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Studies of Solubilities and Liquid-Liquid Equilibria of Ternary Aqueous Solutions Containing Alcohols and Fluorinated Hydrocarbons at Three Temperatures

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Studies of Solubilities and Liquid-Liquid equilibria of Ternary Aqueous Solutions Containing Alcohols and Fluorinated Hydrocarbons at Three Temperatures

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Contents

Abstract

Fluoro-hydrocarbons are taking more important role in many industrial applications.

These green chemicals are accepted in various industries of major applications, such as fuel, medicine, bio-engineering, and technical solvents.

Quantitative knowledge of liquid-liquid equilibrium (LLE) data is much needed in chemical engineering processes; chemical-unit design, simulation, and optimisation of separation operations.

The aim of this work is to report new solubilities and LLE data and investigate the equilibrium phase behaviour for aqueous solutions of fluorinated hydrocarbons with alcohols at three temperatures.

Experimental solubilities and liquid-liquid equilibrium data are obtained for the systems (water + alcohol + fluorobenzene) and (water + alcohol + α,α,α-trifluorotoluene); alcohol = methanol, or ethanol, or 2-propanol. The measurements are carried out in thermostated measuring cells at T = (288.15, 298.15, 308.15; ± 0.05) K and p = 101.2 kPa. The LLE compositions of the conjugate solution phases are obtained using gas-liquid chromatographic analysis.

The experimental solubilities and LLE data for the studied systems at each temperature are well fitted together to empirical equations.

While, the LLE data are correlated apart using the Hand and Othmer-Tobias methods. The critical solution compositions, the distribution coefficients, and the selectivities of each fluorinated hydrocarbon in the ternary solutions are reported.

Résumé

Les fluoro-hydrocarbures ont possèdent très important dans plusieurs applications industrielles. Ces produits chimiques sont acceptés dans diverses industries des applications principales, telles que carburant, médecine, biologie, et dissolvants techniques.

L'étude quantitative des équilibres de phase liquide-liquide est nécessaire dans les processus du génie chimique; simulation, optimisation des opérations de séparation, et études thermodynamiques théoriques.

Le but de ce travail est d'obtenir des résultats expérimentaux des solubilités et des équilibres thermodynamiques liquide-liquide et d'étudier le comportement des équilibres de phase des solutions aqueuses contenant des composés organiques fluorés avec les alcools, à trois températures.

Les résultats expérimentaux des solubilités et des équilibres liquide-liquide sont obtenus pour les systèmes (eau + alcool + fluorobenzene) et (eau + alcool + α,α,α-trifluorotoluene); alcool = méthanol, ou éthanol, ou 2-propanol. Les mesures sont effectuées dans une cellule d'équilibre liquide-liquide à températures T = (288.15, 298.15, 308.15; ± 0.05) K et pression p = 101.2 kPa. Les compositions des équilibres liquide-liquide de chaque phase sont obtenues pour la chromatographie en phase gazeuse.

Les résultats expérimentaux des solubilités et des équilibres liquide-liquide pour les systèmes étudiés sont bien lissés par des équations empiriques.

Les compositions critiques des solutions, les coefficients de la distribution, et les sélectivités de chaque composé fluoré dans les solutions ternaires sont rapportées.

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M.CHAOU

Glossary:

Symbols:

A, B	Hand constants
A_1, B_1	Othmer-Tobias constants
C	number of components
F	degree of freedom
G	Gibbs function
K_0, K	chromatographic constants
M	molar mass
R	universal gas constant
S	entropy
s	selectivity
T	thermodynamic temperature
V	volume
a	activity
d	distribution coefficient
m	mass
n	the number of moles
n_D	refractive index
p	pressure
s	surface area
x	mole fraction

Abbreviations:

LLE	Liquid-Liquid Equilibrium
Exp.	Experimental
Lit.	Literature
GLC	Gas-Liquid Chromatography
mix	mixing
mn	minute
p.p.	plait point

Greek:

Δ	increment
δ	uncertainty
∂	derivation
φ	number of phases
γ	activity coefficient
μ	chemical potential
ρ	density

Subscripts:

A	component A in mixture
B	component B in mixture
i, j	components
i1	component i in aqueous phase
i3	component i in organic phase
m	molar

Superscripts:

c	critical point
cs	critical solution
id	ideal
r	real
E	excess property
α, β, φ	phase

List of tables:

List of Figures:

Experimental results:

CHAPTER 1

INTRODUCTION

Hydrofluorocarbons (HFC's) are seen by industrialists as good replacements for the chlorofluorocarbons (CFC's), which have direct environmental impact to stratospheric ozone depletion.[1] Water is a unique solvent, and numerous chemical and physical studies have been made on it and its solutions than on any other liquid.[2]

Fluorine is the most electronegative of all elements. Therefore, the C−F bond is highly polar, while water has a large dipole moment and is highly self-associated.[2, 3] Generally, in aqueous solutions of hydrocarbons, the organic liquid molecules play the role of the inert diluents. Whereas, adding inert molecules to aqueous solutions reduces the intermolecular associations among the molecules of water.[3]

Solubility of chemical reagents in water is one of the most important physicochemical properties of a substance, and having numerous applications in industry and environment.[4] Generally, solubilities of liquid solutions are affected by temperature.[5, 6]

Many aqueous solutions containing organic substance(s) show partial miscibility and liquid-phase separation. The partial solubility phenomenon in multi-component solutions has important role in separation processes; such as liquid extraction.[7-10] Extraction is a separation method used to obtain highly pure chemicals.[11]

Petrochemical industries, and chemical technologies have very strong interest in liquid solubilities, and liquid-liquid phase equilibria, particularly, the solubility of organics in water and water in organics.[12-14] Nowadays, heterogeneous phase equilibrium data are fundamentally important for design and simulation of all separation processes[15-24] in the petrochemical industry to predict and to avoid phase formation and separation during production and transportation.[25]

Often, when organic solvents are partially miscible, the density difference between components of a solution is significant, facilitating the separation of liquid-liquid phases effectively.[26]

In recent years, liquid-liquid equilibrium studies have become increasingly important in the pharmaceutical and food industries. Liquid-liquid extraction provides an important alternative to distillation for the recovery of valuable materials from solutions using a nonmiscible solvent(s).[27-29] Heterogeneous extractive distillation is one of the effective methods to separate azeotropic mixtures.[17,21] In food industry, various solvents are used for drying and improving food preservation.[30,31]

The problems associated with the development and implementations of the industrial processes are: the complexity of the solution, the heterogeneity of the medium, the chemical materials to be separated, and the availability of thermodynamic property data for simulation and prediction.[32,33]

Light alcohols such as methanol and ethanol are among the compounds used for the production of safe (green) gasoline.[14,34,35] Methanol is widely used as drying solvent in gas industry, and as a starting chemical reagent in chemical synthesis. Thus, the knowledge of the thermodynamic properties of such industrial chemicals in relation to other compounds and conjugate solutions is of a significant importance to chemical engineers.[36]

Ethanol, and 2-propanol are important industrial solvents: a substitute for conventional fuel and recovery for the former, and a cleaning agent in the production of electronic devices for the latter.[17,37,38] The liquid-liquid equilibrium data are therefore essential, at required temperature ranges, to help in designing, and refining of separation units.[39]

For an extraction process, the choice of conditions relies on the chemical nature of solvent molecules and on compositions of solution.[7] The solvent ability to extract light alcohols from their dilute aqueous solutions can be evaluated in terms of two parameters: the distribution coefficient of alcohol, and the solvent selectivity.[40-46]

Fluorobenzene and α,α,α-trifluorotoluene demonstrate very low solubility in water.[47] In this work, we were concentrating on the measurements and correlation of solubilities and liquid-liquid equilibria for (water + alcohol + fluorobenzene) and (water + alcohol + α,α,α-trifluorotoluene) at temperatures T = (288.15, 298.15, 308.15) K and p = 101.2 kPa, where alcohol = methanol, or ethanol, or 2-propanol. We have also discussed the ability of fluorobenzene or α,α,α-trifluorotoluene to extract light alcohols from dilute aqueous solutions.

To the best of our knowledge, no thermodynamic data on these ternary systems are reported in the literature.

CHAPTER 2

PHASE EQUILIBRIUM THERMODYNAMICS

2.1 Fundamental Principles:

Many multi-component solutions containing water show immiscibility gap; existence of two liquid phases, such multi-component two liquid phase solutions are heterogeneous systems. Thermodynamic properties of heterogeneous liquid solutions are very desirable for design and optimization of separation processes in chemical engineering and industrial operations.

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

$$dG_m^{\varphi} = -\sum_{\varphi} S_m^{\varphi} dT^{\varphi} + \sum_{\varphi} V_m^{\varphi} dp^{\varphi} + \sum_{\varphi} \sum_{i} \mu_i^{\varphi} dx_i^{\varphi} , \tag{2.1}$$

where the summations are over all components i and all phase φ.

Since the chemical potential μ for component i is defined by:

$$\mu^{\varphi}_i = \left(\partial G / \partial n_i\right)^{\varphi}_{T,\ p,\ n_i \neq n_j} , \tag{2.2a}$$

so, the chemical potential of component i in phase φ is:

$$\mu_i^{\varphi} = G_m^{\varphi} - x_j^{\varphi} \left(\partial G_m / \partial x_j\right)^{\varphi}_{T,\,p} , \tag{2.2b}$$

then the change in (μ^{φ}_i, T, p) is:

$$d\mu^{\varphi}_i = -S^{\varphi}_{m,i} dT + V^{\varphi}_{m,i} dp , \tag{2.2c}$$

where $S^{\varphi}_{m,i}$ and $V^{\varphi}_{m,i}$ are the molar entropy and molar volume of component i in phase φ, respectively, and the Gibbs-Duhem equation for a phase φ is:

$$S_m^{\varphi} dT - V_m^{\varphi} dp + \sum_i x_i^{\varphi} \mu_i = 0 , \tag{2.3}$$

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

The degree of freedom F of a multi-component multi-phase system is determined by Gibbs phase rule:

$$F = C - \varphi + 2 \geq 0 , \tag{2.4}$$

where C is the number of system component and φ is the number of phases.

For two phase ternary system: F = 3; so three independent variables such as temperature T, pressure p, and composition x_i are needed to study the system precisely and fulfill the equilibrium condition:

$$\mu_i^{\alpha} = \mu_i^{\beta}, \tag{2.5}$$

so we get: $$T^{\alpha} = T^{\beta} = T \tag{2.6}$$

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

In figure (2.1), presents x_A, x_B compositions of coexisting phases. The plot of compositions of coexisting phases gives the binodal curve.

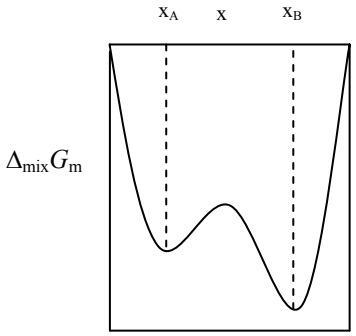


Figure (2.1): Scheme of Gibbs energy of mixing for a binary system with a miscibility gap.

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

$$a_i = x_i \gamma_i, \tag{2.8}$$

where γ_i is the activity coefficient of component i.

The molar Gibbs function of mixing $\Delta_{mix} G_m^r$ of a real solution is given by:

$$\Delta_{mix} G_m^r = RT \sum_{i=1}^{N} x_i \ln a_i \tag{2.9}$$

Thus, the chemical potential of mixing of component i in phase φ is expressed by:

$$\left(\partial \Delta_{mix} G_m / \partial x_i\right)_{T,p}^{\varphi} = \mu_{mix,i}^{\varphi}, \tag{2.10}$$

However, since according to equation (2.10) the derivative of the chemical potential of mixing with respect to the mole fraction of the component i in phase φ is:

$$\left(\partial \mu_{mix,i} / \partial x_i\right)_{T,p}^{\varphi} = \left(\partial^2 \Delta_{mix} G_m / \partial x_i^2\right)_{T,p}^{\varphi} \tag{2.11}$$

where $d\mu_i^{\varphi} < 0$ for a natural mass transfer of component i between phases α and β. Thus $\left(\partial \mu_{mix,i}/\partial x_i\right)_{T,p}^{\varphi} > 0$.

Hence, the condition of material stability for a binary homogeneous mixture is expressed by the inequality:

$$\left(\partial^2 \Delta_{mix} G_m/\partial x_i^2\right)_{T,\ p} > 0 \tag{2.12}$$

So, the mass transfer instability fulfils:

$$\left(\partial^2 \Delta_{mix} G_m/\partial x_i^2\right)_{T,p} < 0 \tag{2.13}$$

The passage from phase stability to instability corresponds to a unique state known as the critical state, where for an infinitesimal change in equilibrium variables (constants), either one stable phase splits into two conjugate phases, or two conjugate phases form one stable phase. The critical state has zero degree of freedom, in which: $x_i^{\alpha} = x_i^{\beta} = x_i^{cs}$, (T, p, constant).

The critical state of a heterogeneous solution is established at unique temperature; which is the critical solution (or consolute) temperature T^{cs}.

The critical solution temperature is the temperature at which a heterogeneous (or homogeneous) solution changes from two phases (or one phase) to yield one phase (or two phases) system.

2.2 Partial Miscibility in Liquid Solutions:

The $(T, x)_p$ phase diagram of a binary liquid solution with a miscibility gap is shown in figure (2. 2).

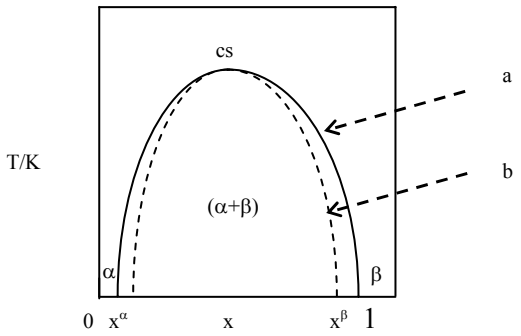


Figure (2.2): Scheme of $(T, x)_p$ phase diagram of a binary solution with miscibility gap: a, binodal; b, spinodal.

The partial miscibility of a binary system at an isotherm T shows the following three composition regions:

- $0 \le x \le x^{\alpha}$: with $\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T,\,p} > 0$, phase α is stable,
- $x^{\beta} \le x \le 1.0$: with $\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T,\,p} > 0$, phase β is stable,
- $x^{\alpha} \le x \le x^{\beta}$: with $\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T,\,p} < 0$, two stable phases coexist; (α +β).

The critical point of a solution justifies:

- $x^{\alpha} = x^{\beta} = x^{cs}$,

$$\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T^{cs},\,P} = 0, \tag{2.14}$$

$$\left(\partial^3 \Delta_{mix} G_m / \partial x^3\right)_{T^{cs},\,P} = 0, \tag{2.15}$$

and $$\left(\partial^4 \Delta_{mix} G_m / \partial x^4\right)_{T^{cs},\,p} > 0 \tag{2.16}$$

T^{cs}, critical solution (consolute) temperature, is the extreme temperature where the heterogeneous solution converges to a homogeneous one. Generally, at temperature $T > T^{cs}$, the solution is homogeneous over the composition range with $\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T,\,p} > 0$.

According to equation (2.9), we have:

$$\Delta_{mix} G_m^r = RT \sum_{i=1}^{N} x_i \ln x_i + RT \sum_{i=1}^{N} x_i \ln \gamma_i, \tag{2.17}$$

The first term in equation (2.17) is the ideal molar Gibbs function of mixing $\Delta_{mix} G_m^{id}$.

Since the excess molar Gibbs function G_m^E is defined by:

$$G_m^E = \Delta_{mix} G_m^r - \Delta_{mix} G_m^{id}, \tag{2.18}$$

Then from equations (2.17) to (2.18) the excess molar Gibbs function G_m^E is given as function of composition x as:

$$G_m^E = RT \sum_{i=1}^{N} x_i \ln \gamma_i, \tag{2.19}$$

where γ_i is the activity coefficient of component i defined by:

$$RT \ln \gamma_i = \left(\frac{\partial G_m^E}{\partial x_i} \right)_{T,\,p,\,x_j \neq x_i} \tag{2.20}$$

Equations (2.19) and (2.20) relate thermodynamically the activity coefficients γ_i and excess molar Gibbs function G_m^E in simple and precise way. Beside the experimental difficulties to

determine excess Gibbs function, the studies of phase equilibrium of multi-component multi-phase systems apply directly the use of excess Gibbs function G_m^E; that is to say the use of activity coefficient γ_i. Many empirical expressions relating G_m^E to composition x, γ_i to composition x, have been proposed for this purpose and find important applications. These empirical expressions are known as G^E models or simply γ_i models. The most known G^E models applied to liquid-liquid equilibrium studies are: UNIQUAC (UNIversal QUAsi Chemical) and NRTL (Non Random Two Liquids) models.

The liquid-liquid equilibrium state for binary solutions is represented by:

$$\left\{\left(1-x^{\alpha}\right)A+x^{\alpha}B\right\}^{\alpha} \leftrightarrow \left\{\left(1-x^{\beta}\right)A+x^{\beta}B\right\}^{\beta} \tag{2.21}$$

The compositions of each phase are joined together by straight lines known as tie lines; such as line MN in figure (2.3).

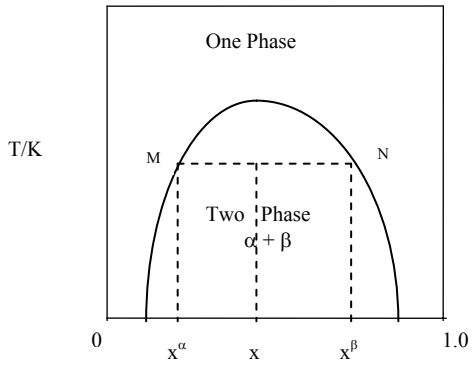


Figure (2.3): Distribution of amount of substance:
liquid-liquid equilibrium in a binary system.

When the thermal and chemical equilibrium is established at temperature T, the distribution of amount of substance of components A and B in solution between phases α and β are:

$$n_A = n_A^{\alpha} + n_A^{\beta} \quad \text{and} \quad n_B = n_B^{\alpha} + n_B^{\beta} \tag{2.22}$$

But, the amount of substance in phase α and β are:

$$n^{\alpha} = n_A^{\alpha} + n_B^{\alpha} \quad \text{and} \quad n^{\beta} = n_A^{\beta} + n_B^{\beta} \tag{2.23}$$

On the other hand, the total amount of substance in the system is:

$$n = n^{\alpha} + n^{\beta}$$
$$n = n_A + n_B \qquad (2.24)$$

Applying equations (2.22 to 2.24) for the isotherm T, the compositions and amount of substance of each phase are related by the following relation:

$$\left(n^{\alpha}/n^{\beta}\right) = \left(x^{\beta} - x\right)/\left(x - x^{\alpha}\right) \qquad (2.25)$$

where x is the overall composition.

Equation (2.25) has important applications in liquid extraction processes applied in chemical engineering and chemical industries.

The distribution coefficient d_i of a solute i between two coexistent phases ($\alpha + \beta$) is related to its phase compositions as:

$$d_i = \frac{x_i^{\alpha}}{x_i^{\beta}} \qquad (2.26)$$

The selectivity S (separation factor), is related to the distribution coefficient of a solvent j for solute i distributed between phases ($\alpha + \beta$) in a multi-component solution:

$$S_{ji} = \frac{d_j}{d_i} = \left(\frac{x_j^{\alpha}/x_j^{\beta}}{x_i^{\alpha}/x_i^{\beta}}\right) \qquad (2.27)$$

2.3 Liquid-Liquid Equilibrium in Ternary Systems:

A ternary system in two phase equilibrium at (T, P, constant) is univariant; $F' = 1$. While the sum of compositions in a phase φ satisfies: $\sum x_i^{\varphi} = 1$, so a two phase diagram in such a system can be represented as: $x_2 = f(x_1)$.

The compositions of ternary system are represented by the Gibbs triangle, where each side of triangle is binary system of compositions ($x_A + x_B = 1$): where as the ternary composition of the system is represented by a single point on the triangle: ($x_A + x_B + x_C = 1$) , (100 %).

Figure (2.4) show a triangular diagram.

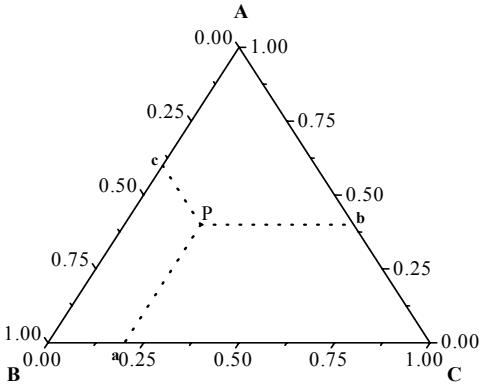
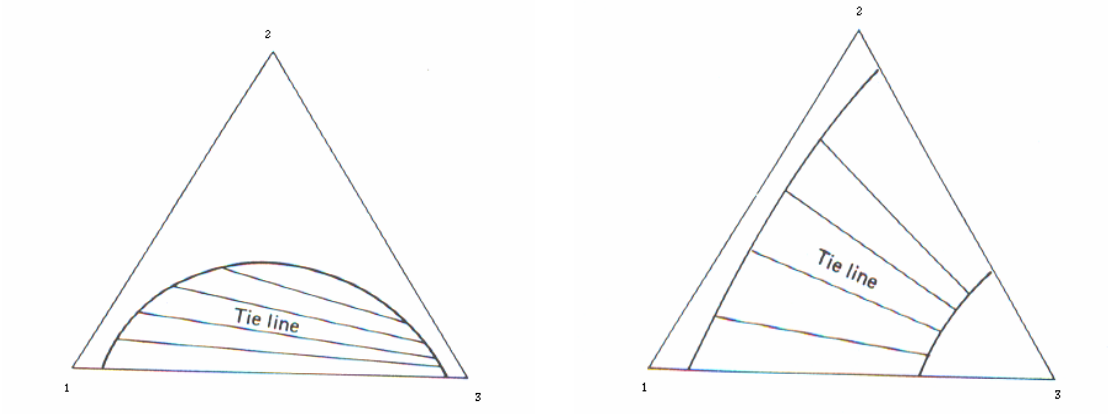


Figure (2.4): Representation of a mixture P in a triangular diagram.

The mutual solubility of a pair of partially miscible liquids is generally affected by the presence of a third component, and consequently changes to their mutual solubility arise.[48-50] Ternary liquid-liquid equilibrium is of two types and usually represented on triangular diagrams:[51]



type 1 type 2

Figure (2.5): Common types of ternary liquid-liquid phase equilibria.

