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A Thermodynamic Study of Phase Equilibria of Aqueous Systems Containing Halogenated Hydrocarbons

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ABSTRACT

Solubility of a liquid in different solvents as well as liquid-liquid equilibrium is most important thermodynamic properties of a pure substance or a solution.

In this work, we report observed and correlated solubility and liquid-liquid equilibrium (or tie-line) data of eleven ternary solutions at different temperatures and atmospheric pressure.

The systems studied at 298.15 K are: (solvent + 2,2,2-trifluoroethanol + water); solvent = toluene, or fluorobenzene, or α,α,α-trifluorotoluene; and (1,4-difluorobenzene + ethanol + water) at 318.15 K, the systems (cyclohexane + alcohol + 2,2,2-trifluoroethanol); where alcohol = ethanol, or 2-propanol, were studied at T = (288.15, 298.15, 308.15) K.

The effect of temperature on solubility and liquid-liquid phase equilibrium was also studied.

A comparison of the extracting capabilities of the solvents is made with respect to distribution coefficient and the selectivity of the solvents. The reliability of data was satisfactorily proved by Hand and Othmer-Tobias methods. The critical solution mole fractions were attained by Othmer-Tobias equation.

The studied temperatures have a small effect on the phase equilibrium properties of the investigated systems. For alcohol-rich solutions, molecular cluster formation by a variety of hydrogen-bonding configurations between water, alcohols, 2,2,2-trifluoroethanol hydroxyl groups and fluorine atoms results in a moderate temperature effect on the phase behaviour of the partially miscible systems.

RESUME

La solubilité d'une substance liquide pure ou une solution dans différents solvants a des propriétés thermodynamiques qui relèvent à des applications techniques importantes.
Le but de ce travail est d'obtenir des résultats expérimentaux des solubilités et des diagrammes de phase liquide- liquide afin d'étudier le comportement des solutions ternaires, contenant des hydrocarbures, alcools, et composés fluoro-organiques, à des différentes températures et à pression atmosphérique.

Les résultas expérimentaux sont obtenus à T = 298.15 K pour les systèmes: (solvant + 2,2,2-trifluorethanol + eau); solvants = toluène, ou fluorobenzene, ou α,α,α-trifluorotoluene; (di-isopropyl éther + éthanol + eau), et (difluorobenzene + éthanol + eau) à 318.15 K, (cyclohexane + alcool + 2,2,2-trifluorethanol); alcool = éthanol, ou 2-propanol à *T* = (288.15, 298.15, 308.15) K.

Les fractions molaires des points critiques des solutions ternaires, les coefficients de distribution, et les sélectivités de chaque système ternaires sont rapportés.
Les binodales ainsi que les diagrammes de phase liquide-liquide ont été favorablement corrélés par des équations empiriques (Hand et Othmer-Tobias).
L'effet de la température et de la structure moléculaire des constituants sur l'immiscibilité gap des systèmes a été évalué.

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GLOSSARY

List of Symbols:

A, A_1, B, B_1	constants
a	activity
C_0, C	chromatographic constants
d	distribution coefficient
F	degree of freedom
G	Gibbs function
n	amount of substance
n_{D}	refractive index
P	pressure
R	universal gas constant
S	entropy, selectivity
T	thermodynamic temperature
V	volume
X	thermodynamic function
x	mole fraction

Abbreviations:

Calc.	calculated
eq.	equation
Expt.	experimental
LLE	liquid-liquid equilibrium
GLC	gas-liquid chromatograph
mix.	mixing
ml	millilitre

mn.	minute
RMSD	root-mean square deviation

Greek Symbols:

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

Subscripts

A, B, C	component
i, j	component
m	molar

Superscripts

cs	critical solution
id	ideal
r	real

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CHAPTER 1

INTRODUCTION

Accurate measurements and capable prediction procedures of thermophysical properties of pure substances and multi-component solutions are of prime importance for the creation of high performance materials and the design and operation of efficient chemical processes.[1]

The liquid-liquid equilibrium data at different temperatures are necessary needed for operations to be carried out in the industrial processes.[2] Liquid extraction provides an important alternative to distillation for the recovery of valuable materials from solutions using nonmiscible solvents.

The use of liquid-liquid equilibrium studies in chemical engineering and production units is fundamentally important to the development of tools used for the synthesis and separation processes applied in solvent absorption and extraction units through water removal and dehydration of solutions.

Liquid extraction is used in the pharmaceutical and food industries, in which the separation factor and mutual solubility of materials play important role in the extraction process.[3-5]

Alcohols are used on gasoline additives to provide antiknock quality and to help reduce harmful combustion emissions.[6-8] The low chain alcohols are important industrial solvents. Propanols are used as solvents in the pharmaceutical industry, cleaning agents in the production of many electronic devices. Ethanol is a natural biodegradable substance and is a favourable alternative to petroleum and coal fuels and greenhouse gases.

The alcohols are polar substances of high solubility in water. The carbon chain of the alcohols resists to some extent their solubility in water.

Cyclohexane is nonpolar solvent with low solubility in water, highly flammable material, [9] and is a dehydrating solvent for alcohols whether obtained from fermentation or synthetic processes. Mixtures of ethanol and cyclohexane are employed as varnish solvents and glossy coatings.

Fluorinated hydrocarbons are non-flammable and non-explosive solvents. They have low toxicity and short environmental lifetime, and are excellent substitutes of chlorinated solvents.[10] As for fluorinated hydrocarbon alcohols, they have high chemical and thermal stability, and find a wide range of technical applications as organic working fluids for thermal engines and heat pumps.[11-16]

Toluene, fluorobenzene, 1.4-difluorobenzene, and α,α,α-trifluorotoluene demonstrate very low solubility in water and may be used to extract light alcohols from their dilute aqueous solutions. While 2,2,2-trifluorethanol demonstrate very low solubility in cyclohexane and finds applications in paints and coatings.

Generally, solubilities of liquid solutions are directly affected by temperature.[17] Numerous investigations of multi-component systems showing low solubilities were carried out in order to understand and provide valuable information about the phase behaviour and the thermodynamic properties of such systems. Furthermore, liquid-liquid equilibrium (LLE) data are essentially required to predict technical data at temperatures and the processes are performed in the industry.[18,19] Liquid extraction techniques in different medium (electrolyte and non-electrolyte) find applications in drying and recovering of technical solvents.[20-25] The solvent ability to extract solutes from solutions can be evaluated in terms of the distribution coefficient of solute and the solvent selectivity.[26]

As a continuation of our studies of the influence of temperature on the liquid-liquid equilibrium of ternary systems of halogenated hydrocarbons,[27-33] this work reports new isobaric experimental and calculated solubility and liquid-liquid equilibrium data for systems of (solvent + 2,2,2-trifluorethanol + water); solvent = toluene, or fluorobenzene, or α,α,α-trifluorotoluene at 298.15 K; (1,4-difluorobenzene + ethanol + water) at 318.15 K; and (cyclohexane + alcohol + 2,2,2-trifluorethanol); alcohol = ethanol; 2-propanol at T = (288.15, 298.15, 308.15) K.

The observed solubility and tie line data of each system were favourably correlated by empirical equations.[34-37]

CHAPTER 2

PHASE EQUILIBRIUM THERMODYNAMICS

2.1 Introduction

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

The thermodynamic functions X depend generally on temperature T, pressure p, and composition n_i: $X = \mathrm{f}\,(T, p, n_i, \ldots)$. Consequently, the change thermodynamic function is:

$$dX = (\partial X / \partial T)_{P,ni}\,\mathrm{d}T + (\partial X \;/\partial p)_{T,ni}\,\mathrm{d}p + \sum(\partial X \;/\partial n_i)_{T,p,nj\neq ni}\mathrm{d}n_i \;, \qquad (2.1)$$

with the partial molar function $X_\mathrm{m,i}$ defines as:

$$X_\mathrm{m,i} = (\partial X/\partial n_\mathrm{i})_{T,\,p,\,xj\,\neq\,xi} \qquad (2.2)$$

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

$$dX = \sum_i X_{m,i} dn_i \; (T, p, const.) \qquad (2.3)$$

It follows that the molar function of a mixture is:

$$X = \sum_i x_i X_{m,i} \; (T, p, const.) \qquad (2.4)$$

Differentiating equation (2.3) gives:

$$dX = \sum_i X_{m,i} dn_i + \sum_i x_i dX_{m,i} \qquad (2.5)$$

Equations (2. 3) and (2.5) give the Gibbs-Duhem relation:

$$\sum_\mathrm{i} x_\mathrm{i} dX_\mathrm{m,i} = 0\,, \; (T, p, \mathrm{const.}) \qquad (2.6)$$

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

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

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

$$\Delta_{mix}X_m(T,p,x) = X_m(T,p,x) - \sum_i x_i X_{m,i}(T,p,x)\,, \tag{2.7}$$

where X_{m} is the molar function of mixture, and $X_{\mathrm{m,i}}$ is the partial molar function of component *i*.

