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Fouzia AMIRECHE

Vapour-Liquid Equilibria and Excess Thermodynamic Properties of Binary Fluorinated Hydrocarbon Mixtures

Soutenu le 03 decembre 2001 devant le Jury d'examination compose de :

Dr. BADJAH HADJ AHMED, A.Y., Professor, USTHB	President
Dr. ATIK, Z., Professor, USTHB	Supervisor
Dr. CIBULKA, I., Professor (Assoc.), Institut of Chemical Technology, Prague	Examinator
Dr. MEGHEZZI, H., Lecturer, USTHB	Examinator
Dr. BENDJEMAA, Z., Lecturer, USTHB	Examinator

التوازنات سائل ـ بخار
و الخواص الترموديناميكية للزيادة
للمزج الثنائية للمركبات الفلورية العضوية

رسالة ماجستير

جامعة العلوم و التكنولوجيا هواري بومدين

الطالبة فوزية عميرش

كلية العلوم ـ الكيمياء
مخبر علم البلورات ـ الترموديناميك
باب الزوار ، الجزائر

Avant tout, El Hamdou Li ALLAH …

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A la mémoire de mon père

A ma mère

A mon mari Salim

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AMIRECHE, F.

ملخص :
تلقى الهيدروكاربونات الفلورية إهتماما متزايدا في مختلف مجالات العلوم التقنية كونها آمنة على البيئة.
هذه المركبات الكيميائية إكتسبت مؤخرا أهمية قصوى في الكثير من التطبيقات الصناعية و البحث العلمي ومعطيات خواصها الترموديناميكية في تطور سريع.
درس هذا العمل المزج الثنائية لبعض من هذه المركبات باستعمال طرق تجريبية متعددة:
غليا نية (توازن أطوار)، حجمية و مسعرية.

في الطريقة الغليانية:
درسنا التوازنات سائل ـ بخار لتسع مزج ثنائية للهيدروكاربونات الفلورية بضغط101 kPa.
حيث عينت تجريبيا لهذه المزج توابع الزيادة الترموديناميكية: G_m^E، n_D^E في مجال التركيب:
$0.0 \le x \le 1.0$
أنشئت لهذه المزج المدروسة مخططات الأطوار :
(T, x, y) ، (x, y) ، $\{Ln(\gamma_1/\gamma_2), x\}$ ، (γ_i, x) و (α_{12}, x).
كما درست النتائج (p, T, x, y) المقاسة نظريا باستعمال نموذجي Wilson و UNIQUAC.
وبهذين النموذجين قدرت قيم الخواص التالية: G_m^E ، H_m^E ، S_m^E ، $C_{p,m}^E$ ، α_{12}^{∞} و γ_i^{∞}.
كان التوافق الترموديناميكي جيدا بين القيم التجريبية و النظرية.

في الطريقة الحجمية :
باستعمال مكثاف الكتروني قيس الحجم الجزيئي للزيادة(V_m^E,x) لست مزج ثنائية لمركبين فلوريين ومركب يودي واحد مع الميثانول و التولوين. كما قيست لها قرينة الانكسار للزيادة ($n_D^E,x,$) بمقياس قرينة انكسار إلكتروني. تمت كل القياسات بدرجة حرارة 298.2 K في مجال التركيب: $0.0 \le x \le 1.0$

في الطريقة المسعرية:
استعمل مسعر لقياس طاقة المزج H_m^E عند تركيب الازيوتروب (T_{az}, x_{az}) للمزج المدروسة بالطريقة الغليانية.

حللت النتائج التجريبية لتوابع الزيادة بالعلاقة: $X_m^E = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i$

حيث: $X_m^E = n_D^E,\ G_m^E/J.mol^{-1},\ V_m^E/cm^3.mol^{-1}$
و كان الانحراف القياسي $\sigma_{X_m^E}$ صغيرا لكل المزج المدروسة كدليل على توافق ترموديناميكي جيد بينها.
لم نحصل على منشورات علمية تجريبية لمعظم الجمل المدروسة قصد مقارنة النتائج المحصل عليها.
يوفر هذا العمل التجريبي معطيات متعددة لهذه المزج الثنائية و نأمل أن تكون نافعة للباحثين.

Abstract

Fluoro-hydrocarbons are environmentally accepted in various fields of science and technology. These chemicals are taking more importance in many industrial applications and research on the thermodynamic properties of their mixtures is progressing fast.

Vapour-Liquid Equilibria (VLE) of nine binary mixtures of fluorinated hydrocarbons were measured at the pressure 101 kPa.

Excess function n_D^E and V_m^E were determined at 298.15 K.

The (p, T, x, y) experimental results of VLE were well represented by the Wilson and UNIQUAC models.

Values of H_m^E, S_m^E and $C_{p,m}^E$ of the azeotropes together with α_{12}^{∞} and γ_i^{∞} were correlated by the above models.

The experimental excess molar properties of the studied mixtures were well

fitted to the equation: $$X_m^E = x(1-x)\sum_{i=0}^{n} A_i (1-2x)^i ,$$

where : $X_m^E = n_D^E$, G_m^E/J.mol^{-1} and V_m^E/cm^3.mol^{-1}.

As far as we know, no literature data are available for most of the studied systems for direct comparison of the results and much work is needed for more progress to be achieved in this field.

The main objective of this work was to obtain sufficient results to evaluate accurately the interaction parameters in these mixtures and consequently better prediction of their (pVT) and thermal behaviour properties

Résumé

Compte tenu de leur aspect écologique, les Fluoro-hydrocarbures sont admis dans divers domaines de la science et de la technologie. Ces produits chimiques ont reçu un intérêt considérable dans plusieurs applications industrielles et la recherche des propriétés thermodynamiques de leurs mélanges est en progrès rapide.

Les équilibres liquide-vapeur (VLE) de neuf mélanges binaires des hydrocarbures fluorés ont été mesurés à la pression de 101 kPa.

Les fonctions d'excès n_D^E et V_m^E ont été déterminées à 298.15 K.

Les résultats expérimentaux (p, T, x, y) des VLE ont été bien représentés par les modèles Wilson et UNIQUAC.

Les valeurs de H_m^E, S_m^E et $C_{p,m}^E$ des azeotropes ainsi que α_{12}^{∞} et γ_i^{∞} ont été corrélés par les modèles ci-dessus.

Les propriétés molaires d'excès expérimentales des mélanges étudiés ont été bien lissés par l'équation: $$X_m^E = x(1-x)\sum_{i=0}^{n} A_i (1-2x)^i ,$$

où : $X_m^E = n_D^E$, G_m^E/J.mol^{-1} et V_m^E/cm^3.mol^{-1}.

Selon notre recherche bibliographique, de tous les systèmes étudiés, un seul a fait l'objet d'une étude thermodynamique. Ceci montre que beaucoup de travaux restent à faire pour plus de progrès dans ce domaine.

L'objectif principal de ce travail est d'obtenir suffisamment de résultats expérimentaux afin d'évaluer de manière exacte les paramètres d'interaction de ces mélanges et par conséquent une meilleure prédiction de leurs (pVT) et de leurs propriétés thermiques.

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Glossary:

Symbols:

A_i	ith coefficient of polynomial
A_{ij}	mixture binary interaction Parameter
A	area
A,B	densimeter constants
A, B, C	Antoine constants
B_{ii}	pure second virial coefficient
B_{ij}	mixture cross second virial coefficient
B(y)	mixture second virial coefficient
C	number of components
C_p	isobaric heat capacity
D	Redlish-Kister consistency test
E	electrical energy
F	degree of freedom, objective function
F(x)	polynomial function in x
G	Gibbs function
H	enthalpy
J	Herington consistency test
M	molar mass
R	universal gas constant
S	entropy, surface
T	temperature
V	volume
X	thermodynamic property
Z_{RA}	Rackett's equation parameter
a	activity
$b^{(0)}$, $b^{(1)}$	Abbot's terms
f	fugacity
$f^{(0)}$, $f^{(1)}$	Tsonopoulos' terms
m	mass
n_D	refractive index
p	pressure
r, q	size and surface area parameters
u	UNIQUAC energy interaction parameter
x	liquid-phase composition
y	vapour-phase composition
z	compressibility factor, coordination number

Abbreviations:

PE	Poynting effect
VLE	vapour-liquid equilibrium
az	azeotrope
id	ideal
mix	mixing
max	maximum
min	minimum
Cal	calculated
Exp	experimental

Greek:

Δ	Increment
Φ	volume fraction
α	relative volatility, phase
δ	residual, uncertainty
ϕ	fugacity coefficient
φ	number of phases
γ	activity coefficient
ι	UNIQUAC parameter
λ	calorimeter constant
λ_{ij}	energy interaction parameter
μ	chemical potential, dipole moment
ν	oscillation
θ	surface area fraction, reduced normal boiling temperature
ρ	density
σ_s	standard deviation
σ^2	variance
ω	acentric factor

Subscripts:

A	component A in mixture
B	component B in mixxture
T	isothermic
b	boiling
i	component i
m	molar
p	isobaric
r	reduced quantity
t	time
0	reference run

Superscripts:

C	combinatorial
E	excess property
R	residual, reference
c	critical point
l	liquid
r	real
v	vapour
α,β	phases
σ	saturation property
∞	infinite dilution
*	pure component
θ	standard state

Chapter 1. Introduction

For over a half century, chlorofluorocarbons (CFC) have found wide range of applications: technical solvents, refrigerants, blowing agents of heat insulators, foaming agents, propellants, grease-removing in the microelectronics industry, and other technological applications.[1, 2] Unfortunately, these compounds have a strong ozone depletion potential, and enhance the greenhouse effect.[3, 4]

The CFC are good absorbers of atmospheric radiation, they are decomposed in the stratosphere and react with ozone, leading to its layer destruction.[5]

These harmful effects on our planet has led to increase concern about the CFC environmental impact and more stringent regulations being imposed on plant design and use of these chemicals together with development of alternative for their replacement. The substitute materials needed should be non-toxic, non-flammable and have an acceptably short environmental lifetime.[6]

The Montreal and Kyoto Protocols[5] which came as a direct consequence of the accumulation of CFC in the atmosphere due to sustained emissions, give a very different environmental regime by careful examination to any CFC substitute.

So far, the growth in CFC replacements has shown to be acceptable by environmentalists and few technical hydro-chloro-fluorocarbons (HCFC) have proven to be less harmful to ozone layer and are currently replacing some CFC.[7]

Hydrofluorocarbons (HFC) have recently taken importance in many industrial implementations,[8] and are already proposed and tested for CFC substitution in refrigerating machines, in heat pumps, and in air conditioning systems.[9] HFC are as cleaning solvents, blowing agents of heat insulators as well as reacting media.[1, 10]

The novel family of hydrofluoropolyethers (HFPE); having a general formula $HCF_2O(CF_2O)_m$-$(CF_2CF_2O)_n$-CF_2H, are being proposed as a promising class of electronic cleaning, foaming, fire extinguishing agents and heat fluids. The studied

HFPE have similar properties of perfluorinated compounds. More important, the HFPE have lower environmental impact in terms of their atmosphere lifetime and global warming potential.[11]

In medicine, some perfluoroorganic compounds; such as perfluorotripropylamine and perfluorodecalin, are being tested as favourable components for blood substitutes and oxygenating media.[12]

Some studies of aqueous solutions of fluorinated alcohols (trifluoroethanol and Pentafluoropropanol) are showing their possible replacement as cleaning agents instead on CFC's and proposed for various applications in heat pumps transformers due to high thermal-stability and safety.[13-15]

Fluorocarbons are distinguished from the homologous hydrocarbons by lower boiling-temperatures, higher densities and higher molar volumes. This might be due to their higher attractive energies in hydrocarbons caused by C—H interactions between inner carbon atoms and hydrogen atoms of different molecules.[16] In fluorocarbons C—F interactions between different molecules are considered very small due to the larger size and stronger electronegativity of the fluorine atom compared to the hydrogen atom.[17]

Several fluorocarbon substances are partially miscible with hydrocarbons of comparable molar mass and are poor solvents for most solid solutes, which may be caused by polarity of C—F bonds, low solubility parameters and differences in ionisation potential.[18] The substitution of hydrogen atoms by fluorine may be the main raison.[19]

Since 1960, scientific experimental and theoretical works has increase on the thermodynamic properties of fluorocarbon-containing mixtures.

The need for thermal data properties of hydrofluorocarbons mixtures, has led to measurements of their permittivities[13] thermodynamic properties; solubilies,[1] phase equilibria,[20] heat capacities, enthalpies and volumes of mixing. [21, 22]

Mixtures of fluorocarbons with hydrocarbons exhibit unusual properties manifested by strong nonideal behaviour forming low boiling azeotropes.[23, 24]

The strong behaviour of (fluorocarbon + hydrocarbon) mixtures are due to the large values of activity coefficients at infinite dilution as well as the separation coefficients

related to the large differences between the solubility parameters of the two liquids[25, 26] and indicating a tendency towards azeotropic behaviour.[18]

The azeotropic point occurs when the composition of component i in the liquid phase is similar to that of the vapour phase, thus separation of such systems using conventional distillation is impossible.[27] Therefore, the ability to predict the relative volatility and also the possible occurrence of an approach to azeotropic condition is an important tool, which enable the designer to select between alternative options for separating azeotropic mixtures.

Alternative distillation processes can employ separation at different pressure, by extractive or azeotropic distillation, pressure swing distillation or hetero-azeotropic distillation and hybrid processes can also be employed.[28] The availability data and data handling procedures for illustrating the phase behaviour and the separation of mixture makes it possible for the process designer to select between these various processing options.[29]

Because azeotropes are important for the synthesis and design of separation processes, the Dortmund Data Bank. (DDB) devotes a large section for azeotropic data.[30]

Published works reveal that binary mixtures of fluorocarbons with hydrocarbons are usually characterised by large and positive values of thermodynamic excess functions.[17, 18]

Knowing that the sign and magnitude of the excess molar properties is an indication of the strength of the unlike interactions in mixtures.[31] In general, large endothermic mixing energies indicate weak unlike interactions whereas large exothermic values of mixing energies are usually found when the unlike interactions are strong.

Differences in the molar volumes of the pure component mixtures do not attribute appreciably to the large value of the excess functions of fluorocarbon + hydrocarbon systems.[32]

It has been indicated that the shape of the hydrocarbon is the predominant factor governing the magnitude of the excess function and that interactions π—π play a secondary role in this respect.[33]

So a reasonable explanation for the experimentally observed trends in the molar excess enthalpy of mixing H^E and the molar excess volume of mixing V_m^E, is that the

enhanced unlike interactions are due solely to an increased contribution from dispersion forces. The strength of such forces is directly proportional to the product of the polarizabilities of the interacting molecules.[34] The strength of the unlike interactions increases with the degree of substitution.

Thermodynamic properties of most hydrocarbon + fluorohydrocarbon mixtures are then interpretable in terms of the presence of normal dispersion and multi-polar intermolecular forces.[35]

Their mixing energies effects are believed to increase with increasing inductive effect of the halogen atom.[36, 37]

On considering the effect of dipole moments of molecules forming aromatic fluorocarbons + hydrocarbons mixtures, from calorimetric measurements, it was found that repulsive effects dominate when a polar molecule dilute another polar molecule leading to endothermic mixing.[38]

The properties of fluid mixtures containing an aromatic fluorocarbon differ in many respects from those of mixtures containing an aliphatic or alicyclic fluorocarbon.[19]

These mixtures showed values of the excess functions G_m^E, H_m^E, and V_m^E for aromatic fluorocarbon + aromatic hydrocarbon mixtures less positive than those of mixtures containing a non-aromatic fluorocarbon.[31, 39]

Much effort, has been spent during the last three decades in obtaining data on fluorocarbon solutions.[17]

However, the data base concerning vapour-liquid equilibria of fluorohydrocarbons is still small despite their great theoretical and technical importance.[14]

More over experimental data are required for reliable process synthesis and design and the development of group contribution methods and excess Gibbs function models.[40]

In order to extend the knowledge of these systems, and to be able to interpret their chemical and physical properties, we have carried out measurements of vapour-liquid equilibria (VLE) and excess thermodynamic functions of binary mixtures: n_D^E, V_m^E, H_m^E as function of temperature at atmospheric pressure.

As far as we know, there are no studies available in the literatures for most of the present studied systems for direct comparison of the results.

For all our measurements: H_m^E, V_m^E the used equipments were tested using standard test systems. The agreement between our experimental data and literature works was quite good.

Chapter 2. Thermodynamics of Phase Equilibrium

2.1 Vapour-Liquid Equilibrium of a Pure component:

The simplest equation of state is that for an ideal gas:

$$pV_m = RT \tag{2.1}$$

The compressibility factor z of a gas is given by:

$$z = \frac{pV_m}{RT} \tag{2.2}$$

For an ideal gas, z = 1.0.

For a real gas, the compressibility factor z is smaller or greater than unity.

The pressure of a real gas is called the fugacity f and it does not equal to the pressure of an ideal gas p.

The fugacity f is related to the pressure p by the relation:

$$f = \phi p \tag{2.3}$$

where ϕ is the fugacity coefficient,

and:

$$\lim_{p \to 0} \left(\frac{f}{p} \right) = 1.0 \tag{2.4}$$

For a multi-component multi-phase system the degree of freedom or variance F, is:

$$F = C + 2 - \varphi \, , \tag{2.5}$$

where: C is number of components, φ is number of phases.

The variance is the number of variables which must be specified in order to fix the intensive state of a pVT system at equilibrium.

For a two-phases pure system, the variance is : F=1; only one intensive variable (temperature T or pressure p) is needed to study the equilibrium: T=f (p) or p =f(T).

Generally, the temperature T is chosen as the independent variable because it is easy to measure with high accuracy.

For a two-phases pure system the conditions of equilibrium are:

$$T^{\alpha} = T^{\beta} = T, \tag{2.6}$$

$$p^{\alpha} = p^{\beta} = p, \tag{2.7}$$

and,

$$\mu^{\alpha} = \mu^{\beta} \tag{2.8}$$

When the temperature T and the pressure p are changed in such away as to maintain equilibrium between the two phases, then for this change:

$$\Delta\mu^{\alpha} = \Delta\mu^{\beta} \tag{2.9}$$

The change in chemical potential of an ideal gas is expressed by:

$$\mu - \mu^{\theta} = RT\ln\left(\frac{p}{p^{\theta}}\right), \tag{2.10}$$

where the standard state is denoted by $^{\theta}$.

For a real behaviour, a new function called fugacity f, is introduced such that the chemical potential is given by:

$$\mu - \mu^{0} = RT\ln\left(\frac{f}{p^{\theta}}\right) \tag{2.11}$$

The condition of vapour-liquid equilibrium can be expressed in term of the fugacity as:

$$f^{v} = f^{l} \tag{2.12}$$

The vapour phase fugacity is expressed through :

$$f^{v} = \phi^{v} p \tag{2.13}$$

and the vapour-phase fugacity coefficient ϕ^{v} is evaluated with sufficient accuracy, through an equation of state.

$$\ln\phi^{v} = \left(\frac{1}{RT}\right)\int_{0}^{p}\left(V_m - \frac{RT}{p}\right)dp \tag{2.14}$$

substitution of equation (2.2) in equation (2.14) yields:

$$\ln\phi = \int_{0}^{p}\frac{(z-1)}{p}dp \tag{2.15}$$

The liquid-phase fugacity of a pure component is given by the equation:

$$f^{*,l}(T,p) = P^{*,\sigma}\phi^{*,\sigma} \exp \int_{p^\sigma}^{p} \left(\frac{V_m^*(T,p)}{RT} \right) dp \qquad (2.16)$$

The exponential term is the correction factor or the poyinting effect (PE).

The poynting factor (PE) is near unity when the total pressure p is sufficiently low.

Vapour-Liquid Equilibrium (VLE) :

The VLE of a pure substance is justified by the Clapeyron equation:

$$\frac{dp^{*,\sigma}}{dT} = \frac{\Delta_l^v H_m^*}{T(\Delta_l^v V_m^*)} \qquad (2.17)$$

where $\Delta_l^v H$: is the enthalpy of vaporisation, and $\Delta_l^v V$ is the change of volume during vaporisation.

Assuming an ideal vapour phase, Clausius wrote the Clapeyron equation (2.17) as:

$$\frac{dp^{*,\sigma}}{dT} = \frac{p^{*,\sigma}\Delta_l^v H_m^*}{RT^2} \qquad (2.18)$$

The equilibrium pressure p is the saturated vapour pressure denoted by p^σ.

The relation (2.18) is the Clausius-Clapeyron equation, which has the differential form:

$$\frac{d\ln p^{*,\sigma}}{d(1/T)} = -\frac{\Delta_l^v H_m^*}{R} \qquad (2.19)$$

Assuming that the molar enthalpy of vaporisation is independent of temperature the integrated form of equation (2.19) is:

$$\ln p^{*,\sigma} = C - \frac{\Delta_l^v H_m^*}{RT} \qquad (2.20)$$

For an ideal gas (vapour) phase, Antoine gave a simple empirical equation similar to equation (2.20) adding a corrective term C:

$$\ln p^{*,\sigma} = A - \frac{B}{T + C} \qquad (2.21)$$

The Antoine equation provides a good empirical equation for correlating vapour pressures of pure components in the range: 2 to 200 kPa.[41] At temperatures below the critical point, the Antoine expression tends to be increasingly inaccurate.[42]

For a moderate pressure VLE, the virial equation of state; in polynomial series in pressure, is commonly used with high efficiency; truncated to the second virial coefficient B:

$$p V_m^* = RT + Bp \tag{2.22}$$

The compressibility factor z is expressed in terms of the second virial coefficient B by:

$$z = 1 + \frac{Bp}{RT} \tag{2.23}$$

and the fugacity coefficient ϕ is related to the second virial coefficient B by:

$$\ln \phi^{*,\sigma} = \frac{Bp}{RT} \tag{2.24}$$

Vapour-liquid equilibrium of pure water is shown in figure (2. 1) as (p, T) phase diagram in the temperature range: $290 \leq T/K \leq T^c$

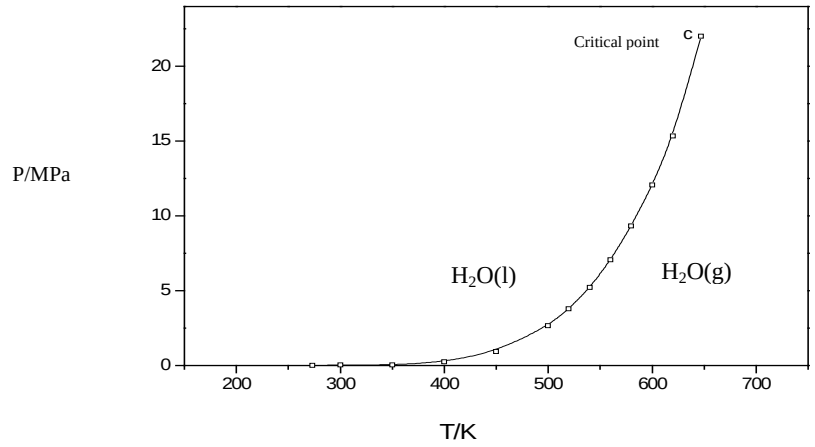


Figure (2. 1): Vapour-liquid equilibrium of pure water.

The (p, V) phase diagram of a vapour (gas) fulfils the partial derivatives:

$$\left(\frac{\partial p}{\partial V_m^*}\right)_{T^c} = 0 \tag{2.25}$$

$$\left(\frac{\partial^2 p}{\partial V_m^{*,2}}\right)_{T^c} = 0 \tag{2.26}$$

Equations (2.25) and (2.26) are used to evaluate critical constants (T^c, p^c, V_m^c) from an equation of state.

Critical constants are of major importance for correlating thermodynamic properties of pure substances as well as mixtures.

Experimental data of critical constants are not always available for all compounds, therefore, they can be calculated using empirical expressions.

A simple critical properties estimation method is used by Lydersen employing group critical-property increments forming the compounds. To evaluate the T^c, p^c and V^c. the relations are:

$$T^c / K = T_b \left\{0.567 + \sum \Delta_T - (\sum \Delta_T)^2\right\}^{-1} \quad (2.27)$$

$$p^c / atm = M.(0.34 + \sum \Delta_p)^{-2} \quad (2.28)$$

$$V_m^{*,c} / cm^3 mol^{-1} = 40 + \sum \Delta_v \quad (2.29)$$

where Δ_T denotes temperature increment effect, Δ_p : pressure increment effect and Δ_V : volume increment effect.

Using the corresponding states principle the critical property X^c is used to define the reduced property X_r: $$X_r = \frac{X}{X^c} \quad (2.30)$$

Common thermodynamic reduced parameters are: T_r , p_r and V_r .

Correlation of Thermodynamic Properties of a Pure Substance:

The standard enthalpy of vaporisation of a substance $\Delta_l^g H_b^*$ is computed from the following relation:

$$\Delta_l^g H_b^* = RT^c \Delta_l^g z_b \left(T_b^\sigma \frac{\ln p^c}{1 - T_b^\sigma} \right), \quad (2.31)$$

where $\Delta_l^g z_b$ is the standard compressibility factor of vaporisation and is given by:

$$\Delta_l^g z_b \approx 1 - (0.97 / p^c T_b^\sigma)$$

The vapour pressure for non-polar compound is estimated according to Pitzer's equation:

$$\ln p_r^{*,\sigma} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (2.32)$$

The functions $f^{(0)}$ and $f^{(1)}$ are expressed by Lee-Kesler as follows:

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6,$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6$$

The acentric factor ω represents the acentricity (non-sphericifity) of a molecule, and it is a measure of the complexity of a molecule with respect to both the geometry and the polarity.

The acentric factor ω, is defined by Pitzer according to the relation:

$$\omega = -\log p_r^{\sigma}(T_r = 0.7) - 1 \qquad (2.33)$$

Using the Clausius-Clapeyron equation (2.19), we get:

$$\omega = \frac{3}{7}\frac{\theta}{1-\theta}\log p^c - 1 \qquad (2.34)$$

where $\theta \equiv T_b/T^c$, is the reduced normal boiling temperature.

When the Lee-Kesler vapour-pressure correlation is used, we get:

$$\omega = \frac{-\ln p^c - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.169347\theta^6}{15.2518 - 15.6875\theta^{-1} - 13.4721 \ln \theta + 0.43577\theta^6} \qquad (2.35)$$

The acentric factor is not an exact constant, variation of 1% in the value selected for the critical pressure leads to a change in ω of 0.004.[43]

The critical compressibility factor z^c is related to the acentric factor ω is related to by:

$$z^c = 0.291 - 0.080\omega \qquad (2.36)$$

The second virial coefficient (B_{ij}) is not measured.

For the estimation of second virial coefficients an empirical equation is proposed by Tsonopoulos for non-polar compounds :

$$\frac{BP^c}{RT^c} = f^{(0)} + \omega f^{(1)}, \qquad (2.37)$$

with: $$f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \quad ,$$

$$f^{(1)} = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8}$$

For polar and hydrogen bonded compounds, Tsonopoulos added one corrective term to equation (2.37) to become as:

$$\frac{BP^c}{RT^c} = f^{(0)} + \omega f^{(1)} + f^{(2)}, \qquad (2.38)$$

where: $$f^{(2)} = \frac{a}{T_r^6} - \frac{b}{T_r^8} \qquad (2.39)$$

Abbott-Van Ness' expression for estimation of second virial coefficients is given by:

$$\frac{Bp^c}{RT^c} = b^{(0)}(T_r) + \omega b^{(1)}(T_r) \quad , \qquad (2.40)$$

where : $$b^{(0)} = 0.083 - \frac{0.442}{(T_r)_{ij}^{1.6}} \quad ,$$

$$b^{(1)} = 0.139 - \frac{0.172}{(T_r)_{ij}^{4.2}}$$

The saturated-liquid molar volume $V_m^{*,\sigma}$ is given by Rackett equation as:

$$V_m^{*,\sigma} = \left(\frac{RT^c}{p^c}\right)(z_{RA})^{\tau} , \qquad (2.41)$$

where: z_{RA} = Rackett's equation parameter:

$$z_{RA} = 0.29056 - 0.08775\omega ,$$

and, in the range: $T/T^c \le 0.75$: $\qquad \tau = 1 + \left(1 - \frac{T}{T^c}\right)^{2/7}$

Gun-Yamada refined the Rackett's equation (2.41) as:

$$V_m^{*,\sigma} = V_m^R z^c \exp\left\{\phi(T_r, T_r^R)\right\} , \qquad (2.42)$$

where: $z^c = 0.29056 - 0.08775.\omega$,

$$\phi(T_r, T_r^R) = (1 - T_r)^{2/7} - \left(1 - T_r^R\right)^{2/7}$$

V_R = liquid molar volume at a reference temperature T_r^R.

2.2 Thermodynamic Properties of Mixtures:

The total molar property X_m is expressed by:

$$X_m = \sum_i x_i . X_{m,i} \tag{2.43}$$

where, $x_{i:}$ the composition of component i; $X_{m,i:}$ the partial molar property (V, H,…).

Differentiation of equation (2.43) at constant temperature and pressure gives the Gibbs-Duhem relation:

$$0 = \sum_i x_i dX_{m,i} \tag{2.44}$$

For a binary mixture {(1-x) A + x B}, equation (2.44) can be written as:

$$dX_m = (X_{m,B} - X_{m,A})dx \tag{2.45}$$

The molar functions of mixing $\Delta_{mix}X_m$, for a binary mixture {(1-x)A + x B}, are defined by:

$$\Delta_{mix}X_m = (1-x)(X_A - X_A^*) + x(X_B - X_B^*), \tag{2.46}$$

where X_i^* is the partial molar property of a thermodynamic function X, with

X = G, H, S or V.

Differentiation of equation (2.46) gives:

$$d(\Delta_{mix}X_m) = \left\{(1-x)(X_A - X_A^*) + x(X_B - X_B^*)\right\}dx \tag{2.47}$$

Solution of derived equations (2.45) and (2.47) yields:

$$(X_A - X_A^*) = \Delta_{mix}X_m - x\left(\frac{\partial X_m}{\partial x}\right)_{T,p} \tag{2.48}$$

$$(X_B - X_B^*) = \Delta_{mix}X_m + (1-x)\left(\frac{\partial X_m}{\partial x}\right)_{T,p} \tag{2.49}$$

The molar volume of mixing $\Delta_{mix}V_m$, for a binary mixture {(1-x)A + x B}, is calculated by:

$$\Delta_{mix}V_m = V_m - (1-x)V_A^* - xV_B^* \tag{2.50}$$

The experimental molar volume of mixture $V_m(x)$ is for a composition x is given by the relation:

$$V_m(x) = \left\{(1-x)M_A + xM_B\right\}/\rho(x) \tag{2.51}$$

where:

$\rho(x)$: mixture density, M_i : molar mass of component i,

and the molar volume of pure component i, is : $V_i^* = M_i / \rho_i^*$

The equation (2.50) becomes:

$$\Delta_{mix} V_m = \{(1-x)M_A + xM_B\}/\rho(x) - (1-x)M_A/\rho_A^* - xM_B/\rho_B^* \qquad (2.52)$$

Equation (2.52) is an exact relation.

Excess molar functions are derived from thermodynamic functions of mixing to describe the real behaviour of a mixture.

The excess molar function X_m^E is defined by:

$$X_m^E(T, p, x) = \Delta_{mix} X_m^r(T, P, x) - \Delta_{mix} X_m^{id}(T, P, x) \qquad (2.53)$$

For an ideal mixture: $\Delta_{mix} X_m^{id} = 0$; X = V or H (2.54)

The excess molar volume V_m^E is given by:

$$V_m^E = \Delta_{mix} V_m^r \qquad (2.55)$$

The excess refractive index n_D^E for a binary mixture is given by:

$$n_D^E = n_D(x) - \{(1\text{-}x)\ n_{D,2}^* + x\, n_{D,1}^*\} \qquad (2.56)$$

The excess molar enthalpy H_m^E is given by:

$$H_m^E = \Delta_{mix} H_m^r \qquad (2.57)$$

The excess molar Gibbs function G_m^E is given by:

$$G_m^E = \Delta_{mix} G_m^r - RT\{(1-x)\ln(1-x) + x \ln x\} \qquad (2.58)$$

For binary mixtures the excess molar Gibbs function G_m^E is given by:

$$G_m^E = RT\{(1-x)\ln\gamma_A + x \ln\gamma_B\} \qquad (2.59)$$

Usual classical thermodynamic equations are still holding among excess functions:

$$\left(\frac{\partial G_m^E}{\partial p}\right)_{T,x} = V_m^E \quad , \qquad (2.60)$$

$$\left(\frac{\partial H_m^E}{\partial T}\right)_{p,x} = C_{p,m}^E \quad , \tag{2.61}$$

$$\left(\frac{\partial G_m^E}{\partial T}\right)_{p,x} = -S_m^E \quad , \tag{2.62}$$

and

$$\left\{\frac{\partial\left(G_m^E/T\right)}{\partial(T)}\right\}_{p,x} = \frac{-H_m^E}{T^2} \tag{2.63}$$

One of the commonly used analytical expressions for the excess functions of binary mixtures is:

$$X_m^E = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i \tag{2.64}$$

or,

$$X_m^E = x(1-x)F(x) \tag{2.65}$$

where A_i is a polynomial parameter.

The partial excess molar functions for a binary mixture are:

$$X_{m,A}^E = x^2\left\{F(x) + 2(1-x)\left(\frac{\partial F(x)}{\partial(1-2x)}\right)\right\} \tag{2.66}$$

$$X_{m,B}^E = (1-x)^2\left\{F(x) - 2x\left(\frac{\partial F(x)}{\partial(1-2x)}\right)\right\} \tag{2.67}$$

The sign and magnitude of the excess functions are a good indication of the unlike interactions energies in the mixture. Large endothermic mixing is indicated by weak unlike interactions, whereas large exothermic mixing is accomplished by strong unlike interactions in the mixture.[30]

For an ideal gas mixture, the partial pressure of a component i, is expressed by Dalton's law as:

$$p_i = y_i\, p \quad , \text{with: } p = \sum_{i=1}^{n} p_i \tag{2.68}$$

For an isothermal ideal mixture, Raoult's law gives the vapour pressure of component i, as:

$$p_i = x_i p_i^* \tag{2.69}$$

When the equilibrium l↔g is established we have:

$$y_i p = x_i p_i^* \tag{2.70}$$

The relative volatility α_{ij} of component i with respect to j is conventionally defined as:

$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} \tag{2.71}$$

If equations of state are used, the expression for the relative volatility becomes:

$$\alpha_{ij} = \frac{\varphi_i^l / \phi_i^v}{\phi_j^l / \phi_j^v} \tag{2.72}$$

The relative volatility α_{ij} indicates the ease of separation by distillation of components i and j. The relative volatility is also referred to as the separation factor.[40]

Equation (2.71), solved for y, becomes:

$$y = \frac{\alpha.x}{1+(\alpha-1).x} \tag{2.73}$$

with: $x = x_1$; $y = y_1$; $\alpha = \alpha_{12}$;

and component 1, is the component with the lower boiling point (the more volatile component).

Equation (2.73) indicated that the type of phase behaviour exhibited by a binary system will be determined largely by the manner in which the relative volatility α varies with composition.

The chemical potential of an ideal liquid mixture is expressed by Raoult's law:

$$\mu_i^l = \mu_i^* + RT \ln\left(\frac{p_i}{p_i^*}\right) \tag{2.74}$$

Substitution of equation (2.69) yields:

$$\mu_i^l = \mu_i^* + RT \ln x_i \tag{2.75}$$

The Raoult's law in equation (2.74) for a real liquid mixture is:

$$\mu_i^l = \mu_i^* + RT \ln a_i \quad , \tag{2.76}$$

where a_i is the activity of component i,:

$$a_i = p_i / p_i^* \quad ,$$

or:

$$a_i = \gamma_i x_i \tag{2.77}$$

with γ_i is the activity coefficient of component i at a composition x_i.

The activity coefficient γ_i describes the deviation from ideality.

The activity coefficient γ_i may be positive or negative.

When γ_i of a mixture is greater than one ($\gamma_i > 1.0$) the mixture has a positive deviation from ideality, whereas when it is less than one ($\gamma_i < 1.0$) the deviation from ideality is negative.

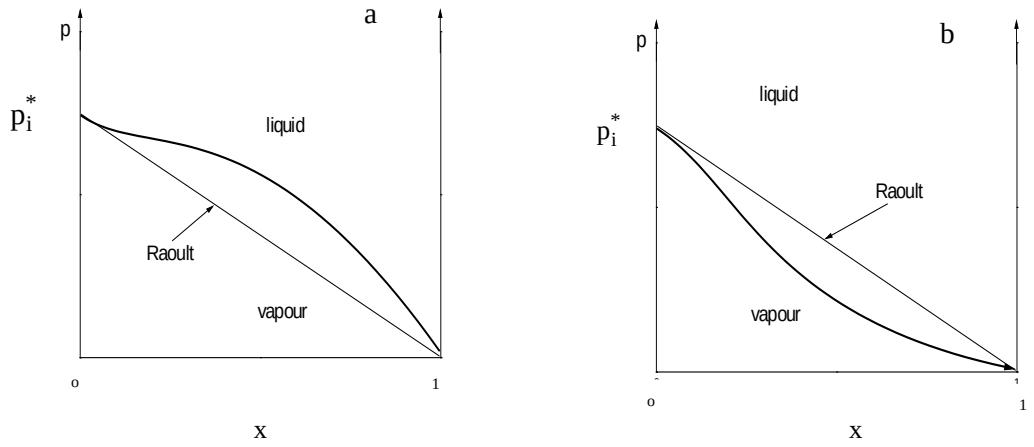


Figure (2. 2): $(p_i, x)_T$ phase diagram having :
a- positive , b- negative deviations from Raoult law

We note that when: $x_i \rightarrow 0.0$, $\gamma_i \rightarrow \gamma_i^{\infty}$

where γ_i^{∞} is the activity coefficient at infinite dilution.

VLE Phase Diagrams:

a). Ideal mixture :

For an ideal mixture, The relative volatility α_{12} is always greater than unity ($\alpha_{12} > 1.0$), and has a constant value through all composition range at constant T, and a nearly constant value at constant p.

An example of the type of phase diagram exhibited by an ideal solution is shown in figure (2. 3).

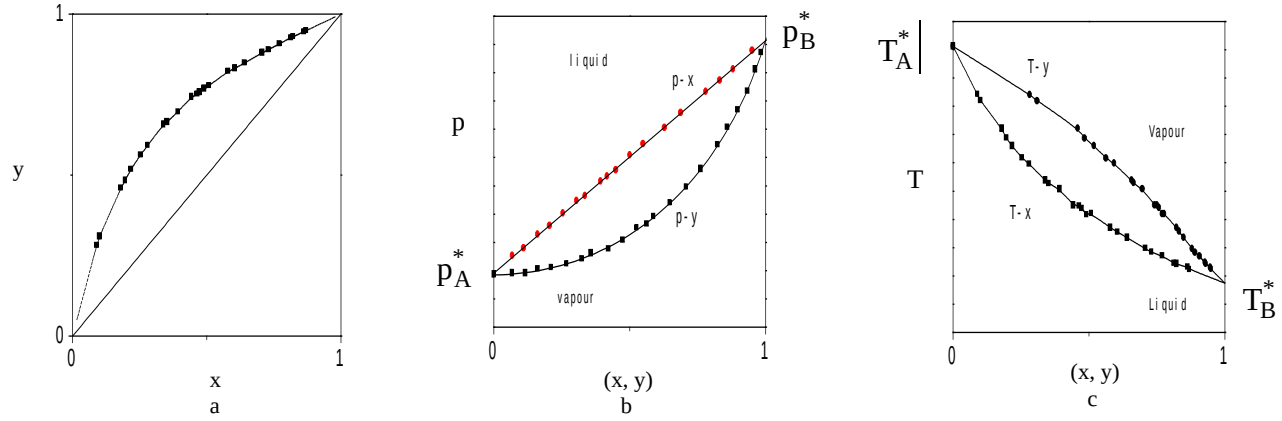


Figure (2. 3): Phase diagrams for ideal mixture: a- (y, x), b- $(p, x, y)_T$, c- $(T, x, y)_p$.

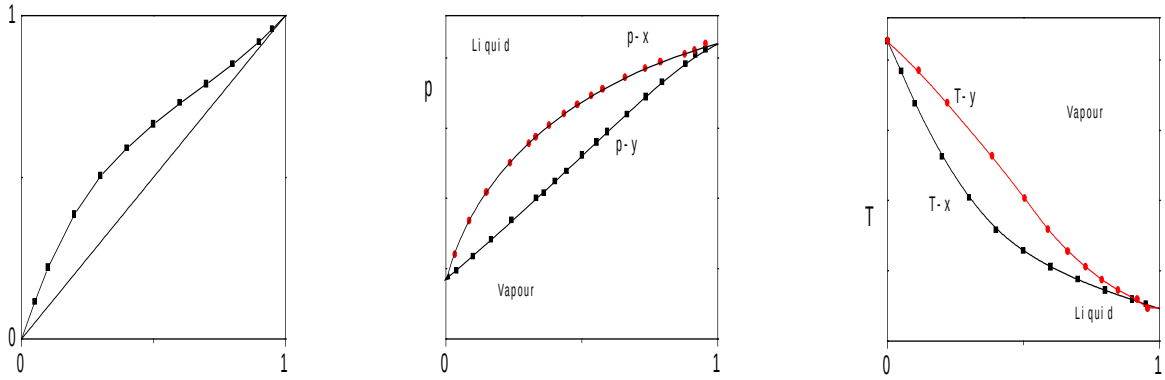
For such a system, the (y, x) curve lies above the isoline x = y, and exhibits no minima or maxima.

