380	0.190	0.051	0.841	-1.249
0.360	0.360	0.180	0.101	0.838	-1.186
0.320	0.320	0.160	0.200	0.834	-1.113
0.280	0.280	0.140	0.301	0.829	-1.016
0.240	0.240	0.120	0.399	0.826	-0.986
0.221	0.221	0.110	0.449	0.822	-0.857
0.200	0.200	0.100	0.501	0.819	-0.810
0.180	0.180	0.090	0.550	0.816	-0.740
0.160	0.160	0.080	0.601	0.814	-0.705
0.139	0.139	0.070	0.652	0.810	-0.609
0.119	0.119	0.060	0.702	0.807	-0.543
0.099	0.099	0.049	0.753	0.804	-0.461
0.080	0.080	0.040	0.801	0.801	-0.390
0.040	0.040	0.020	0.900	0.794	-0.218
0.020	0.020	0.010	0.950	0.791	-0.126

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.2.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(123+4)}$ $\{(x_1C_2H_5OH + x_2H_2O + x_3(CH_3)_2CO) + CH_3OH\}$ at 298.15 K and 101kPa

	C_{1q}	C_{2q}	C_{3q}	C_{4q}	C_{5q}	C_{6q}	C_{7q}	σ_s
eq. (2.22)	-5.439	6.232	-17.838	-11.212	13.309	-1.342	7.986	0.024

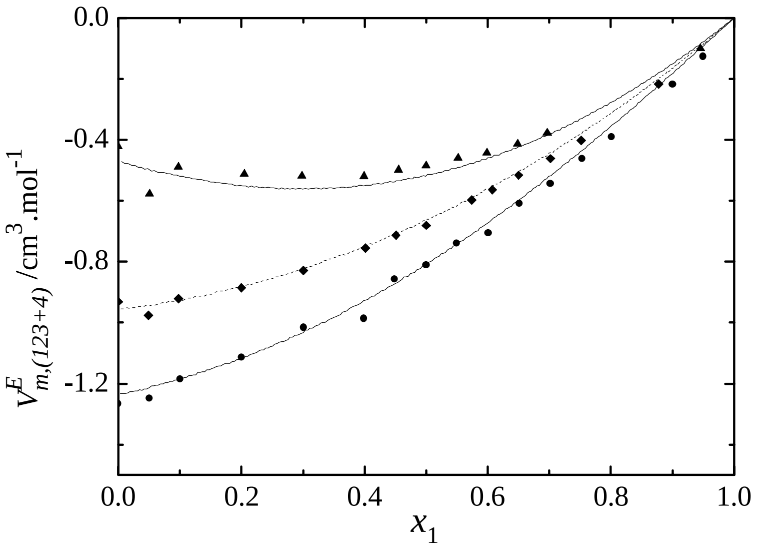

Figure (A.27): Excess molar volumes $V^E_{m,(123+4)}$of {($x_1C_2H_5OH$ + x_2H_2O + $x_3(CH_3)_2CO$) + CH_3OH} at 298.15 K and 101kPa for sections: ●, S1; ▲,S2; ♦, S3; _ ,Colinet; …,Kohler

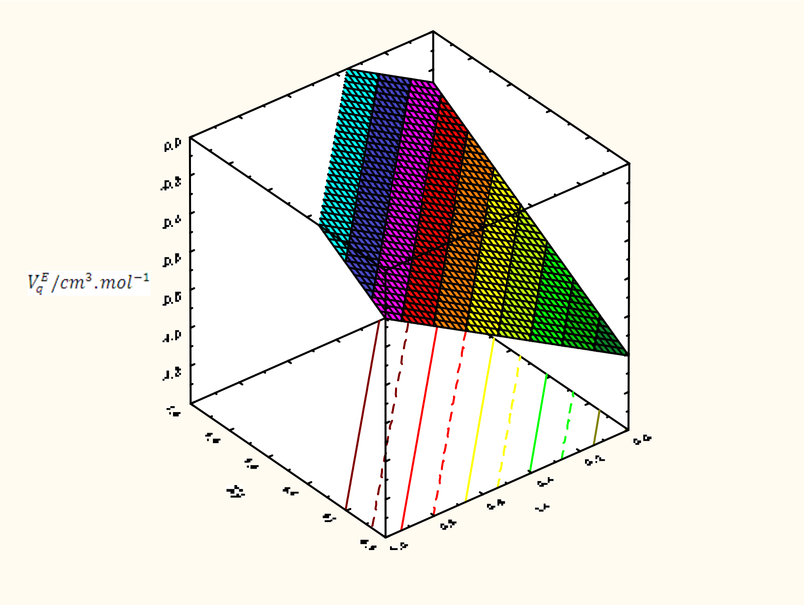

Figure (A.28): Surface of excess molar volumes $V^E_{m,(123+4)}$of {($x_1C_2H_5OH$ + x_2H_2O + $x_3$2-C_3H_7OH) + $(CH_3)_2CO$} at 298.15 K and 101kPa for sections: S1