The most common thermodynamic functions in experimental thermodynamics are: Gibbs function *G*, enthalpy *H*, entropy *S*, volume *V*. The ideal mixture has mixing thermodynamic properties $\Delta_{\mathrm{mix}}X_m^{id}$ given by:

$$\Delta_{mix}G_{\mathrm{m}}^{\mathrm{id}} = RT\sum_i x_{\mathrm{i}} \ln x_{\mathrm{i}} \tag{2.8a}$$

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

$$\Delta_{mix}H_m^{id} = 0, \quad \Delta_{mix}V_m^{id} = 0 \tag{2.8c}$$

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

$$dG^{\varphi} = -\sum_{\varphi} S^{\varphi} dT^{\varphi} + \sum_{\varphi} V^{\varphi} dp^{\varphi} + \sum_{\varphi}\sum_i \mu_i^{\varphi} dn_i^{\varphi}\,, \tag{2.9}$$

where the summations are over all components *i* and all phases

Since the chemical potential μ for component *i* and phase φ.is defined by:

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

then, the change in ($\mu^{\varphi}_{\mathrm{i}}$, *T*, *p*) is:

$$d\mu_i^{\varphi} = -S_{m,i}^{\varphi}dT + V_{m,i}^{\varphi}dp\,, \tag{2.10b}$$

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

$$S_m^{\varphi}dT - V_m^{\varphi}dp + \sum_i x_i^{\varphi} d\mu_i = 0\,, \tag{2.11}$$

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

For a binary phase ternary system, its degree of freedom: 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 conditions:

$$\mu_\mathrm{i}^{\alpha} = \mu_\mathrm{i}^{\beta} , \tag{2.12}$$

$$T^{\alpha} = T^{\beta} \tag{2.13}$$

$$p^{\alpha} = p^{\beta} \tag{2.14}$$

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

$$a_\mathrm{i} = x_\mathrm{i}\, \gamma_\mathrm{i} , \tag{2.15}$$

where γ_i is the activity coefficient of component i.

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

$$\Delta_\mathrm{mix} G_\mathrm{m}^\mathrm{r} = RT \sum_{i=1}^{N} x_\mathrm{i} \ln a_\mathrm{i} \tag{2.16}$$

The change in the chemical potential of mixing of the component i with respect to the mole fraction in phase φ is:

$$\left(\partial \mu_{mix,i} / \partial x_i \right)_{T,\ p}^{\varphi} = \left(\partial^2 \Delta_{mix} G_m / \partial x_i^2 \right)_{T,\ p}^{\varphi} \tag{2.17}$$

Equation (2.17) is used to predict the phase stability of the solution, where $d\,\mu_i^{\varphi} < 0$ for a natural process.

Many liquids are partially miscible to yield heterogeneous liquid solutions. The change in the Gibbs energy function of mixing $\Delta_{mix} G_m$ to give away mutual solubility of liquid phases (α + β) is outlined in the following. The natural mass transfer of component i between phases α and β implies:

$$\left(\partial \mu_{mix,i} / \partial x_i \right)_{T,p}^{\varphi} > 0 , \tag{2.18}$$

The condition of material stability in homogeneous mixtures is expressed by the inequality:[38]

$$\left(\partial^2 \Delta_{mix} G_m / \partial x_i^2 \right)_{T,\ p} > 0 , \tag{2.19}$$

and the instable mixture fulfills:

$$\left(\partial^2 \Delta_{mix} G_m / \partial x_i^2\right)_{T,p} < 0 , \tag{2.20}$$

The passage from phase stability to phase instability corresponds to 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).

For a heterogeneous system at constant temperature and pressure, the critical point of a ternary solution is established at unique point, the plait point, and is identified by critical solution mole fractions x_i^{cs}.

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

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

In general, the plait point of a solution justifies:[38, 39]

- $x^{\alpha} = x^{\beta} = x^{cs}$,
- $\left(\partial^2 \Delta_{mix} G_m / \partial x^2\right)_{T^{cs},p} = 0$, (2.21)
- $\left(\partial^3 \Delta_{mix} G_m / \partial x^3\right)_{T^{cs},P} = 0$, (2.22)
- $\left(\partial^4 \Delta_{mix} G_m / \partial x^4\right)_{T^{cs},p} > 0$, (2.23)

where T^{cs}, denotes critical solution temperature, is the extreme temperature where the heterogeneous mixtures converge to a homogeneous one.

2.2 Liquid-Liquid Equilibrium in Ternary Systems

For a ternary system in this work, the liquid-liquid equilibrium is studied at constant temperature and atmospheric pressure. The mole fractions of ternary system are represented by the Gibbs triangle, where each side of the triangle represents a binary system; (*A* + *B*), (*B* + *C*), (*A* + *C*). Where as the ternary system (*A* + *B* + *C*) is represented by a single point on the triangle surface. Figure (2.1) represents the phase diagram for a ternary system.

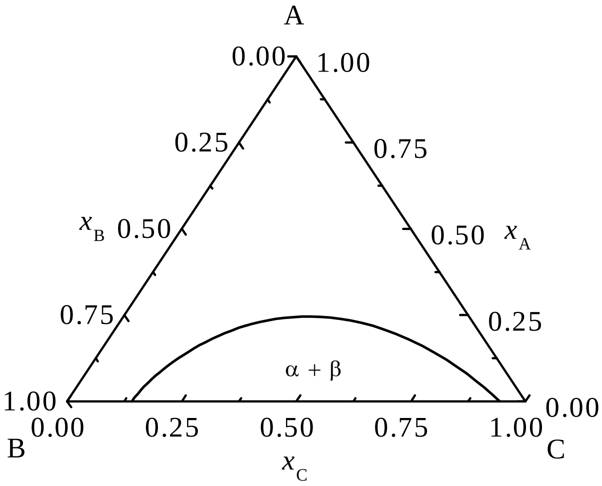


Figure (2.1): Schematic representation of a ternary liquid-liquid phase equilibrium

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

$$a_i^{\alpha} = a_i^{\beta}, \tag{2.24}$$

where a_i^{φ} is the activity of component *i* in phase φ ($\varphi = \alpha$, or β).

According to equation (2.24), the component *i* in a two phase system is represented by:

$$\gamma_i^{\alpha} x_i^{\alpha} = \gamma_i^{\beta} x_i^{\beta}, \tag{2.25}$$

where x_i^{φ} and γ_i^{φ} are the equilibrium mole fraction and the activity coefficient of component *i* in phase φ ($\varphi = \alpha$, or β), respectively.

Applying equation (2.25) for a ternary system we get:

$$(\gamma_1 x_1)^{\alpha} = (\gamma_1 x_1)^{\beta} \tag{2.26}$$

$$(\gamma_2 x_2)^{\alpha} = (\gamma_2 x_2)^{\beta} \tag{2.27}$$

$$(\gamma_3 x_3)^\alpha = (\gamma_3 x_3)^\beta \tag{2.28}$$

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

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

The selectivity S, or the separation factor, of a solvent j to extract the solute i from a multi-component solution is defined as:

$$S = \frac{d_j}{d_i} = \frac{x_j^\alpha / x_j^\beta}{x_i^\alpha / x_i^\beta} \tag{2.30}$$

2.3 Solubility Data Correlation

The experimental binodal curve for the ternary phase equilibrium is correlated by the empirical equation:[34, 35]

$$x_2 = a + bx_3^{0.5} + cx_3 + dx_3^2 + ex_3^3, \tag{2.31}$$

where x_i represents the mole fraction of component i in the solution, and a, b, c,..., are regression constants.

2.4 Liquid-Liquid Equilibrium Data Correlation

In this work, the reliability of experimentally measured liquid-liquid equilibrium data is ascertained by applying two empirical equations.

The tie-lines of the studied systems were satisfactorily correlated by the methods of:

Hand:[36]

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

and Othmer-Tobias:[37]

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

where x_i^φ denotes the observed mole fraction of component i in liquid phase φ.

The fitting parameters of equations (2.31) to (2.33) were determined using a linear least squares method

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Chemical Substances

Chemical substances used in this work are: α,α,α-trifluorotoluene, 2,2,2-tifluoroethanol, toluene, fluorobenzene, 1,4-difluorobenzene, and benzene, supplied by Fluka, and 2-propanol from Labosi, and ethanol, di-isopropyl ether, were from Merck and cyclohexane from Panreac. Triple-distilled are used throughout the study. Solutions were prepared by mass using an OHAUS balance (model: Explorer) with a precision of ± 0.1 mg. The uncertainty in the compositions of the prepared solutions was estimated to be $\pm 3.10^{-4}$. The purities of the chemicals was verified by gas chromatography to better than 99.6 %.

Measurements of density were made using an Anton-Paar vibrating-tube densimeter DMA 5000, having a precision of $\pm 5.10^{-5}$ $g.cm^{-3}$. The refractive indices for pure components and solutions were measured with a precision of $\pm 2.10^{-4}$ using an Abbe-type refractometer (Phywe, No.990649), at temperature (298.15 ± 0.03) K.