The $(p, x, y)_T$ phase diagrams are equally well behaved. The (p, x) curve is always above the (p, y) curve.

The $(T, x, y)_p$ phase diagrams are similar to each other with the (T, y) curve lies above the (T, x) curve.

b). Real zeotropic mixture:

For this mixture, the relative volatility α_{12} is always greater than unity ($\alpha_{12} > 1.0$) throughout the composition range. Its phase diagrams are resented by figure (2.4):



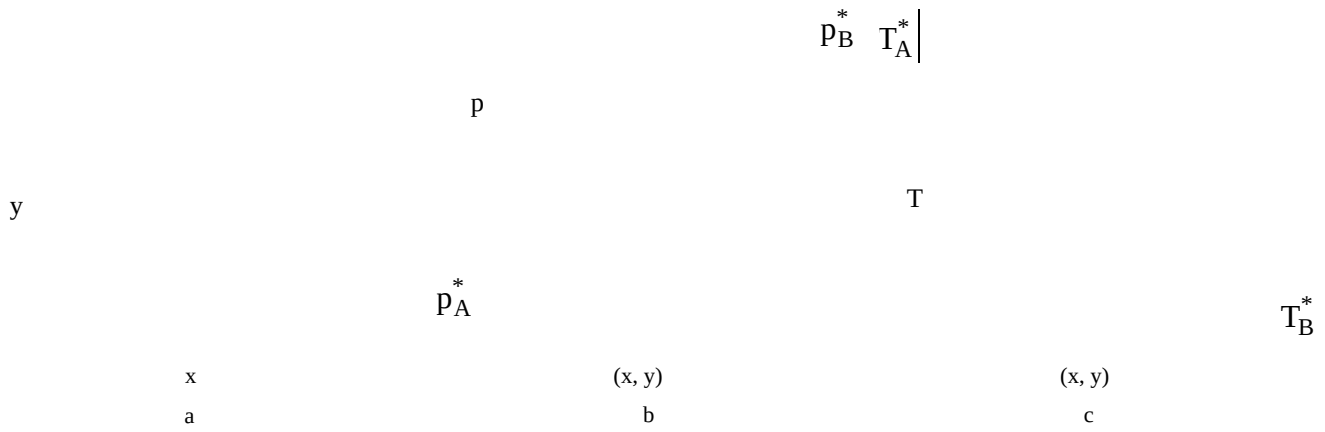


Figure (2. 4): Phase diagrams for real mixture: a- (y, x), b- $(p, x, y)_T$, c - $(T, x, y)_p$

t is noted that for theses mixtures their phase diagrams have a tendency to inflect when the mixture composition x_i tends to 1.0 ($x \approx y$).

c). Azeotropic Mixture

In a binary vapour-liquid equilibrium an azeotrope is a mixture which satisfies:

$$y = x \quad , \quad \alpha_{12} = 1.0 \tag{2.78}$$

and :

$$\frac{p_1^\sigma}{p_2^\sigma} = \frac{\gamma_2}{\gamma_1} \tag{2.79}$$

therefore,

$$\left(\frac{dT}{dx}\right)_p = 0 \quad ; \quad \left(\frac{dp}{dx}\right)_p = 0 \tag{2.80}$$

The continuous distillation of this particular mixture produces no composition change. Common azeotropes are those of low boiling temperatures.

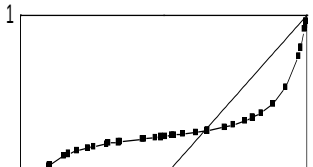
The azeotrope composition changes as the equilibrium temperature and pressure are changed.

An azeotrope will occur in a binary system when one of the following conditions is fulfilled:

- for $(p, x)_T$ phase diagram with pressure minimum azeotrpe:

$$\gamma_2^\infty \le p_1^\sigma / p_2^\sigma \le 1/\gamma_1^\infty \tag{2.81}$$

where α_{12} varies with composition in such a way that it is less than unity before (p_{az}, x_{az}) and greater than unity after (p_{az}, x_{az}).



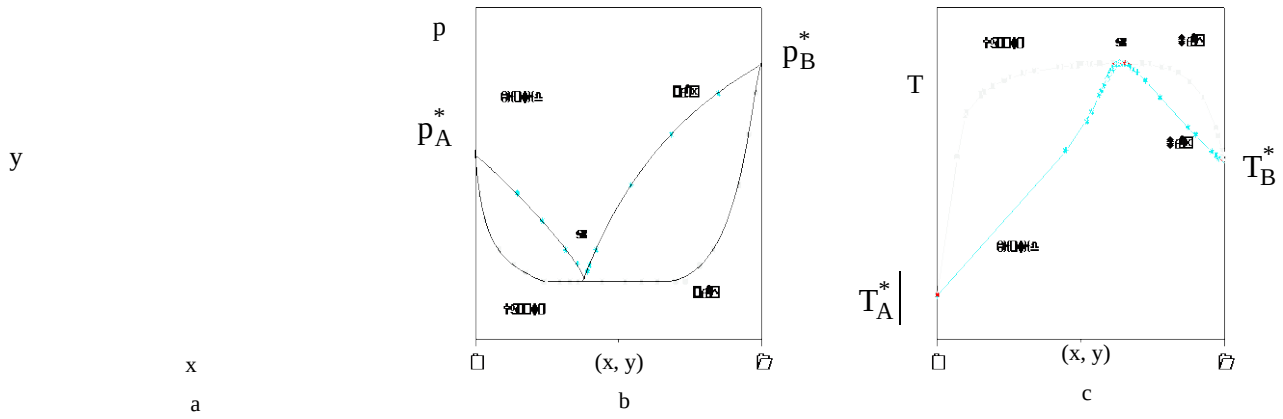


Figure (2. 5): Phase diagrams for pressure minimum azeotrope system:

a- (y, x), b- $(p, x, y)_T$, c- $(T, x, y)_p$

- for $(p, x)_T$ phase diagram with pressure maximum azeotrope:

$$\gamma_2^{\infty} \geq p_1^{\sigma} / p_2^{\sigma} \geq 1/\gamma_1^{\infty} \qquad (2.82)$$

where α_{12} >1.0 before (p_{az}, x_{az}) and α_{12} <1.0 after (p_{az}, x_{az}).

Binary azeotropes can also occur in almost ideal mixtures, when the two components have nearly equal vapour pressures.

Large deviations from ideal mixing can also lead to partial miscibility. In most cases, heterogeneous azeotropes are formed when miscibility gaps occur. However, in some binary mixtures both homogeneous azeotropes and miscibility gaps may be found. Types of binary azeotropes are reported in details by Gmehling.[40]

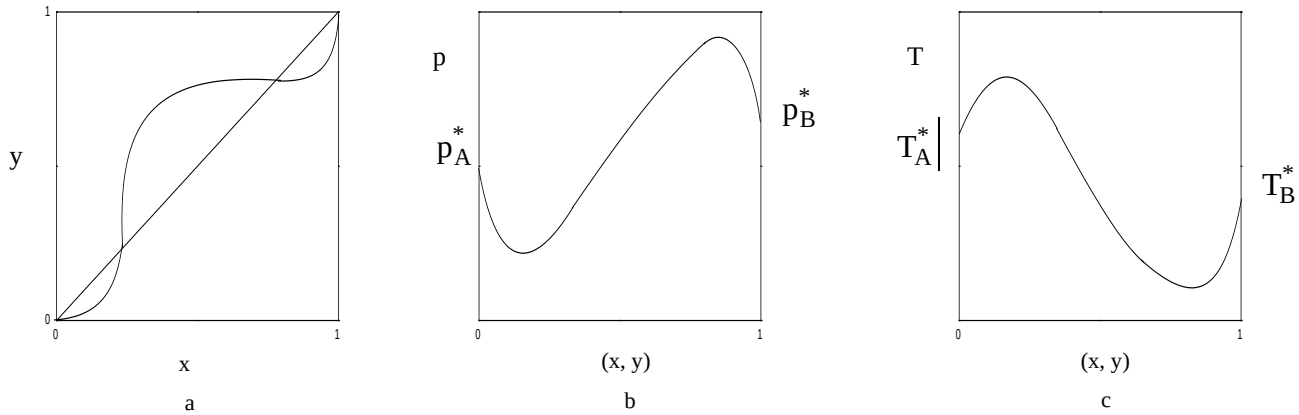


Figure (2. 6): Phase diagrams for a double azeotropic mixture:

a- (y, x), b- $(p, x, y)_T$, c- $(T, x, y)_p$.

The prediction of azeotropic composition is given by the Prigogine equation:

$$\frac{(1-x_{az})}{x_{az}} = \left(\frac{\Delta_l^g S_{m,1}}{\Delta_l^g S_{m,2}}\right)^{1/2} \left(\frac{T_1 - T_{az}}{T_2 - T_{az}}\right)^{1/2} \tag{2.83}$$

Equation (2.83) shows that the prediction of the azeotropic composition requires a prior knowledge of the azeotropic temperature.

There are more complicated equations to evaluate azeotropic data of complicated systems using different models.

2.3 Vapour-Liquid Equilibrium of Binary Mixtures:

For a two-phases multi-component mixture in equilibrium: l = v , chemical equilibrium equation (2.12) for component i becomes :

$$f_i^v = f_i^l \tag{2.84}$$

Considering the real behaviour of the liquid and vapour phases in a mixture, and combining equations (2.13) and (2.16), therefore equation (2.84) becomes:

$$\phi_i^v y_i p = \gamma_i x_i p_i^\sigma \phi_i^\sigma (PE)_i \tag{2.85}$$

For convenience, the sign * for pure component properties will be omitted in the text.

The vapour phase fugacity coefficient ϕ_i^v is evaluated through the virial equation of state as:

$$\ln \phi_i^v = \frac{p}{RT}\left(2\sum_i y_i B_{ij} - B(y)\right) \tag{2.86}$$

and the fugacity coefficient ϕ_i^σ of saturated pure component i can be again evaluated from the virial equation of state using equation (2.24).

from equation (2.16) of pure component the poynting effect $(PE)_i$ is expressed by:

$$(PE)_i \cong \exp\left\{(V_i^l - B_{ii})(p - p_i^\sigma)/RT\right\} \tag{2.87}$$

where V_i^l is the average molar volume of pure liquid i at T from P_i^σ to the system pressure p.

The second virial coefficient for mixtures, B (y) is given by the relation:

$$B(y) = \sum_i \sum_j y_i y_j B_{ij} \tag{2.88}$$

where B_{ii} and B_{jj} are the second virial coefficient of pure i and pure j, and B_{ij} is the crossed second virial coefficient for the pair of molecules i-j.

Crossed virial coefficient B_{ij} is correlated from the empirical equation of Tsonopoulos (2.38):

$$B_{ij} = \left(\frac{RT_{ij}^c}{p_{ij}^c} \right) \left\{ f^{(0)}(T_r)_{ij} + \omega_{ij} f^{(1)}(T_r)_{ij} \right\} \quad , \tag{2.89}$$

where the empirical expressions of $f^{(0)}$ and $f^{(1)}$ terms are similar to those given previously.

with the empirical expressions of $f^{(0)}$ and $f^{(1)}$ terms are similar to those given previously:

The critical constants of mixing are correlated by different methods. Tsonopoulos and Abbott correlation are given by the following mixing rules:

$$T_{ij}^c = (T_i^c T_j^c)^{1/2} \tag{2.90}$$

$$p_{ij}^c = \frac{z_{ij}^c R T_{ij}^c}{V_{ij}^c} \tag{2.91}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{2.92}$$

$$z_{ij}^c = \frac{z_i^c + z_j^c}{2} \tag{2.93}$$

$$V_{ij}^c = \left(\frac{(V_i^c)^{1/3} + (V_j^c)^{1/3}}{2} \right)^3 \tag{2.94}$$

When using Pitzer's correlation, the following mixture rules are employed:

$$T^c(y) = \frac{1}{8V_m^c} \sum\sum y_i y_j \left\{ (V_i^c)^{1/3} + (V_j^c)^{1/3} \right\}^3 (T_i^c T_j^c)^{1/2} \tag{2.95}$$

$$p^c(y) = \{0.2905 + 0.085\omega(y)\} \frac{RT^c(y)}{V^c(y)} \tag{2.96}$$

$$z^c(y) = \sum y_i z_i^c \tag{2.97}$$

$$z_i^c = 0.291 - 0.08.\omega(y) \tag{2.98}$$

$$\omega(y) = \sum y_i \omega_i \tag{2.99}$$

$$V^c(y) = \frac{1}{8}\sum_i \sum_j y_i y_j \left\{(V_i^c)^{1/3} + (V_j^c)^{1/3}\right\}^3 \tag{2.100}$$

$$V_i^c = (0.2905 + 0.085\omega_i)\frac{RT_i^c}{P_i^c} \tag{2.101}$$

Activity coefficient γ_i expresses the deviation from ideality. It is evaluated from equation (2.85) by:

$$\gamma_i = \frac{y_i \phi_i^v p}{x_i p_i^\sigma \phi_i^\sigma (PE)_i} \tag{2.102}$$

All the quantities on the right side of equation (2.102) are experimentally determined or computed with high accuracy.

In the limit as $x_i \to 0.0$, $p \to p_j^\sigma$, equation (2.102) becomes:

$$\gamma_i^\infty = \phi_i^\infty \frac{p_j^\sigma}{p_i^\sigma}\left(\frac{dy_i}{dx_i}\right)^\infty \tag{2.103}$$

where ϕ_i^∞ is the fugacity coefficient of component i at infinite dilution.

Equation (2.103) shows that the infinite-dilution value of an activity coefficient γ_i^∞ is directly related to the limiting slope of the (y, x) curve for VLE.

Thermodynamic Consistency:

The activity coefficients of the components of an equilibrium mixture must satisfy Gibbs Duhem equation if they are to be thermodynamically consistent. The Gibbs-Duhem equation is given by:

$$0 = \int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right)dx - \int_0^1 \left(\frac{H^E}{RT^2}\right)dT + \int_0^1 \left(\frac{V^E}{RT}\right)dp \quad ; \tag{2.104}$$

The effect of composition on VLE is treated by Redlich-Kister as:

$$D = \int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 \qquad (2.105)$$

by integration equation (2.105) becomes :

$$D = \left|\frac{A_p - A_n}{A_p + A_n}\right| x100, \qquad (2.106)$$

where A is areas above and below zero.

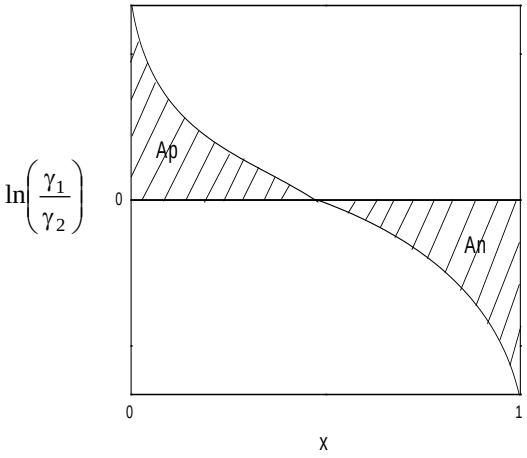


Figure (2. 7): The area test for binary mixtures of Redlish-Kister

Herington, extended the concept symmetrical area test proposed by Redlich-Kister to much more detailed analysis of thermodynamic consistency which may be used over parts of the composition range for both isothermal and isobaric data.

The effect of temperature is treated by Herington as:

$$J = \int_0^1 \left(\frac{H^E}{RT^2}\right) dT \qquad (2.107)$$

or,

$$J = 150\frac{\left|T_{max} - T_{min}\right|}{T_{min}} x100 \qquad (2.108)$$

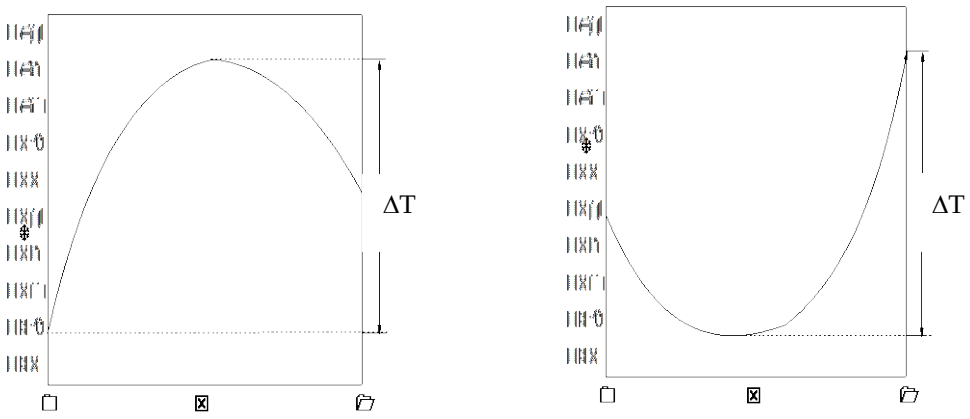


Figure (2. 8) : The (T, x) phase diagram for a binary mixture

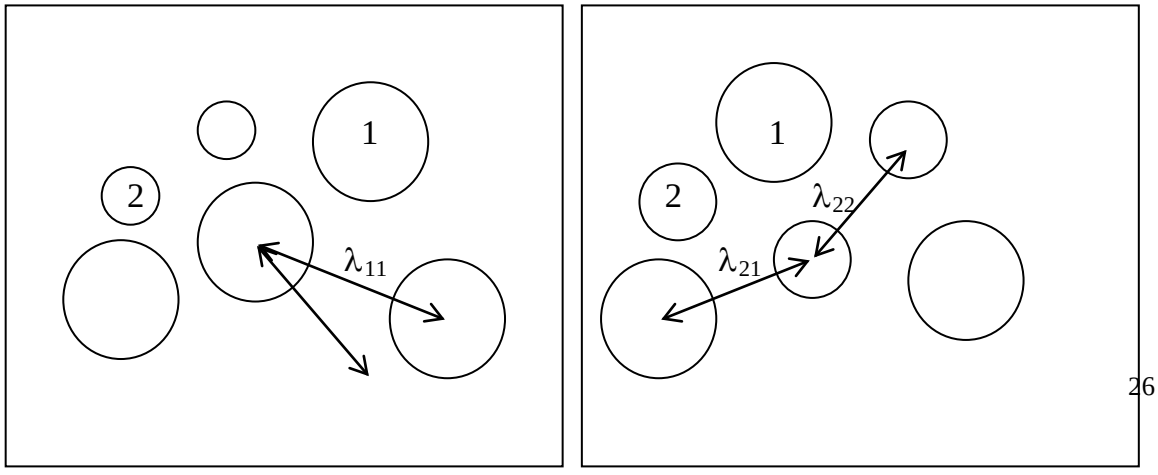
where T_{max} and T_{min} are the temperature extrema in the binary mixture including the boiling points of the pure components and the azeotrope, if present.

For thermodynamic data that satisfy (D-J)≤10, are considered to be consistent. However, in many publications,[45] systems with (D-J)≤20, were consistent because it still depends on boiling points of pure compounds: $T^*_{b,i} >> T^*_{b,j}$ (including azeotrope) yields always J>10.00.

Vapour-Liquid Equilibrium Data Reduction :

Many equations have been developed to represent the relation of (γ_i, x_i). These equations are known as activity coefficients γ_i models. These models contain a number of adjustable interaction parameters which can only be determined from experimental VLE data.

The concept of "local composition" of a mixture was introduced in the Flory-Huggins theory and was refined by Wilson, and it is represented by the simple schematic diagram:



(a) (b)

Figure (2. 9): Scheme of a Fluid structure on the local level*

For a binary mixture in a random liquid state, the probability of finding a molecule of type i relative to finding a molecule of type j about a central molecule j is:

$$\frac{x_{ij}}{x_{ii}} = \left(\frac{x_j}{x_i}\right)\left\{\frac{\exp(-\Delta\lambda_{ij}/RT)}{\exp(-\Delta\lambda_{ii}/RT)}\right\}, \qquad (2.109)$$

where: x_{ij} denotes the 'local' mole fraction,

x_i and x_j are the overall compositions of the mixture,

$\Delta\lambda_{ii}$ and $\Delta\lambda_{ij}$ are interaction energies of pure and crossed molecules.

With: $\Delta\lambda_{ij} \neq \Delta\lambda_{ji}$, so $A_{ij} \neq A_{ji}$. and $A_{ii} = A_{jj} = 0.0$

The local composition theory also provides the approximate temperature dependence of the Wilson's adjustable parameters:

$$A_{ij} = \left(\frac{V_j}{V_i}\right)\exp\left\{\frac{-(\lambda_{ij} - \lambda_{ii})}{RT}\right\} \quad , \qquad (2.110)$$

where V_j and V_i are the liquid molar volumes at temperature T of the pure j and i, and $\Delta\lambda_{ij} = (\lambda_{ij} - \lambda_{ii})$ is taken as constant over a short temperature range.

The Wilson equation (2.110) provides good predictions for the vapour-liquid properties using only two binary interaction parameters: The excess Gibbs function is given as follows:

$$\frac{G_m^E}{RT} = -\sum_i^n x_i \ln\left(\sum_j^n x_j A_{ij}\right) \qquad (2.111)$$

For a binary mixture equation (2.111) yields:

$$G_m^E = -RT\{x_1 \ln(x_1 + x_2 A_{12}) + x_2 \ln(x_2 + x_1 A_{21})\} \quad , \qquad (2.112)$$

* Tassios, D.P., 1993.

with:

$$A_{12} = \left(\frac{V_2^l}{V_1^l}\right)\exp\left(-\frac{\Delta\lambda_{12}}{RT}\right)$$

$$A_{21} = \left(\frac{V_1^l}{V_2^l}\right)\exp\left(-\frac{\Delta\lambda_{21}}{RT}\right)$$

The activity coefficient of component i, is derived from the Wilson's expression as:

$$\ln\gamma_i = 1 - \ln(\sum x_j A_{ij}) - \sum\frac{x_k A_{ki}}{\sum x_j A_{kj}} \qquad (2.113)$$

The summation is carried out over all the components of the mixture.

For a binary mixture, equation (2.113) yields :

$$\ln\gamma_1 = -\ln(x_1 + x_2 A_{12}) + x_2\left(\frac{A_{12}}{x_1 + x_2 A_{12}} - \frac{A_{21}}{x_2 + x_1 A_{21}}\right) \qquad (2.114)$$

$$\ln\gamma_2 = -\ln(x_2 + x_1 A_{21}) + x_1\left(\frac{A_{21}}{x_2 + x_1 A_{21}} - \frac{A_{12}}{x_1 + x_2 A_{12}}\right) \qquad (2.115)$$

The interaction parameters A_{12} and A_{21} are the differences of interaction energies between the molecules 1-2 and 1-1 or 2-2, respectively.

The Wilson model is not applied to mixtures having miscibility gap.

The UNIQUAC model (UNIversal Quasi-Chemical) was developed by Prausnitz and is based on Guggenheim's model and the local composition principle of Wilson. The resulting equation also accounts for the effects of molecular size through structural parameters obtainable from pure compound data, in addition to the molecular interactions. (46)

The UNIQUAC model gives the excess Gibbs energy G_m^E in two terms:

$$G_m^E = (G_m^E)^C + (G_m^E)^R \qquad (2.116)$$

Therefore :

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (2.117)$$

$(G_m^E)^C$ and γ_i^C: combinatorial parts, reflecting the difference in size and shape of the molecules of the mixture,

$(G_m^E)^R$ and γ_i^R : residual parts, reflecting the difference in energy interaction between the molecules in the mixture.

The main UNIQUAC G_m^E model equations are summarised bellow:

$$\frac{(G_m^E)^C}{RT} = \sum_i^n x_i \ln\frac{\Phi_i}{x_i} + \frac{Z}{2}\sum_i^n q_i x_i \ln\frac{\theta_i}{\Phi_i} \qquad (2.118)$$

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum x_j l_j \qquad (2.119)$$

$$\frac{(G_m^E)^R}{RT} = -\sum_i^n q_i x_i \ln\left(\sum_j^n \theta_j \tau_{ji}\right) \qquad (2.120)$$

$$\ln\gamma_i^R = -q_i \ln(\sum\theta_j\tau_{ij}) + q_i - q_i \sum\left(\frac{\theta_j\tau_{ij}}{\sum\theta_k\tau_{kj}}\right) \qquad (2.121)$$

The surface fraction θ_i and the volume fraction Φ_i are defined as :

$$\theta_i = \frac{q_i x_i}{\sum q_j x_j} \quad , \quad \Phi_i = \frac{r_i x_i}{\sum r_j x_j}$$

$$\tau_{ij} = \exp\left\{\frac{-(u_{ij}-u_{jj})}{RT}\right\} = \exp\left(\frac{-\Delta u_{ij}}{RT}\right)$$

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$$

with:

u_{ij} : energy parameters, They are reffered to as characteristic exchange energies of the interacting molecules.

z : coordination number, set equal to 10;

r, q : size and surface area parameters obtained from Bondi's method.

The values of r and q are normalised and can be obtained for each species as the sum of the group volume (R_i) and surface area (Q_i) parameter values given by literature.

For a binary system, equation (2.121) becomes :

$$\ln\gamma_1 = \ln\frac{\Phi_1}{x_1} + \frac{z}{2} q_1 \ln\frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2} l_2\right) -$$

$$q_1 \ln(\theta_1 + \theta_2\tau_{12}) + q_1\theta_2\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) \qquad (2.122)$$

The expression for $\ln\gamma_2$ is obtained by rotating the subscripts.

with $\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}$, $\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$

$\ln\tau_{21} = -\frac{\Delta u_{21}}{RT}$, $\ln\tau_{12} = -\frac{\Delta u_{12}}{RT}$

In case of binary mixture, there are only two adjustable interaction parameters ι_{ij}, and ι_{ji} which are computed by VLE data.

The UNIQUAC equation is applicable to both, miscible and partially miscible mixtures.

The parameters chosen of a (γ_i, x_i) or G_m^E model are determined from (p, T, x, y) experimental data by the maximum-likelihood principle and are those that minimise the objective function F given by:

$$F = \sum_{i=1}^{n}\left\{\frac{(p_{i,exp.} - p_{i,cal.})^2}{\sigma_{p_i}^2} + \frac{(T_{i,exp.} - T_{i,cal.})^2}{\sigma_{T_i}^2} + \frac{(x_{i,exp.} - xi,_{cal.})^2}{\sigma_{x_i}^2} + \frac{(y_{i,exp.} - y_{i,cal.})^2}{\sigma_{y_i}^2}\right\} \qquad (2.123)$$

where $\sigma_{p_i}^2$, $\sigma_{T_i}^2$, $\sigma_{x_i}^2$ and $\sigma_{y_i}^2$ are the variances of the corresponding variables for a set of a reading point i.

Convergence in equation (2.123) is obtained when $\delta F \approx 10^{-5}$.

By use of the above γ_i-models, the thermodynamic quantities γ_i^∞, H_m^E, C_p^E are evaluated through the equations given in table (2.1).

Table (2.1): Thermodynamic properties of binary mixtures using Wilson and UNIQUAC models

Model	$\ln\gamma_1^{\infty} =$ $\ln\gamma_2^{\infty} =$	
WILSON		
	$1-\ln A_{12}-A_{21}$ $1-\ln A_{21}-A_{12}$	(2.124)
UNIQUAC		
	$1-\frac{r_1}{r_2}+\ln\frac{r_1}{r_2}-5q_1\left(\ln\frac{r_1q_2}{r_2q_1}-\frac{r_1q_2}{r_2q_1}\right)-q_1\left(4+\ln\tau_{21}+\tau_{12}\right)$ $1-\frac{r_2}{r_1}+\ln\frac{r_2}{r_1}-5q_2\left(\ln\frac{r_2q_1}{r_1q_2}-\frac{r_2q_1}{r_1q_2}\right)-q_2\left(4+\ln\tau_{21}+\tau_{21}\right)$	(2.125)

Model	$H_m^E =$	
WILSON		
	$x_1x_2\left\{\frac{A_{12}\lambda_{12}}{x_1+x_2A_{12}}+\frac{A_{21}\lambda_{21}}{x_2+x_1A_{21}}\right\}$	(2.126)
UNIQUAC		
	$x_1x_2\left\{\frac{q_1\theta_2\tau_{21}\Delta u_{21}}{\theta_1x_1+\theta_2x_2\tau_{21}}+\frac{q_2\theta_1\tau_{12}\Delta u_{12}}{\theta_2x_2+\theta_1x_1\tau_{12}}\right\}$	(2.127)

Model	$C^{E}_{p,m}$ =
WILSON	$\frac{x_1 x_2}{RT^2}\left\{\frac{x_1 A_{12}(\lambda_{12})^2}{(x_1 + x_2 A_{12})^2} + \frac{x_2 A_{21}(\lambda_{21})^2}{(x_2 + x_1 A_{21})^2}\right\}$ (2.128)
UNIQUAC	$\frac{x_1 x_2}{RT^2}\left\{\frac{q_1 x_1 \theta_1^2 \tau_{21}(\Delta u_{21})^2}{(\theta_1 x_1 + \theta_2 x_2 \tau_{21})^2} + \frac{q_2 x_2 \theta_2^2 \tau_{12}(\Delta u_{12})^2}{(\theta_2 x_2 + \theta_1 x_1 \tau_{12})^2}\right\}$ (2.129)

Vapour-Liquid Equilibrium Data Correlation

Models for (γ_i, x_i) store much information for liquid mixtures. Given such a model, computer calculation methods of VLE properties are devised for isobaric and isothermic systems.

For a given set of (T_i, x_i) the objective function F, equation (2.123) becomes:

$$F = \sum_{i=1}^{n}\left\{\frac{(p_{i,exp.} - p_{i,cal.})^2}{\sigma_{p_i}^2} + \frac{(y_{i,exp.} - y_{i,cal.})^2}{\sigma_{y_i}^2}\right\} \qquad (2.130)$$

and a set of (p , y_i) is obtained by minimising equation (2.130), the optimum values for the (p, y_i) satisfies: $\delta p \le 10\%$, $\delta y \le 2\%$.[47]

Equation (2.85) provides the basis of calculation, written either as:

$$y_i = \frac{x_i \gamma_i p_i^{\sigma}}{\phi_i p} \quad \text{or as} \quad x_i = \frac{y_i \phi_i p}{\gamma_i p_i^{\sigma}} \qquad (2.131)$$

Since: $\sum y_i = 1.0$ and $\sum x_i = 1.0$, we also have the following expressions:

and: $$1 = \sum \frac{y_i \phi_i p}{\gamma_i p_i^{\sigma}} \quad \text{or} \quad p = \frac{1}{\sum y_i \phi_i / \gamma_i p_i^{\sigma}} \qquad (2.132)$$

For a given set of (T_i, x_i), the calculation of (p, y_i) is proceeded through the equations (2.131) and (2.132) by iteration:

$$p = \frac{1}{y_1 \phi_1 / \gamma_1 p_1^{\sigma} + y_2 \phi_2 / \gamma_2 p_2^{\sigma}} \qquad (2.133)$$

The iteration is started with the ideal behaviour phase condition:

$$\gamma_i = 1.0 \ , \ \phi_i = 1.0.$$

Thus choosing a gamma model, initial calculation of p; Raoult's-law, by equation (2.133) and of x_i by equation (2.131), with the computed (p, x_i) now we can evaluate γ_i from the chosen model and ϕ_i from equation (2.86) and then a new value of p is obtained from equation (2.133) to start the next iteration. This computing process is continued until convergence is achieved in p (10^{-3}) and y_i (10^{-4}).

This correlation process is represented by the block diagram in figure (2.9).

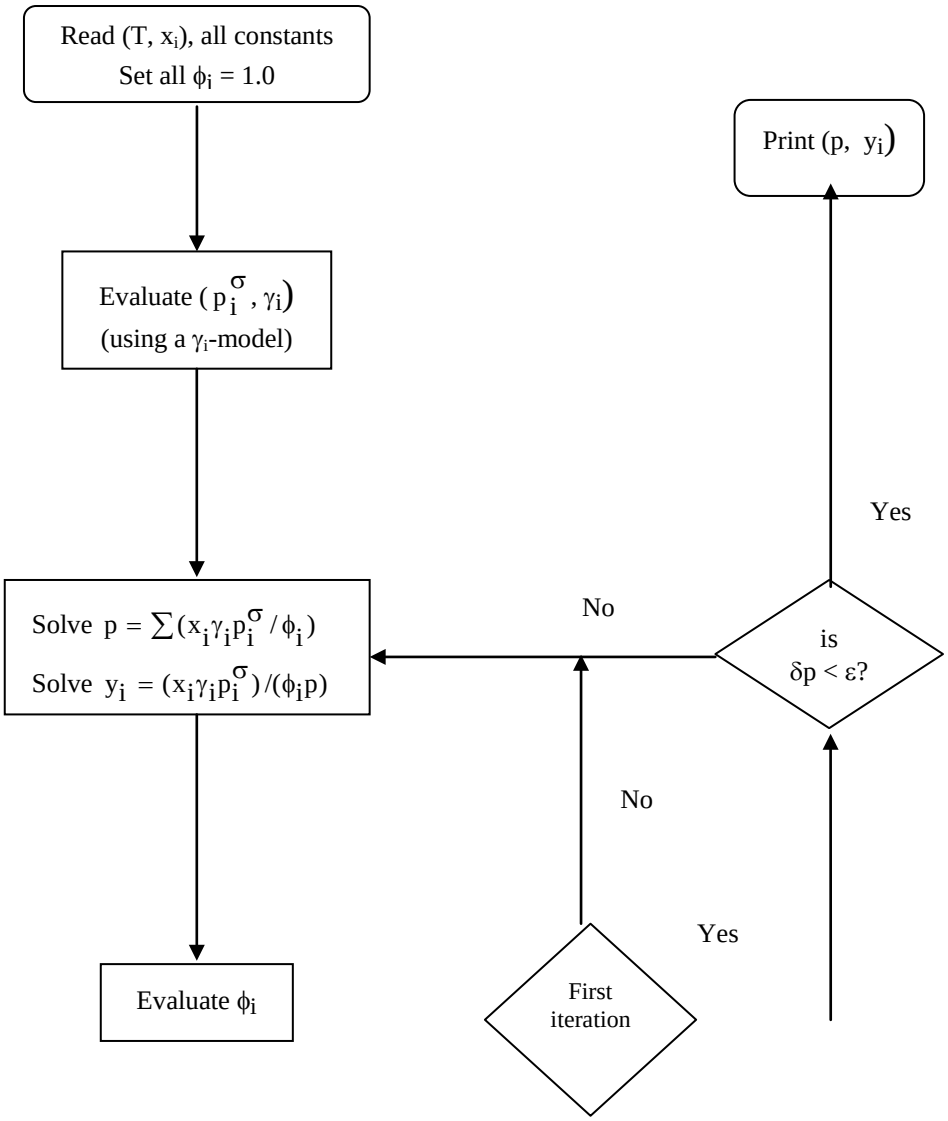


Figure (2. 10): The block diagram for data correlation of isobaric Vapour-liquid equilibrium [*]

[*] Van Ness, Abbott, **1982**

Chapter 3. Experimental Techniques

3.1 Materials:

The chemicals used for this investigation were chosen of relatively simple chemical structures with low boiling temperatures, so the quantitative analysis, for pure compounds and mixtures, could be performed fairly rapidly with equipment available to us.

The original purities of the pure substances declared by the suppliers (Fluka, Merk, J. Chemica and Prolabo) were better than 99.5% (GC). Hence, chemicals were used with no further purification.

The experimental boiling temperatures, densities and refractive indices are listed in table (3. 1). The over all physico-chemical properties of pure components needed for calculations and discussion are listed in tables (3. 2a) and (3. 2b).

3.2 Equipments and Procedures.

Refractometry :

Refractive index is the relative velocity of light in the substance under examination.

Refractive indices of pure substances and binary mixtures were determined at 298.2 K using an Abbe-type refractometer, with an accuracy of 0.001, and an electronic refractometer-DUR, with the precision of 0.0002.

For Abbe refractometer: the water bath temperature was kept constant by LAUDA PID-temperature-controller (models R25-R3) and stirrerd Heidolph- motor (model: RZR1). Water was circulated through the measuring prisms by a B-BRAUN-thermomix-1441.

Table (3.1): Pure Component Properties

Component	Symbol	n_D (298.2 K)		ρ(298.2 K)/g.cm^{-3}	
		Exp.	Lit.	Exp.	Lit.
Water	H_2O	1.3334	--	--	0.9970751[48]
Benzene	C_6H_6	1.4974	1.4978[49]	0.8735	0.87370[50]
Cyclohexane	C_6H_{12}	1.4243	1.4235[51]	0.7735	0.77383[52]
Hexane	C_6H_{14}	1.3720	1.3723[50]	--	0.6548[50]
Toluene	C_7H_8	1.4936	1.4941[53]	0.8622	0.8623[49]
Heptane	C_7H_{16}	1.3855		--	
Metnanol	CH_4O	1.3287*	1.32691[48]	0.7876	0.7864[54]
Chloroform	$CHCl_3$	1.4429		1.4773	
Ethanol	C_2H_5OH	1.3604	1.35941[55]	0.7895	0.7851[56]
Acetone	C_3H_6O	1.3560		--	
Fluorobenzene	C_6H_5F	1.4625		--	1.01893[57]
Difluorobenzene	1,4-$C_6H_4F_2$	1.4393		1.1635	
Fluorotoluene	2-C_7H_7F	1.4713		0.9987	
Trifluorotoluene	α,α,α-$C_7H_5F_3$	1.4132		1.1887	
Trifluoroethanol	2,2,2-$C_2H_2F_3OH$	1.2910		1.3813	1.38091[15]
Iodoethane	C_2H_5I	1.5087		1.9241	1.9264[58]

* extrapolated from (n_D, x) curve of the methanol mixtures.

Table (3. 2a): Physico-chemical properties of pure components

Component	T^c/K	p^c/bar	V_m^c ($cm^3.mol^{-1}$)	ω	A	B	C
					lnp (p/mmHg , T/K)		
H_2O	647.3	217.6	56.0	0.344	18.3036	3816.44	-46.13
C_6H_6	562.1	48.3	259.0	0.212	15.9008	2788.51	-52.36
C_6H_{12}	553.4	40.2	308.0	0.273	15.7527	2766.63	-50.50
C_6H_{14}	507.4	29.3	370.0	0.296	15.8366	2697.55	-48.78
C_7H_8	591.7	40.6	316.0	0.257	16.0137	3096.52	-53.67
C_7H_{16}	540.2	27.0	432.0	0.351	15.8737	2911.32	-56.51
CH_4O	512.6	79.9	118.0	0.559	18.5875	3626.55	-34.29
$CHCl_3$	536.4	54.0	239.0	0.216	15.9732	2696.79	-46.16
C_2H_5OH	516.2	63.0	167.0	0.635	18.9119	3803.98	-
41.68							
C_3H_6O	508.1	46.4	209.0	0.309	16.6513	2940.46	-35.93
C_6H_5F	560.1	44.9	271.0	0.245	16.5487	3181.78	-37.59
α,α,α-$C_7H_5F_3$	565.0	33.5	356.0	0.282	16.6110	3357.63	-
38.88							
2,2,2-$C_2H_2F_3OH$	499.3	47.8	205.4	0.635	18.4330	3441.63	-55.30

Table (3. 2b): Physico-chemical properties of pure components

Component	M/g.mol^{-1}	$r^{(59)}$	$q^{(59)}$	$\Delta_l^g H_m^*$ /kJ.mol^{-1}	μ/D
H_2O	18.015	0.920	1.400	40.62	1.8
C_6H_6	78.114	2.400	3.188	30.76	0.0
C_6H_{12}	84.162	3.240	4.046	29.92	0.3
C_6H_{14}	86.178	4.500	3.860	28.83	0.0
C_7H_8	92.141	3.923	2.968	33.15	0.4
C_7H_{16}	100.205	5.1742	4.396	31.67	0.0
CH_4O	32.042	1.4311	1.432	35.22	1.7
$CHCl_3$	119.378	2.870	2.410	29.68	1.1
C_2H_5OH	46.069	2.106	1.972	38.71	1.7
C_3H_6O	58.080	2.574	2.336	29.09	2.9
1,4-C_6H_5F	96.099	3.404	2.572	30.32	1.6
α,α,α-$C_7H_5F_3$	146.110	4.428	3.512	31.04	2.9
2,2,2-$C_2H_2F_3OH$	100.040	2.610	2.504	35.39	1.0

* at normal boiling temperature.

For reading n_D, day-light was used.

Whereas, for DUR-refractometer, a LAUDA RC6-type refrigerated circulation thermostat was used with controlling temperature within 0.2 K.

The binary mixture compositions were prepared gravimetrically with a precision of 2.10^{-4} g using a Mettler balance (model: AE-160).

The reported refractive index values of a given composition x were the mean values of at least three readings for three different mixture samples.

For vapour-liquid equilibria, calibration measurements (n_D, x) at 298.2 K were performed usually 18 mixture points.

Later, the compositions of liquid and vapour phases were read from the fitted (n_D, x) equation of the calibration data.

The measured phase compositions were considered to be accurate within 0.0005.

Densimetry:

The principle of the vibrating-tube densimeter is based on mechanical oscillations of U-shaped glass tube.[60] Oscillations are equivalent to the resonant frequency of the tube and are related to the density of the fluid inside.

This type of densimeters are able to measure densities of liquid and gaseous samples (2 ml) with high precision within very short time (less than 10 min).