Table (A.3.3.a): Densities ρ and excess molar volumes $V^E_{m,(123+4)}$ of {(x_1H_2O + $x_2$2-C_3H_7OH + x_3 CF_3CH_2OH) + $x_4C_2H_5OH$} at 298.15 K and 101kPa

x_1	x_2	x_3	x_4	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,(123+4)}}{\text{cm}^3.\text{mol}^{-1}}$
Section 1: ($x°_1$= 0.15 , $x°_2$= 0.75 , $x°_3$= 0.10)					
0.150	0.750	0.100	0.000	0.857	-0.189
0.134	0.670	0.089	0.107	0.850	-0.185
0.118	0.593	0.079	0.210	0.844	-0.188
0.105	0.525	0.070	0.300	0.838	-0.201
0.090	0.451	0.060	0.399	0.832	-0.189
0.083	0.413	0.055	0.449	0.828	-0.172
0.079	0.397	0.053	0.471	0.827	-0.168
0.074	0.369	0.049	0.508	0.824	-0.165
0.067	0.335	0.045	0.553	0.821	-0.153
0.060	0.300	0.041	0.599	0.818	-0.135
0.045	0.223	0.031	0.701	0.810	-0.112
0.037	0.184	0.025	0.754	0.806	-0.090
0.030	0.150	0.021	0.799	0.802	-0.080
0.015	0.074	0.010	0.901	0.794	-0.041
0.007	0.036	0.005	0.952	0.790	-0.020
Section 2: ($x°_1$= 0.35 , $x°_2$= 0.60 , $x°_3$= 0.05)					
0.349	0.599	0.052	0.000	0.857	-0.694
0.331	0.569	0.050	0.050	0.854	-0.693
0.313	0.538	0.048	0.101	0.850	-0.690
0.279	0.478	0.042	0.201	0.844	-0.674
0.243	0.418	0.037	0.302	0.837	-0.635
0.209	0.358	0.032	0.401	0.830	-0.587
0.191	0.329	0.029	0.451	0.827	-0.563
0.174	0.299	0.026	0.501	0.823	-0.530
0.156	0.268	0.024	0.552	0.819	-0.496
0.090	0.154	0.014	0.742	0.805	-0.321
0.139	0.239	0.021	0.601	0.815	-0.420
0.122	0.209	0.018	0.651	0.812	-0.379
0.112	0.193	0.017	0.678	0.810	-0.346
0.086	0.147	0.013	0.754	0.804	-0.297
0.069	0.119	0.010	0.802	0.800	-0.236
0.051	0.088	0.008	0.853	0.797	-0.172
0.035	0.061	0.005	0.899	0.793	-0.138
0.017	0.029	0.003	0.951	0.789	-0.070

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.3.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(123+4)}$ of $\{(x_1H_2O + x_2\ 2\text{-}C_3H_7OH + x_3CF_3CH_2OH) + x_4C_2H_5OH\}$ at 298.15 K and 101kPa

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	σ_s
eq. (2.22)	-4.212	4.580	-3.946	2.895	-0.283	3.280	2.303	0.010