The atmospheric pressure was measured with a mercury barometer (Prolabo: Fortin, No 02025008).

The experimental densities and refractive indices values 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 components at temperature 298.15 K.

Component	Chemical Formula	ρ(298.15 K)/g.cm^{-3}		n_D(298.15 K)	
		Expt.	Lit.	Expt.	Lit.
Water	H_2O	0.9971	0.9971 [40]	1.3325	1.3328 [40]
Ethanol	C_2H_5OH	0.7856	0.7851 [40]	1.3592	1.3594 [40]
2-Propanol	C_3H_7OH	0.7811	0.7813 [40]	1.3710	1.3752 [40]
Benzene	C_6H_6	0.8739	0.8736 [40]	1.4982	1.4979 [40]
Cyclohexane	C_6H_{12}	0.7741	0.7745 [41]	1.4243	1.4235 [41]
Toluene	C_7H_8	0.8670	0.8669 [42]	1.4959	1.4961 [42]
Di-isopropyl ether	$((CH_3)_2CH)_2O$	0.7192	0.7187 [7]	1.3661	1.3655 [7]
Fluorobenzene	C_6H_5F	1.0191	1.0189 [28]	1.4636	
1,4-Difluorobenzene	$C_6H_4F_2$	1.1631	1.1634 [33]	1.4785	
α,α,α-Trifluorotoluene	$C_7H_5F_3$	1.1820	1.1813 [40]	1.4124	1.4122 [40]
2,2,2-Trifluoroethanol	$CF_3\ CH_2OH$	1.3824	1.3818 [41]	1.2910	1.2910 [41]

3.2 Experimental Procedures

The solubility measurements (binodal curve) of the ternary solutions are determined visually by the titration [28,43-44] method in an equilibrium glass cell equiped with a magnetic bar and connected to a thermocryostat. [6,26] The temperature of the circulating water is controlled to ± 0.03 K by a cryothermostat (LAUDA, model: RC6CP-Edition 2000) and measured with a digital thermistor-thermometer (Cole-Parmer Instrument, model: 8502-16, thermistor: YSI-400) with precision better than ± 0.03 K. The glass equilibrium cell used in this work was built by SOMIVER-Thenia (Algeria). The scheme of the measuring cell is shown in figure (3.1).

For the determination of the mutual solubility data on the α-rich phase side, the titration method was applied. Accurately known masses of the three components forming a heterogeneous (turbid) solution, with component *A* being the dominant, were stirred continuously at the desired temperature, and the third component (titrant) was titrated progressively into the cell from a syringe, through septum of the injection arm, until the turbidity disappears, and amount of mass of the titrant was precisely recorded.

This end point corresponded to the equilibrated point of the solubility curve on the α-rich phase side.

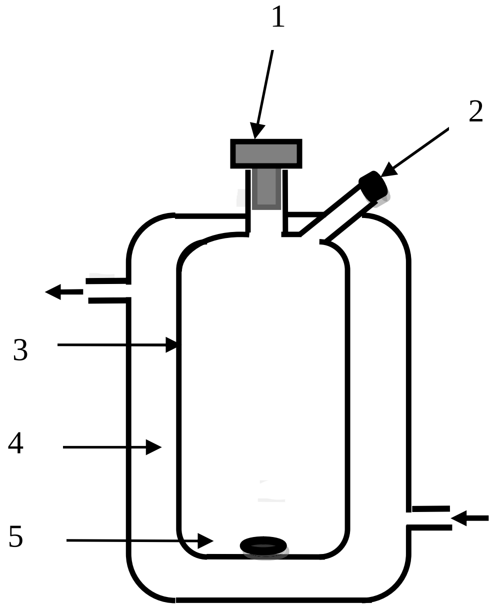


Figure (3.1): Scheme of the equilibrium cell made from Pyrex Glass:
1- stopper, 2- sample inlet (symptom), 3- measuring cell,
4- thermostated jacket, 5- magnetic bar.

For the β-rich phase side, the same measuring procedure was employed starting with larger mass of component *B* and quantities of known masses of components *A* and *C* to form turbid solutions. The end point of the solubility curve was attained by adding the titrating component progressively to the stirred heterogeneous solution until the turbidity disappeared. This end point corresponded to the equilibrated point of the solubility curve on the β-rich phase side.

During the titration, the visual inspection of the transition between the heterogeneous and homogeneous zones permits to obtain the phase mole fraction to ($x \pm 0.005$).[29]

In this work, the titrating solvent was either ethanol, or 2-propanol, or 2,2,2-trifluoroethanol, depending on the solution studied.

For the liquid-liquid equilibrium measurements, the feed solutions were vigorously stirred in stoppered ampoules for 5 h, and were then submerged in the cryostat bath which controls the temperature to ± 0.03 K and allowed to attain phase equilibrium for six days at the desired temperature until the solutions in bottles were clear.[29,45] Then, samples of the upper and lower liquid layers were collected and then analyzed by means of gas chromatography [30,31].

3.3 Liquid-Liquid Equilibrium Data Analysis

The samples from the two-phase mixture were analyzed by gas chromatography.[21,35]

The chromatograph was from Perkin Elmer, Model Clarus 500, and it was run by a computer using Total Chrom Workstation software.

To obtain quantitative results on liquid-liquid equilibrium, the gas chromatography was calibrated applying the internal standard method. The synthesized solutions corresponding to the binodal curve data for a measuring system at constant temperature were used to calibrate the gas chromatograph. The calibration equation for the chromatograph is:

$$\frac{s_i}{s_{st}} = c + c_0 \frac{n_i}{n_{st}}, \tag{3.1}$$

where s_i and s_st are the percentage peak area of the component *i* and of the internal standard, respectively, n_i and n_st are the number of moles of the component *i* and of the internal standard in the calibration mixture, respectively, *C* and C_O are the chromatograph constants.

For the cyclohexane systems, the mole fraction of the equilibrated liquid phases was analyzed with a thermal conductivity detector (TCD) and a packed column (carbopack β 80/100 mesh, 5% carbowax 20 M). The column temperature was 423 K, the injector block temperature was 513 K, and detector temperature was 473 K. Nitrogen was the carrier gas, and was flowing at 25 $\mathrm{ml.mn^{-1}}$, The retention times for the compounds were: 2.46 mn, for ethanol, 3.75 mn for 2-propanol, 6.52 mn for cyclohexane, and 9.29 mn for 2,2,2-trifluoroethanol.

For the aqueous solutions studied in this work, the mole fractions of components of ternary systems were determined by a thermal conductivity detector (TCD) and a packed column: Porapack, 0.6 m, Q80/100 Mesh: the column temperature was 423 K, injector block temperature was 513 K, and detector temperature was 473 K. Nitrogen was the carrier gas and was flowing at 20 $\mathrm{ml.mn^{-1}}$. The component mean-retention time were: 0.492 mn for water, 1.621 mn for ethanol, 2.840 mn for 2-propanol, and 15.645 mn for α,α,α-trifluorotoluene.

For quantitative chromatographic-data analysis, the standard component for this work was ethanol or 2-propanol

For the technical procedure, solubility and liquid-liquid equilibrium measurement for three tests systems were performed: (water + ethanol + benzene) at 303.15 K, and (water + ethanol + di-isopropyl ether) at 298.15 K. The experimental LLE data obtained for these test systems showed good agreement with literature values.[6,7,26]

For test system: water (1) + ethanol (2) + benzene (3) at 303.15 K, the observed critical mole fractions (x_{1}^{cs} = 0.295, x_2^{cs} = 0.371), which compare well with the literature values at 303.15 K: (x_1^{cs} = 0.282, x_2^{cs} = 0.365).[26]

In this work, the solubility and liquid-liquid equilibrium measurements of nine new ternary systems were studied at isothermal conditions and atmospheric pressure 101.2 kPa. The systems are: (solvent + 2,2,2-trifluorethanol + water), where solvent = toluene, or fluorobenzene, or α,α,α-trifluorotoluene; (1,4-difluorobenzene + ethanol + water) at 318.15 K; (cyclohexane + alcohol + 2,2,2-trifluorethanol) with alcohol = ethanol or 2-propanol at temperatures (288.15, 298.15, 308.15) K.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Experimental Results

The solubility and liquid-liquid equilibrium of ternary solutions were investigated at various temperatures and atmospheric pressure.

For liquid-liquid equilibrium measurements, the chromatograph was calibrated with solutions of known amount of substances containing three components forming the mixtures together with the standard. For a component *i*, the calibrating equation have the form:

$$\frac{s_i}{s_{st}} = c + c_0 \frac{n_i}{n_{st}}, \tag{4.1}$$

or, for a liquid phase φ :

$$y_i^{\varphi} = c_i^{\varphi} + c_o^{\varphi} n_i, \tag{4.2}$$

where n_i, s_i and n_{st}, s_{st} are the number of moles and the percentage peak area of the compound *i* and standard *st* in the calibrating mixture, respectively, c and c_0 are the chromatograph constants. The mole fractions of ternary solutions were then precisely determined for phases α and β of a liquid-liquid equilibrium system.