The density ρ of the sample depends on the period of oscillation ν of the U-tube according to:

$$\rho = \frac{\nu^2 - B}{A} \qquad (3.1)$$

where the densimeter constants A($pls.cm^3.g^{-1}$), B($pls.cm^3.g^{-1}$) were determined by measuring the period of pure water and air samples and are given by the relations:

$$A = \frac{\nu_{H2O}^2 - \nu_{air}^2}{\rho_{H2O} - \rho_{air}} \qquad (3.2)$$

The constants A and B were stored in the calibration constant block.

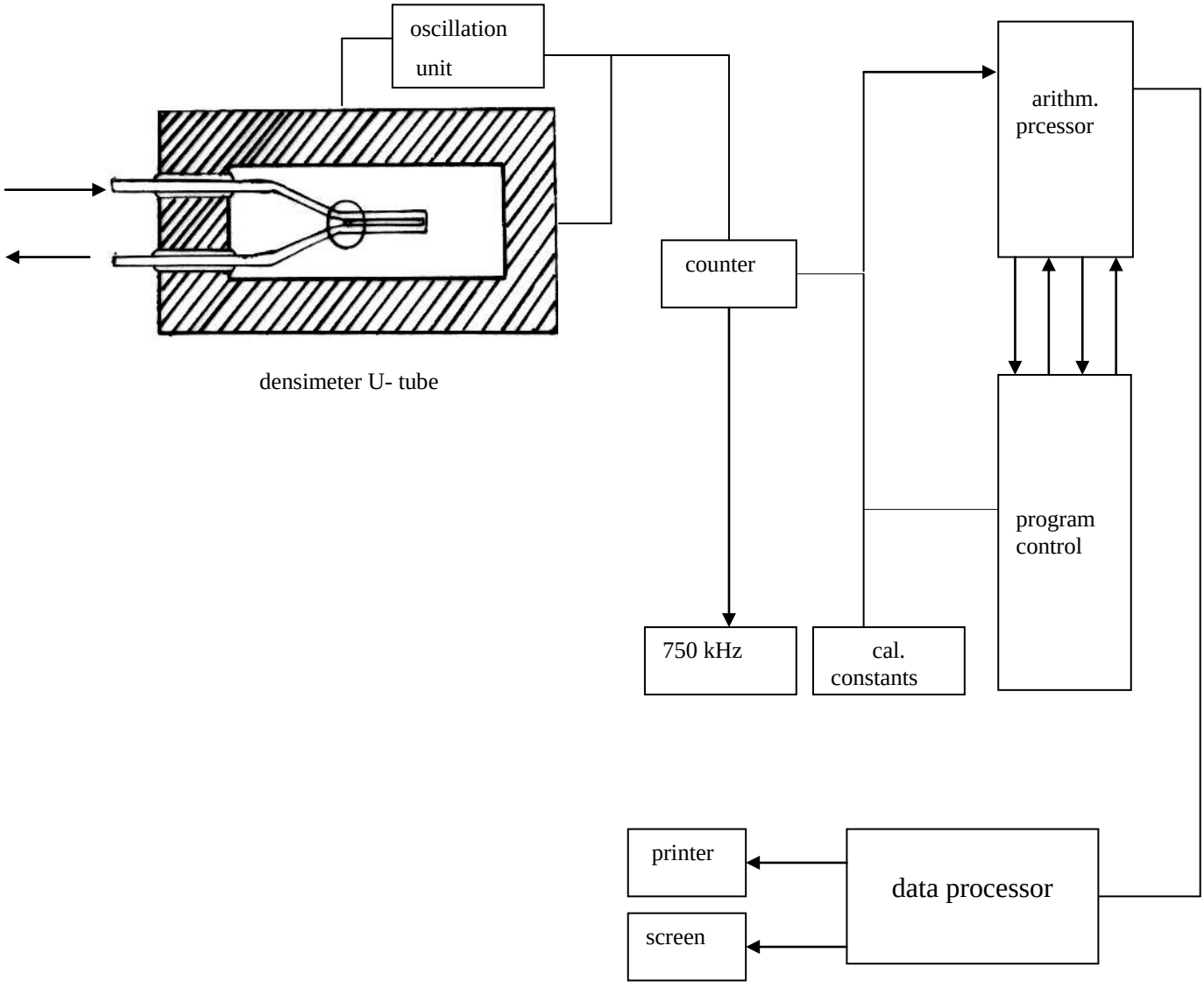


Figure (3. 1): Schematic diagram of a vibrating-tube densimeter[61]

The density of air was evaluated as:

$$\rho_{air} = \left(\frac{0.0012930}{1 + 0.00367.\vartheta} \right) \frac{p}{760} \qquad (3.3)$$

where: θ : temperature, p : atmospheric pressure (torr).

In this work, densities of liquids were measured by an Anton-Paar DMA-45 vibrating-tube densimeter given by schematic diagram (3. 1) at 298.2 K with a precision of 2.10^{-4} g.cm^{-3}.

The temperature of densimeter was controlled to 0.5 K using a Braun immersion thermomix thermostat, model: 1441.

The liquid samples were introduced into the densimeter U- tube with an hypodermic syringe.

The reported density and refractive index values of a given composition x were the mean values of at least three readings of three different samples.

The densimetric techniques were checked by measuring the excess molar volumes (V_m^E, x) of the standard test system: {(1-x) C_6H_{12} + x C_6H_6} at 298 K:

V_m^E(298.2 K, x = 0.500)/ cm^3.mol^{-1} = (0.6420 ± 0.0002); (0.6494 ± 0.0007).[62]

Electronic refractometry and densimetry were used for VLE measurements.

The excess molar volumes V_m^E were determined through equation (2. 52).

Calorimetry:

A chemical-physical energy is developed when two liquids are mixed at a given temperature and pressure.

Three types of calorimeters are employed: adiabatic-batch, conduction, flow and isothermal–continuous calorimeters.

For a real solution, the energy shown is excess enthalpy of mixing H_m^E.

Conduction calorimetry is used for phase-transition and mixing energies.[63- 65]

In this work, an isothermal-conduction calorimeter (C-80 SETARAM, 1982), was used for the measurements of enthalpies of mixing H_m^E.

The principle of conduction calorimetry is based on the thermal-energy equation:

$$E = \lambda \int_{-\infty}^{+\infty} \Delta T dt \qquad (3.4)$$

where λ is the calorimetric constant.

Figures (3. 2) and (3. 3) show the principle of thermal conduction calorimeter and the twin calorimeter cell's block respectively.

To determine the calorimetric constant λ, a known electrical energy E_0 is added to the calorimeter-cell, then:

$$E_0 = \lambda \int_{-\infty}^{+\infty} (\Delta T)_0 \, dt \qquad (3.5)$$

ΔT corresponds to the temperature change of the calorimeter cell ($\Delta T \rightarrow 0$, at the end of the run, $t \rightarrow \infty$).

$$S_0 = \int_{-\infty}^{+\infty} (\Delta T)_0 dt \, , \qquad (3.6)$$

where S_0 is area of calibration thermogram.

Therefore, a known area S_0 , obtained by integration, corresponds to the energy E_0. The calorimetric constant λ is:

$$\lambda = E_0 / S_0 \qquad (3.7)$$

The mean value for calorimetric constant λ of (C-80 SETARAM, 1982) was found to be 4.073 10^{-3} J.pls^{-1}.

Figure (3. 4) shows the schematic diagram of a twin-conduction calorimeter.

For a mixture, the enthalpy of mixing $\Delta_{mix} H_m$ corresponds to a thermal energy E that is identical to the area S_1 under the thermogram (ΔT, t):

$$S_1 = \int_{-\infty}^{+\infty} \Delta T dt \qquad (3.8)$$

$$\Delta_{mix} H_m = \left(\frac{E_0}{S_0} \right) S_1 \ , \qquad (3.9)$$

ΔT corresponds to the temperature change of the calorimeter cell due to mixing of liquids, where S_1 is area of the mixing thermogram (figure (3. 5)).

The excess molar enthalpies H_m^E were evaluated through the following equation:

$$H_m^E = \frac{\lambda S}{n} \qquad (3.10)$$

n denotes the total amount of substance.

The mixing cell is divided into two compartments as shown in figure (3. 6).

For a run, known masses of liquids 1 and 2 were accommodate in compartments 1 and 2 of the calorimetric cell. The two liquids were prevented from premature mixing by a film of mercury placed on the top of the mobile disc.

Liquid masses were weighed to 2.10^{-3} g by a Mettler balance model: PE-160.

The thermal equilibrium of the calorimetric bloc was achieved within 3h, so only 2 runs of measurements can be carried out within a day.

The calorimetric experimental techniques were checked by measuring excess molar enthalpies of the standard binary system $\{(1-x)\ C_6H_{12} + x\ C_6H_6\}$ at 298.15K.

Experimental data:

this work: H_m^E(298.2 K, x = 0.500) = 784 J.mol^{-1},

literature: H_m^E(298.2 K, x = 0.500) = 800 J.mol^{-1}.[66- 68]

The agreement between the two values was ≈ 2.0 %.

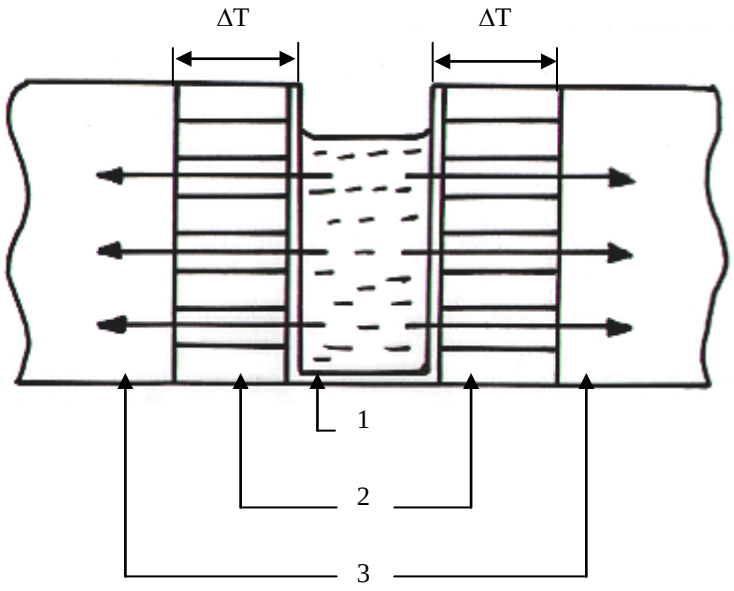
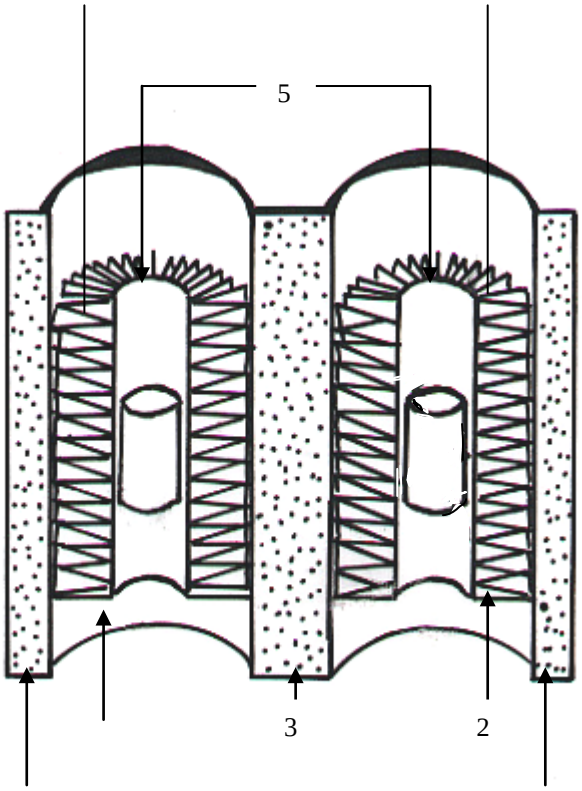


Figure (3. 2): Principle of thermal conduction calorimeter

1) sample cell, 2) heat conductor, 3) heat sink



1

4

Figure (3. 3): Twin cell conduction calorimeter block
1) Rrference cell; 2) sample cell: 3) thermopile
4) thermostated calorimetric block;
5) heat fux transducers

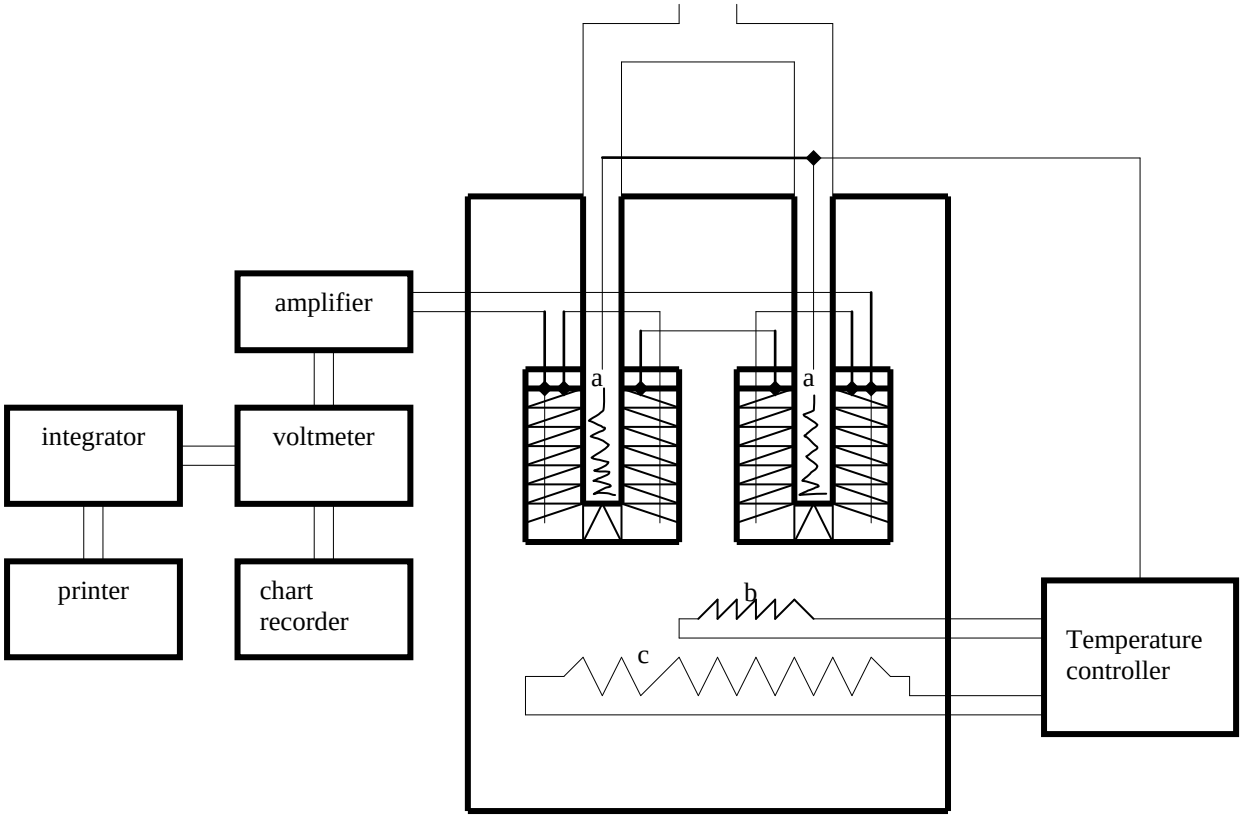
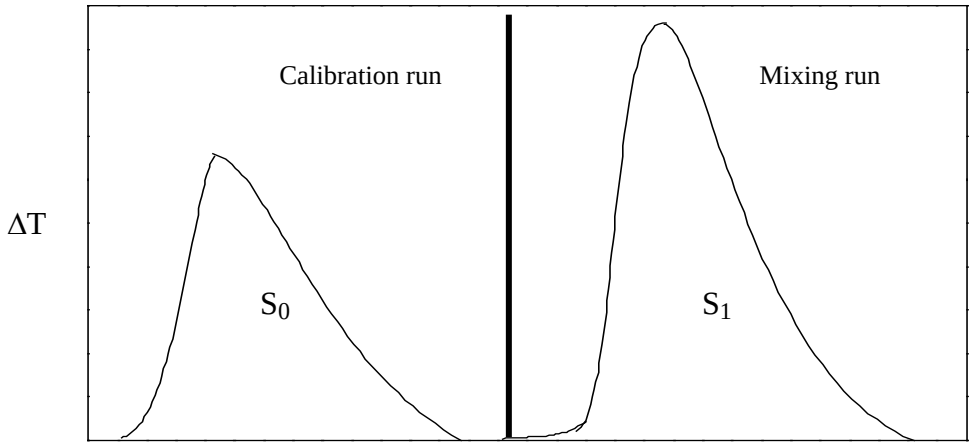


Figure (3. 4) : Block diagram of twin conduction calorimeter:[63]
a : calibration heater, b : Pt-thermometer, c : control heater



t t

Figure (3. 5): (ΔT, t) thermogram of a twin-conduction calorimeter

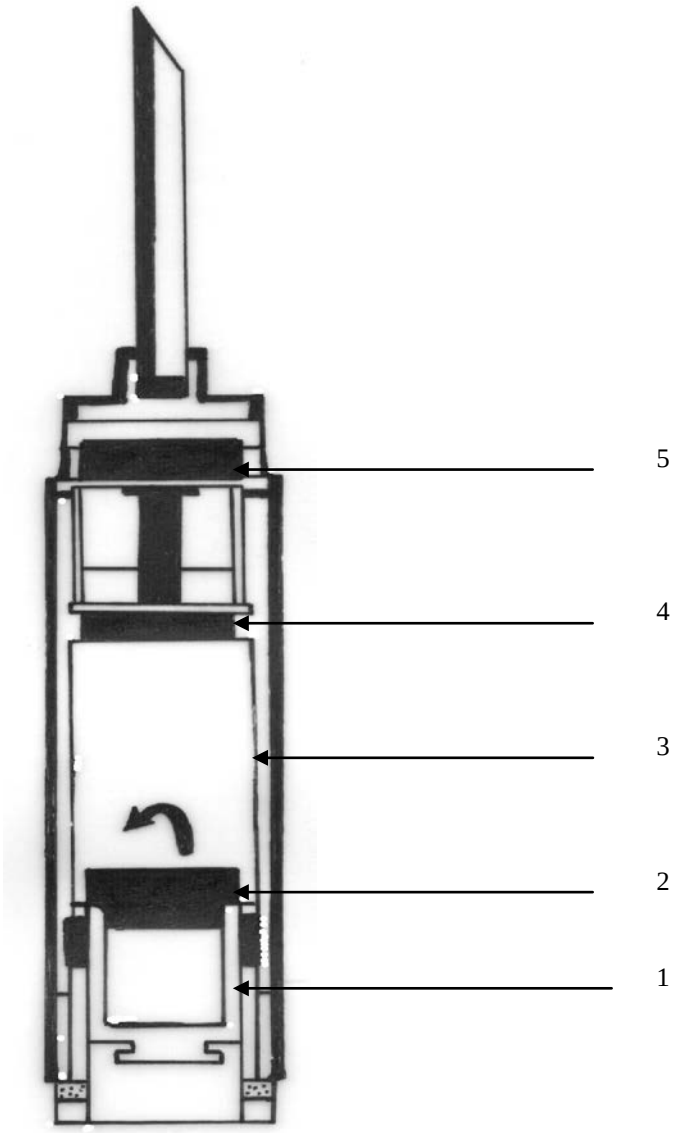


Figure (3. 6) : Mixing cell with mobile disc

1) lower compartment; 2) metallic disc;
3) upper compartment; 4) gasket in teflon;
5) obturator

Experimental Methods of Vapour-Liquid Equilibria:

The state of a two-phase, two-component system can be characterised by the determination of two independent variables (F=2). In our case, the experimental variables of interest are: pressure p, temperatureT, liquid-phase composition x and vapour-phase composition y.

For vapour liquid equilibria studies, dynamic and static methods are commonly used.

The dynamic method is used chiefly at low and moderate pressures and when it is proposed to determine the composition of both liquid and vapour phases. It is usually successful when the relative volatility of the mixture is not high.

In this method, a mixture is boiled to produce a flow of liquid and vapour in intimate contact with the thermometer. The vapour is totally condensed and the condensate is returned to the re-circulating still via a hold up trap with sampling neck.

The still is operated until a phase equilibrium is reached at which the pressure and the temperature are constant. In this state of equilibrium, the liquid and vapour compositions are those of equilibrium.

A schematic diagram of dynamic method ebulliometer is shown in figure (3. 7).

The static method is appropriate when one component is less volatile than the other, where the relative volatilities become high and the dynamic method is of little use.

This method has been extensively used for vapour pressures at temperatures from 300 K to 800 K and pressures up to the critical and requires highly degassed liquids, to insure total absence of air that would contribute in the pressure of the system.

The sample can be visually observed and allows for a direct determination of the critical point.

A schematic diagram of static method ebulliometer is shown in figure (3. 8).

In the present work, the dynamic method was used for our vapour liquid equilibria studies. The ebulliometer used was a refined version of the successful design of

Eckert-Gmehling which enables the sampling of the two-coexisting phases[69] and is shown in figure (3. 9).

Our ebulliometer was built by SOMIVER Company-Thenia Boumerdes. Its glass work was done with great expertise.

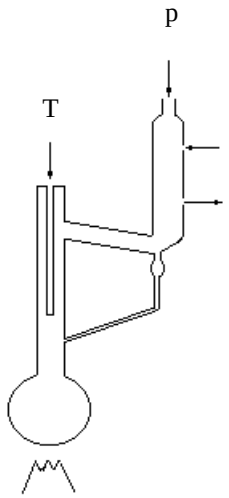


Figure (3. 7): Scheme of dynamic method ebulliometry

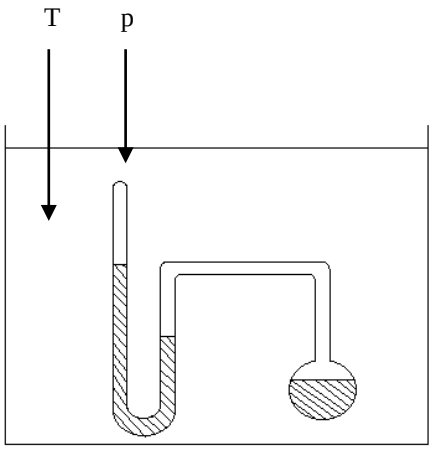


Figure (3. 8): Scheme of static method ebulliometry

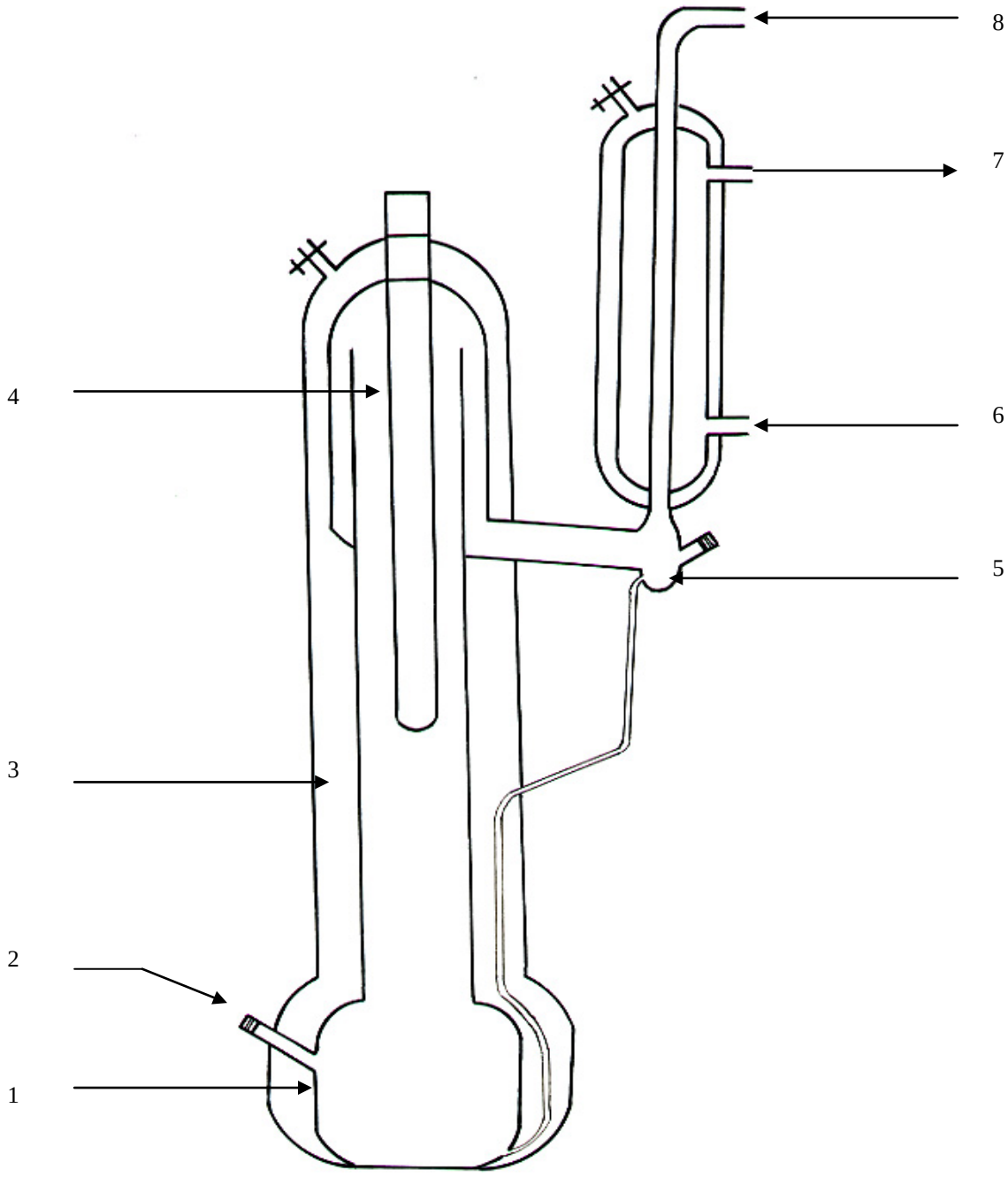

8
7
4
6
5
3
2
1

Figure 8: Eckert-Gmehling Ebulliometer

1) boiler,	2) liquid feeding and sampling,
3) vacuum jacket,	4) thermometer well,
5) condensate receiver,	6) Refrigerant Inlet
7) Refrigerant Outlet	8) connection to pressure

During a run, the volume of a mixture in the re-circulating still was kept less than two thirds of its total volume (about 285 cm^3).

The condensate returned to the recirculating still via a capillary tube (ϕ = 1.5 mm).

For isobaric VLE measurements, when the phase equilibrium was obtained , equilibrium temperature was noted and samples of liquid and vapour phases were taken out for composition analysis .

Before each use, the ebulliometer was cleaned thoroughly with acetone dried of 6 h under vacuum using Pfeiffer-Balzers rotary vacuum pump, model: UNO 004B, with ultimate pressure less than 0.5 mbar.

In this ebulliometer, the flow volume of condensate was about 2 cm^3 and good steady state was established within 20 min.[70]

Heating of the ebulliometer was achieved by a hot plate (IKA-Labour Technik, model: RH) equipped with magnetic stirrer.

The vapour phase was cooled to a temperature of 267 K by a LAUDA refrigerated circulation cryostat (model: RC6) with water-ethylene glycol mixture as refrigerant with controlling temperature within 0.2 K.

Equilibrium temperatures were measured using a digital thermistor-thermometer (Cole-Parmer Instrument, model: 8502-16, thermistor: YSI-400 with temperature range is from 273 to 373 K having a precision 0.25 K) and a precision mercury thermometer (range : 273 $\rightarrow$ 373 K) with an accuracy of 0.05 K.

The atmospheric pressure was determined by a mercury barometer (Prolabo Fortin n° 02025008) to 20 Pa. The laboratory pressure readings agreed well with the values obtained from the National Weather Centre (Algiers).

The liquid and vapour mixture samples were stored in a refrigerator to minimize changes in compositions.

A great care was taken through out the run and the measurement to insure safety and a real equilibrium state.

The ebulliometric techniques and data calculation and correlation were checked with literature data by measuring four test systems over the entire range of composition: $0.0 \leq x \leq 1.0$ at atmospheric pressure:

$\{(1-x)H_2O+xC_2H_5OH\}$, $\{(1-x)CHCl_3+ xC_3H_6O\}$, $\{(1-x)C_6H_{12}+ xC_6H_6\}$ and $\{(1-x)C_7H_8+xCH_4O\}$.

In this work, the VLE measurements of nine fluoro-hydrocarbon binary mixtures were carried out. They were:

$\{(1-x)C_6H_5F+xC_6H_{14}\}$, $\{(1-x)C_6H_5F+xC_7H_{16}\}$, $\{(1-x)C_2H_2F_3OH+xCHCL_3\}$,

$\{(1-x)C_2H_2F_3OH+xC_6H_6\}$, $\{(1-x)C_2H_2F_3OH+xC_7H_8\}$, $\{(1-x)C_2H_2F_3OH+xC_7H_5F_3\}$,

$\{(1-x)C_7H_5F_3+xCHCL_3\}$, $\{(1-x)C_7H_5F_3+xC_2H_5OH\}$, $\{(1-x)\ C_7H_5F_3+xC_6H_6\}$.

3.3 Experimental uncertainty analysis

The errors on the individual measurements affect the final results.

For a thermodynamic function: U = f(x, y, …) the error δU introduced when changes occur in its variables (δx, δy, …) is:

$$\delta U^2 = \left(\frac{\partial U}{\partial x}\right)^2 (\delta x)^2 + \left(\frac{\partial U}{\partial y}\right)^2 (\delta y)^2 + ... \qquad (2.11)$$

Barometric pressure p(T, h, ρ):

The pressure p is calculated from :

$$p = \rho g h \quad , \qquad (2.12)$$

The uncertainty in pressure p from the barometer is:

$$\delta p^2 = \left(\frac{\partial p}{\partial \rho}\right)^2 (\delta \rho)^2 + \left(\frac{\partial p}{\partial h}\right)^2 (\delta h)^2 + \left(\frac{\partial p}{\partial T}\right)^2 (\delta T)^2 \ , \qquad (2.13)$$

where: $\left(\frac{\partial p}{\partial \rho}\right) = gh$, $\left(\frac{\partial p}{\partial h}\right) = \rho g$

Liquid composition x_i:

The liquid composition x_i is calculated from:

$$x_i = (m_i / M_i) / \sum_{i=1}^{n} (m_i / M_i) \qquad (2.14)$$

The uncertainty in liquid composition is:

$$(\delta x_i)^2 = \sum_{i=1}^{n} \left\{ \left(\frac{\partial x_i}{\partial m_i}\right)^2 (\delta m_i)^2 \right\}, \qquad (2.15)$$

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

Excess molar volume V_m^E(T, p, x, ρ):

The excess molar volume is calculated from equation (2.52):

$$V_m^E = \frac{\sum_{i=1}^{n} x_i M_i}{\rho(x)} - \sum_{i=1}^{n}\left(\frac{x_i M_i}{\rho_i}\right)$$

The uncertainty in excess molar volume from densimetry is:

$$(\delta V_m^E)^2 = \left(\frac{\partial V_m^E}{\partial \rho}\right)^2 (\delta\rho)^2 + \sum_{i=1}^{n}\left\{\left(\frac{\partial V_m^E}{\partial \rho_i}\right)^2 (\delta\rho_i)^2\right\} + \sum_{i=1}^{n}\left\{\left(\frac{\partial V_m^E}{\partial x_i}\right)^2 (\delta x_i)^2\right\}, \qquad (2.16)$$

where: $\left(\partial V_m^E / \partial \rho(x)\right) = -\frac{\sum_{i=1}^{n} x_i M_i}{\rho^2(x)}$, $\left(\partial V_m^E / \partial \rho_i\right) = \frac{x_i M_i}{\rho_i^2}$, $\left(\partial V_m^E / \partial x_i\right) = M_i / \left(\rho - \frac{M_i}{\rho_i}\right)$

Activity coefficient $\gamma_i(T, p, x, y)$:

The activity coefficient is calculated from:

$$\ln \gamma_i = \ln\left(\frac{y_i p}{x_i p_i^*}\right) + \frac{\left(B_{ii} - V_i^*\right)\left(p - p_i^*\right)}{RT} \qquad (2.17)$$

The uncertainty in activity coefficient from VLE is:

$$(\delta \ln \gamma_i)^2 = \left(\frac{\partial \ln \gamma_i}{\partial p}\right)^2 (\delta p)^2 + \sum_{i=1}^{n}\left\{\left(\frac{\partial \ln \gamma_i}{\partial p_i^*}\right)^2 (\delta p_i^*)^2\right\} + \sum_{i=1}^{n}\left\{\left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)^2 (\delta x_i)^2\right\} +$$

$$\sum_{i=1}^{n}\left\{\left(\frac{\partial \ln \gamma_i}{\partial y_i}\right)^2 (\delta y_i)^2\right\} + \left(\frac{\partial \ln \gamma_i}{\partial T}\right)^2 (\delta T)^2 + \sum_{i=1}^{n}\left\{\left(\frac{\partial \ln \gamma_i}{\partial (B_{ii} - V_i^*)}\right)^2 (\delta(B_{ii} - V_i^*))^2\right\}, \qquad (2.18)$$

where:

$\left(\partial \ln \gamma_i / \partial p\right) = 1/p$, $\left(\partial \ln \gamma_i / \partial p_i^*\right) = -1/p_i^*$, $\left(\partial \ln \gamma_i / \partial x_i\right) = -1/x_i$

$\left(\partial \ln \gamma_i / \partial T\right) = \left(B_{ii} - V_i^*\right)\left(p - p_i^*\right)/RT^2$, $\left(\partial \ln \gamma_i / \partial (B_{ii} - V_i^*)\right) = \left(p - p_i^*\right)/RT$.

Excess Gibbs function G_m^E (T, p, x, y) from VLE

The excess Gibbs function is calculated from equation (2.59):

$$G_m^E = RT\sum_{i=1}^{n} x_i \ln \gamma_i$$

The uncertainty in excess Gibbs function from VLE is:

$$(\delta G_m^E)^2 = RT\left[\sum_{i=1}^{n}\left\{\left(\frac{\partial G_m^E}{\partial x_i}\right)^2(\delta x_i)^2\right\} + \sum_{i=1}^{n}\left\{\left(\frac{\partial G_m^E}{\partial \ln\gamma_i}\right)^2(\delta \ln\gamma_i)^2\right\} + \left(\frac{\partial G_m^E}{\partial T}\right)^2(\delta T)^2\right], \quad (2.19)$$

where: $(\partial G_m^E / \partial x_i) = \sum_{\substack{i=1 \\ i\neq j}}^{n} \ln\gamma_i - \ln\gamma_j$, $(\partial G_m^E / \partial \ln\gamma_i) = x_i/\gamma_i$, $(\partial G_m^E / \partial T) = R\sum_{i=1}^{n}(x_i \ln\gamma_i)$.

$$(\delta G_m^E / G_m^E)^2 = \left\{\sum_{\substack{i=1 \\ i\neq j}}^{n}(\ln\gamma_i - \ln\gamma_j)/\sum_{i=1}^{n}(x_i \ln\gamma_i)\right\}^2 (\delta x_i)^2 +$$

$$\left\{\sum_{\substack{i=1 \\ i\neq j}}^{n} x_i/\gamma_i \sum_{i=1}^{n}(x_i \ln\gamma_i)\right\}^2 (\delta \ln\gamma_i)^2 + \left(\frac{1}{T}\right)^2(\delta T)^2$$

Excess molar enthalpy $H_m^E(T, p, x)$:

The excess enthalpy is calculated from equation :

$$H_m^E = \frac{\lambda S}{n} \quad (2.20)$$

The uncertainty in excess enthalpy from calorimetry is:

$$(\delta H_m^E)^2 = \left\{\left(\frac{\partial H_m^E}{\partial \lambda}\right)^2(\delta\lambda)^2 + \left(\frac{\partial H_m^E}{\partial S}\right)^2(\delta S)^2 + \left(\frac{\partial H_m^E}{\partial n}\right)^2(\delta n)^2\right\} \quad , \quad (2.21)$$

where:

$$(\partial H_m^E / \partial\lambda) = S/n \quad , \quad (\partial H_m^E / \partial S) = \lambda/n \quad , \quad (\partial H_m^E / \partial n) = -\lambda S/n^2 .$$

For binary mixtures:

$\delta m_1 = \delta m_2 = \delta m$, $\delta x = \delta x_1 = \delta x_2$,

$\delta m = 0.002$ g , $\delta x = \delta y = 2\ 10^{-4}$,

$\delta\rho_1^* = \delta\rho_2^* = \delta\rho$, $\delta p_1^* = \delta p_2^* = \delta p$,

$\delta\rho = 2.10^{-4}$ g.cm^{-3} , $\delta p = 0.05$ torr ,

$\delta(B_{11} - V_1^*) = \delta(B_{22} - V_2^*) = \delta(B - V_m^*)$, $\delta T = 0.05$ K ,

$\delta(B - V_m^*) = 50$ cm^{-3} mol^{-1}.•

• Williamson, A.G., in Le Neindre, B., Vodar, B. (eds.), 1975.

Chapter 4. Experimental Results

Reductions and correlations of experimental data :

We refer to chapter 3 for the calculation of each appropriate thermodynamic property presented in this thesis.

The investigated systems will be referred in the next sections by numbering them as follows :

For VLE : $(T, x, y)_p$, n_D^E (298 K, x) and H_m^E (T, x = 0.500):

1. {(1-x)C_6H_5F+ xC_6H_{14}},
2. {(1-x)C_6H_5F + xC_7H_{16}},
3. {(1-x)$C_2H_2F_3OH$+ x$CHCL_3$},
4. {(1-x)$C_2H_2F_3OH$+xC_6H_6},
5. {(1-x)$C_2H_2F_3OH$+xC_7H_8},
6. {(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$},
7. {(1-x)$C_7H_5F_3$+$CHCL_3$},
8. {(1-x)$C_7H_5F_3$+xC_2H_5OH},
9. {(1-x)$C_7H_5F_3$+xC_6H_6}.

For V_m^E (298 K, x) :

10. {(1-x)2-C_7H_7F+xC_7H_8},
11. {(1-x)C_7H_7F+xCH_3OH},
12. {(1-x)1,4-$C_6H_4F_2$+xC_7H_8},
13. {(1-x)1,4-$C_6H_4F_2$+xCH_3OH},
14. {(1-x)C_2H_5I+xC_7H_8},
15. {(1-x)C_2H_5I+xCH_3OH}.

Results of Vapour-Liquid Equilibria:

The physico-chemical properties of pure components were mainly from the Dortmunder Data Bank.[30]

The experimental VLE data, calculations and correlation of the studied binary mixtures n; $1 \leq n \leq 9$, together with their consistency tests are given in details in appendix A in tables (A, n, 1) to (A, n, 12), and graphs (A, n).

In this chapter and for convenience, only the summaries of the thermodynamic properties are reported in tables (4, n, 12)and the energy interaction parameters of the

two used models are denoted by $\Delta\lambda_{ij}$. In addition, we report experimental phase diagrams for nine mixtures in figures (4. 1) to (4. 3).

The experimental excess molar volumes $(V_m^E, x)_T$ are reported in figure (4. 4).

The reported tables contain:

- experimental results: (n_D, x, y), $(T, x, y, \gamma_i)_p$
- smoothing (n_D^E, x), (G_m^E, x), (x, α_{12}), (T, x, ϕ_1, ϕ_2)
- data reduction and correlation $(\Delta\gamma_i\%, x)$, $(\Delta p\%, x)$, $(\Delta y, x)$.

The reported figures contain:

- phase diagrams $(T, x, y)_p$, $(y, x)_p$
- consistency test $[\ln(\gamma_1/\gamma_2), x]$
- (γ_i, x), (G_m^E, x), (α_{12}, x), (n_D^E, x), $(\Delta p\%, x)$, $(\Delta y, x)$.

All experimental VLE were found to be thermodynamically consistent as (D-J) < 20 with: $\left|\frac{1}{N}\left(\frac{\Delta\gamma_i}{\gamma_i}\right)\right| x100 < 5\%$.

To include the highly dilute regions of the mixtures, values of γ_i^∞ and α_{12}^∞ were estimated from experimental $(\gamma_i, x)_p$ and $(\alpha_{12}, x)_p$ data at boiling temperatures of pure liquids. Correlation of γ_i^∞ using the two models were in good accordance. It may be concluded that the two models describe the experimental data very well.

For VLE mixtures, assuming negligible temperature effect on the model interaction parameters $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$, an appropriate estimation of: H_m^E, S_m^E and $C_{p,m}^E$ were correlated for the azeotrope (T_{az}, x_{az}) and at mid-compositions; x = 0.500.

We note that $\{(1-x)C_7H_5F_3 + x\ C_6H_6\}$mixture was studied before[9].

The uncertainty in activity coefficient $\ln\gamma_1$ was 0.03 and in excess molar Gibbs function G_m^E was $\left(\delta G_m^E / G_m^E\right) = 0.02$.

The uncertainty calculation is given in appendix B.

Results of Excess Molar Properties X_m^E:

The experimental excess molar properties X_m^E of the studied mixtures were well fitted to the equation (2.80):

$$X_m^E = x(1-x)\sum_{i=0}^{n} A_i(1-2x)^i ,$$

where : $X_m^E = n_D^E$, $V_m^E/cm^3.mol^{-1}$ and $G_m^E/J.mol^{-1}$,

with the corresponding standard deviations in the range:

$1.10^{-4} < \sigma n_D^E < 5.10^{-4}$,

$2.10^{-4} < \sigma V_m^E/cm^3.mol^{-1} < 5.10^{-4}$,

$5 < \sigma G_m^E/J.mol^{-1} < 90$.