Figure (2.6) represents the phase diagram for the system {water(1) + ethanol(2) + benzene(3)} at 303.15 K.

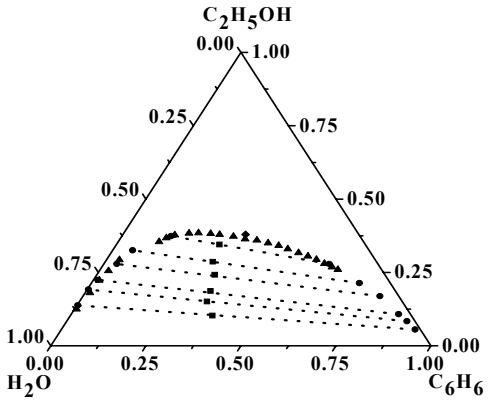


Figure (2.6): Liquid-liquid equilibrium phase diagram for the system {water(1) + ethanol(2) + benzene(3)}at 303.15 K.

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

$$a_i^{\alpha} = a_i^{\beta}, \tag{2.28}$$

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

According to equation (2.28), it holds for component i in two phase system:

$$\gamma_i^{\alpha} x_i^{\alpha} = \gamma_i^{\beta} x_i^{\beta}, \tag{2.29}$$

where x_i^{φ} and γ_i^{φ} (φ = α, or β) are the equilibrium mole fractions and the activity coefficient of component i in phases φ, respectively.

Applying equation (2.29) for ternary system we get:

$$\left(\gamma_1 x_1\right)^{\alpha} = \left(\gamma_1 x_1\right)^{\beta} \tag{2.30a}$$

$$\left(\gamma_2 x_2\right)^{\alpha} = \left(\gamma_2 x_2\right)^{\beta} \tag{2.30b}$$

$$\left(\gamma_3 x_3\right)^{\alpha} = \left(\gamma_3 x_3\right)^{\beta} \tag{2.30c}$$

In addition to equations (2.30) the material balances in liquid-liquid equilibrium of a ternary system fulfil:

$$n^{\alpha} + n^{\beta} = n \tag{2.31}$$

$$n_1^{\alpha} + n_1^{\beta} = n_1 \tag{2.32}$$

$$n_2^{\alpha} + n_2^{\beta} = n_2 \tag{2.33}$$

where n is the number of moles.

2.4 Liquid-Liquid Equilibrium Data Correlation:

The binodal curve and liquid-liquid equilibrium data of a ternary system {x_1 water(1) + x_2 alcohol(2) + x_3 solvent(3)}, at (T, p, constant), are fitted to the equation (2.34) refined by us:[52,53]

$$x_2 = a + bx_3^{0..5} + cx_3 + dx_3^2 + ex_3^3, \tag{2.34}$$

where x_i represent the mole fraction of component i.

Liquid-liquid equilibrium data for all systems are satisfactorily correlated by the methods of Hand and Othmer-Tobias. [9, 54, 55]

The Hand correlation equation is:

$$\ln\left(\frac{x_{23}}{x_{33}}\right) = A + B\ln\left(\frac{x_{21}}{x_{11}}\right) \tag{2.35}$$

The Othmer-Tobias correlation equation is:

$$\ln\left\{\frac{\left(1 - x_{33}\right)}{x_{33}}\right\} = A_1 + B_1 \ln\left\{\frac{\left(1 - x_{11}\right)}{x_{11}}\right\}, \tag{2.36}$$

where $x_{i\varphi}$ is the mole fraction of component i in a phase φ; (aqueous, φ = 1; organic, φ = 3).

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Chemicals:

Chemicals used in this investigation are: methanol, ethanol, 2-propanol, benzene, fluorobenzene, and α,α,α-trifluorotoluene. They are supplied by Fluka, Merck, and Panreac and are used without any further purification. Triply-distilled water is used throughout the experimental work.

The purities of the chemicals are verified by gas-liquid chromatographically to better than 99.8%.

Physico-chemical properties of pure components are determined at 298.15 K and atmospheric pressure. The refractive indices are measured using an Abbe-type refractometer (Phywe, No. 990646). The densities are measured using an Anton-Paar Vibrating-tube densimeter: DMA 5000. The accuracy in refractive index and density measurements are $\pm 5.10^{-4}$ and $\pm 2.10^{-5}$ $g \cdot cm^{-3}$, respectively.

The experimental densities and refractive indices of pure components at 298.15 K are listed in table (3.1) together with the literature data.

Table (3.1): experimental values of density (ρ), refractive index (n_D) of pure componaents at tempertaure T = 298.15 K, and dipole moment (μ).

Component	Chemical formulea	ρ (298.15 K)/g·cm^{-3}		n_D (298.15 K)		μ/D
		Exp.	Lit.	Exp.	Lit.	
Water	H_2O	0.99708	0.99705[56]	1.3325	1.33250[56]	1.82[56]
Methanol	CH_3OH	0.78662	0.78637[56]	1.3263	1.32652[56]	2.87[56]
Ethanol	C_2H_5OH	0.78579	0.78493[56]	1.3590	1.35941[56]	1.66[56]
2-Propanol	C_3H_7OH	0.78109	0.78126[56]		1.37520[56]	1.66[56]
Benzene	C_6H_6	0.87399	0.78360[56]	1.4976	1.49792[56]	0.00[56]
Fluorobenzene	C_6H_5F	1.01906	1.01893[57]			1.48[56]
α,α,α-Trifluorotoluene	$C_7H_5F_3$	1.18198	1.18129[56]		1.41225[56]	2.86[56]

3.2 Experimental Procedure of Liquid-Liquid Equilibrium:

The solubility (binodal) curves of the ternary aqueous solutions are determined visually by the titration method in a glass measuring cell equipped with a water jacket to maintain isothermal condition and a magnetic stirrer.[58-61] Various mixtures are studied using the continuous method by injecting the titrant solvent through a side arm in the cell.

The glass equilibrium cell used in this work is similar to that reported in literature,[62,63] and is built by SOMIVER-Thenia (Algeria). The scheme of the measuring cell is shown in figure (3.1).

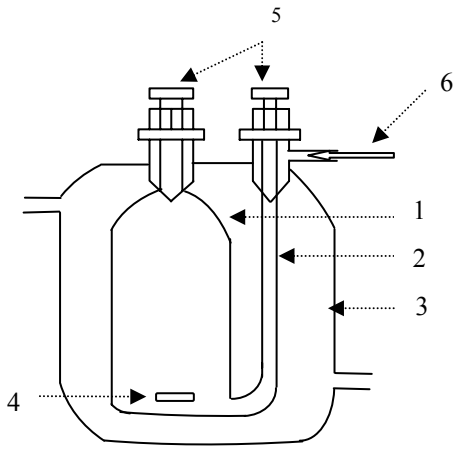


Figure (3.1): Scheme of the equilibrium cell:
1. cell body, 2. side tube, 3. thermostated jacket,
4. magnetic stirrer, 5. Teflon stoppers, 6. syringe.

The mixture compositions are computed from precise masses using an electronic balance OHAUS (model: Explorer, δm = ± 0.1 mg). Prior to titration of a heterogeneous mixture (water + alcohol + fluorohydrocarbon), the cell mixture is stirred vigorously for at least 30 mn,[64] then the titrant component (alcohol) is progressively added until the turbidity has disappeared, keeping the stirring on.

The cell is connected to a thermocryostat (LAUDA, model: RC6CP- Edition 2000, δT = ± 0.01K). The cell temperature is measured with a digital thermistor-thermometer (Cole-Parmer instrument, model: 8502-16, thermistor: YSI-400) with precision better than ±0.05 K.

Tie line data (LLE) are obtained by preparing two-phase ternary mixtures of known overall compositions in glass flasks. All heterogeneous mixtures are prepared by mass. After being stirred vigorously for at least 4 h,[16,31,60,65] the two-phase mixtures are left to stand for more than 24 h to attain liquid-liquid equilibrium with complete separation into aqueous and organic phases.[66-69] Finally, samples of each phase is withdrawn out and stored in small glass bottles, then analysed by gas-liquid chromatography.

Chromatographic Analysis:

The composition of liquid samples from the conjugate phases are analysed using a gas-liquid chromatography (GLC); Perkin Elmer, Model Clarus 500. The chromatograph is equipped with two injects, for packed and capillary columns, and two detectors, flame ionization FID and thermal conductivity TCD, and is run by computer software: Total Chrom Workstation.

For aqueous solutions, the composition analyses are performed using a packed column: Porapak, Q80/100 Mesh, length of the column = 0.6 m, and the thermal conductivity detector. For an optimum analysis of a sample, pure component or mixture, the GLC conditions are: temperatures: column = 423.15 K; detector = 473.15 K, injector = 513.15 K, nitrogen as carrier gas, flow rate = 20 ml/mn. The injected volume of each sample is 0.2 µl. Retention times (mn) for the pure components are: 0.492 for water, 0.938 for methanol, 1.621 for ethanol, 2.845 for 2-propanol, 8.809 for fluorobenzene, and 15.645 for α,α,α-trifluorotoluene. For an optimum analysis, the injector and the detector temperatures are set higher by 50 K than that of the highest boiling point of components, and to that of the column, respectively.[70]

To obtain quantitative results of LLE, the internal standard method is used for GLC analysis. [63,71-75] Samples with known compositions are used to calibrate the chromatography in the compositions range of solubility data.[21,30,76] The solute used as the internal standard

calibration are either ethanol or 2-propanol; which corresponds to a studied system. The calibration equation is:

$$\frac{s_i}{s_{st}} = K_0 + K\frac{n_i}{n_{st}} \quad , \tag{3.1}$$

where s_i and s_{st} are the percentage peak areas of the measured compound and of the internal standard respectively, n_i and n_{st} are the number of moles of the measured compound and of the internal standard in the calibration mixture respectively, K_0 and K are the chromatographic constants. Three measurements are performed for each sample, and the mean composition values are obtained within $x_i^{\varphi} = \pm 0.002$.

For technical procedure, tow test systems were performed: solubility and LLE measurement for: (water + ethanol + benzene) system at 303.15 K, and solubility measurement for (water + methanol + benzene) at 293.15 K. The experimental data obtained for the two test systems showed good agreement with literature values.[77,78]

In this work, the solubility and liquid-liquid equilibrium measurements of fifteen ternary aqueous solutions containing water, benzene, fluorobenzene, α,α,α-trifluorotoluene, methanol, ethanol, and 2-propanol are studied at isothermal conditions and atmospheric pressure. They are:

{water(1) + ethanol(2) + benzene(3)}, {water(1) + alcohol(2) + fluorobenzene(3)}, and {water(1) + alcohol(2) + α,α,α-trifluorotoluene(3)}; alcohol = methanol, or ethanol, or 2-propanol.

3.3 Experimental Uncertainty Analysis:

Liquid phase composition x_i:

The composition x_i in multi-component system is defined by:

$$x_i = \left(m_i / M_i\right) / \sum_{i=1}^{N} \left(m_i / M_i\right), \tag{3.2}$$

Therefore, the uncertainty in composition x_i is:

$$\left(\delta x_i\right)^2 = \sum_{i=1}^{N} \left\{ \left\{ \frac{1}{M_i} \sum_{i=1}^{N} \left(\frac{m_i}{M_i}\right) - \frac{m_i}{M_i^2} \right\} / \left\{ \sum_{i=1}^{N} \left(\frac{m_i}{M_i}\right) \right\}^4 \left(\delta m_i\right)^2 \right\}, \tag{3.3}$$

where N, M, and m are the number of components, the molar mass, and experimental masses, respectively.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Results of Solubilities and Liquid-Liquid Equilibrium Data:

The solubilities and liquid-liquid equilibrium data of fifteen ternary aqueous solutions containing water, benzene, fluorobenzene, α,α,α-trifluorotoluene, methanol, ethanol, and 2-propanol are investigated at isothermal conditions and atmospheric pressure:

T = 303.15 K:

1. {water(1) + ethanol(2) + benzene(3)}.

T = (288.15, 298.15, 308.15) K:

2. {water(1) + ethanol(2) + fluorobenzene(3)}.
3. {water(1) + 2-propanol(2) + fluorobenzene(3)}.
4. {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}.
5. {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}.

T = (288.15, 298.15) K:

6. {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)}.

4.2 Reductions and Correlations of Experimental Data:

The experimental solubilities, liquid-liquid equilibrium data, and correlation for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 288.15 K, are given in this chapter in tables and figures. The experimental solubilities (binodal curve) and fitting parameters of equation (2.34) are reported in table (4.1). The data of liquid-liquid equilibrium, selectivity, and correlation parameters of Hand and Othmer-Tobias methods, together with the critical solution compositions $\left(x_1^{cs}, x_2^{cs}\right)$ are given in table (4.2).

Critical solution compositions (plait point), at the measuring temperatures, are correlated by the Othmer-Tobias method.[40,43,79,80] The distribution coefficient and selectivity (separation factors) are evaluated over the immiscibility region.

In this study, the alcohol distribution coefficients, d_2, is defined as the ratio of the alcohols mole fraction in the aqueous phase (x_{21}) to that in the organic phase (x_{23}), and selectivity is determined as the ratio of the distribution coefficients of water (d_1) to the distribution coefficients (d_2) of alcohol. [45,81]

$$d_i = \frac{x_{i1}}{x_{i3}}, \qquad S_{12} = \frac{d_1}{d_2} \tag{4.1}$$

Due to the specificity of the infinite dilution regions, the thermodynamic properties corresponding to the measured compositions are not taken for correlation procedures in this work.

The experimental and correlated solubilities and liquid-liquid equilibrium data for the ternary systems are plotted in figure (4.1). Hand and Othmer-Tobias plots are shown in figure (4.2). The distribution coefficients for ethanol and selectivity are shown in figure (4.3). The distribution of ethanol between water and fluorohydrocabon are plotted in figure (4.4).

The effect of temperature on solubilities and liquid-liquid equilibrium data of all our studies systems are represented in figures (4.5) to (4.9).

The correlation factor for the linear regression R^2 is varying between 0.9953 and 0.9998.

Table (4.1): Experimental solubilities at 288.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component:	1. water	H_2O
	2. ethanol	C_2H_5OH
	3. fluorobenzene	C_6H_5F

x_1	x_2	x_3
0.0355	0.1661	0.7984
0.0557	0.2180	0.7263
0.0723	0.2457	0.6820
0.0921	0.2715	0.6364
0.1114	0.2898	0.5988
0.1275	0.3071	0.5654
0.1537	0.3267	0.5196
0.1798	0.3439	0.4763
0.2151	0.3586	0.4263
0.2527	0.3702	0.3771
0.2900	0.3775	0.3325
0.3276	0.3830	0.2894
0.3710	0.3844	0.2446
0.4118	0.3838	0.2044
0.4497	0.3792	0.1711
0.4894	0.3705	0.1401
0.5367	0.3533	0.1100
0.5790	0.3371	0.0839
0.6132	0.3239	0.0629
0.6612	0.2911	0.0477
0.6988	0.2668	0.0344
0.7442	0.2319	0.0239

Equation: (2.34)

a	b	c	d	e	σ
0.0304	1.6404	-2.0691	1.0229	-0.6431	0.00002

Table (4.2): Experimental liquid-liquid equilibrium data at 288.15 K
for solutions of {water(1) + ethanol(2) + Fluorobenzene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.3056	0.3474	0.4851	0.3731	0.1585	0.3274	2.69
0.3530	0.3390	0.5337	0.3555	0.1338	0.3084	3.46
0.3851	0.2903	0.6290	0.3140	0.0875	0.2607	5.97
0.4016	0.2528	0.6772	0.2803	0.0674	0.2298	8.24
0.4191	0.2123	0.7406	0.2354	0.0448	0.1904	13.37
0.4395	0.1750	0.7972	0.1921	0.0306	0.1509	20.46
0.4817	0.1140	0.8621	0.1336	0.0182	0.0916	32.48
0.4979	0.0758	0.8999	0.0972	0.0082	0.0570	64.36
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
-0.1675	1.0711			-0.1043	1.0220	
Plait point for the {water(1) + ethanol(2) + fluorobenzene(3)} solutions at T						
T/K	$(x_1)^{cs}$	$(x_2)^{cs}$				
288.15	0.3007	0.3803				
298.15	0.3902	0.3897				
308.15	0.3050	0.3493				

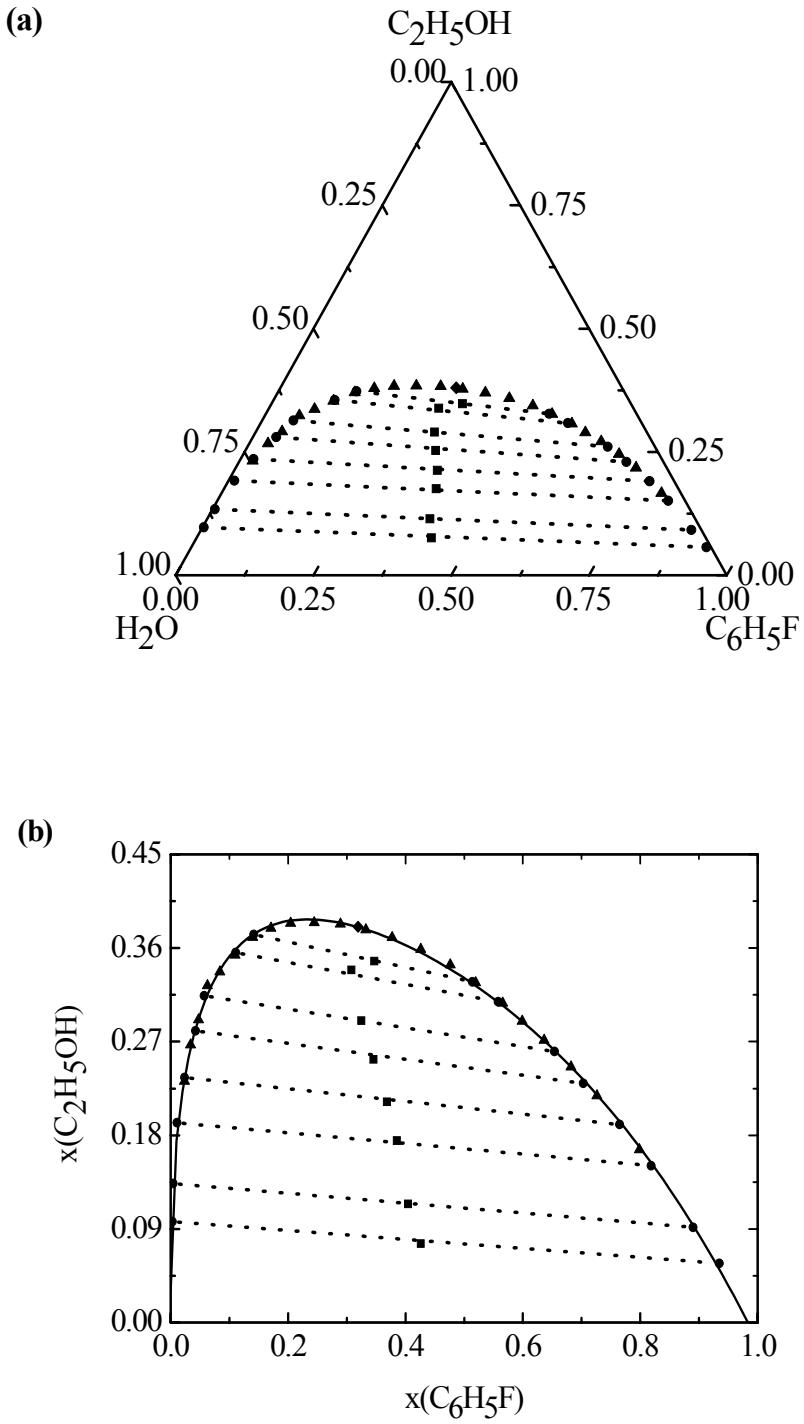


Figure (4.1): Solubilities and LLE data for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34).

(a), ternary representation; **(b)**, binary representation

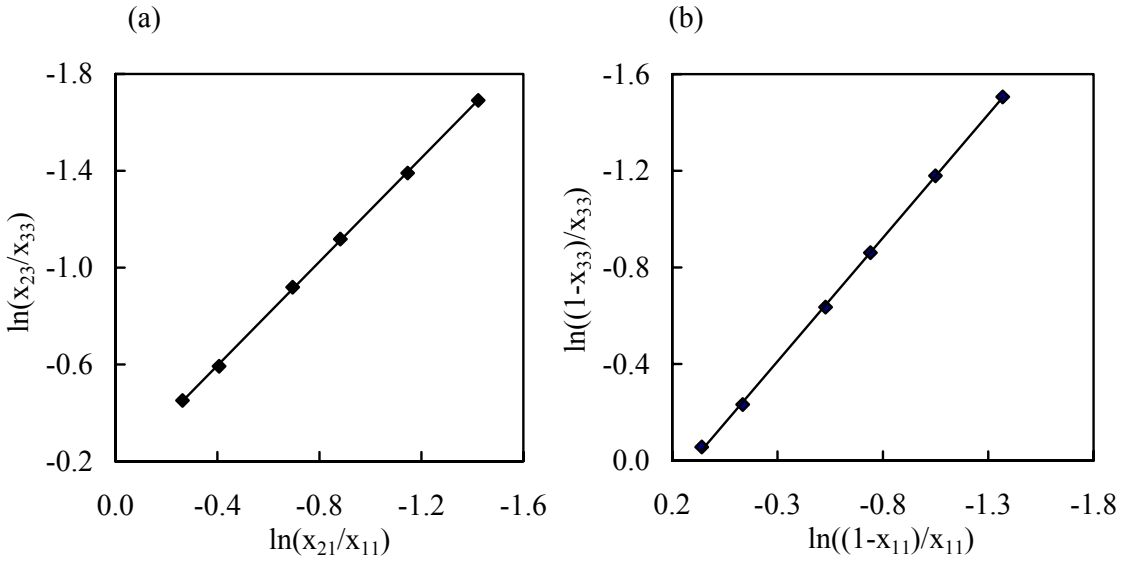


Figure (4.2): correlation of the LLE data for {water(1) + ethanol(2) + fluorobenzene(3)} solutions at 288.15 K: (a), hand; —, equation (2.35); (b), Othmer-Tobias; —, equation (2.36).

