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PHASE DIAGRAMS OF MULTI-COMPONENTS MIXTURES CONTAINING FLUORINATED HYDROCARBON

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PHASE DIAGRAMS OF MULTI-COMPONENTS MIXTURES CONTAINING FLUORINATED HYDROCARBON

CONTENTS

ABSTRACT

Phase diagrams of multicomponents mixtures are important in both theoretical studies and industrial applications. They are frequently encountered in liquid-liquid extraction processes. The fluorinated hydrocarbons, such as 2.2.2-trifluoroethanol, are non-toxic non ozone depleting and non-flammable, and excellent substitutes of chlorinated solvents. They are used in medicine, pharmaceutical, chemical industries and fuels.

The measurements and predictions of multicomponent liquid-liquid equilibrium were important for the design of solvent extraction processes.

This work is carried out in order to report solubility and phase diagrams data for ternary and quaternary aqueous mixtures containing: 2.2.2-trifluoroethanol, 1-hexanol, 1-butanol, ethanol, cyclohexane, acetone, and water at temperatures (T =283.15 and T =298.15 , ±0.05) K and pressure P = 101kPa.

For technical procedure, two testes of ternary systems were performed and were in good agreement with literature values.

Complete phase diagrams from solubility (binodal) and tie-line data of the studied systems are obtained by titration and gas chromatography, respectively. Selectivity (S), distribution coefficient (d), and critical solution compositions are reported.

The binodal and liquid-liquid equilibrium data curves were well constructed using by Hand and Othmer-Tobias correlation methods.

RESUME

Les diagrammes de phases de mélanges de multi-composants sont importants aussi bien dans les études théoriques que dans les applications industrielles. Ils sont fréquemment rencontrés dans des processus de l'extraction liquides-liquides. Les hydrocarbures fluorés, comme 2.2.2-trifluoroethanol sont non inflammables, non toxiques ne détruisent pas l'ozone et sont même d'excellents remplaçants des solvants chlorés. On les utilise en médecine, et dans les industries pharmaceutiques, chimiques.

Les mesures et les prédictions d'équilibre liquide-liquide de multi-composants sont importants pour la conception du processus d'extraction.

Ce travail est effectué pour rapporter la solubilité et les diagrammes de phase liquide-liquide de mélanges ternaire et quaternaire contenant : 2.2.2-trifluoroethanol, 1-hexanol, 1-butanol, éthanol, cyclohexane, acétone, et l'eau à différentes températures (T =283.15 and T =298.15 , ±0.05) K et à une pression de 101Kpa.

Pour la procédure technique, des mesures effectuées sur deux systèmes ternaires étalons nous ont permis de confirmer que les résultats obtenus étaient en bon accord avec les données de la littérature.

Des diagrammes de phases complets de la solubilité (binodal) et les données des droites conjuguées (tie-line) des systèmes étudiés sont obtenus par titration et par chromatographie en phase gazeuse, respectivement. Le facteur de sélectivité (S), le coefficient de distribution (d) et les compositions de solution critiques sont rapportés.

Les courbes binodales et les données d'équilibre liquide-liquide ont été bien corrélées par les méthodes de Hand et Othmer-Tobias.

DEDICATION

This thesis would not have been possible without the emotional support of my family:

Special thanks go to my dearest PARENTS, for giving birth to me in the first place, bore me, raised me, taught me, and loved me, thank you for rekindling dreams.

Then and most importantly, I thank my husband, without his understanding, encouragement and patience my thesis would never have been possible, and to my sweetheart, my baby daughter SYRINE, whose love is worth it all.

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L.TELLI

GLOSSERY

List of Symbols

A, B	Hand constants
A_1, B_1	Othmer-Tobias constants
a	activity
C	number of components
d	distribution coefficient
F	degree of freedom
G	Gibbs function
H	enthalpy
M	molar mass
n_D	refractive index
n	mole numbers
p	thermodynamic pressure
Q^0, Q	chromatograph constants
R	universal gas constant
S	entropy, selectivity
s	surface area
T	thermodynamic temperature
V	volume
x	composition
Z	thermodynamic function
z	thermodynamic function

Abbreviations

Calc.	Calculated
eq.	equation
Expt.	Experimental

GLC	Gas-Liquid Chromatograph
LLE	Liquid-Liquid Equilibrium
mix	mixing
mn	minute
p.p.	plait point
TFE	2.2.2-trifluoroethanol
const.	constant

Greek letters

Δ	total change
α, β, φ	phases
δ	uncertainty
∂	derivation
γ	activity coefficient
μ	chemical potential
ρ	density

Lower scripts

A, B, C	components in solutions
i, j	components
m	molar

Upper scripts

cs	critical solution
E	excess property
id	ideal
r	real

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CHAPTER 1

INTRODUCTION

Precise liquid-liquid equilibrium (LLE) data are necessary for the design of many chemical operations and to optimize extraction processes. [1,2,3,4,5,6] Investigation of various kinds of multi-component systems are taking place in many research laboratories in order to understand and provide further information on their phase behavior and thermodynamic properties. Moreover Liquid–liquid extraction is applied in many chemical, pharmaceutical and medicinal processes. [7,8,9] and extraction methods are used to separate compounds on the basis of their relative solubilities in different immiscible liquids. Thus, it is an important operation in chemical and petrochemical processes and for laboratory use. [10,11,12] Extraction is based on liquid-liquid equilibrium. Solvent extraction technique is an alternative method to distillation.

The liquid extraction of aqueous solution is industrially and scientifically important. [13,14,15] Solvents with high selectivity factors and distribution coefficients are considered potential candidates to carry out the extraction. [16]

Among them, fluoroalcohols, are good solvent. They form technical mixture solvents which are taking an important branch in chemical engineering research and unit development.

For example, 2.2.2-trifluoroethanol, wich (TFE) is an expensive substance, it is a solvent of strong hydrogen-bond donor capacity and undergoes chemical and thermal stability. It is reported as an effective solvent in bioengineering, and is considered as a novel and clean energetic fluid [17].

Alcohols are some of the promissory compounds in order to produce lead free gasolines. They are among the most important organic compounds, because they are of central importance in organic chemistry and biochemistry. Due to the presence of the –OH group in the molecule, the solution chemistry of these compounds can be strongly influenced by the intermolecular hydrogen bond formation, which can play an important role in the physical

properties of these molecules. Therefore, they have been subject to extensive practical and theoretical investigations to study intermolecular hydrogen bonding. [18,19]

- Alcohols have applications in industry and science as reagents or solvents. Concerning the liquids, we have used in the mixtures under study, we remember here some of their characteristics. Because of its low toxicity and ability to dissolve non-polar substances, ethanol has widespread use as a solvent of substances intended for human contact or consumption, including scents, flavourings, colourings, and medicines. In chemistry, it is both an essential solvent and a feedstock for the synthesis of other products. [20]
However, the use of ethanol in gasoline blends can raise phase separation problems.[21,22]

-Water is miscible with many liquids. Water is also one of the best solvent due to its polarity.

-Butanol is used as a solvent for a wide variety of chemical and textile processes, and in organic synthesis as a chemical intermediate. It is also used as paint and a solvent in other coating applications where it is used as a relatively slow evaporating latent solvent in lacquers and ambient-cured enamels. It finds other uses such as a component of hydraulic and brake fluids.

-Hexanol has a high boiling point and is used to improve the flow and surface properties of paints. It is also used in the perfume industry and as a solvent for fats, waxes, and dyes.[23]

-Acetone is a mobile, and flammable liquid. It is the simplest ketone. It is soluble in water and also good solvent for most organic components and polymers and itself serves as an important solvent. It is often used as a degreaser in the preparation of metal prior to painting as well as a cleaning solvent of glassware. Acetone is also used to make plastic, fibers, drugs, and other chemicals. Acetone is also found naturally in the environment, and in small amounts, in the human body.[24]

-Cyclohexane is used as a chemical intermediate to produce target molecules. Cyclohexane derivatives can be used for the synthesis of pharmaceuticals, dyes, herbicides, plant growth regulator, plasticizers, rubber chemicals, cycloamines and other organic compounds. It is a nonpolar solvent which is often used as a standard. [25] It is virtually insoluble in 2,2,2-

trifluoroethanol. On an industrial scale, cyclohexane is produced by reacting benzene with hydrogen, owing to its unique chemical and conformational properties.

This work is a continuation of our laboratory research concerning studies on liquid-liquid equilibrium of halogenated hydrocarbons and fluorohydrocarbons: Iodoethane, α,α,α-trifluorotoluene, fluorobenzen and 2.2.2-trifluoroethanol. Now we present complete phase diagrams of aqueous, organic ternary and quaternary solutions for systems of 2.2.2 trifluoroethanol at temperature 288.15K and 298.15 K and pressure 101kPa. The solubility data were obtained by titration method and were correlated using empirical equations; Tie-lines were obtained by gas chromatography and were correlated by using the Hand and Othmer–Tobias equations.

CHAPTER 2

Fundamentals of phase diagrams of multicomponents mixtures

2.1 Introduction

Mixtures are characterized by many thermodynamic properties and show wide range of behaviour which leads to major applications in chemical and industrial technologies.

The total thermodynamic functions Z_m depend generally on temperature *T*, pressure *p*, and composition n_i: $Z_m = f(T, p, n_i, \ldots)$. Consequently, the change in a molar thermodynamic function is:

$$dZ_m = (\partial Z_m / \partial T)_{P,ni}\, dT + (\partial Z_m / \partial p)_{T,ni}\, dp + \sum (\partial Z_m / \partial n_i)_{T,p,n_{j\neq i}}\, dn_i \qquad (2.1)$$

where $(\partial Z_m / \partial n_i)_{T,p,n_{j\neq i}}$ (2.2)

is the partial molar function $\bar{z}_{m,i}$

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

$$dZ_m = \sum_i \bar{z}_{m,i}\, dn_i \ (T,p, \text{const.}) \qquad (2.3)$$

It follows that the total function of a mixture is:

$$Z_m = \sum_i n_i \bar{z}_{m,i} \ (T, p, \text{const.}) \qquad (2.4)$$

Differentiating equation (2.4) gives:

$$dZ_m = \sum_i \bar{z}_{m,i}\, dn_i + \sum_i n_i d\, \bar{z}_{m,i} \qquad (2.5)$$

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

$$\sum_i x_i d\, \bar{z}_{m,i} = 0, \ (T, p, \text{const.}) \qquad (2.6)$$

The Gibbs-Duhem equation (2.6) is valid for any total molar thermodynamic property z_m in a homogeneous phase.

$$\Delta_{mix} z_m(T,p,x_i) = z_m(T,p,x_i) - \sum_i x_i \bar{z}_{m,i}(T,p,x_i) \tag{2.7}$$

Where z_m is the total molar function of mixture, and $\bar{z}_{m,i}$ is the partial molar function of component *i*.

Common thermodynamic functions are: Gibbs function *G*, enthalpy *H*, entropy *S*, volume *V*.

The ideal mixtures have mixing thermodynamic properties $\Delta_{mix} z_m^{id}$ given by:

$$\Delta_{mix} g_m^{id} = RT \sum_i x_i \ln x_i \tag{2.8a}$$

$$\Delta_{mix} s_m^{id} = -R \sum_i x_i \ln x_i \tag{2.8b}$$

$$\Delta_{mix} h_m^{id} = 0,\ \Delta_{mix} v_m^{id} = 0 \tag{2.8c}$$

For a system of heterogeneous liquid solutions, the change in the total Gibbs energy function *G* is given as follows:

$$dG_m^{\varphi} = -S_m^{\varphi} dT^{\varphi} + V_m^{\varphi} dp^{\varphi} + \sum_i \mu_i^{\varphi} dn_i^{\varphi} \tag{2.9}$$

where the summation is over all components *i* .

The chemical potential μ for component *i* is defined by:

$$\mu_i^{\varphi} = \left(\partial G / \partial n_i\right)_{T, p, n_j \neq n_i}^{\varphi} \tag{2.10}$$

The Gibbs-Duhem relation (eq. 2.6) for a phase φ *is then*:

$$\sum_i x_i^{\varphi} d\mu_i = 0 \tag{2.11}$$

where x_i^{φ} is the mole fraction of component *i* in phase φ.

The phase rule allows the determination of the least number of variables to study a thermodynamic system of φ phases that coexist in equilibrium. The phase rule defines the degree of freedom of the system as:

$$F = C + 2 - \varphi \tag{2.12}$$

where φ is the number of phases in thermodynamic equilibrium, C is the number of components. The degree of freedom F corresponds to the number of intensive variables, (T, p, x_i,..), that must be specified to fix the state of a system.

The activity a_i of a component i in a real mixture is related to the mole fraction x_i as:

$$a_i = x_i \gamma_i \tag{2.13}$$

where γ_i is the activity coefficient of component i in mixture.

For an ideal solution:

$$\gamma_i = 1.0 \text{ and } a_i = x_i \tag{2.14}$$

The molar Gibbs function of mixing of real solution $\Delta_{mix} g_m^r$ is:

$$\Delta_{mix} g_m^r = RT \sum_{i=1}^{N} x_i \ln a_i \tag{2.15}$$

The molar excess function $z_m^E(T, p, x_i)$ is defined by:

$$z_m^E(T, p, x_i) = \Delta_{mix} z_m^r(T, p, x_i) - \Delta_{mix} z_m^{id}(T, p, x_i) \tag{2.16}$$

The excess molar Gibbs function g_m^E is:

$$g_m^E(T, p, x_i) = \Delta_{mix} g_m^r(T, p, x_i) - \Delta_{mix} g_m^{id}(T, p, x_i) \tag{2.17}$$

with:

$$\Delta_{mix} g_m^r = RT \sum_{i}^{N} x_i \ln x_i + RT \sum_{i}^{N} x_i \ln \gamma_i \tag{2.18}$$

and we get:

$$g_m^E = RT \sum_{i}^{N} x_i \ln \gamma_i \tag{2.19}$$

with the activity coefficient γ_i of component i:

$$\bar{g}_{m,i}^E = RT \ln \gamma_i \tag{2.20}$$

Molar excess Gibbs function g_m^E is difficult thermodynamic quantity to measure. However, the studies of phase equilibrium of multi-component multi-phase systems apply directly its determination, as shown in equations (2.19) and (2.20).

The liquid-liquid phase equilibrium of multi-component solution is expressed in term of the activity as:

$$a_i^{\alpha} = a_i^{\beta} \tag{2.21}$$

Where a_i^{φ} is the activity of component i in phase φ (φ=α or β)

According to equation (2.21), it holds for component i in two phases in system:

$$\gamma_i^{\alpha} x_i^{\alpha} = \gamma_i^{\beta} x_i^{\beta} \tag{2.22}$$

where x_i^{φ} and γ_i^{φ} are the equilibrium composition and the activity coefficient of component *i* in phase φ, respectively.

Applying equation (2.22) for ternary system we get:

$$\left(\gamma_1 x_1\right)^{\alpha} = \left(\gamma_1 x_1\right)^{\beta} \tag{2.23}$$

$$\left(\gamma_2 x_2\right)^{\alpha} = \left(\gamma_2 x_2\right)^{\beta} \tag{2.24}$$

$$\left(\gamma_3 x_3\right)^{\alpha} = \left(\gamma_3 x_3\right)^{\beta} \tag{2.25}$$

Critical state

In a two-phases system, at liquid-liquid equilibrium, the state where coexisting phases become identical is known as the of critical state .

In thermodynamic studies of solutions, the variables of critical state are: the critical pressure p^c, critical temperature T^c, and critical composition x^c. The values of (T^c, p^c , x^c) constants are unique for each system or solution.

Critical point

In phase equilibrium, for a given set of fixed parameters it always exists a thermodynamic potential having a minimum in the states, denotes the limit of the two-phases region of the phase diagram. The temperature, pressure and composition corresponding to critical point are known as the critical temperature, critical pressure, critical composition.

$$T^{\alpha} = T^{\beta} = T, \quad (2.26)$$

$$p^{\alpha} = p^{\beta} = p, \quad (2.27)$$

$$x_i^{\alpha} = x_i^{\beta} = x_i^{cs}, \text{ (}T\text{, }p\text{, constant)} \quad (2.28)$$

2.2 Liquid liquid phase equilibrium:

According to Treybal's classification [Sorensen and Arlt, 1980], all ternary and quaternary solutions in this study were formed type 1 having a plait point. [26]

For two phases in ternary system: the variance is $F = 3$

$\varphi = 2$, $C = 3$, so $F = 3$

For a ternary system at constant temperature, $F = 2$, so only two mole fractions x_1 and x_2 are needed to well identify the system since $x_3 = 1 - (x_1 + x_2)$

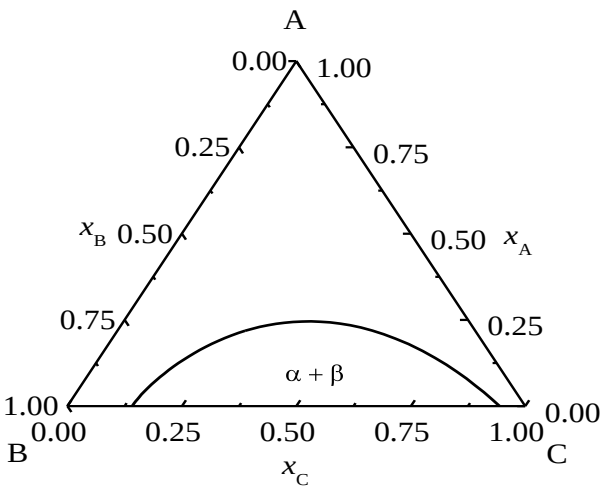

FIGURE (1.2.1) : Schematic representation of a ternary liquid-liquid phase equilibrium

For a quaternary system at constant temperature, $F = 3$, so only three mole fractions x_1 , x_2 and x_3 are needed to well identify the system since $x_4 = 1 - (x_1 + x_2 + x_3)$

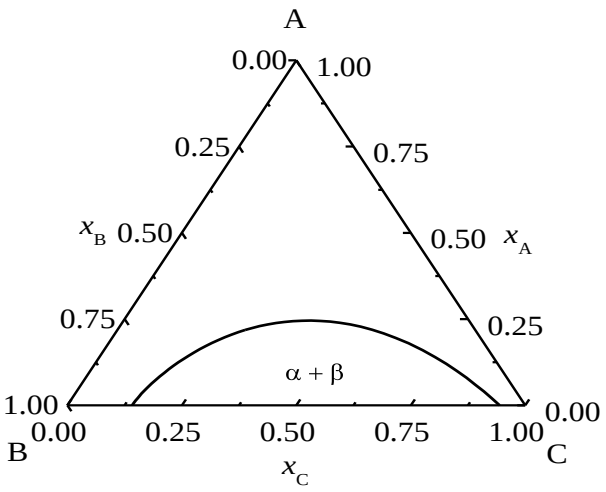

FIGURE (1.2.2) : Schematic representation of a quaternary liquid-liquid phase equilibrium, With: $C = c + d$

The distribution coefficient d_i is defined by:

$$d_i = \frac{x_i^{\alpha}}{x_i^{\beta}} \tag{2.29}$$

The selectivity S (separation factor) is:

$$S_{ij} = \frac{d_i}{d_j} = \left(\frac{x_i^{\alpha} / x_i^{\beta}}{x_j^{\alpha} / x_j^{\beta}} \right) \tag{2.30}$$

2.3 Solubility Data Correlation:

The binodal curve and liquid-liquid equilibrium data of ternary and quaternary mixtures were well fitted and correlated by the empirical equation:

$$x_i = a + bx_j^{0.5} + cx_j + dx_j^2 + ex_j^3 \tag{2.31}$$

where x_i, x_j represent the compositions of component i, j in the ternary and quaternary solutions respectively, and $a,b,c,e...$ are regression constants.