Excess refractive indices (n_D^E, x) of the binary mixtures were evaluated using equation (2.56). The experimental results are given in tables (4, 10) to (4, 17) and are plotted together with their smoothing equations in the figure (4, 4).

The uncertainty on H_m^E was 0.04.[71]

With reference to error analysis, the mean uncertainties in excess molar volume V_m^E was $(\delta V_m^E / V_m^E) = 0.03$.

Table (4.1.12): Summary of physico-chemical properties of {(1-x)C_6H_5F + xC_6H_{14}} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	Exp.	-	-	2.28	1.58	2.01
exp.	341.6	0.9563	WILSON	-126.26	367.20	2.61	1.15	1.91
cal.	-	0.8793	UNIQUAC	275.05	-145.89	2.61	1.95	2.34

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
6.93	WILSON	0.259	0.016
	UNIQUAC	0.261	0.001

Correlated X_m^E(T, x):

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.9563	WILSON	82	77	-0.01	0.01
T_{az} = 341.6 K	UNIQUAC	82	246	0.48	0.39
x = 0.500	WILSON	412	239	-0.50	1.17
T = 347.1 K	UNIQUAC	421	11	-1.18	2.14

Experimental X_m^E(T, x = 0.500):

n_D^E (298.2 K)	V_m^E(298.2 K) (cm^3.mol^{-1})	H_m^E(313.2 K) (J.mol^{-1})	G_m^E(347.1 K) (J.mol^{-1})
-0.0067	-	832	440

G_m^E(cal.)/J.mol-1 = [1762.5.x(1-x) ± 23.60]

n_D^E = [-0.0268 x(1 – x) ± 0.0001]

Literature X_m^E(T=298.15 K, x=0.500):[70]

V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})
0.2462 ± 0.003	868 ± 1.2

Table (4.2.12): Summary of physico-chemical properties of {(1-x)C_6H_5F + xC_7H_{16}} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	exp.	-	-	1.35	2.23	1.59
Exp.	357.7	0.1115	WILSON	212.30	75.71	1.43	2.17	1.60
cal.	-	0.1979	UNIQUAC	16.18	50.24	1.43	2.34	1.59

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
5.86	WILSON	0.328	0.003
	UNIQUAC	0.332	0.003

Correlated X_m^E(T, x):

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.1115	WILSON	208	221	0.04	0.10
T_{az} = 357.7 K	UNIQUAC	220	206	-0.04	0.01
x = 0.500	WILSON	403	409	0.02	0.32
T = 361.7 K	UNIQUAC	432	417	-0.04	0.14

Experimental X_m^E(T, x = 0.500):

n_D^E (298.2 K)	V_m^E(298.2 K) (cm^3.mol^{-1})	H_m^E(313.2 K) (J.mol^{-1})	G_m^E(361.7 K) (J.mol^{-1})
-0.0108	-	955	390

G_m^E(cal.)/J.mol^{-1} = [x(1 - x){1562.13 + 268.62(1 - 2x) + 1091.77(1 - 2x)^2} ± 30.13]

n_D^E = [x (1 - x){-0.0432 + 0.0006(1 - 2x)} ± 0.0001]

Literature X_m^E(T=298.15 K, x=0.500): [70]

V_m^E (cm^3.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
0.4314 ± 0.002)	-1.18 ± 0.01

Table (4.3.12): Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$+ x$CHCL_3$} at 102 kPa

Method	azeotrope			Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}		exp.	-	-	7.40	5.02	10.13
exp.	327.5	0.6965		WILSON	218.49	717.07	7.45	4.90	10.27
cal.	-	0.6447		UNIQUAC	252.89	37.47	6.83	5.06	9.94

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
8.98	WILSON	0.661	0.002
	UNIQUAC	0.541	0.004

Correlated $X_m^E(T, x)$:

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x_{az} = 0.6965	WILSON	1128	624	-1.54	2.51
T_{az} = 327.5 K	UNIQUAC	1121	1187	0.20	0.42
x = 0.500	WILSON	1235	634	-1.81	2.43
T = 332.2 K	UNIQUAC	1241	1015	-0.68	1.31

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.4998	313.2 K, 0.499	332.2 K, 0.500
	n_D^E	V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	G_m^E ($J.mol^{-1}$)
	-0.0061	1.0032	2843	1272

G_m^E (cal.)/$J.mol^{-1}$ = [x(1 - x){5088.8 - 320.70(1 - 2x) + 2061.20(1 - 2x)²} ± 16.30]

n_D^E = [x(1 - x){-0.0245 - 0.0013(1 - 2x)} ± 0.0001]

Table (4.4.12): Summary of physico-chemical properties of {(1-x) $C_2H_2F_3OH$+xC_6H_6} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	X_{az}	exp.	-	-	4.76	6.46	8.84
exp.	337.8	0.4681	WILSON	279.07	619.87	4.69	5.97	9.15
cal.	-	0.4549	UNIQUAC	183.56	107.38	4.81	6.42	8.62

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
6.77	WILSON	0.513	0.002
	UNIQUAC	0.842	0.002

Correlated $X_m^E(T, x)$:

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x_{az} = 0.4681	WILSON	1269	729	-1.60	2.52
T_{az} = 337.8 K	UNIQUAC	1301	1109	-0.60	1.02
x = 0.500	WILSON	1279	742	-1.60	2.57
T = 338.1 K	UNIQUAC	1313	1146	-0.49	0.97

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5108	313.2 K, 0.513	338.1 K, 0.500
	n_D^E	V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	G_m^E ($J.mol^{-1}$)
	0.0011	1.0561	1909	1245

G_m^E(cal.)/$J.mol^{-1}$ = [4981.21 x(1 - x) ± 22.89]

n_D^E = [0.0044 x(1 - x) ± 0.0001]

Literature X_m^E(T = 298.15 K, x = 0.500):

V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
1.1392 ± 0.009[71] 1.1005 ± 0.006[72]	1569 ± 0.002[71] (298.15 K) 1748 ± 0.001[72] (318.15K)	13.06 ± 0.1[71]

Table (4.5.12):Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$ + xC_7H_8} at 102 kPa

Method	azeotrope			Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}		exp.	-	-	2.97	9.30	7.35
exp.	345.4	0.2003		WILSON	362.38	655.52	2.56	8.19	9.43
cal.	-	0.1811		UNIQUAC	204.65	93.63	2.81	10.80	8.83

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
16.25	WILSON	0.723	0.003
	UNIQUAC	1.128	0.004

Correlated X_m^E(T, x):

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x_{az} = 0.2003	WILSON	964	529	-1.20	1.74
T_{az} = 345.4 K	UNIQUAC	966	556	-1.19	0.75
x = 0.500	WILSON	1424	841	-1.61	2.88
T = 360.8 K	UNIQUAC	1497	1312	-0.51	0.92

Experimental X_m^E(T, x):

T, x	298.2 K, 0.500	298.2 K, 0.5024	313.2 K, 0.499	360.8 K, 0.500
	n_D^E	V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	G_m^E ($J.mol^{-1}$)
	0.0137	1.0249	1656	1353

G_m^E(calc.)/$J.mol^{-1}$ = [x (1 - x){5410.19 + 873.48 (1 - 2x)} ± 90.15]

n_D^E = [x (1 - x){0.0549 + 0.0005 (1 - 2x) } ± 0.0001]

Table(4.6.12):Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$}at102 kPa

Method	azeotrope			Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}		exp.	-	-	2.98	7.43	5.24
exp.	344.8	0.2186		WILSON	282.90	535.45	2.86	6.35	6.14
cal.	-	0.2284		UNIQUAC	179.18	58.60	3.04	8.17	5.37

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
13.28	WILSON	0.718	0.018
	UNIQUAC	0.871	0.026

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.2186	WILSON	888	582	-0.89	1.71
T_{az} = 344.8 K	UNIQUAC	942	509	-1.26	0.65
x = 0.500	WILSON	1218	881	-0.95	2.36
T = 356.2 K	UNIQUAC	1312	1178	-0.38	0.60

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5054	313.2 K, 0.501	356.2 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	0.0123	-0.2588	1830	1281

G_m^E(cal.)/J.mol^{-1} = [4727.50 x(1 - x) ± 83.19]

n_D^E = [x (1 - x){0.0486 + 0.0055(1 - 2x) – 0.0133(1 – 2x)^2 } ± 0.0004]

Table (4.7.12): Summary of physico-chemical properties of $\{(1-x)C_7H_5F_3 + xCHCL_3\}$ at 102 kPa

Method	azeotrope			Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}		exp.	-	-	6.51	2.03	1.85
exp.	-	-		WILSON	410.19	-126.01	6.39	2.37	2.03
cal.	-	-		UNIQUAC	-116.19	256.74	6.30	1.80	1.55

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
18.33	WILSON	0.615	0.002
	UNIQUAC	0.636	0.002

Correlated $X_m^E(T, x)$:

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x = 0.500	WILSON	518	371	-0.41	1.38
T = 357.6 K	UNIQUAC	539	242	-0.83	1.42

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.4992	313.2 K, 0.503	357.6 K, 0.500
	n_D^E	V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	G_m^E ($J.mol^{-1}$)
	-0.0059	2.2626	1289	527

$$G_m^E(cal.)/J.mol^{-1} = [x(1 - x)\{2108.56 - 42.80(1 - 2x) -252.83(1 - 2x)^2 - 153.66 (1 - 2x)^3 +1988.74(1- 2x)^4\} \pm 5.87]$$

$$n_D^E = [x(1 - x)\{-0.0236 - 0.0005(1 - 2x)\} \pm 0.0001]$$

Table (4.8.12):Summary of physico-chemical properties of {(1-x)$C_7H_5F_3$ + xC_2H_5OH} at 100 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	Exp.	-	-	10.29	4.87	5.55
Exp.	348.6	0.7115	WILSON	667.39	105.14	11.29	5.49	6.04
cal.	-	0.7239	UNIQUAC	-47.57	375.99	11.59	4.41	5.17

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
11.48	WILSON	0.412	0.003
	UNIQUAC	0.419	0.003

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.7115	WILSON	994	610	-1.10	2.46
T_{az} = 348.6 K	UNIQUAC	1078	78	-2.87	1.57
x = 0.500	WILSON	118	853	-0.94	2.96
T = 355.1 K	UNIQUAC	1292	905	-1.09	1.33

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5113	313.2 K, 0.500	355.1 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	0.0068	2.4575	1206	1226

G_m^E(cal.)/J.mol^{-1} = [x(1 - x){4904.51 + 624.56(1 - 2x) + 736.79(1 –2x)^2} ± 29.66]

n_D^E = [x(1 - x){0.0270 + 0.0061(1 - 2x) } ± 0.0003]

Table (4.9.12):Summary of physico-chemical properties of {(1-x)$C_7H_5F_3$ + xC_6H_6} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	Exp.	-	-	2.57	1.53	5.61
Exp.	353.7	0.9013	WILSON	-70.84	772.43	2.69	1.29	4.86
cal.	-	0.8780	UNIQUAC	435.46	-196.54	2.66	1.40	5.35

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
9.18	WILSON	1.129	0.002
	UNIQUAC	1.143	0.002

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az}=0.9013	WILSON	334	186	-0.42	1.00
T_{az} = 353.7 K	UNIQUAC	339	1079	2.09	1.03
x= 0.500	WILSON	474	67	-1.12	1.41
T = 362.3 K	UNIQUAC	479	-319	-2.21	4.77

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5097	313.2 K, 0.499	362.3 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	-0.0110	1.2041	435	425

G_m^E(cal.)/J.mol^{-1} = [x (1 - x){1699.31 + 15.22 (1 - 2x) + 1091.87 (1 - 2x)^2} ± 5.83]

n_D^E = [x(1 - x){-0.0438 - 0.0036(1 - 2x) – 0.0079(1- 2x)^2 } ± 0.0001]

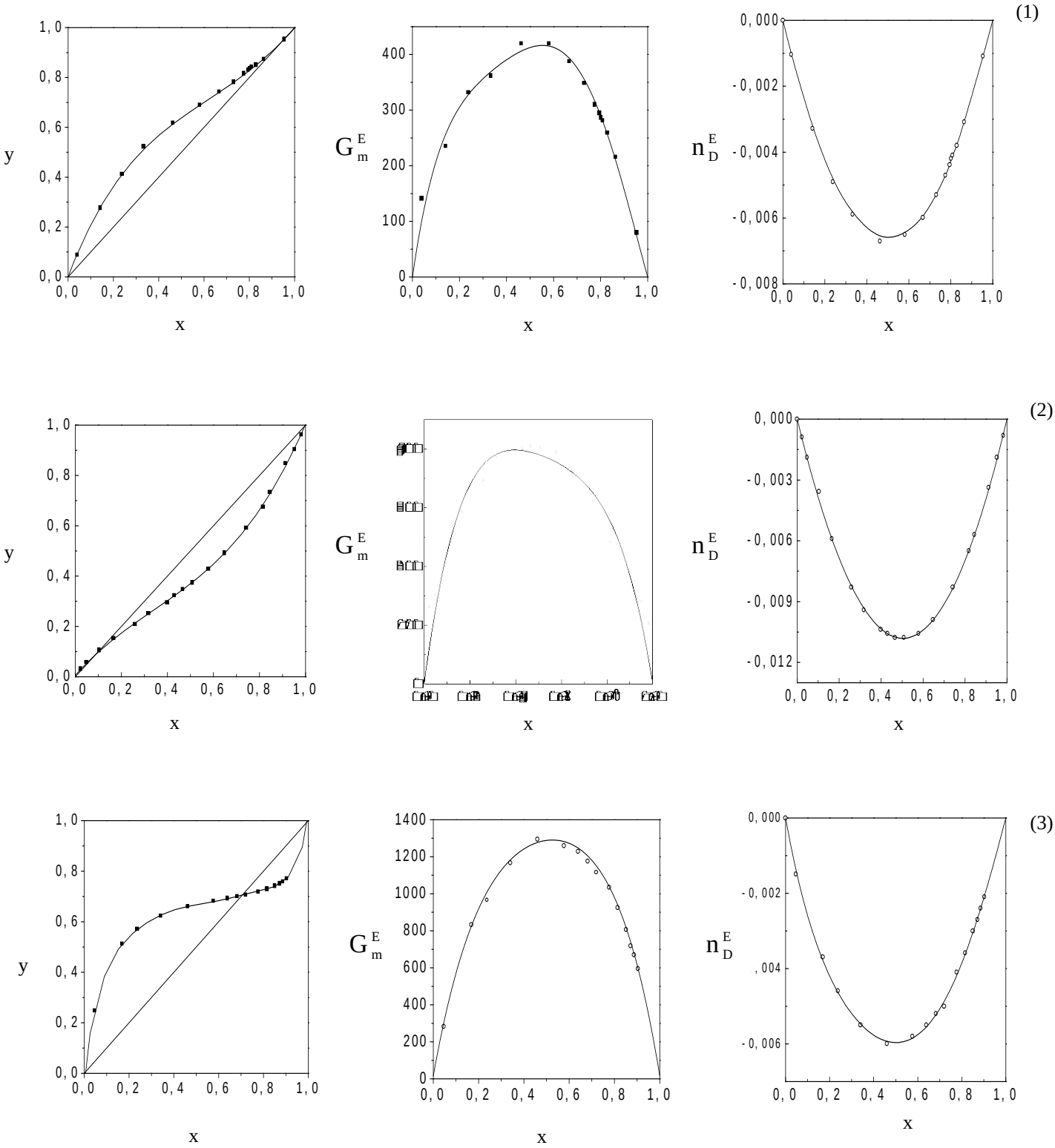


Figure (4. 1): Vapour-Liquid Equilibria at 102 kPa :
(1): {(1-x)C_6H_5F+xC_6C_{14}} ;
(2): {(1-x)C_6H_5F+xC_7H_{16}};
(3): {(1-x)$C_2H_2F_3OH$+x$CHCL_3$}.

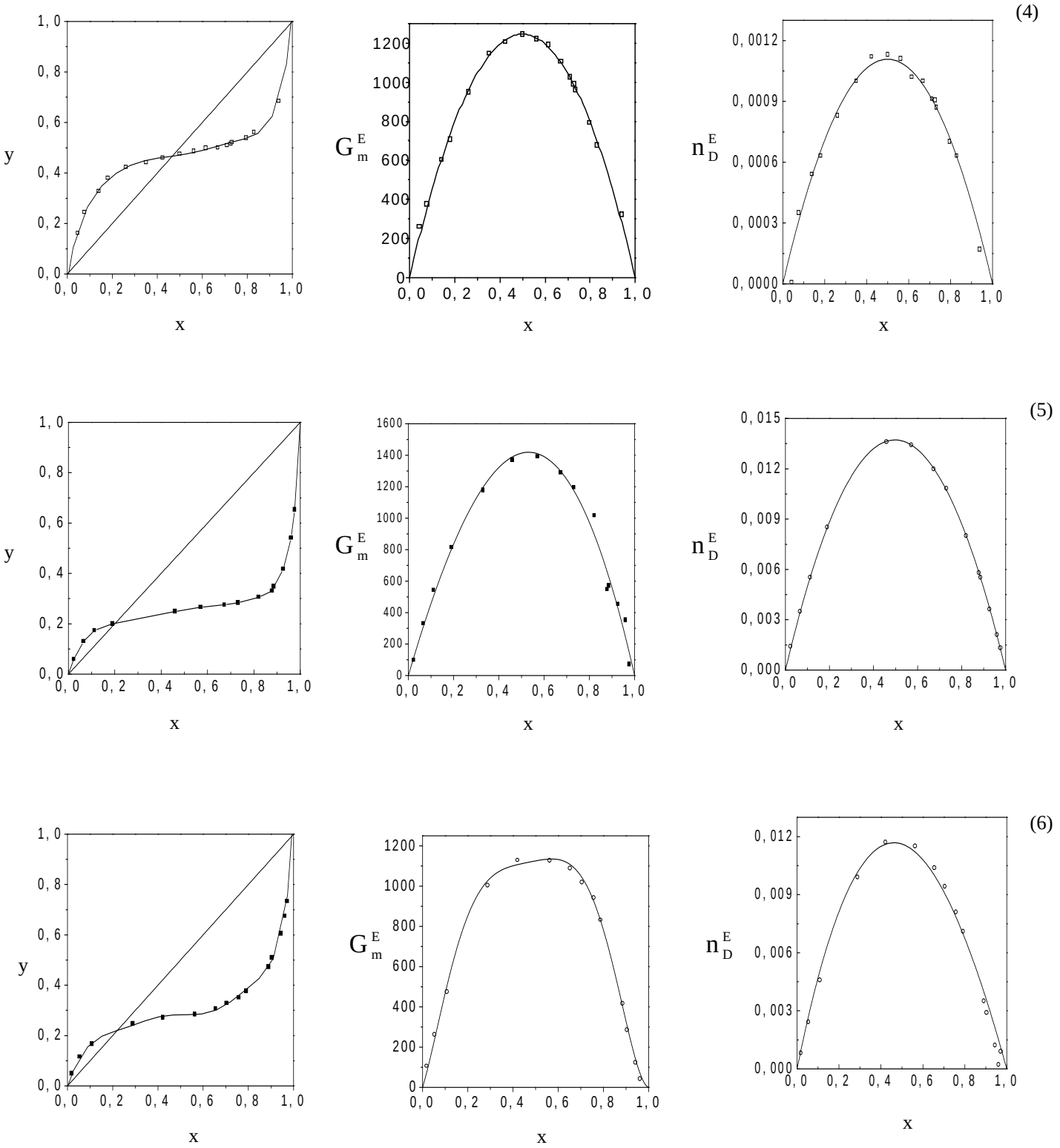


Figure (4. 2): Vapour-Liquid Equilibria at 102 kPa :
(4): {(1-x)$C_2H_2F_3OH$+xC_6H_6} ;
(5): {(1-x)$C_2H_2F_3OH$+xC_7H_8};
(6): {(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$}.

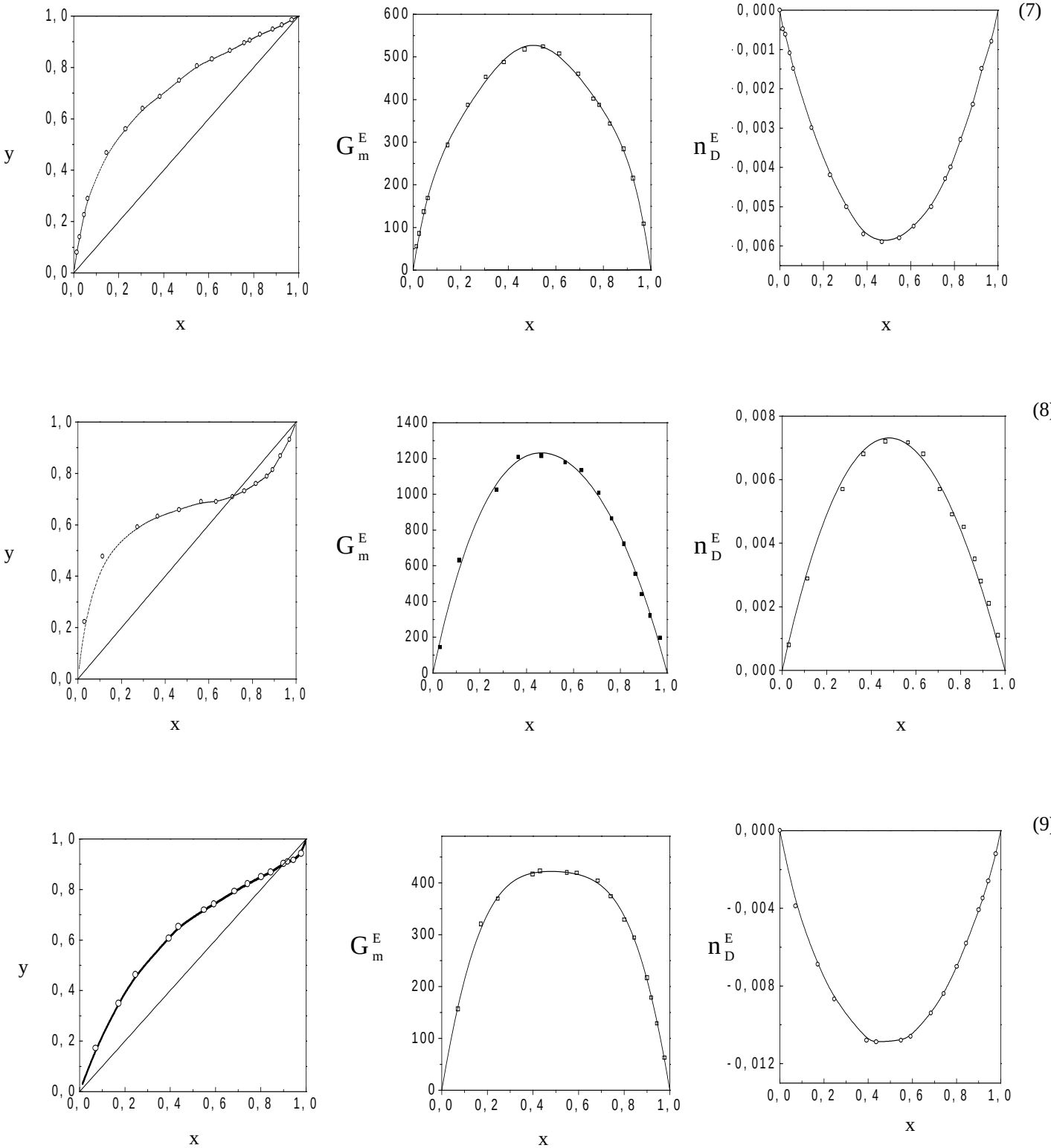


Figure (4. 3): Vapour-Liquid Equilibria at 102 kPa :
(7): {(1-x)$C_7H_5F_3$+x$CHCL_3$} ;
(8): {(1-x)$C_7H_5F_3$+xC_2H_5OH};
(9): {(1-x)$C_7H_5F_3$+xC_6H_6}.

Table (4.10): Excess properties n_D^E and V_m^E : {(1-x)2-C_7H_7F+x C_7H_8} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0547	-0.0007	0.0085
0.1093	-0.0082	0.0160
0.1411	-0.0008	0.0199
0.2114	-0.0083	0.0274
0.2353	-0.0009	0.0296
0.2876	-0.0008	0.0337
0.3839	-0.0008	0.0389
0.5022	-0.0008	0.0411
0.5935	-0.0007	0.0397
0.7041	-0.0006	0.0343
0.6768	-0.0007	0.0360
0.8189	-0.0008	0.0244
0.8948	-0.0004	0.0155
0.9450	-0.0005	0.0085

Table (4.11): Excess properties n_D^E and V_m^E : {(1-x)2-C_7H_7F+x CH_3OH} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0543	0.0117	-0.6057
0.1053	0.0215	-1.1113
0.1536	0.0297	-1.5335
0.2096	0.0378	-1.9542
0.2580	0.0437	-2.2581
0.3115	0.0490	-2.5298
0.3650	0.0529	-2.7339
0.4032	0.0549	-2.8384
0.5050	0.0571	-2.9486
0.6044	0.0546	-2.8203
0.7012	0.0478	-2.4714
0.8031	0.0361	-1.8652
0.9049	0.0196	-1.0151
0.9584	0.0091	-0.4703

Table (4.12): Excess properties n_D^E and V_m^E : {(1-x)1,4-$C_6H_4F_2$+xC_7H_8} at 298.2 K

x	n_D^E *	V_m^E / $cm^3.mol^{-1}$
0.0509	0.0002	0.0468
0.1111	0.0004	0.0956
0.1512	0.0006	0.1229
0.1973	0.0007	0.1532
0.2573	0.0008	0.1845
0.3031	0.0007	0.2039
0.3548	0.0006	0.2211
0.4121	0.0005	0.2335
0.4981	0.0002	0.2417
0.6070	-0.0003	0.2303
0.7102	-0.0006	0.1987
0.8076	-0.0007	0.1503
0.9079	-0.0004	0.0810
0.9653	-0.0002	0.0322

* $n_D^E = (0.0000 \pm 0.0005)$

Table (4.13): Excess properties n_D^E and V_m^E : {(1-x)1,4-$C_6H_4F_2$+xCH_3OH} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0589	0.0033	-0.0380
0.1098	0.0061	-0.0684
0.1584	0.0088	-0.0938
0.2038	0.0118	-0.1145
0.2619	0.0156	-0.1363
0.3018	0.0183	-0.1484
0.4076	0.0255	-0.1699
0.5111	0.0307	-0.1754
0.6274	0.0322	-0.1640
0.7062	0.0297	-0.1456
0.8057	0.0225	-0.1111
0.8631	0.0165	-0.0830
0.9211	0.0094	-0.0511
0.9618	0.0046	-0.0252

Table (4.14): Excess properties n_D^E and V_m^E : $\{(1-x)C_2H_5I+xC_7H_8\}$ at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0666	-0.0010	0.1257
0.1065	-0.0016	0.1928
0.1527	-0.0020	0.2623
0.2508	-0.0028	0.3803
0.1819	-0.0023	0.3015
0.3011	-0.0032	0.4268
0.3966	-0.0034	0.4842
0.4960	-0.0035	0.5061
0.5951	-0.0034	0.4882
0.6908	-0.0029	0.4326
0.7914	-0.0021	0.3349
0.9014	-0.0010	0.1801
0.9397	-0.0006	0.1146

Table (4.15): Excess properties n_D^E and V_m^E : $\{(1-x)C_2H_5I+xCH_3OH\}$ at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0534	0.0046	0.2427
0.1098	0.0089	0.4680
0.1533	0.0118	0.6213
0.2066	0.0148	0.7856
0.2460	0.0168	0.8882
0.2943	0.0188	0.9949
0.3959	0.0217	1.1458
0.5195	0.0226	1.1951
0.6403	0.0209	1.1027
0.6933	0.0193	1.0180
0.8017	0.0144	0.7613
0.8458	0.0118	0.6247
0.8990	0.0082	0.4343
0.9471	0.0045	0.2400

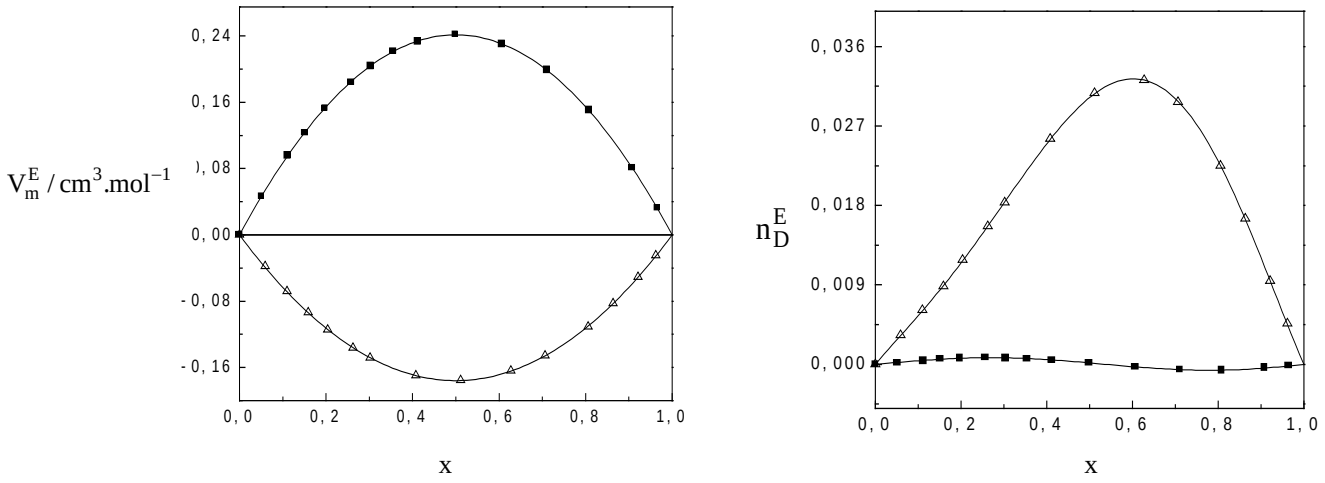
Table (4.17):Smoothing parameters of n_D^E at 298.2 K

A_0	A_1	A_2	A_3	σs	n_D^E (x = 0.500)
(1-x)2-C_7H_8F + xC_7H_8					
-0.0028	-0.0008	-0.0066	--	0.0001	-0.0007
(1-x)2-C_7H_8F + xCH_3OH					
0.2283				0.00002	0.0571
(1-x)1,4-$C_6H_4F_2$ + xC_7H_8					
0.0006	0.0071	-0.0018	--	0.0001	0.0002
(1-x)1,4-$C_6H_4F_2$ + xCH_3OH					
0.1209	-0.0786	-0.0362	0.5152	0.0001	0.0302
(1-x)C_2H_5I + xC_7H_8					
-0.0141	-0.0022	--	--	0.0001	-0.0035
(1-x)C_2H_5I + xCH_3OH					
0.0905				0.0006	0.0226

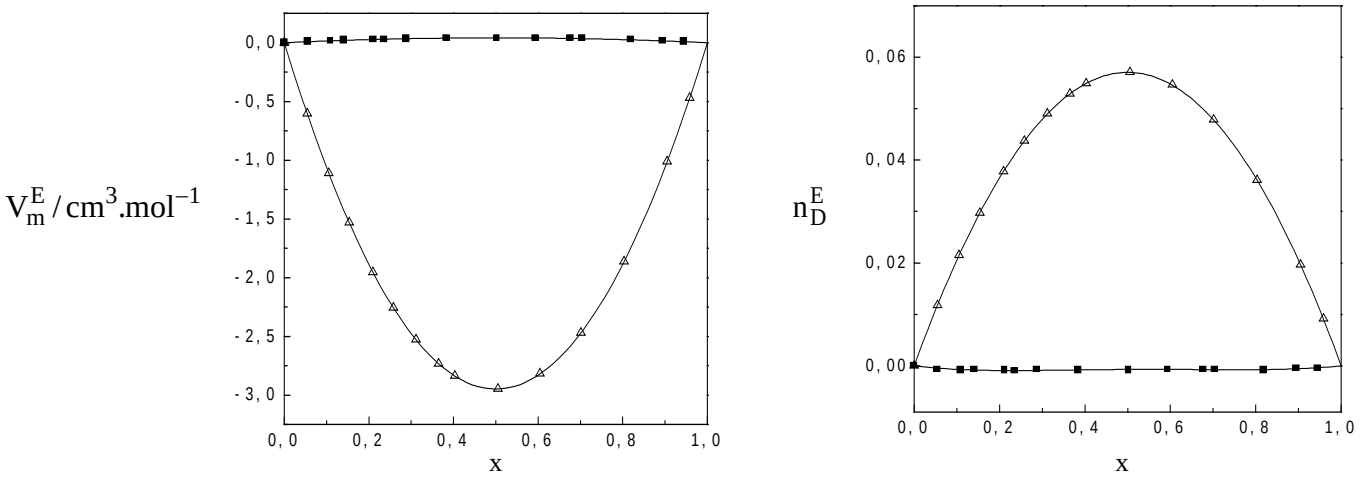
Table (4.16):Smoothing parameters of V_m^E at 298.2 K

A_0	A_1	A_2	σs	V_m^E (x = 0.500) ($cm^3.mol^{-1}$)
(1-x)2-C_7H_8F + xC_7H_8				
0.1646	-0.0014		0.0002	0.0412
(1-x)2-C_7H_8F + xCH_3OH				
-11.7959			0.0002	-2.9490
(1-x)1,4-$C_6H_4F_2$ + xC_7H_8				
0.9654			0.0003	0.2414
(1-x)1,4-$C_6H_4F_2$ + xCH_3OH				
-0.7032			0.0005	-0.1758
(1-x)C_2H_5I + xC_7H_8				
2.0255			0.0003	0.5064
(1-x)C_2H_5I + xCH_3OH				
4.7889	0.0020		0.0003	1.1972

(1)



(2)



(3)

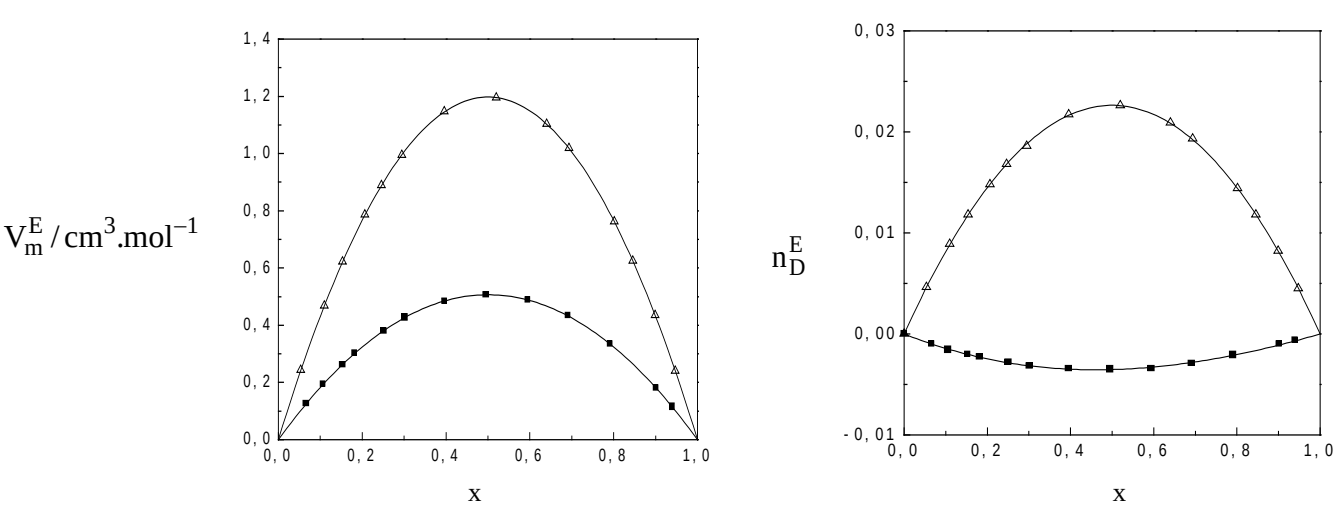


Figure (4. 4) : Excess properties V_m^E and n_D^E at 298.2 K:
(1) : {(1-x)1,4-$C_6H_4F_2$ + xB} ; (2) : {(1-x)2-C_7H_7F + xB} ;
(3) : {(1-x)C_2H_5I + xB} ; B = C_7H_8 (■) or CH_3OH (Δ)

Chapter 5. Discussion

Fluorine is the most electronegative of all elements, and the C—F bond is highly polar and molecules adjacent to fluoro-hydrocarbons must be affected by strong local dipoles, with C—H bond dipole moment is negligibly small in comparison.[23]

Thus, in dealing with mixing energies in systems consisting of fuoro-hydrocarbons and hydrocarbons dipole-dipole interactions and dipole-induced dipole interactions must be considered, with dipole-induced dipole interaction is possible in pure and mixed molecules.[34]

In a mixture of a fluoro-hydrocarbon with an inert solvent species such as benzene and toluene, the F—C bonding causes the fluoro-hydrocarbon to form a distribution of aggregated complexes of pure molecules and that this distribution changes as the mole fraction of the inert species changes.[35]

The highly positive non-ideal behaviour shown for all the VLE mixtures is thought to be attributed to F—C bonding of the fluorinated molecules caused by the low polarizability of florine atom[19] and to lower mixing energies of mixed-molecular interaction in these mixtures.[17] In such systems the forces attracting like pairs of molecules are stronger than forces between unlike pairs of molecules.[39] This is leading to activity coefficients of the mixture components exceeding unity,[23] and to excess Gibbs function: $82 \leq G_m^E / J.mol^{-1} \leq 1497$.[75,76] As consequence, a minimum boiling azeotrope was formed by these binary systems indicating poor proton-accepting abilities of the solvents used. Only $\{(1-x)C_7H_5F_3 + xCHCL_3\}$ mixture was zeotrope. The azeotropic mole fractions were evaluated graphically; $(y, x)_p$ and were in accordance with the estimated value from equation (2.83) within 14%.

The Wilson and UNIQUAC equations were chosen for correlation of activity coefficients data, although other models may be appropriate. Binary interaction parameters A_{ij} were computed, the values were summarised in table (A, n, 12).

For the mixture $\{(1-x)C_7H_5F_3 + xC_6H_6\}$we have clearly observed an azeotrope at (T_{az} = 53.7 K, x_{az} =0.9013), while Fraiha et al. did not mention any presence of azeotrope for the above mixture.[9]

The excess molar enthalpy H_m^E is a macroscopic property which consists of the sum of a positive (endothermic) contribution due to the non-spherical physical interaction and a negative one (exothermic) due to the specific chemical interaction.[32] The origin of the enthalpy of mixing H_m^E is the polarizabilities of the solute and solvent molecules giving the dispersion forces with exothermic effect.[77] For mixtures of molecules differing in size and shape, the H_m^E depends on the total molecular configuration and the microscopic structure of the mixture.

In this work most mixtures show to be moderately endothermic which support the existence of molecular aggregation where beside the small dispersion force contribution due to mutual polarization of the two components, the π—π interactions of the aromatic orbitals and electrostatic interaction of the C—F bond dipoles of the fluorinated hydrocarbons interacting to the π-electron-quadrupole of the aromatic hydrocarbon are of major importance in the azeotrope formation.[33]

For azeotropes, where like molecules are assembled near each other, the mixing energies H_m^E are large and positive: $435 \leq H_m^E/\text{J.mol}^{-1} \leq 2843$, indicating the absence of formation of specific physical or chemical attraction energies between the fluoro-hydrocarbon (solute) and the solvent, probably because of a weak electron-accepting ability of the solute in inert and non-inert solvents.[24]

Mixing with more or less non-polar molecules, such as benzene and cyclohexane result in a corresponding smaller positive H_m^E.

Experimental excess molar enthalpies H_m^E show that the introduction of a group —F into C_6H_6 molecule resulted in an endothermic effect its value increases with increasing inductive effect of the Fluorine atom[36, 37] and that introduction of another halogen atom into the halogenated molecule causes an increasing endothermic effect

in the same sequence as the dipole moment. Still these effects are small in the aromatic fluoro-hydrocarbon mixtures when the number fluorine atoms per molecule is small.[31]

Comparison with experimental H_m^E data, the two used activity coefficients γ_i models are yielding H_m^E values with reasonable accordance. Both analyses lead to the conclusion that, in these mixtures, the energy of the unlike interactions are similar within 5 %.

All excess molar volumes (V_m^E, x) were symmetrical around mid-composition except for the {(1-x)C_7H_7F + xC_7H_8} mixture which exhibits almost an ideal behaviour for all compositions x.

For {(1-x)C_7H_7F + xCH_3OH} and {(1-x)1,4-$C_6H_4F_2$ + xC_7H_8} mixtures, the excess molar volumes were found negative, indicating interactions between unlike molecules,[78] whereas they were positive for the other studied mixtures.

For methanol mixtures the excess molar volumes were very large around:

$-2.95 \leq V_m^E/cm^3.mol^{-1} \leq 1.20$. While for toluene mixtures they were within : $0.04 \leq V_m^E/cm^3.mol^{-1} \leq 0.51$. The large and negative V_m^E values indicate very strong attractive forces and volume compression due to mixing.

Excess refractive indices were large and positive for halogenated mixtures with methanol mixtures: {(1-x)C_7H_7F + xCH_3OH}; {(1-x)1,4-$C_6H_4F_2$ + xCH_3OH}; {(1-x)C_2H_5I + xCH_3OH}, and around zero for halogenated mixtures with toluene mixtures.