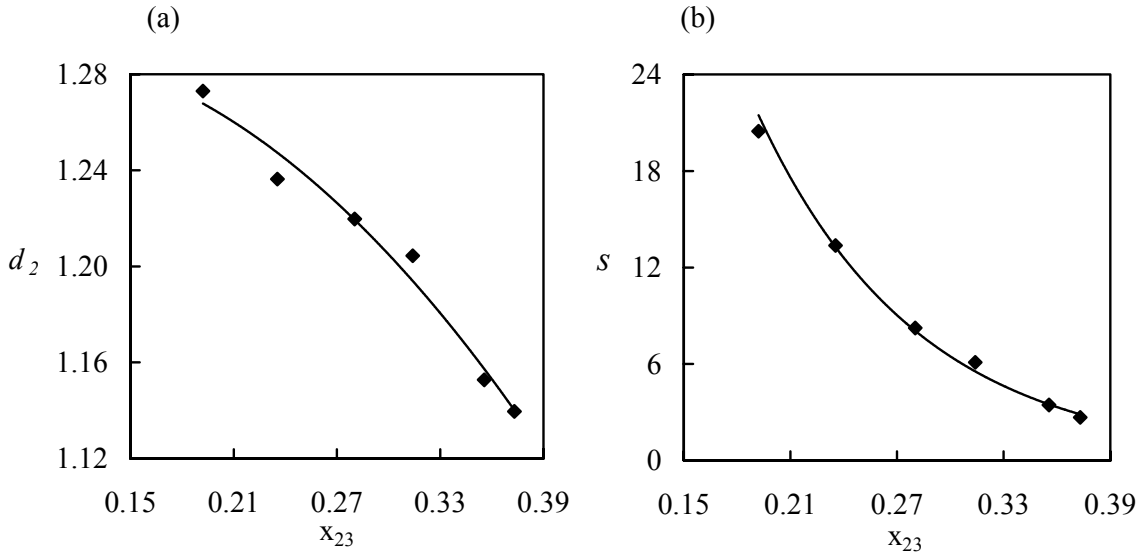


Figure (4.3): Experimental distribution coefficient d2 of ethanol and selectivity s for LLE of {water(1) + ethanol(2) + fluorobenzene(3)} solutions at T = 288.15 K.
(a): distribution coefficient d_2; (b): selectivity s; —, exponential fit.

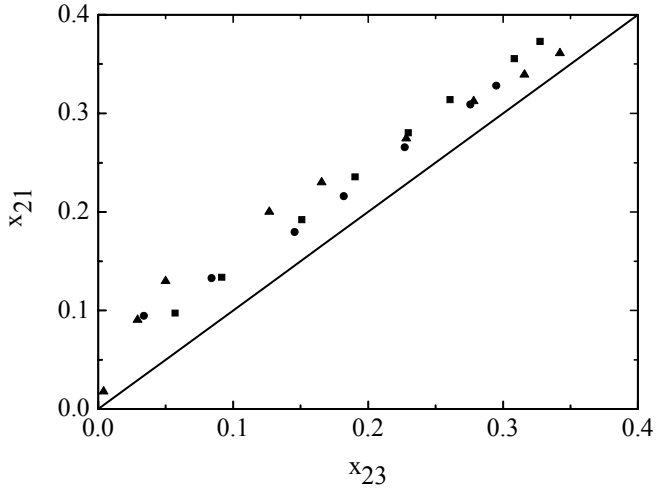


Figure (4.4): distribution of ethanol between water and fluorobenzene at T = (■, 288.15; ▲, 298.15; ●, 308.15) K

The effect of temperature on solubilities and liquid-liquid equilibrium data of our studies systems in the range T = 288.15 K to T = 298.15 K is particularly small, and becomes slightly important at T = 308.15 K as can be seen in the figures (4.5) to (4.9) given below:

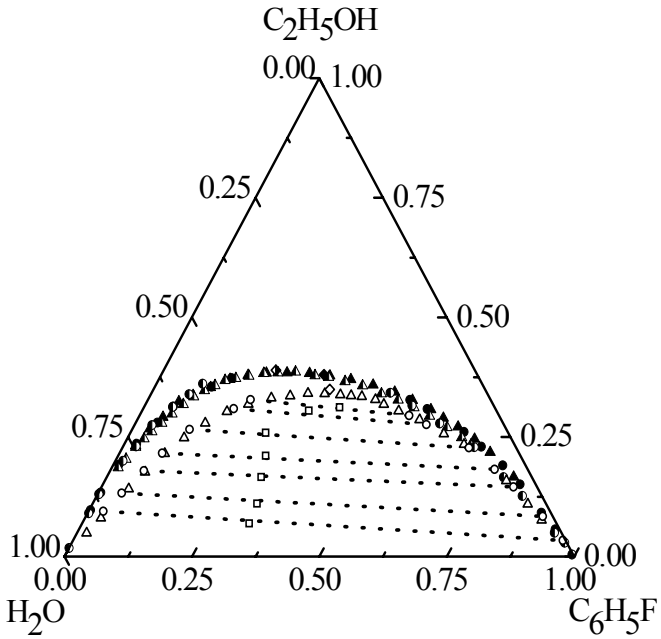


Figure (4.5): solubilities and LLE data for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 288.15 (solid symbol), 298.15 (half solid symbol), and 308.15(open symbol) K, ▲, solubility; ●, LLE; ■, overall composition; ♦, p.p; …, tie line.

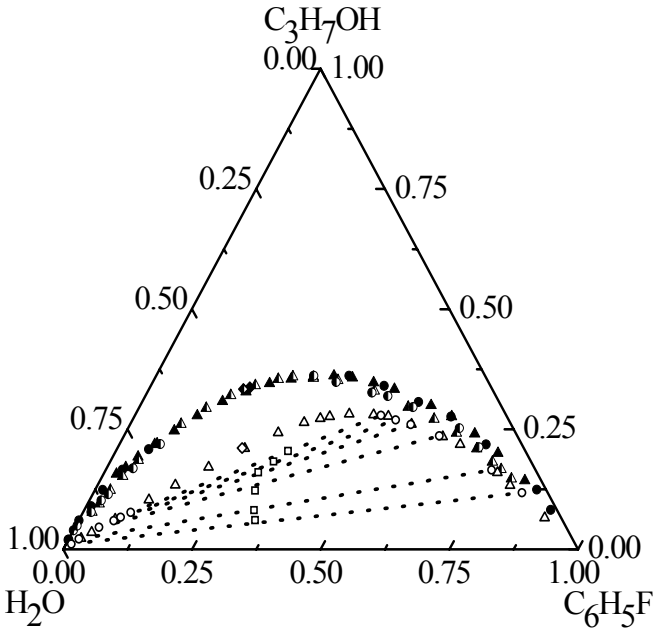


Figure (4.6): solubilities and LLE data for the system {water(1) + 2-propanol(2) + fluorobenzene(3)} at 288.15 (solid symbol), 298.15 (half solid symbol), and 308.15(open symbol) K, ▲, solubility; ●, LLE; ■, overall composition; ♦, p.p; …, tie line.

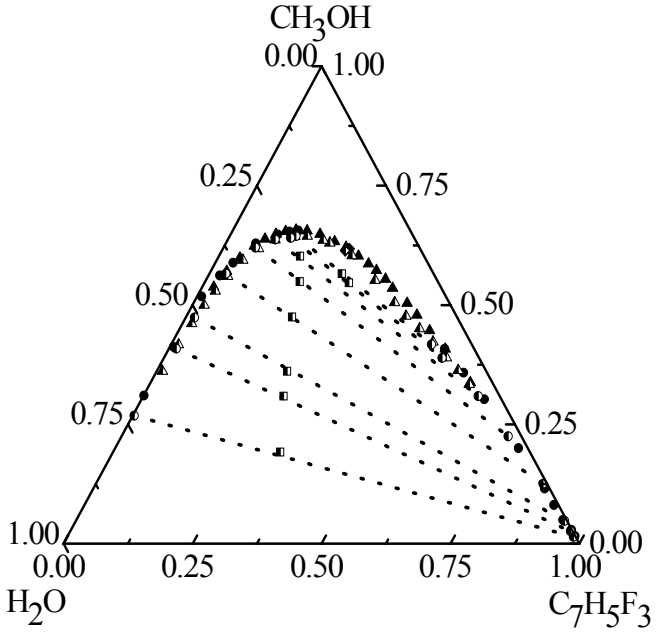


Figure (4.7): solubilities and LLE data for the system {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)} at 288.15 (solid symbol), 298.15 (half solid symbol) K, ▲, solubility; ●, LLE; ■, overall composition; ♦, p.p; …, tie line.

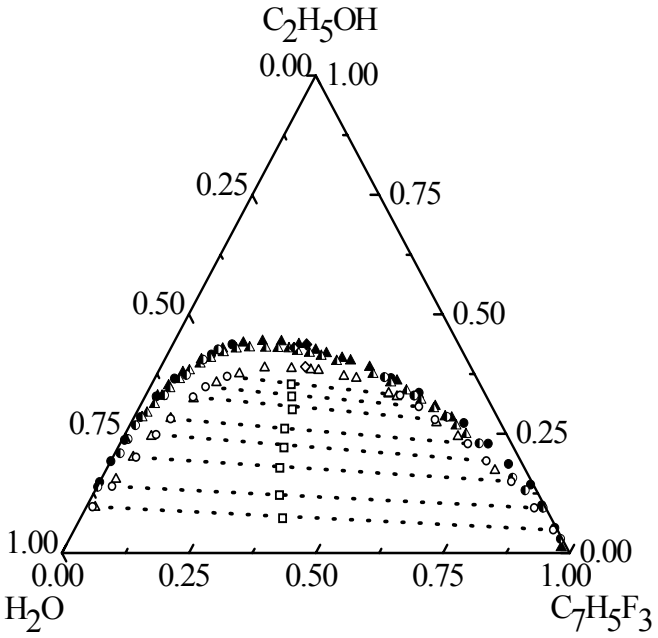


Figure (4.8): solubilities and LLE data for the system {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} at 288.15 (solid symbol), 298.15 (half solid symbol), and 308.15 (open symbol) K, ▲, solubility; ●, LLE; ■, overall composition; ♦, p.p; …, tie line.

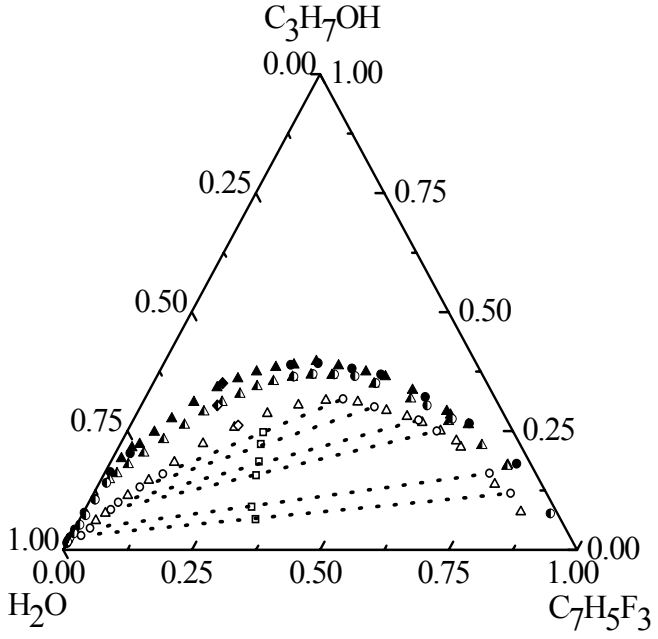


Figure (4.9): solubilities and LLE data for the system {water(1) + 2-propanol + α,α,α-trifluorotoluene(3)} at 288.15 (solid symbol), 298.15 (half solid symbol), and 308.15 (open symbol) K, ▲, solubility; ●, LLE; ■, overall composition; ♦, p.p; …, tie line.

The immiscibility gap decreases with increasing the alcohol-molecular mass as can be seen in the figures (4.10) and (4.11) given below:

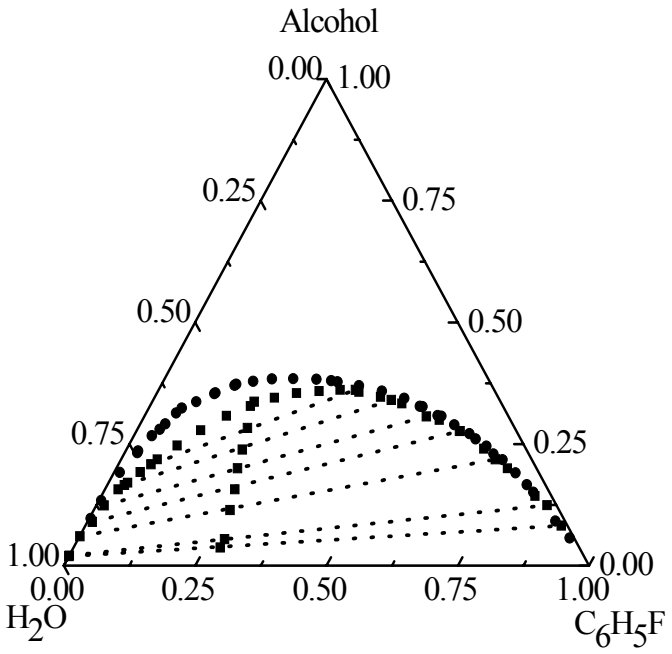


Figure (4.10): Solubilities and LLE data for the system {water(1) + alcohol(2) + fluorobenzene(3)} at 288.15 K; ●, ethanol; ■, 2-PrOH.

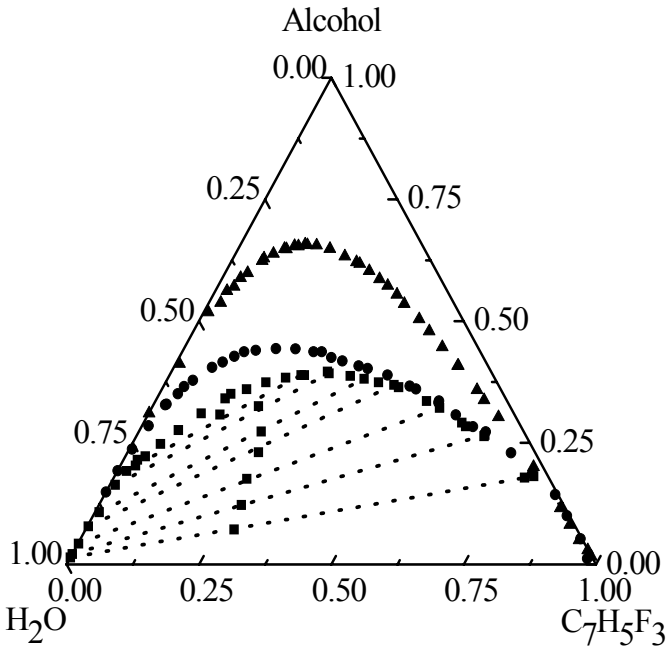


Figure (4.11): Solubilities and LLE data for the system {water(1) + alcohol(2) + α,α,α-trifluorotoluene(3)} at 288.15 K; ▲, methanol; ●, ethanol; ■, 2-propanol.

The experimental and correlated solubilities and liquid-liquid equilibrium data at 303.15 K for solutions of {water(1) + ethanol(2) + benzene(3)} are given in appendix A in tables (A_0.1), (A_0.2), and graphs (A_0.1).

Hand and Othmer-Tobias plots of equations (2.35) and (2.36) are shown in figure (A_0.2). The distribution coefficients for ethanol and selectivity are shown in figure (A_0.3).

The experimental and correlated solubilities and liquid-liquid equilibrium data for each ternary system at each temperature are listed in the appendix A; tables (A.1.1) to (A.2.6), (A.3.1) to (A.3.4), and (A.4.1) to (A.5.6) and represented in figures (A.1.1) to (A.2.3), (A.3.1), (A.3.2), and (A.4.1) to (A.5.3).

Hand and Othmer-Tobias plots of equations (2.35) and (2.36), respectively, at three temperatures are shown in figures (A.1.4), (A.2.4), (A.3.3), (A.4.4), and (A.5.4).

The distribution coefficients for alcohols (methanol, or ethanol, or 2-propanol) and selectivity plots at three temperatures are shown in figures (A.1.5), (A.2.5), (A.3.4), (A.4.5), and (A.5.5).

CHAPTER 5

DISCUSSION

In a liquid solution, forces of attraction determine the solubility of substances in each other. When the forces of attraction between solute-solute are stronger than the forces between solvent-solvent and solvent-solute a liquid-liquid phase separation occurs.[82]

Water and fluorinated hydrocarbons (HFC's) are strong polar components.[3] In aqueous solutions, self-self intermolecular attractions exists between water and FHC molecules and consequently affect the thermodynamic properties of their multi-component solutions to a great extent and produce large miscibility gaps. Adding an alcohol to water affects the polar characteristics of the aqueous solution formed.

All the systems studies in this work exhibit type 1 phase equilibrium behaviour, having one pair of partially miscible component (water + fluorobenzene) or (water + α,α,α-trifluorotoluene) and two pairs of homogeneous solutions: (water + alcohol); alcohol = methanol, or ethanol, or 2-propanol, and (fluorohydrocarbon + alcohol) at the temperatures of investigation. Hence the mutual solubility of the ternary aqueous systems increases significantly when heating the system; the region of partial miscibility becomes smaller as temperature increases.[83,84] This effect being more obvious in the aqueous phase rather than in the organic phase.

In this work, the effect of temperature on the miscibility gap is negligible as temperature is increased from 288.15 K to 298.15 K and becomes moderately significant at 308.15 K. This behaviour is observed in systems containing branched ethers, ethanol, and water.[85]

It is observed that the immiscibility gap decreases with increasing the alcohol-molecular mass.

It is also shown that the aqueous phase is richer in methanol and ethanol, compared with 2-propanol which is more concentrated in the organic phase.

The effect of the water concentration on the solute-distribution coefficients in the two mutual liquid phases, and on the selectivity of a solvent is important for dilute aqueous solutions.[79,80,86-95]

The capability of solvents as extractive agents is evaluated from distribution coefficients and selectivities.[90,94]

From the liquid-liquid phase equilibrium data of the systems (water + alcohol + fluorobenzene) and (water + alcohol + α,α,α-trifluorotoluene) at the temperatures T = (288.15, 298.15, 308.15) K: it has been found that the distribution coefficients of methanol, ethanol, are similar in magnitude (1.1 → 10.5), whereas for 2-propanol are smaller < 0.61, with large selectivities of fluorobenzene or α,α,α-trifluorotoluene for an alcohol (2 → 70).

Therefore, fluorobenzene and α,α,α-trifluorotoluene are good candidates for drying alcohols.

(water + ethanol + benzene, 303.15 K)/(water + ethanol + fluorobenzene, 298.15 K): p.p.: (0.2976, 0.3798)/(0.3902, 0.3897); *s*: (2.89 → 25.02)/(2.7 → 111.0).

At the critical solution compositions (plait point), the compositions of alcohols change very slightly within the range of temperature (288.15 → 298.15) K[84] but it becomes slightly lower at 308.15 K.

The reliability of the experimental LLE data is checked by the Hand and Othmer-Tobias correlation and is thermodynamically consistent. On the other hand, the small influence of temperature on these ternary systems may indicate the unnecessary to use higher temperatures for a possible extraction process.[94]

This work confirms the applicability of fluorobenzene and α,α,α-trifluorotoluene as drying agents to obtain absolute alcohols from dilute aqueous solutions.

CONCLUSION

- This work reports new solubilities and LLE data of the ternary systems containing water, fluorobenzene, α,α,α-trifluorotoluene, and alcohol (methanol, ethanol, and 2-propanol) at temperatures T = (288.15, 298.15, 308.15) K, and pressure p = 101.2 kPa.
- Generally, the ambient temperatures have practically small effect on the system miscibilities, where the surfaces underneath the binodal curves decrease slightly with increasing temperature.
- The binodal curve and LLE data are well fitted to empirical equations and are thermodynamically consistent.
- Fluorobenzene and α,α,α-trifluorotoluene are suitable separating agents for alcohols from dilute aqueous solutions just like as benzene, yet they are more expensive, but environmentally accepted.