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

- **Test systems:**

4.2 Results for (water + ethanol + benzene)

In this work, to ensure a good accuracy of the measured solubility and liquid-liquid equilibrium data, we have checked our measuring techniques by carrying out a test system of water (1) + ethanol (2) + benzene (3) at 303.15 K. For chromatograph calibration the standard component was 2-propanol. The calibration points of the chromatograph are represented in Figures (4.2.1) by the fitting equations for ethanol:

water-rich phase: $y_2^{\alpha} = 0.291 + 0.251\,x^{\alpha}$, benzene-rich phase: $y_2^{\beta} = 0.936 + 0.241\,x^{\beta}$.

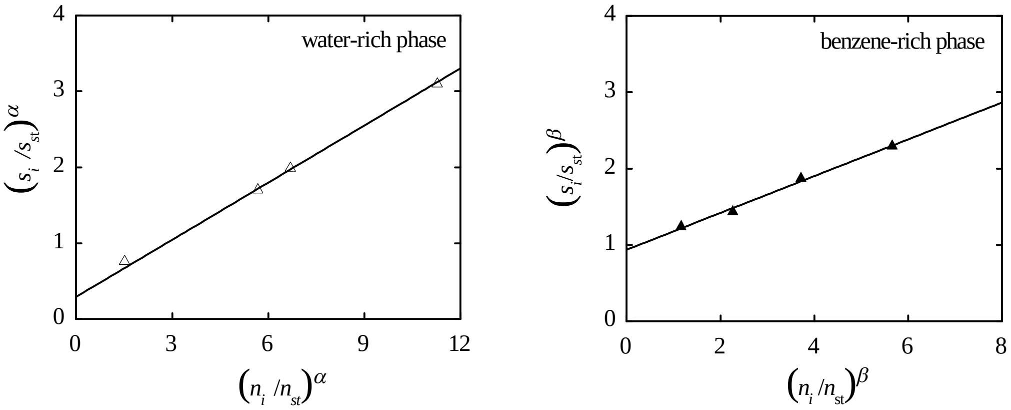


Figure (4.2.1): Chromatograph calibration for {water (1) + ethanol (2) + benzene(3)} at 303.15 K: (Δ, ▲), ethanol.

The solubility data were correlated by equation (2.31). The standard deviation $\sigma(x_i)$ of solubility measurements is estimated by the expression:[46]

$$\sigma(x_{\mathrm{i}}) = \left\{ \frac{\sum \left(x_i^{Expt.} - x_i^{Calc.}\right)^2}{n - 1} \right\}^{0.5} , \qquad (4.\ 3)$$

where x_i^{Expt} and $x_i^{Calc.}$ denote the experimental and correlated mole fraction of component *i*, in phase φ, *n* denotes data points.

The experimental solubility and fitting parameters are reported in Table (4.2.1), is shown in Figure (4.2.2). The liquid-liquid equilibrium values are given in Table (4.2.2).

The correlations of Hand and Othmer-Tobias are given in Table (4.2.3) and are shown in Figure (4.2.3). While distribution coefficient d_i,, and selectivity S values are outlined in Table (4.2.4), and are shown in Figure (4.2.4). The critical solution plait point of water (1) + ethanol (2) + benzene (3) at 303.15 K is: experimental value: $(x_1^{cs} = 0.295,\ x_2^{cs} = 0.371)$ and literature value: $(x_1^{\mathrm{cs}} = 0.282,\ x_2^{\mathrm{cs}} = 0.365\ )$.[26]

Table (4.2.1): Experimental solubility data for solutions of {water (1) + ethanol (2) + benzene (3)}at 303.15 K and 0.1MPa

x_1	x_2	x_3
0.7020	0.2730	0.0250
0.6460	0.3150	0.0390
0.5750	0.3430	0.0820
0.5030	0.3700	0.1270
0.4610	0.3850	0.1540
0.3660	0.3780	0.2560
0.3067	0.3641	0.3292
0.2778	0.3601	0.3621
0.2528	0.3506	0.3966
0.2297	0.3418	0.4285
0.2112	0.3303	0.4585
0.2360	0.3490	0.4150
0.1720	0.3020	0.5260
0.1530	0.3020	0.5450
0.1570	0.2880	0.5550
0.1310	0.2740	0.5950
0.0960	0.2420	0.6620
0.0850	0.2030	0.7120
0.0810	0.1940	0.7250
0.0530	0.1660	0.7810
0.0460	0.1380	0.8160
0.0310	0.1230	0.8460
0.0120	0.0530	0.9350

Equation: (2. 31)					
a	b	c	d	e	σ
0.0722	1.4699	-1.8672	0.7745	-0.4596	0.0002

Table (4.2.2): Experimental liquid-liquid equilibrium data and plait point for solutions of {water (1) + ethanol (2) + benzene (3)}at 303.15 K

Feed Solution		Water-Rich Phase		Benzene-Rich Phase	
x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
0.390	0.344	0.502	0.370	0.131	0.280
0.435	0.279	0.620	0.320	0.066	0.199
0.452	0.240	0.691	0.282	0.049	0.170
0.480	0.192	0.760	0.231	0.032	0.112
0.516	0.149	0.810	0.190	0.022	0.088
0.526	0.099	0.865	0.141	0.014	0.060
	x^{cs}	0.295	0.371	0.295	0.371

Table (4.2.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + benzene (3)} at 303.15 K

Hand: Equation (2.32)			Othmer -Tobias: Equation (2.33)		
A	B	R^2	A_1	B_1	R^2
-0.352	1.382	0.994	-0.342	1.254	0.995

Table (4.2.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) + ethanol (2) + benzene (3)}at 303.15 K

d_1	d_2	S
3.82	1.32	2.90
9.46	1.61	5.88
14.06	1.66	8.47
23.54	2.06	11.43
36.89	2.16	17.08
61.02	2.35	25.97

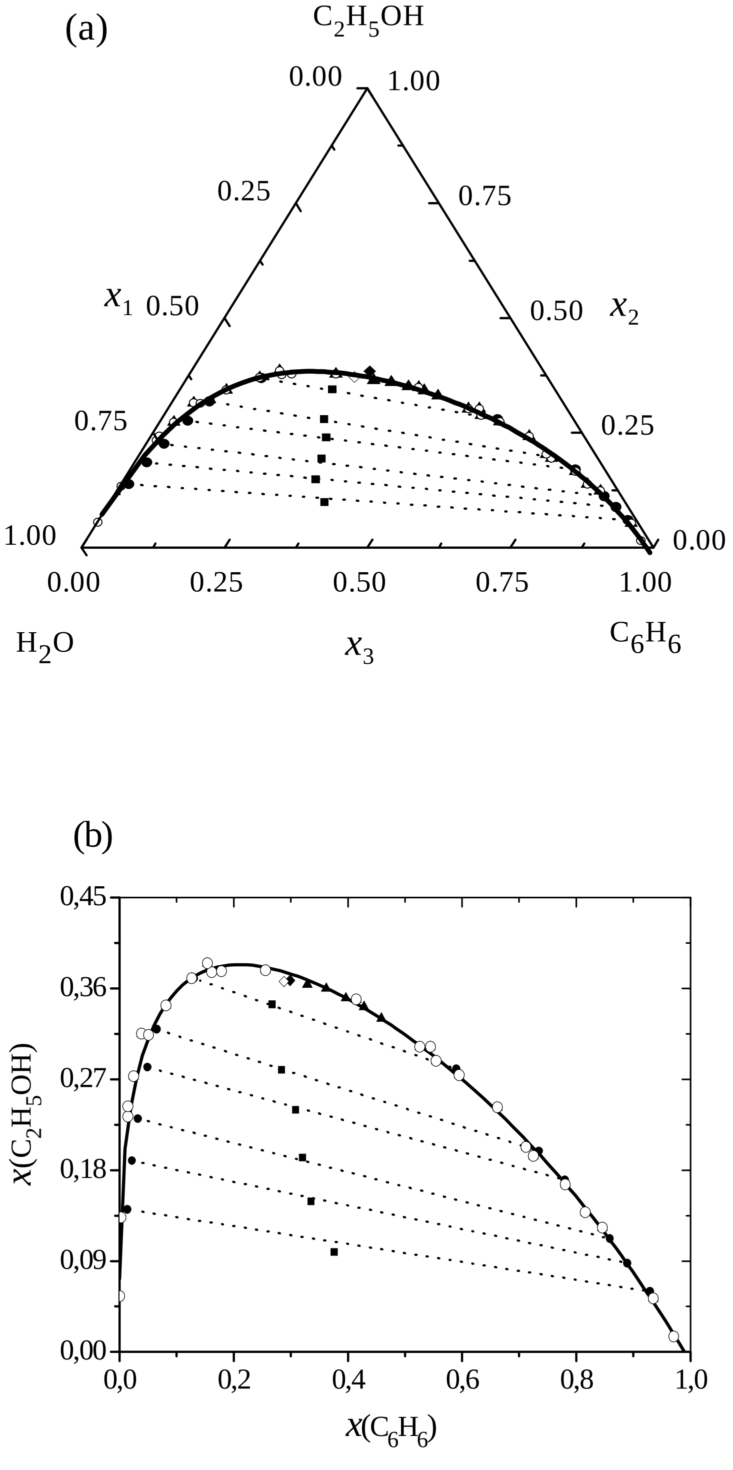


Figure (4.2.2): Solubility and liquid-liquid equilibrium data for solutions of (water + ethanol + benzene) at 303.15 K: ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line; — eq (2.31); ○, LLE literature point [26]: (a), ternary graph; (b), binary graph.