Calorimetric measurements reporting interaction energies H_m^E for iodoethane mixtures {(1-x)C_2H_5I + xC_7H_8}and {(1-x)C_2H_5I + xCH_3OH} were :

$+190 \leq H_m^E/J.mol^{-1} \leq +1034$, with H_m^E (295.15 K, x = 0.500): 500 and 50 $J.mol^{-1}$, respectively.[79] Also, excess molar volumes V_m^E of the two mixtures at (293.15 K, x = 0.500) were equal to 0.3129 and 1.1739 $cm^3.mol^{-1}$, respectively.

Both results indicate the existence of moderate repulsive energies among the iodoethane, toluene and methanol molecules in the binary solutions. This can be attributed to the strong polar dipole of iodoethane.

The results of binary VLE experiments showed that the mixture $\{(1\text{-}x)C_2H_5I + xC_7H_8\}$exhibits strong positive deviations with a homogeneous azeotrope. Whereas the mixture $\{(1\text{-}x)C_2H_5I + xCH_3OH\}$ shows only weak interactions with slightly positive deviations from ideal mixing behaviour.

Owing to the polarity of molecules, methanol and fluorotoluene have compact effect on mixing, as for difluorobenzene some volumetric expansion was built up.

The high excess molar volume V_m^E values of (fluoro-hydrocarbon + hydrocarbon) mixtures were the largest for nonpolar–nonelectrolyte mixtures.

The large value of the excess molar volumes of (fluoro-hydrocarbon + hydrocarbon) mixtures was mainly caused by the large differences in molecular sizes and mixing energies.[17]

Endothermic mixing leads to large volume expansion observed when the fluoro-hydrocarbons and hydrocarbons are mixed.[80, 81]

Iodoethane mixtures have strong real behaviour revealed by V_m^E and excess molar enthalpies H_m^E.[38, 79]

As for excess refractive indices n_D^E, the results are:

For mixtures 1. to 9., excess refractive indices were found in the range:

$0.012 \leq n_D^E \leq 0.014$. While for mixtures 10. to 15.:

excess refractive indices for halogenated mixtures with methanol were found in

the range: $0.023 \leq n_D^E \leq 0.06$

These values of n_D^E explain the effect of mixed molecular structure on the refraction of light in the solution.

For halogenated mixtures with toluene, excess refractive indices n_D^E were found around zero indicating the absence of influence of molecular structure on the refraction of light in the corresponding solutions.

Conclusion:

- An outcome of this study is the measurement and correlation of thermodynamic properties of systems which are mostly needed for their technical applications.
- Report data sets of VLE, G_m^E, n_D^E and V_m^E over the whole composition range for fifteen binary halogenated hydrorcarbon mixtures together with their smoothing functions and error analysis
- The experimental results suggest that the equipments in use were performing properly.
- The present mixtures show large deviations from ideality with low boiling azeotropes.
- The thermodynamic consistency, reduction and correlation of our data are reliable and allow successfully for the estimation of various thermodynamic properties.
- This work will provide efficient tools and knowledge to carry out a good research works on applied sciences.

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Table (A.1.1): Refractive indices n_D of VLE of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.4625	0.0000	1.4625	0.0000
1.4578	0.0393	1.4522	0.0891
1.4463	0.1418	1.4320	0.2763
1.4359	0.2387	1.4185	0.4127
1.4263	0.3328	1.4083	0.5233
1.4138	0.4628	1.4000	0.6190
1.4032	0.5814	1.3942	0.6895
1.3960	0.6672	1.3900	0.7427
1.3909	0.7311	1.3870	0.7819
1.3875	0.7753	1.3845	0.8155
1.3860	0.7952	1.3835	0.8291
1.3855	0.8020	1.3830	0.8360
1.3850	0.8087	1.3826	0.8415
1.3835	0.8291	1.3820	0.8499
1.3810	0.8639	1.3803	0.8739
1.3748	0.9543	1.3748	0.9530
1.3720	1.0000	1.3720	1.0000

Table (A.1.2): Experimental results: VLE of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr.

T/K	x	y	γ_1	γ_2
355.7	0.0393	0.0891	1.5810	1.0314
352.0	0.1418	0.2763	1.4882	1.0285
348.9	0.2387	0.4127	1.4301	1.0387
346.9	0.3328	0.5233	1.3725	1.0304
344.9	0.4628	0.6190	1.2333	1.0960
343.6	0.5814	0.6895	1.1311	1.1974
342.9	0.6672	0.7427	1.0830	1.2821
342.5	0.7311	0.7819	1.0533	1.3682
342.2	0.7753	0.8155	1.0437	1.4008
342.1	0.7952	0.8291	1.0386	1.4317
342.0	0.8020	0.8360	1.0392	1.4232
342.0	0.8087	0.8415	1.0388	1.4266
341.9	0.8291	0.8499	1.0245	1.5152
341.8	0.8639	0.8739	1.0134	1.6061
341.8	0.9543	0.9530	1.0013	1.7971

comp. (1) = C_6H_{14}, comp. (2) = C_6H_5F

Table (A.1.3): Excess refractive indices n_D^E of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 298.2 K

x	n_D^E
0.0393	-0.0010
0.1418	-0.0033
0.2387	-0.0049
0.3328	-0.0059
0.4628	-0.0067
0.5814	-0.0065
0.6672	-0.0060
0.7311	-0.0053
0.7753	-0.0047
0.7952	-0.0044
0.8020	-0.0042
0.8087	-0.0041
0.8291	-0.0038
0.8639	-0.0031
0.9543	-0.0011

$n_D^E = -0.0268\ x(1 - x) \pm 0.0001$

$n_D^E (x = 0.500) = -0.0067 \pm 0.0001$

Table (A.1.4): Excess Gibbs function G_m^E of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0393	141.05	40.65
0.1418	235.58	-21.68
0.2387	331.57	3.23
0.3328	361.65	-7.14
0.4628	419.47	13.35
0.5814	419.99	4.83
0.6672	387.46	-5.61
0.7311	348.24	-6.58
0.7753	309.84	-6.32
0.7952	294.64	-0.84
0.8020	286.37	-1.59
0.8087	280.92	0.59
0.8291	259.00	3.24
0.8639	216.01	6.42
0.9543	79.57	7.63

G_m^E (cal.)/J.mol^{-1} = [1762.5x (1 - x) ± 23.60]

$G_m^E (x = 0.500) = (440.63 \pm 23)$ J.mol^{-1}

Table (A.1.5): VLE data reduction: Evaluation of WILSON parameters of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
355.7	0.0393	1.581	1.588	-0.46	1.031	1.001	2.99
352.0	0.1418	1.488	1.478	0.68	1.028	1.008	2.00
348.9	0.2387	1.430	1.385	3.13	1.039	1.024	1.44
346.9	0.3328	1.372	1.304	4.96	1.030	1.049	-1.81
344.9	0.4628	1.233	1.207	2.12	1.096	1.105	-0.83
343.6	0.5814	1.131	1.133	-0.17	1.197	1.185	1.00
342.9	0.6672	1.083	1.088	-0.48	1.282	1.268	1.06
342.5	0.7311	1.053	1.060	-0.63	1.368	1.349	1.41
342.2	0.7753	1.044	1.043	0.05	1.401	1.417	-1.14
342.1	0.7952	1.039	1.036	0.21	1.432	1.451	-1.36
342.0	0.8020	1.039	1.034	0.48	1.423	1.463	-2.83
342.0	0.8087	1.039	1.032	0.64	1.427	1.476	-3.46
341.9	0.8291	1.025	1.026	-0.15	1.515	1.516	-0.05
341.9	0.8639	1.013	1.017	-0.35	1.606	1.592	0.87
341.8	0.9543	1.001	1.002	-0.08	1.797	1.849	-2.89

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.004 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 0.97\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.005 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 1.68\ \%$$

WILSON's interaction parameters are:

$$\Delta\lambda_{12}/R = -126.26\ K$$
$$\Delta\lambda_{21}/R = 367.21\ K$$

Table (A.1.6): VLE data reduction: evaluation of UNIQUAC parameters of $\{(1-x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
355.7	0.0393	1.581	1.571	0.60	1.031	1.000	3.00
352.0	0.1418	1.488	1.471	1.15	1.028	1.007	2.09
348.9	0.2387	1.430	1.383	3.29	1.039	1.022	1.65
346.9	0.3328	1.372	1.304	4.96	1.030	1.046	-1.49
344.9	0.4628	1.233	1.207	2.10	1.096	1.101	-0.43
343.6	0.5814	1.131	1.132	-0.10	1.197	1.181	1.35
342.9	0.6672	1.083	1.087	-0.36	1.282	1.265	1.36
342.5	0.7311	1.053	1.059	-0.50	1.368	1.345	1.69
342.2	0.7753	1.044	1.042	0.18	1.401	1.412	-0.81
342.1	0.7952	1.039	1.035	0.34	1.432	1.446	-1.00
342.0	0.8020	1.039	1.033	0.60	1.423	1.458	-2.45
342.0	0.8087	1.039	1.031	0.76	1.427	1.470	-3.07
341.9	0.8291	1.025	1.025	-0.04	1.515	1.509	0.38
341.9	0.8639	1.013	1.016	-0.27	1.606	1.583	1.44
341.8	0.9543	1.001	1.002	-0.06	1.797	1.825	-1.53

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0043 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 1.02\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0047 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 1.58\ \%$$

UNIQUAC interaction parameters are:

$$\Delta u_{12}/R = 275.05\ K$$
$$\Delta u_{21}/R = -145.89\ K$$

Table (A.1.7): Evaluation of relative volatility α_{12} of $\{(1-x)C_6H_5F + xC_6H_{14}\}$ mixtures at 760.0 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	σs
Experimental	2.2852	0.919	-5.1124	2.869	0.0399
WILSON	0.0005	0.005	0.0114	0.007	0.0004
UNIQUAC	2.6078	-1.486	-0.6095	0.321	0.0006

Table (A.1.8): VLE data reduction of $\{(1\text{-}x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
355.7	0.0393	2.56	0.0891	-0.0053
352.0	0.1418	1.07	0.2763	-0.0064
348.9	0.2387	1.44	0.4127	0.0019
346.9	0.3328	0.95	0.5233	0.0168
344.9	0.4628	0.19	0.6190	0.0084
343.6	0.5814	-0.60	0.6895	-0.0001
342.9	0.6672	-0.82	0.7427	0.0001
342.5	0.7311	-0.86	0.7819	-0.0002
342.2	0.7753	-0.78	0.8155	0.0051
342.1	0.7952	-0.63	0.8291	0.0056
342.0	0.8020	-0.62	0.8360	0.0079
342.0	0.8087	-0.55	0.8415	0.0089
341.9	0.8291	-0.65	0.8499	0.0031
341.9	0.8639	-0.65	0.8739	0.0017
341.8	0.9543	-0.41	0.9530	0.0029

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.259 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.016$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 2.267$$

$$\left|\frac{(\Delta y_1)}{N}\right| = 0.008 \quad ; \quad \left|\frac{(\Delta y_2)}{N}\right| = 0.008$$

Table (A.1.9): VLE data reduction of $\{(1\text{-}x)C_6H_5F + xC_6H_{14}\}$at 760.0 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
355.66	0.0393	2.67	0.0891	-0.0044
351.97	0.1418	1.28	0.2763	-0.0056
348.90	0.2387	1.64	0.4127	0.0018
346.86	0.3328	1.12	0.5233	0.0160
344.85	0.4628	0.34	0.6190	0.0074
343.63	0.5814	-0.44	0.6895	-0.0007
342.91	0.6672	-0.64	0.7427	-0.0003
342.47	0.7311	-0.68	0.7819	-0.0005
342.20	0.7753	-0.60	0.8155	0.0049
342.06	0.7952	-0.45	0.8291	0.0053
342.03	0.8020	-0.45	0.8360	0.0076
341.98	0.8087	-0.37	0.8415	0.0085
341.94	0.8291	-0.48	0.8499	0.0027
341.85	0.8639	-0.49	0.8739	0.0011
341.80	0.9543	-0.32	0.9530	0.0022

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.261 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.001$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 0.798$$

$$\left|\frac{(\Delta y_1)}{N}\right| = 0.045 \quad ; \quad \left|\frac{(\Delta y_2)}{N}\right| = 0.045$$

Table (A.1.10): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_6H_5F + xC_6H_{14}\}$mixtures at 760.0 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0393	2.3111	2.5482	2.5214
0.1418	2.3107	2.3853	2.3759
0.2387	2.2412	2.2237	2.2246
0.3328	2.2008	2.0576	2.0642
0.4628	1.8859	1.8201	1.8278
0.5814	1.5988	1.5996	1.6040
0.6672	1.4398	1.4390	1.4421
0.7311	1.3186	1.3201	1.3225
0.7753	1.2810	1.2388	1.2404
0.7952	1.2494	1.2016	1.2041
0.8020	1.2585	1.1893	1.1918
0.8087	1.2559	1.1765	1.1799
0.8291	1.1671	1.1394	1.1429
0.8639	1.0918	1.0752	1.0810
0.9543	0.9710	0.9118	0.9255

Table (A.1.11): Reduction of VLE of $\{(1\text{-}x)C_6H_5F + xC_6H_{14}\}$mixtures at 760.0 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
355.66	0.0393	0.987	0.955	0.960	0.964
351.97	0.1418	0.977	0.955	0.958	0.962
348.90	0.2387	0.969	0.957	0.957	0.961
346.86	0.3328	0.964	0.959	0.956	0.960
344.85	0.4628	0.960	0.962	0.955	0.959
343.63	0.5814	0.958	0.965	0.954	0.958
342.91	0.6672	0.956	0.968	0.953	0.957
342.47	0.7311	0.955	0.970	0.953	0.957
342.20	0.7753	0.955	0.973	0.953	0.957
342.06	0.7952	0.954	0.973	0.953	0.957
342.03	0.8020	0.954	0.974	0.953	0.957
341.98	0.8087	0.954	0.974	0.953	0.957
341.94	0.8291	0.954	0.975	0.953	0.957
341.85	0.8639	0.954	0.977	0.953	0.957

341.80	0.9543	0.953	0.983	0.953	0.957

Table (A.1.12): Summary of physico-chemical properties of $\{(1-x)C_6H_5F + xC_6H_{14}\}$ at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	Exp.	-	-	2.28	1.58	2.01
Exp.	341.6	0.9563	WILSON	-126.26	367.20	2.61	1.15	1.91
cal.	-	0.8793	UNIQUAC	275.05	-145.89	2.61	1.95	2.34

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
6.93	WILSON	0.259	0.016
	UNIQUAC	0.261	0.001

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.9563	WILSON	82	77	-0.01	0.01
T_{az} = 341.6 K	UNIQUAC	82	246	0.48	0.39
x = 0.500	WILSON	412	239	-0.50	1.17
T = 347.1 K	UNIQUAC	421	11	-1.18	2.14

Experimental $X_m^E(T, x = 0.500)$:

n_D^E (298.2 K)	V_m^E (298.2 K) (cm^3.mol^{-1})	H_m^E (313.2 K) (J.mol^{-1})	G_m^E (347.1 K) (J.mol^{-1})
-0.0067	-	832	440

G_m^E(cal.)/J.mol-1 = [1762.5.x(1-x) ± 23.60]

n_D^E = [-0.0268 x(1 – x) ± 0.0001]

Literature $X_m^E(T=298.15\ K, x=0.500)$:[70]

V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})
0.2462 ± 0.003	868 ± 1.2

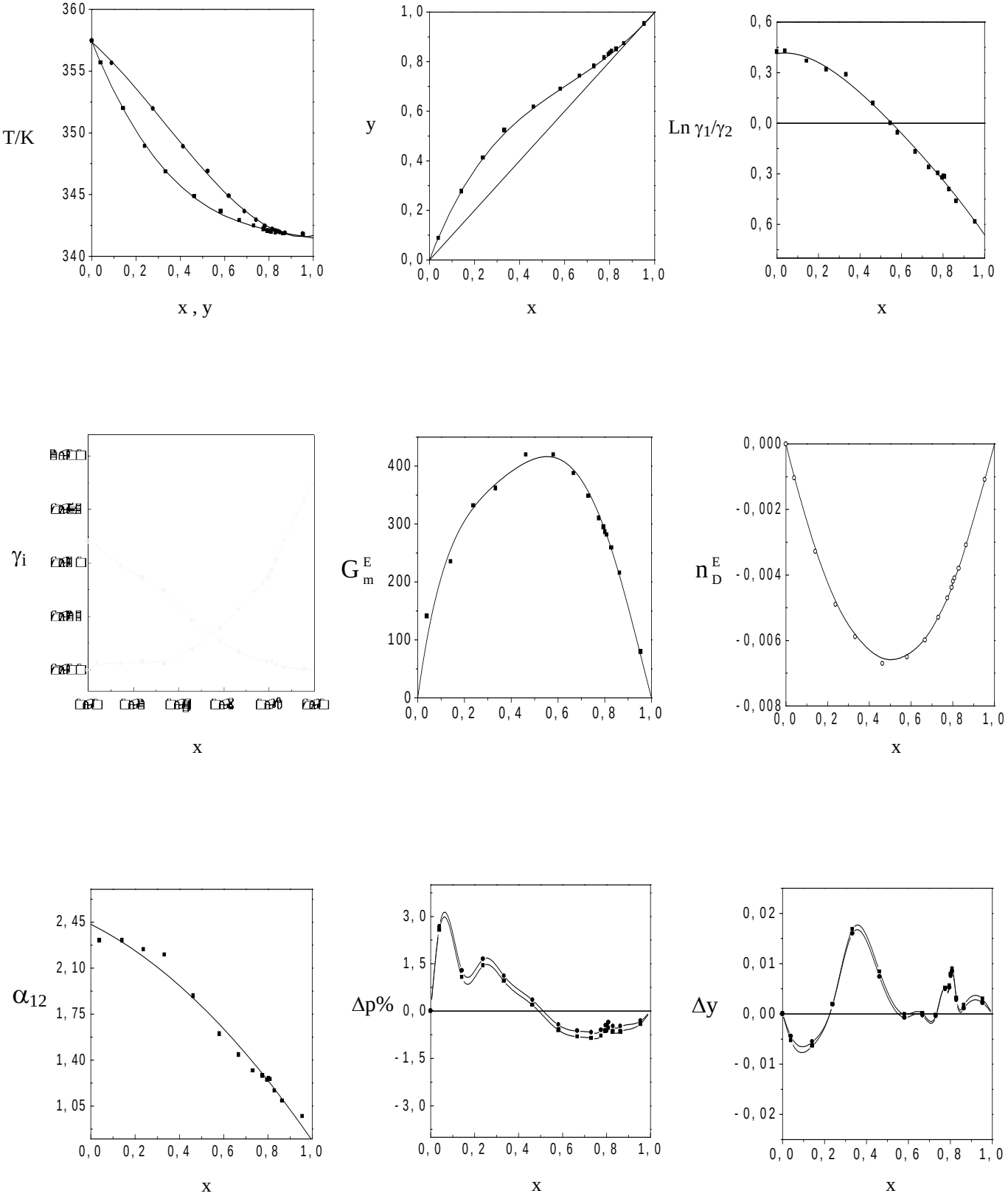


Figure (A, 1): Vapour-Liquid Equilibria of {(1-x)C_6H_5F+xC_6C_{14}} at 102 kPa

Table (A.2.1): Refractive indices n_D of VLE of $\{(1-x)C_6H_5F + xC_7H_{16}\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.4615	0.0000	1.4615	0.0000
1.4588	0.0233	1.4580	0.0310
1.4560	0.0479	1.4550	0.0565
1.4500	0.1037	1.4495	0.1055
1.4430	0.1656	1.4443	0.1533
1.4335	0.2590	1.4385	0.2091
1.4280	0.3177	1.4342	0.2523
1.4208	0.3991	1.4300	0.2962
1.4182	0.4299	1.4275	0.3227
1.4153	0.4664	1.4252	0.3481
1.4120	0.5090	1.4230	0.3735
1.4070	0.5782	1.4183	0.4286
1.4024	0.6476	1.4133	0.4913
1.3968	0.7424	1.4061	0.5910
1.3930	0.8158	1.4005	0.6752
1.3916	0.8453	1.3973	0.7336
1.3887	0.9129	1.3918	0.8400
1.3872	0.9523	1.3891	0.9023
1.3861	0.9823	1.3868	0.9630
1.3855	1.0000	1.3855	1.0000

Table (A.2. 2): Experimental results : VLE of $\{(1-x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr

T/K	x	y	γ_1	γ_2
357.52	0.0233	0.0310	2.0970	1.0278
357.64	0.0479	0.0565	1.8484	1.0231
357.54	0.1037	0.1055	1.5932	1.0337
357.69	0.1656	0.1533	1.4380	1.0469
358.14	0.2590	0.2091	1.2321	1.0876
358.36	0.3177	0.2523	1.2005	1.1103
358.88	0.3991	0.2962	1.1013	1.1698
359.20	0.4299	0.3227	1.1014	1.1763
359.48	0.4664	0.3481	1.0843	1.2006
359.78	0.5090	0.3735	1.0550	1.2438
360.51	0.5782	0.4286	1.0398	1.2950
361.60	0.6476	0.4913	1.0272	1.3400
363.32	0.7424	0.5910	1.0207	1.4084
356.04	0.8158	0.6752	1.0068	1.4951
365.91	0.8453	0.7336	1.0281	1.4288
368.00	0.9129	0.8400	1.0250	1.4457
369.00	0.9523	0.9023	1.0255	1.5736
370.18	0.9823	0.9630	1.0262	1.5603

comp. (1) = C_7H_{16} , comp. (2) = C_6H_5F

Table (A.2.3): Excess refractive indices n_D^E of $\{(1-x)C_6H_5F + xC_7H_{16}\}$at 298.2 K

x	n_D^E
0.0000	0.0000
0.0233	-0.0009
0.0479	-0.0019
0.1037	-0.0036
0.1656	-0.0059
0.2590	-0.0083
0.3177	-0.0094
0.3991	-0.0104
0.4229	-0.0106
0.4664	-0.0108
0.5090	-0.0108
0.5782	-0.0106
0.6476	-0.0099
0.7424	-0.0083
0.8158	-0.0065
0.8453	-0.0057
0.9129	-0.0034
0.9523	-0.0019
0.9823	-0.0008
1.0000	0.0000

$n_D^E = [x(1 - x)\{-0.0432 + 0.0006(1 - 2x)\} \pm 0.0001]$

$n_D^E (x = 0.500) = -0.0108 \pm 0.0001$

Table (A.2.4): Excess Gibbs function G_m^E of $\{(1-x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0000	0.0000	0.00
0.0233	130.79	66.82
0.0479	152.25	29.22
0.1037	231.87	3.13
0.1656	292.64	-15.51
0.2590	346.31	-27.01
0.3177	385.55	-5.75
0.3991	396.26	-2.03
0.4229	400.49	3.14
0.4664	404.39	9.90
0.5090	402.04	12.75
0.5782	394.46	17.21
0.6476	362.28	2.16
0.7424	312.35	-10.56
0.8158	241.59	-33.10
0.8453	239.13	-8.97
0.9129	167.06	1.28
0.9523	139.90	39.39
0.9823	102.49	62.17
1.0000	0.0000	0.00

G_m^E (cal.)/J.mol^{-1} = $[x(1 - x)\{1562.13 + 268.62(1 - 2x) + 1091.77(1 - 2x)^2\} \pm 30.13]$

$G_m^E (x = 0.500) = (390.53 \pm 30)$ J.mol^{-1}

Table (A.2.5): VLE data reduction: evaluation of WILSON parameters of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
357.5	0.0233	2.097	2.040	2.74	1.028	1.001	2.63
357.6	0.0479	1.848	1.912	-3.43	1.023	1.003	1.95
357.5	0.1037	1.593	1.687	-5.89	1.034	1.013	1.96
357.7	0.1656	1.438	1.509	-4.92	1.047	1.031	1.52
358.1	0.2590	1.232	1.328	-7.75	1.088	1.067	1.93
358.4	0.3177	1.201	1.249	-4.01	1.110	1.093	1.54
358.9	0.3991	1.101	1.168	-6.07	1.170	1.134	3.05
359.2	0.4299	1.101	1.144	-3.89	1.176	1.151	2.19
359.5	0.4664	1.084	1.120	-3.26	1.201	1.171	2.49
359.8	0.5090	1.055	1.095	-3.84	1.244	1.195	3.92
360.5	0.5782	1.040	1.064	-2.36	1.295	1.236	4.56
361.6	0.6476	1.027	1.041	-1.36	1.340	1.278	4.61
363.3	0.7424	1.021	1.020	0.09	1.408	1.338	5.02
365.0	0.8158	1.007	1.009	-0.25	1.495	1.384	7.41
365.9	0.8453	1.028	1.006	2.11	1.429	1.403	1.81
368.0	0.9129	1.025	1.002	2.25	1.446	1.446	0.01
369.0	0.9523	1.023	1.001	2.15	1.574	1.471	6.53
370.2	0.9823	1.026	1.000	2.55	1.560	1.489	4.55

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.026 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 3.27\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.024 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 3.20\ \%$$

WILSON's interaction parameters:

$\Delta\lambda_{12}/R = 212.30$ K

$\Delta\lambda_{21}/R = 75.71$ K

Table (A.2.6): VLE data reduction: evaluation of UNIQUAC parameters of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
357.5	0.0233	2.097	2.027	3.34	1.028	1.001	2.63
357.6	0.0479	1.848	1.906	-3.12	1.023	1.003	1.97
357.5	0.1037	1.593	1.689	-6.00	1.034	1.013	2.01
357.7	0.1656	1.438	1.512	-5.18	1.047	1.030	1.58
358.1	0.2590	1.232	1.330	-7.96	1.088	1.066	1.98
358.4	0.3177	1.201	1.250	-4.14	1.110	1.093	1.56
358.9	0.3991	1.101	1.168	-6.09	1.170	1.135	3.01
359.2	0.4299	1.101	1.144	-3.87	1.176	1.151	2.13
359.5	0.4664	1.084	1.119	-3.22	1.201	1.172	2.40
359.8	0.5090	1.055	1.095	-3.77	1.244	1.196	3.81
360.5	0.5782	1.040	1.063	-2.27	1.295	1.238	4.43
361.6	0.6476	1.027	1.040	-1.28	1.340	1.280	4.48
363.3	0.7424	1.021	1.019	0.15	1.408	1.339	4.94
365.0	0.8158	1.007	1.009	-0.22	1.495	1.384	7.40
365.9	0.8453	1.028	1.006	2.14	1.429	1.403	1.84
368.0	0.9129	1.025	1.002	2.26	1.446	1.444	0.14
369.0	0.9523	1.023	1.001	2.15	1.574	1.468	6.73
370.2	0.9823	1.026	1.000	2.55	1.560	1.485	4.81

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0268 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 3.32\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0248 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 3.21\ \%$$

UNIQUAC interaction parameters:

$\Delta u_{12}/R = 16.18$ K

$\Delta u_{21}/R = 50.24$ K

Table (A.2.7): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$ mixtures at 765.5 torr : parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	σs
Experimental	1.35	-3.17	4.17	-1.91	0.027
WILSON	1.43	-3.09	3.76	-1.66	0.013
UNIQUAC	1.43	-3.09	3.76	-1.66	0.013

0.9823	0.4690	0.4625		0.4625

Table (A.2.8): VLE data reduction of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
357.5	0.0233	2.65	0.0310	-0.0011
357.6	0.0479	1.50	0.0565	-0.0049
357.5	0.1037	0.79	0.1055	-0.0107
357.7	0.1656	0.01	0.1533	-0.0123
358.1	0.2590	-0.83	0.2091	-0.0201
358.4	0.3177	-0.66	0.2523	-0.0144
358.9	0.3991	-0.53	0.2962	-0.0226
359.2	0.4299	-0.70	0.3227	-0.0164
359.5	0.4664	-0.45	0.3481	-0.0158
359.8	0.5090	0.09	0.3735	-0.0206
360.5	0.5782	0.66	0.4286	-0.0184
361.6	0.6476	0.74	0.4913	-0.0151
363.3	0.7424	1.26	0.5910	-0.0103
365.0	0.8158	1.52	0.6752	-0.0141
365.9	0.8453	1.38	0.7336	0.0042
368.0	0.9129	1.48	0.8400	0.0066
369.0	0.9523	2.67	0.9023	-0.0011
370.2	0.9823	2.64	0.9630	0.0005

$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.328$; $\left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.003$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 1.141$, $\left|\frac{(\Delta y_1)}{N}\right| = 0.012$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.012$

Table (A.2.9): VLE data reduction of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$at 765.5 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
357.52	0.0233	1.66	0.0453	0.0012
357.64	0.0479	1.54	0.0565	-0.0048
357.54	0.1037	0.82	0.1055	-0.0109
357.69	0.1656	0.03	0.1533	-0.0127
358.14	0.2590	-0.83	0.2091	-0.0206
358.36	0.3177	-0.68	0.2523	-0.0146
358.88	0.3991	-0.56	0.2962	-0.0225
359.20	0.4299	-0.73	0.3227	-0.0163
359.48	0.4664	-0.49	0.3481	-0.0155
359.78	0.5090	0.05	0.3735	-0.0202
360.51	0.5782	0.63	0.4286	-0.0179
361.60	0.6476	0.72	0.4913	-0.0146
363.32	0.7424	1.26	0.5910	-0.0099
365.04	0.8158	1.54	0.6752	-0.0141
365.91	0.8453	1.41	0.7336	0.0042
368.00	0.9129	1.51	0.8400	0.0064
369.00	0.9523	2.70	0.9023	-0.0013
370.18	0.9823	2.65	0.9630	0.0004

$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.332$; $\left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.003$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 1.156$, $\left|\frac{(\Delta y_1)}{N}\right| = 0.011$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.011$

Table (A.2.10): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$ mixtures at 765.5 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0233	1.3410	1.3902	1.3902
0.0479	1.1903	1.3003	1.3003
0.1037	1.0194	1.1364	1.1364
0.1656	0.9123	1.0000	1.0000
0.2590	0.7564	0.8507	0.8507
0.3177	0.7247	0.7811	0.7811
0.3991	0.6337	0.7046	0.7046
0.4299	0.6318	0.6804	0.6804
0.4664	0.6109	0.6545	0.6545
0.5090	0.5751	0.6274	0.6274
0.5782	0.5472	0.5897	0.5897
0.6476	0.5256	0.5583	0.5583
0.7424	0.5014	0.5233	0.5233
0.8158	0.4694	0.5009	0.5009
0.8453	0.5040	0.4933	0.4933
0.9129	0.5009	0.4773	0.4773
0.9523	0.4626	0.4684	0.4684

Table (A.2.11): Reduction of VLE of $\{(1\text{-}x)C_6H_5F + xC_7H_{16}\}$ mixtures at 765.5 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
357.52	0.0233	0.981	0.956	0.946	0.965
357.64	0.0479	0.975	0.956	0.945	0.964
357.54	0.1037	0.965	0.959	0.944	0.964
357.69	0.1656	0.962	0.961	0.944	0.964
358.14	0.2590	0.955	0.967	0.944	0.964
358.36	0.3177	0.960	0.962	0.944	0.964
358.88	0.3991	0.951	0.977	0.944	0.964
359.20	0.4299	0.950	0.986	0.944	0.964
359.48	0.4664	0.950	0.990	0.944	0.965
359.78	0.5090	0.950	0.994	0.945	0.965
360.51	0.5782	0.979	0.956	0.945	0.965
361.60	0.6476	0.972	0.957	0.946	0.966
363.32	0.7424	0.968	0.958	0.947	0.967
365.04	0.8158	0.959	0.963	0.948	0.968
365.91	0.8453	0.957	0.965	0.948	0.968

368.00	0.9129	0.963	0.960	0.950	0.969
369.00	0.9523	0.952	0.972	0.951	0.970
370.18	0.9823	0.950	0.980	0.951	0.970

Table (A.2.12): Summary of physico-chemical properties of $\{(1-x)C_6H_5F + xC_7H_{16}\}$ at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	exp.	-	-	1.35	2.23	1.59
Exp.	357.7	0.1115	WILSON	212.30	75.71	1.43	2.17	1.60
cal.	-	0.1979	UNIQUAC	16.18	50.24	1.43	2.34	1.59

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
5.86	WILSON	0.328	0.003
	UNIQUAC	0.332	0.003

Correlated $X_m^E(T, x)$:

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x_{az} = 0.1115	WILSON	208	221	0.04	0.10
T_{az} = 357.7 K	UNIQUAC	220	206	-0.04	0.01
x = 0.500	WILSON	403	409	0.02	0.32
T = 361.7 K	UNIQUAC	432	417	-0.04	0.14

Experimental $X_m^E(T, x = 0.500)$:

n_D^E (298.2 K)	V_m^E (298.2 K) ($cm^3.mol^{-1}$)	H_m^E (313.2 K) ($J.mol^{-1}$)	G_m^E (361.7 K) ($J.mol^{-1}$)
-0.0108	-	955	390

$G_m^E(cal.)/J.mol^{-1} = [x(1 - x)\{1562.13 + 268.62(1 - 2x) + 1091.77(1 - 2x)^2\} \pm 30.13]$

$n_D^E = [x (1 - x)\{-0.0432 + 0.0006(1 - 2x)\} \pm 0.0001]$

Literature $X_m^E(T=298.15\ K, x=0.500)$: [70]

V_m^E ($cm^3.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
0.4314 ± 0.002)	-1.18 ± 0.01

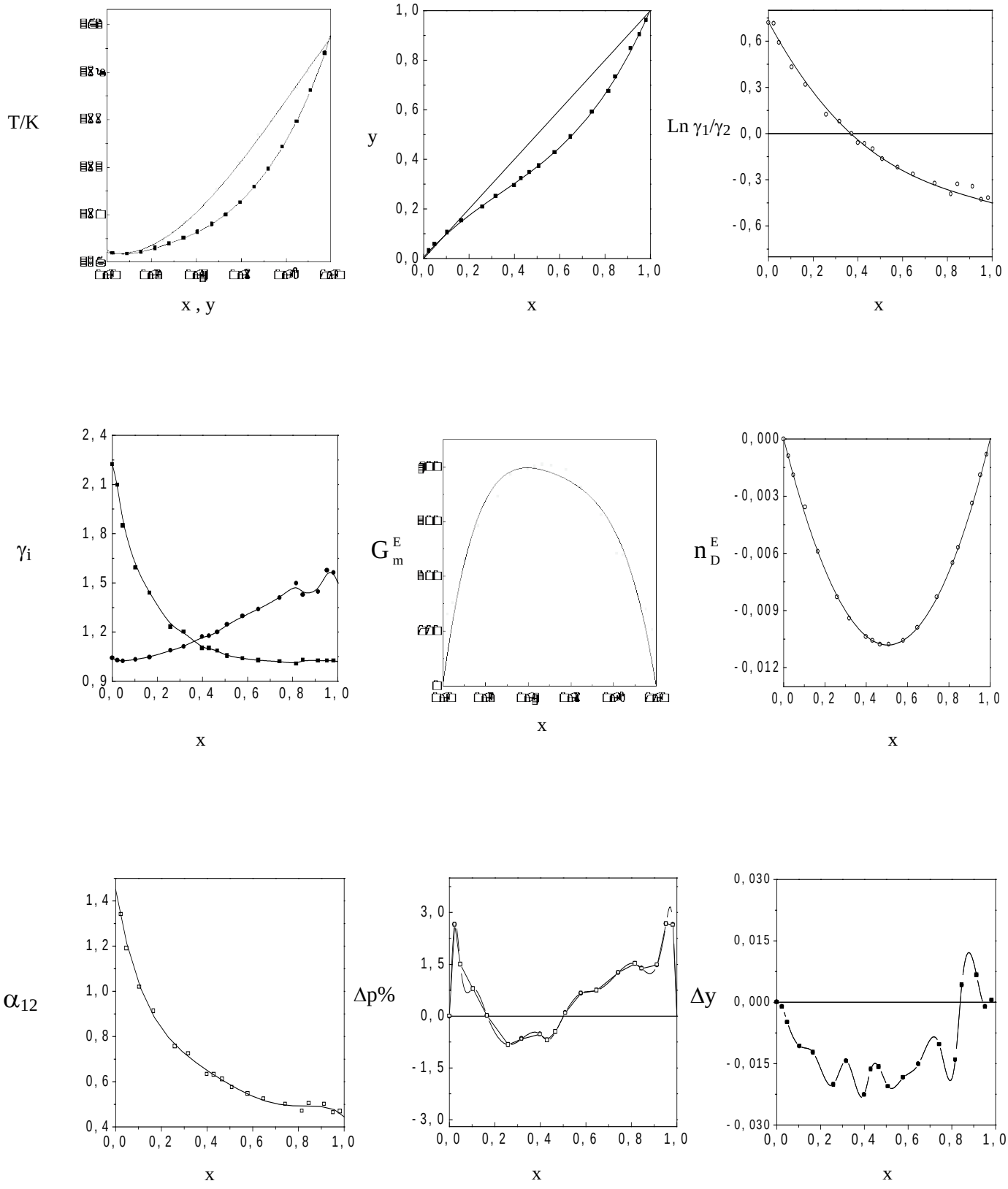


Figure (A. 2) : Vapour-Liquid Equilibria of {(1-x)C_6H_5F+xC_7H_{16}} at 102 kPa

Table (A.3.1): Refractive indices n_D of VLE of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.2880	0.0000	1.2880	0.0000
1.2937	0.0467	1.3205	0.2434
1.3104	0.1692	1.3590	0.5015
1.3200	0.2374	1.3688	0.5630
1.3350	0.3409	1.3765	0.6112
1.3530	0.4610	1.3848	0.6629
1.3710	0.5769	1.3918	0.7062
1.3810	0.6396	1.3925	0.7100
1.3880	0.6828	1.3930	0.7142
1.3940	0.7207	1.3930	0.7134
1.4035	0.7768	1.3940	0.7207
1.4100	0.8155	1.3960	0.7316
1.4160	0.8508	1.3985	0.7467
1.4195	0.8713	1.3990	0.7498
1.4220	0.8859	1.4010	0.7618
1.4250	0.9033	1.4040	0.7798
1.4420	1.0000	1.4420	1.0000

Table (A.3.2): Experimental results: VLE of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$ at 766.9 torr.