2.4 Liquid-Liquid Equilibrium Data Correlation Using Empirical Equations: Othmer-Tobias and Hand Correlation Method:

In the multicomponent mixtures, the reliability of experimentally measured tie-line data can be ascertained by applying the Hand [1930], and Othmer-Tobias [1942] equations. The Hand and the Othmer-Tobias correlation are given by the following equation, respectively. [27]

$$\ln\left(\frac{x_2^{\beta}}{x_3^{\beta}}\right) = A + B\ln\left(\frac{x_2^{\alpha}}{x_1^{\alpha}}\right) \tag{2.32}$$

$$\ln\left\{\frac{(1-x_3^{\beta})}{x_3^{\beta}}\right\} = A_1 + B_1\ln\left\{\frac{(1-x_1^{\alpha})}{x_1^{\alpha}}\right\} \tag{2.33}$$

where x_i^{φ} is composition of component *i* in phase φ.

CHAPTER 3

EXPERIMENTAL SECTION

3.1 Chemical Substances:

The chemical substances and their compositions purities are: ethanol, 1-hoxanol, toluene, 1-butanol, 2.2.2-trifluoroethanol, acetone, and 2-propanol, supplied by Riedel deHaën and cyclohexane from Panreac. Pure water is used throughout the study.

The refractive indices of pure components were measured at the temperature 298.15 K using an Abbe-type refractometer (Phywe, No.990646).

Densities of the pure chemicals were measured at the temperature 298.15 K with an Anton Paar vibrating tube densimeter (model DMA5000) with a precision of $\pm 2.10^{-5}$ g.cm^{-3} at a temperature controlled to ± 2 mK, which was calibrated with triple-distilled and dry air.

The densities are measured at 298.15 K compared to $\pm 5.10^{-4}$ cm^3.mol^{-1} with the literature values. The atmospheric pressure was determined to ±0.1 kPa with a mercury barometer (Prolabo: Fortin, no. 02025008).

The purities and refractive indices of all chemicals used in this study are presented in table (1) together with the literature data.

TABLE (3.1): Experimental values of density (ρ), refractive index (n_D) of pure components at T= 298.15 K:

Component	Symbol	ρ (298.15K)g.cm^{-3}		n_D (298.15K)	
		Exp.	Lit.	Exp.	Lit.
Acetone	CH_3COCH_3	0.7846	0.7844 [118]	1.3563	1.3560 [118]
1-Butanol	C_4H_9OH	0.8055	0.8057 [118]	1.3971	1.3974 [118]
Cyclohexane	C_6H_{12}	0.7740	0.7739 [118]	1.4233	1.4235 [118]
Toluene	C_7H_8	0.8630	0.8622 [118]	1.4944	1.4941 [118]
Ethanol	C_2H_5OH	0.7852	0.7849 [118]	1.3593	1.3594 [118]
1-Hexanol	$C_6H_{13}OH$	0.8158	0.8153 [118]	1.4158	1.4157 [118]
2-Propanol	C_3H_7OH	0.7811	0.7813 [118]	1.3757	1.3752 [118]
2.2.2Trifluoroethanol	CF_3CH_2OH	1.3820	1.3827 [137]	1.2910	1.2907 [137]
Water	H_2O	0.9970	0.9971 [118]	1.3327	1.3325 [118]

3.2 Apparatus and procedure

3.2.1 Extraction runs

The binodal curve of the ternary and the quaternary solutions were performed by the titration method in an equilibrium glass cell (built by SOMIVER-Thenia (Algeria),the scheme of this liquid-liquid equilibrium cell is shown in figure (1)), equipped with a magnetic stirrer and connected to Lauda cryostat (model: RC6CP Edition 2000) and measured with a calibrated digital thermistor-thermometer (Cole-Parmer Instrument, model: 8502–16, thermistor: YSI-400) with a precision better than ± 0.03 K.

The tie-line data were obtained by preparing ternary and quaternary solutions of known overall compositions lying within the two-phase region.
The continuous visual-titration method was used to construct the solubility curves (binodal).

All mixtures were prepared by weighing using an OHAUS balance (model: Explorer) with a precision of ± 0.1 mg. The error in compositions of the prepared solutions was estimated to be (± 3.10^{-4}) and after being stirred vigorously in stoppered ampoules the mixture was stirred

vigorously for least 20 min and then where submerged in the cryostat bath, and allowed phase equilibrium to be attained for three days at the desired temperature.

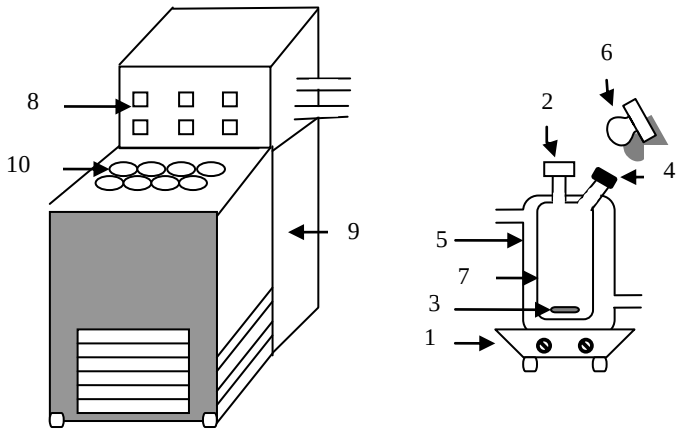

FIGURE (3.1): Liquid-liquid equilibrium cell.

1- Magnetic stirrer	2- Stopper
3- Magnetic stirring bar	4- Symptom pore
5- Water jacket	6- Lamp
7- Cell body	8-Temperature control
9- Cryostat bath	10- Samples

The samples of organic-rich and aqueous-rich phase were taken by a glass hypodermic syringe (5 μ l), and were kept in bottles protected from light (sample injection: 0.2 μ l). Three analyses were performed for each sample.
The composition of liquid Samples of phases were collected and were analyzed using Gas-Liquid Chromatography (GLC).

3.2.2 Measurements of phase compositions using Chromatographic Analysis

The composition of phases was determined by Gas-Liquid Chromatography (G.L.C.) analysis (Perkin-Elmer, model: Clarus 500 is shown in Figure (2)). The chromatograph was equipped with a thermal conductivity detector (T.C.D.) and flame ionisation detector (FID),Two filters

were attached to the carrier-gas line to protect the chromatograph detector TCD from any traces of water and oxygen in the carrier gas (Supelco Park Bellefonte, PA 16823 (814) 359-3441; Moisture Trap Model 23987).

TABLE (3.2.1): Operating conditions for gas-liquid chromatography measurements using Porapak packed column:

Column	Porapak packed column, 0.6m, Q80/100 Mesh
Detector temperature	473.15 K
Injector temperature	513.15 K
Oven temperature	423.15 K
Carrier gas	Nitrogen
Flow rate	25 $ml.min^{-1}$

For the ternary and quaternary solutions containing cyclohexane and 2.2.2-trifluoroethanol the two liquid phase samples were analysed by:

TABLE (3.2.2): Operating conditions for gas-liquid chromatography measurements using Carbopak column:

Column	Carbopak (B 80/100 Mesh, 5 % Carboix 20M)
Detector temperature	473.15 K
Injector temperature	513.15 K
Oven temperature	403.15 K
Carrier gas	Nitrogen
Flow rate	20 $ml.min^{-1}$

The compositions of samples of pure components as well as solutions were obtained using by applying the internal standard calibration method.

The internal standard calibration method was used for phase-composition analysis. The gas chromatograph was calibrated by means of standard mixtures.

2-propanol was used as a solvent for the gas chromatograph internal standard calibration.

The chromatograph calibration equation is:

$$\frac{s_i}{s_{st}} = Q + Q^0 \frac{n_i}{n_{st}} \qquad (3.1)$$

Where s_i and s_{st} are the percentage peak area of the compound and of the internal standard, respectively, n_i and n_{std} are the number of moles of the measured compound and of the internal standard in the calibration mixture respectively, Q and Q^0 are the chromatograph constants.

The chromatographic-technical procedures were checked by two ternary tests systems for: (water + ethanol + cyclohexane), and (water + ethanol + toluene) at 298.15 K.

The experimental data obtained for these test systems showed good agreement with literature values.

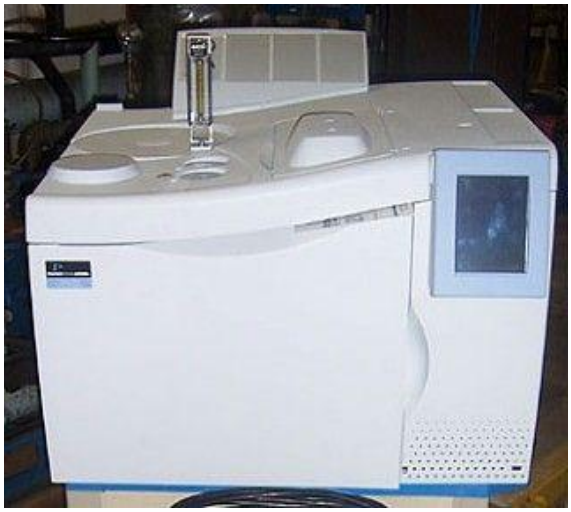

FIGURE (3.2.2): Gas-Liquid Chromatography

CHAPTER 4

Experimental Results

4.1 Experimental data of liquid-liquid equilibrium

This thesis reports new solubility and liquid-liquid equilibrium data for ternary and quaternary mixtures containing water, ethanol, 1-propanol, 1-butanol, 1-hoxanol, toluene, acetone, cyclohexane, 2.2.2-trifluoroethanol, at temperatures 283.15 K, 298.15 K and atmospheric pressure.

The Test systems:

T = 298.15 K

water (1) + ethanol (2) + toluene (3),

water (1) + ethanol (2) + cyclohexane (3).

The studied systems:

-Ternary systems:

T = 298.15 K

water (1) + 2.2.2-trifluoroethanol (2) + 1-butanol (3),

water (1) + 2.2.2-trifluoroethanol (2) + 1-hexanol (3),

2.2.2-trifluoroethanol (1) + acetone (2) + cyclohexane (3),

-Quaternary systems:

T = 283.15 K

cyclohexane (1) + ethanol (2) +2.2.2-trifluoroethanol (3) + acetone (4),

T = 298.15 K

cyclohexane (1) + ethanol (2) +2.2.2-trifluoroethanol (3) + acetone (4) ,

water (1) + 2.2.2-trifluoroethanol (2) + 1-hexanol (3) + acetone (4),

2.2.2-trifluoroethanol (1) + acetone (2) + water (3) + 1-butanol (4).

4.2 Liquid-liquid equilibrium correlation

The selectivity S_{ji} of the solvent *j* to extract the solute *i* from its liquid solution was obtained by equation (2.30).

The experimental solubility and liquid–liquid equilibrium data of ternary and quaternary mixtures at the measured temperatures for the studied systems are given bellow.

The solubility data were correlated by equation (2.31). The liquid-liquid equilibrium data were correlated by: Hand, equation (2.32), and Othmer-Tobias, equation (2.33).

The distribution coefficient of component *i*; d_i, was estimated from liquid-liquid equilibrium data using equation (2.29).

4.3 Results and analysis for ternary and quaternary mixtures

4.3.1 Results and analysis for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.1.1), are shown in Figure (4.3.1.1). The liquid-liquid equilibrium values are given in Table (4.3.1.2).

The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.1.2) and are shown in Figures (4.3.1.2) and (4.3.1.3) successively. While distribution coefficient d_i, selectivity *S* values are outlined in Table (4.3.1.3), and are shown in Figure (4.3.1.4) and (4.3.1.5). The critical solution plait point of (water + ethanol + cyclohexane) at 298.15 K is: experimental value: ($x_1^{cs} = 0.129$, $x_2^{cs} = 0.574$)

TABLE (4.3.1.1): Binodal curve data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa

x_1	x_2	x_3	x_1	x_2	x_3
0.530	0.448	0.022	0.185	0.627	0.189
0.511	0.465	0.024	0.174	0.618	0.207
0.480	0.491	0.030	0.164	0.613	0.224
0.466	0.500	0.033	0.157	0.608	0.235
0.448	0.514	0.038	0.151	0.610	0.238
0.437	0.523	0.041	0.146	0.597	0.257
0.431	0.527	0.042	0.139	0.587	0.274
0.421	0.535	0.045	0.127	0.569	0.304
0.411	0.542	0.047	0.126	0.583	0.292
0.387	0.562	0.051	0.121	0.560	0.319
0.384	0.564	0.052	0.117	0.551	0.332
0.381	0.566	0.053	0.114	0.543	0.343
0.377	0.568	0.055	0.097	0.524	0.379
0.375	0.569	0.056	0.097	0.524	0.379
0.369	0.574	0.058	0.093	0.510	0.397
0.364	0.576	0.059	0.093	0.510	0.397
0.358	0.580	0.062	0.084	0.481	0.435
0.356	0.581	0.064	0.084	0.481	0.435
0.352	0.583	0.065	0.068	0.440	0.493
0.341	0.590	0.069	0.065	0.401	0.534
0.339	0.591	0.070	0.065	0.401	0.534
0.331	0.595	0.074	0.045	0.331	0.624
0.321	0.603	0.076	0.045	0.329	0.626
0.311	0.606	0.084	0.045	0.329	0.626
0.306	0.608	0.085	0.037	0.308	0.655
0.293	0.615	0.092	0.035	0.301	0.664
0.279	0.620	0.101	0.027	0.250	0.723
0.265	0.624	0.110	0.019	0.203	0.779
0.240	0.634	0.126	0.013	0.102	0.885
0.217	0.628	0.154	0.012	0.135	0.853
0.216	0.633	0.151	0.011	0.014	0.975
0.201	0.627	0.172	0.011	0.014	0.975

Binodal curve eq: $x_2 = 0.115 + 2.914x_3^{0.5} - 4.367x_3 + 2.183x_3^2 - 0.860x_3^3;\ R^2 = 1.0$

TABLE (4.3.1.2): liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa

Feed Composition			Water-Rich Phase			Cyclohexane-Rich Phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
0.471	0.114	0.415	0.802	0.186	0.012	0.006	0.017	0.978
0.444	0.175	0.381	0.724	0.266	0.009	0.006	0.030	0.964
0.405	0.247	0.348	0.619	0.364	0.018	0.011	0.066	0.923
0.359	0.334	0.307	0.526	0.454	0.020	0.010	0.115	0.875
0.316	0.407	0.277	0.438	0.525	0.037	0.020	0.166	0.814
0.283	0.478	0.239	0.369	0.574	0.057	0.025	0.214	0.761
0.257	0.521	0.222	0.327	0.605	0.069	0.015	0.272	0.713
0.233	0.567	0.200	0.281	0.619	0.100	0.039	0.350	0.612
	x^{cs}		0.129	0.574	0.297	0.129	0.574	0.297

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
-1.857	1.534	0.997	-1.848	1.406	0.997

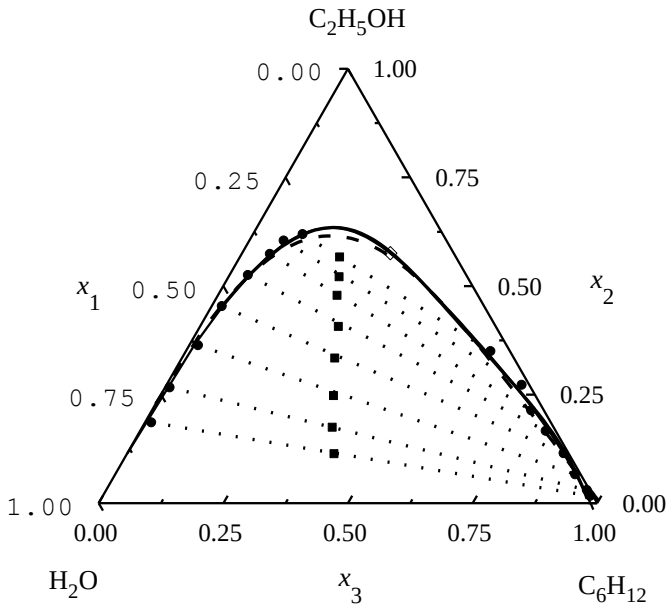

FIGURE (4.3.1.1): Solubility and liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa: —, eq. (2.31); -.-, eq. (2.31) from ref [28]; ■, feed composition; ●, LLE; …, tie line; ◊, p.p.