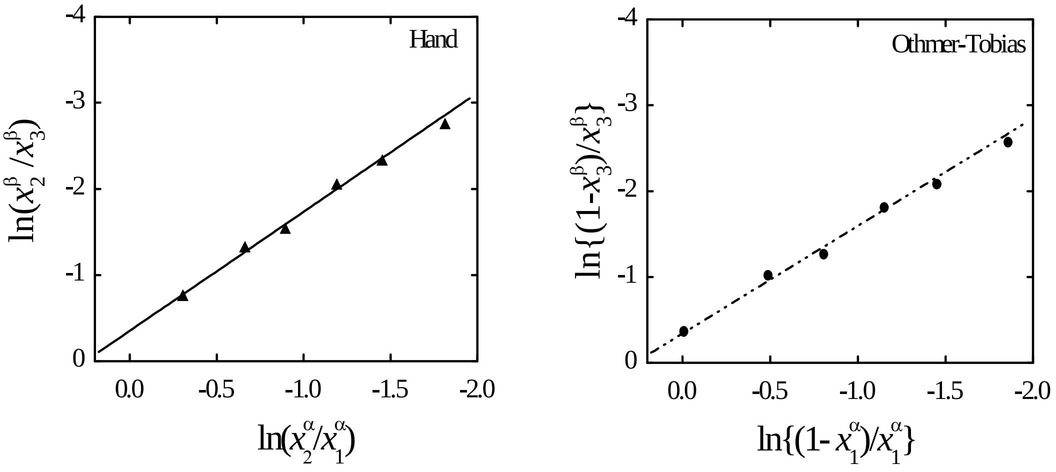


Figure (4.2.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + benzene (3)} at 303.15 K: —, eq (2.32); …, eq (2.33).

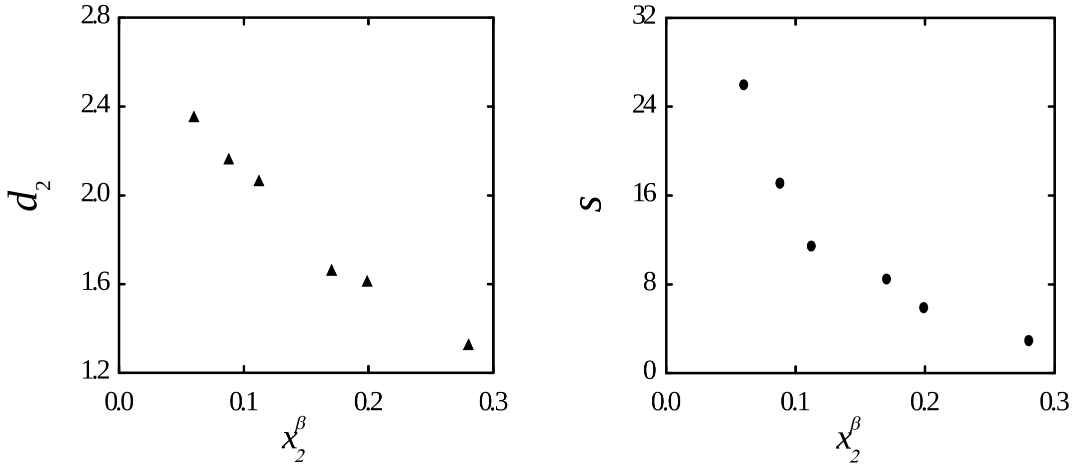


Figure (4.2.4): Distribution coefficient d_2 and selectivity S for solutions of {water (1) + ethanol (2) + benzene (3)} at 303.15 K.

4.3 Results for (water + ethanol + di-isopropyl ether)

The solubility and the liquid-liquid equilibrium of the water (1) + ethanol (2) + di-isopropyl ether (3) were investigated at 298.15 K and pressure 0.1 MPa. The experimental solubility and fitting parameters are reported in Table (4.3.1) and are shown in Figure (4.3.2).

For liquid-liquid equilibrium measurements, we have checked our measuring techniques by carrying out a test system, the chromatograph calibration was performed by 2-propanol as standard.

The calibration points of the chromatograph are represented in Figures (4.3.1) by the fitting equations for ethanol: $y_2^{\alpha} = 0.245 + 0.421\,x^{\beta}$ water-rich phase, di-isopropyl ether-rich phase: $y_2^{\beta} = 0.269 + 0.433\,x^{\beta}$

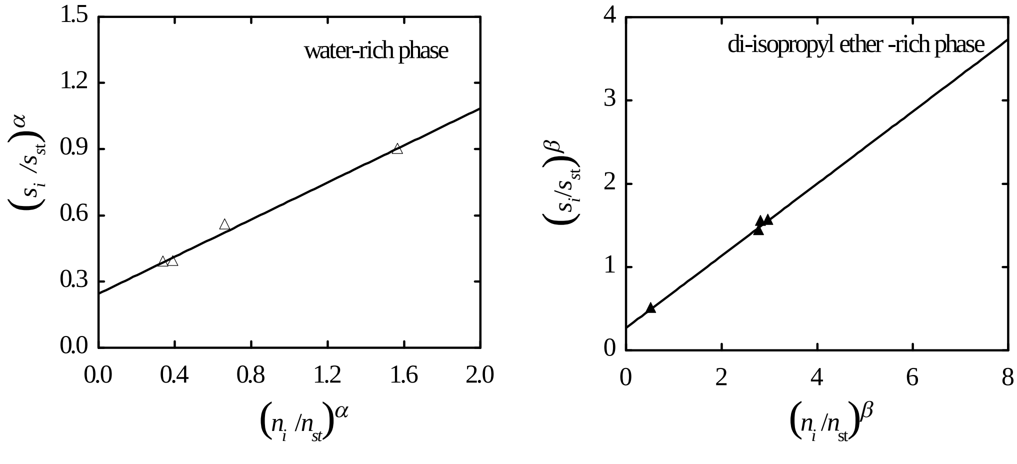


Figure (4.3.1): Chromatograph calibration for {(water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K: (Δ, ▲), ethanol.

The liquid-liquid equilibrium values are given in Table (4.3.2). The correlations of Hand and Othmer-Tobias are given in Table (4.3.3) and shown in Figure (4.3.3). While distribution coefficient d_i, selectivity S values are outlined in Table (4.3.4), and are shown in Figure (4.3.4). The plait point of water (1) + ethanol (2) + di-isopropyl ether (3) at 298.15 K is: $(x_1^{cs} = 0.177,\ x_2^{cs} = 0.335)$.

Table (4.3.1): Experimental solubility data for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K and 0.1 MPa

x_1	x_2	x_3
0.0957	0.1176	0.7865
0.1165	0.1625	0.7209
0.1694	0.2276	0.6030
0.2076	0.2641	0.5283
0.2587	0.3063	0.4350
0.2996	0.3301	0.3703
0.3313	0.3417	0.3271
0.3599	0.3476	0.2925
0.3941	0.3444	0.2615
0.2837	0.4747	0.2416
0.2488	0.4722	0.2790
0.2002	0.4517	0.3481
0.4225	0.3440	0.2335
0.4473	0.3403	0.2124
0.5052	0.3265	0.1683
0.5404	0.3180	0.1417
0.5765	0.3017	0.1218
0.6358	0.2749	0.0893
0.7139	0.2352	0.0509
0.7612	0.2115	0.0274
0.7718	0.2060	0.0222

Equation: (2.31)			
a	b	c	σ
0.0323	1.2804	-1.3245	0.0002

Table (4.3.2): Experimental liquid-liquid equilibrium data and plait point for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K

Feed Solution		Water-Rich Phase		Di-isopropyl ether-Rich Phase	
x_1	x_2	x_1^α	x_2^α	x_1^β	x_2^β
0.286	0.205	0.868	0.129	0.207	0.281
0.320	0.176	0.881	0.116	0.186	0.243
0.343	0.131	0.891	0.109	0.138	0.180
0.360	0.092	0.918	0.080	0.085	0.094
0.367	0.061	0.941	0.057	0.071	0.065
x^{cs}		0.177	0.335	0.177	0.335