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APPENDIX A

EXPERIMENTAL RESULTS

Table (A_0.1): Experimental solubilities at 303.15 K for solutions of{water(1) + ethanol(2) + benzene(3)}

Component: 1. water		H_2O
2. ethanol		C_2H_5OH
3. benzene		C_6H_6

x_1	x_2	x_3
0.1147	0.2598	0.6255
0.1258	0.2689	0.6053
0.1396	0.2805	0.5799
0.1538	0.2942	0.5520
0.1710	0.3054	0.5236
0.1897	0.3172	0.4931
0.2112	0.3303	0.4585
0.2297	0.3418	0.4285
0.2528	0.3506	0.3966
0.2778	0.3601	0.3621
0.3067	0.3641	0.3292
0.3331	0.3729	0.2940
0.3662	0.3798	0.2540
0.3884	0.3825	0.2291
0.4187	0.3849	0.1964
0.4444	0.3839	0.1717
0.4850	0.3776	0.1374
0.5120	0.3675	0.1205
0.5378	0.3546	0.1076
0.6730	0.2930	0.0340
0.7200	0.2560	0.0240
0.7610	0.2230	0.0160
0.8065	0.1807	0.0128
0.8700	0.1250	0.0050

Equation: (2.34)

a	b	c	d	e	σ
0.0719	1.4721	-1.8665	0.7732	-0.4594	0.0002

Table (A_0.2): Experimental liquid-liquid equilibrium data at 303.15 K for solutions of {water(1) + ethanol(2) + benzene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. benzene		C_6H_6				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	s
0.3837	0.3454	0.4958	0.3744	0.1277	0.2788	2.89
0.4303	0.2867	0.6220	0.3256	0.0814	0.2135	5.01
0.4479	0.2420	0.6867	0.2789	0.0496	0.1696	8.42
0.4866	0.1873	0.7640	0.2250	0.0312	0.1078	11.73
0.5139	0.1509	0.8050	0.1916	0.0209	0.0841	16.91
0.5234	0.1030	0.8600	0.1380	0.0138	0.0554	25.02
x^{cs}		0.2976	0.3798	0.2976	0.3798	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
-0.3412		1.3763		-0.3320	1.2503	

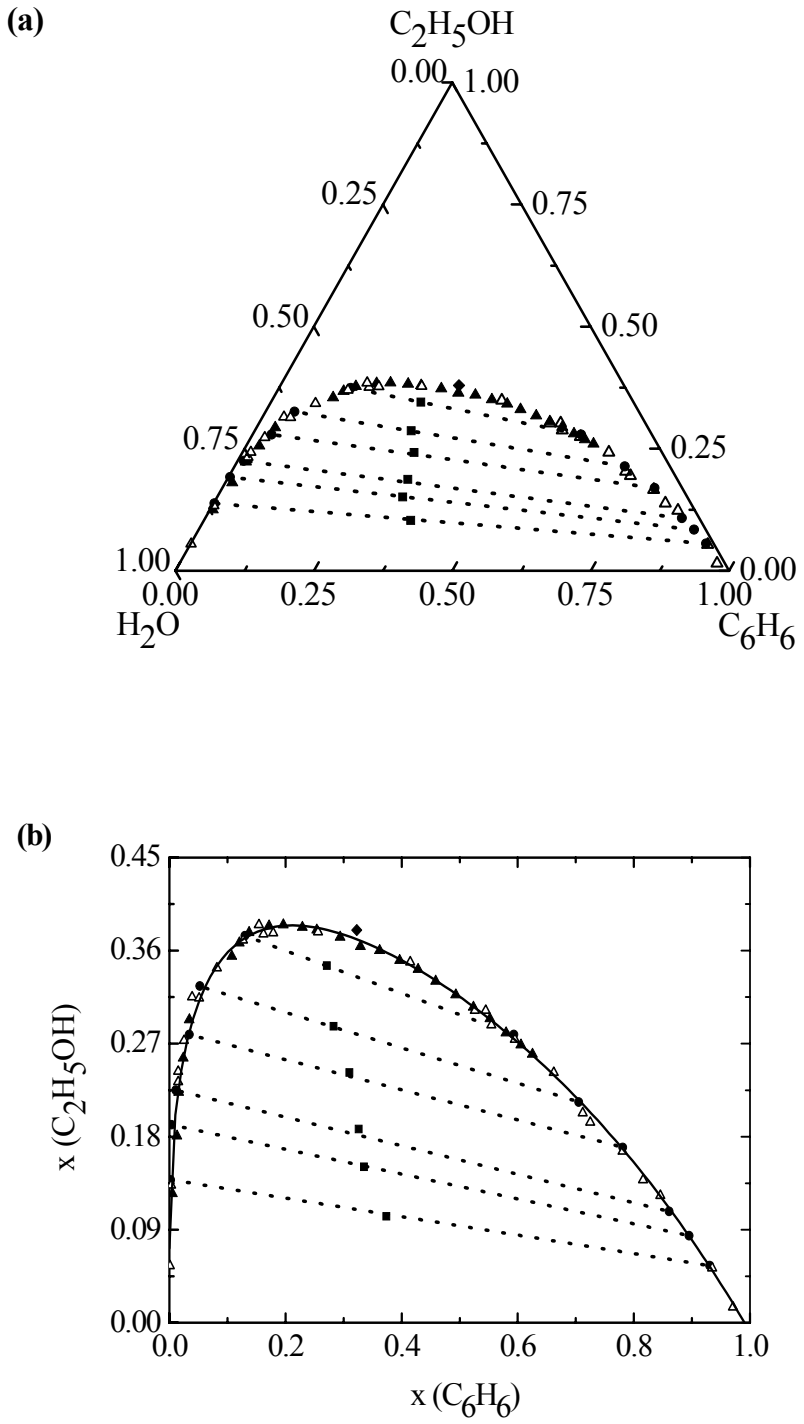

Figure (A_0.1): Solubilities and LLE data for the system {water(1) + ethanol(2) + benzene(3)} at 303.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); Δ, LLE literature[77]; **(a)**, ternary representation; **(b)**, binary representation.

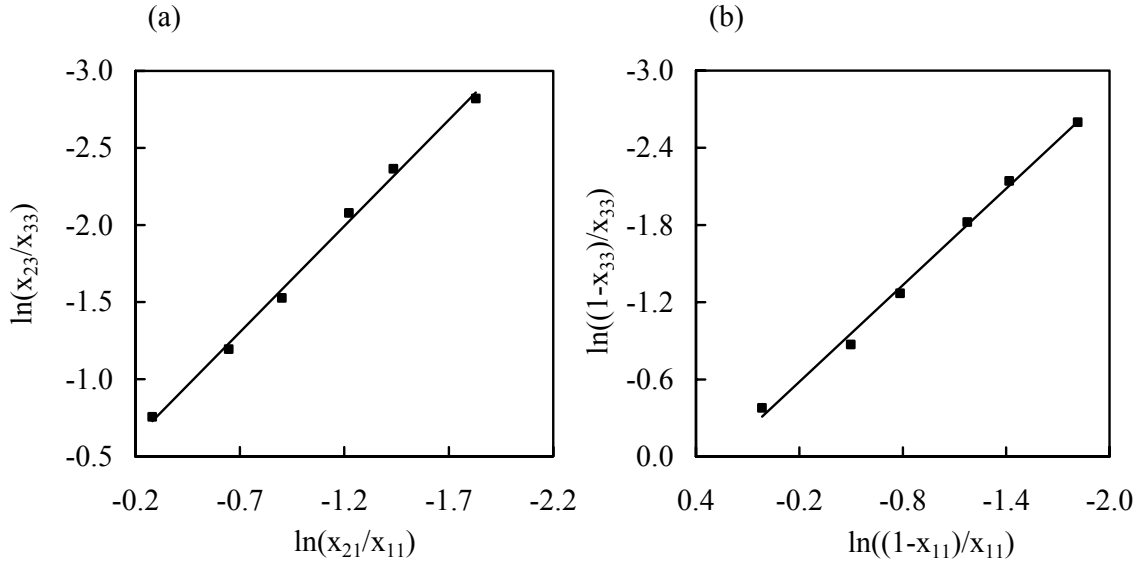

Figure (A_0.2): correlation of the LLE data for {water(1) + ethanol(2) + benzene(3)}solutions at T = 303.15 K: (a), Hand; ——, equation (2.35); (b), Othmer-Tobias; ——, equation (2.36).

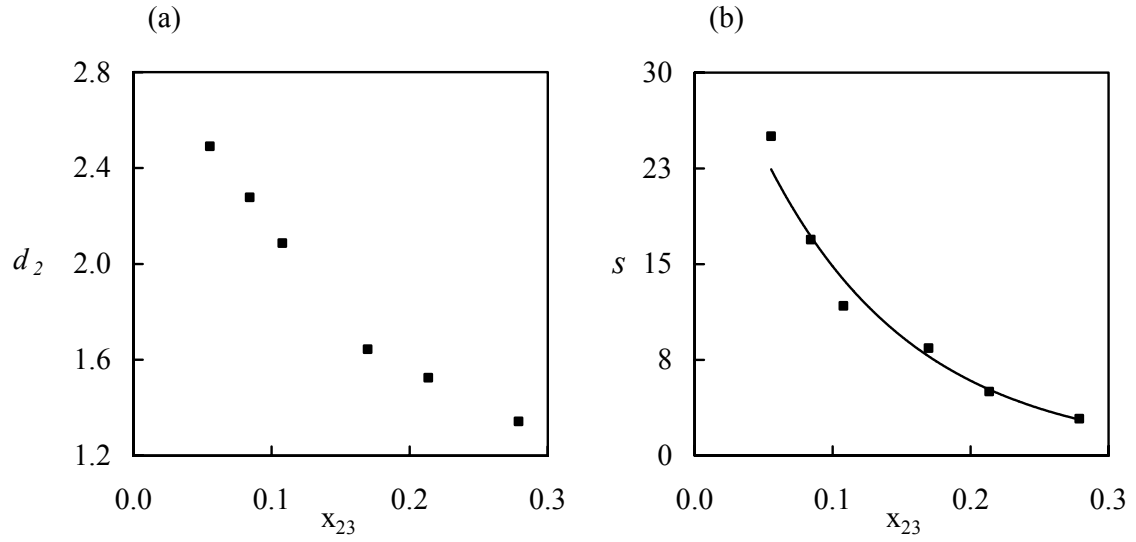

Figure (A_0.3): Experimental distribution coefficient d2 of Ethanol and selectivity s for LLE of {water(1) + ethanol(2) + benzene(3)} solutions at T = 303.15 K;
(a): distribution coefficient d_2; (b): selectivity s; —, exponential fit.

Table (A.1.1): Experimental solubilities at 288.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component: 1. water	H_2O
2. ethanol	C_2H_5OH
3. fluorobenzene	C_6H_5F

x_1	x_2	x_3
0.0355	0.1661	0.7984
0.0557	0.2180	0.7263
0.0723	0.2457	0.6820
0.0921	0.2715	0.6364
0.1114	0.2898	0.5988
0.1275	0.3071	0.5654
0.1537	0.3267	0.5196
0.1798	0.3439	0.4763
0.2151	0.3586	0.4263
0.2527	0.3702	0.3771
0.2900	0.3775	0.3325
0.3276	0.3830	0.2894
0.3710	0.3844	0.2446
0.4118	0.3838	0.2044
0.4497	0.3792	0.1711
0.4894	0.3705	0.1401
0.5367	0.3533	0.1100
0.5790	0.3371	0.0839
0.6132	0.3239	0.0629
0.6612	0.2911	0.0477
0.6988	0.2668	0.0344
0.7442	0.2319	0.0239

Equation: (2.34)

a	b	c	d	e	σ
0.0304	1.6404	-2.0691	1.0229	-0.6431	0.00002

Table (A.1.2): Experimental liquid-liquid equilibrium data at 288.15 K
for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.3056	0.3474	0.4851	0.3731	0.1585	0.3274	2.69
0.3530	0.3390	0.5337	0.3555	0.1338	0.3084	3.46
0.3851	0.2903	0.6290	0.3140	0.0875	0.2607	5.97
0.4016	0.2528	0.6772	0.2803	0.0674	0.2298	8.24
0.4191	0.2123	0.7406	0.2354	0.0448	0.1904	13.37
0.4395	0.1750	0.7972	0.1921	0.0306	0.1509	20.46
0.4817	0.1140	0.8621	0.1336	0.0182	0.0916	32.48
0.4979	0.0758	0.8999	0.0972	0.0082	0.0570	64.36
x^{cs}		0.3007	0.3803	0.3007	0.3803	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
-0.1675	1.0711			-0.1043	1.0220	

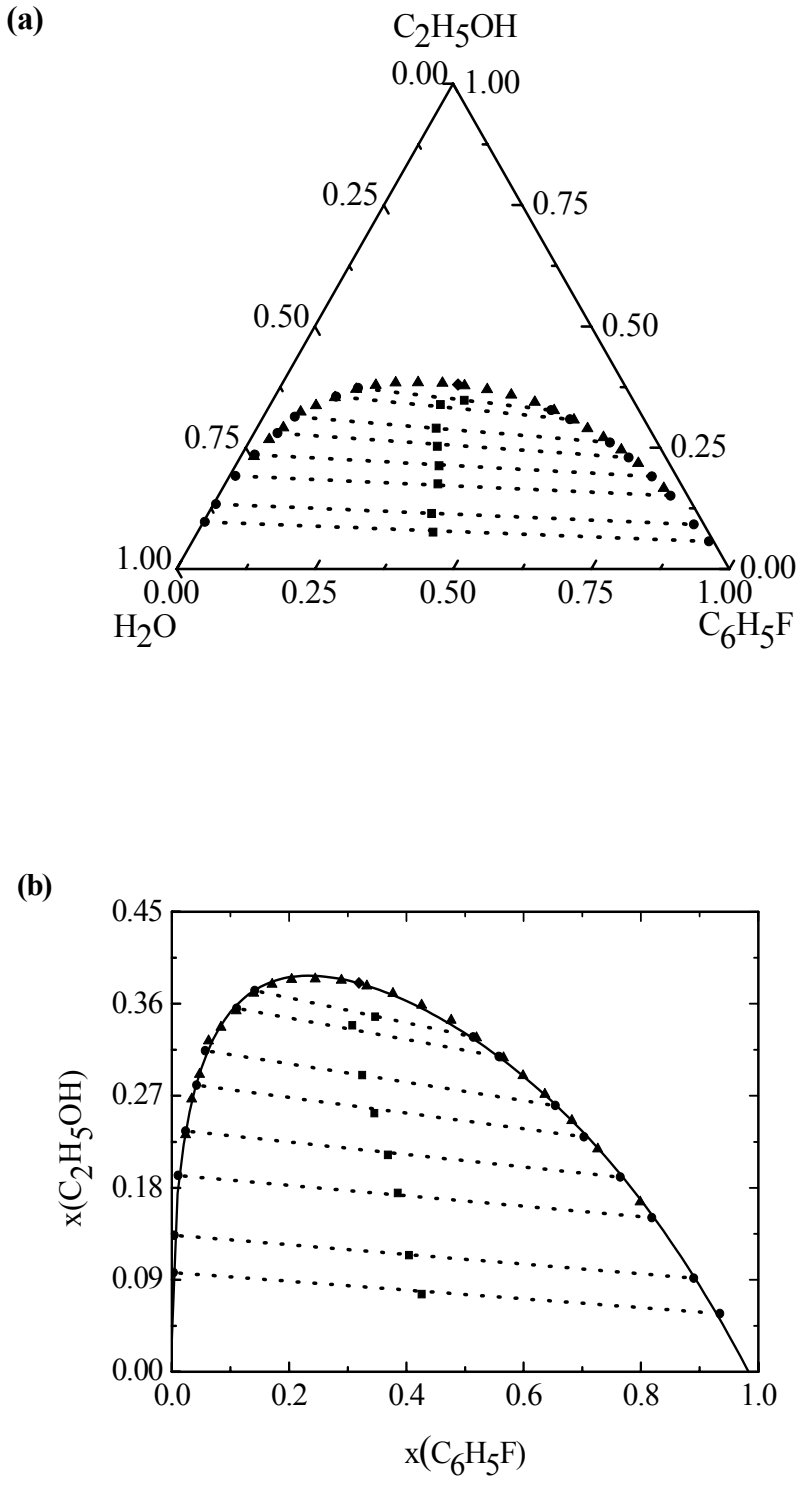

Figure (A.1.1): Solubilities and LLE data for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

Table (A.1.3): Experimental solubilities at 298.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component: 1. water	H_2O
2. ethanol	C_2H_5OH
3. fluorobenzene	C_6H_5F

x_1	x_2	x_3
0.0856	0.2335	0.6809
0.0963	0.2486	0.6551
0.1143	0.2699	0.6158
0.1367	0.2938	0.5695
0.1580	0.3112	0.5308
0.1813	0.3277	0.4910
0.2078	0.3405	0.4517
0.2364	0.3569	0.4067
0.2662	0.3660	0.3678
0.2940	0.3749	0.3311
0.3192	0.3784	0.3024
0.3537	0.3859	0.2604
0.3888	0.3845	0.2267
0.4172	0.3831	0.1997
0.4496	0.3771	0.1733
0.4773	0.3722	0.1505
0.5006	0.3684	0.1310
0.5258	0.3579	0.1163
0.5515	0.3468	0.1017
0.5791	0.3338	0.0871
0.6076	0.3181	0.0743
0.6395	0.2983	0.0622
0.6693	0.2790	0.0517
0.6978	0.2611	0.0411
0.7205	0.2466	0.0329
0.7455	0.2287	0.0258
0.7770	0.2039	0.0191
0.8013	0.1862	0.0125

Equation (2.34)

a	b	c	d	e	σ
0.0189	1.6492	-1.9779	0.7057	-0.4009	0.0001

Table (A.1.4): Experimental liquid-liquid equilibrium data at 298.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.4138	0.3502	0.5480	0.3611	0.1895	0.3421	2.7
0.4611	0.3330	0.5858	0.3393	0.1598	0.3159	3.4
0.4804	0.2984	0.6317	0.3124	0.1244	0.2783	4.5
0.5668	0.2680	0.6908	0.2745	0.0817	0.2283	7.0
0.6026	0.2238	0.7446	0.2302	0.0558	0.1657	9.6
0.5871	0.1789	0.7851	0.2003	0.0381	0.1268	13.0
0.6364	0.1078	0.8673	0.1300	0.0135	0.0500	24.7
0.6678	0.0696	0.9070	0.0905	0.0040	0.0293	73.4
0.7000	0.0396	0.9821	0.0177	0.0020	0.0040	111.0
x^{cs}		0.3902	0.3897	0.3902	0.3897	1.0
LLE Correlation Equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
0.4461		1.7271		0.5110	1.6888	

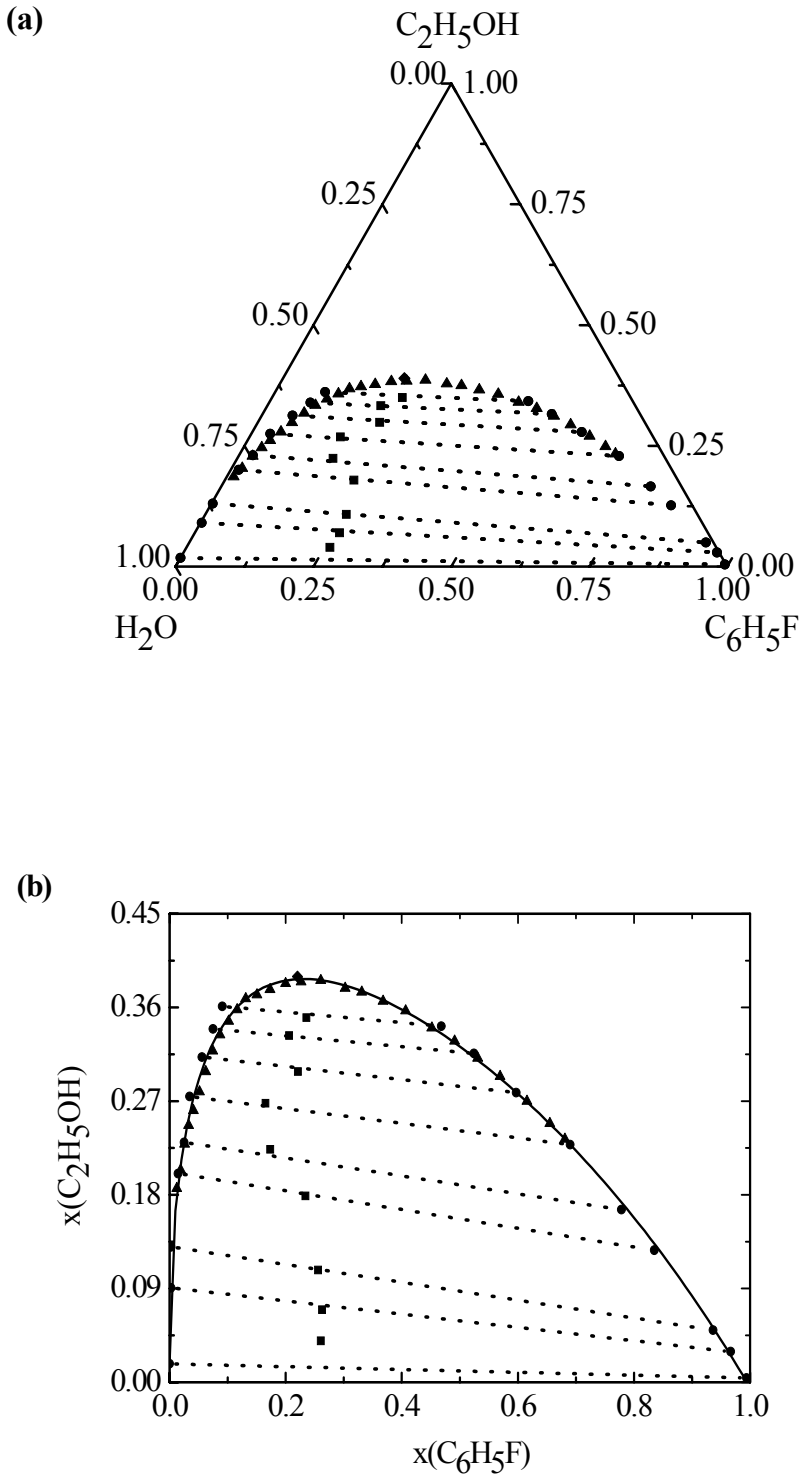

Figure (A.1.2): Solubilities and LLE data for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 298.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

Table (A.1.5): Experimental solubilities at 308.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component:	1. water	H_2O
	2. ethanol	C_2H_5OH
	3. fluorobenzene	C_6H_5F

x_1	x_2	x_3
0.0251	0.0766	0.8983
0.0359	0.1095	0.8546
0.0535	0.1588	0.7877
0.0986	0.2343	0.6671
0.1272	0.2564	0.6164
0.1602	0.2858	0.5540
0.1917	0.3044	0.5039
0.2142	0.3182	0.4676
0.2257	0.3279	0.4464
0.2488	0.3348	0.4164
0.2695	0.3362	0.3943
0.2895	0.3383	0.3722
0.3188	0.3405	0.3407
0.3517	0.3411	0.3072
0.3891	0.3357	0.2752
0.4281	0.3319	0.2400
0.4795	0.3187	0.2018
0.5296	0.3031	0.1673
0.5842	0.2788	0.1370
0.6414	0.2479	0.1107
0.6955	0.2153	0.0892
0.7532	0.1764	0.0704
0.8032	0.1415	0.0553
0.8879	0.0808	0.0313
0.9319	0.0494	0.0187

Equation: (2.34)

a	b	c	d	e	σ
-0.1826	1.8113	-1.5285	-0.1006		0.00004

Table (A.1.6): Experimental liquid-liquid equilibrium data at 308.15 K for solutions of {water(1) + ethanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.3039	0.3122	0.4710	0.3280	0.1760	0.2951	2.41
0.3678	0.3051	0.5130	0.3089	0.1518	0.2758	3.02
0.4756	0.2587	0.6214	0.2657	0.0928	0.2272	5.73
0.4997	0.2110	0.7000	0.2160	0.0649	0.1821	9.09
0.5304	0.1664	0.7541	0.1795	0.0464	0.1456	13.18
0.5667	0.1107	0.8212	0.1327	0.0193	0.0841	26.97
0.6028	0.0690	0.8762	0.0946	0.0052	0.0339	60.38
x^{cs}		0.3050	0.3493	0.3050	0.3493	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
-0.2014	1.0476			-0.2342	1.0594	