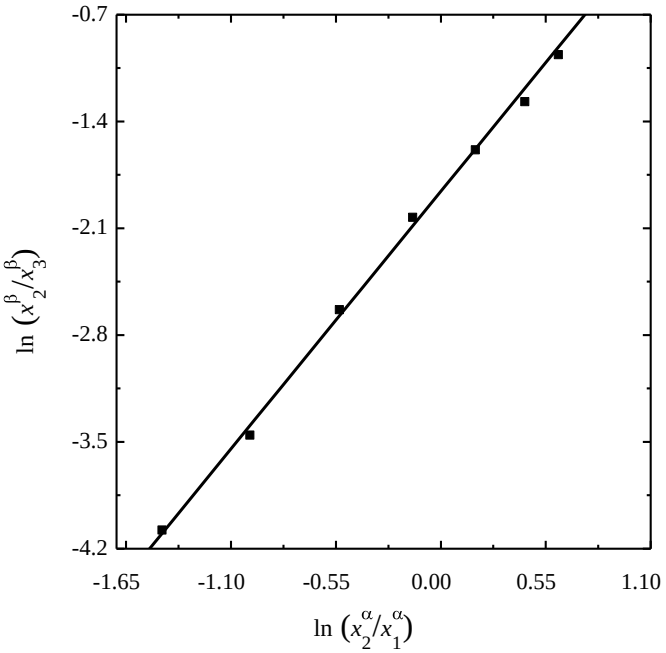

FIGURE (4.3.1.2): Hand correlation of liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

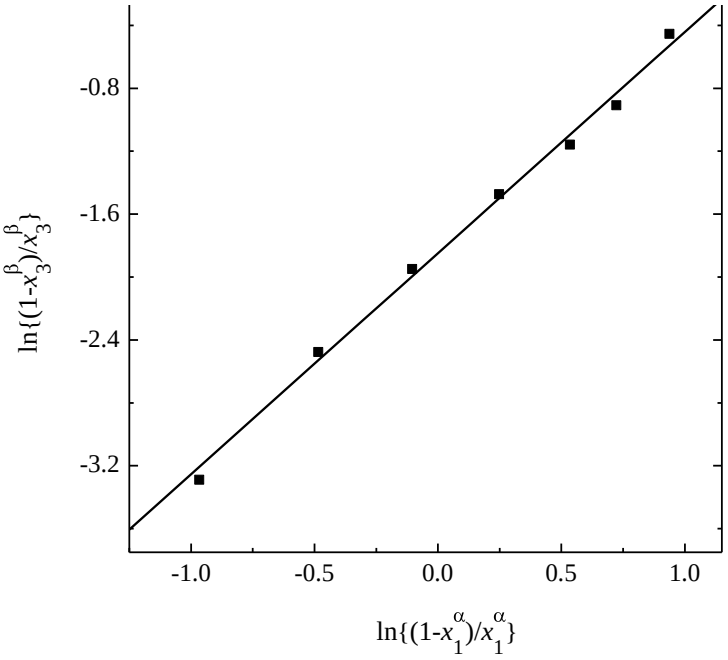

FIGURE (4.3.1.3): Othmer-Tobias correlation of liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

TABLE (4.3.1.3): Distribution coefficient d_i and selectivity S for liquid-liquid equilibrium data for ternary mixtures {x_1 water (1) + x_2 ethanol (2) + x_3 cyclohexane (3)} at 298.15 K and 101Kpa

d_1	141.9	131.4	55.3	54.9	22.1	14.6	21.9	7.3
d_2	11.2	8.8	5.5	3.9	3.2	2.7	2.2	1.8
S	12.6	15.0	10.1	13.9	7.0	5.4	9.9	4.1

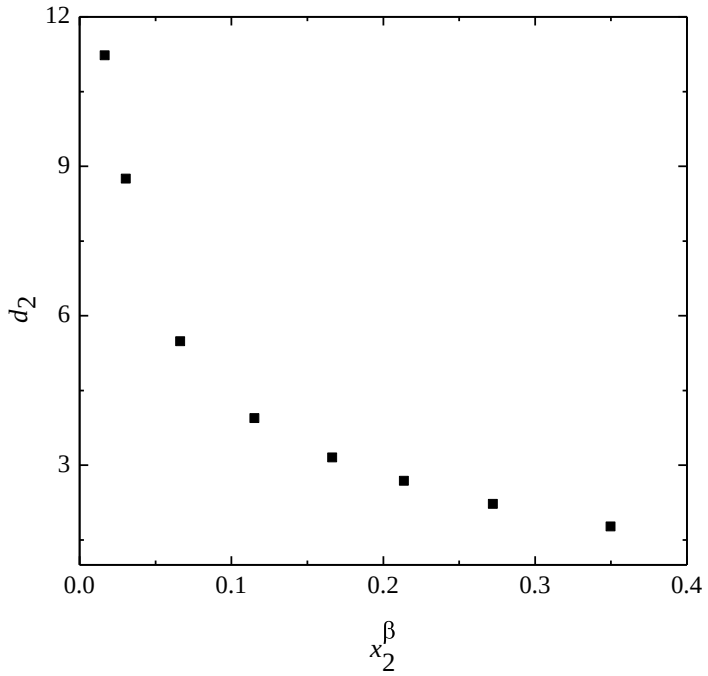

FIGURE (4.3.1.4): Distribution coefficient for liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

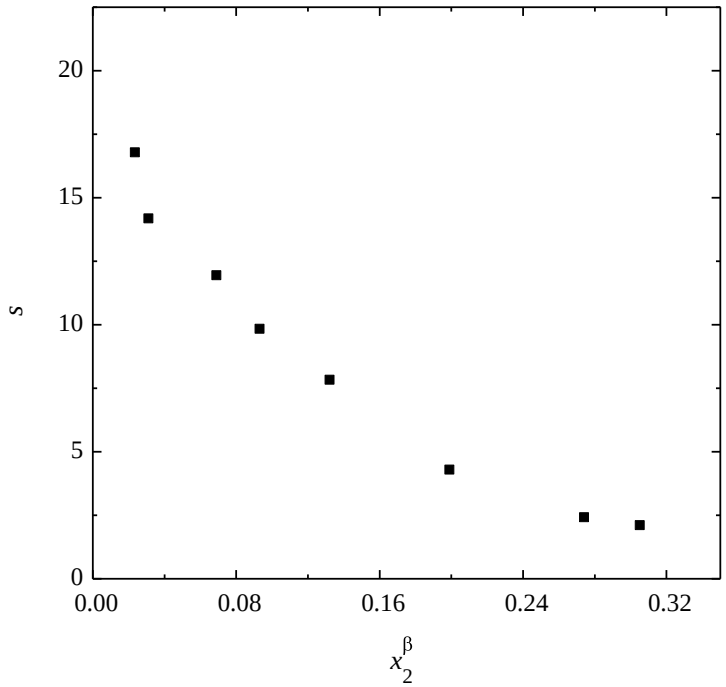

FIGURE (4.3.1.5): Selectivity *S* for liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

4.3.2 Results and analysis for ternary mixtures {water (1) + ethanol (2) + toluene (3)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.2.1), are shown in Figure (4.3.2.1). The liquid-liquid equilibrium values are given in Table (4.3.2.2). The critical solution plait point of {water (1) + ethanol (2) + toluene (3)} at 298.15 K is: experimental value: ($x_1^{cs} = 0.152$, $x_2^{cs} = 0.370$).

TABLE (4.3.2.1): Binodal curve data for ternary mixtures { water (1) + ethanol (2) + toluene (3)} at 298.15 K and 101Kpa

x_1	x_2	x_3	x_1	x_2	x_3
0.649	0.335	0.016	0.212	0.425	0.363
0.610	0.362	0.028	0.198	0.403	0.399
0.570	0.396	0.035	0.172	0.383	0.445
0.522	0.432	0.047	0.157	0.363	0.480
0.480	0.452	0.068	0.136	0.345	0.519
0.431	0.478	0.091	0.122	0.318	0.560
0.382	0.485	0.133	0.099	0.287	0.614
0.337	0.482	0.181	0.090	0.273	0.637
0.311	0.472	0.217	0.071	0.240	0.689
0.274	0.460	0.266	0.053	0.199	0.747
0.247	0.450	0.303	0.028	0.169	0.803
0.232	0.435	0.333			

Binodal curve eq: $x_2 = 0.118 - 3.070x_3^{0.5} + 2.054x_3 + 1.633x_3^2 - 0.738x_3^3;\ R^2 = 0.999$

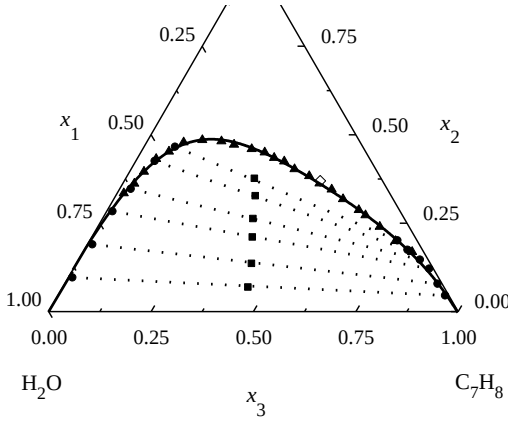

FIGURE (4.3.2.1) : Solubility and liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + toluene (3)} at 298.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.2.2): liquid-liquid equilibrium data for ternary mixtures {water (1) + ethanol (2) + toluene (3)} at 298.15 K and 101Kpa at 298.15 K and 101Kpa

Feed Composition			Water-Rich Phase			Toluene-Rich Phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
0.452	0.069	0.479	0.894	0.096	0.010	0.009	0.045	0.945
0.427	0.136	0.436	0.798	0.190	0.012	0.011	0.079	0.910
0.392	0.211	0.397	0.702	0.284	0.014	0.010	0.121	0.868
0.368	0.263	0.370	0.626	0.347	0.027	0.020	0.147	0.834
0.341	0.327	0.332	0.528	0.426	0.046	0.036	0.175	0.789
0.314	0.377	0.309	0.459	0.466	0.076	0.047	0.201	0.751
	x^{cs}		0.152	0.370	0.478	0.152	0.370	0.478

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
-1.314	0.769	0.998	-1.231	0.767	0.999

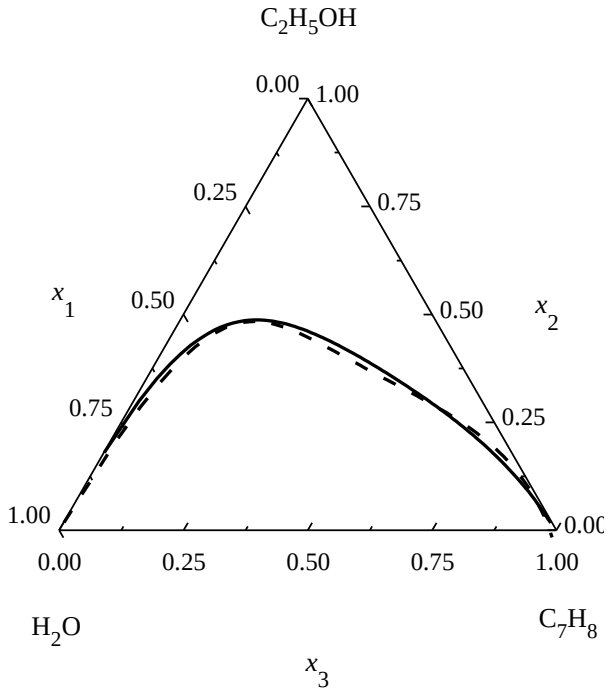

FIGURE (4.3.2.2): — binodal curve eq; .... from ref [29] binodal curve eq for ternary mixtures { water (1) + ethanol (2) + toluene (3)} at 298.15 K and 101Kpa.

4.3.3 Results and analysis for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.3.1), are shown in Figure (4.3.3.1). The liquid-liquid equilibrium values are given in Table (4.3.3.2).

The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.3.2) and are shown in Figures (4.3.3.2) and (4.3.3.3) successively. While distribution coefficient d_i,, selectivity S values are outlined in Table (4.3.3.3), and are shown in Figure (4.3.3.4) and (4.3.3.5). The critical solution plait point of {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K is: experimental value: $(x_1^{cs} = 0.578,\ x_2^{cs} = 0.217)$.

TABLE (4.3.3.1): Binodal curve data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa

x_1	x_2	x_3	x_1	x_2	x_3
0.496	0.016	0.488	0.577	0.215	0.209
0.495	0.032	0.474	0.592	0.219	0.189
0.494	0.044	0.463	0.616	0.214	0.170
0.494	0.050	0.456	0.643	0.208	0.149
0.496	0.063	0.442	0.666	0.202	0.131
0.496	0.085	0.420	0.697	0.187	0.116
0.499	0.113	0.389	0.712	0.181	0.107
0.503	0.132	0.364	0.741	0.165	0.094
0.508	0.146	0.345	0.774	0.148	0.078
0.510	0.158	0.333	0.804	0.135	0.061
0.508	0.166	0.326	0.846	0.107	0.048
0.515	0.181	0.304	0.876	0.088	0.037
0.523	0.192	0.285	0.900	0.073	0.027
0.537	0.199	0.264	0.913	0.063	0.024
0.554	0.210	0.236	0.931	0.049	0.021
0.553	0.212	0.235	0.972	0.009	0.019

Binodal curve eq: $x_2 = -0.099 + 0.993x_3^{0.5} - 0.050x_3 - 3.468x_3^2 + 2.331x_3^3;\ R^2 = 0.991$

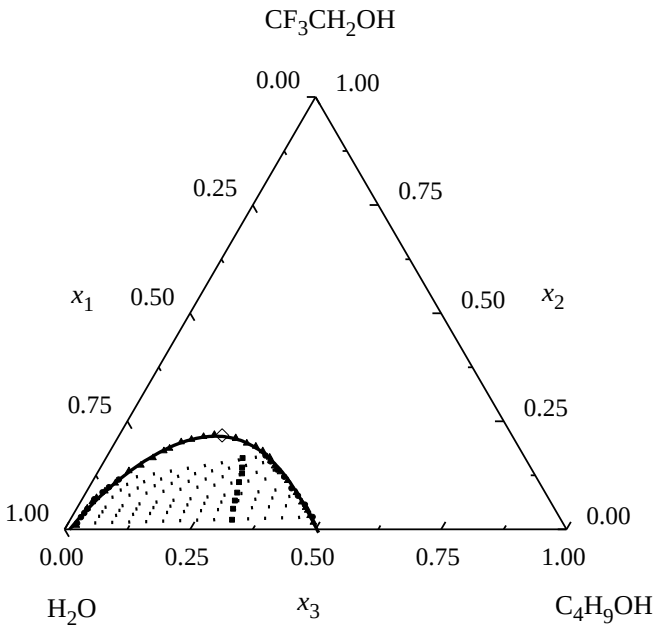

FIGURE (4.3.3.1) : Solubility and liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa:▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

Table (4.3.3.2): liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa

Feed Composition			Water-Rich Phase			BuOH-Rich Phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
0.655	0.022	0.323	0.968	0.014	0.018	0.491	0.029	0.480
0.641	0.047	0.312	0.953	0.028	0.019	0.493	0.057	0.451
0.628	0.066	0.306	0.942	0.037	0.021	0.496	0.077	0.426
0.614	0.085	0.301	0.931	0.047	0.022	0.500	0.095	0.405
0.598	0.109	0.293	0.906	0.069	0.025	0.502	0.121	0.377
0.582	0.129	0.289	0.882	0.085	0.033	0.507	0.138	0.355
0.575	0.143	0.283	0.863	0.097	0.040	0.511	0.157	0.333
0.563	0.164	0.273	0.835	0.115	0.051	0.514	0.171	0.315
	x^{cs}		0.578	0.217	0.205	0.578	0.217	0.205

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
1.350	0.966	0.995	1.406	0.395	0.997

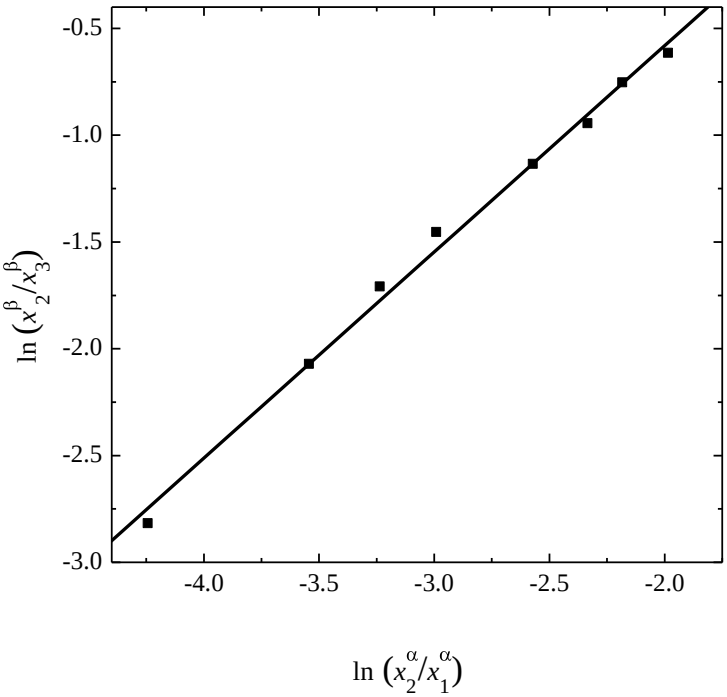

FIGURE (4.3.3.2): Hand correlation of liquid-liquid equilibrium data of ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa.

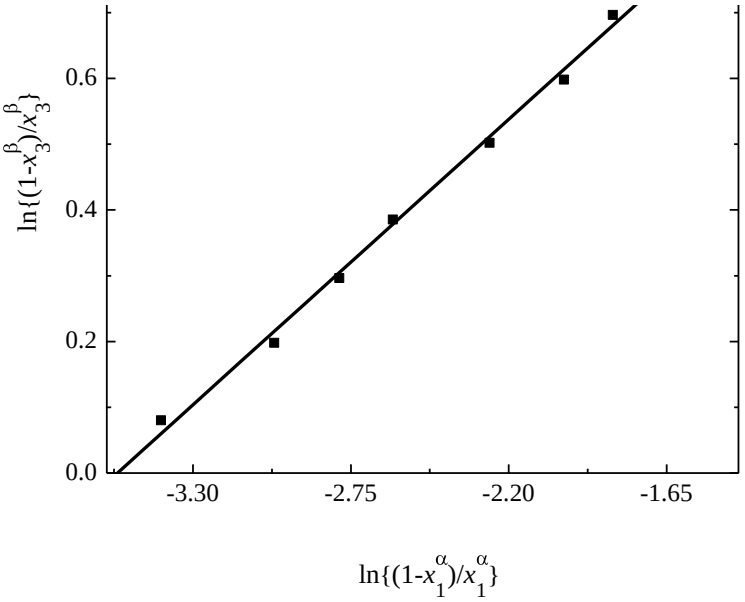

FIGURE (4.3.3.3): Othmer-Tobias correlation of liquid-liquid equilibrium data ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa.

TABLE (4.3.3.3): Distribution coefficient d_i and selectivity S for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa

d_1	2.0	1.9	1.9	1.9	1.8	1.7	1.7	1.6
d_2	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.7
S	4.1	4.0	4.0	3.8	3.2	2.8	2.7	2.4

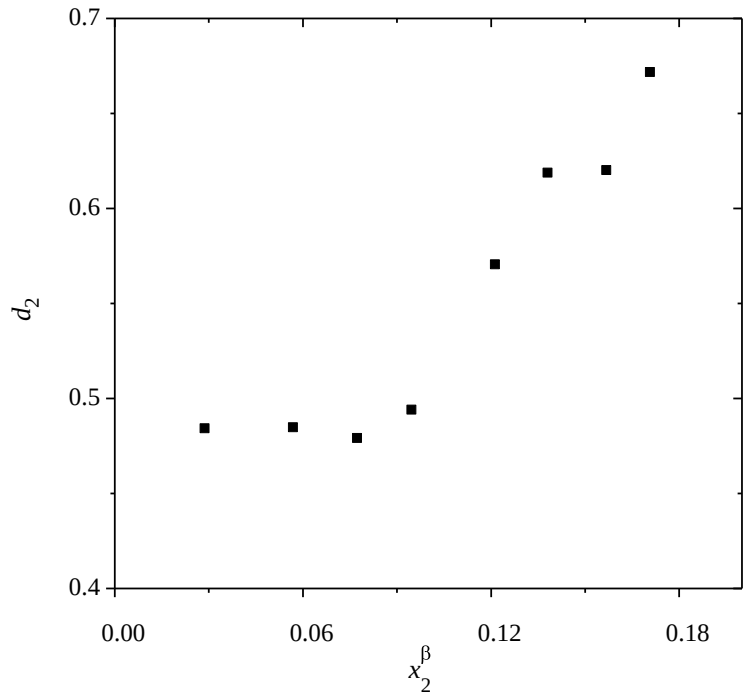

FIGURE (4.3.3.4): Distribution coefficient for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa.