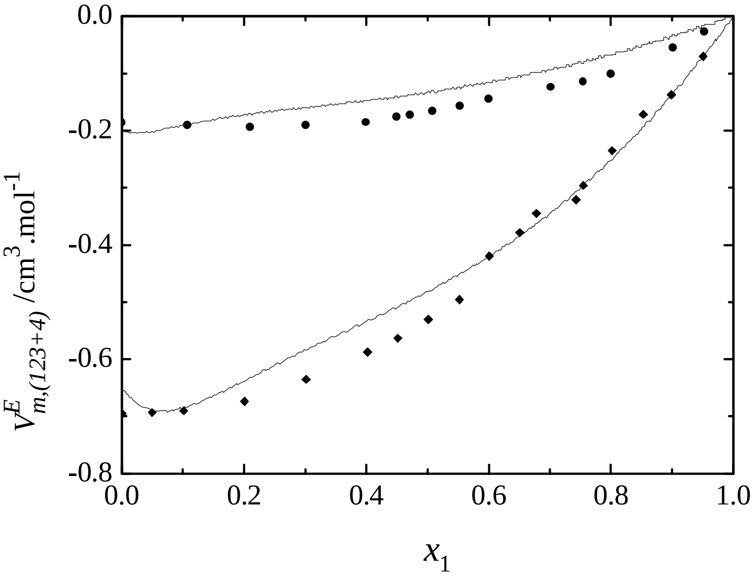

Figure (A.29): Excess molar volumes $V^E_{m,(123+4)}$of $\{(x_1H_2O + x_22\text{-}C_3H_7OH + x_3CF_3CH_2OH) + x_4C_2H_5OH\}$ at 298.15 K and 101kPa for sections: ●, S1; ▲,S2; ♦ , S3; _,Kohler’s eq

Table (A.3.4.a): Densities ρ and excess molar volumes $V^E_{m,(123+4)}$ of $\{(x_1H_2O + x_2(CH_3)_2CO + x_3CF_3CH_2OH) + C_2H_5OH\}$ at 298.15 K and 101kPa

x_1	x_2	x_3	x_4	$\frac{\rho}{g.cm^{-3}}$	$\frac{V^E_{m,(123+4)}}{cm^3.mol^{-1}}$
Section 1: ($x°_1$= 0.15 , $x°_2$= 0.75 , $x°_3$= 0.10)					
0.150	0.750	0.100	0.000	0.864	-0.356
0.135	0.675	0.090	0.100	0.858	-0.366
0.120	0.599	0.080	0.201	0.850	-0.338
0.105	0.526	0.070	0.299	0.843	-0.305
0.090	0.450	0.060	0.400	0.836	-0.267
0.083	0.412	0.055	0.450	0.832	-0.248
0.075	0.375	0.050	0.500	0.828	-0.234
0.068	0.337	0.045	0.550	0.824	-0.218
0.060	0.300	0.040	0.600	0.820	-0.199
0.053	0.262	0.035	0.650	0.816	-0.177
0.038	0.188	0.025	0.749	0.808	-0.146
0.015	0.075	0.010	0.900	0.795	-0.074
Section 2: ($x°_1$= 0.20 , $x°_2$= 0.50 , $x°_3$= 0.30)					
0.200	0.500	0.300	0.000	1.009	-0.260
0.180	0.450	0.270	0.100	0.987	-0.184
0.160	0.400	0.240	0.200	0.965	-0.136
0.140	0.350	0.210	0.300	0.943	-0.084
0.117	0.292	0.175	0.416	0.918	-0.063
0.100	0.250	0.150	0.500	0.900	-0.054
0.090	0.225	0.135	0.550	0.888	-0.048
0.080	0.200	0.120	0.600	0.877	-0.046
0.070	0.175	0.105	0.650	0.866	-0.039
0.060	0.150	0.090	0.700	0.855	-0.037
0.040	0.099	0.060	0.801	0.832	-0.037
0.030	0.074	0.045	0.851	0.821	-0.039
0.020	0.050	0.030	0.900	0.809	-0.031
0.010	0.025	0.015	0.950	0.798	-0.026

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.4.a): contd.

x_1	x_2	x_3	x_4	$\frac{\rho}{\text{g.cm}^{-3}}$	$\frac{V^E_{m,(123+4)}}{\text{cm}^3.\text{mol}^{-1}}$
Section 3: ($x°_1$= 0.35 , $x°_2$= 0.60 , $x°_3$= 0.05)					
0.350	0.600	0.050	0.000	0.866	-1.033
0.315	0.540	0.045	0.100	0.858	-1.013
0.280	0.480	0.040	0.200	0.851	-0.953
0.245	0.420	0.035	0.300	0.842	-0.839
0.210	0.361	0.030	0.399	0.834	-0.740
0.193	0.330	0.028	0.449	0.830	-0.683
0.182	0.311	0.026	0.481	0.827	-0.649
0.158	0.270	0.023	0.549	0.822	-0.587
0.141	0.241	0.020	0.598	0.818	-0.534
0.124	0.212	0.018	0.646	0.814	-0.480
0.106	0.182	0.015	0.697	0.810	-0.431
0.053	0.090	0.008	0.849	0.798	-0.245

x_i^0, x_j^0, x_k^0 : initial ternary mixture

Table (A.3.4.b): Smoothing coefficients and standard deviation σ_s for $V^E_{m,(123+4)}$of {(x_1H_2O + $x_2(CH_3)_2CO$ + $x_3CF_3CH_2OH$) + C_2H_5OH} at 298.15 K and 101kPa