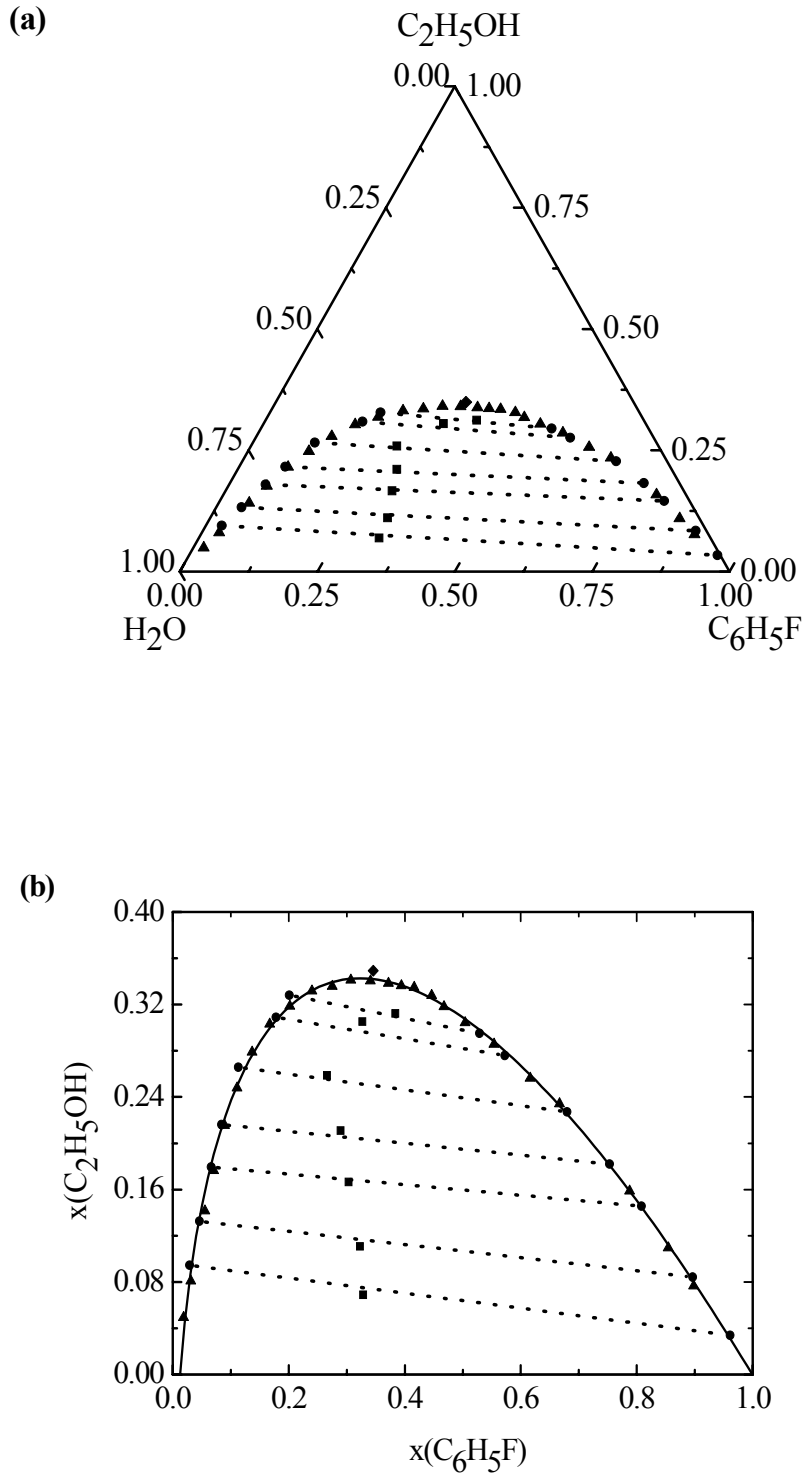

Figure (A.1.3): Solubilities and LLE data for the system {water(1) + ethanol(2) + fluorobenzene(3)} at 308.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

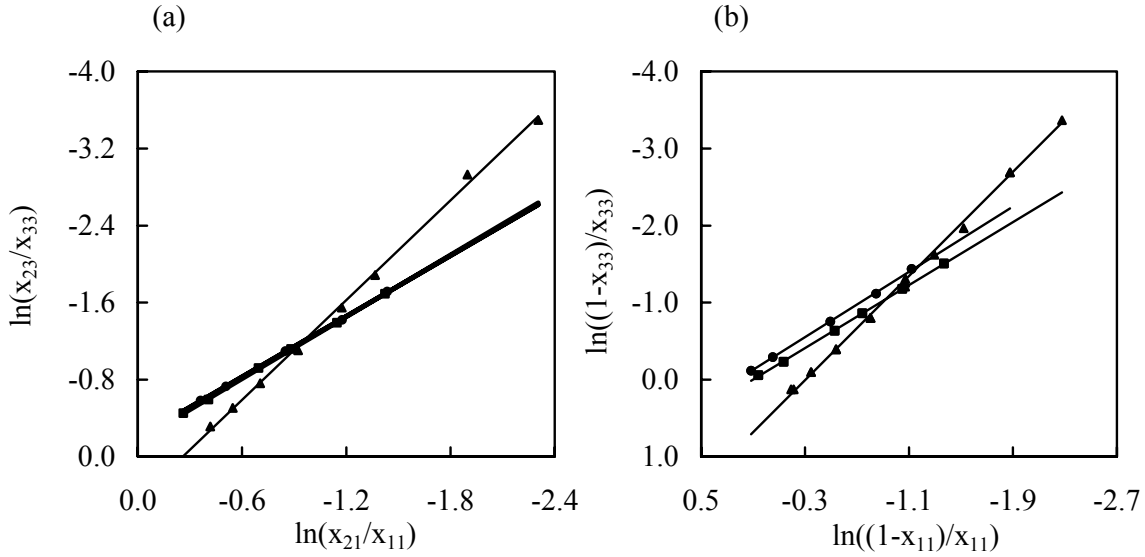

Figure (A.1.4): correlation of the LLE data for the {water(1) + ethanol(2) + fluorobenzene(3)} solutions at T = (■, 288.15; ▲, 298.15; ●, 308.15) K;
(a), Hand; ──, equation (2.35); (b), Othmer-Tobias; ──, equation (2.36).

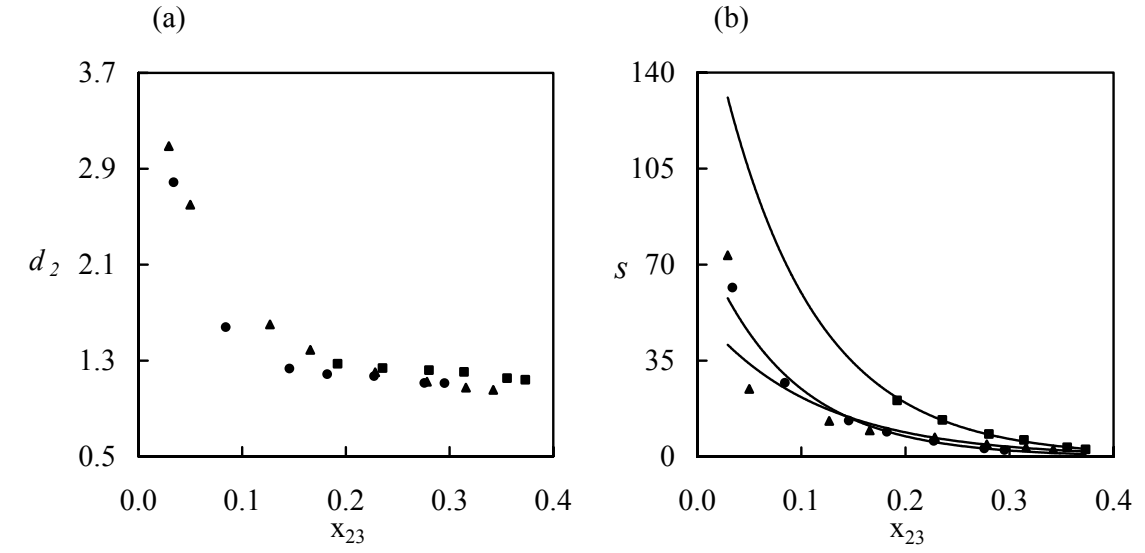

Figure (A.1.5): Experimental distribution coefficient d2 of Ethanol and selectivity s for LLE of {water(1) + ethanol(2) + fluorobenzene(3)} solutions at T = (■, 288.15; ▲, 298.15; ●, 308.15) K;
(a): distribution coefficient d_2; (b): selectivity s; —, exponential fit.

Table (A.2.1): Experimental solubilities at 288.15 K for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component:		
1. water	H_2O	
2. 2-propanol	C_3H_7OH	
3. fluorobenzene	C_6H_5F	

x_1	x_2	x_3
0.0553	0.2003	0.7444
0.0805	0.2402	0.6793
0.1072	0.2763	0.6165
0.1352	0.2994	0.5654
0.1895	0.3335	0.4770
0.2232	0.3471	0.4297
0.2591	0.3572	0.3837
0.2929	0.3614	0.3457
0.3342	0.3589	0.3069
0.3793	0.3548	0.2659
0.4265	0.3451	0.2284
0.4804	0.3281	0.1915
0.5364	0.3077	0.1559
0.6004	0.2786	0.1210
0.6603	0.2471	0.0926
0.7131	0.2183	0.0686
0.7580	0.1924	0.0496
0.7932	0.1707	0.0361
0.8183	0.1567	0.0250

Equation: (2.34)

a	b	c	d	e	σ
0.0181	0.9089	-0.3761	-0.5729		0.0001

Table (A.2.2): Experimental liquid-liquid equilibrium data at 288.15 K for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.5088	0.2833	0.7295	0.2082	0.2639	0.3611	4.79
0.5405	0.2386	0.8020	0.1657	0.2064	0.3403	7.98
0.5691	0.2000	0.8610	0.1240	0.1562	0.3068	13.64
0.5959	0.1570	0.9005	0.0903	0.1085	0.2768	25.44
0.6263	0.1141	0.9390	0.0606	0.0692	0.2185	48.93
0.6667	0.0546	0.9790	0.0209	0.0177	0.1243	328.95
0.6831	0.0375	0.9803	0.0197	0.0115	0.0823	356.12
x^{cs}		0.4691	0.3368	0.4691	0.3368	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
0.8687	0.7329			1.3233	0.8129	

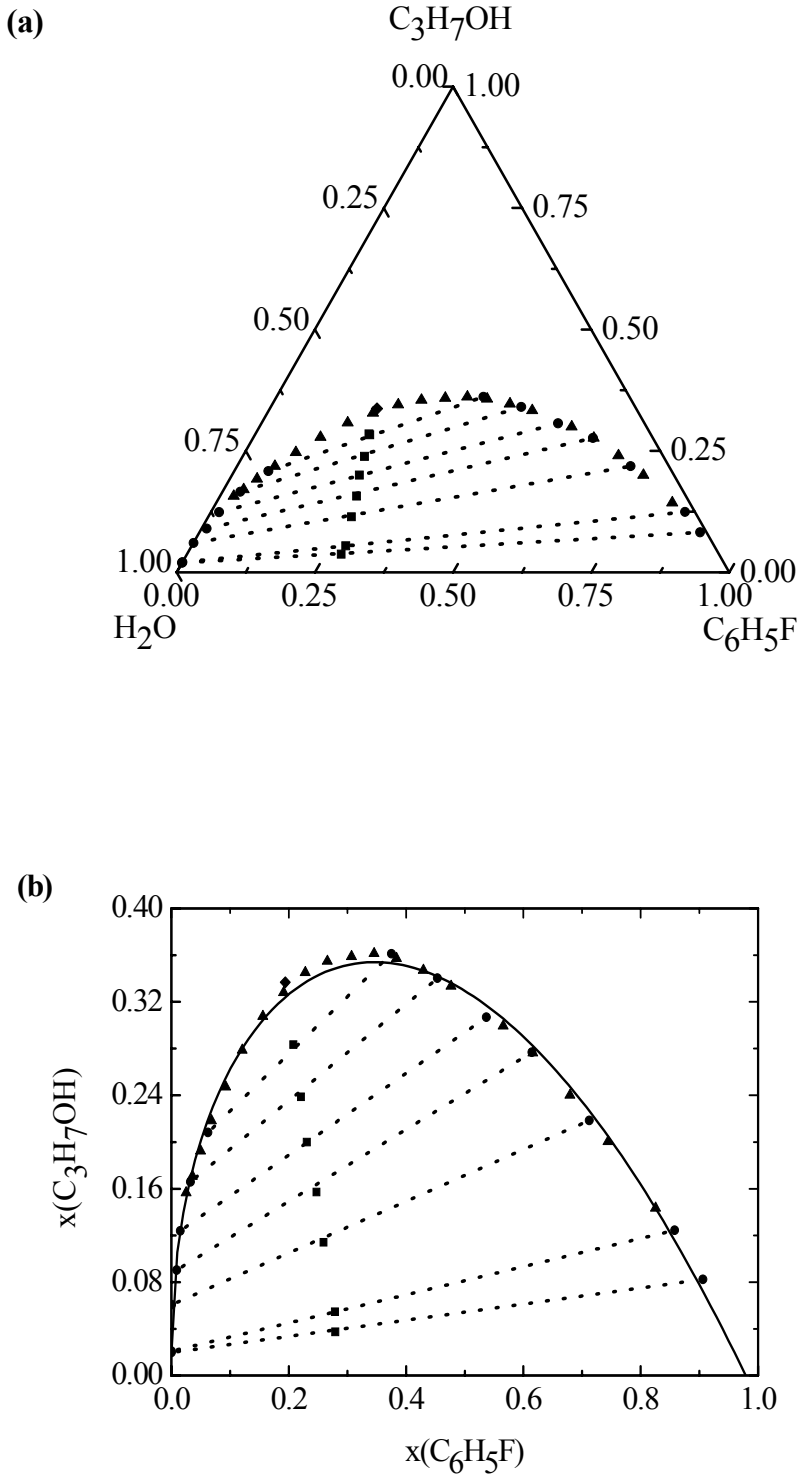

Figure (A.2.1): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + fluorobenzene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

Table (A.2.3): Experimental solubilities at 298.15 K for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component:		
1. water	H_2O	
2. 2-propanol	C_3H_7OH	
3. fluorobenzene	C_6H_5F	

x_1	x_2	x_3
0.0557	0.1468	0.7975
0.0662	0.1662	0.7676
0.0756	0.1815	0.7429
0.0915	0.2094	0.6991
0.1150	0.2420	0.6430
0.1441	0.2712	0.5847
0.1818	0.2961	0.5221
0.2302	0.3299	0.4399
0.2902	0.3520	0.3578
0.3358	0.3562	0.3080
0.3741	0.3597	0.2662
0.4048	0.3543	0.2409
0.4562	0.3413	0.2025
0.5140	0.3203	0.1657
0.5754	0.2937	0.1309
0.6404	0.2606	0.0990
0.7073	0.2199	0.0728
0.7613	0.1855	0.0532
0.8079	0.1519	0.0402
0.8466	0.1229	0.0305
0.8826	0.0945	0.0229
0.9047	0.0776	0.0177

Equation: (2.34)

a	b	c	d	e	σ
-0.1362	1.7613	-1.5539	-0.0833		0.00001

Table (A.2.4): Experimental liquid-liquid equilibrium data at 298.15 K for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.5460	0.2837	0.7016	0.2190	0.3329	0.3611	3.48
0.4294	0.2580	0.7800	0.1687	0.2954	0.3484	5.45
0.5689	0.2495	0.8546	0.1150	0.2369	0.3262	10.23
0.4225	0.2479	0.8750	0.1021	0.2096	0.3192	13.05
0.4538	0.2068	0.9068	0.0775	0.1723	0.2961	20.11
0.4941	0.1496	0.9486	0.0489	0.1045	0.2520	46.78
0.4991	0.1279	0.9603	0.0397	0.0858	0.2126	59.94
x^{cs}		0.4834	0.3332	0.4834	0.3332	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
0.9083	0.6119			1.4476	0.6912	

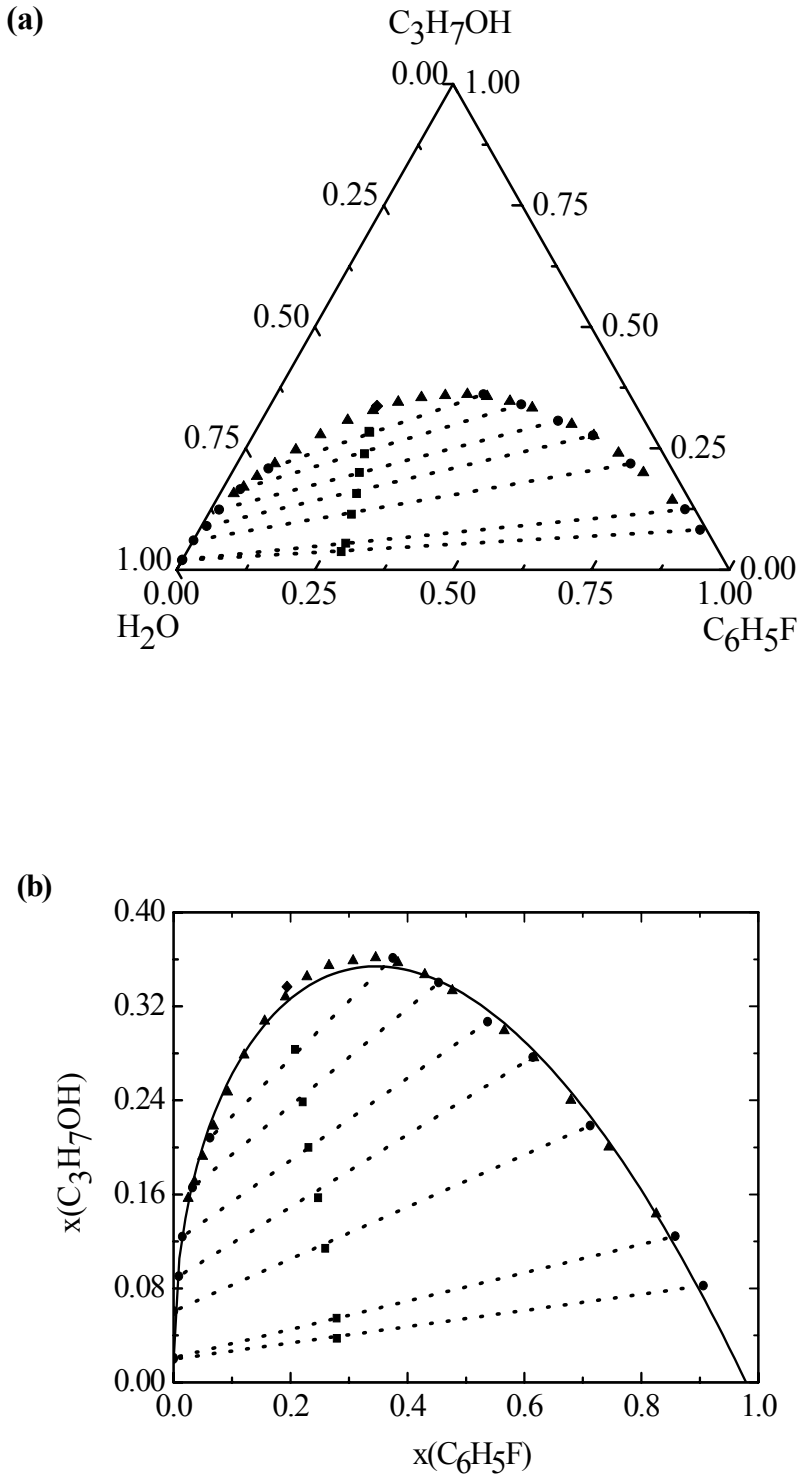

Figure (A.2.2): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + fluorobenzene(3)}at 298.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

Table (A.2.5): Experimental solubilities at 308.15 K for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component:	1. water	H_2O
	2. 2-propanol	C_3H_7OH
	3. fluorobenzene	C_6H_5F

x_1	x_2	x_3
0.0320	0.0657	0.9023
0.0652	0.1334	0.8014
0.0768	0.1597	0.7635
0.1194	0.2183	0.6623
0.1454	0.2344	0.6202
0.1928	0.2607	0.5465
0.2296	0.2772	0.4932
0.2570	0.2803	0.4627
0.3031	0.2821	0.4148
0.3437	0.2768	0.3795
0.3644	0.2722	0.3634
0.3996	0.2643	0.3361
0.4606	0.2430	0.2964
0.5421	0.2100	0.2479
0.6319	0.1712	0.1969
0.7150	0.1341	0.1509
0.7819	0.1031	0.1150
0.8677	0.0630	0.0693
0.9269	0.0353	0.0378
0.9534	0.0231	0.0235

Equation: (2.34)

a	b	c	d	e	σ
0.0610	-0.6574	2.6729	-3.1950	1.1126	0.00002

Table (A.2.6): Experimental liquid-liquid equilibrium data at 308.15 K
for solutions of {water(1) + 2-propanol(2) + fluorobenzene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. fluorobenzene		C_6H_5F				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.4605	0.2052	0.8300	0.0770	0.2433	0.2787	12.35
0.4997	0.1829	0.8545	0.0669	0.2190	0.2693	15.71
0.5409	0.1604	0.8717	0.0600	0.1945	0.2600	19.42
0.5659	0.1226	0.9070	0.0464	0.1510	0.2360	30.55
0.5883	0.0818	0.9580	0.0220	0.0849	0.1651	84.68
0.5968	0.0607	0.9785	0.0115	0.0496	0.1178	202.08
x^{cs}		0.5468	0.2108	0.5468	0.2108	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
1.1075		0.6913		1.2824	0.7588	