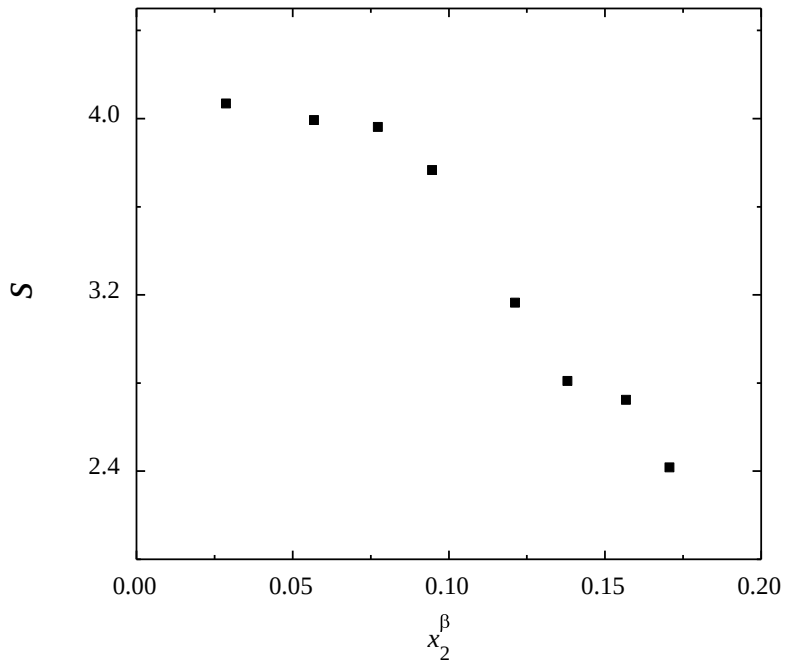

FIGURE (4.3.3.5): Selectivity *S* for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-butanol (3)} at 298.15 K and 101Kpa.

4.3.4 Results and analysis for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.4.1), are shown in Figure (4.3.4.1). The liquid-liquid equilibrium values are given in Table (4.3.4.2).
The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.4.2) and are shown in Figures (4.3.4.2) and (4.3.4.3) successively. While distribution coefficient d_i,, selectivity *S* values are outlined in Table (4.3.4.3), and are shown in Figure (4.3.4.4) and (4.3.4.5). The critical solution plait point of {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K is: experimental value: $(x_1^{cs} = 0.378,\ x_2^{cs} = 0.278)$.

TABLE (4.3.4.1): Binodal curve data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa

x_1	x_2	x_3	x_1	x_2	x_3
0.938	0.061	0.001	0.524	0.307	0.169
0.917	0.081	0.002	0.498	0.312	0.190
0.887	0.105	0.008	0.471	0.311	0.218
0.867	0.120	0.013	0.461	0.309	0.230
0.841	0.140	0.019	0.448	0.305	0.247
0.809	0.164	0.027	0.427	0.304	0.269
0.765	0.196	0.039	0.400	0.296	0.304
0.723	0.226	0.051	0.397	0.289	0.314
0.708	0.235	0.057	0.384	0.283	0.333
0.688	0.247	0.065	0.369	0.269	0.362
0.669	0.258	0.073	0.358	0.260	0.382
0.652	0.267	0.081	0.331	0.243	0.426
0.651	0.262	0.087	0.320	0.235	0.445
0.634	0.270	0.096	0.315	0.232	0.453
0.623	0.278	0.099	0.304	0.222	0.474
0.585	0.290	0.125	0.293	0.211	0.496
0.570	0.296	0.134	0.275	0.201	0.524
0.559	0.299	0.142	0.254	0.179	0.567
0.552	0.301	0.147	0.237	0.158	0.605
0.553	0.300	0.147	0.213	0.134	0.653
0.542	0.303	0.155	0.189	0.099	0.712
0.532	0.305	0.163	0.136	0.044	0.820

Binodal curve eq: $x_2 = -0.003 + 1.384x_3^{0.5} - 1.581x_3 + 0.123x_3^2;\ R^2 = 0.991$

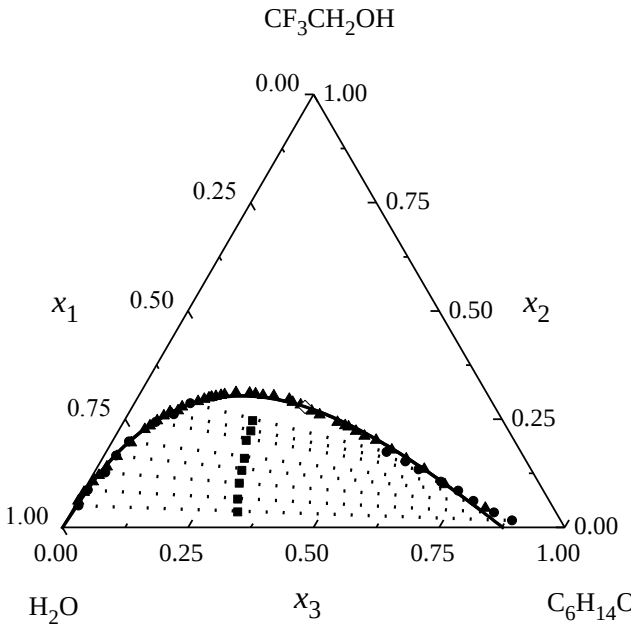

FIGURE (4.3.4.1): Solubility and liquid-liquid equilibrium data ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa:▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

Table (4.3.4.2): liquid-liquid equilibrium data ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa

Feed Composition			Water-Rich Phase			HexOH-Rich Phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
0.633	0.035	0.331	0.942	0.050	0.007	0.097	0.016	0.887
0.618	0.065	0.317	0.906	0.087	0.007	0.124	0.034	0.842
0.597	0.102	0.301	0.851	0.127	0.022	0.151	0.061	0.788
0.577	0.131	0.292	0.810	0.166	0.024	0.170	0.085	0.746
0.558	0.159	0.283	0.768	0.198	0.033	0.194	0.106	0.701
0.534	0.201	0.266	0.692	0.243	0.064	0.224	0.134	0.642
0.513	0.223	0.264	0.647	0.261	0.092	0.241	0.152	0.607
0.498	0.246	0.256	0.602	0.287	0.112	0.267	0.174	0.559
	x^{cs}		0.378	0.278	0.344	0.378	0.278	0.344

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
-0.189	1.283	0.998	0.040	0.761	0.999

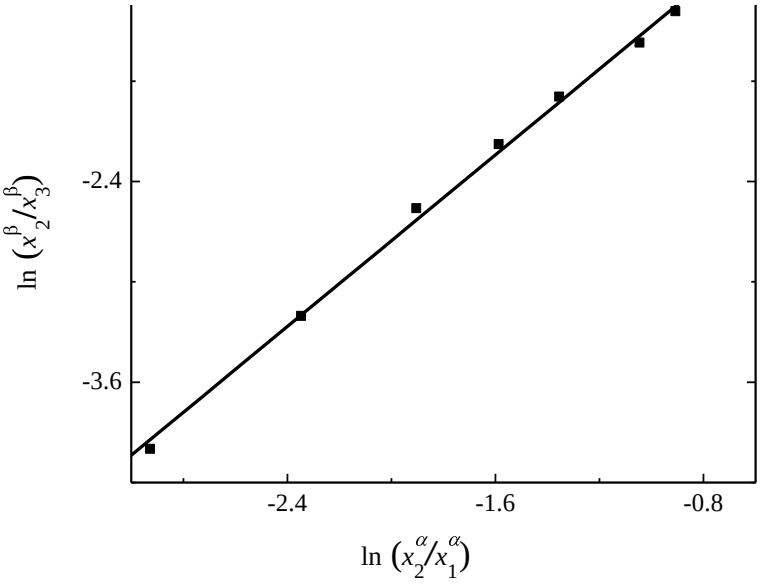

FIGURE (4.3.4.2): Hand correlation of liquid-liquid equilibrium data of ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa.

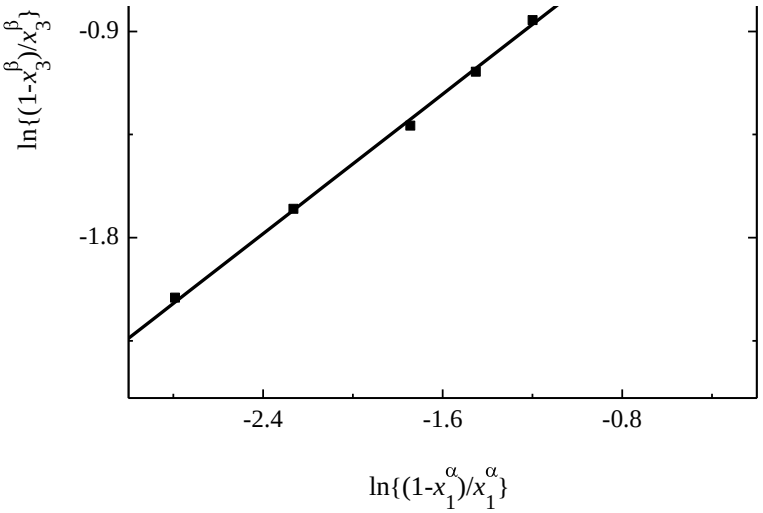

FIGURE (4.3.4.3): Othmer-Tobias correlation of liquid-liquid equilibrium data ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa.

TABLE (4.3.4.3): Distribution coefficient d_i and selectivity S for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa

d_1	13.3	9.6	6.0	4.8	4.0	2.9	2.5	2.3
d_2	3.1	2.5	2.1	2.0	1.9	1.8	1.7	1.6
S	4.3	3.8	2.9	2.4	2.1	1.6	1.5	1.4

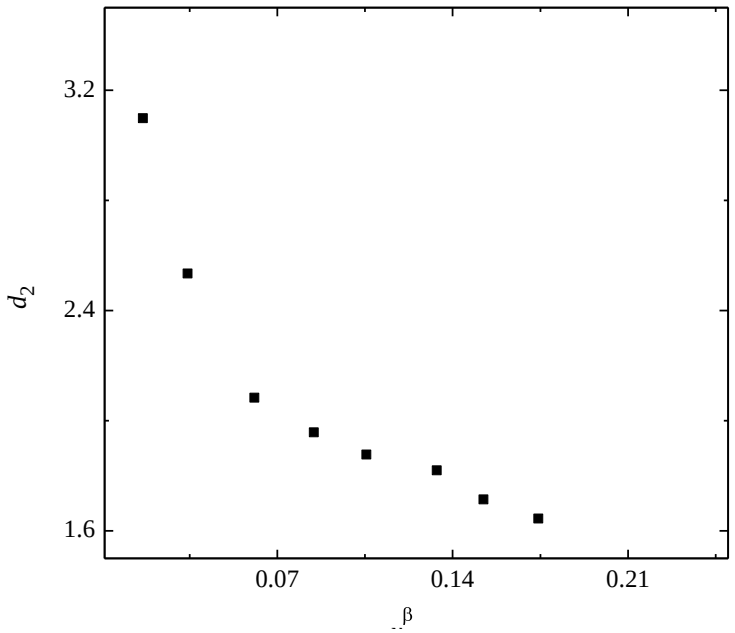

FIGURE (4.3.4.4): Distribution coefficient for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa.

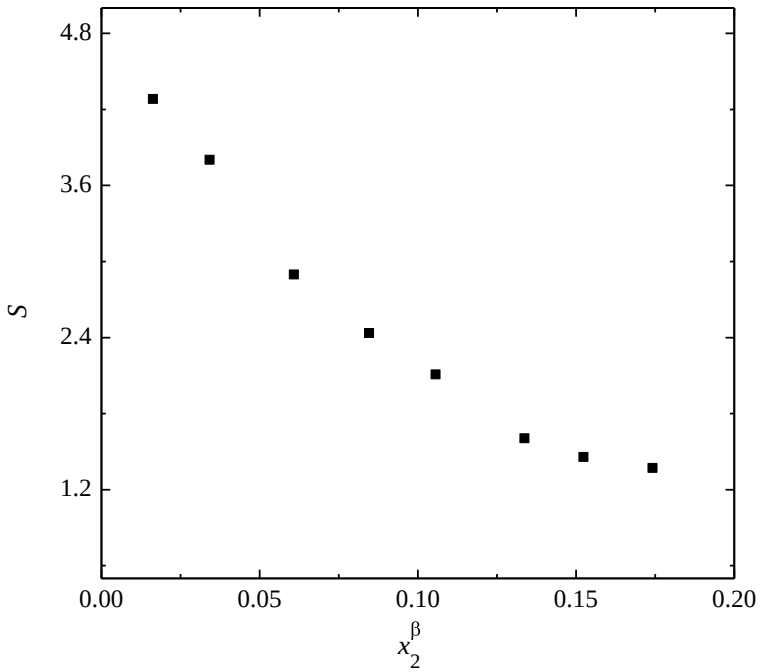

FIGURE (4.3.4.5): Selectivity *S* for liquid-liquid equilibrium data for ternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3)} at 298.15 K and 101Kpa.

4.3.5 Results and analysis for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.5.1), are shown in Figure (4.3.5.1). The liquid-liquid equilibrium values are given in Table (4.3.5.2).

The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.5.2) and are shown in Figures (4.3.5.2) and (4.3.5.3) successively. While distribution coefficient d_i, selectivity S values are outlined in Table (4.3.5.3), and are shown in Figure (4.3.5.4) and (4.3.5.5). The critical solution plait point of {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K is: experimental value: $(x_1^{cs} = 0.337,\ x_2^{cs} = 0.358)$.

TABLE (4.3.5.1): Binodal curve data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa

x_1	x_2	x_3	x_1	x_2	x_3
0.961	0.005	0.033	0.348	0.370	0.282
0.865	0.092	0.043	0.332	0.370	0.297
0.789	0.160	0.051	0.327	0.368	0.306
0.720	0.209	0.071	0.310	0.360	0.330
0.689	0.229	0.082	0.291	0.352	0.356
0.664	0.246	0.090	0.270	0.335	0.395
0.599	0.284	0.117	0.257	0.326	0.417
0.581	0.294	0.125	0.239	0.311	0.450
0.563	0.302	0.135	0.216	0.292	0.492
0.536	0.314	0.150	0.202	0.275	0.524
0.532	0.320	0.148	0.186	0.251	0.563
0.498	0.332	0.171	0.163	0.224	0.613
0.463	0.346	0.191	0.148	0.212	0.640
0.458	0.349	0.193	0.132	0.195	0.672
0.446	0.350	0.205	0.107	0.159	0.734
0.436	0.351	0.212	0.089	0.145	0.766
0.420	0.359	0.220	0.083	0.128	0.790
0.400	0.365	0.235	0.068	0.109	0.823
0.388	0.368	0.244	0.050	0.083	0.866
0.385	0.371	0.244	0.032	0.039	0.929
0.362	0.372	0.265	0.008	0.013	0.979
0.355	0.370	0.275			

Binodal curve eq: $x_2 = -0.506 + 3.785x_3^{0.5} - 4.459x_3 + 1.601x_3^2 - 0.421x_3^3;\ R^2 = 0.993$

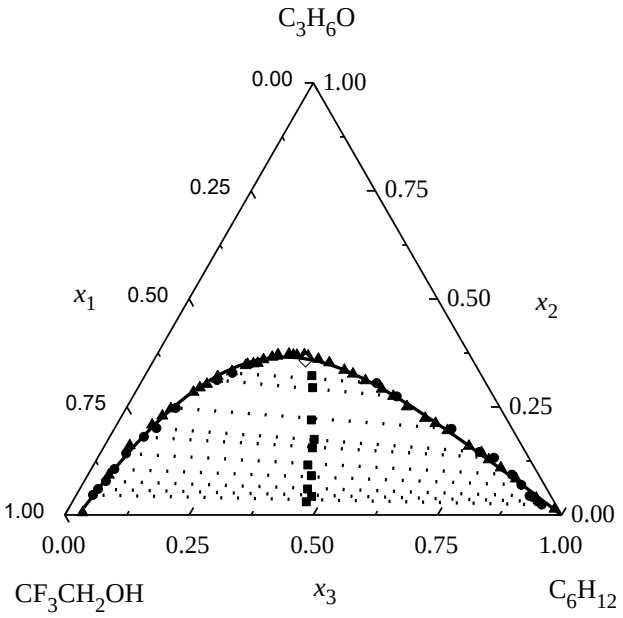

FIGURE (4.3.5.1): Solubility and liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.5.2): liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa

Feed Composition			TFE-Rich Phase			Cyclohexane-Rich Phase		
x_1	x_2	x_3	x_1^{α}	x_2^{α}	x_3^{α}	x_1^{β}	x_2^{β}	x_3^{β}
0.499	0.030	0.471	0.920	0.046	0.034	0.028	0.024	0.949
0.482	0.042	0.475	0.903	0.060	0.037	0.033	0.031	0.936
0.481	0.060	0.459	0.878	0.078	0.044	0.043	0.044	0.914
0.458	0.090	0.451	0.847	0.106	0.047	0.046	0.069	0.885
0.453	0.116	0.432	0.805	0.142	0.053	0.054	0.093	0.853
0.424	0.155	0.421	0.750	0.181	0.069	0.070	0.132	0.798
0.411	0.175	0.415	0.715	0.201	0.084	0.092	0.146	0.762
0.394	0.219	0.387	0.653	0.248	0.100	0.122	0.199	0.679
0.354	0.294	0.352	0.537	0.312	0.151	0.195	0.274	0.531
0.341	0.322	0.336	0.498	0.329	0.173	0.220	0.305	0.475
	x^{cs}		0.337	0.358	0.306	0.337	0.358	0.306

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
0.058	1.252	0.998	0.028	1.220	0.998