T/K	x	y	γ_1	γ_2
340.7	0.0467	0.2434	4.4788	1.0313
332.1	0.1692	0.5015	3.2961	1.1269
330.5	0.2374	0.5630	2.7680	1.1548
329.0	0.3409	0.6112	2.1922	1.2713
327.7	0.4610	0.6629	1.8363	1.4359
327.5	0.5769	0.7062	1.5700	1.6090
327.5	0.6396	0.7100	1.4232	1.8640
327.6	0.6828	0.7142	1.3387	2.0829
327.6	0.7207	0.7134	1.2644	2.3656
327.3	0.7768	0.7207	1.1975	2.9280
327.5	0.8155	0.7316	1.1508	3.3780
327.8	0.8508	0.7467	1.1156	3.8973
328.0	0.8713	0.7498	1.0863	4.4213
328.1	0.8859	0.7618	1.0796	4.7165
328.5	0.9033	0.7798	1.0701	5.0620

comp. (1) = $CHCL_3$, comp. (2) = $C_2H_2F_3OH$

Table (A.3.3): Excess refractive indices n_D^E of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$ at 298.2 K

x	n_D^E
0.0467	0.0467
0.1692	0.1692
0.2374	0.2374
0.3409	0.3409
0.4610	0.4610
0.5769	0.5769
0.6396	0.6396
0.6828	0.6828
0.7207	0.7207
0.7768	0.7768
0.8155	0.8155
0.8508	0.8508
0.8713	0.8713
0.8859	0.8859
0.9033	0.9033

$n_D^E = [x\,(1 - x)\{-0.0245 - 0.0013\,(1 - 2x) \pm 0.0001]$

$n_D^E\,(x = 0.500) = -0.0061 \pm 0.0001$

Table (A.3.4): Excess Gibbs function G_m^E of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$ at 766.9 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0467	281.53	-17.36
0.1692	831.28	-1.37
0.2374	4965.86	-47.30
0.3409	1164.82	-15.77
0.4610	1294.59	29.58
0.5769	1256.65	-5.53
0.6396	1225.64	1.23
0.6828	1176.26	-3.76
0.7207	1115.74	-10.47
0.7768	1033.55	17.91
0.8155	923.30	9.85
0.8508	806.61	8.39
0.8713	718.24	-2.14
0.8859	667.84	8.22
0.9033	595.42	14.44

G_m^E (cal.)/J.mol^{-1} = [x (1 - x){5088.8 - 320.70(1 - 2x) + 2061.20 (1 - 2x)²} ± 16.30]

$G_m^E\,(x = 0.500) = (1272 \pm 16)$ J.mol^{-1}

Table (A.3.5): VLE data reduction:
Evaluation of WILSON parameters of
{(1-x)$C_2H_2F_3OH$ + x$CHCL_3$} at 766.9 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
340.7	0.0467	4.479	4.509	-0.68	1.031	1.004	2.68
332.1	0.1692	3.296	3.248	1.45	1.127	1.047	7.10
330.5	0.2374	2.768	2.760	0.28	1.155	1.092	5.41
329.0	0.3409	2.192	2.220	-1.25	1.271	1.195	6.00
327.7	0.4610	1.836	1.789	2.59	1.436	1.383	3.67
327.5	0.5769	1.570	1.496	4.69	1.609	1.678	-4.31
327.5	0.6396	1.423	1.374	3.48	1.864	1.917	-2.86
327.6	0.6828	1.339	1.300	2.87	2.083	2.134	-2.44
327.6	0.7207	1.264	1.243	1.71	2.366	2.374	-0.34
327.3	0.7768	1.197	1.168	2.45	2.928	2.859	2.36
327.5	0.8155	1.151	1.123	2.40	3.378	3.331	1.39
327.8	0.8508	1.116	1.087	2.56	3.897	3.921	-0.60
328.0	0.8713	1.086	1.068	1.67	4.421	4.367	1.23
328.1	0.8859	1.080	1.056	2.20	4.716	4.749	-0.68
328.5	0.9033	1.070	1.042	2.61	5.062	5.293	-4.56

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0089 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 2.19\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0200 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 2.81\ \%$$

WILSON's interaction parameters are:

$\Delta\lambda_{12}/R$ = 218.49 K
$\Delta\lambda_{21}/R$ = 717.07 K

Table (A.3.6): VLE data reduction:
evaluation of UNIQUAC parameters of
{(1-x)$C_2H_2F_3OH$ + x$CHCL_3$} at 766.9 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
340.7	0.0467	4.479	4.130	7.80	1.031	1.003	2.78
332.1	0.1692	3.296	3.220	2.32	1.127	1.037	7.98
330.5	0.2374	2.768	2.792	-0.86	1.155	1.077	6.76
329.0	0.3409	2.192	2.266	-3.36	1.271	1.174	7.62
327.7	0.4610	1.836	1.810	1.45	1.436	1.369	4.64
327.5	0.5769	1.570	1.487	5.26	1.609	1.694	-5.28
327.5	0.6396	1.423	1.353	4.93	1.864	1.963	-5.30
327.6	0.6828	1.339	1.274	4.80	2.083	2.206	-5.90
327.6	0.7207	1.264	1.214	3.97	2.366	2.472	-4.48
327.3	0.7768	1.197	1.139	4.87	2.928	2.993	-2.22
327.5	0.8155	1.151	1.097	4.70	3.378	3.471	-2.75
327.8	0.8508	1.116	1.064	4.59	3.897	4.025	-3.28
328.0	0.8713	1.086	1.048	3.48	4.421	4.414	0 .17
328.1	0.8859	1.080	1.038	3.81	4.716	4.727	-0.23
328.5	0.9033	1.070	1.028	3.94	5.062	5.144	-1.61

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0280 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 4.01\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0333 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 4.07\ \%$$

UNIQUAC interaction parameters are:

$\Delta u_{12}/R$ = 252.89 K
$\Delta u_{21}/R$ = 37.47 K

Table (A.3.7): Evaluation of relative volatility α_{12} of {(1-x)$C_2H_2F_3OH$ + x$CHCL_3$}
at 766.9 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	b_4	σs
Exp.	7.40	-18.29	22.34	-16.34	5.48	0.062
Wilson	7.45	-15.27	7.07	5.79	-5.04	0.022
UNIQUAC	6.83	-7.22	-18.55	35.20	-16.67	0.028

Table (A.3.8): VLE data reduction of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$ at 766.9 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
340.7	0.0467	1.96	0.2434	-0.0051
332.1	0.1692	4.63	0.5015	-0.0104
330.5	0.2374	2.90	0.5630	-0.0080
329.0	0.3409	1.96	0.6112	-0.0123
327.7	0.4610	3.41	0.6629	0.0027
327.5	0.5769	2.46	0.7062	0.0239
327.5	0.6396	2.03	0.7100	0.0174
327.6	0.6828	1.73	0.7142	0.0145
327.6	0.7207	1.51	0.7134	0.0071
327.3	0.7768	2.89	0.7207	0.0017
327.5	0.8155	2.64	0.7316	0.0023
327.8	0.8508	2.34	0.7467	0.0050
328.0	0.8713	2.20	0.7498	-0.0014
328.1	0.8859	2.21	0.7618	0.0023
328.5	0.9033	1.78	0.7798	0.0084

With:

$\left(\frac{\sum(\Delta p)^2}{N}\right)^{1/2} = 0.661$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.002$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 0.024$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.008$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.008$

Table (A.3.9): VLE data reduction of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$at 766.9 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
340.7	0.0467	3.25	0.2434	0.0037
332.1	0.1692	4.00	0.5015	-0.0175
330.5	0.2374	1.30	0.5630	-0.0197
329.0	0.3409	-0.15	0.6112	-0.0246
327.7	0.4610	1.73	0.6629	-0.0037
327.5	0.5769	1.43	0.7062	0.0273
327.5	0.6396	1.24	0.7100	0.0265
327.6	0.6828	1.01	0.7142	0.0273
327.6	0.7207	0.82	0.7134	0.0225
327.3	0.7768	2.25	0.7207	0.0193
327.5	0.8155	2.10	0.7316	0.0193
327.8	0.8508	2.05	0.7467	0.0192
328.0	0.8713	2.15	0.7498	0.0099
328.1	0.8859	2.39	0.7618	0.0108
328.5	0.9033	2.30	0.7798	0.0129

With:

$\left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 0.541$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.004$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 1.878$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.017$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.017$

Table (A.3.10): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$ at 766.9 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0467	6.5670	6.7501	6.4357
0.1692	4.9397	5.1496	5.2981
0.2374	4.1385	4.2756	4.4855
0.3409	3.0394	3.2018	3.3752
0.4610	2.2992	2.2716	2.3377
0.5769	1.7629	1.5751	1.5506
0.6396	1.3795	1.2696	1.2169
0.6828	1.1609	1.0824	1.0192
0.7207	0.9647	0.9320	0.8662
0.7768	0.7414	0.7352	0.6749
0.8155	0.6167	0.6095	0.5601
0.8508	0.6170	0.5036	0.4682
0.8713	0.4427	0.4460	0.4202
0.8859	0.4119	0.4067	0.3885
0.9033	0.3791	0.3612	0.3522

Table (A.3.11): Reduction of VLE of $\{(1\text{-}x)C_2H_2F_3OH + xCHCL_3\}$at 766.9 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
340.7	0.0467	0.985	0.963	0.970	0.963
332.1	0.1692	0.975	0.963	0.968	0.959
330.5	0.2374	0.972	0.965	0.967	0.958
329.0	0.3409	0.971	0.965	0.966	0.956
327.7	0.4610	0.969	0.967	0.966	0.956
327.5	0.5769	0.968	0.969	0.966	0.956
327.5	0.6396	0.968	0.969	0.966	0.955
327.6	0.6828	0.968	0.969	0.966	0.955
327.6	0.7207	0.968	0.969	0.966	0.955
327.3	0.7768	0.968	0.969	0.966	0.956
327.5	0.8155	0.968	0.970	0.966	0.956
327.8	0.8508	0.968	0.971	0.966	0.956

Table (A.3.12): Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$+ x$CHCL_3$} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	exp.	-	-	7.40	5.02	10.13
exp.	327.5	0.6965	WILSON	218.49	717.07	7.45	4.90	10.27
cal.	-	0.6447	UNIQUAC	252.89	37.47	6.83	5.06	9.94

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
8.98	WILSON	0.661	0.002
	UNIQUAC	0.541	0.004

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.6965	WILSON	1128	624	-1.54	2.51
T_{az} = 327.5 K	UNIQUAC	1121	1187	0.20	0.42
x = 0.500	WILSON	1235	634	-1.81	2.43
T = 332.2 K	UNIQUAC	1241	1015	-0.68	1.31

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.4998	313.2 K, 0.499	332.2 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	-0.0061	1.0032	2843	1272

G_m^E (cal.)/J.mol^{-1} = [x(1 - x){5088.8 - 320.70(1 - 2x) + 2061.20(1 - 2x)²} ± 16.30]

n_D^E = [x(1 - x){-0.0245 - 0.0013(1 - 2x)} ± 0.0001]

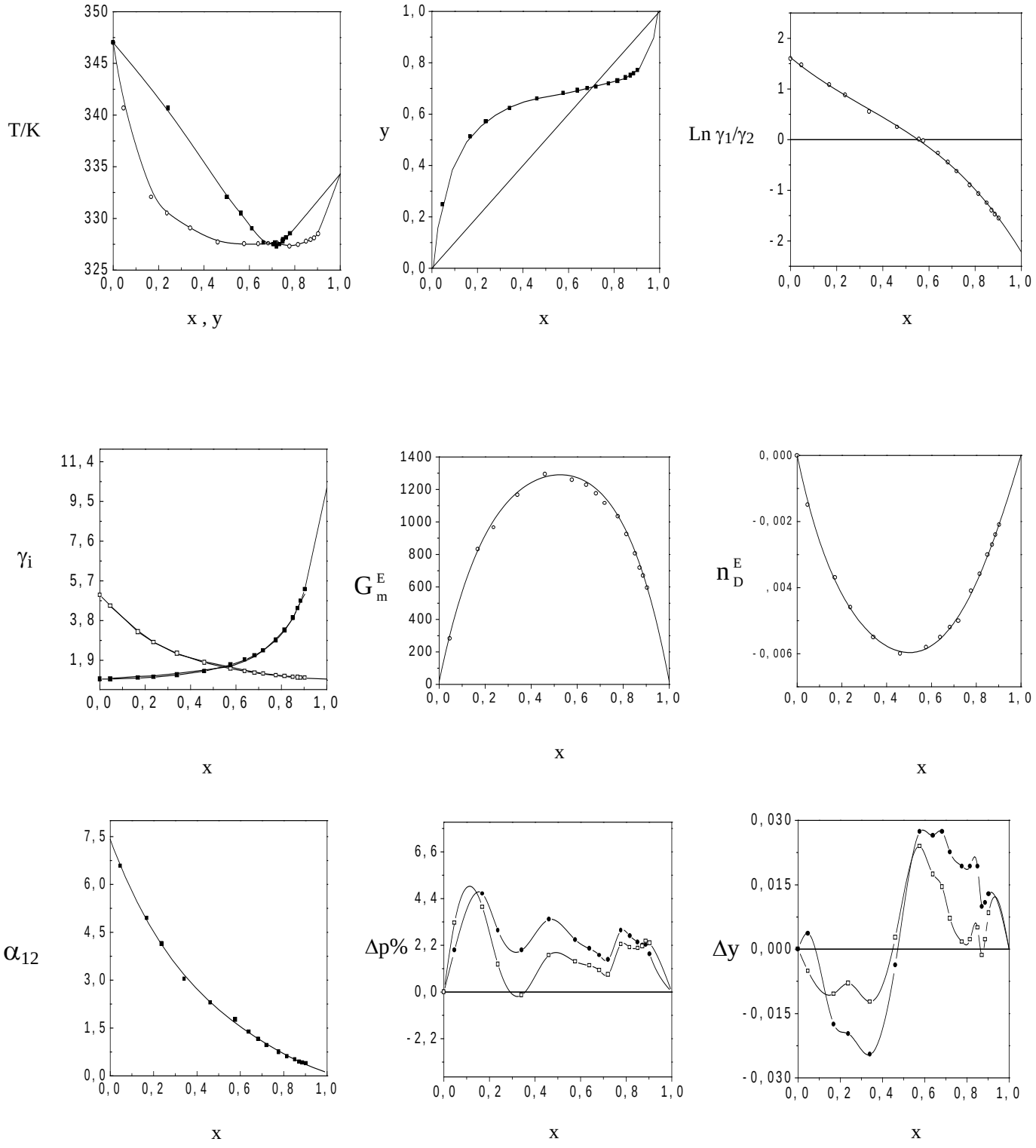


Figure (A. 3) : Vapour-Liquid Equilibria of {(1-x)$C_2H_2F_3OH$+x$CHCL_3$} at 102 kPa

Table (A.4.1): Refractive indices n_D of VLE of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.2885	0.0000	1.2885	0.0000
1.2972	0.0426	1.3220	0.1609
1.3044	0.0767	1.3395	0.2452
1.3175	0.1393	1.3570	0.3281
1.3260	0.1795	1.3681	0.3810
1.3430	0.2612	1.3770	0.4237
1.3616	0.3502	1.3809	0.4423
1.3770	0.4232	1.3845	0.4595
1.3930	0.5001	1.3880	0.4763
1.4060	0.5623	1.3900	0.4858
1.4170	0.6148	1.3927	0.4987
1.4283	0.6688	1.3930	0.5001
1.4370	0.7104	1.3950	0.5097
1.4400	0.7262	1.3960	0.5145
1.4415	0.7321	1.3975	0.5216
1.4548	0.7955	1.4010	0.5384
1.4620	0.8293	1.4059	0.5619
1.4850	0.9390	1.4315	0.6841
1.4975	1.0000	1.4975	1.0000

Table (A.4.2): Experimental results: VLE of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr.

T/K	x	y	γ_1	γ_2
343.2	0.0426	0.1609	5.2766	1.0230
341.7	0.0767	0.2452	4.6754	1.0162
340.0	0.1393	0.3281	3.6282	1.0415
339.2	0.1795	0.3810	3.3531	1.0426
338.2	0.2612	0.4237	2.6401	1.1225
337.7	0.3502	0.4423	2.0887	1.2617
337.8	0.4232	0.4595	1.7910	1.3748
337.7	0.5001	0.4763	1.5743	1.5429
337.8	0.5623	0.4858	1.4224	1.7227
337.9	0.6148	0.4987	1.3323	1.9044
338.0	0.6688	0.5001	1.2216	2.1941
338.3	0.7104	0.5097	1.1629	2.4384
338.4	0.7262	0.5145	1.1436	2.5415
338.7	0.7321	0.5216	1.1366	2.5231
339.2	0.7955	0.5384	1.0629	3.1308
340.0	0.8293	0.5619	1.0359	3.4470
343.1	0.9390	0.6841	1.0038	6.1492

comp. (1) = C_6H_6, comp. (2) = $C_2H_2F_3OH$

Table (A.4.3): Excess refractive indices n_D^E of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 298.2 K

x	n_D^E
0.0426	0.0000
0.0767	0.0004
0.1393	0.0005
0.1795	0.0006
0.2612	0.0008
0.3502	0.0010
0.4232	0.0011
0.5001	0.0011
0.5623	0.0011
0.6148	0.0010
0.6688	0.0010
0.7104	0.0009
0.7262	0.0009
0.7321	0.0008
0.7955	0.0007
0.8293	0.0006
0.9390	0.0002

$n_D^E = [0.0044.x\,(1 - x) \pm 0.0001]$

$n_D^E\,(x = 0.500) = 0.0011 \pm 0.0001$

Table (A.4.4): Excess Gibbs function G_m^E of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr.

x	G_m^E/J.mol^{-1}	ΔG_m^E/J.mol^{-1}
0.0426	264.27	61.11
0.0767	378.14	25.38
0.1393	606.37	9.14
0.1795	708.95	-24.68
0.2612	953.30	-7.94
0.3502	1148.45	14.92
0.4232	1208.19	-7.73
0.5001	1245.81	0.50
0.5623	1225.15	-0.81
0.6148	1192.50	12.84
0.6688	1107.62	4.24
0.7104	1027.38	2.58
0.7262	992.58	2.14
0.7321	962.34	-14.62
0.7955	795.00	-15.34
0.8293	679.85	-25.29
0.9390	326.37	41.05

G_m^E (cal.)/J.mol^{-1} = [4981.21.x (1 - x) ± 22.89]

$G_m^E\,(x = 0.500) = (1246 \pm 23)$ J.mol^{-1}

Table (A.4.5): VLE data reduction:
Evaluation of WILSON parameters of
$\{(1\text{-}x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
343.2	0.0426	5.277	5.420	-2.71	1.023	1.004	1.83
341.7	0.0767	4.675	4.720	-0.96	1.016	1.013	0.27
340.0	0.1393	3.628	3.764	-3.76	1.041	1.042	-0.06
339.2	0.1795	3.353	3.311	1.25	1.043	1.068	-2.46
338.2	0.2612	2.640	2.636	0.16	1.122	1.140	-1.56
337.7	0.3502	2.089	2.140	-2.46	1.262	1.250	0.93
337.8	0.4232	1.791	1.848	-3.20	1.375	1.371	0.29
337.7	0.5001	1.574	1.615	-2.62	1.543	1.539	0.27
337.8	0.5623	1.422	1.467	-3.14	1.723	1.716	0.38
337.9	0.6148	1.332	1.363	-2.32	1.904	1.906	-0.09
338.0	0.6688	1.222	1.273	-4.20	2.194	2.155	1.80
338.3	0.7104	1.163	1.213	-4.32	2.438	2.396	1.72
338.4	0.7262	1.144	1.192	-4.27	2.542	2.503	1.51
338.7	0.7321	1.137	1.185	-4.24	2.523	2.544	-0.83
339.2	0.7955	1.063	1.114	-4.80	3.131	3.104	0.86
340.0	0.8293	1.036	1.082	-4.49	3.447	3.506	-1.71
343.1	0.9390	1.004	1.013	-0.87	6.149	5.839	5.05

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = -0.0179 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 2.93\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = -0.0051 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 1.27\ \%$$

WILSON's interaction parameters are:

$$\Delta\lambda_{12}/R = 297.07\ K$$
$$\Delta\lambda_{21}/R = 619.87\ K$$

Table (A.4.6): VLE data reduction:
evaluation of UNIQUAC parameters of
$\{(1\text{-}x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
343.2	0.0426	5.277	4.941	6.35	1.023	1.003	1.97
341.7	0.0767	4.675	4.484	4.10	1.016	1.009	0.67
340.0	0.1393	3.628	3.767	-3.81	1.041	1.032	0.95
339.2	0.1795	3.353	3.382	-0.87	1.043	1.053	-1.03
338.2	0.2612	2.640	2.747	-4.05	1.122	1.118	0.40
337.7	0.3502	2.089	2.231	-6.80	1.262	1.226	2.81
337.8	0.4232	1.791	1.909	-6.56	1.375	1.353	1.59
337.7	0.5001	1.574	1.646	-4.53	1.543	1.537	0.41
337.8	0.5623	1.422	1.478	-3.88	1.723	1.736	-0.76
337.9	0.6148	1.332	1.361	-2.17	1.904	1.952	-2.48
338.0	0.6688	1.222	1.262	-3.33	2.194	2.233	-1.79
338.3	0.7104	1.163	1.199	-3.06	2.438	2.504	-2.69
338.4	0.7262	1.144	1.177	-2.92	2.542	2.622	-3.16
338.7	0.7321	1.137	1.169	-2.86	2.523	2.666	-5.67
339.2	0.7955	1.063	1.098	-3.31	3.131	3.260	-4.13
340.0	0.8293	1.036	1.068	-3.13	3.447	3.660	-6.18
343.1	0.9390	1.004	1.009	-0.50	6.149	5.595	9.01

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0277 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 3.64\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0224 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 2.76\ \%$$

UNIQUAC interaction parameters are:

$$\Delta u_{12}/R = 183.56\ K$$
$$\Delta u_{21}/R = 107.38\ K$$

Table (A.4.7): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_2H_2F_3OH + xC_6H_6\}$ at 765.3 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	σs
Exp.	4.76	-13.65	14.61	-5.63	0.063
WILSON	4.69	-12.32	11.68	-3.94	0.014
UNIQUAC	1.81	-13.82	15.08	-5.99	0.075

Table (A.4.8): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
343.2	0.0426	1.36	0.1609	-0.0041
341.7	0.0767	0.16	0.2452	-0.0002
340.0	0.1393	-1.34	0.3281	-0.0074
339.2	0.1795	-1.24	0.3810	0.0086
338.2	0.2612	-1.23	0.4237	0.0023
337.7	0.3502	-1.09	0.4423	-0.0116
337.8	0.4232	-1.94	0.4595	-0.0126
337.7	0.5001	-1.75	0.4763	-0.0115
337.8	0.5623	-2.00	0.4858	-0.0131
337.9	0.6148	-1.88	0.4987	-0.0097
338.0	0.6688	-1.91	0.5001	-0.0188
338.3	0.7104	-2.11	0.5097	-0.0184
338.4	0.7262	-2.24	0.5145	-0.0175
338.7	0.7321	-3.46	0.5216	-0.0114
339.2	0.7955	-3.13	0.5384	-0.0154
340.0	0.8293	-4.37	0.5619	-0.0071
343.1	0.9390	-0.25	0.6841	-0.0070

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.513 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.002$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 0.018, \left|\frac{(\Delta y_1)}{N}\right| = 0.010 ; \left|\frac{(\Delta y_2)}{N}\right| = 0.010$$

Table (A.4.9): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$at 765.3 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
343.24	0.0426	2.37	0.1609	0.0033
341.70	0.0767	0.99	0.2452	0.0034
340.00	0.1393	-1.40	0.3281	-0.0130
339.17	0.1795	-1.83	0.3810	-0.0016
338.22	0.2612	-2.42	0.4237	-0.0121
337.72	0.3502	-2.39	0.4423	-0.0245
337.78	0.4232	-3.15	0.4595	-0.0206
337.70	0.5001	-2.94	0.4763	-0.0126
337.81	0.5623	-3.28	0.4858	-0.0080
337.87	0.6148	-3.34	0.4987	0.0006
338.03	0.6688	-3.58	0.5001	-0.0039
338.26	0.7104	-3.92	0.5097	-0.0009
338.38	0.7262	-4.08	0.5145	0.0007
338.73	0.7321	-5.31	0.5216	0.0070
339.19	0.7955	-4.76	0.5384	0.0025
339.99	0.8293	-5.56	0.5619	0.0081
343.13	0.9390	1.94	0.6841	-0.0187

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.842 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.002$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 3.225, \left|\frac{(\Delta y_1)}{N}\right| = 0.082 ; \left|\frac{(\Delta y_2)}{N}\right| = 0.082$$

Table (A.4.10): Evaluation of relative volatility α_{12} of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$ at 765.3 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0426	4.3095	4.4410	4.2046
0.0767	3.9105	3.9148	3.8390
0.1393	3.0172	3.1196	3.1986
0.1795	2.8135	2.7123	2.8326
0.2612	2.0795	2.0600	2.1848
0.3502	1.4716	1.5422	1.6244
0.4232	1.1587	1.2189	1.2586
0.5001	0.9091	0.9520	0.9562
0.5623	0.7354	0.7750	0.7593
0.6148	0.6233	0.6480	0.6218
0.6688	0.4954	0.5341	0.5032
0.7104	0.4238	0.4562	0.4253
0.7262	0.3996	0.4286	0.3984
0.7321	0.3990	0.4177	0.3879
0.7955	0.2998	0.3191	0.2968
0.8293	0.2640	0.2717	0.2555
0.9390	0.1407	0.1453	0.1536

Table (A.4.11): Reduction of VLE of $\{(1-x)C_2H_2F_3OH + xC_6H_6\}$ at 765.3 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
343.24	0.0426	0.981	0.963	0.960	0.964
341.70	0.0767	0.977	0.963	0.960	0.963
340.00	0.1393	0.973	0.964	0.958	0.961
339.17	0.1795	0.971	0.965	0.958	0.961
338.22	0.2612	0.969	0.965	0.958	0.960
337.72	0.3502	0.969	0.965	0.958	0.960
337.78	0.4232	0.968	0.966	0.958	0.960
337.70	0.5001	0.967	0.966	0.958	0.960
337.81	0.5623	0.967	0.967	0.958	0.959
337.87	0.6148	0.967	0.967	0.958	0.960
338.03	0.6688	0.967	0.967	0.958	0.960
338.26	0.7104	0.967	0.968	0.958	0.960
338.38	0.7262	0.966	0.968	0.958	0.960

338.73	0.7321	0.966	0.968	0.958	0.959
339.19	0.7955	0.966	0.969	0.958	0.960
339.99	0.8293	0.966	0.970	0.958	0.959
343.13	0.9390	0.964	0.976	0.961	0.962

Table (A.4.12): Summary of physico-chemical properties of {(1-x) $C_2H_2F_3OH$+xC_6H_6} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	X_{az}	exp.	-	-	4.76	6.46	8.84
exp.	337.8	0.4681	WILSON	279.07	619.87	4.69	5.97	9.15
cal.	-	0.4549	UNIQUAC	183.56	107.38	4.81	6.42	8.62

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
6.77	WILSON	0.513	0.002
	UNIQUAC	0.842	0.002

Correlated $X_m^E(T, x)$:

x	Method	G_m^E ($J.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	S_m^E ($J.K^{-1}.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
x_{az} = 0.4681	WILSON	1269	729	-1.60	2.52
T_{az} = 337.8 K	UNIQUAC	1301	1109	-0.60	1.02
x = 0.500	WILSON	1279	742	-1.60	2.57
T = 338.1 K	UNIQUAC	1313	1146	-0.49	0.97

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5108	313.2 K, 0.513	338.1 K, 0.500
	n_D^E	V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	G_m^E ($J.mol^{-1}$)
	0.0011	1.0561	1909	1245

G_m^E(cal.)/$J.mol^{-1}$ = [4981.21 x(1 - x) ± 22.89]

n_D^E = [0.0044 x(1 - x) ± 0.0001]

Literature X_m^E(T = 298.15 K, x = 0.500):

V_m^E ($cm^3.mol^{-1}$)	H_m^E ($J.mol^{-1}$)	$C_{p,m}^E$ ($J.K^{-1}.mol^{-1}$)
1.1392 ± 0.009[71] 1.1005 ± 0.006[72]	1569 ± 0.002[71] (298.15 K) 1748 ± 0.001[72] (318.15K)	13.06 ± 0.1[71]

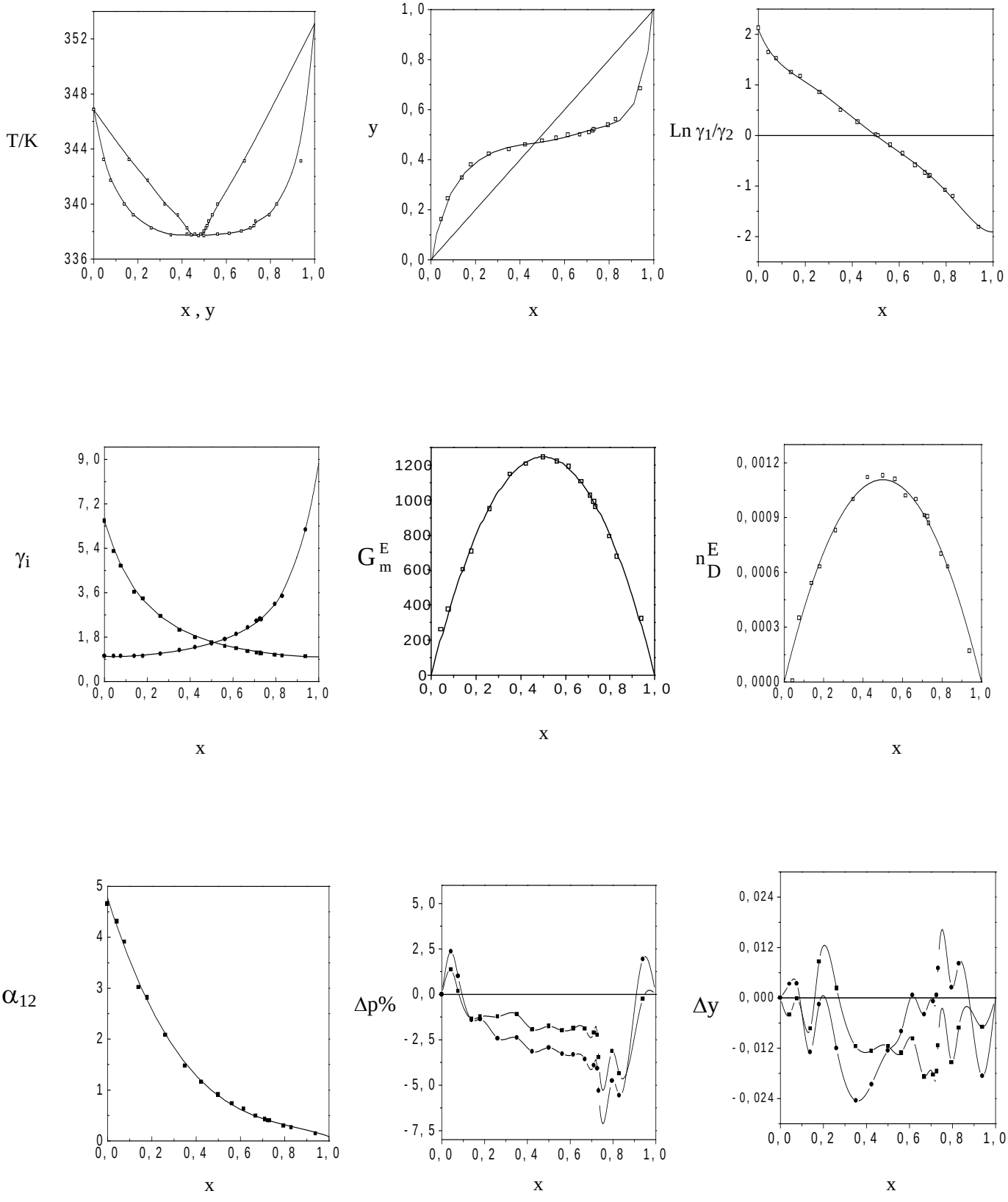


Figure (A. 4): Vapour-Liquid Equilibria of $\{(1-x)C_2H_2F_3OH+xC_6H_6\}$ at 102 kPa

Table (A.5.1): Refractive indices n_D of VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$ at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.2870	0.0000	1.2870	0.0000
1.2932	0.0233	1.3025	0.0593
1.3042	0.0665	1.3200	0.1299
1.3156	0.1119	1.3307	0.1735
1.3347	0.1904	1.3370	0.1998
1.3953	0.4597	1.3487	0.2493
1.4180	0.5711	1.3525	0.2659
1.3477	0.6732	1.3548	0.2759
1.4484	0.7311	1.3595	0.2963
1.4642	0.8213	1.3560	0.2807
1.4739	0.8790	1.3673	0.3307
1.4751	0.8865	1.3710	0.3478
1.4815	0.9269	1.3862	0.4170
1.4870	0.9605	1.4120	0.5412
1.4894	0.9763	1.4340	0.6534
1.4930	1.0000	1.4930	1.0000

Table (A.5.2): Experimental results: VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$ at 764.0 torr.

T/K	x	y	γ_1	γ_2
346.5	0.0233	0.0593	8.3418	0.9845
345.6	0.0665	0.1299	6.5814	0.9879
345.2	0.1119	0.1735	5.2824	1.0021
345.5	0.1904	0.1998	3.5390	1.0546
345.8	0.4597	0.2493	1.8038	1.4658
346.2	0.5711	0.2659	1.5228	1.7747
346.8	0.6732	0.2759	1.3149	2.2507
347.0	0.7311	0.2963	1.2885	2.6357
347.8	0.8213	0.2807	1.0593	3.9364
351.9	0.8790	0.3307	1.0071	4.6157
352.6	0.8865	0.3478	1.0263	4.6798
356.5	0.9269	0.4170	1.0325	5.6459
362.9	0.9605	0.5412	1.0476	6.5635
370.4	0.9763	0.6534	0.9860	6.4310

comp. (1) = C_7H_8, comp. (2) = $C_2H_2F_3OH$

Table (A.5.3): Excess refractive indices n_D^E of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$ at 298.2 K

x	n_D^E
0.0233	0.0014
0.0665	0.0035
0.1119	0.0055
0.1904	0.0085
0.4597	0.0136
0.5711	0.0134
0.6732	0.0120
0.7311	0.0108
0.8213	0.0080
0.8790	0.0058
0.8865	0.0055
0.9269	0.0036
0.9605	0.0021
0.9763	0.0013

$$n_D^E = [x\,(1 - x)\{0.0549 + 0.0005\,(1 - 2x)\} \pm 0.0001]$$

$$n_D^E\,(x = 0.500) = 0.0137 \pm 0.0001$$

Table (A.5.4): Excess Gibbs function G_m^E of $\{(1-x)C_2H_2F_3OH+xC_7H_8\}$ at 764.0 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0233	98.54	-43.53
0.0665	327.32	-55.54
0.1119	539.93	-65.10
0.1904	814.92	-105.83
0.4597	1373.69	112.45
0.5711	1399.66	38.41
0.6732	1295.70	0.92
0.7311	1286.46	162.77
0.8213	844.85	-139.38
0.8790	559.78	-151.87
0.8865	581.05	76.04
0.9269	462.92	-13.50
0.9605	359.06	43.01
0.9763	93.32	-81.41

$$G_m^E\,(\text{cal.})/\text{J.mol}^{-1} = [x\,(1 - x)\{5410.19 + 873.48(1- 2x)\} \pm 90.15]$$

$$G_m^E\,(x = 0.500) = (1352.53 \pm 90)\ \text{J.mol}^{-1}$$

Table (A.5.5): VLE data reduction:
Evaluation of WILSON parameters of
$\{(1\text{-}x)C_2H_2F_3OH + xC_7H_8\}$at 764.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
346.5	0.0233	8.342	8.224	1.41	0.984	1.002	-1.79
345.6	0.0655	6.581	6.268	4.76	0.988	1.015	-2.72
345.2	0.1119	5.282	5.144	2.62	1.002	1.033	-3.12
345.5	0.1904	3.539	3.511	0.80	1.055	1.102	-4.51
345.8	0.4597	1.804	1.735	3.79	1.466	1.532	-4.54
346.2	0.5711	1.523	1.440	5.42	1.775	1.867	-5.20
346.8	0.6732	1.315	1.256	4.48	2.251	2.338	-3.87
347.0	0.7311	1.288	1.177	8.64	2.636	2.723	-3.30
347.8	0.8213	1.059	1.084	-2.29	3.936	3.627	7.87
351.9	0.8790	1.007	1.040	-3.31	4.616	4.505	2.39
352.6	0.8865	1.026	1.036	-0.93	4.680	4.646	0.73
356.5	0.9269	1.033	1.016	1.64	5.646	5.547	1.76
362.9	0.9605	1.048	1.005	4.10	6.563	6.467	1.48
370.4	0.9763	0.986	1.002	-1.59	6.431	6.859	-6.65

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = -0.021 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 3.27\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.023 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 3.57\ \%$$

WILSON's interaction parameters are:

$$\Delta\lambda_{12}/R = 362.38\ K$$
$$\Delta\lambda_{21}/R = 655.52\ K$$

Table (A.5.6): VLE data reduction:
evaluation of UNIQUAC parameters of
$\{(1\text{-}x)C_2H_2F_3OH + xC_7H_8\}$at 764.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
346.5	0.0233	8.342	7.254	13.04	0.984	1.001	-1.70
345.6	0.0655	6.581	6.089	7.48	0.988	1.010	-2.20
345.2	0.1119	5.282	5.269	0.25	1.002	1.023	-2.10
345.5	0.1904	3.539	3.805	-7.52	1.055	1.082	-2.55
345.8	0.4597	1.804	1.799	0.27	1.466	1.548	-5.58
346.2	0.5711	1.523	1.448	4.89	1.775	1.946	-9.68
346.8	0.6732	1.315	1.241	5.62	2.251	2.506	-11.30
347.0	0.7311	1.288	1.158	10.12	2.636	2.947	-11.79
347.8	0.8213	1.059	1.068	-0.78	3.936	3.897	1.00
351.9	0.8790	1.007	1.030	-2.30	4.616	4.676	-1.31
352.6	0.8865	1.026	1.027	-0.02	4.680	4.790	-2.35
356.5	0.9269	1.033	1.011	2.10	5.646	5.459	3.31
362.9	0.9605	1.048	1.003	4.25	6.563	6.012	8.40
370.4	0.9763	0.986	1.001	-1.53	6.431	6.158	4.24

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.047 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 4.30\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.051 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 4.83\ \%$$

UNIQUAC interaction parameters are:

$$\Delta u_{12}/R = 204.65\ K$$
$$\Delta u_{21}/R = 93.63\ K$$

Table (A.5.7): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_2H_2F_3OH + xC_7H_8\}$ at 764.0 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	b_4	σs
Exp.	2.97	-15.27	34.20	-35.16	13.34	0.017
Wilson	2.56	-10.55	18.94	-16.48	5.58	0.005
UNIQUAC	2.81	-14.74	33.67	-35.10	13.43	0.029

Table (A.5.8): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$at 764.0 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
346.5	0.0233	-1.58	0.0593	0.0024
345.6	0.0665	-1.79	0.1299	0.0087
345.2	0.1119	-2.00	0.1735	0.0138
345.5	0.1904	-3.83	0.1998	0.0042
345.8	0.4597	-2.84	0.2493	0.0085
346.2	0.5711	-2.82	0.2659	0.0137
346.8	0.6732	-2.15	0.2759	0.0105
347.0	0.7311	-0.48	0.2963	0.0201
347.8	0.8213	3.99	0.2807	-0.0246
351.9	0.8790	-1.37	0.3307	-0.0126
352.6	0.8865	-1.85	0.3478	-0.0030
356.5	0.9269	-0.69	0.4170	0.0046
362.9	0.9605	0.39	0.5412	0.0167
370.4	0.9763	-5.96	0.6534	0.0230

With:

$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.723$; $\left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.003$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 2.267$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.011$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.011$

0.9269	0.0564	0.0554	0.0574
0.9605	0.0485	0.0454	0.0505
0.9763	0.0458	0.0414	0.0482

Table (A.5.9): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$at 764.0 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
346.5	0.0233	-1.04	0.0593	0.0065
345.6	0.0665	-1.38	0.1299	0.0083
345.2	0.1119	-2.05	0.1735	0.0059
345.5	0.1904	-4.39	0.1998	-0.0116
345.8	0.4597	-5.07	0.2493	0.0068
346.2	0.5711	-6.86	0.2659	0.0234
346.8	0.6732	-7.76	0.2759	0.0283
347.0	0.7311	-6.35	0.2963	0.0402
347.8	0.8213	-0.26	0.2807	-0.0069
351.9	0.8790	-2.53	0.3307	-0.0049
352.6	0.8865	-2.44	0.3478	0.0027
356.5	0.9269	2.14	0.4170	-0.0042
362.9	0.9605	5.71	0.5412	-0.0102
370.4	0.9763	-0.10	0.6534	-0.0115

With:

$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 1.128$; $\left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.004$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 3.434$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.012$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.012$

Table (A.5.10): Evaluation of relative volatility α_{12} of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$ at 764.0 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0233	2.6425	2.5291	2.3367
0.0665	2.0957	1.9356	1.9433
0.1119	1.6661	1.5084	1.5280
0.1904	1.0617	1.0340	1.1399
0.4597	0.3903	0.3728	0.3763
0.5711	0.2720	0.2533	0.2404
0.6732	0.1850	0.1754	0.1597
0.7311	0.1549	0.1404	0.1266
0.8213	0.0849	0.0956	0.0878
0.8790	0.0680	0.0720	0.0695
0.8865	0.0683	0.0692	0.0675

Table (A.5.11): Reduction of VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_8\}$at 764.0 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
346.54	0.0233	0.975	0.964	0.943	0.964
345.63	0.0665	0.970	0.964	0.942	0.964
345.24	0.1119	0.967	0.965	0.942	0.964
345.48	0.1904	0.966	0.965	0.941	0.963
345.79	0.4597	0.963	0.966	0.941	0.964
346.24	0.5711	0.963	0.967	0.942	0.964
346.77	0.6732	0.962	0.967	0.943	0.964
347.00	0.7311	0.961	0.968	0.944	0.965
347.75	0.8213	0.962	0.968	0.947	0.967

351.94	0.8790	0.962	0.970	0.946	0.967
352.60	0.8865	0.961	0.971	0.946	0.967
356.45	0.9269	0.960	0.974	0.949	0.969
362.90	0.9605	0.959	0.980	0.953	0.971
370.44	0.9763	0.960	0.985	0.954	0.972

Table (A.5.12):Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$+ xC_7H_8} at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	exp.	-	-	2.97	9.30	7.35
exp.	345.4	0.2003	WILSON	362.38	655.52	2.56	8.19	9.43
cal.	-	0.1811	UNIQUAC	204.65	93.63	2.81	10.80	8.83

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
16.25	WILSON	0.723	0.003
	UNIQUAC	1.128	0.004

Correlated X_m^E(T, x):

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.2003	WILSON	964	529	-1.20	1.74
T_{az} = 345.4 K	UNIQUAC	966	556	-1.19	0.75
x = 0.500	WILSON	1424	841	-1.61	2.88
T = 360.8 K	UNIQUAC	1497	1312	-0.51	0.92

Experimental X_m^E(T, x):

T, x	298.2 K, 0.500	298.2 K, 0.5024	313.2 K, 0.499	360.8 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	0.0137	1.0249	1656	1353

G_m^E(calc.)/J.mol^{-1} = [x (1 - x){5410.19 + 873.48 (1 - 2x)} ± 90.15]

n_D^E = [x (1 - x){0.0549 + 0.0005 (1 - 2x) } ± 0.0001]

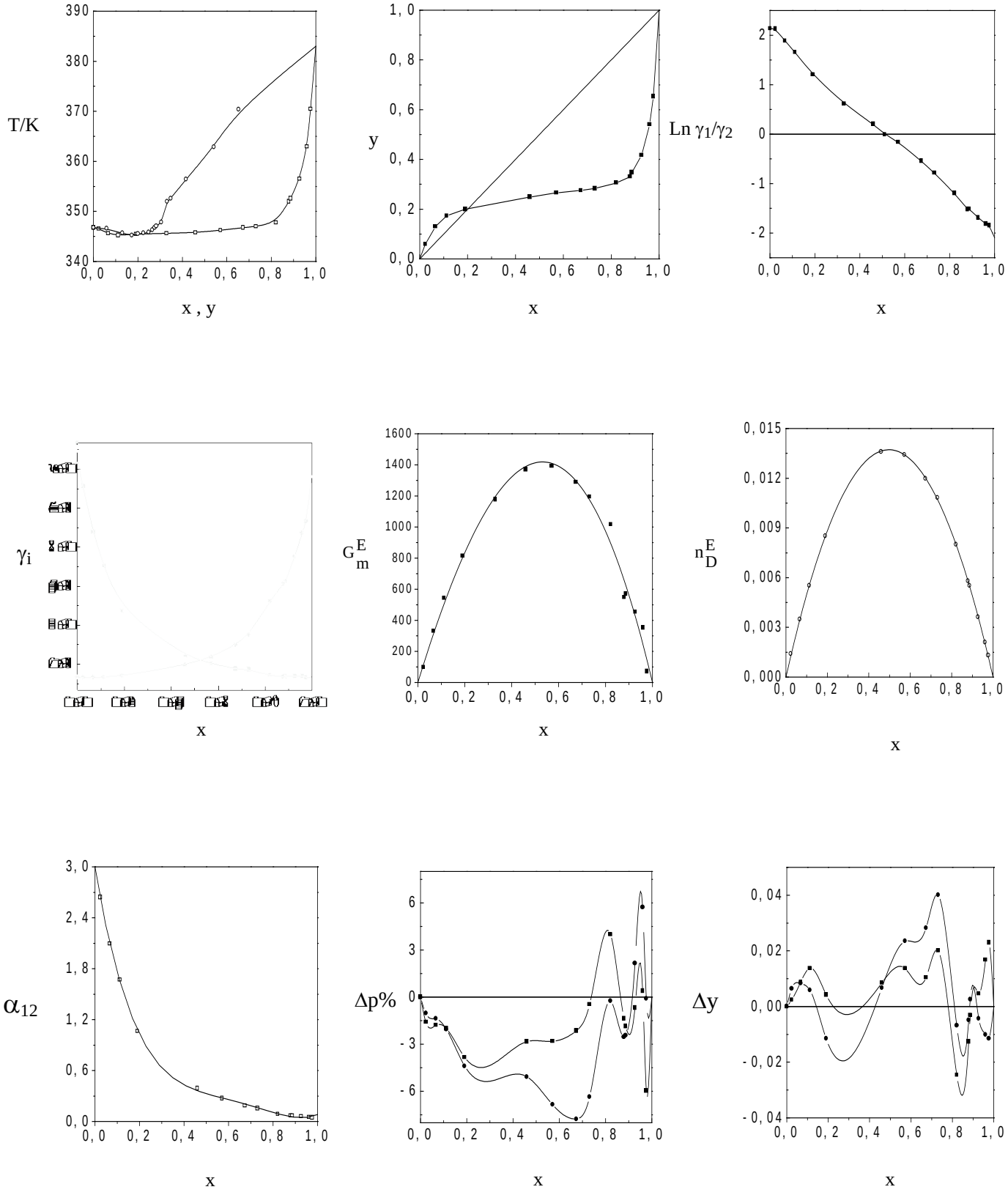


Figure (A. 5): Vapour-Liquid Equilibria of {(1-x)$C_2H_2F_3OH$+xC_7H_8} at 102 kPa

Table (A.6.1): Refractive indices n_D of VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.2910	0.0000	1.2910	0.0000
1.2940	0.0184	1.2990	0.0493
1.3000	0.0543	1.3100	0.1149
1.3088	0.1087	1.3178	0.1663
1.3360	0.2890	1.3300	0.2467
1.3540	0.4226	1.3334	0.2713
1.3710	0.5634	1.3350	0.2836
1.3810	0.6552	1.3386	0.3077
1.3860	0.7044	1.3415	0.3290
1.3911	0.7572	1.3450	0.3511
1.3942	0.7913	1.3480	0.3763
1.4027	0.8904	1.3600	0.4723
1.4038	0.9042	1.3646	0.5091
1.4068	0.9434	1.3755	0.6045
1.4080	0.9617	1.3830	0.6752
1.4100	0.9721	1.3890	0.7336
1.4125	1.0000	1.4125	1.0000

Table (A.6.2): Experimental results: VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr.