Table (4.3.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K

Hand: Equation (2.32)			Othmer -Tobias: Equation (2.33)		
A	B	R^2	A_1	B_1	R^2
3.356	2.153	0.983	1.685	1.299	0.983

Table (4.3.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K

d_1	d_2	S
4.19	0.46	9.14
4.74	0.48	9.92
6.45	0.61	10.65
10.81	0.85	12.70
13.21	0.88	14.97

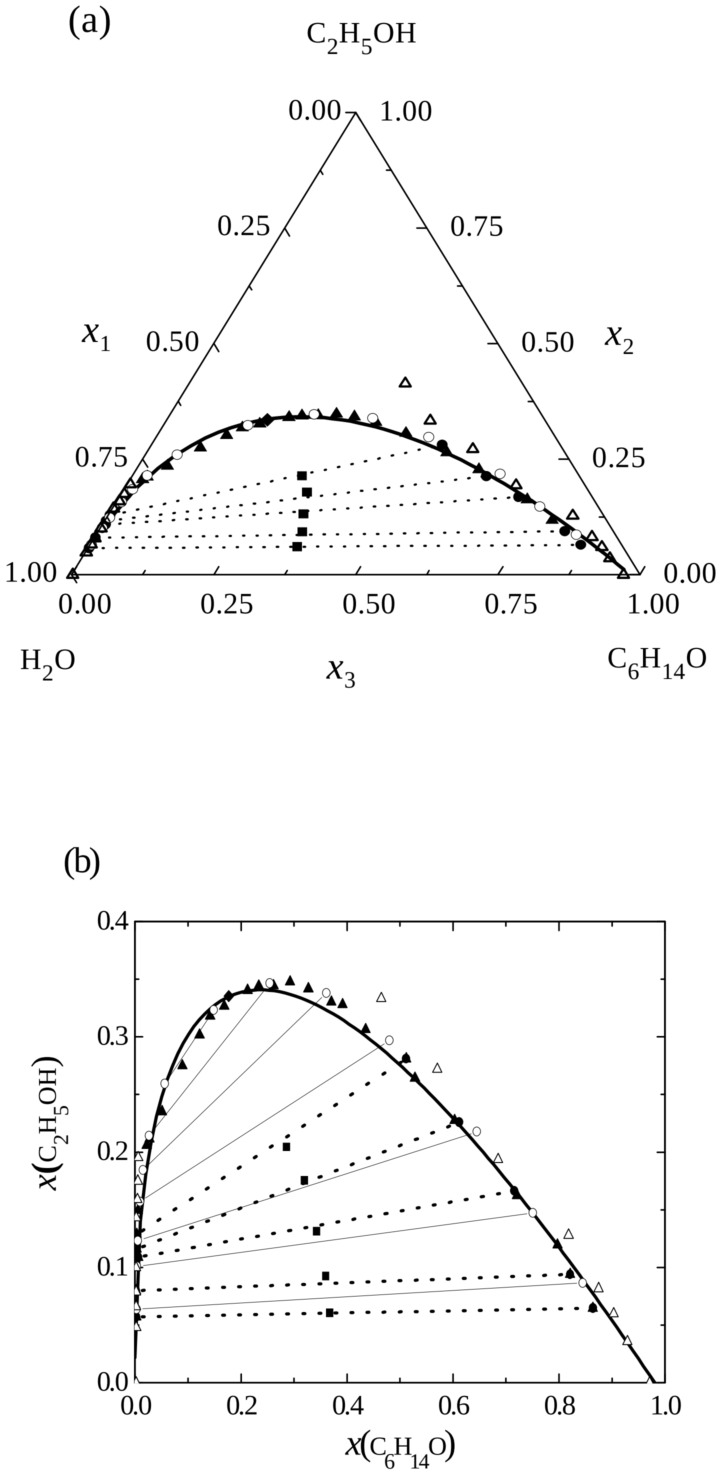


Figure (4.3.2): Solubility and liquid-liquid equilibrium data for solutions of (water + ethanol + di-isopropyl ether) at 298.15 K. ▲, solubility; ■, feed solution; ●, LLE; ○, LLE literature[6]; Δ, literature[7]; ♦, plait point; …, tie line: (a), ternary graph; (b), binary graph.

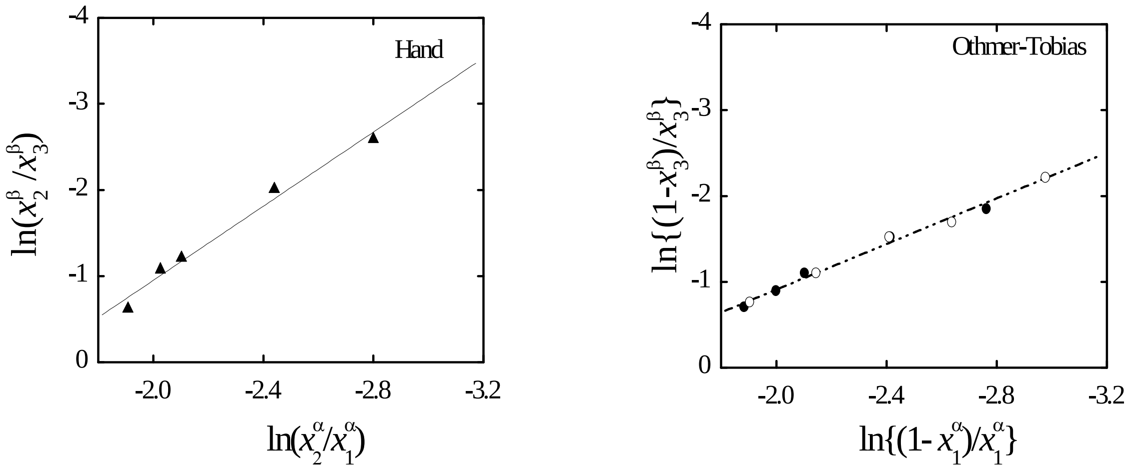


Figure (4.3.3): Correlation of the liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)) at 298.15 K: —, eq (2.31); ---, eq (2.32); …, eq (2.32) from literature.[6]

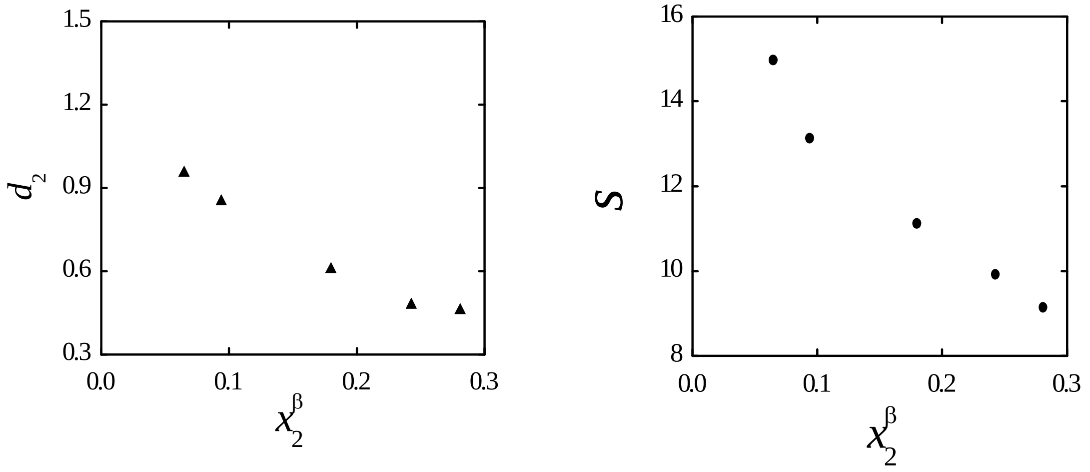


Figure (4.3.4): Distribution coefficient d_2 and selectivity S for solutions of {water (1) + ethanol (2) + di-isopropyl ether (3)} at 298.15 K.

- **New systems:**

4.4 Results for (water + 2,2,2-trifluoroethanol + fluorobenzene)

The solubility and the liquid-liquid equilibrium of the water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3) were investigated at 298.15 K and pressure 0.1 MPa. The experimental solubility and fitting parameters are reported in Table (4.4.1) and are shown in Figure (4.4.2). For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by ethanol as standard.

The calibration points of the chromatograph are represented in Figure (4.4.1) by the fitting equations for 2,2,2,-trifluoroethanol: water-rich phase: $y_2^{\alpha} = 0.654 + 0.298\,x^{\alpha}$, fluorobenzene-rich phase: $y_2^{\beta} = 0.1982 + 0.436\,x^{\beta}$.