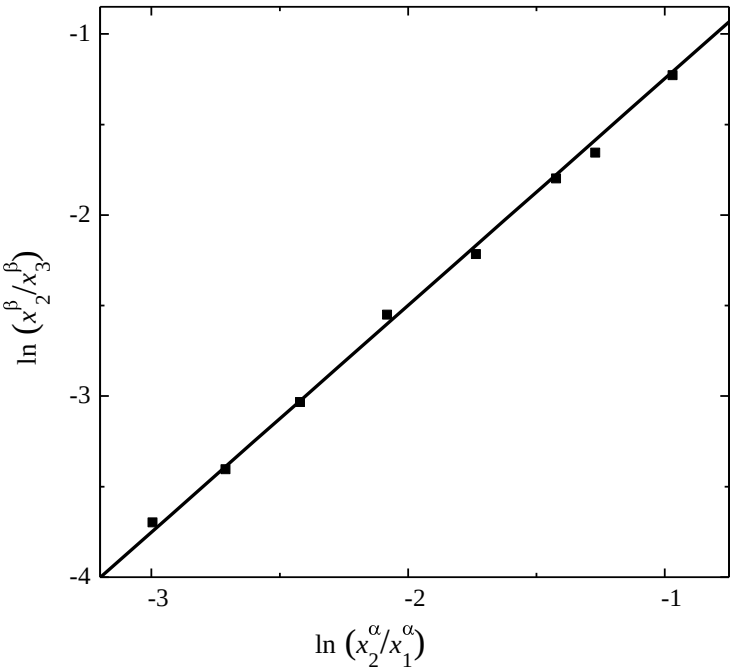

FIGURE (4.3.5.2): Hand correlation of liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

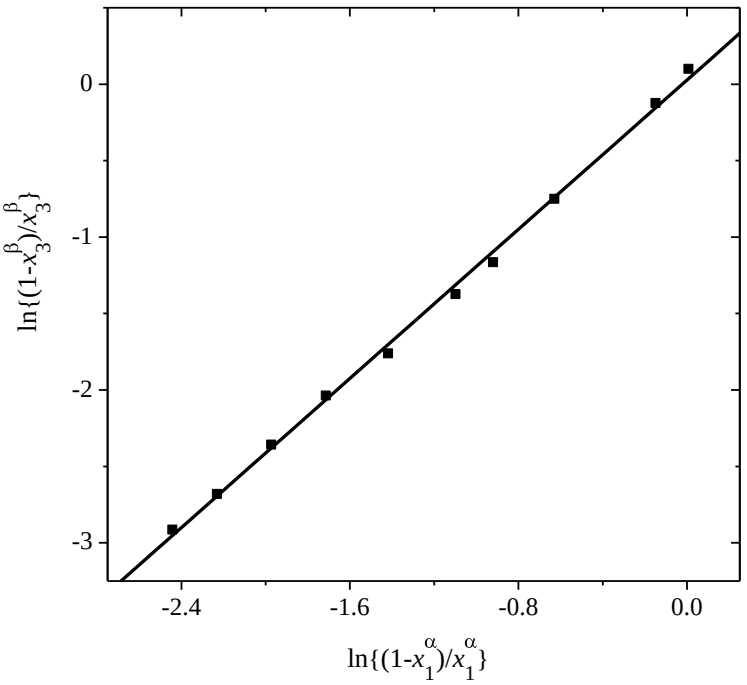

FIGURE (4.3.5.3): Othmer-Tobias correlation of liquid-liquid equilibrium data for ternary mixtures

{2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

TABLE (4.3.5.3): Distribution coefficient d_i and selectivity S for liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa

d_1	2.3	2.8	5.3	7.8	10.7	15.0	18.3	20.7	27.4	32.9
d_2	1.1	1.1	1.2	1.4	1.4	1.5	1.5	1.8	1.9	2.0
S	2.1	2.4	4.3	5.6	7.8	9.8	11.9	11.7	14.2	16.8

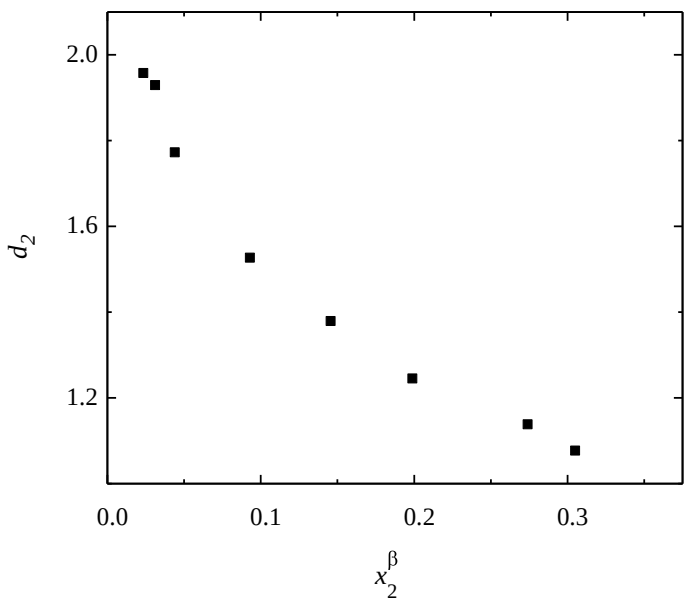

FIGURE (4.3.5.4): Distribution coefficient for liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

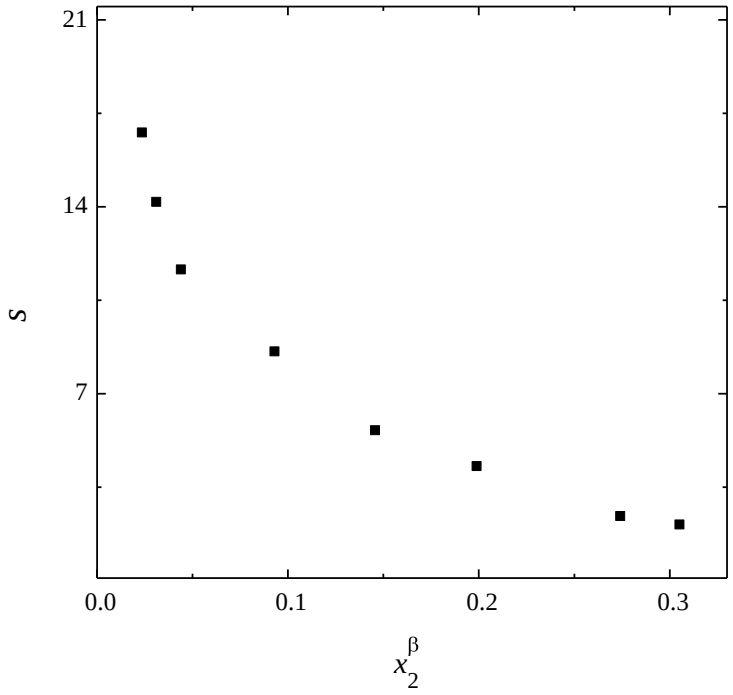

FIGURE (4.3.5.5): Selectivity *S* for liquid-liquid equilibrium data for ternary mixtures {2.2.2 trifluoroethanol (1) + acetone (2) + cyclohexane (3)} at 298.15 K and 101Kpa.

4.3.6 Results and analysis for ternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.6.1), are shown in Figure (4.3.6.1). The liquid-liquid equilibrium values are given in Table (4.3.6.2).

The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.6.2) and are shown in Figures (4.3.6.2) and (4.3.6.3) successively. While distribution coefficient d_i, selectivity *S* values are outlined in Table (4.3.6.3), and are shown in Figure (4.3.6.4) and (4.3.6.5). The critical solution plait point of (water + ethanol + cyclohexane) at 298.15 K is: experimental value: $(x_1^{cs} = 0.235,\ x_2^{cs} = 0.362, x_3^{cs} = 0.256)$.

TABLE (4.3.6.1): Binodal curve data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa

x_3/x_4 = (0.635/0.365)							
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.112	0.045	0.535	0.307	0.477	0.340	0.117	0.067
0.137	0.125	0.469	0.269	0.535	0.311	0.098	0.056
0.144	0.191	0.422	0.243	0.580	0.289	0.083	0.048
0.162	0.235	0.383	0.220	0.329	0.393	0.176	0.101
0.184	0.287	0.336	0.193	0.296	0.400	0.193	0.111
0.206	0.327	0.296	0.170	0.267	0.393	0.216	0.124
0.225	0.353	0.268	0.154	0.898	0.079	0.014	0.008
0.239	0.370	0.248	0.143	0.840	0.121	0.025	0.014
0.259	0.386	0.226	0.130	0.796	0.152	0.033	0.019
0.364	0.380	0.163	0.093	0.731	0.199	0.044	0.025
0.385	0.374	0.154	0.088	0.680	0.233	0.055	0.032
0.417	0.365	0.139	0.080	0.633	0.264	0.066	0.038
0.452	0.347	0.127	0.073				

Binodal curve eq: $x_2 = -0.050 + 0.687x_{(3+4)}^{0.5} + 1.188x_{(3+4)} - 3.890x_{(3+4)}^2 + 2.051x_{(3+4)}^3$; $R^2 = 0.997$

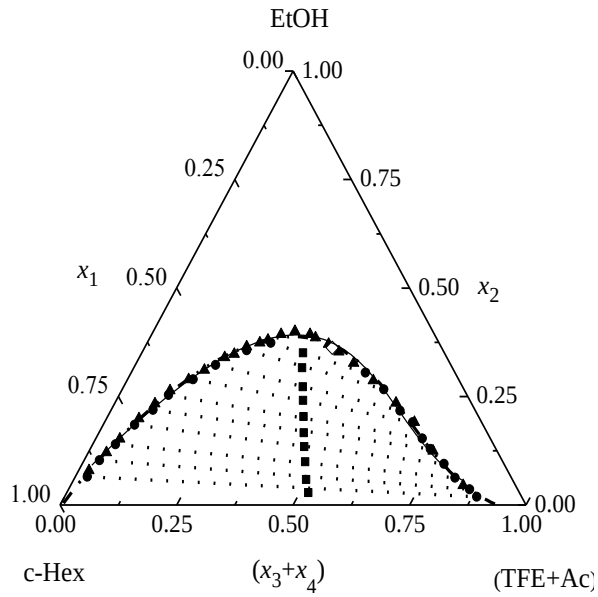

FIGURE (4.3.6.1): Solubility and liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.6.2): liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa

x_3/x_4 = (0.635/0.365)											
Feed Composition				(Ac-TFE)-Rich Phase				Cyclohexane-Rich Phase			
x_1	x_2	x_3	x_4	x_1^{α}	x_2^{α}	x_3^{α}	x_4^{α}	x_1^{β}	x_2^{β}	x_3^{β}	x_4^{β}
0.453	0.029	0.329	0.189	0.096	0.019	0.562	0.323	0.909	0.065	0.016	0.009
0.442	0.059	0.317	0.182	0.103	0.036	0.547	0.314	0.864	0.103	0.021	0.012
0.424	0.100	0.303	0.174	0.121	0.063	0.519	0.298	0.811	0.140	0.031	0.018
0.409	0.135	0.290	0.167	0.129	0.095	0.493	0.283	0.748	0.185	0.043	0.025
0.394	0.166	0.280	0.161	0.141	0.129	0.464	0.266	0.691	0.219	0.057	0.033
0.376	0.204	0.267	0.153	0.146	0.154	0.445	0.256	0.641	0.254	0.067	0.039
0.358	0.241	0.255	0.146	0.148	0.191	0.420	0.241	0.569	0.290	0.090	0.051
0.343	0.273	0.244	0.140	0.162	0.218	0.394	0.226	0.505	0.323	0.110	0.063
0.322	0.316	0.230	0.132	0.172	0.266	0.357	0.205	0.422	0.356	0.141	0.081
0.303	0.350	0.220	0.126	0.192	0.305	0.319	0.183	0.361	0.373	0.169	0.097
	x^{cs}			0.235	0.362	0.256	0.147	0.235	0.362	0.256	0.147
Hand Equation								Othmer-Tobias Equation			
A	B	R^2						A_1	B_1	R^2	
0.348	0.797	0.992						0.638	1.406	0.998	

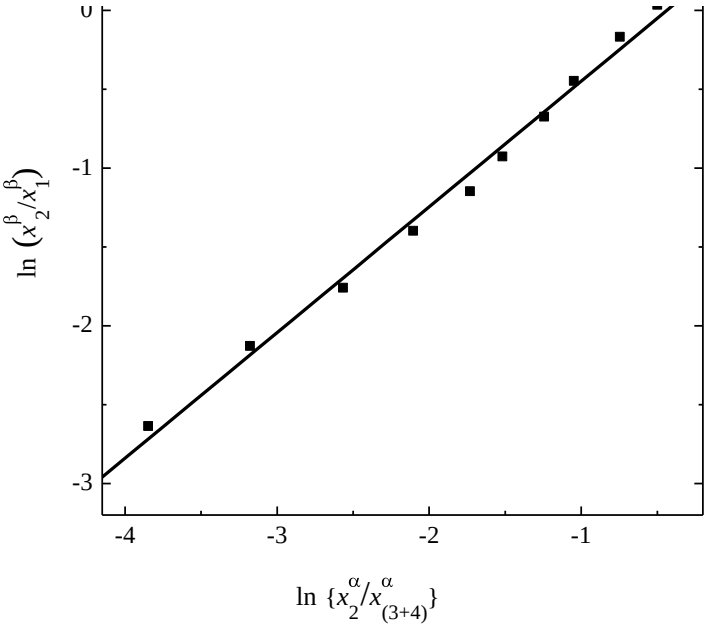

FIGURE (4.3.6.2): Hand correlation of liquid-liquid equilibrium data for quaternary mixtures of {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa.

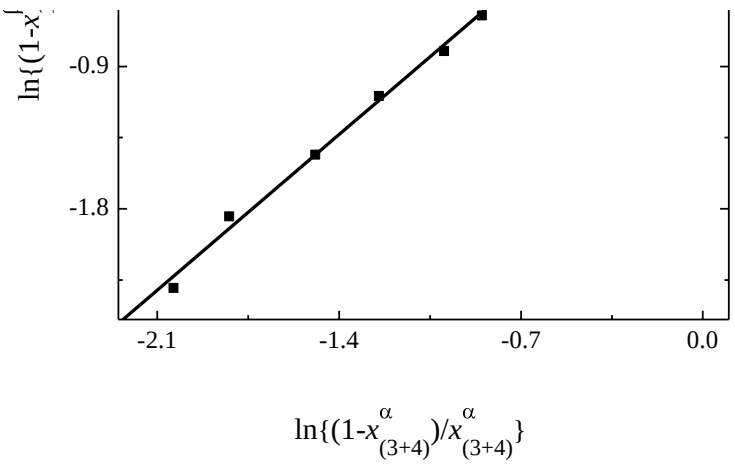

FIGURE (4.3.6.3): Othmer-Tobias correlation of liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa.

TABLE (4.3.6.3): Distribution coefficient and selectivity of pure and mixed solvents for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa

x_3/x_4= (0.635/0.365)										
d_1	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.5
d_2	0.3	0.3	0.4	0.5	0.6	0.6	0.7	0.7	0.7	0.8
S	2.7	2.9	3.0	3.0	2.9	2.7	2.5	2.1	1.8	1.5

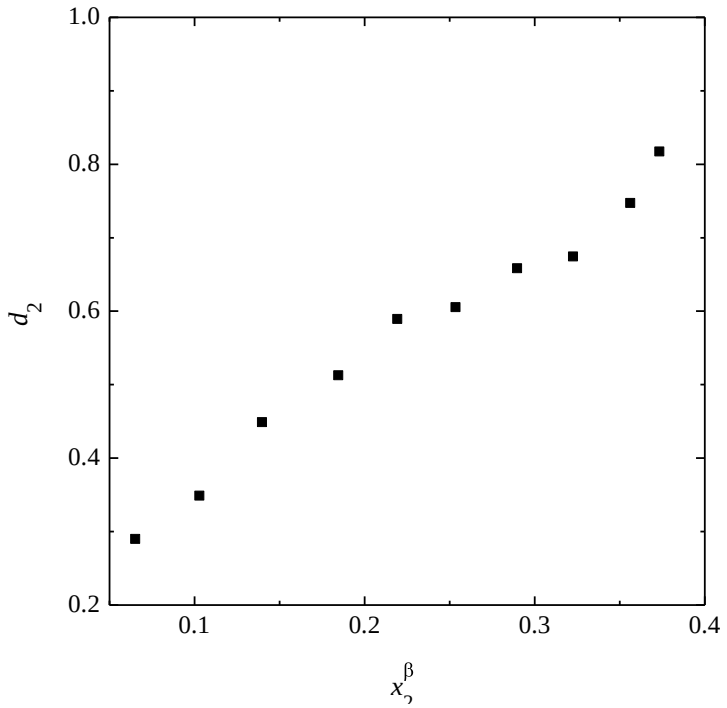

FIGURE (4.3.6.4): Distribution coefficient for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa.

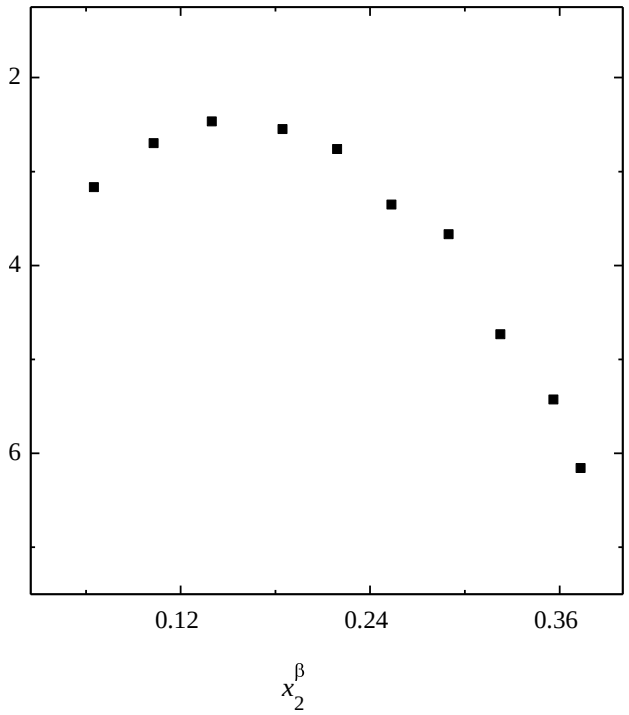

FIGURE (4.3.6.5): Selectivity *S* for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 283.15 K and 101Kpa.

4.3.7 Results and analysis for for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.7.1), are shown in Figure (4.3.7.1). The liquid-liquid equilibrium values are given in Table (4.3.7.2). The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.7.2) and are shown in Figures (4.3.7.2) and (4.3.7.3) successively. While distribution coefficient d_i, selectivity S values are outlined in Table (4.3.7.3), and are shown in Figure (4.3.7.4) and (4.3.7.5). The critical solution plait point of {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K is: experimental value: $(x_1^{cs} = 0.263,\ x_2^{cs} = 0.274, x_3^{cs} = 0.294)$.