T/K	x	y	γ_1	γ_2
346.1	0.0184	0.0493	6.9309	1.0064
345.3	0.0543	0.1149	5.6004	1.0036
345.0	0.1087	0.1663	4.0749	1.0147
344.7	0.2890	0.2467	2.2910	1.1673
345.1	0.4226	0.2713	1.6967	1.3693
345.6	0.5634	0.2836	1.3048	1.7433
346.2	0.6552	0.3077	1.1908	2.0847
346.7	0.7044	0.3290	1.1628	2.3124
347.4	0.7572	0.3511	1.1254	2.6499
348.4	0.7913	0.3763	1.1162	2.8581
354.8	0.8904	0.4723	1.0039	3.6324
357.5	0.9042	0.5091	0.9742	3.5013
362.0	0.9434	0.6045	0.9593	4.0787
365.1	0.9617	0.6752	0.9562	4.4670
367.5	0.9721	0.7336	0.9540	4.6399

comp. (1) = $C_7H_5F_3$, comp. (2) = $C_2H_2F_3OH$

Table (A.6.3): Excess refractive indices n_D^E of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 298.2 K

x	n_D^E
0.0184	0.0008
0.0543	0.0024
0.1087	0.0046
0.2890	0.0099
0.4226	0.0117
0.5634	0.0115
0.6552	0.0104
0.7044	0.0094
0.7572	0.0081
0.7913	0.0071
0.8904	0.0035
0.9042	0.0029
0.9434	0.0012
0.9617	0.0002
0.9721	0.0009

$$n_D^E = [x\,(1 - x)\{0.0486 + 0.0055\,(1 - 2x) - 0.0133(1-2x)^2\} \pm 0.0003]$$

$$n_D^E\,(x = 0.500) = 0.0123 \pm 0.0003$$

Table (A.6.4): Excess Gibbs function G_m^E of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0184	120.58	45.03
0.0543	278.21	33.54
0.1087	475.36	-32.84
0.2890	1001.89	-26.01
0.4226	1161.71	53.99
0.5634	1127.90	-6.74
0.6552	1058.47	-46.87
0.7044	1020.50	-23.69
0.7572	942.00	16.78
0.7913	856.93	41.66
0.8904	427.09	51.63
0.9042	286.54	-22.19
0.9434	121.61	-13.41
0.9617	43.41	-27.08
0.9721	-9.17	-50.47

$$G_m^E\,(\text{cal.})/\text{J.mol}^{-1} = [4727.50x\,(1 - x) \pm 83.19]$$

$$G_m^E\,(x = 0.500) = (1281.88 \pm 83)\ \text{J.mol}^{-1}$$

Table (A.6.5): VLE data reduction: Evaluation of WILSON parameters of $\{(1\text{-}x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
346.1	0.0184	6.931	6.803	1.85	1.006	1.001	0.52
345.3	0.0543	5.600	5.472	2.29	1.004	1.009	-0.58
345.0	0.1087	4.075	4.157	-2.01	1.015	1.034	-1.93
344.7	0.2890	2.291	2.248	1.86	1.167	1.199	-2.73
345.1	0.4226	1.697	1.697	1.03	1.369	1.407	-2.74
345.6	0.5634	1.305	1.347	-3.21	1.743	1.741	0.13
346.2	0.6552	1.191	1.209	-1.49	2.085	2.059	1.26
346.7	0.7044	1.163	1.152	0.94	2.312	2.277	1.55
347.4	0.7572	1.125	1.102	2.05	2.650	2.561	3.37
348.4	0.7913	1.116	1.076	3.62	2.858	2.777	2.84
354.8	0.8904	1.004	1.021	-1.72	3.632	3.586	1.28
357.5	0.9042	0.974	1.016	-4.30	3.501	3.709	-5.93
362.0	0.9434	0.959	1.006	-4.83	4.079	4.136	-1.42
365.1	0.9617	0.956	1.003	-4.85	4.467	4.348	2.66
367.5	0.9721	0.954	1.001	-4.97	4.640	4.464	3.79

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.014 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 2.73\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.010 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 2.18\ \%$$

WILSON's interaction parameters are:

$$\Delta\lambda_{12}/R = 282.90\ K$$
$$\Delta\lambda_{21}/R = 535.45\ K$$

Table (A.6.7): Evaluation of relative volatility α_{12} of $\{(1\text{-}x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	b_4	σs
Exp.	2.98	-14.87	33.82	-35.83	14.04	0.044
Wilson	2.86	-12.06	-21.02	5.79	7.45	0.010
UNIQUAC	3.04	-15.50	-38.08	35.20	14.94	0.038

Table (A.6.6): VLE data reduction: evaluation of UNIQUAC parameters of $\{(1\text{-}x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
346.1	0.0184	6.931	6.403	7.62	1.006	1.001	0.56
345.3	0.0543	5.600	5.466	2.40	1.004	1.007	-0.33
345.0	0.1087	4.075	4.366	-7.15	1.015	1.027	-1.24
344.7	0.2890	2.291	2.397	-4.61	1.167	1.191	-1.99
345.1	0.4226	1.697	1.733	-2.16	1.369	1.422	-3.84
345.6	0.5634	1.305	1.351	-3.54	1.743	1.808	-3.71
346.2	0.6552	1.191	1.200	-0.81	2.085	2.170	-4.07
346.7	0.7044	1.163	1.142	1.83	2.312	2.410	-4.23
347.4	0.7572	1.125	1.092	2.97	2.650	2.712	-2.35
348.4	0.7913	1.116	1.066	4.46	2.858	2.932	-2.57
354.8	0.8904	1.004	1.017	-1.32	3.632	3.669	-1.00
357.5	0.9042	0.974	1.013	-3.97	3.501	3.762	-7.46
362.0	0.9434	0.959	1.004	-4.70	4.079	4.091	-0.30
365.1	0.9617	0.956	1.002	-4.79	4.467	4.239	5.11
367.5	0.9721	0.954	1.001	-4.93	4.640	4.312	7.06

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.027 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 3.82\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.021 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 3.05\ \%$$

UNIQUAC interaction parameters are:

$$\Delta u_{12}/R = 179.18\ K$$
$$\Delta u_{21}/R = 58.60\ K$$

Table (A.6.8): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
346.1	0.0184	0.44	0.0493	-0.0010
345.3	0.0543	-0.65	0.1149	-0.0001
345.0	0.1087	-2.58	0.1663	-0.0038
344.7	0.2890	-2.39	0.2467	0.0047
345.1	0.4226	-2.57	0.2713	0.0037
345.6	0.5634	-1.67	0.2836	-0.0103
346.2	0.6552	-0.41	0.3077	-0.0090
346.7	0.7044	0.56	0.3290	-0.0042
347.4	0.7572	2.18	0.3511	-0.0055
348.4	0.7913	2.41	0.3763	0.0000
354.8	0.8904	-1.06	0.4723	-0.0078
357.5	0.9042	-6.29	0.5091	0.0039
362.0	0.9434	-4.48	0.6045	-0.0064
365.1	0.9617	-3.25	0.6752	-0.0138
367.5	0.9721	-3.38	0.7336	-0.0141

With:

$\left(\frac{\sum(\Delta p)^2}{N}\right)^{1/2} = 0.718$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.018$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 2.287$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.005$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.005$

Table (A.6.10): Evaluation of relative volatility α_{12} of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$
at 764.0 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0184	2.7664	2.8255	2.6604
0.0543	2.2609	2.2631	2.2653
0.1087	1.6356	1.3806	1.7780
0.2890	0.8057	0.7854	0.8439
0.4226	0.5087	0.4992	0.5100
0.5634	0.3068	0.3226	0.3118
0.6552	0.2339	0.2439	0.2302
0.7044	0.2058	0.2097	0.1965
0.7572	0.1735	0.1777	0.1664
0.7913	0.1591	0.1591	0.1496
0.8904	0.1102	0.1137	0.1107
0.9042	0.1099	0.1082	0.1063
0.9434	0.0917	0.0942	0.0951
0.9617	0.0828	0.0882	0.0905
0.9721	0.0790	0.0851	0.0880

Table (A.6.9): VLE data reduction of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
346.1	0.0184	0.78	0.0493	0.0018
345.3	0.0543	-0.40	0.1149	-0.0002
345.0	0.1087	-2.89	0.1663	-0.0119
344.7	0.2890	-3.52	0.2467	-0.0087
345.1	0.4226	-4.34	0.2713	-0.0005
345.6	0.5634	-4.67	0.2836	-0.0033
346.2	0.6552	-4.07	0.3077	0.0034
346.7	0.7044	-3.21	0.3290	0.0101
347.4	0.7572	-1.38	0.3511	0.0095
348.4	0.7913	-0.81	0.3763	0.0144
354.8	0.8904	-2.13	0.4723	-0.0012
357.5	0.9042	-6.91	0.5091	0.0082
362.0	0.9434	-3.93	0.6045	-0.0087
365.1	0.9617	-2.35	0.6752	-0.0191
367.5	0.9721	-2.42	0.7336	-0.0204

With:

$\left(\frac{\sum(\Delta p)^2}{N}\right)^{1/2} = 0.871$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.026$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 2.921$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.081$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.081$

Table (A.6.11): Reduction of VLE of $\{(1-x)C_2H_2F_3OH + xC_7H_5F_3\}$at 764.0 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
346.11	0.0184	0.975	0.964	0.942	0.967
345.32	0.0543	0.970	0.964	0.941	0.966
345.04	0.1087	0.967	0.965	0.940	0.966
344.68	0.2890	0.962	0.966	0.940	0.966
345.08	0.4226	0.960	0.966	0.940	0.966
345.62	0.5634	0.960	0.967	0.941	0.966
346.22	0.6552	0.959	0.968	0.942	0.967
346.72	0.7044	0.958	0.968	0.943	0.967
347.43	0.7572	0.957	0.969	0.944	0.968

348.38	0.7913	0.957	0.970	0.945	0.969
354.75	0.8904	0.956	0.975	0.947	0.970
357.50	0.9042	0.956	0.977	0.945	0.970
362.03	0.9434	0.955	0.982	0.949	0.972
365.08	0.9617	0.955	0.985	0.951	0.973
367.53	0.9721	0.955	0.988	0.952	0.974

Table(A.6.12):Summary of physico-chemical properties of {(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$}at102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	exp.	-	-	2.98	7.43	5.24
exp.	344.8	0.2186	WILSON	282.90	535.45	2.86	6.35	6.14
cal.	-	0.2284	UNIQUAC	179.18	58.60	3.04	8.17	5.37

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
13.28	WILSON	0.718	0.018
	UNIQUAC	0.871	0.026

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.2186	WILSON	888	582	-0.89	1.71
T_{az} = 344.8 K	UNIQUAC	942	509	-1.26	0.65
x = 0.500	WILSON	1218	881	-0.95	2.36
T = 356.2 K	UNIQUAC	1312	1178	-0.38	0.60

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5054	313.2 K, 0.501	356.2 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	0.0123	-0.2588	1830	1281

G_m^E(cal.)/J.mol^{-1} = [4727.50 x(1 - x) ± 83.19]

n_D^E = [x (1 - x){0.0486 + 0.0055(1 - 2x) – 0.0133(1 – 2x)^2 } ± 0.0004]

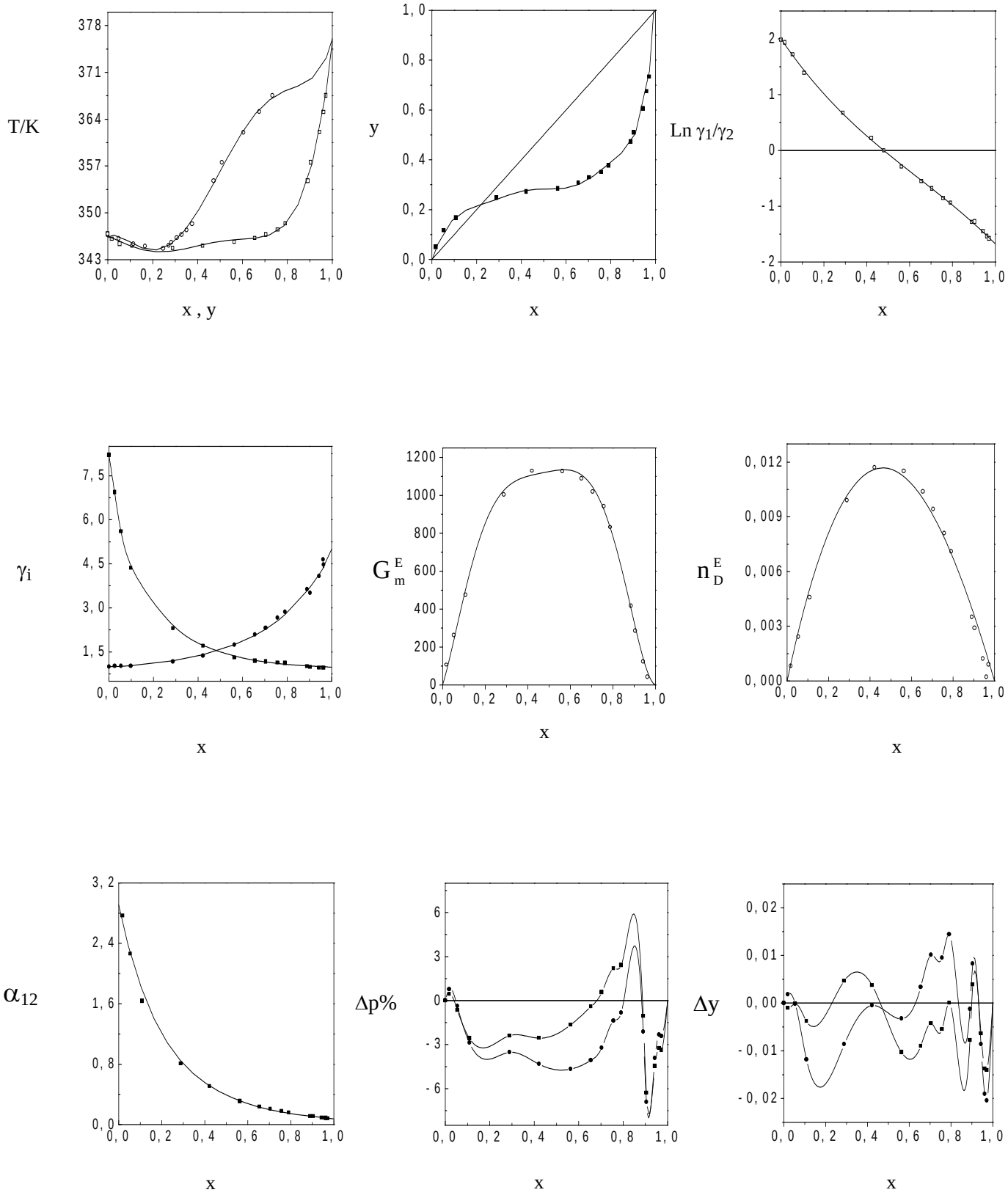


Figure (A. 6): Vapour-Liquid Equilibria of $\{(1\text{-}x)C_2H_2F_3OH+xC_7H_5F_3\}$ at 102 kPa

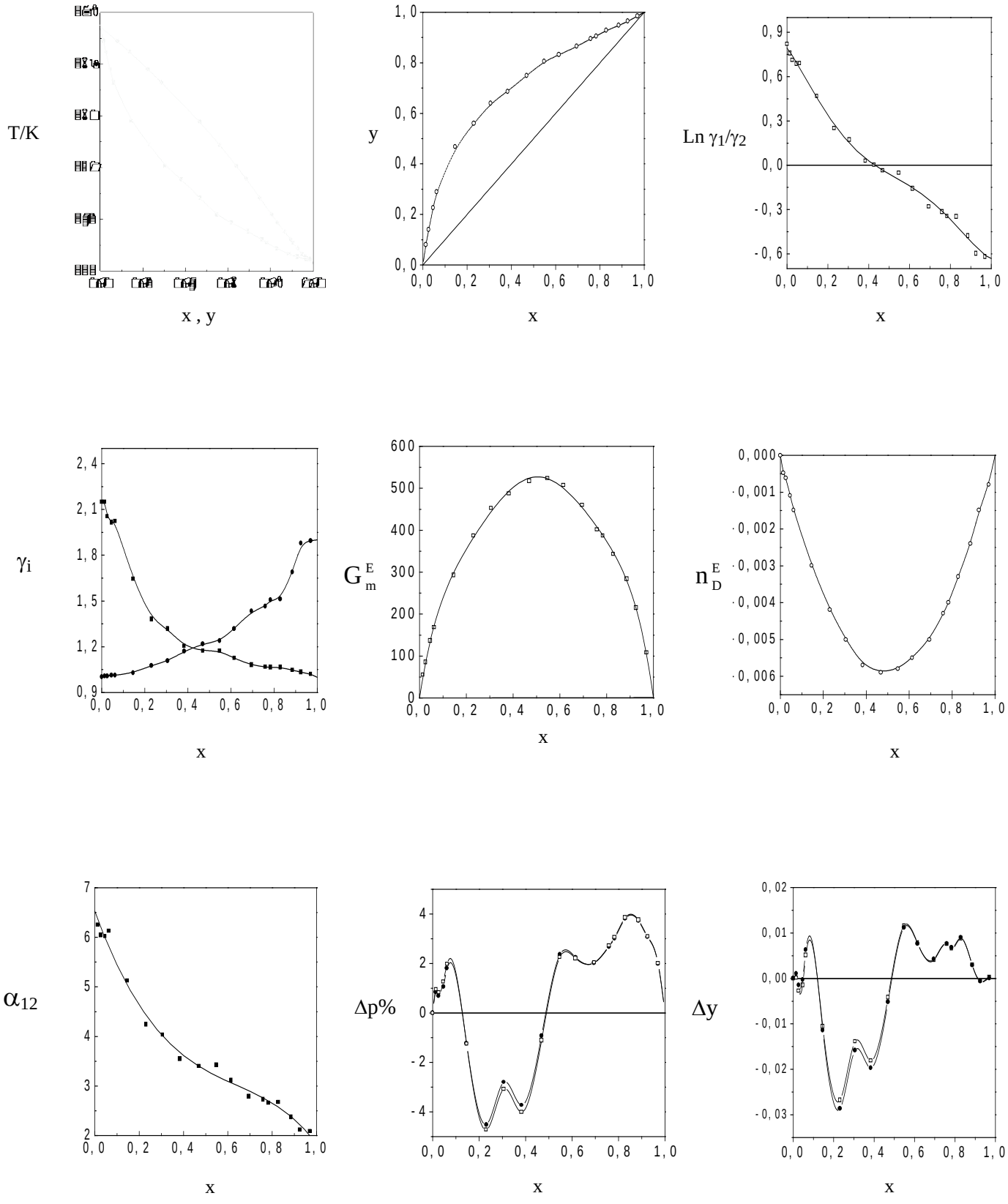


Figure (A. 7) : Vapour-Liquid Equilibria of {(1-x)$C_7H_5F_3$+x$CHCL_3$} at 100 kPa

Table (A.8.1): Refractive indices n_D of VLE of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.4140	0.0000	1.4140	0.0000
1.4110	0.0303	1.4057	0.2233
1.4090	0.1132	1.3955	0.4759
1.4040	0.2724	1.3895	0.5923
1.4000	0.3650	1.3873	0.6311
1.3960	0.4644	1.3857	0.6588
1.3910	0.5654	1.3840	0.6889
1.3872	0.6343	1.3838	0.6881
1.3827	0.7088	1.3827	0.7096
1.3793	0.7634	1.3813	0.7308
1.3758	0.8161	1.3800	0.7600
1.3724	0.8654	1.3777	0.7881
1.3705	0.8919	1.3760	0.8134
1.3679	0.9280	1.3723	0.8676
1.3648	0.9694	1.3677	0.9307
1.3620	1.0000	1.3620	1.0000

Table (A.8.2): Experimental results: VLE of {(1-x) $C_7H_5F_3$ + x C_2H_5OH } at 772.5 torr.

T/K	x	y	γ_1	γ_2
368.1	0.0303	0.2233	4.1968	1.0032
356.0	0.1132	0.4759	3.6508	1.0776
351.3	0.2724	0.5923	2.2456	1.1961
349.4	0.3650	0.6311	1.9195	1.3236
349.2	0.4644	0.6588	1.5855	1.4641
348.8	0.5654	0.6889	1.3817	1.6712
348.6	0.6343	0.6881	1.2400	2.0043
348.5	0.7088	0.7096	1.1480	2.3556
348.7	0.7634	0.7308	1.0883	2.6744
348.8	0.8161	0.7600	1.0537	3.0652
349.1	0.8654	0.7881	1.0176	3.6699
349.5	0.8919	0.8134	1.0026	3.9798
350.0	0.9280	0.8676	1.0070	4.1913
350.0	0.9694	0.9307	1.0175	5.1263

comp. (1) = C_2H_5OH, comp. (2) = $C_7H_5F_3$

Table (A.8.3): Excess refractive indices n_D^E of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 298.2 K

x	n_D^E
0.0303	0.0008
0.1132	0.0029
0.2724	0.0057
0.3650	0.0068
0.4644	0.0072
0.5654	0.0068
0.6343	0.0053
0.7088	0.0049
0.7634	0.0045
0.8161	0.0035
0.8654	0.0028
0.8919	0.0021
0.9280	0.0011
0.9694	0.0010

$n_D^E = [x (1 - x)\{0.0270 + 0.0061 (1 - 2x) \} \pm 0.0003]$

$n_D^E (x = 0.500) = 0.0068 \pm 0.0003$

Table (A.8.4): Excess Gibbs function G_m^E of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0303	142.62	-37.82
0.1132	630.17	45.06
0.2724	1024.34	-34.33
0.3650	1208.50	20.22
0.4644	1214.20	-17.70
0.5654	1177.43	-10.74
0.6343	1132.40	21.31
0.7088	1006.33	21.33
0.7634	861.94	-1.41
0.8161	721.25	0.24
0.8654	551.78	-12.18
0.8919	440.53	-28.77
0.9280	319.23	-8.82
0.9694	194.61	47.25

G_m^E (cal.)/J.mol^{-1} = [x (1 - x){4904.51 + 624.56 (1 - 2x) + 736.79 (1 - 2x)^2} ± 29.66]

$G_m^E (x = 0.500) = (1226 \pm 30)$ J.mol^{-1}

Table (A.8.5): VLE data reduction:
Evaluation of WILSON parameters of
{(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
368.1	0.0303	4.197	4.503	-7.29	1.003	1.002	0.14
356.0	0.1132	3.651	3.535	3.16	1.078	1.025	4.91
351.3	0.2724	2.246	2.318	-3.23	1.196	1.136	5.00
349.4	0.3650	1.919	1.911	0.44	1.324	1.246	5.83
349.2	0.4644	1.586	1.604	-1.18	1.464	1.411	3.60
348.8	0.5654	1.382	1.384	-0.17	1.671	1.652	1.16
348.6	0.6343	1.240	1.271	-2.49	2.004	1.878	6.29
348.5	0.7088	1.148	1.174	-2.28	2.356	2.209	6.22
348.7	0.7634	1.088	1.118	-2.70	2.674	2.534	5.23
348.8	0.8161	1.054	1.073	-1.88	3.065	2.949	3.80
349.1	0.8654	1.018	1.041	-2.30	3.670	3.466	5.56
349.5	0.8919	1.003	1.027	-2.45	3.980	3.815	4.14
350.0	0.9280	1.007	1.013	-0.56	4.191	4.405	-5.09
350.4	0.9694	1.018	1.002	1.48	5.126	5.311	-3.60

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.011 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 2.26\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.030 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 4.33\ \%$$

WILSON's interaction parameters are:

$\Delta\lambda_{12}/R$ = 667.39 K
$\Delta\lambda_{21}/R$ = 105.14 K

Table (A.8.6): VLE data reduction:
evaluation of UNIQUAC parameters of
{(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
368.1	0.0303	4.863	4.641	4.56	1.003	1.002	0.16
356.00	0.1132	3.651	3.720	-1.90	1.078	1.023	5.07
351.30	0.2724	2.246	2.415	-7.56	1.196	1.138	4.82
349.40	0.3650	1.919	1.957	-1.93	1.324	1.259	4.85
349.20	0.4644	1.586	1.612	-1.64	1.464	1.445	1.28
348.80	0.5654	1.382	1.371	0.81	1.671	1.718	-2.78
348.60	0.6343	1.240	1.251	-0.90	2.004	1.970	1.72
348.50	0.7088	1.148	1.154	-0.50	2.356	2.326	1.27
348.70	0.7634	1.088	1.100	-1.04	2.674	2.658	0.61
348.80	0.8161	1.054	1.059	-0.54	3.065	3.056	0.29
349.10	0.8654	1.018	1.032	-1.38	3.670	3.514	4.23
349.50	0.8919	1.003	1.020	-1.77	3.980	3.802	4.47
350.00	0.9280	1.007	1.009	-0.20	4.191	4.251	-1.43
350.40	0.9694	1.018	1.002	1.56	5.126	4.868	5.04

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.0099 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 1.88\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0152 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 2.72\ \%$$

UNIQUAC interaction parameters are:

$\Delta u_{12}/R$ = -47.57 K
$\Delta u_{21}/R$ = 375.99 K

Table (A.8.7): Evaluation of relative volatility α_{12} of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }
at 772.5 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	b_4	σs
Exp.	10.29	-35.36	57.32	-47.79	15.96	0.085
Wilson	11.29	-41.91	75.23	-68.65	24.46	0.039
UNIQUAC	11.59	-40.62	65.03	-52.77	17.19	0.016

Table (A.8.8): VLE data reduction of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
368.1	0.0303	-2.10	0.2233	-0.0171
356.00	0.1132	3.53	0.4759	-0.0079
351.30	0.2724	-0.68	0.5923	-0.0206
349.40	0.3650	1.75	0.6311	-0.0130
349.20	0.4644	-0.32	0.6588	-0.0101
348.80	0.5654	-0.53	0.6889	-0.0015
348.60	0.6343	-0.51	0.6881	-0.0176
348.50	0.7088	-0.55	0.7096	-0.0158
348.70	0.7634	-1.31	0.7308	-0.0133
348.80	0.8161	-1.23	0.7600	-0.0077
349.10	0.8654	-1.30	0.7881	-0.0102
349.50	0.8919	-1.86	0.8134	-0.0068
350.00	0.9280	-1.69	0.8676	0.0084
350.40	0.9694	0.88	0.9307	0.0056

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.412 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.003$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 1.303$$

$$\left|\frac{(\Delta y_1)}{N}\right| = 0.001 \quad ; \quad \left|\frac{(\Delta y_2)}{N}\right| = 0.001$$

Table (A.8.10): Evaluation of relative volatility α_{12} of {(1-x) $C_7H_5F_3$ + x C_2H_5OH}
at 772.5 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0303	9.2009	10.1285	10.4414
0.1132	7.1135	7.3422	7.7312
0.2724	3.8805	4.2291	4.3934
0.3650	2.9763	3.1485	3.1887
0.4644	2.2269	2.3300	2.2843
0.5654	1.7021	1.7141	1.6319
0.6343	1.2719	1.3825	1.2978
0.7088	1.0039	1.0853	1.0132
0.7634	0.8414	0.9012	0.8457
0.8161	0.7136	0.7447	0.7089
0.8654	0.5785	0.6156	0.6017
0.8919	0.5283	0.5529	0.5514
0.9280	0.5084	0.4735	0.4887
0.9694	0.4239	0.3899	0.4252

Table (A.8.9): VLE data reduction of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
368.1	0.0303	-2.87	0.2233	-0.0227
356.00	0.1132	1.07	0.4759	-0.0208
351.30	0.2724	-3.46	0.5923	-0.0296
349.40	0.3650	-0.20	0.6311	-0.0159
349.20	0.4644	-1.47	0.6588	-0.0057
348.80	0.5654	-1.11	0.6889	0.0091
348.60	0.6343	-0.87	0.6881	-0.0043
348.50	0.7088	-0.75	0.7096	-0.0019
348.70	0.7634	-1.36	0.7308	-0.0010
348.80	0.8161	-1.06	0.7600	0.0012
349.10	0.8654	-0.84	0.7881	-0.0065
349.50	0.8919	-1.22	0.8134	-0.0064
350.00	0.9280	-0.85	0.8676	0.0046
350.40	0.9694	1.60	0.9307	-0.0002

With:

$$\left(\frac{\Sigma(\Delta p)^2}{N}\right)^{1/2} = 0.419 \quad ; \quad \left(\frac{\Sigma(\Delta y)^2}{N}\right)^{1/2} = 0.003$$

$$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 1.338$$

$$\left|\frac{(\Delta y_1)}{N}\right| = 0.009 \quad ; \quad \left|\frac{(\Delta y_2)}{N}\right| = 0.009$$

Table (A.8.11): Reduction of VLE of {(1-x) $C_7H_5F_3$ + x C_2H_5OH }at 772.5 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
368.10	0.0303	1.002	0.941	0.978	0.952
356.00	0.1132	0.988	0.938	0.975	0.948
351.30	0.2724	0.982	0.940	0.972	0.943
349.40	0.3650	0.980	0.941	0.972	0.944
349.20	0.4644	0.978	0.942	0.972	0.943
348.80	0.5654	0.977	0.944	0.972	0.943
348.60	0.6343	0.977	0.944	0.972	0.943
348.50	0.7088	0.976	0.946	0.972	0.943
348.70	0.7634	0.967	0.947	0.971	0.943
348.80	0.8161	0.975	0.950	0.971	0.943
349.10	0.8654	0.974	0.953	0.971	0.943

Table (A.8.12):Summary of physico-chemical properties of {(1-x)$C_7H_5F_3$ + xC_2H_5OH} at 100 kPa

Method	azeotrope			Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}		Exp.	-	-	10.29	4.87	5.55
Exp.	348.6	0.7115		WILSON	667.39	105.14	11.29	5.49	6.04
cal.	-	0.7239		UNIQUAC	-47.57	375.99	11.59	4.41	5.17

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
11.48	WILSON	0.412	0.003
	UNIQUAC	0.419	0.003

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az} = 0.7115	WILSON	994	610	-1.10	2.46
T_{az} = 348.6 K	UNIQUAC	1078	78	-2.87	1.57
x = 0.500	WILSON	118	853	-0.94	2.96
T = 355.1 K	UNIQUAC	1292	905	-1.09	1.33

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5113	313.2 K, 0.500	355.1 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	0.0068	2.4575	1206	1226

G_m^E(cal.)/J.mol^{-1} = [x(1 - x){4904.51 + 624.56(1 - 2x) + 736.79(1 –2x)^2} ± 29.66]

n_D^E = [x(1 - x){0.0270 + 0.0061(1 - 2x) } ± 0.0003]

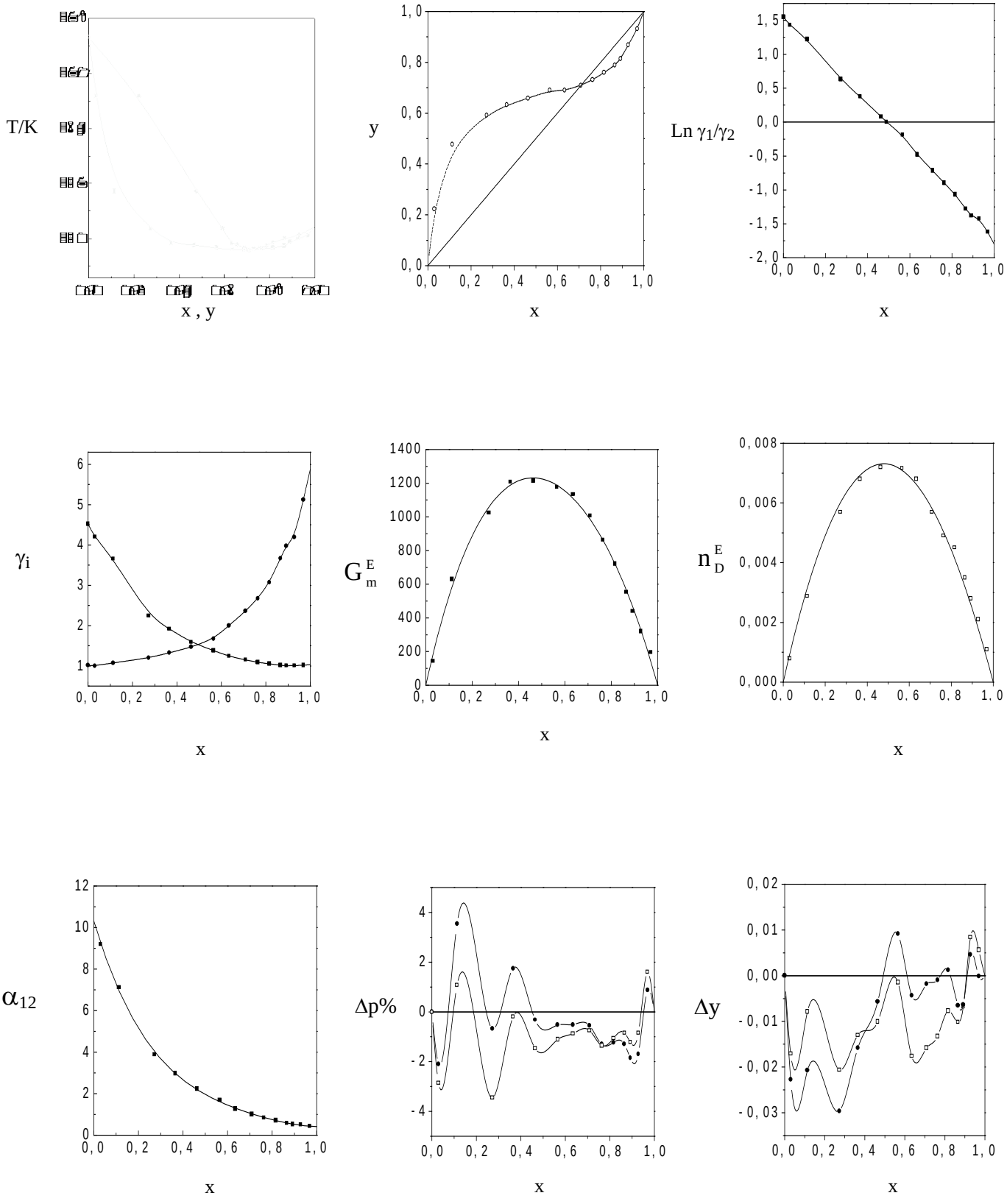


Figure (A. 8) : Vapour-Liquid Equilibria of {(1-x)$C_7H_5F_3$+xC_2H_5OH} at 100 kPa

Table (A.9.1): Refractive indices n_D of VLE of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 298.2 K

n_D (liq.)	x	n_D (vap.)	y
1.4140	0.0000	1.4140	0.0000
1.4160	0.0717	1.4212	0.1717
1.4212	0.1719	1.4324	0.3486
1.4255	0.2466	1.4410	0.4624
1.4355	0.3933	1.4533	0.6072
1.4390	0.4366	1.4575	0.6515
1.4482	0.5493	1.4640	0.7188
1.4520	0.5930	1.4663	0.7409
1.4605	0.6844	1.4718	0.7931
1.4665	0.7419	1.4750	0.8214
1.4727	0.8015	1.4780	0.8506
1.4774	0.8447	1.4800	0.8675
1.4838	0.9007	1.4840	0.9023
1.4859	0.9185	1.4848	0.9097
1.4889	0.9440	1.4856	0.9163
1.4930	0.9779	1.4898	0.9517
1.4960	1.0000	1.4960	1.0000

Table (A.9.2): Experimental results: VLE of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr.

T/K	x	y	γ_1	γ_2
371.2	0.0717	0.1717	1.5130	1.0229
366.1	0.1719	0.3486	1.4561	1.0503
363.3	0.2466	0.4624	1.4489	1.0415
359.8	0.3933	0.6072	1.3074	1.0572
358.7	0.4366	0.6515	1.3021	1.0478
357.3	0.5493	0.7188	1.1872	1.1096
356.8	0.5930	0.7409	1.1505	1.1530
355.5	0.6844	0.7931	1.1054	1.2401
355.0	0.7419	0.8214	1.0727	1.3351
354.5	0.8015	0.8506	1.0429	1.4791
354.1	0.8447	0.8675	1.0210	1.7009
353.7	0.9007	0.9023	1.0059	1.9895
353.7	0.9185	0.9097	0.9944	2.2418
353.5	0.9440	0.9163	0.9803	3.0457
353.3	0.9779	0.9517	0.9879	4.4935

comp. (1) = C_6H_6, comp.(2) = $C_7H_5F_3$

Table (A.9.3): Excess refractive indices n_D^E of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 298.2 K

x	n_D^E
0.0717	-0.0039
0.1719	-0.0069
0.2466	-0.0087
0.3933	-0.0108
0.4366	-0.0109
0.5493	-0.0108
0.5930	-0.0106
0.6844	-0.0094
0.7419	-0.0084
0.8015	-0.0070
0.8447	-0.0058
0.9007	-0.0041
0.9185	-0.0035
0.9440	-0.0026
0.9779	-0.0012

$$n_D^E = [x\,(1-x)\{-0.0438 - 0.0036\,(1-2x) - 0.0079\,(1-2x)^2\} \pm 0.0001]$$

$$n_D^E\,(x = 0.500) = -0.0110 \pm 0.0001$$

Table (A.9.4): Excess Gibbs function G_m^E of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr.

x	G_m^E /J.mol^{-1}	ΔG_m^E /J.mol^{-1}
0.0717	156.48	-10.81
0.1719	320.22	9.97
0.2466	368.77	-0.47
0.3933	416.42	-2.57
0.4366	422.30	-0.10
0.5493	419.15	-3.80
0.5930	418.53	-0.03
0.6844	403.46	5.54
0.7419	373.92	1.00
0.8015	328.01	-4.05
0.8447	294.37	4.75
0.9007	216.44	2.82
0.9185	178.21	-5.30
0.9440	128.15	-6.48
0.9779	62.57	4.60

$$G_m^E\,(\text{cal.})/\text{J.mol}^{-1} = [x\,(1-x)\{1699.31 + 15.22(1-2x) + 1091.87\,(1-2x)^2\} \pm 5.83]$$

$$G_m^E\,(x = 0.500) = (425 \pm 6)\ \text{J.mol}^{-1}$$

Table (A.9.5): VLE data reduction: Evaluation of WILSON parameters of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
371.2	0.0717	1.513	1.456	3.75	1.023	1.001	2.19
366.1	0.1719	1.456	1.425	2.14	1.050	1.004	4.44
363.3	0.2466	1.449	1.399	3.45	1.041	1.009	3.16
359.8	0.3933	1.307	1.340	-2.46	1.057	1.030	2.57
358.7	0.4316	1.302	1.322	-1.55	1.048	1.040	0.79
357.3	0.5493	1.187	1.264	-6.43	1.110	1.087	2.04
356.8	0.5930	1.151	1.240	-7.75	1.153	1.115	3.28
355.5	0.6844	1.105	1.186	-7.29	1.240	1.207	2.63
355.0	0.7419	1.073	1.150	-7.19	1.335	1.305	2.24
354.5	0.8015	1.043	1.111	-6.51	1.479	1.469	0.67
354.1	0.8447	1.021	1.082	-5.96	1.701	1.663	2.23
353.7	0.9007	1.006	1.045	-3.88	1.990	2.120	-6.56
353.7	0.9185	0.994	1.034	-3.96	2.242	2.362	-5.36
353.5	0.9440	0.980	1.019	-3.96	3.046	2.874	5.64
353.3	0.9779	0.988	1.004	-1.63	4.494	4.206	6.39

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.037 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 4.53\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.022 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 3.35\ \%$$

WILSON's interaction parameters are:

$$\Delta\lambda_{12}/R = -70.84\ K$$
$$\Delta\lambda_{21}/R = 772.43\ K$$

Table (A.9.6): VLE data reduction: evaluation of UNIQUAC parameters of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr.