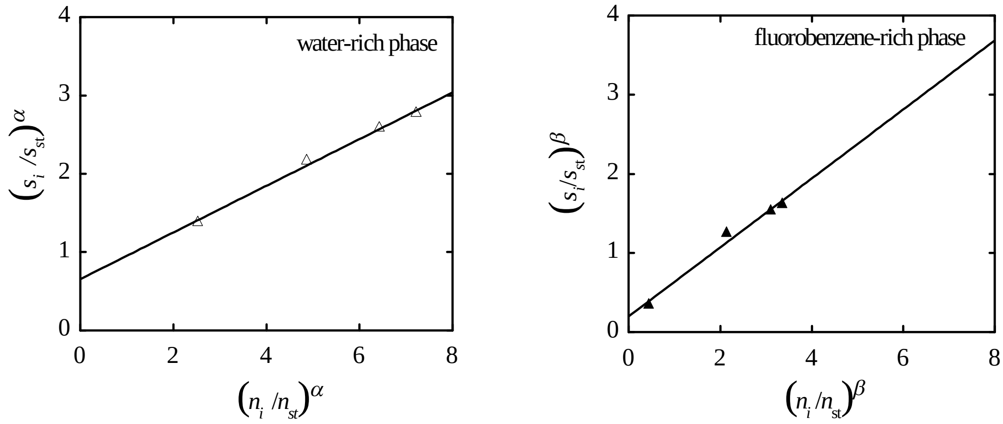


Figure (4.4.1): Chromatograph calibration for {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K: (Δ, ▲), 2,2,2-trifluoroethanol.

The liquid-liquid equilibrium values are given in Table (4.4.2). The correlations of Hand and Othmer-Tobias are given in Table (4.4.3) and in Figure (4.4.3). The values of distribution coefficient d_i and selectivity S are given in Table (4.4.4), and are shown in Figure (4.4.4). The critical solution plait point of water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3) at 298.15 K is: $(x_1^{cs} = 0.286,\ x_2^{cs} = 0.365)$.

Table (4.4.1): Experimental solubility data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K and 0.1MPa

x_1	x_2	x_3
0.9099	0.0872	0.003
0.8731	0.1216	0.0053
0.8000	0.1865	0.0135
0.7700	0.2099	0.0201
0.7020	0.2617	0.0363
0.6493	0.3009	0.0498
0.5875	0.3343	0.0782
0.5568	0.3512	0.0920
0.5247	0.3650	0.1103
0.4796	0.3801	0.1403
0.4401	0.3862	0.1737
0.4114	0.3877	0.2009
0.4796	0.4517	0.3481
0.4401	0.3862	0.1737
0.4114	0.3877	0.2009
0.3572	0.3817	0.2611
0.3252	0.3754	0.2994
0.3084	0.3723	0.3193
0.2683	0.3491	0.3806
0.2372	0.3351	0.4277
0.2106	0.3189	0.4705
0.1867	0.3021	0.5112
0.1381	0.2603	0.6016

Equation: (2.31)

a	*b*	*c*	*d*	*e*	σ
-0.0537	2.1671	-2.9022	1.4524	-0.6646	0.0003

Table (4.4.2): Experimental liquid-liquid equilibrium and plait point data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K

Feed Solution		Water-Rich Phase		Fluorobenzene -Rich Phase	
x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
0.465	0.293	0.604	0.328	0.097	0.223
0.508	0.255	0.670	0.280	0.061	0.183
0.539	0.208	0.731	0.235	0.037	0.138
0.562	0.181	0.754	0.215	0.029	0.103
0.584	0.151	0.792	0.191	0.021	0.084
0.635	0.082	0.973	0.117	0.013	0.003
x^{cs}		0.286	0.365	0.286	0.365

Table (4.4.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K

Hand: Equation (2.32)			Othmer -Tobias: Equation (2.33)		
A	B	R^2	A_1	B_1	R^2
-0.123	1.538	0.996	-0.325	1.262	0.994

Table (4.4.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K

d_1	d_2	S
6.22	1.47	4.23
10.99	1.53	7.17
20.03	1.70	11.76
25.73	2.09	12.33
38.64	2.28	16.94
173.71	8.43	20.61

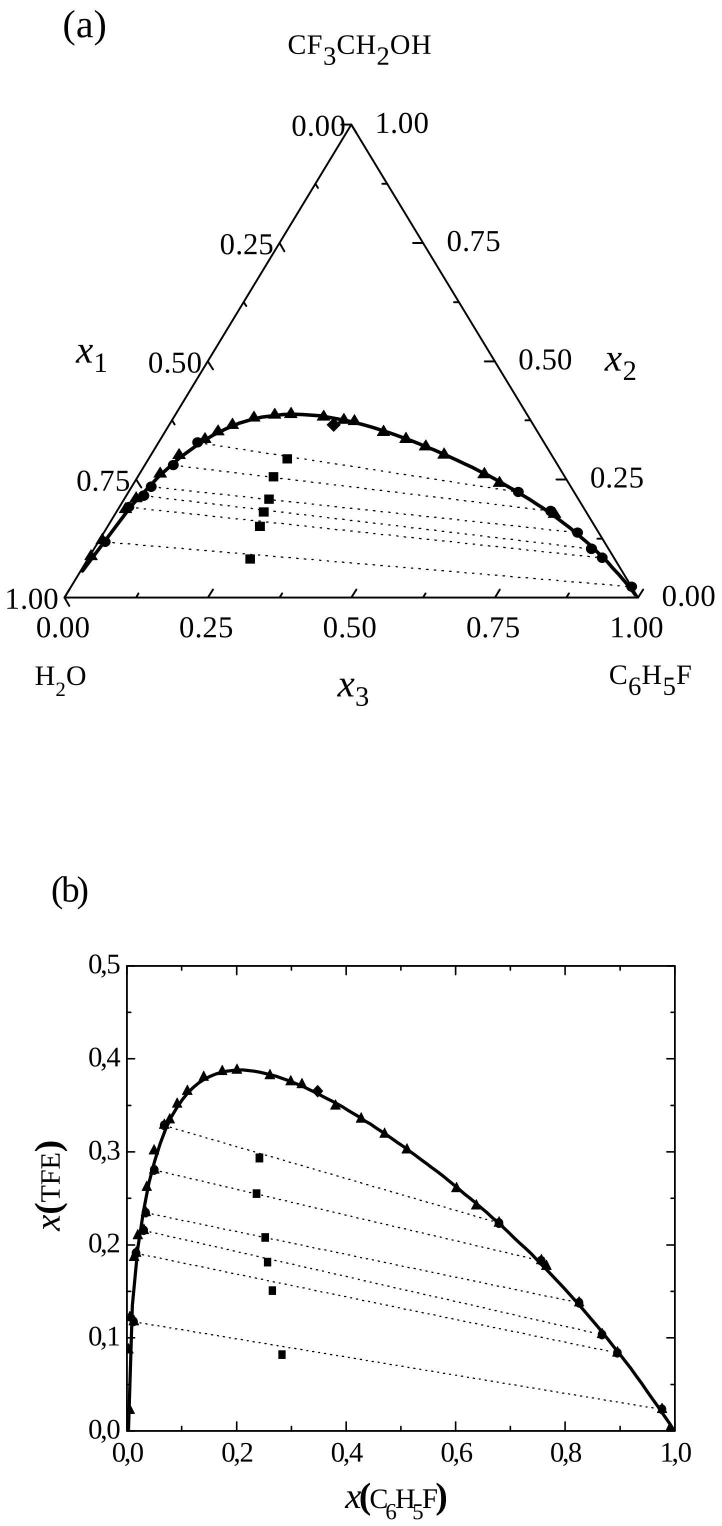


Figure (4.4.2): Solubility and liquid-liquid equilibrium data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K: ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line, —, eq (2.31): (a), ternary graph; (b), binary graph.

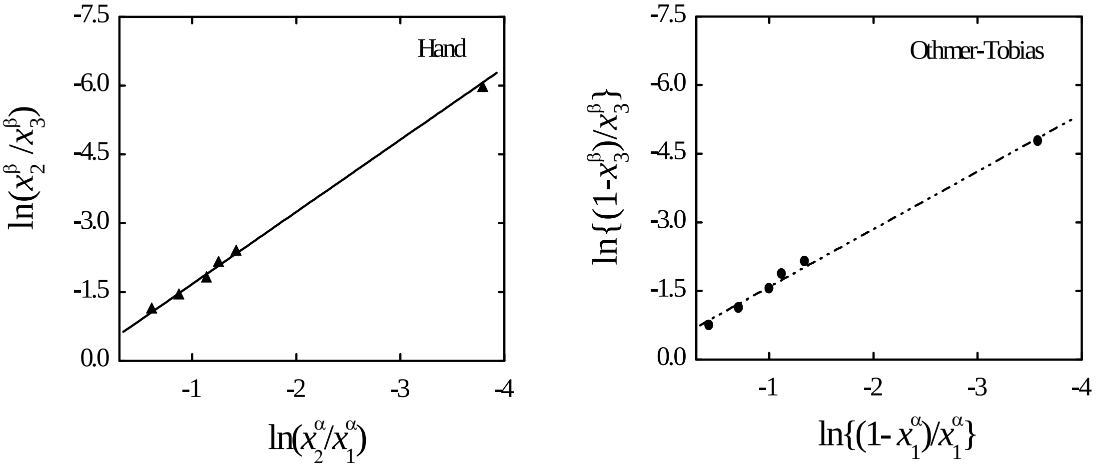


Figure (4.4.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 *K*: : —, eq (2.31); …, eq (2.32).