	C_{1q}	C_{2q}	C_{3q}	C_{4q}	C_{5q}	C_{6q}	C_{7q}	σ_s
eq. (2.22)	-5.200	-5.023	-4.209	3.773	-0.407	3.125	16.620	0.016

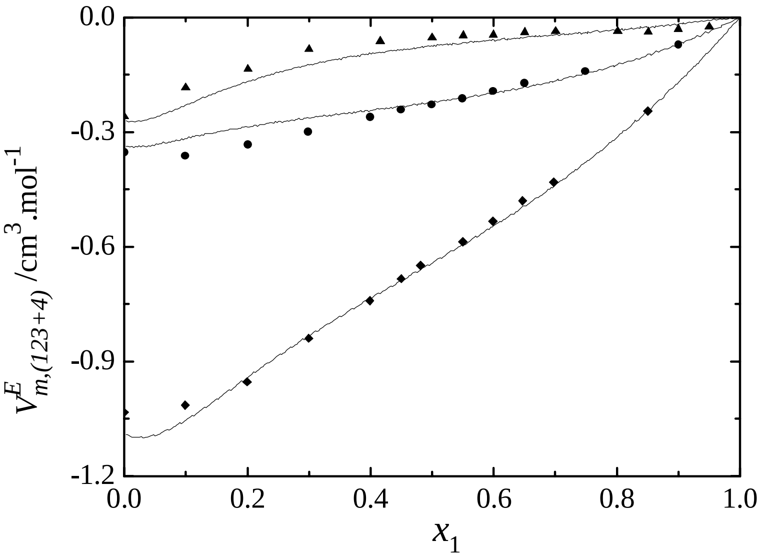

Figure (A.30): Excess molar volumes $V^E_{m,(123+4)}$of {(x_1H_2O + $x_2(CH_3)_2CO$ + $x_3CF_3CH_2OH$) + C_2H_5OH} at 298.15 K and 101kPa for sections: ●, S1; ▲, S2; ♦, S3; _,Kohler

Table (A.3.5): Summary of standard deviation σ_s; infinite dilution for $V^E_{(123+4)}$ of quaternary systems calculated from eq. (2.22) at 298.15 K and 101kPa

Mixtures	σ_s	$V^{E\infty}_{m,1}$	$V^{E\infty}_{m,2}$	$V^{E\infty}_{m,3}$	$V^{E\infty}_{m,4}$
	$cm^3.mol^{-1}$				
$(x_1C_2H_5OH + x_2H_2O + x_3\text{2-}C_3H_7OH) + x_4(CH_3)_2CO$	0.024	-4.267	-5.856	-1.512	-2.783
$\{x_1C_2H_5OH + x_2H_2O + x_3(CH_3)_2CO\} + x_4CH_3OH$	0.024	-5.193	-3.480	-1.851	-6.279
$(x_1H_2O + x_2\text{2-}C_3H_7OH + x_3CF_3CH_2OH) + x_4C_2H_5OH$	0.010	-106.321	-35.245	32.700	-54.093
$\{x_1H_2O + x_2(CH_3)CO + x_3CF_3CH_2OH\} + x_4C_2H_5OH$	0.016	-3.773	-2.198	-1.469	-1.948

Table (A.3.6): Standard deviations $\sigma(V^E_m/cm^3\cdot mol^{-1})$ of predicted V^E_m for ternary and quaternary systems at 298.15 K and 101kPa.

	$\sigma(V^E_m/cm^3\cdot mol^{-1})$						
	Ternary Mixture			Quaternary Mixture			
System n°	13	14	15	16	17	18	19
Redlich-Kister, eq (2.24)	0.014	0.024	0.030	0.030	0.040	0.038	0.027
Kohler, eq (2.25)	0.036	0.028	0.030	0.088	0.032	0.024	0.024
Colinet, eq (2.26)	0.033	0.029	0.046	0.081	0.038	0.030	0.035
Mggianu:, eq (2.27)	0.014	0.024	0.030	0.032	0.039	0.032	0.025
$\overline{\sigma}(V^E_m/cm^3\cdot mol^{-1})$	0.024	0.026	0.034	0.058	0.037	0.031	0.028