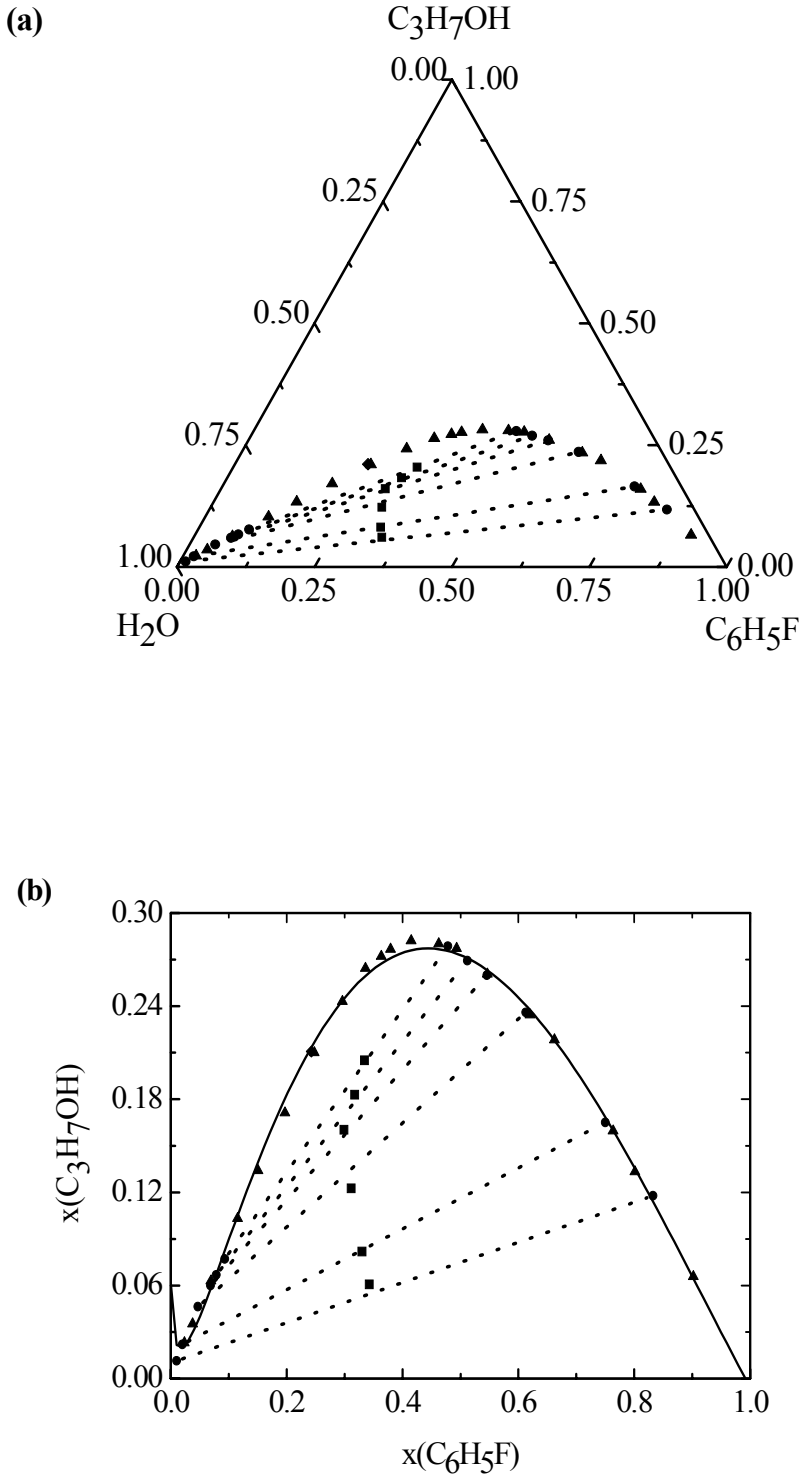

Figure (A.2.3): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + fluorobenzene(3)} at 308.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

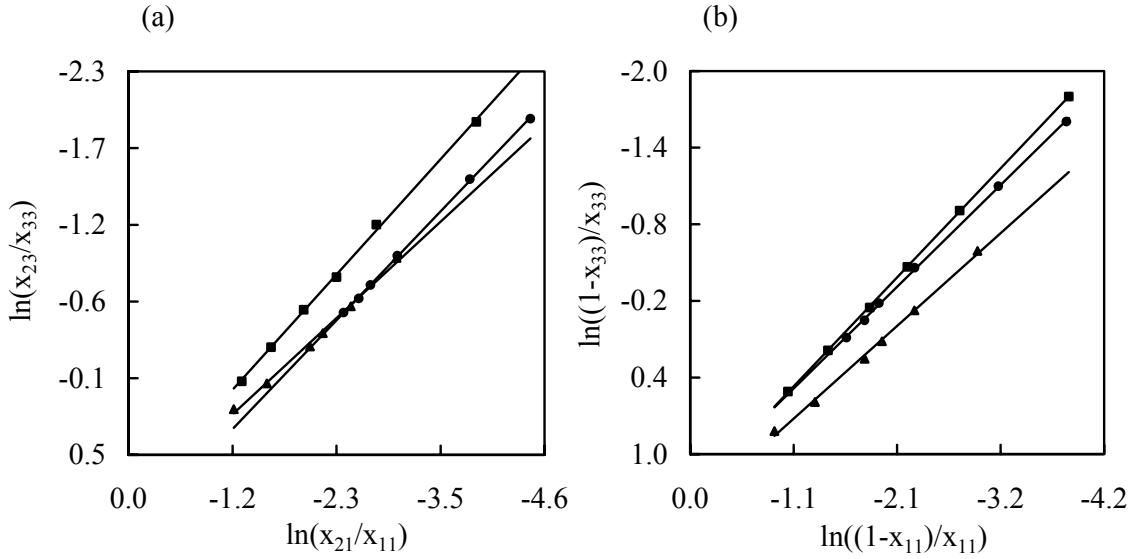

Figure (A.2.4): Correlation of the LLE data for the {water(1) + 2-propanol(2) + fluorobenzene(3)} solutions at T = (■, 288.15; ▲, 298.15; ●, 308.15) K;
(a), Hand, ──, equation (2.35); (b), Othmer-Tobias, ──, equation(2.36).

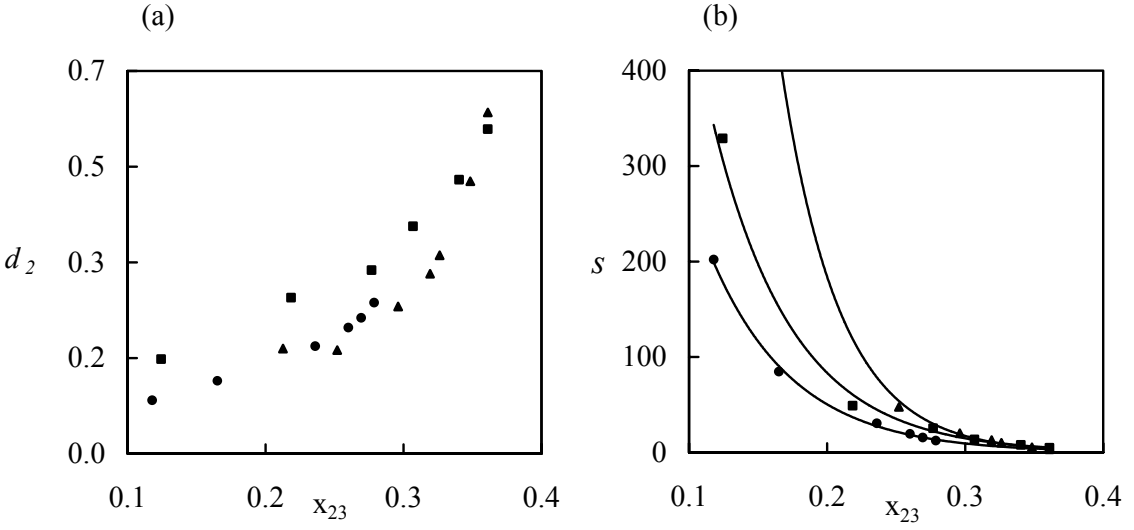

Figure (A.2.5): Experimental distribution coefficient d_2 of 2-propanol and selectivity s for LLE of {water(1) + 2-propanol(2) + fluorobenzene(3)} solutions at T = (■, 288.15; ▲, 298.15; ●, 308.15) K; (a), distribution coefficient d_2; (b), selectivity s ; —, exponential fit.

Table (A.3.1): Experimental solubilities at 288.15 K for solutions of {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)}

Component:	1. water	H_2O
	2. methanol	CH_3OH
	3. α,α,α-trifluorotoluene	$C_7H_5F_3$

x_1	x_2	x_3
0.0424	0.3377	0.6199
0.0562	0.4078	0.5360
0.0670	0.4465	0.4865
0.0753	0.4788	0.4459
0.0816	0.5042	0.4142
0.0943	0.5352	0.3705
0.0991	0.5540	0.3469
0.1069	0.5725	0.3206
0.1156	0.5861	0.2983
0.1269	0.6028	0.2703
0.1417	0.6214	0.2369
0.1577	0.6331	0.2092
0.1786	0.6484	0.1730
0.1999	0.6553	0.1448
0.2206	0.6572	0.1222
0.2422	0.6545	0.1033
0.2642	0.6483	0.0875
0.2902	0.6381	0.0717
0.3183	0.6238	0.0579
0.3589	0.5984	0.0427
0.3985	0.5706	0.0309
0.4398	0.5375	0.0227

Equation: (2.34)

a	b	c	d	e	σ
0.2757	2.3186	-3.6954	1.8410	-0.7476	0.0002

Table (A.3.2): Experimental liquid-liquid equilibrium data at 288.15 K for solutions of {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. methanol		CH_3OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.1388	0.5484	0.2170	0.6560	0.0570	0.4080	2.37
0.1947	0.6000	0.2351	0.6539	0.0456	0.3584	2.83
0.2272	0.6130	0.2610	0.6477	0.0326	0.3027	3.74
0.2559	0.5645	0.3131	0.6286	0.0181	0.2000	5.50
0.2874	0.5054	0.3770	0.5888	0.0095	0.1150	7.75
0.3156	0.4610	0.4161	0.5617	0.0085	0.0811	7.07
0.3497	0.4133	0.4732	0.5184	0.0070	0.0500	6.52
0.4134	0.3091	0.5804	0.4121	0.0007	0.0292	58.75
0.4644	0.2348	0.6888	0.3105	0.0005	0.0161	71.43
x^{cs}		0.1371	0.6179	0.1371	0.6179	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
-3.1952		2.6359		-3.0741	2.2830	

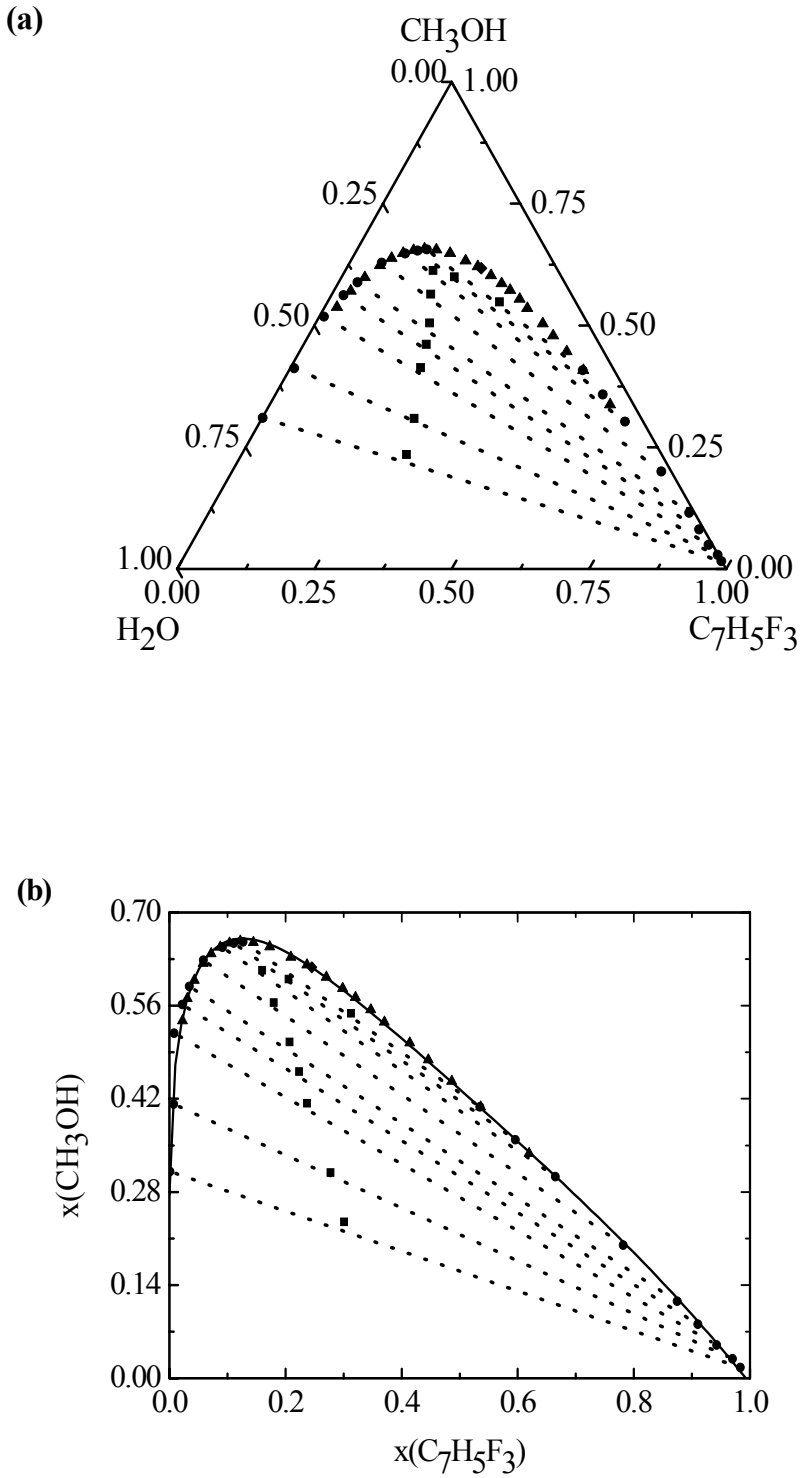

Figure (A.3.1): Solubilities and LLE data for the system {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

Table (A.3.3): Experimental solubilities at 298.15 K for solutions of {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water	H_2O
2. methanol	CH_3OH
3. α,α,α-trifluorotoluene	$C_7H_5F_3$

x_1	x_2	x_3
0.0464	0.3342	0.6194
0.0535	0.3627	0.5838
0.0627	0.3897	0.5476
0.0721	0.4228	0.5051
0.0845	0.4504	0.4651
0.0979	0.4764	0.4257
0.1057	0.5049	0.3894
0.1201	0.5516	0.3283
0.1388	0.6032	0.2580
0.1686	0.6301	0.2013
0.1785	0.6362	0.1853
0.2052	0.6444	0.1504
0.2292	0.6437	0.1271
0.2715	0.6364	0.0921
0.3126	0.6182	0.0692
0.3553	0.5938	0.0509
0.4018	0.5599	0.0383
0.4408	0.5295	0.0297
0.4773	0.4996	0.0231
0.5207	0.4610	0.0183
0.5685	0.4167	0.0148
0.6274	0.3611	0.0115

Equation: (2.34)

a	b	c	d	e	σ
0.1072	3.3120	-5.4012	3.4078	-1.4391	0.0002

Table (A.3.4): Experimental liquid-liquid equilibrium data at 298.15 K for solutions of {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. methanol		CH_3OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.1732	0.5466	0.2273	0.6440	0.0778	0.4173	1.89
0.1775	0.5658	0.2392	0.6405	0.0716	0.3889	2.03
0.2405	0.6021	0.2712	0.6370	0.0411	0.3091	3.20
0.2677	0.5488	0.3177	0.6205	0.0255	0.2250	4.52
0.3197	0.4747	0.4022	0.5654	0.0072	0.1257	12.42
0.3857	0.3615	0.5093	0.4735	0.0050	0.0477	10.26
0.4185	0.3092	0.5775	0.4084	0.0042	0.0258	8.69
0.4841	0.1921	0.7288	0.2685	0.0044	0.0142	8.76
x^{cs}		0.1471	0.6128	0.1471	0.6128	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
-2.7941		2.4627		-2.7888	2.2446	

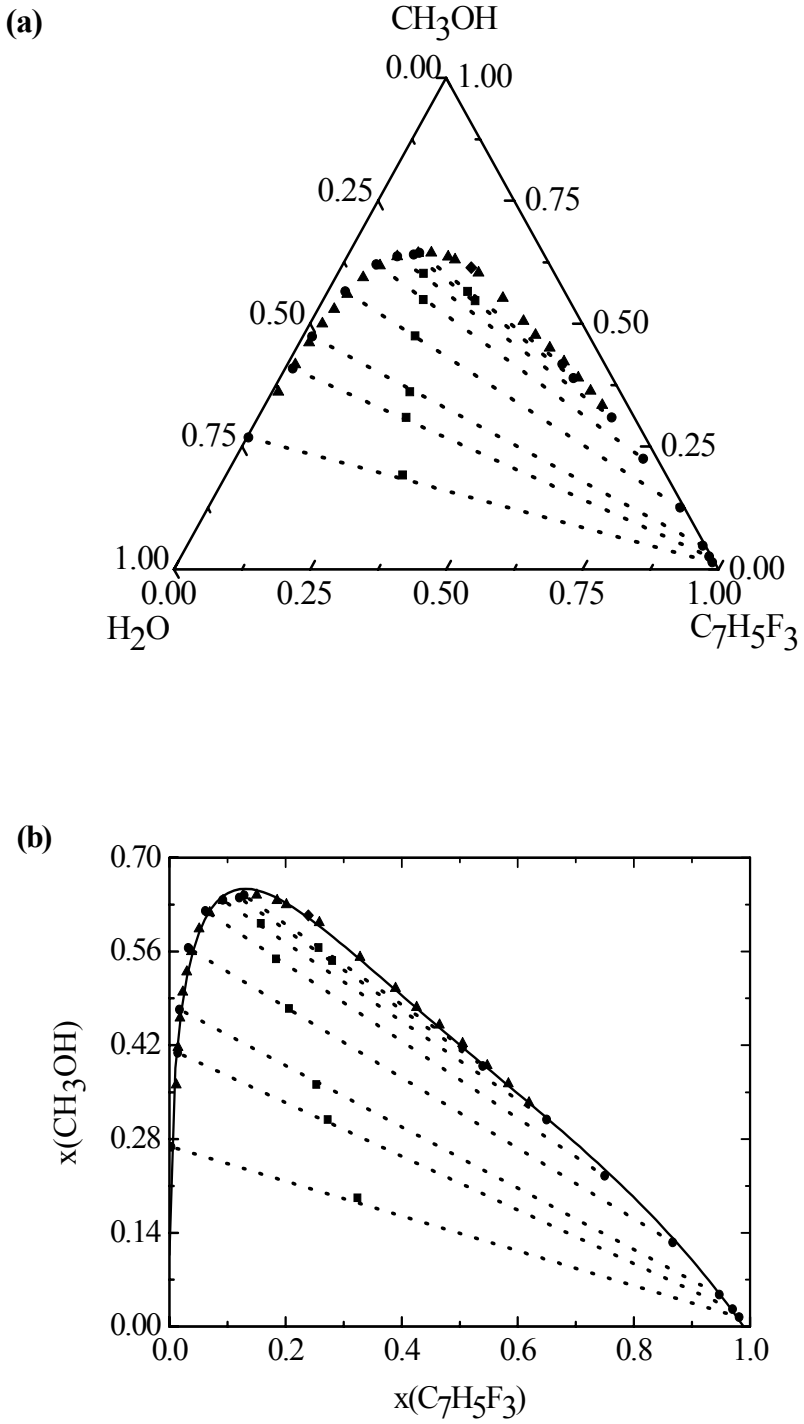

Figure (A.3.2): Solubilities and LLE data for the system {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)} at 298.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

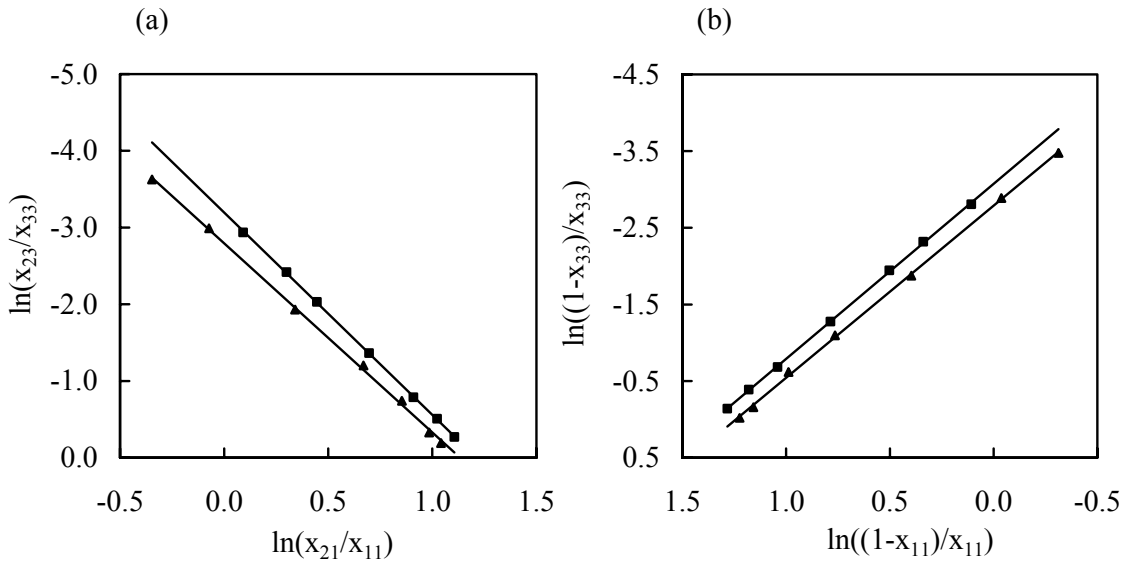

Figure:(A.3.3): Correlation of the LLE data for the {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)} solutions at T = (■, 288.15; ▲, 298.15) K; (a), Hand; ──, equation (2.35); (b), Othmer-Tobias; ──, equation (2.36).

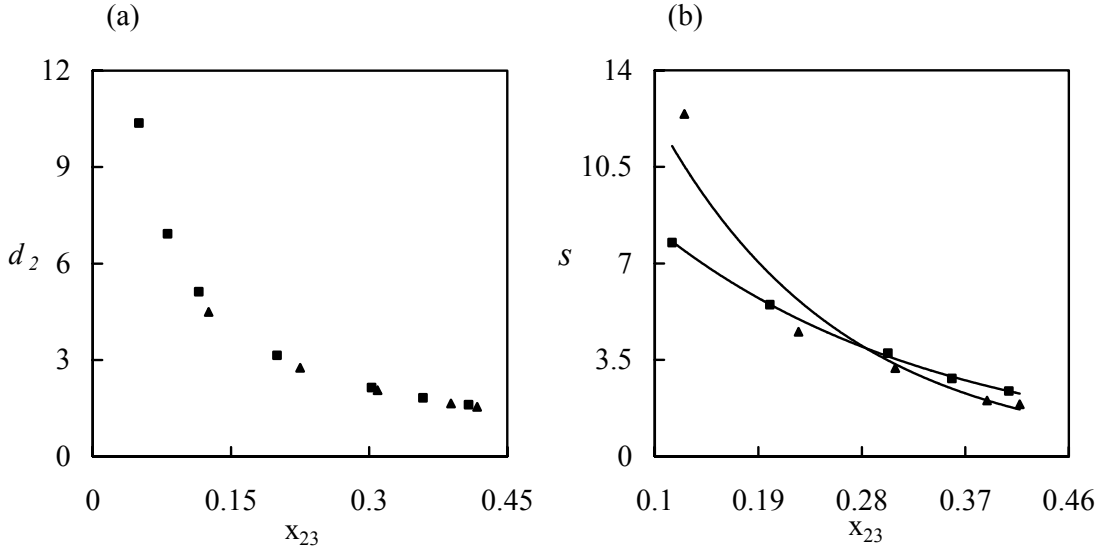

Figure (A.3.4): Experimental distribution coefficient d_2 of methanol and selectivity s for LLE of {water(1) + methanol(2) + α,α,α-trifluorotoluene(3)} solutions at T = (■, 288.15; ▲, 298.15) K; (a), distribution coefficient d_2; (b), selectivity s; —, exponential fit.