TABLE (4.3.7.1): Binodal curve data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.635/0.365)							
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.109	0.021	0.552	0.317	0.419	0.260	0.204	0.117
0.126	0.045	0.526	0.302	0.443	0.257	0.191	0.110
0.143	0.083	0.492	0.282	0.460	0.253	0.182	0.105
0.160	0.129	0.452	0.259	0.489	0.243	0.170	0.098
0.171	0.139	0.439	0.252	0.521	0.232	0.157	0.090
0.174	0.170	0.417	0.239	0.542	0.224	0.149	0.085
0.197	0.197	0.385	0.221	0.563	0.215	0.141	0.081
0.213	0.227	0.356	0.204	0.581	0.206	0.135	0.078
0.227	0.247	0.334	0.192	0.596	0.203	0.128	0.074
0.235	0.265	0.317	0.182	0.619	0.194	0.119	0.068
0.248	0.274	0.303	0.174	0.664	0.169	0.106	0.061
0.261	0.284	0.289	0.166	0.677	0.167	0.099	0.057
0.291	0.281	0.272	0.156	0.692	0.162	0.093	0.053
0.306	0.282	0.262	0.150	0.717	0.152	0.083	0.048
0.337	0.277	0.245	0.141	0.757	0.128	0.073	0.042
0.359	0.273	0.234	0.134	0.787	0.112	0.064	0.037
0.372	0.269	0.228	0.131	0.817	0.101	0.052	0.030
0.383	0.267	0.222	0.128	0.850	0.078	0.046	0.026
0.401	0.265	0.212	0.122	0.912	0.047	0.026	0.015

Binodal curve eq:$x_2 = -0.339 + 0.062x_{(3+4)}^{0.5} + 1.667x_{(3+4)} - 2.662x_{(3+4)}^2 + 0.909x_{(3+4)}^3;\ R^2 = 0.989$

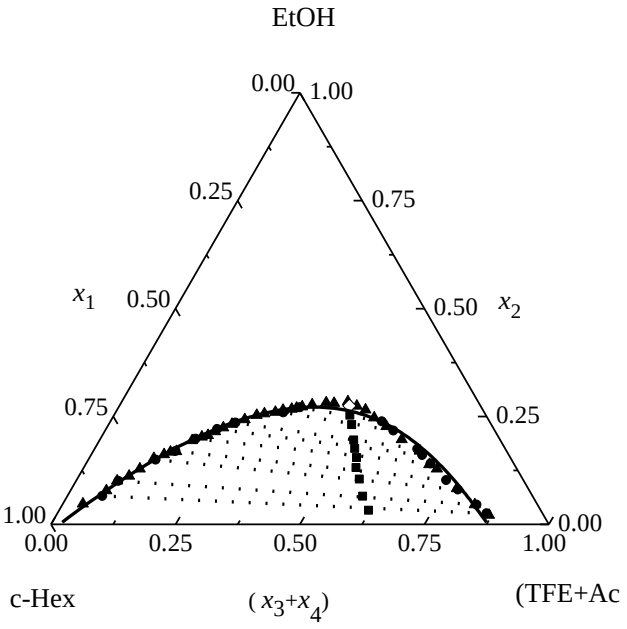

FIGURE (4.3.7.1): Solubility and liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.7.2): Liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.635/0.365)											
Feed Composition				(Ac+TFE)-Rich Phase				Cyclohexane-Rich Phase			
x_1	x_2	x_3	x_4	x_1^{α}	x_2^{α}	x_3^{α}	x_4^{α}	x_1^{β}	x_2^{β}	x_3^{β}	x_4^{β}
0.346	0.032	0.395	0.227	0.112	0.026	0.548	0.314	0.864	0.066	0.045	0.026
0.341	0.065	0.377	0.216	0.122	0.046	0.529	0.303	0.815	0.101	0.054	0.031
0.328	0.105	0.360	0.207	0.142	0.081	0.494	0.283	0.715	0.150	0.086	0.049
0.322	0.131	0.348	0.200	0.155	0.102	0.472	0.271	0.665	0.170	0.105	0.060
0.309	0.155	0.341	0.196	0.167	0.141	0.440	0.252	0.610	0.198	0.122	0.070
0.302	0.176	0.332	0.191	0.174	0.160	0.423	0.243	0.556	0.221	0.142	0.081
0.294	0.195	0.324	0.186	0.177	0.174	0.412	0.237	0.512	0.235	0.161	0.092
0.281	0.231	0.310	0.178	0.204	0.217	0.368	0.211	0.403	0.259	0.214	0.123
0.273	0.253	0.301	0.173	0.216	0.239	0.346	0.199	0.365	0.271	0.231	0.133
x^{cs}				0.2633	0.274	0.2936	0.1686	0.2633	0.274	0.2936	0.1686

Hand Equation			Othmer-Tobias Equation		
A	B	R^2	A_1	B_1	R^2
0.310	0.8359	0.994	0.814	1.440	0.996

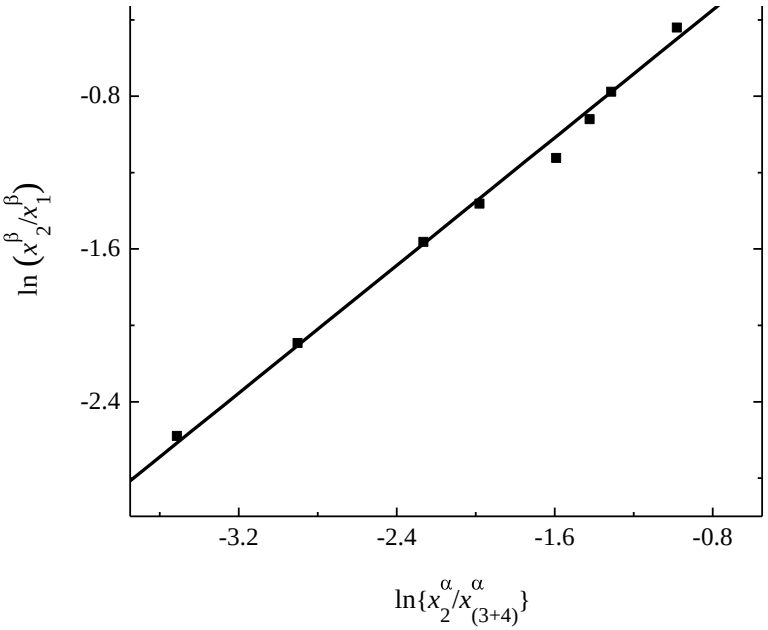

FIGURE (4.3.7.2) : Hand correlation of liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa.

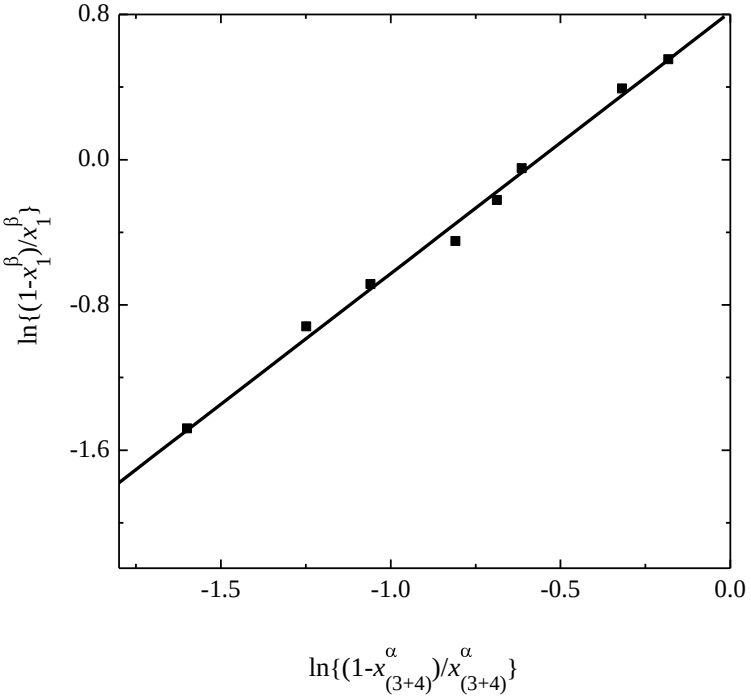

FIGURE (4.3.7.3) : Othmer-Tobias correlation of liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa.

TABLE (4.3.7.3): Distribution coefficient d_i and selectivity for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol(2) + 2.2.2 trifluoroethanol (3) + acetone (4)}at 298.15 K and 101Kpa

	x_3/x_4= (0.635/0.365)								
d_1	0.13	0.15	0.20	0.23	0.27	0.31	0.35	0.51	0.59
d_2	0.4	0.5	0.5	0.6	0.7	0.7	0.7	0.8	0.9
S	3.0	3.0	2.7	2.6	2.6	2.3	2.1	1.7	1.5

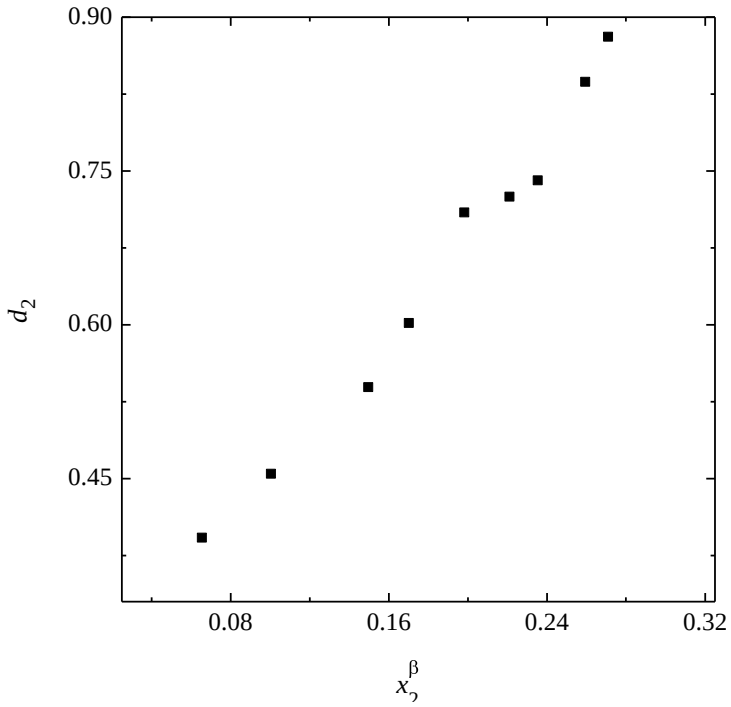

FIGURE (4.3.7.4): Distribution coefficient for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa.

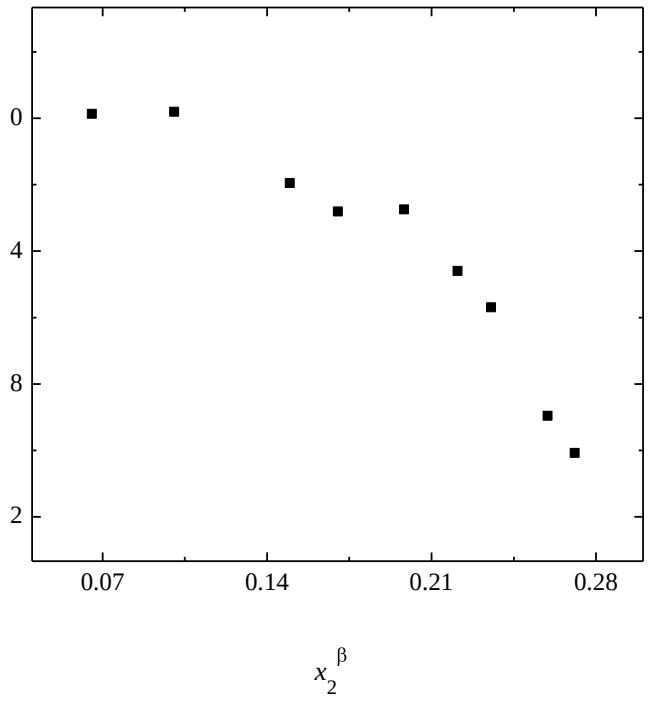

FIGURE (4.3.7.5): Selectivity *S* for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 101Kpa.

4.3.8 Results and analysis for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.8.1), are shown in Figure (4.3.8.1). The liquid-liquid equilibrium values are given in Table (4.3.8.2). The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.8.2) and are shown in Figures (4.3.8.2) and (4.3.8.3) successively. While distribution coefficient d_i, selectivity *S* values are outlined in Table (4.3.8.3), and are shown in Figure (4.3.8.4) and (4.3.8.5). The critical solution plait point of quaternary {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K is: experimental value:

$(x_1^{cs} = 0.618,\ x_2^{cs} = 0.093, x_3^{cs} = 0.233)$.

TABLE (4.3.8.1): Binodal curve data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.802/0.198)							
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.966	0.011	0.018	0.004	0.804	0.078	0.095	0.023
0.953	0.022	0.020	0.005	0.783	0.084	0.106	0.026
0.943	0.029	0.023	0.006	0.758	0.088	0.123	0.030
0.933	0.033	0.027	0.007	0.737	0.092	0.137	0.034
0.923	0.039	0.031	0.008	0.718	0.095	0.150	0.037
0.911	0.044	0.036	0.009	0.689	0.098	0.171	0.042
0.896	0.050	0.043	0.011	0.690	0.097	0.171	0.042
0.886	0.054	0.048	0.012	0.663	0.097	0.193	0.048
0.880	0.056	0.052	0.013	0.637	0.096	0.214	0.053
0.871	0.059	0.056	0.014	0.621	0.094	0.229	0.056
0.866	0.060	0.059	0.015	0.603	0.088	0.247	0.061
0.858	0.063	0.063	0.016	0.572	0.076	0.282	0.070
0.846	0.066	0.071	0.017	0.561	0.071	0.295	0.073
0.835	0.069	0.077	0.019	0.550	0.066	0.308	0.076
0.823	0.073	0.083	0.021	0.529	0.049	0.338	0.083
0.815	0.076	0.088	0.022	0.511	0.030	0.368	0.091

Binodal curve eq: $x_2 = -0.035 + 0.359x_{(3+4)}^{0.5} + 0.039x_{(3+4)} - 0.931x_{(3+4)}^2;\ R^2 = 0.993$

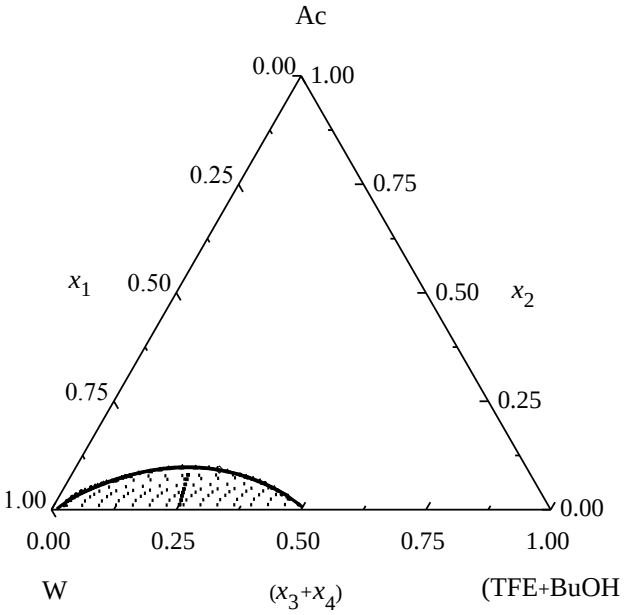

FIGURE (4.3.8.1): Solubility and liquid-liquid equilibrium data for quaternary mixtures{water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.8.2): Liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.802/0.198)											
Feed Composition				Water-Rich Phase				(TFE+BuOH)-Rich Phase			
x_1	x_2	x_3	x_4	x_1^{α}	x_2^{α}	x_3^{α}	x_4^{α}	x_1^{β}	x_2^{β}	x_3^{β}	x_4^{β}
0.737	0.011	0.050	0.202	0.9693	0.0102	0.0165	0.0041	0.4984	0.0121	0.3926	0.097
0.729	0.022	0.049	0.200	0.9591	0.0197	0.017	0.0042	0.510	0.025	0.373	0.0921
0.723	0.031	0.049	0.197	0.944	0.0291	0.0216	0.0053	0.5212	0.035	0.3559	0.0879
0.717	0.039	0.048	0.196	0.9329	0.0351	0.0257	0.0063	0.5253	0.0436	0.3457	0.0854
0.711	0.047	0.048	0.194	0.9187	0.0421	0.0314	0.0078	0.5333	0.0506	0.3337	0.0824
0.703	0.058	0.047	0.192	0.895	0.0511	0.0432	0.0107	0.5418	0.0608	0.3187	0.0787
0.694	0.070	0.047	0.190	0.8377	0.0671	0.0763	0.0189	0.570	0.0741	0.2851	0.070
0.686	0.080	0.046	0.188	0.8028	0.0771	0.0963	0.0238	0.5818	0.080	0.2708	0.0669
x^{cs}				0.6175	0.0925	0.2326	0.0574	0.6175	0.0925	0.2326	0.0574
Hand Equation								Othmer-Tobias Equation			
A	B	R^2						A_1	B_1	R^2	
1.036	1.027	0.998						1.089	0.305	0.998	

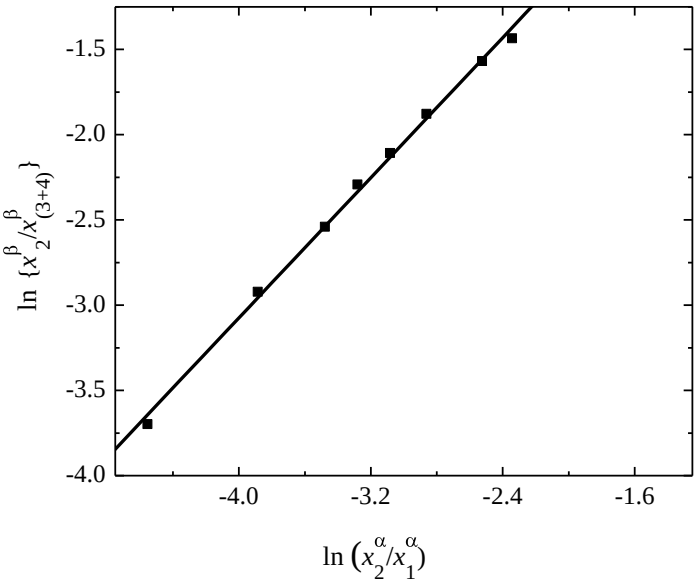

FIGURE (4.3.8.3): Hand correlation of liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa.