T/K	x	γ_1 (exp.)	γ_1 (cal.)	$\Delta\gamma_1$%	γ_2 (exp.)	γ_2 (cal.)	$\Delta\gamma_2$%
371.2	0.0717	1.513	1.410	6.80	1.023	1.000	2.24
366.1	0.1719	1.456	1.394	4.25	1.050	1.000	4.77
363.3	0.2466	1.449	1.381	4.70	1.041	1.001	3.84
359.8	0.3933	1.307	1.344	-2.82	1.057	1.012	4.26
358.7	0.4316	1.302	1.331	-2.20	1.048	1.018	2.82
357.3	0.5493	1.187	1.280	-7.79	1.110	1.057	4.78
356.8	0.5930	1.151	1.256	-9.17	1.153	1.083	6.11
355.5	0.6844	1.105	1.198	-8.42	1.240	1.176	5.20
355.0	0.7419	1.073	1.158	-7.91	1.335	1.282	4.01
354.5	0.8015	1.043	1.113	-6.68	1.479	1.466	0.89
354.1	0.8447	1.021	1.080	-5.77	1.701	1.685	0.92
353.7	0.9007	1.006	1.040	-3.41	1.990	2.186	-9.88
353.7	0.9185	0.994	1.029	-3.49	2.242	2.437	-8.69
353.5	0.9440	0.980	1.015	-3.57	3.046	2.928	3.85
353.3	0.9779	0.988	1.003	-1.51	4.494	3.996	11.08

With:

$$\Sigma\left(\frac{\Delta\gamma_1}{\gamma_1}\right)^2 = 0.02436 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_1}{\gamma_1}\right)\right| x100 = 4.91\ \%$$

$$\Sigma\left(\frac{\Delta\gamma_2}{\gamma_2}\right)^2 = 0.0367 \quad ; \quad \left|\frac{1}{N}\left(\frac{\Delta\gamma_2}{\gamma_2}\right)\right| x100 = 4.40\ \%$$

UNIQUAC interaction parameters are:

$$\Delta u_{12}/R = 435.46\ K$$
$$\Delta u_{21}/R = -196.54\ K$$

Table (A.9.7): Evaluation of relative volatility α_{12} of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$ at 770.5 torr: parameters for the smoothing polynomial

Method	a_0	b_1	b_2	b_3	b_4	σs
Exp.	2.57	1.79	-9.25	11.71	-6.49	0.054
Wilson	2.69	0.24	-2.31	2.00	-2.32	0.002
UNIQUAC	2.66	-0.82	4.70	-9.59	3.37	0.014

Table (A.9.8): VLE data reduction of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr
Method of gamma estimation used: WILSON

T/K	x	Δp%	y	Δy
371.2	0.0717	2.20	0.1717	-0.0009
366.1	0.1719	3.16	0.3486	-0.0086
363.3	0.2466	2.70	0.4624	-0.0009
359.8	0.3933	-1.30	0.6072	-0.0110
358.7	0.4366	-1.47	0.6515	-0.0029
357.3	0.5493	-4.95	0.7188	-0.0139
356.8	0.5930	-5.80	0.7409	-0.0174
355.5	0.6844	-6.08	0.7931	-0.0125
355.0	0.7419	-6.30	0.8214	-0.0101
354.5	0.8015	-6.15	0.8506	-0.0057
354.1	0.8447	-5.52	0.8675	-0.0062
353.7	0.9007	-4.68	0.9023	0.0049
353.7	0.9185	-4.59	0.9097	0.0036
353.5	0.9440	-3.57	0.9163	-0.0050
353.3	0.9779	-1.46	0.9517	-0.0022

With:

$\left(\frac{\sum(\Delta p)^2}{N}\right)^{1/2} = 1.129$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.002$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 3.994$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.007$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.007$

Table (A.9.10): Evaluation of relative volatility α_{12} of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$ at 770.5 torr

x	α_{12} (exp)	α_{12} (Wilson)	α_{12} (UNIQUAC)
0.0717	2.6838	2.7007	2.6180
0.1719	2.5780	2.6770	2.6283
0.2466	2.6278	2.6373	2.6225
0.3933	2.3846	2.4977	2.5513
0.4366	2.4124	2.4434	2.5128
0.5493	2.0973	2.2491	2.3426
0.5930	1.9626	2.1533	2.2480
0.6844	1.7676	1.9110	1.9826
0.7419	1.6000	1.7167	1.7593
0.8015	1.4100	1.4758	1.4806
0.8447	1.2037	1.2718	1.2525
0.9007	1.0182	0.9643	0.9308
0.9185	0.8939	0.8562	0.8270
0.9440	0.6494	0.6945	0.6794
0.9779	0.4453	0.4676	0.4922

Table (A.9.9): VLE data reduction of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$at 770.5 torr
Method of gamma estimation used: UNIQUAC

T/K	x	Δp%	y	Δy
371.2	0.0717	2.80	0.1717	0.0035
366.1	0.1719	4.16	0.3486	-0.0044
363.3	0.2466	3.70	0.4624	0.0005
359.8	0.3933	-0.82	0.6072	-0.0160
358.7	0.4366	-1.18	0.6515	-0.0092
357.3	0.5493	-5.15	0.7188	-0.0218
356.8	0.5930	-6.12	0.7409	-0.0252
355.5	0.6844	-6.44	0.7931	-0.0182
355.0	0.7419	-6.57	0.8214	-0.0135
354.5	0.8015	-6.27	0.8506	-0.0061
354.1	0.8447	-5.53	0.8675	-0.0045
353.7	0.9007	-4.58	0.9023	0.0082
353.7	0.9185	-4.46	0.9097	0.0066
353.5	0.9440	-3.35	0.9163	-0.0034
353.3	0.9779	-1.09	0.9517	-0.0044

With:

$\left(\frac{\sum(\Delta p)^2}{N}\right)^{1/2} = 1.143$; $\left(\frac{\sum(\Delta y)^2}{N}\right)^{1/2} = 0.002$

$\left|\frac{1}{N}\left(\frac{\Delta p}{p}\right)\right| x100 = 4.016$

$\left|\frac{(\Delta y_1)}{N}\right| = 0.008$; $\left|\frac{(\Delta y_2)}{N}\right| = 0.008$

Table (A.9.11): Reduction of VLE of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$ at 770.5 torr: Fugacity coefficients ϕ_i

		Experimental		Wilson UNIQUAC	
T/K	x	ϕ_1	ϕ_2	ϕ_1	ϕ_2
371.20	0.0717	0.994	0.948	0.973	0.965
366.10	0.1719	0.985	0.947	0.971	0.954
363.25	0.2466	0.979	0.949	0.970	0.953
359.80	0.3933	0.973	0.952	0.967	0.949
358.70	0.4366	0.972	0.954	0.967	0.949
357.28	0.5493	0.970	0.957	0.965	0.946
356.75	0.5930	0.969	0.958	0.964	0.945
355.50	0.6844	0.968	0.960	0.964	0.945
354.95	0.7419	0.967	0.962	0.964	0.944
354.45	0.8015	0.967	0.964	0.963	0.944
354.05	0.8447	0.966	0.965	0.964	0.944
353.70	0.9007	0.966	0.967	0.964	0.945

Table (A.9.12):Summary of physico-chemical properties of $\{(1-x)C_7H_5F_3 + xC_6H_6\}$ at 102 kPa

Method	azeotrope		Method	$\Delta\lambda_{12}/R$ (K)	$\Delta\lambda_{21}/R$ (K)	α_{12}^{∞}	γ_1^{∞}	γ_2^{∞}
	T_{az}/K	x_{az}	Exp.	-	-	2.57	1.53	5.61
Exp.	353.7	0.9013	WILSON	-70.84	772.43	2.69	1.29	4.86
cal.	-	0.8780	UNIQUAC	435.46	-196.54	2.66	1.40	5.35

Consistency test and correlation:

(CI-J)%	Method	σp/torr	σy
9.18	WILSON	1.129	0.002
	UNIQUAC	1.143	0.002

Correlated $X_m^E(T, x)$:

x	Method	G_m^E (J.mol^{-1})	H_m^E (J.mol^{-1})	S_m^E (J.K^{-1}.mol^{-1})	$C_{p,m}^E$ (J.K^{-1}.mol^{-1})
x_{az}=0.9013	WILSON	334	186	-0.42	1.00
T_{az} = 353.7 K	UNIQUAC	339	1079	2.09	1.03
x= 0.500	WILSON	474	67	-1.12	1.41
T = 362.3 K	UNIQUAC	479	-319	-2.21	4.77

Experimental $X_m^E(T, x)$:

T, x	298.2 K, 0.500	298.2 K, 0.5097	313.2 K, 0.499	362.3 K, 0.500
	n_D^E	V_m^E (cm^3.mol^{-1})	H_m^E (J.mol^{-1})	G_m^E (J.mol^{-1})
	-0.0110	1.2041	435	425

$$G_m^E(\text{cal.})/\text{J.mol}^{-1} = [x\,(1 - x)\{1699.31 + 15.22\,(1 - 2x) + 1091.87\,(1 - 2x)^2\} \pm 5.83]$$

$$n_D^E = [x(1 - x)\{-0.0438 - 0.0036(1 - 2x) - 0.0079(1- 2x)^2\} \pm 0.0001]$$

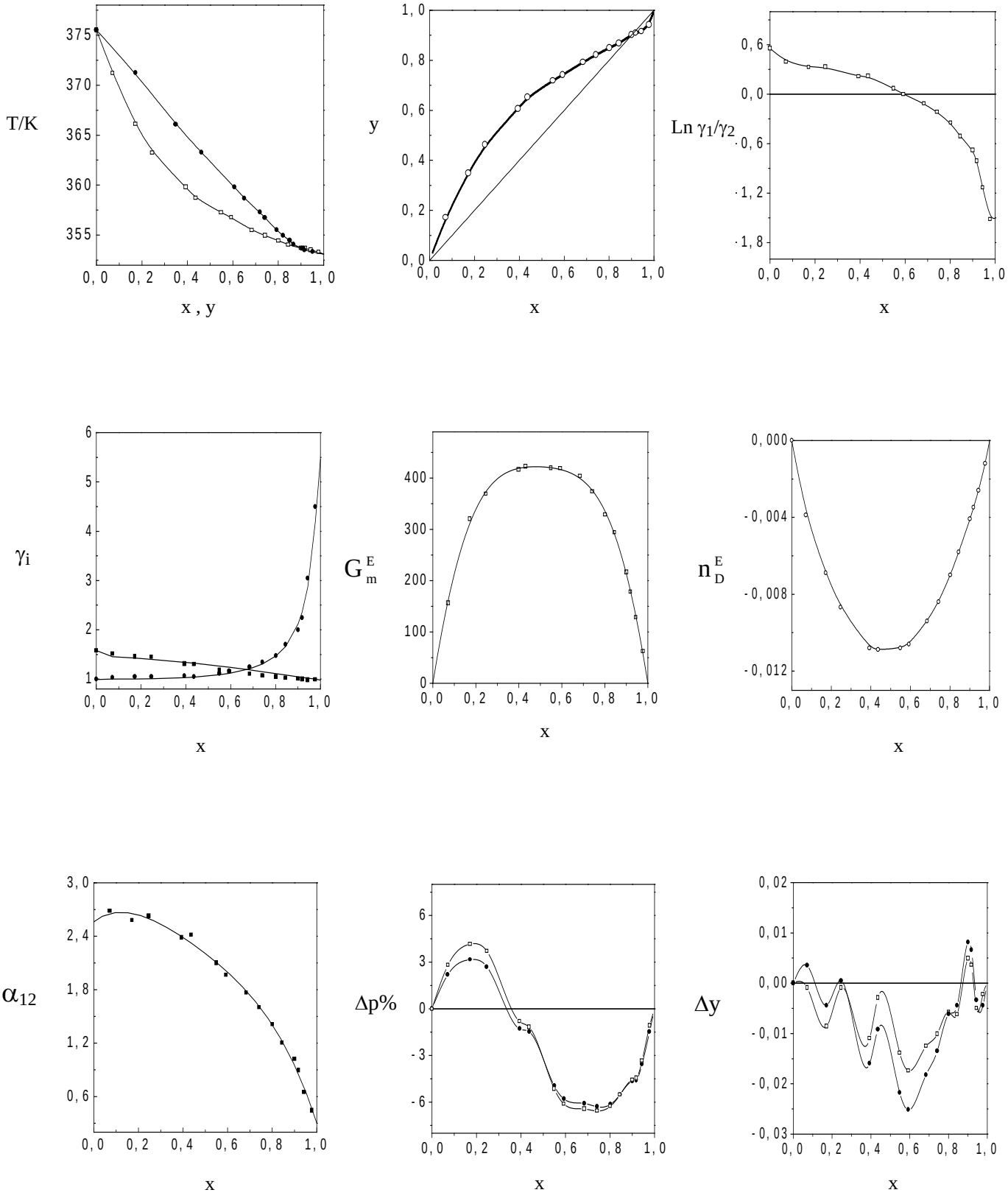


Figure (A. 9) : Vapour-Liquid Equilibria of {(1-x)$C_7H_5F_3$+xC_6H_6} at 102 kPa

Table (A.10): Excess properties n_D^E and V_m^E : {(1-x)2-C_7H_7F+x C_7H_8} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0547	-0.0007	0.0085
0.1093	-0.0082	0.0160
0.1411	-0.0008	0.0199
0.2114	-0.0083	0.0274
0.2353	-0.0009	0.0296
0.2876	-0.0008	0.0337
0.3839	-0.0008	0.0389
0.5022	-0.0008	0.0411
0.5935	-0.0007	0.0397
0.7041	-0.0006	0.0343
0.6768	-0.0007	0.0360
0.8189	-0.0008	0.0244
0.8948	-0.0004	0.0155
0.9450	-0.0005	0.0085

Table (A.11): Excess properties n_D^E and V_m^E : {(1-x)2-C_7H_7F+x CH_3OH} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0543	0.0117	-0.6057
0.1053	0.0215	-1.1113
0.1536	0.0297	-1.5335
0.2096	0.0378	-1.9542
0.2580	0.0437	-2.2581
0.3115	0.0490	-2.5298
0.3650	0.0529	-2.7339
0.4032	0.0549	-2.8384
0.5050	0.0571	-2.9486
0.6044	0.0546	-2.8203
0.7012	0.0478	-2.4714
0.8031	0.0361	-1.8652
0.9049	0.0196	-1.0151
0.9584	0.0091	-0.4703

Table (A.12): Excess properties n_D^E and V_m^E : {(1-x)1,4-$C_6H_4F_2$+xC_7H_8} at 298.2 K

x	n_D^E *	V_m^E / $cm^3.mol^{-1}$
0.0509	0.0002	0.0468
0.1111	0.0004	0.0956
0.1512	0.0006	0.1229
0.1973	0.0007	0.1532
0.2573	0.0008	0.1845
0.3031	0.0007	0.2039
0.3548	0.0006	0.2211
0.4121	0.0005	0.2335
0.4981	0.0002	0.2417
0.6070	-0.0003	0.2303
0.7102	-0.0006	0.1987
0.8076	-0.0007	0.1503
0.9079	-0.0004	0.0810
0.9653	-0.0002	0.0322

* $n_D^E = (0.0000 \pm 0.0005)$

Table (A.13): Excess properties n_D^E and V_m^E : {(1-x)1,4-$C_6H_4F_2$+xCH_3OH} at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0589	0.0033	-0.0380
0.1098	0.0061	-0.0684
0.1584	0.0088	-0.0938
0.2038	0.0118	-0.1145
0.2619	0.0156	-0.1363
0.3018	0.0183	-0.1484
0.4076	0.0255	-0.1699
0.5111	0.0307	-0.1754
0.6274	0.0322	-0.1640
0.7062	0.0297	-0.1456
0.8057	0.0225	-0.1111
0.8631	0.0165	-0.0830
0.9211	0.0094	-0.0511
0.9618	0.0046	-0.0252

Table (A.14): Excess properties n_D^E and V_m^E : $\{(1-x)C_2H_5I+xC_7H_8\}$ at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0666	-0.0010	0.1257
0.1065	-0.0016	0.1928
0.1527	-0.0020	0.2623
0.2508	-0.0028	0.3803
0.1819	-0.0023	0.3015
0.3011	-0.0032	0.4268
0.3966	-0.0034	0.4842
0.4960	-0.0035	0.5061
0.5951	-0.0034	0.4882
0.6908	-0.0029	0.4326
0.7914	-0.0021	0.3349
0.9014	-0.0010	0.1801
0.9397	-0.0006	0.1146

Table (A.15): Excess properties n_D^E and V_m^E : $\{(1-x)C_2H_5I+xCH_3OH\}$ at 298.2 K

x	n_D^E	V_m^E / $cm^3.mol^{-1}$
0.0534	0.0046	0.2427
0.1098	0.0089	0.4680
0.1533	0.0118	0.6213
0.2066	0.0148	0.7856
0.2460	0.0168	0.8882
0.2943	0.0188	0.9949
0.3959	0.0217	1.1458
0.5195	0.0226	1.1951
0.6403	0.0209	1.1027
0.6933	0.0193	1.0180
0.8017	0.0144	0.7613
0.8458	0.0118	0.6247
0.8990	0.0082	0.4343
0.9471	0.0045	0.2400

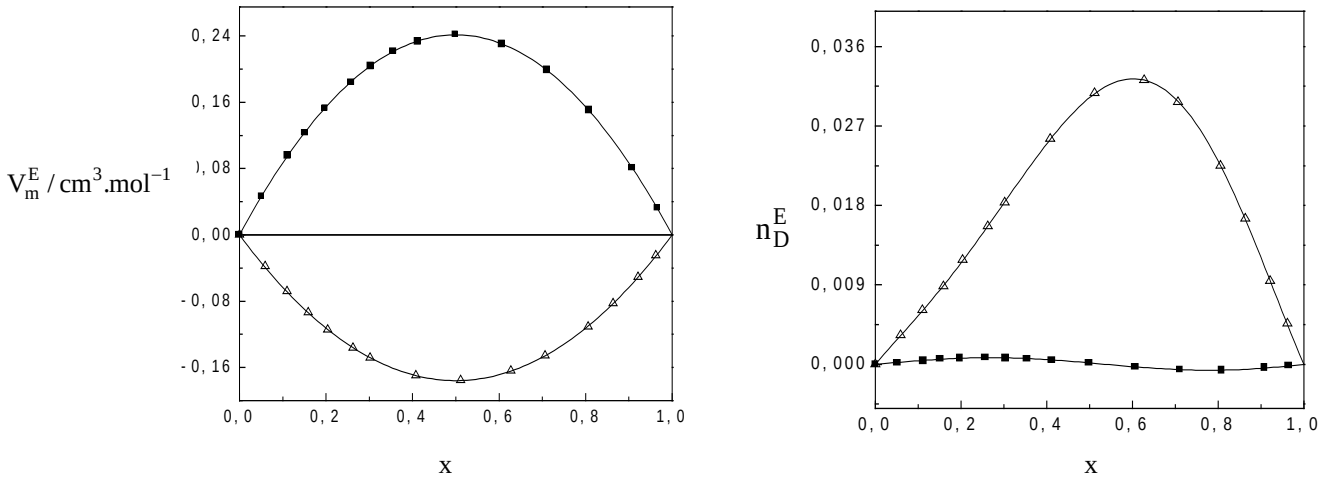
Table (A.17):Smoothing parameters of n_D^E at 298.2 K

A_0	A_1	A_2	A_3	σs	n_D^E (x = 0.500)
(1-x)2-C_7H_8F + xC_7H_8					
-0.0028	-0.0008	-0.0066	--	0.0001	-0.0007
(1-x)2-C_7H_8F + xCH_3OH					
0.2283				0.00002	0.0571
(1-x)1,4-$C_6H_4F_2$ + xC_7H_8					
0.0006	0.0071	-0.0018	--	0.0001	0.0002
(1-x)1,4-$C_6H_4F_2$ + xCH_3OH					
0.1209	-0.0786	-0.0362	0.5152	0.0001	0.0302
(1-x)C_2H_5I + xC_7H_8					
-0.0141	-0.0022	--	--	0.0001	-0.0035
(1-x)C_2H_5I + xCH_3OH					
0.0905				0.0006	0.0226

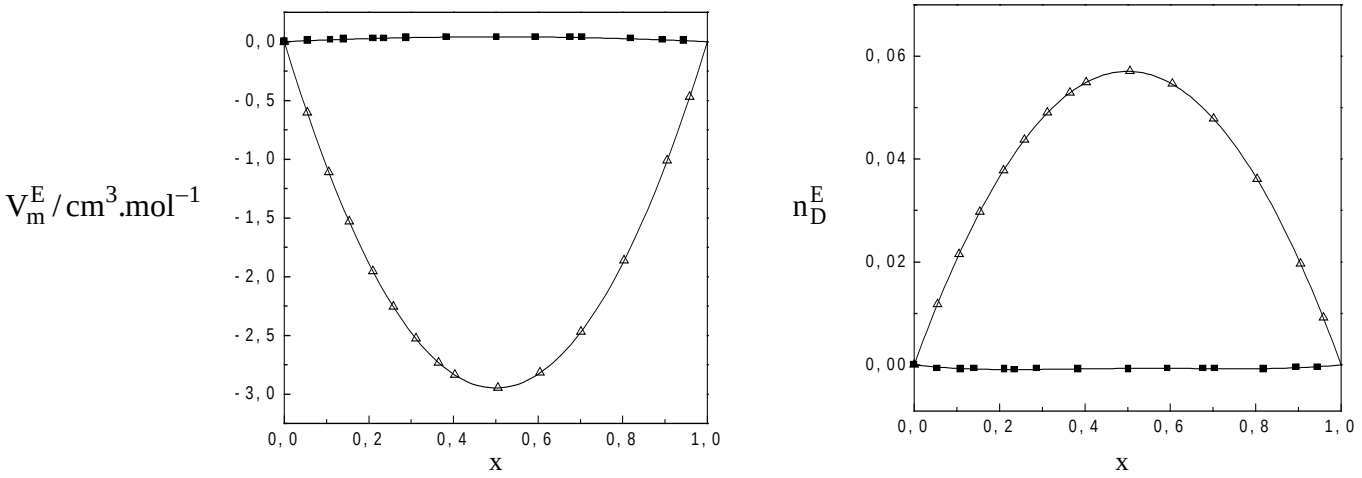
Table (A.16):Smoothing parameters of V_m^E at 298.2 K

A_0	A_1	A_2	σs	V_m^E (x = 0.500) ($cm^3.mol^{-1}$)
(1-x)2-C_7H_8F + xC_7H_8				
0.1646	-0.0014		0.0002	0.0412
(1-x)2-C_7H_8F + xCH_3OH				
-11.7959			0.0002	-2.9490
(1-x)1,4-$C_6H_4F_2$ + xC_7H_8				
0.9654			0.0003	0.2414
(1-x)1,4-$C_6H_4F_2$ + xCH_3OH				
-0.7032			0.0005	-0.1758
(1-x)C_2H_5I + xC_7H_8				
2.0255			0.0003	0.5064
(1-x)C_2H_5I + xCH_3OH				
4.7889	0.0020		0.0003	1.1972

(1)



(2)



(3)

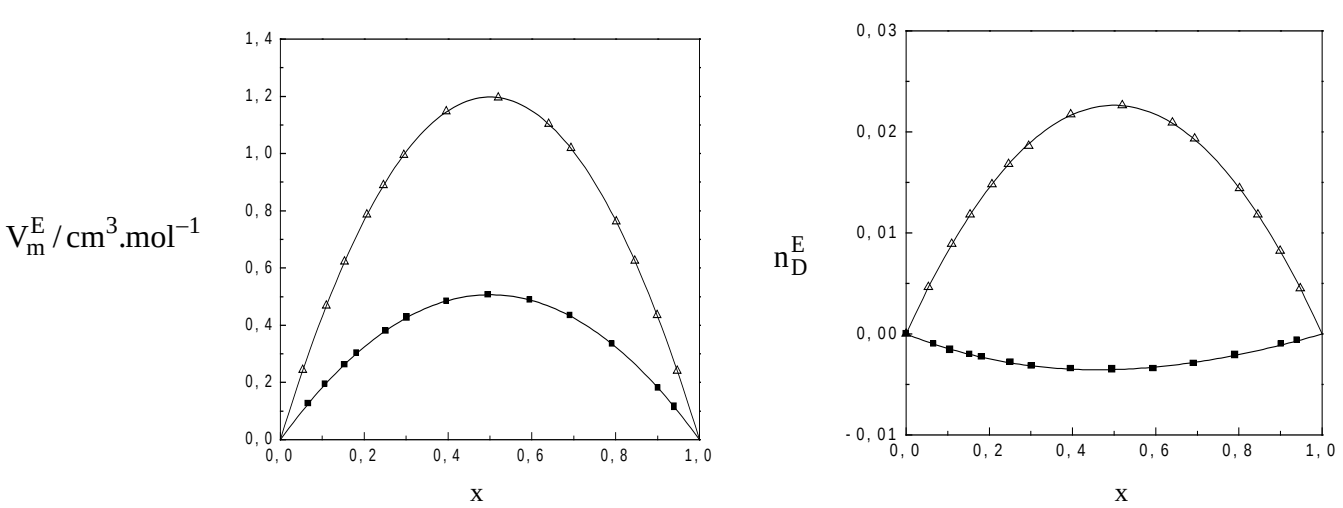


Figure (A. 10) : Excess properties V_m^E and n_D^E at 298.2 K:
(1) : {(1-x)1,4-$C_6H_4F_2$ + xB} ; (2) : {(1-x)2-C_7H_7F + xB} ;
(3) : {(1-x)C_2H_5I + xB} ; B = C_7H_8 (■) or CH_3OH (Δ)

Table(B. 1): uncertainty calculations for V_m^E measurements

Uncertainty From	{(1-x)2-C_7H_7F+xC_7H_8 }			{(1-x)2-C_7H_7F+xCH_3OH}			{(1-x)1,4-$C_6H_4F_2$+xC_7H_8}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
δx	$2.0\ 10^{-5}$	$4.0\ 10^{-4}$	$5.0\ 10^{-4}$	$1.0\ 10^{-4}$	$5.5\ 10^{-4}$	$7.0\ 10^{-4}$	$3.5\ 10^{-5}$	$3.0\ 10^{-4}$	$7.5\ 10^{-4}$

Uncertainty From	{(1-x)1,4-$C_6H_4F_2$+xCH_3OH}			{(1-x)C_2H_5I+xC_7H_8}			{(1-x)C_2H_5I+xCH_3OH}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
δx	$1.0\ 10^{-4}$	$4.5\ 10^{-4}$	$5.5\ 10^{-4}$	$6.0\ 10^{-5}$	$4.5\ 10^{-4}$	$6.0\ 10^{-4}$	$1.0\ 10^{-4}$	$8.0\ 10^{-4}$	$6.5\ 10^{-4}$

So, the mean uncertainty on composition x is : $\overline{\delta x} = 0.0004$

uncertainty from	{(1-x)2-C_7H_7F+xC_7H_8 }			{(1-x)2-C_7H_7F+xCH_3OH}			{(1-x)1,4-$C_6H_4F_2$+xC_7H_8}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
Contrib.ρ	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$	$2.5\ 10^{-2}$	$2.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.5\ 10^{-2}$	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$
Contrib.x	$6.5\ 10^{-3}$	$3.0\ 10^{-3}$	$5.5\ 10^{-4}$	$4.5\ 10^{-3}$	$4.0\ 10^{-3}$	$1.0\ 10^{-3}$	$1.5\ 10^{-3}$	$7.5\ 10^{-3}$	$4.5\ 10^{-3}$
$\frac{\delta V_m^E}{V_m^E}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$2.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$
δV_m^E /cm^3.mol^{-1}	0.0012			0.0530			0.0064		
σV_m^E /cm^3.mol^{-1}	0.0002			0.0002			0.0003		

Source of Error	{(1-x)1,4-$C_6H_4F_2$+xCH_3OH}			{(1-x)C_2H_5I+xC_7H_8}			{(1-x)C_2H_5I+xCH_3OH}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
Contrib.ρ	$1.5\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$9.0\ 10^{-3}$	$1.5\ 10^{-2}$	$2.0\ 10^{-2}$	$8.0\ 10^{-3}$	$8.0\ 10^{-3}$	$9.5\ 10^{-3}$
Contrib.x	$3.5\ 10^{-4}$	$5.0\ 10^{-3}$	$2.0\ 10^{-2}$	$2.0\ 10^{-3}$	$1.5\ 10^{-2}$	$4.0\ 10^{-2}$	$8.0\ 10^{-4}$	$1.0\ 10^{-2}$	$4.5\ 10^{-2}$
$\frac{\delta V_m^E}{V_m^E}$	$2.5\ 10^{-3}$	$1.5\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$5.0\ 10^{-2}$	$1.5\ 10^{-2}$	$1.5\ 10^{-2}$	$4.5\ 10^{-2}$
δV_m^E /cm^3.mol^{-1}	0.003			0.015			0.022		
σV_m^E / cm^3.mol^{-1}	0.0004			0.0003			0.0003		

Therefore, the mean uncertainty on excess molar volume V_m^E is : $\frac{\overline{\delta V_m^E}}{V_m^E} = 3.0\ 10^{-2}$

Table(B.2): uncertainty calculations for G_m^E measurements :

Uncertainty from	{(1-x)C_6H_5F+xC_6H_{14} }			{(1-x)C_6H_5F+xC_7H_{16} }			{(1-x)$C_2H_2F_3OH$+x$CHCL_3$ }		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.p	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$
contrib.x	$5.0\ 10^{-2}$	$4.0\ 10^{-3}$	$2.0\ 10^{-3}$	$8.5\ 10^{-2}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$	$4.0\ 10^{-2}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$
contrib.y	$2.0\ 10^{-2}$	$3.0\ 10^{-3}$	$2.0\ 10^{-3}$	$6.5\ 10^{-2}$	$5.0\ 10^{-3}$	$2.0\ 10^{-3}$	$8.0\ 10^{-3}$	$2.5\ 10^{-3}$	$2.0\ 10^{-3}$
contrib.T	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$9.0\ 10^{-3}$	$9.5\ 10^{-3}$	$1.0\ 10^{-2}$	$6.0\ 10^{-3}$	$5.0\ 10^{-3}$	$5.5\ 10^{-3}$
contrib.									
$\delta(B - V_m^*)$	$1.5\ 10^{-2}$	$1.0\ 10^{-2}$	$1.5\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$
$\delta\ln\gamma$	$6.0\ 10^{-2}$	$1.5\ 10^{-2}$	$1.5\ 10^{-2}$	$1.0\ 10^{-1}$	$1.5\ 10^{-2}$	$1.5\ 10^{-2}$	$4.5\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$

Uncertainty from	{(1-x)$C_2H_2F_3OH$+xC_6H_6}			{(1-x)$C_2H_2F_3OH$+xC_7H_8}			{(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.p	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$
contrib.x	$4.5\ 10^{-2}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$	$8.5\ 10^{-2}$	$4.5\ 10^{-3}$	$2.0\ 10^{-3}$	$2.0\ 10^{-1}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$
contrib.y	$1.0\ 10^{-2}$	$4.0\ 10^{-3}$	$3.0\ 10^{-3}$	$3.0\ 10^{-2}$	$8.0\ 10^{-3}$	$3.0\ 10^{-3}$	$4.0\ 10^{-2}$	$7.0\ 10^{-3}$	$2.5\ 10^{-3}$
contrib.T	$6.0\ 10^{-3}$	$5.5\ 10^{-3}$	$6.0\ 10^{-3}$	$3.5\ 10^{-3}$	$3.5\ 10^{-3}$	$5.5\ 10^{-3}$	$2.0\ 10^{-3}$	$2.5\ 10^{-3}$	$4.0\ 10^{-3}$
contrib.									
$\delta(B - V_m^*)$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$1.0\ 10^{-2}$	$5.5\ 10^{-3}$	$5.5\ 10^{-3}$	$8.5\ 10^{-3}$	$3.0\ 10^{-3}$	$3.0\ 10^{-3}$	$5.5\ 10^{-3}$
$\delta\ln\gamma_1$	$5.0\ 10^{-1}$	$1.0\ 10^{-2}$	$1.0\ 10^{-3}$	$3.0\ 10^{-2}$	$1.0\ 10^{-3}$	$1.0\ 10^{-2}$	$1.0\ 10^{-1}$	$8.5\ 10^{-3}$	$7.5\ 10^{-3}$

Uncertainty from	{(1-x)$C_7H_5F_3$+x$CHCL_3$}			{(1-x)$C_7H_5F_3$+xC_2H_5OH}			{(1-x) $C_7H_5F_3$+xC_6H_6}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.p	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$	$6.5\ 10^{-5}$
contrib.x	$1.5\ 10^{-1}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$	$6.5\ 10^{-3}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$	$5.5\ 10^{-2}$	$3.5\ 10^{-3}$	$2.0\ 10^{-3}$
contrib.y	$2.5\ 10^{-2}$	$2.5\ 10^{-3}$	$2.0\ 10^{-3}$	$8.5\ 10^{-3}$	$2.5\ 10^{-3}$	$2.0\ 10^{-3}$	$2.5\ 10^{-2}$	$2.0\ 10^{-3}$	$2.0\ 10^{-3}$
contrib.T	$1.0\ 10^{-2}$	$6.5\ 10^{-3}$	$5.5\ 10^{-3}$	$7.0\ 10^{-3}$	$4.5\ 10^{-3}$	$1.0\ 10^{-2}$	$9.5\ 10^{-3}$	$7.5\ 10^{-3}$	$7.0\ 10^{-3}$
contrib.									
$\delta(B - V_m^*)$	$2.0\ 10^{-2}$	$1.5\ 10^{-2}$	$1.0\ 10^{-2}$	$2.0\ 10^{-2}$	$1.5\ 10^{-3}$	$3.5\ 10^{-2}$	$1.5\ 10^{-2}$	$1.5\ 10^{-2}$	$1.0\ 10^{-2}$
$\delta\ln\gamma$	$1.5\ 10^{-1}$	$1.5\ 10^{-2}$	$1.0\ 10^{-3}$	$7.0\ 10^{-2}$	$1.5\ 10^{-2}$	$3.5\ 10^{-2}$	$6.5\ 10^{-2}$	$1.5\ 10^{-3}$	$1.5\ 10^{-2}$

Therefore, the mean uncertainty on activity coefficient lnγ is : $\overline{\delta \ln \gamma_i} = 5.0\ 10^{-2}$

Uncertainty From	{(1-x)C_6H_5F+xC_6H_{14} }			{(1-x)C_6H_5F+xC_7H_{16} }			{(1-x)$C_2H_2F_3OH$+x$CHCL_3$ }		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.x	$8.5\ 10^{-4}$	$2.5\ 10^{-4}$	$1.0\ 10^{-4}$	$1.0\ 10^{-3}$	$3.0\ 10^{-4}$	$8.0\ 10^{-4}$	$2.5\ 10^{-3}$	$5.0\ 10^{-5}$	$3.5\ 10^{-3}$
contrib.γ	$7.5\ 10^{-4}$	$1.5\ 10^{-2}$	$7.5\ 10^{-4}$	$3.0\ 10^{-4}$	$1.5\ 10^{-2}$	$2.5\ 10^{-2}$	$3.0\ 10^{-4}$	$1.0\ 10^{-2}$	$2.5\ 10^{-2}$
contrib.T	$2.0\ 10^{-2}$	$6.0\ 10^{-2}$	$1.0\ 10^{-2}$	$2.0\ 10^{-2}$	$6.0\ 10^{-2}$	$1.0\ 10^{-2}$	$4.0\ 10^{-2}$	$2.0\ 10^{-2}$	$4.0\ 10^{-2}$
$\frac{\delta G_m^E}{G_m^E}$	$2.5\ 10^{-2}$	$1.5\ 10^{-2}$	$2.5\ 10^{-2}$	$2.5\ 10^{-2}$	$2.0\ 10^{-2}$	$3.0\ 10^{-2}$	$2.5\ 10^{-2}$	$1.5\ 10^{-2}$	$2.5\ 10^{-2}$
δG_m^E /J.mol^{-1}		9			8			18	
σG_m^E /J.mol^{-1}		23			30			16	

Uncertainty From	{(1-x)$C_2H_2F_3OH$+xC_6H_6}			{(1-x)$C_2H_2F_3OH$+xC_7H_8}			{(1-x)$C_2H_2F_3OH$+x$C_7H_5F_3$}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.x	$3.0\ 10^{-3}$	$4.0\ 10^{-5}$	$3.5\ 10^{-3}$	$4.0\ 10^{-3}$	$4.0\ 10^{-4}$	$3.5\ 10^{-3}$	$3.5\ 10^{-3}$	$5.5\ 10^{-4}$	$3.0\ 10^{-3}$
contrib.γ	$2.0\ 10^{-4}$	$9.5\ 10^{-3}$	$2.5\ 10^{-2}$	$8.0\ 10^{-5}$	$7.5\ 10^{-3}$	$3.0\ 10^{-2}$	$8.0\ 10^{-5}$	$1.0\ 10^{-2}$	$3.0\ 10^{-2}$
contrib.T	$3.0\ 10^{-2}$	$9.0\ 10^{-2}$	$4.0\ 10^{-2}$	$1.0\ 10^{-2}$	$9.0\ 10^{-2}$	$1.0\ 10^{-2}$	$2.0\ 10^{-2}$	$9.0\ 10^{-2}$	$1.0\ 10^{-2}$
$\frac{\delta G_m^E}{G_m^E}$	$3.0\ 10^{-3}$	$1.5\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$1.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$1.5\ 10^{-2}$	$3.0\ 10^{-2}$
δG_m^E /J.mol^{-1}		17			18			20	
σG_m^E /J.mol^{-1}		23			90			83	

Uncertainty from	{(1-x)$C_7H_5F_3$+x$CHCL_3$}			{(1-x)$C_7H_5F_3$+xC_2H_5OH}			{(1-x) $C_7H_5F_3$+xC_6H_6}		
x	0.01	0.50	0.95	0.01	0.50	0.95	0.01	0.50	0.95
contrib.x	$1.5\ 10^{-3}$	$1.0\ 10^{-4}$	$1.0\ 10^{-3}$	$3.0\ 10^{-3}$	$3.5\ 10^{-4}$	$3.0\ 10^{-3}$	$4.0\ 10^{-4}$	$4.0\ 10^{-5}$	$4.5\ 10^{-4}$
contrib.γ	$2.0\ 10^{-4}$	$1.5\ 10^{-2}$	$2.0\ 10^{-2}$	$2.0\ 10^{-4}$	$4.0\ 10^{-3}$	$2.5\ 10^{-2}$	$8.0\ 10^{-4}$	$1.5\ 10^{-2}$	$2.5\ 10^{-3}$
contrib.T	$1.0\ 10^{-2}$	$7.0\ 10^{-2}$	$1.0\ 10^{-2}$	$2.0\ 10^{-2}$	$9.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$2.0\ 10^{-2}$	$1.0\ 10^{-2}$
$\frac{\delta G_m^E}{G_m^E}$	$3.0\ 10^{-2}$	$2.0\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$1.5\ 10^{-2}$	$3.0\ 10^{-2}$	$3.0\ 10^{-2}$	$2.0\ 10^{-2}$	$2.5\ 10^{-2}$
δG_m^E /J.mol^{-1}		9			18			8	
σG_m^E /J.mol^{-1}		6			29			6	

The mean uncertainty on excess Gibbs function G_m^E is : $\overline{\frac{\delta G_m^E}{G_m^E}} = 2.0\ 10^{-2}$