Table (A.4.1): Experimental solubilities at 288.15 K for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O
2. ethanol		C_2H_5OH
3. α,α,α-trifluorotoluene		$C_7H_5F_3$

x_1	x_2	x_3
0.0108	0.0116	0.9776
0.0908	0.2831	0.6261
0.1109	0.3074	0.5817
0.1314	0.3320	0.5366
0.1597	0.3607	0.4796
0.1992	0.3889	0.4119
0.2298	0.4029	0.3673
0.2440	0.4079	0.3481
0.2701	0.4182	0.3117
0.2873	0.4253	0.2874
0.3146	0.4371	0.2483
0.3460	0.4431	0.2109
0.3828	0.4438	0.1734
0.4227	0.4401	0.1372
0.4693	0.4276	0.1031
0.5226	0.4050	0.0724
0.5721	0.3786	0.0493
0.6146	0.3508	0.0346
0.6464	0.3295	0.0241

Equation: (2.34)

a	b	c	d	e	σ
0.1631	1.3630	-1.7785	0.6683	-0.4173	0.0001

Table (A.4.2): Experimental liquid-liquid equilibrium data at 288.15 K
for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	s
0.3326	0.4061	0.4460	0.4368	0.1682	0.3668	2.23
0.3767	0.3890	0.4970	0.4158	0.1282	0.3360	3.13
0.4129	0.3422	0.5950	0.3655	0.0719	0.2723	6.17
0.4331	0.2963	0.6500	0.3280	0.0459	0.2293	9.90
0.4699	0.2498	0.7030	0.2846	0.0270	0.1867	17.08
0.4922	0.2055	0.7580	0.2370	0.0055	0.1431	83.21
0.5218	0.1627	0.8075	0.1925	0.0048	0.1003	87.65
0.5549	0.1159	0.8512	0.1488	0.0027	0.0527	111.65
x^{cs}		0.2993	0.4372	0.2993	0.4372	1.00
LLE corrrelation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
-0.2129		1.3658		-0.1459	1.3800	

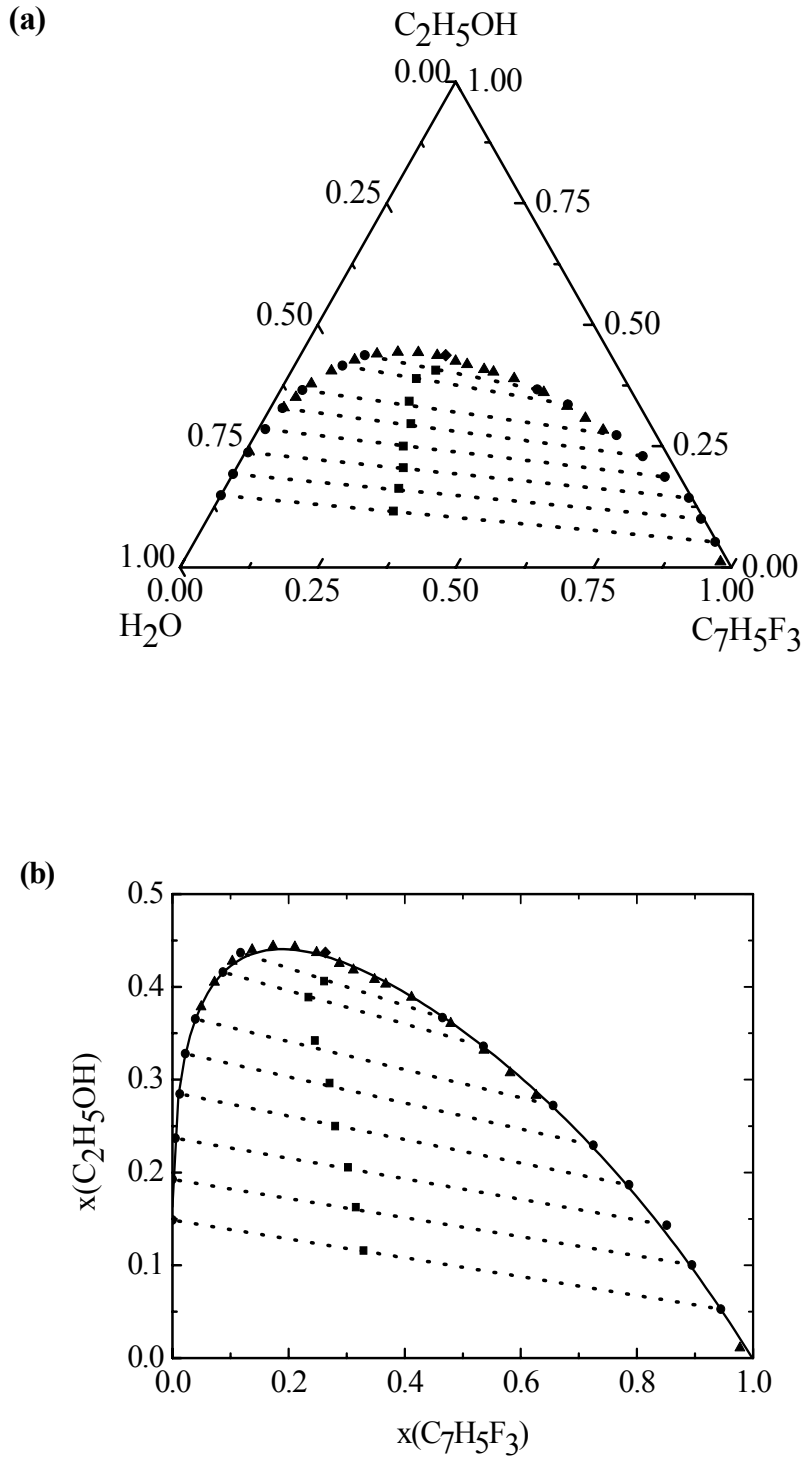

Figure (A.4.1): Solubilities and LLE data for the system {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

Table (A.4.3): Experimental solubilities at 298.15 K for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component:	1. water	H_2O
	2. ethanol	C_2H_5OH
	3. α,α,α-trifluorotoluene	$C_7H_5F_3$

x_1	x_2	x_3
0.0797	0.2489	0.6714
0.0903	0.2666	0.6431
0.1023	0.2854	0.6123
0.1165	0.3026	0.5809
0.1327	0.3206	0.5467
0.1515	0.3397	0.5088
0.1740	0.3566	0.4694
0.2000	0.3743	0.4257
0.2581	0.4017	0.3402
0.2832	0.4121	0.3047
0.3030	0.4184	0.2786
0.3245	0.4226	0.2529
0.3388	0.4283	0.2329
0.3599	0.4286	0.2115
0.3839	0.4292	0.1869
0.4154	0.4298	0.1548
0.4430	0.4273	0.1297
0.4722	0.4196	0.1082
0.5029	0.4079	0.0892
0.5297	0.3964	0.0739
0.5577	0.3817	0.0606
0.5867	0.3634	0.0499
0.6148	0.3444	0.0408
0.6383	0.3286	0.0331
0.6619	0.3112	0.0269
0.6857	0.2931	0.0212
0.7001	0.2836	0.0163

Equation: (2.34)

a	b	c	d	e	σ
0.0723	1.8912	-2.6807	1.4566	-0.7454	0.00005

Table (A.4.4): Experimental liquid-liquid equilibrium data at 298.15 K for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	s
0.3731	0.4144	0.4790	0.4266	0.1805	0.3681	2.29
0.3946	0.3811	0.5195	0.4050	0.1414	0.3296	2.99
0.4353	0.3336	0.5683	0.3732	0.0993	0.2852	4.37
0.4615	0.2951	0.6328	0.3307	0.0629	0.2298	6.99
0.4867	0.2349	0.7208	0.2678	0.0335	0.1574	12.65
0.5235	0.2034	0.7506	0.2386	0.0221	0.1312	18.68
0.6646	0.1727	0.7805	0.2093	0.0051	0.0947	69.24
0.7116	0.1104	0.8596	0.1388	0.0030	0.0299	61.72
x^{cs}		0.3274	0.4301	0.3274	0.4301	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
-0.0663	1.5892			0.0105	1.5680	

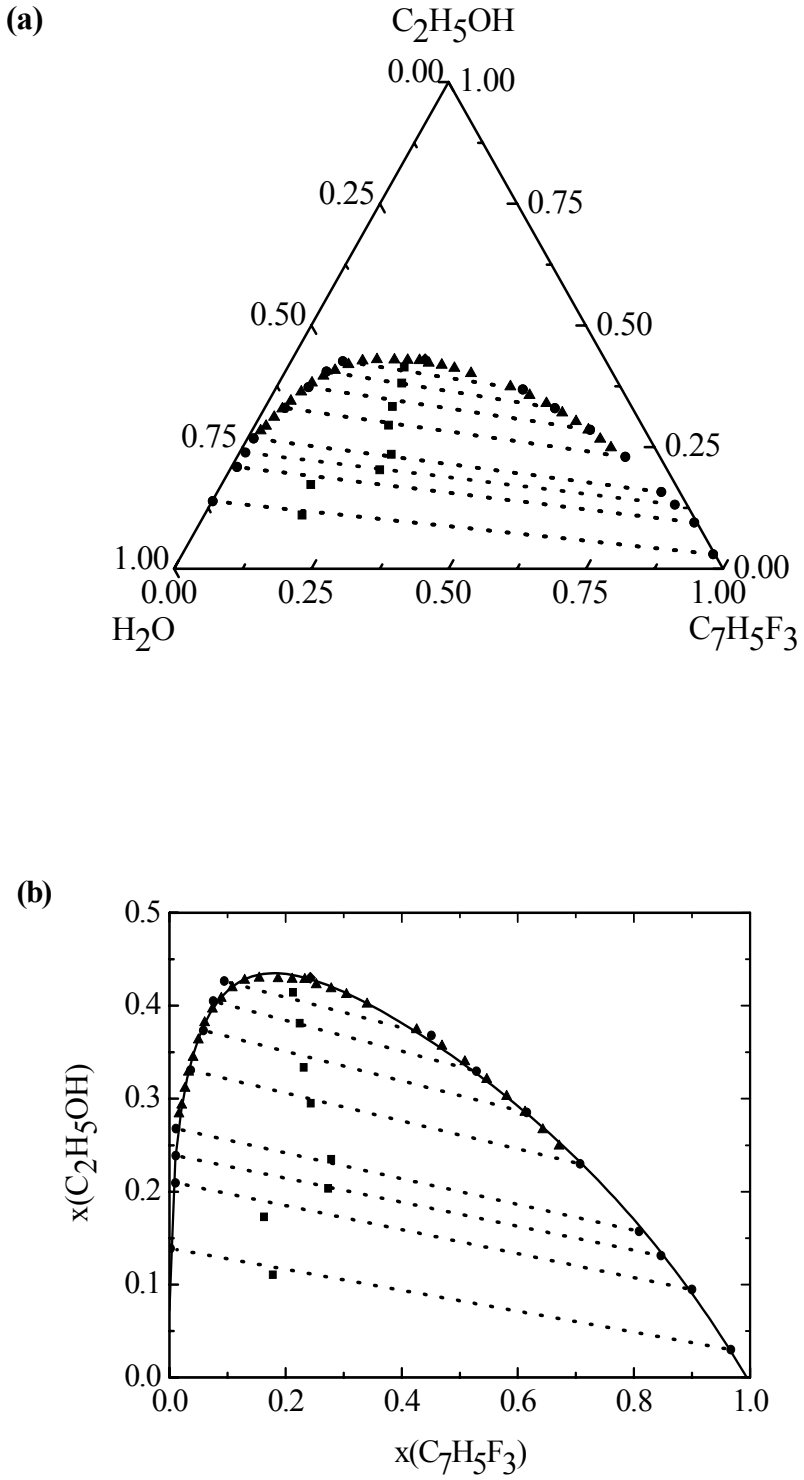

Figure (A.4.2): Solubilities and LLE data for the system {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} at 298.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

Table (A.4.5): Experimental solubilities at 308.15 K for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component:	1. water	H_2O
	2. ethanol	C_2H_5OH
	3. α,α,α-trifluorotoluene	$C_7H_5F_3$

x_1	x_2	x_3
0.0604	0.1732	0.7664
0.0981	0.2440	0.6579
0.1257	0.2731	0.6012
0.1762	0.3276	0.4962
0.1900	0.3331	0.4769
0.1890	0.3345	0.4765
0.2369	0.3661	0.3970
0.2597	0.3702	0.3701
0.3033	0.3824	0.3143
0.3179	0.3839	0.2982
0.3544	0.3864	0.2592
0.4067	0.3881	0.2052
0.4626	0.3757	0.1617
0.5172	0.3568	0.1260
0.5789	0.3235	0.0976
0.6445	0.2820	0.0735
0.7012	0.2444	0.0544
0.7593	0.2008	0.0399
0.8160	0.1547	0.0293
0.8863	0.0962	0.0175

Equation: (2.34)

a	b	c	d	e	σ
-0.1017	1.8784	-1.7866			0.0001

Table (A.4.6): Experimental liquid-liquid equilibrium data at 308.15 K for solutions of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. ethanol		C_2H_5OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.3711	0.3538	0.4890	0.3703	0.1684	0.3304	2.59
0.3832	0.3281	0.5425	0.3484	0.1433	0.3070	3.34
0.3957	0.3006	0.5781	0.3269	0.1256	0.2793	3.93
0.4306	0.2605	0.6452	0.2812	0.0861	0.2291	6.11
0.4524	0.2208	0.6901	0.2483	0.0677	0.1932	7.93
0.4814	0.1783	0.7536	0.2010	0.0399	0.1500	14.09
0.5107	0.1212	0.8310	0.1398	0.0223	0.0949	25.30
0.5290	0.0727	0.8908	0.0974	0.0078	0.0488	57.22
x^{cs}		0.3254	0.3902	0.3254	0.3902	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
-0.0683	1.2214			-0.0006	1.2796	

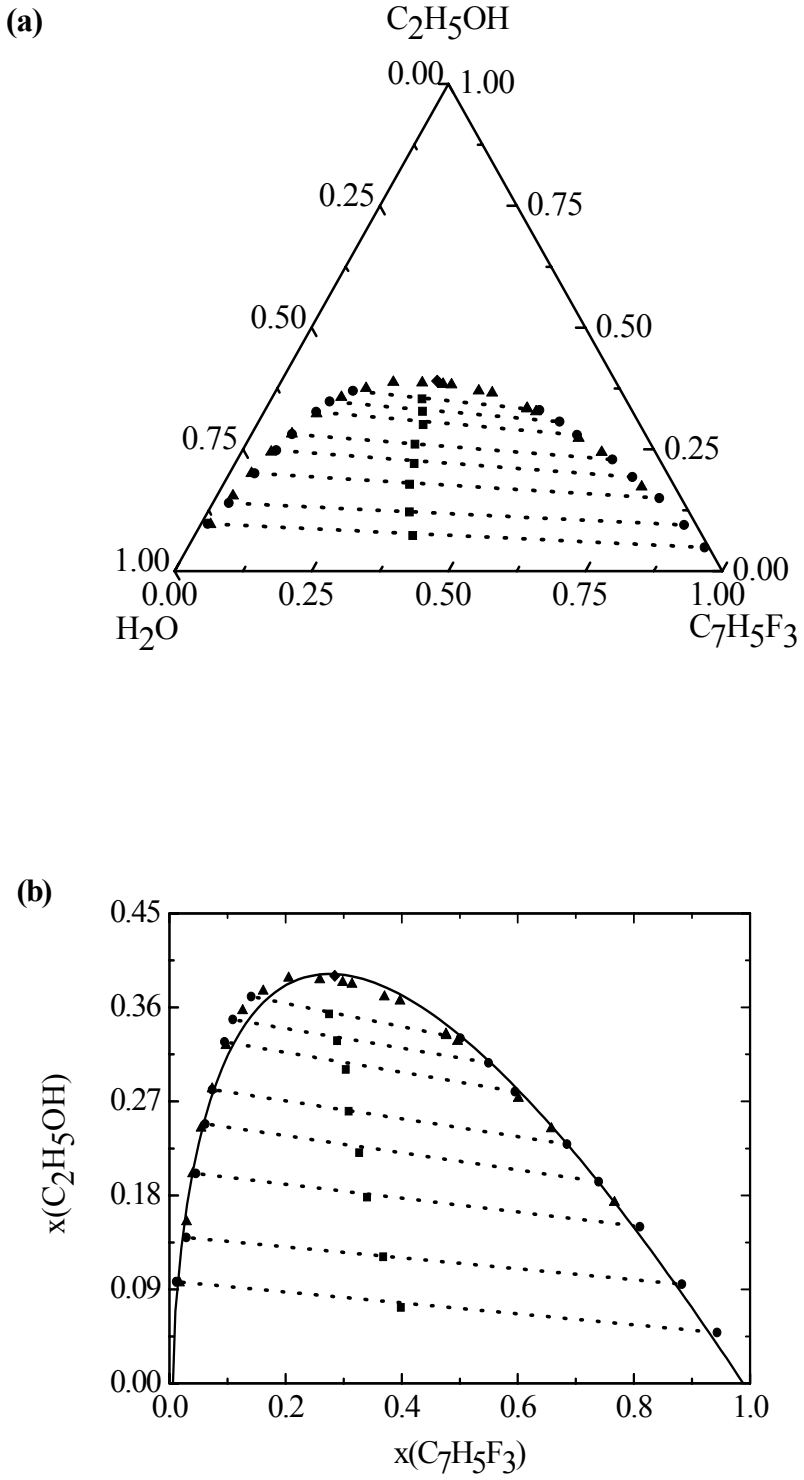

Figure (A.4.3): Solubilities and LLE data for the system {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} at 308.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

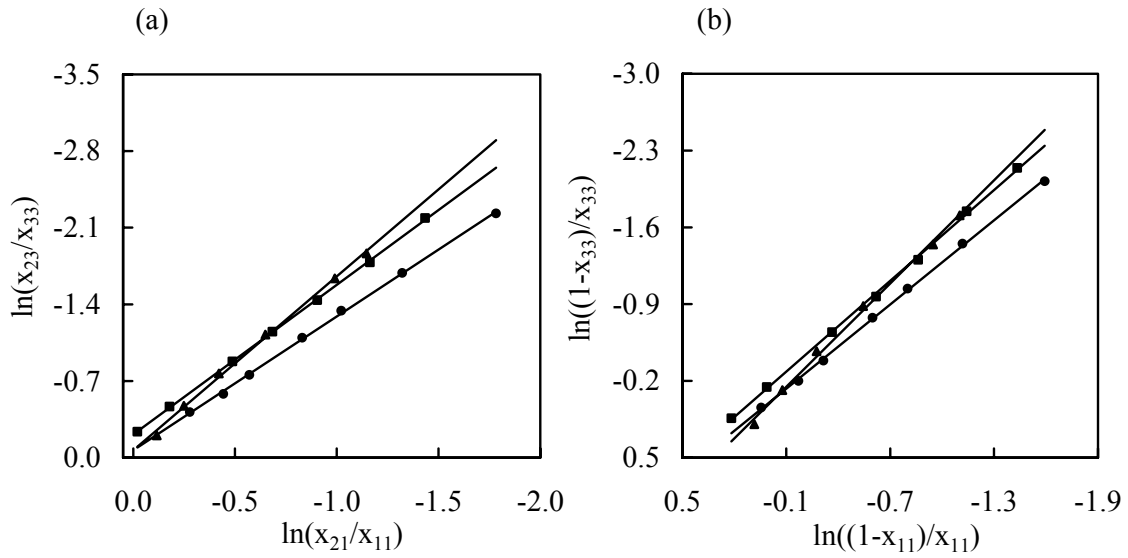

Figure (A.4.4): Correlation of the LLE data for the {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} solutions at T = (■, 288.15; ▲, 298.15; ●, 308.15) K; (a), Hand; ──, equation (2.35); (b), Othmer-Tobias; ──, equation (2.36).

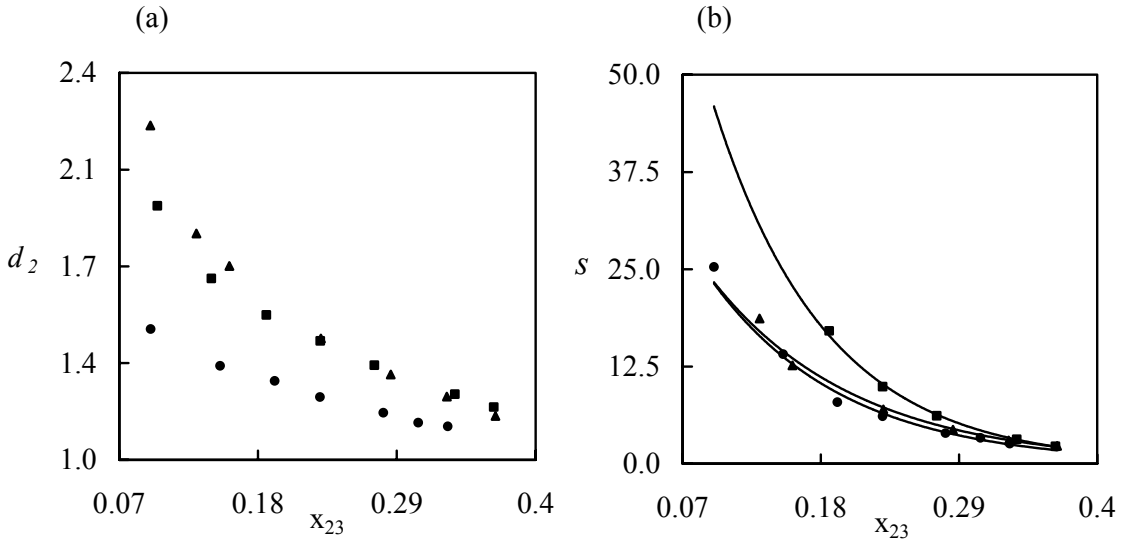

Figure (A.4.5): Experimental distribution coefficient d_2 of ethanol and selectivity s for LLE of {water(1) + ethanol(2) + α,α,α-trifluorotoluene(3)} at T = (■, 288.15; ▲, 298.15; ●, 308.15) K; (a), distribution coefficient d_2; (b), selectivity s; —, exponential fit.