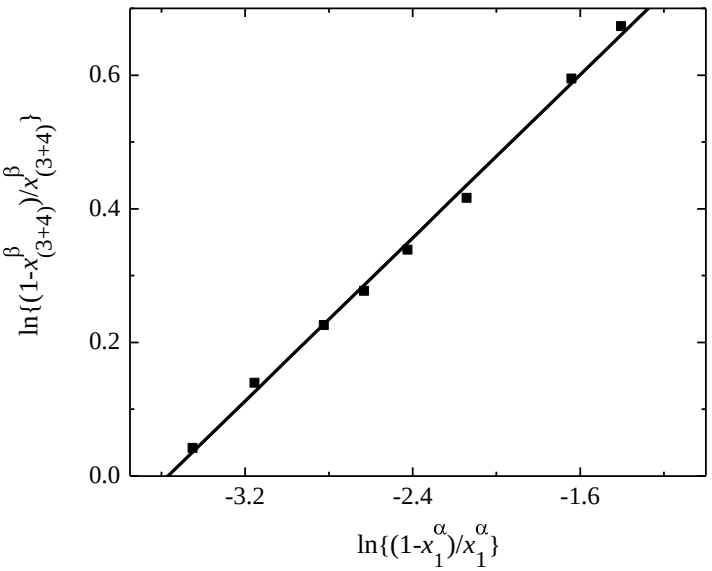

FIGURE (4.3.8.4): Othmer-Tobias correlation of liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa.

TABLE (4.3.8.3): Distribution coefficient d_i and selectivity for liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.802/0.198)								
d_1	1.9	1.9	1.8	1.8	1.7	1.7	1.5	1.4
d_2	1.2	1.3	1.2	1.2	1.2	1.2	1.1	1.0
S	1.6	1.5	1.5	1.4	1.4	1.4	1.3	1.3

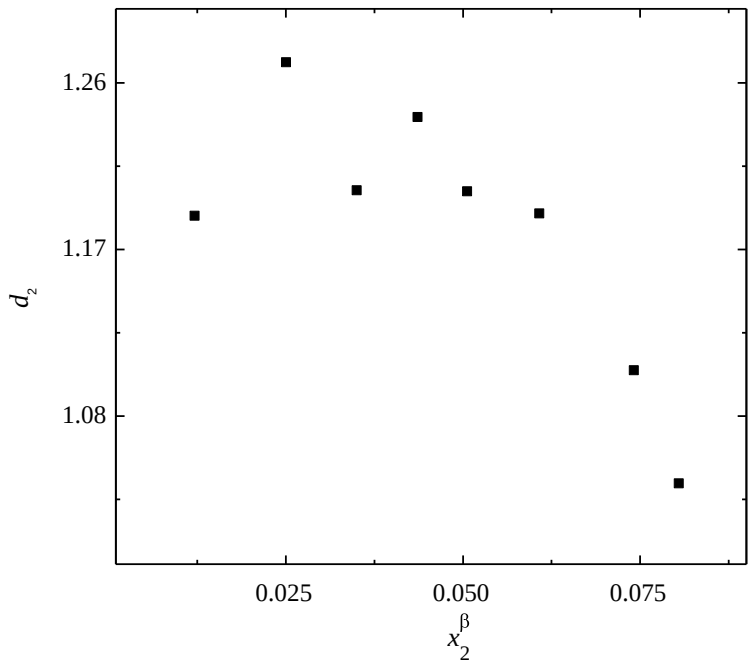

FIGURE (4.3.8.5): Distribution coefficient liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa.

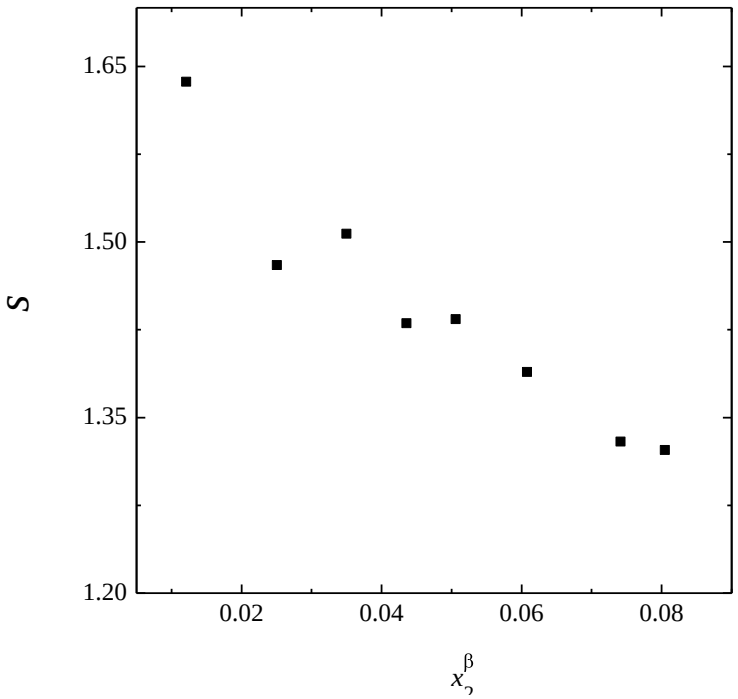

FIGURE (4.3.8.6): Selectivity *S* for liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa.

4.3.9 Results and analysis for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa

The binodal curve and fitting parameters are reported in Table (4.3.9.1), are shown in Figure (4.3.9.1). The liquid-liquid equilibrium values are given in Table (4.3.9.2).

The correlation parameters of Hand and Othmer-Tobias are given in Table (4.3.9.2) and are shown in Figures (4.3.9.2) and (4.3.9.3) successively. While distribution coefficient d_i,, selectivity S values are outlined in Table (4.3.9.3), and are shown in Figure (4.3.9.4) and (4.3.9.5). The critical solution plait point of quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K is: experimental value: $(x_1^{cs} = 0.357,\ x_2^{cs} = 0.345, x_3^{cs} = 0.188)$.

TABLE (4.3.9.1): Binodal curve data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.630/0.370)							
x_1	x_2	x_3	x_4	x_1	x_2	x_3	x_4
0.346	0.351	0.191	0.112	0.887	0.097	0.01	0.006
0.459	0.337	0.128	0.075	0.851	0.12	0.019	0.011
0.548	0.302	0.095	0.055	0.811	0.143	0.029	0.017
0.605	0.272	0.078	0.046	0.746	0.186	0.042	0.025
0.677	0.232	0.057	0.034	0.656	0.244	0.063	0.037
0.736	0.194	0.044	0.026	0.143	0.181	0.426	0.25
0.765	0.178	0.036	0.021	0.167	0.246	0.371	0.217
0.796	0.155	0.031	0.018	0.201	0.293	0.319	0.187
0.815	0.142	0.027	0.016	0.255	0.317	0.269	0.158
0.842	0.125	0.021	0.012	0.298	0.337	0.231	0.135
0.860	0.113	0.017	0.010	0.421	0.343	0.149	0.087
0.872	0.105	0.014	0.008	0.511	0.321	0.106	0.062
0.893	0.090	0.011	0.006	0.575	0.293	0.083	0.049
0.909	0.081	0.006	0.003				

Binodal curve eq: $x_2 = -0.0343 + 0.854x_{(3+4)}^{0.5} + 0.337x_{(3+4)} - 2.424x_{(3+4)}^2 + 1.279x_{(3+4)}^3;\ R^2 = 0.988$

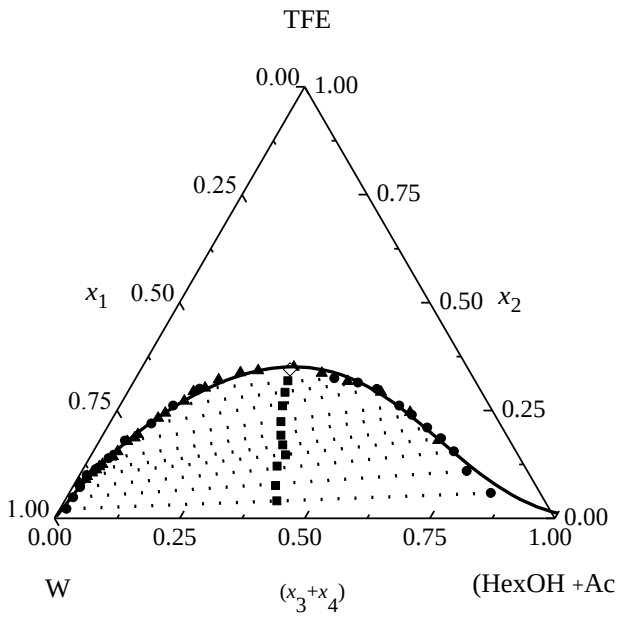

FIGURE (4.3.9.1): Solubility and liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa: ▲, solubility; ■, feed composition; ●, LLE; ◊, p.p.; …, tie line; — eq. (2.21)

TABLE (4.3.9.2): liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.630/0.370)											
Feed Composition				Water-Rich Phase				(Ac+HexOH)-Rich Phase			
x_1	x_2	x_3	x_4	x_1^{α}	x_2^{α}	x_3^{α}	x_4^{α}	x_1^{β}	x_2^{β}	x_3^{β}	x_4^{β}
0.535	0.040	0.268	0.157	0.965	0.022	0.008	0.005	0.098	0.059	0.531	0.312
0.520	0.076	0.255	0.149	0.938	0.049	0.008	0.005	0.121	0.109	0.485	0.284
0.495	0.121	0.242	0.142	0.913	0.072	0.010	0.006	0.124	0.155	0.455	0.267
0.464	0.147	0.245	0.144	0.885	0.100	0.009	0.005	0.135	0.185	0.429	0.251
0.459	0.170	0.234	0.137	0.860	0.114	0.016	0.010	0.150	0.210	0.403	0.237
0.451	0.192	0.225	0.132	0.822	0.139	0.024	0.014	0.166	0.240	0.375	0.220
0.435	0.224	0.215	0.126	0.769	0.180	0.032	0.019	0.180	0.261	0.352	0.207
0.414	0.261	0.205	0.120	0.696	0.220	0.053	0.031	0.206	0.300	0.312	0.183
0.393	0.292	0.198	0.116	0.632	0.261	0.067	0.040	0.236	0.314	0.283	0.166
0.374	0.318	0.194	0.114	0.560	0.300	0.088	0.052	0.278	0.325	0.250	0.147
	x^{cs}			0.3568	0.3452	0.188	0.110	0.3568	0.3452	0.188	0.110
Hand Equation								Othmer-Tobias Equation			
A	B	R^2							A_1	B_1	R^2
-0.485	1.290	0.997							-0.886	1.504	0.999

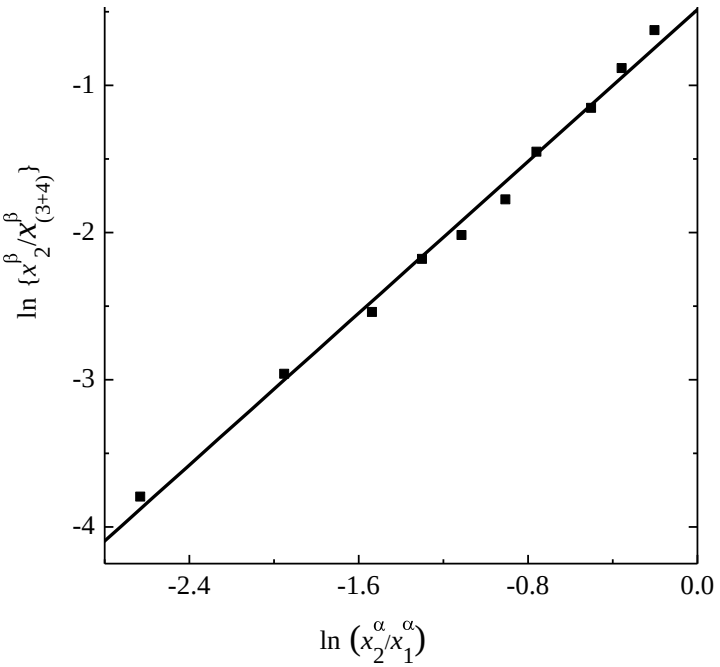

FIGURE (4.3.9.2): Hand correlation of liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa.

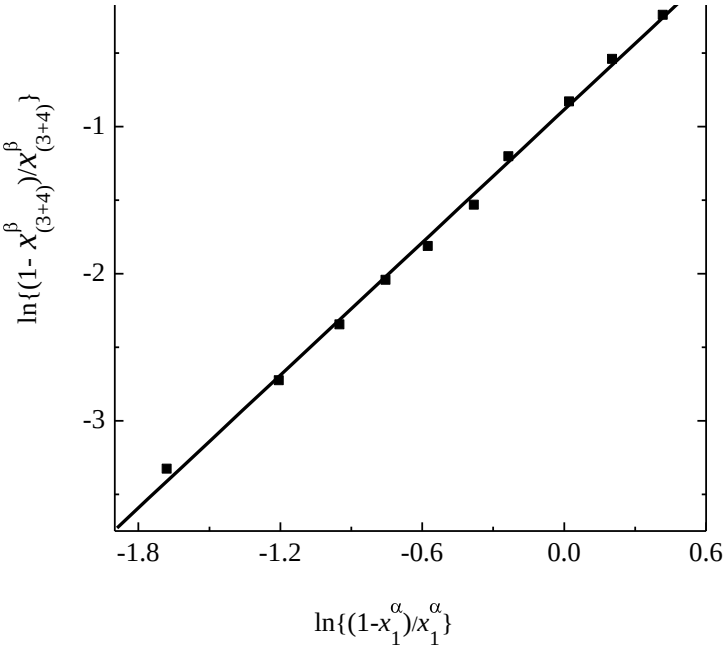

FIGURE (4.3.9.3): Othmer-Tobias correlation of liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa.

TABLE (4.3.9.3): Distribution coefficient d_i and selectivity S for liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa

x_3/x_4 = (0.630/0.370)										
$d_{(3+4)}$	9.8	7.8	7.4	6.6	5.7	5.0	4.3	3.4	2.7	2.0
d_2	0.4	0.4	0.5	0.5	0.5	0.6	0.7	0.7	0.8	0.9
S	26.6	17.4	15.9	12.2	10.5	8.5	6.2	4.6	3.2	2.2

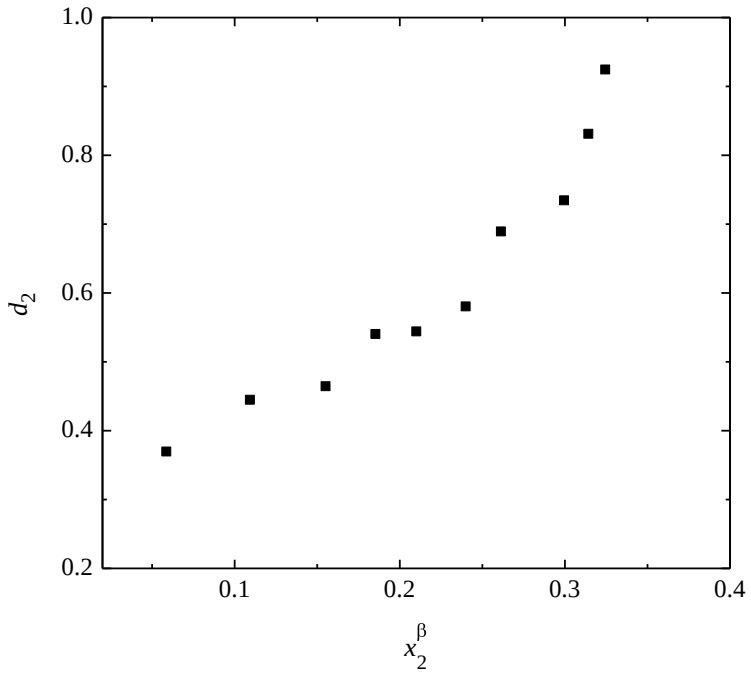

FIGURE (4.3.9.4): Distribution coefficient for liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa.

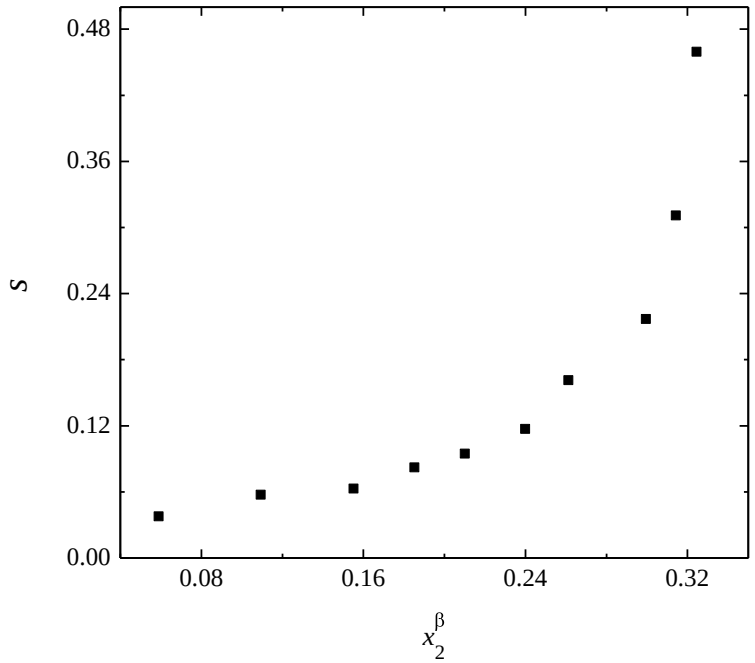

FIGURE (4.3.9.5): Selectivity diagram for liquid-liquid equilibrium data for quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa.

DISCUSSION

The thermodynamic properties multi-component solutions containing water and fluorinated hydrocarbons (HFC's) are diverse from large to small miscibility gaps. [30]

The thermodynamic properties of mixtures reflect the physico-chemical interactions between like and unlike molecules, in particular hydrogen bonding. The intermolecular forces enhance the solubility of substances in solutions. [31]

The cluster formation involving molecular like-like and like-dislike hydrogen bonding interactions between ethanol and trifluoroethanol hydroxyl groups and fluorine atoms results in a moderate temperature effect on the phase behavior of the alcohol-rich region of the partially miscible solutions.

Alcohols, and fluoro-alcohols are highly polar molecules. Fluorine is the most electronegative atom and it a hydrogen bond generator. The three atoms of fluorine in TFE molecule make it more self-associated in the pure state than alcohols. In aqueous solutions containing TFE and alcohols hydrogen bondings are well established and total miscibility is dominating the systems. [32]

The hydrogen bond interactions are considered to be dominant in the pure component liquids, and on the other hand, the three dimensional hydrogen bond structure of the water in the pure state by the mixing of TFE may be broken in solution, and although the hydrogen bond intermolecular interaction between the dissimilar molecules is newly formed with TFE, it is weaker than the similar intermolecular hydrogen bond interactions in the pure components, and then solution becomes thermally unstable.