Table (A.5.1): Experimental solubilities at 288.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O			
2. 2-propanol		C_3H_7OH			
3. α,α,α-trifluorotoluene		$C_7H_5F_3$			
x_1		x_2		x_3	
0.0460		0.1781		0.7759	
0.0795		0.2635		0.6570	
0.1042		0.2839		0.6119	
0.1075		0.2912		0.6013	
0.1520		0.3355		0.5125	
0.1897		0.3621		0.4428	
0.2235		0.3744		0.4021	
0.2707		0.3870		0.3423	
0.3093		0.3962		0.2945	
0.3562		0.3893		0.2545	
0.3945		0.3835		0.2220	
0.4367		0.3741		0.1892	
0.4802		0.3601		0.1597	
0.5297		0.3412		0.1291	
0.5903		0.3105		0.0991	
0.6507		0.2762		0.0731	
0.6989		0.2475		0.0536	
0.7405		0.2220		0.0375	
0.7585		0.2151		0.0264	
0.7906		0.1917		0.0177	
Equation: (2.34)					
a	b	c	d	e	σ
0.0185	1.2892	-1.0365	-0.2756		0.0001

Table (A.5.2): Experimental liquid-liquid equilibrium data at 288.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	s
0.4752	0.3249	0.8265	0.1636	0.3079	0.3929	6.45
0.5562	0.3082	0.7684	0.2030	0.3623	0.3890	4.06
0.4959	0.2732	0.8850	0.1073	0.2476	0.3812	12.70
0.5226	0.2301	0.9200	0.0780	0.1972	0.3691	22.08
0.5719	0.1756	0.9562	0.0428	0.1347	0.3218	53.37
0.6087	0.1217	0.9785	0.0215	0.0768	0.2660	157.63
0.6475	0.0718	0.9858	0.0142	0.0270	0.1813	466.16
x^{cs}		0.5147	0.3504	0.5147	0.3504	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A	B			A_1	B_1	
1.1665	0.5429			1.9012	0.6704	

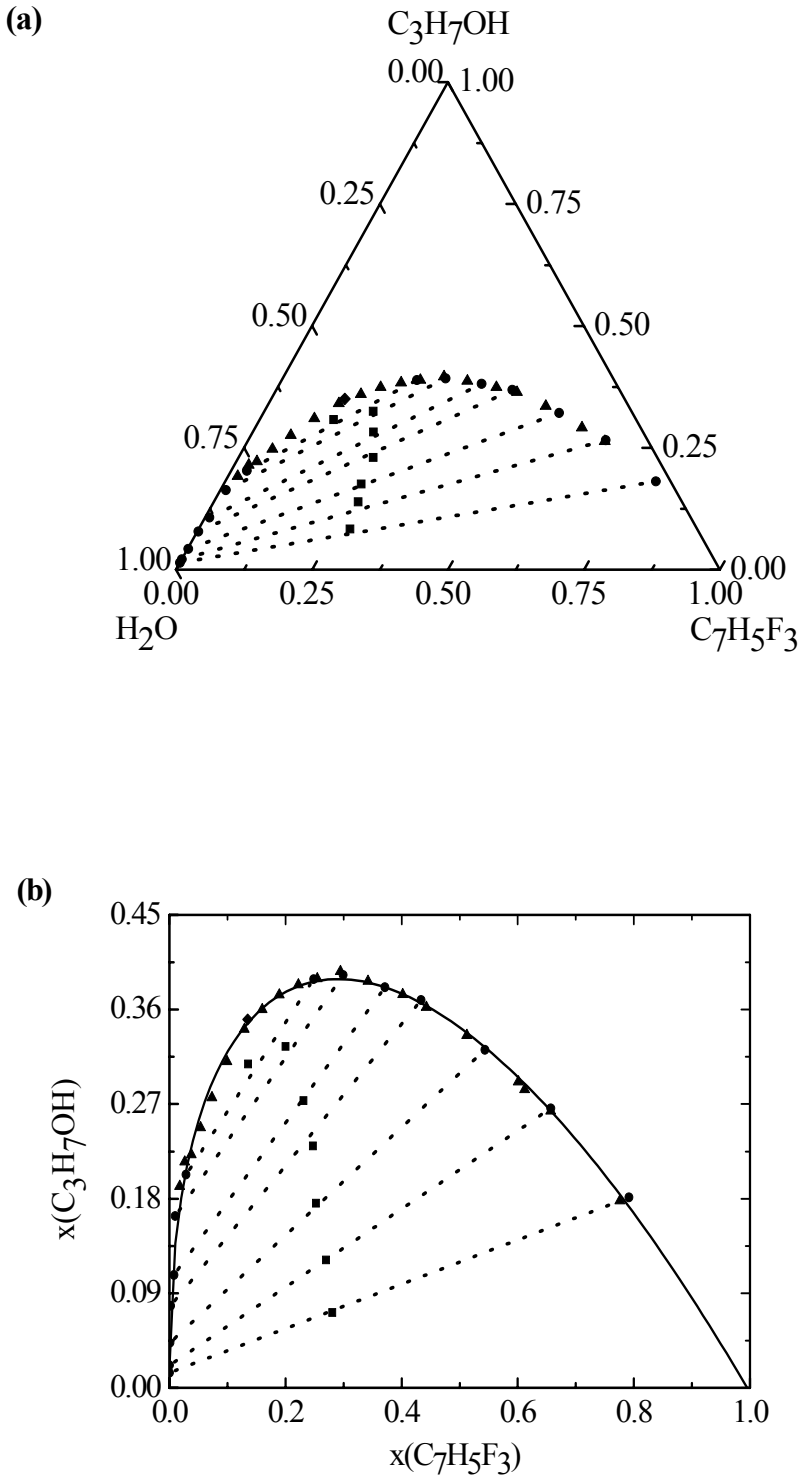

Figure (A.5.1): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)} at 288.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

Table (A.5.3): Experimental solubilities at 298.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O
2. 2-propanol		C_3H_7OH
3. α,α,α-trifluorotoluene		$C_7H_5F_3$

x_1	x_2	x_3
0.0754	0.2199	0.7047
0.1148	0.2698	0.6154
0.1648	0.3173	0.5179
0.2206	0.3489	0.4305
0.2933	0.3671	0.3396
0.3335	0.3680	0.2985
0.3726	0.3630	0.2644
0.4137	0.3540	0.2323
0.4510	0.3434	0.2056
0.4922	0.3277	0.1801
0.5358	0.3104	0.1538
0.5811	0.2902	0.1287
0.6328	0.2623	0.1049
0.6883	0.2323	0.0794
0.7415	0.2036	0.0549
0.7837	0.1793	0.0370
0.8151	0.1605	0.0244
0.8358	0.1481	0.0161
0.0486	0.1759	0.7755

Equation: (2.34)

a	b	c	d	e	σ
0.0094	0.9902	-0.4728	-0.5598		0.0002

Table (A.5.4): Experimental liquid-liquid equilibrium data at 298.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	S
0.5969	0.2559	0.8456	0.1408	0.3692	0.3642	5.92
0.4631	0.3017	0.8856	0.1052	0.3291	0.3697	9.46
0.4213	0.2999	0.9197	0.0730	0.2876	0.3692	16.17
0.4176	0.2888	0.9415	0.0528	0.2496	0.3652	26.09
0.4480	0.2454	0.9616	0.0349	0.2164	0.3506	44.64
0.4842	0.1887	0.9732	0.0268	0.1401	0.3038	78.74
0.5075	0.1574	0.9800	0.0200	0.1053	0.2751	128.01
0.7405	0.0321	0.9831	0.0169	0.0136	0.0765	327.22
x^{cs}		0.5479	0.3038	0.5479	0.3038	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
0.9350		0.3437		1.8476	0.4923	

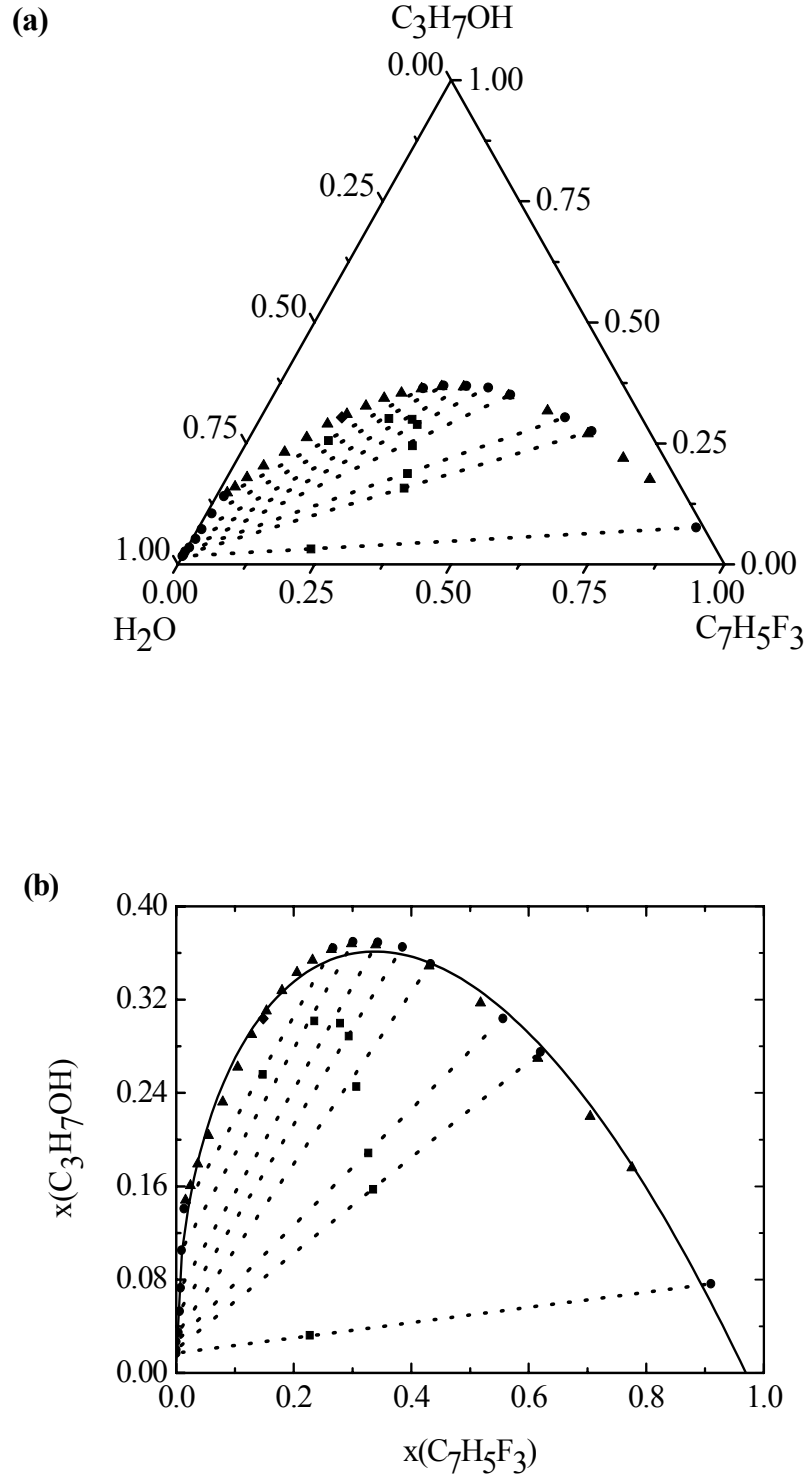

Figure (A.5.2): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)} at 298.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34);
(a), ternary representation; **(b)**, binary representation.

Table (A.5.5): Experimental solubilities at 308.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O			
2. 2-propanol		C_3H_7OH			
3. α,α,α-trifluorotoluene		$C_7H_5F_3$			
x_1		x_2		x_3	
0.0693		0.0801		0.8506	
0.0912		0.1378		0.7710	
0.1178		0.2162		0.6660	
0.1203		0.2290		0.6507	
0.1405		0.2500		0.6095	
0.1675		0.2675		0.5650	
0.1903		0.2805		0.5292	
0.2241		0.2929		0.4830	
0.2712		0.3107		0.4181	
0.3317		0.3144		0.3539	
0.3901		0.3043		0.3056	
0.4592		0.2864		0.2544	
0.5380		0.2573		0.2047	
0.6157		0.2235		0.1608	
0.6914		0.1841		0.1245	
0.7604		0.1462		0.0934	
0.8170		0.1143		0.0687	
0.8795		0.0768		0.0437	
0.9058		0.0617		0.0325	
Equation: (2.34)					
a	b	c	d	e	σ
-0.0225	0.1862	1.4502	-2.6797	1.0404	0.00002

Table (A.5.6): Experimental liquid-liquid equilibrium data at 308.15 K for solutions of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)}

Component: 1. water		H_2O				
2. 2-propanol		C_3H_7OH				
3. α,α,α-trifluorotoluene		$C_7H_5F_3$				
overall composition		aqueous phase		organic phase		
x_1	x_2	x_{11}	x_{21}	x_{13}	x_{23}	s
0.4867	0.2478	0.7259	0.1600	0.2965	0.3175	4.86
0.5041	0.2227	0.7847	0.1323	0.2442	0.3008	7.31
0.5261	0.1859	0.8430	0.0999	0.1715	0.2730	13.43
0.5462	0.1569	0.8650	0.0848	0.1480	0.2501	17.24
0.5880	0.0908	0.9251	0.0456	0.0900	0.1610	36.29
0.5936	0.0644	0.9500	0.0300	0.0699	0.1191	53.96
x^{cs}		0.5287	0.2618	0.5287	0.2618	1.00
LLE correlation equations						
Hand				Othmer-Tobias		
A		B		A_1	B_1	
1.1844		0.8978		1.4419	0.9937	

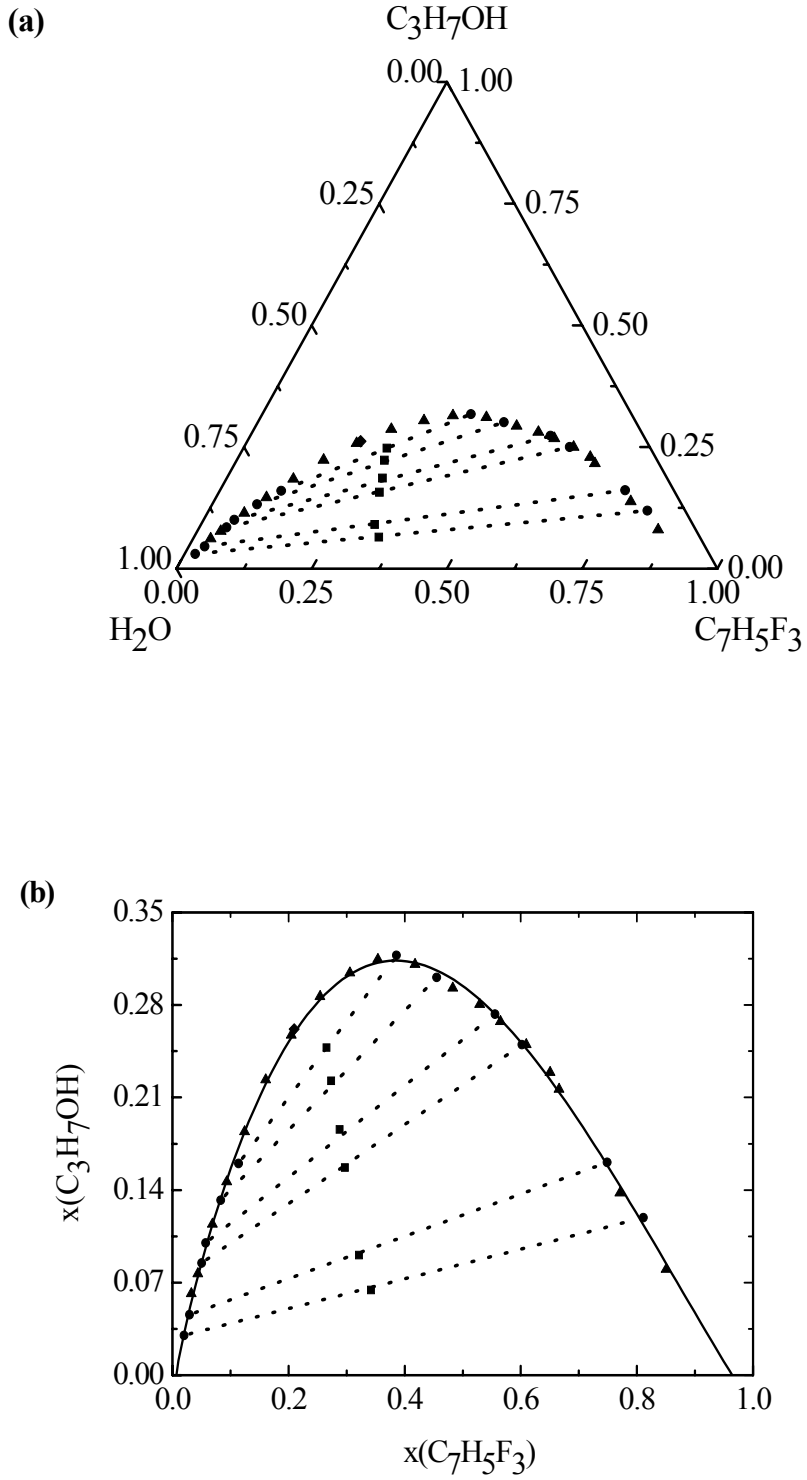

Figure (A.5.3): Solubilities and LLE data for the system {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)} at 308.15 K, ▲, solubility; ■, overall composition; ●, LLE; ♦, p.p.; …, tie line; —, equation (2.34); **(a)**, ternary representation; **(b)**, binary representation.

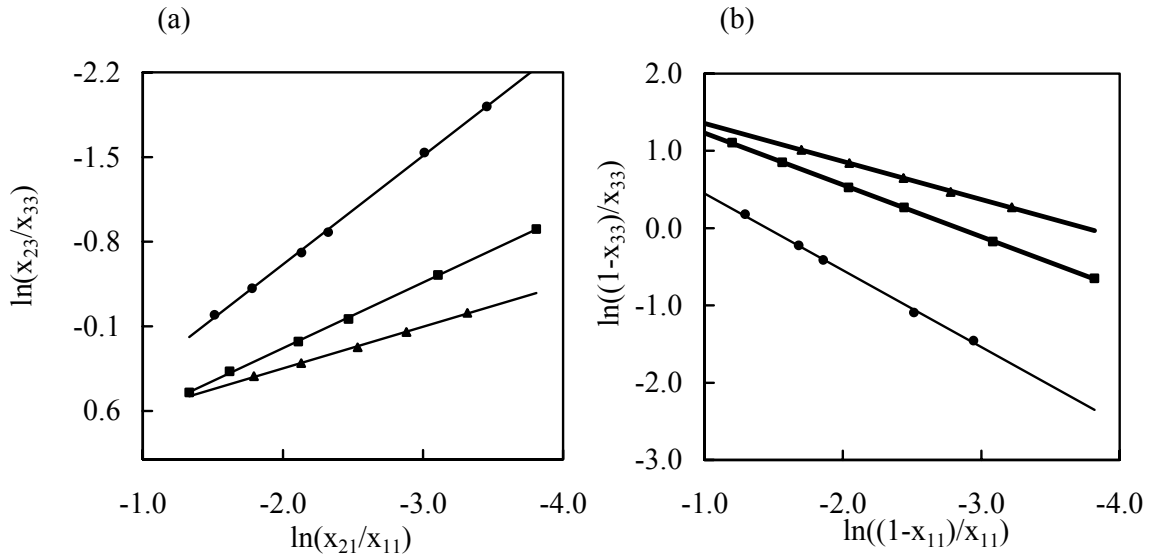

Figure (A.5.4): Correlation of the LLE data for the {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)} at T = (■, 288.15; ▲, 298.15; ●, 308.15) K; (a), Hand; —, equation (2.35); (b), Othmer-Tobias; —, equation (2.36).

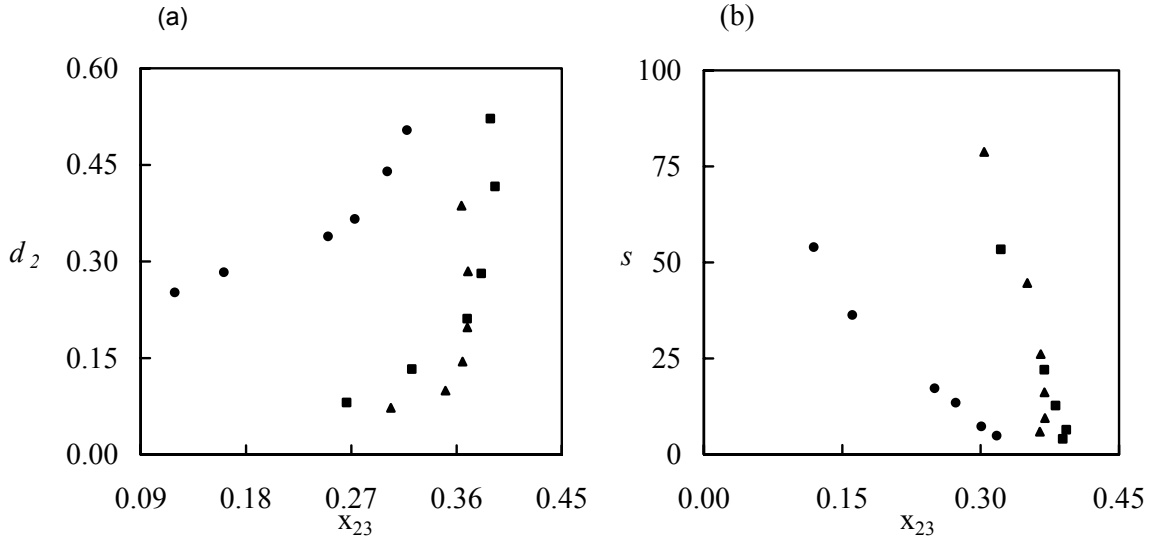

Figure (A.5.5): Experimental distribution coefficient d_2 of 2-propanol and selectivity s for LLE of {water(1) + 2-propanol(2) + α,α,α-trifluorotoluene(3)} solutions at T = (■ , 288.15; ▲, 298.15; ●, 308.15) K; (a), distribution coefficient d_2; (b), selectivity s .