The mutual solubility of heterogeneous systems increases with heating them; where the region of partial miscibility becomes smaller as temperature increases.[33]

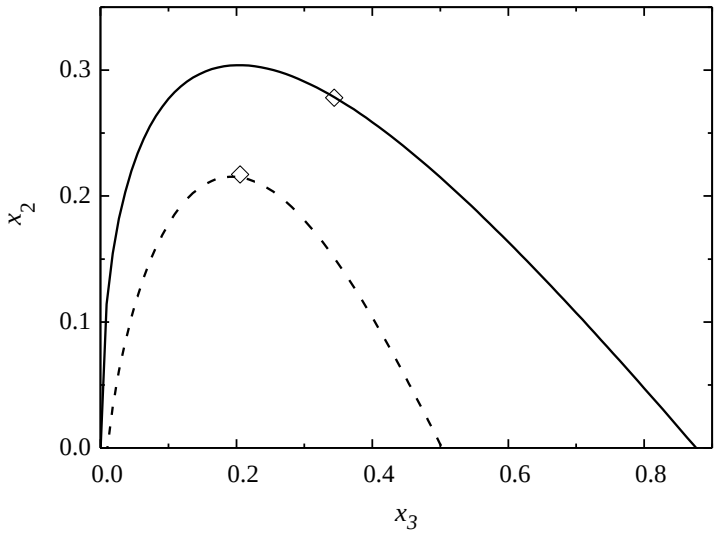

FIGURE (5.1): Comparison of liquid-liquid equilibrium data for {water (1) + 2.2.2 trifluoroethanol (2) + alcohol (3)} at 298.15 K and 0.1MP: ─, 1-hexanol; ---**,** 1-butanol; ◊, p.p.

For the ternary systems (water + 2.2.2 trifluoroethanol + alcohol) at 298.15 K, were alcohol is 1-butanol or 1-hexanol, it is observed that the immiscibility region decreases significantly with increasing of the alcohol molecular chain, as illustrated in figure (5.1), it is caused mainly by breaking hydrogen bonding between the alcohol–alcohol molecules and repulsive effects of the extra negative charges of oxygen and fluorine atoms [34], and also show that the aqueous phase richer in 1-butanol compared with 1-hexanol which is more concentrate in organic phase. So solubility of water in alcohols depends on the carbon number of alcohols, in the order 1-hexanol‹butanol.[35]

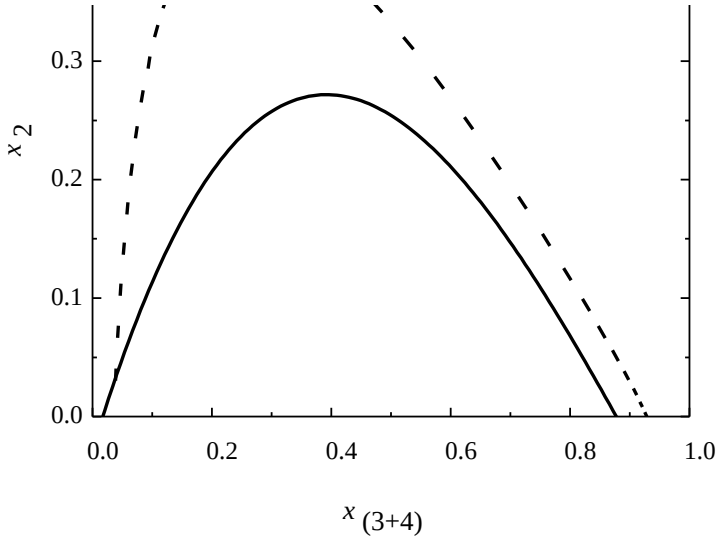

FIGURE (5.2): The binodal curve of liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at 298.15 K and 0.1MP:—, (x_3/x_4) = (0.635/0.365); ---, UNIQUAC ($x_4 = 0$) from ref.[36]

In figure (5.2) it can be observed that the ternary system{cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3)} show a large miscibility than the quaternary system {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at the same temperature and pressure: 298.15 K and 0.1MP. Where the hydrogen bonding of the self-associations in trifluoroethanol are broken and new hydrogen bonding OH---F, OH---O=C are generated. [37] Figure (5.2) also shows that the solubility of cyclohexane in ethanol increases with amounts of acetone added to solution. Acetone behaves as a common solvent in solution.

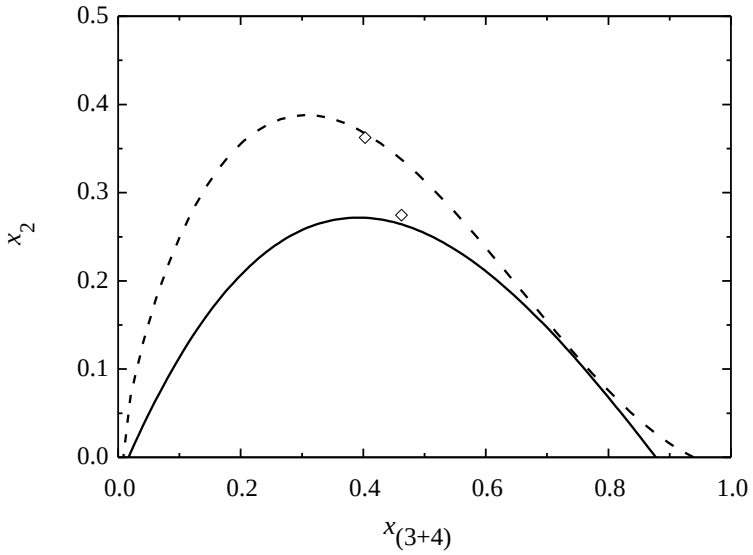

FIGURE (5.3): The effect of temperature on the solubility for solutions of quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)}, —, 298.15 K; ---, 283.15 K; ◊, p.p.

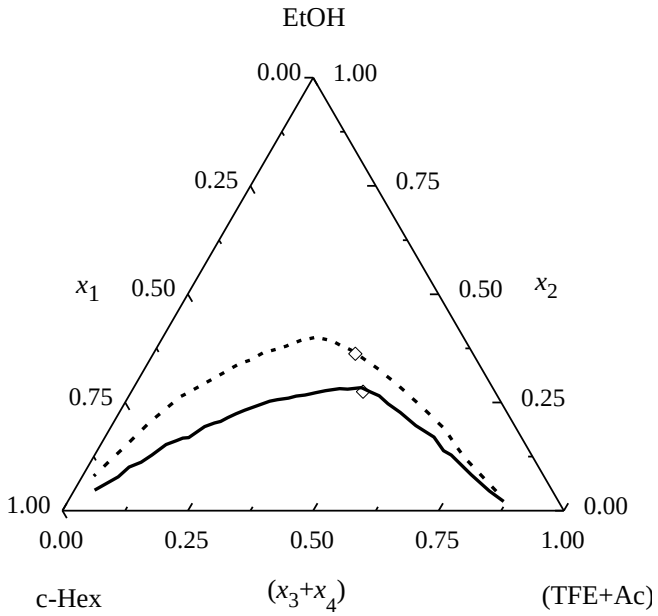

FIGURE (5.4): Binodal curve eq of quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)}; ---, at 283.15 K; — at 298.15 K and 101Kpa: ◊, p.p.

The miscibility gap of a heterogeneous system is slightly affected by temperature.[38]

For the systems {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)}, the miscibility gap decreases with increasing temperature.

For the apolar molecules of cyclohexane with the temperature increase weaken the macrocluster stability of the self- and cross-associations formed by hydrogen bonding which are existing in 2.2.2-trifluoroethanol and mixed (2.2.2-trifluoroethanol +acetone) in the presence of the hydroxyl group of the ethanol molecules. The capacity of mixed solvent (2.2.2-trifluoroethanol + acetone) to extract ethanol from its cyclohexane solutions is high[39].The temperature effect on liquid-liquid equilibrium is shown in Figure (5.3) and Figure (5.4).

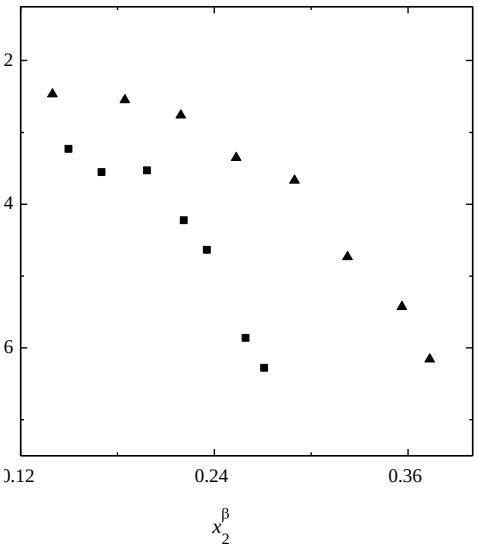

FIGURE (5.5): Selectivity *S* for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at T =▲ , 283.15 K ; ■, 298.15 K.

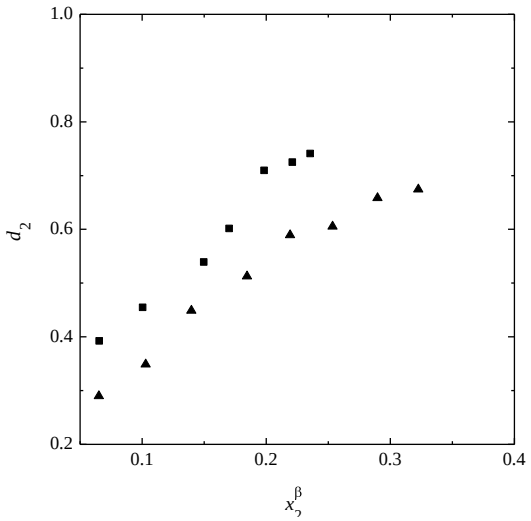

FIGURE (5.6): Distribution coefficient for liquid-liquid equilibrium data for quaternary mixtures {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at T =▲ , 283.15 K ; ■, 298.15 K.

The experimental selectivity factor and distribution coefficient for the quaternary system {cyclohexane (1) + ethanol (2) + 2.2.2 trifluoroethanol (3) + acetone (4)} at two temperatures (283.15, 298.15) K are represented in figures (5.5) and (5.6), respectively. According to these figures, increasing the temperature decreases the selectivity, and therefore, it is better to perform the extraction at lower temperatures.

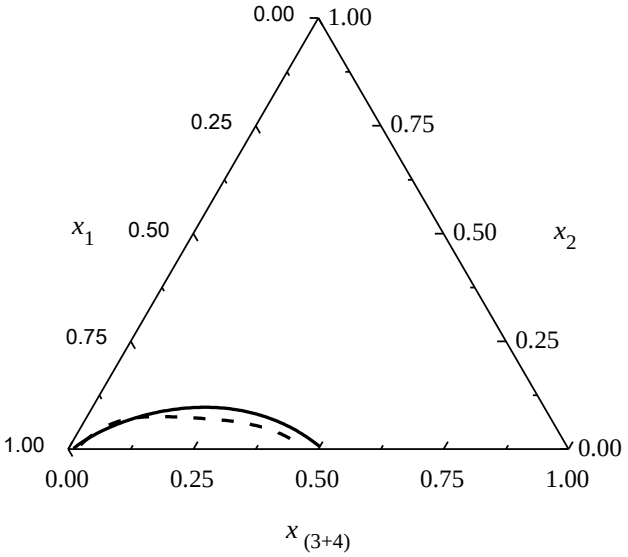

FIGURE (5.7): Binodal curve eq. of quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)}; —— , (x_3/x_4) = (0.802/0.198); ---, (x_4 = 0) from ref .[40]

The quaternary system{water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)}show a large miscibility than the ternary system {water (1) + acetone (2) + 1-butanol (3)} at the same temperature and pressure: 298.15 K and 0.1MP. The hydrogen bonding of the self-associations in mixed solvent containing trifluoroethanol is formed as seen in Figure (5.7).

For the systems {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} the solutions containing TFE have fairly stable structures due to significant dipole-dipole intermolecular interactions with water molecules giving a large immiscibility gap , as illustrated in Figure (5.8).

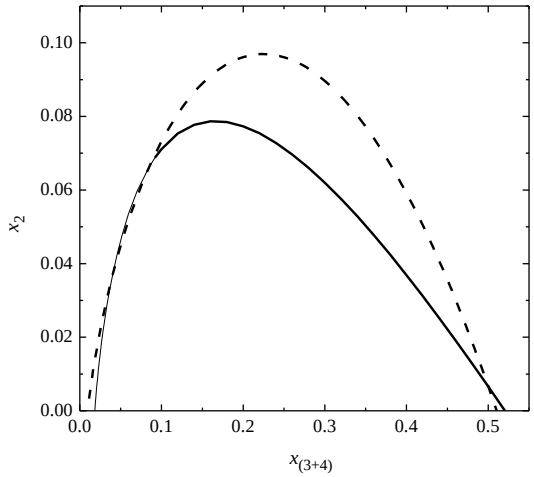

FIGURE (5.8) : The binodal of liquid-liquid equilibrium data for quaternary mixtures {water (1) + acetone (2) + 1-butanol (3) + 2.2.2 trifluoroethanol (4)} at 298.15 K and 101Kpa : ---, (x_3/x_4) = (0.802/0.198); — , NRTL (x_4 = 0) from ref [40] .

In the region of $0.10 \leq x \leq 0.70$, the immiscibility region of the system mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} is significantly important with presence of acetone as illustrated in Figure (5.9).

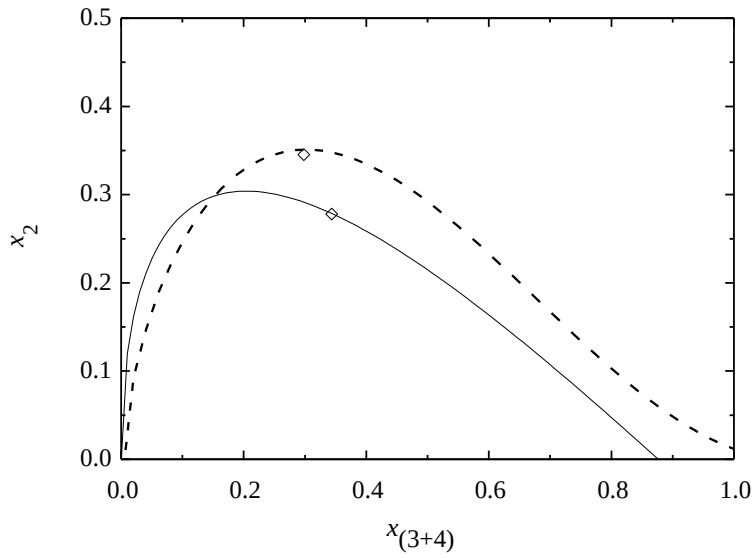

FIGURE (5.9) : Binodal curve eq. of quaternary mixtures {water (1) + 2.2.2 trifluoroethanol (2) + 1-hexanol (3) + acetone (4)} at 298.15 K and 101Kpa: ---, (x_3/x_4) = (0.63/0.37); — , (x_4 = 0), ◊, p.p.

CONCLUSION

The study of the liquid–liquid equilibrium in multi-components mixtures is not only of interest in order to provide necessary useful data in process design but also to check the thermodynamic models for the treatment of these data.

This thesis reports new solubility and liquid-liquid phase diagrams data for aqueous solutions of multi-components mixtures (ternary and quaternary mixtures) containing fluorinated hydrocarbons at atmospheric pressure and temperatures. The packing of the mixtures is resulting from moderate energetic effects due to formation/breaking of hydrogen bonding, in addition to repulsions of extra negative charges of oxygen and fluorine atoms.

The experimental data are discussed in terms intermolecular interactions.

Liquid-liquid phase equilibrium diagrams of ternary and quaternary mixtures were obtained by titration and analyzed by gas chromatographic methods.

The binodal curves data were well fitted using empirical equations and were correlated using the Hand and Othmer-Tobias equations.

Distribution coefficients and separation factors were evaluated for the immiscibility region.

Critical solution compositions are reported.

Compositions of critical points of LLE were determined for solutions investigating.

The effect of the mixed solvents in extraction process was investigate.

Solubility of solutions dependent on the structure and polarity of the solvent.

The immiscibility region of the systems decreases significantly with increasing of the alcoholic molecular chain.

Fluorinated hydrocarbons are more expensive, but environmentally accepted.

Water and fluorinated hydrocarbons HFC’s are strong polar components.

This work will provide efficient tools and knowledge to carry out a good research works on applied sciences.

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مخطط الأطوار لمزج متعددة لمكونات تحوي مركب فلوروهيدروكربوني

الملخص:

يعد مخطط الأطوار لمزج متعددة مهم في الدراسات النظرية و كذا في التطبيقات الصناعية، كثيرا ما نجدها في عمليات الاستخلاص

سائل- سائل.إن الهيدروكربونات الفلورية مثل 2-2-2 ثلاثي فلويوروإثانول لا قابلة للاشتعال ،غير سامة و لا مدمرة للأوزون وهي بدائل ممتازة للمركبات الكلورية.تستخدم في الطب وكثير من الأحيان في صناعة الدواء،الكيماويات و الوقود.

إن القياسات للتوازن سائل- سائل متعدد المركبات مهمة في عمليات الاستخلاص.

درس هذا العمل لتوفير قياسات للانحلالية والتوازنات سائل ـ مرفقة بمعطيات ترموديناميكية لمزج ثلاثية و رباعية سائلة تحوي 2-2-2 ثلاثي فلويوروإثانول،1 هكزانول،1 بوثانول،إيثانول، سيكلوهكزان، اسيتون، و الماء. بدرجات حرارة مختلفة وضغط 0.1MPa .

أجريت قياسات عيارية لمزج ثلاثية و رباعية وأعطت قياسات متوافقة جدا مع المنشورات العلمية.

استعملت طريقتي المعايرة و الكروماتوغرافيا لدراسة مخططات الأطوار سائل ـ سائل لمجموع المحاليل.

استخرجت قيم معاملات التوزيع و الانتقائية لكل محلول ثلاثي في هذه الدراسة، و كذا النقاط الحرجة لهذه المحاليل.

تم الحصول على قيم ذات نوعية جيدة للتوازن سائل- سائل و هذا باستعمال معادلات تجريبية لـ Hand وOthmer-Tobias .

وزارة التعليم العالي والبحث العلمي

جامعة العلوم والتكنولوجيا هواري بومدين

مذكرة ماجستير

تلي ليلى

مخطط الأطوار لمزج متعددة لمكونات تحوي مركب فلوروهيدروكربوني

كلية الكيمياء

مخبر علم البلورات الترمود يناميك