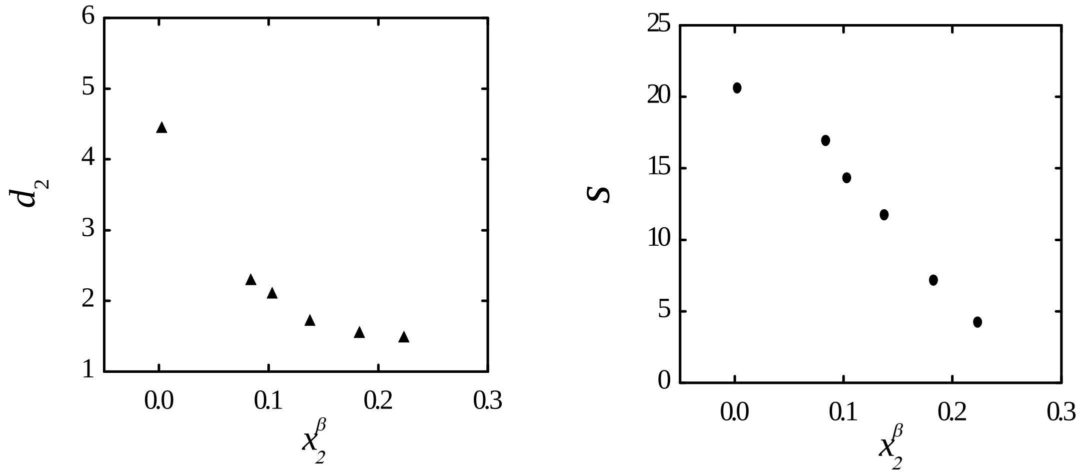


Figure (4.4.4): Distribution coefficient d_2 and selectivity *S* for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + fluorobenzene (3)} at 298.15 K.

4.5 Results for (water + 2,2,2-trifluoroethanol + toluene)

The solubility and the liquid-liquid equilibrium of the water (1) + 2,2,2-trifluoroethanol (2) + toluene (3) were investigated at 298.15 K and pressure 0.1 MPa. The experimental solubility and fitting parameters are reported in Table (4.5.1) and are shown in Figure (4.5.2).

For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by ethanol as standard.

The calibration points of the chromatograph are represented in Figure (4.5.1) by the fitting equations for 2,2,2-trifluoroethanol: water-rich phase: $y_2^{\alpha} = 0.546 + 0.314\, x^{\alpha}$, toluene-rich phase: $y_2^{\beta} = 0.175 + 0.377\, x^{\beta}$

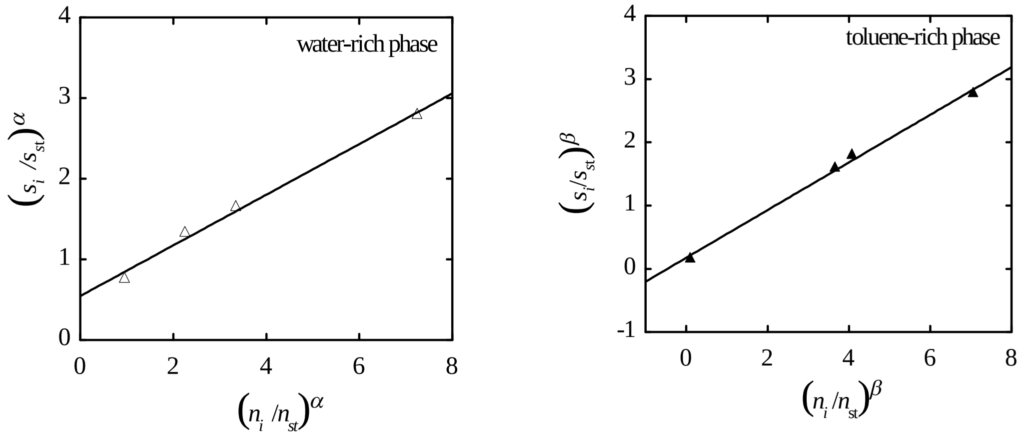


Figure (4.5.1): Chromatograph calibration for{water (1) + 2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K: (Δ, ▲), 2,2,2-trifluoroethanol.

The liquid-liquid equilibrium values are given in Table (4.5.2). The correlations of Hand and Othmer-Tobias are given in Table (4.5.3) and shown in Figure (4.5.3). While distribution coefficient d_i, selectivity S values are outlined in Table (4.5.4), and are shown in Figure (4.5.4). The plait point of water (1) + 2,2,2-trifluoroethanol (2) + toluene (3) at 298.15 K is: $(x_1^{cs} = 0.243,\ x_2^{cs} = 0.541)$.

Table (4.5.1): Experimental solubility data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K and 0.1 MPa

x_1	x_2	x_3
0.6025	0.3741	0.0234
0.5879	0.3841	0.0280
0.5655	0.3995	0.0350
0.5286	0.4248	0.0465
0.4544	0.4760	0.0696
0.3913	0.5122	0.0965
0.3327	0.5396	0.1278
0.2978	0.5542	0.1480
0.3012	0.5492	0.1496
0.2837	0.4747	0.2416
0.2488	0.4722	0.2790
0.2002	0.4517	0.3481
0.2641	0.5543	0.1816
0.2111	0.5437	0.2352
0.1819	0.5236	0.2945
0.1584	0.4917	0.3497
0.1319	0.4259	0.4422
0.1165	0.3919	0.4916
0.1018	0.3543	0.5440
0.0800	0.2552	0.6646

Equation: (2.31)

a	b	c	d	e	σ
0.0703	2.3347	-2.9276	0.5167	-	0.0004

Table (4.5.2): Experimental liquid-liquid equilibrium data and plait point for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K

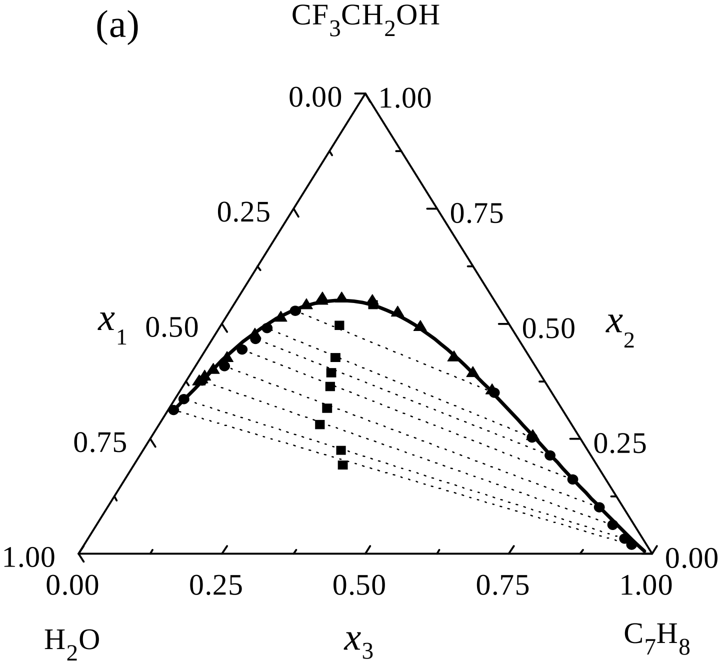
Feed solution		Water-Rich Phase		Toluene-Rich Phase	
x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
0.207	0.496	0.358	0.528	0.100	0.349
0.235	0.426	0.425	0.490	0.084	0.258
0.257	0.363	0.457	0.467	0.071	0.215
0.276	0.316	0.492	0.444	0.057	0.161
0.281	0.281	0.541	0.408	0.041	0.101
0.244	0.393	0.596	0.376	0.037	0.063
0.345	0.225	0.648	0.336	0.031	0.033
0.368	0.194	0.677	0.312	0.026	0.019
x^{cs}		0.243	0.541	0.243	0.541

Table (4.5.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) +2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K

Hand: Equation (2.32)			Othmer -Tobias: Equation (2.33)		
A	B	R^2	A_1	B_1	R^2
-1.331	2.970	0.997	-1.371	2.174	0.995

Table (4.5.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) +2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K

d_1	d_2	S
3.58	1.51	2.37
5.05	1.90	2.66
6.02	2.18	2.76
8.28	2.75	3.00
13.94	4.04	3.45
22.75	5.97	3.81
42.31	10.17	4.15
75.29	16.44	4.58



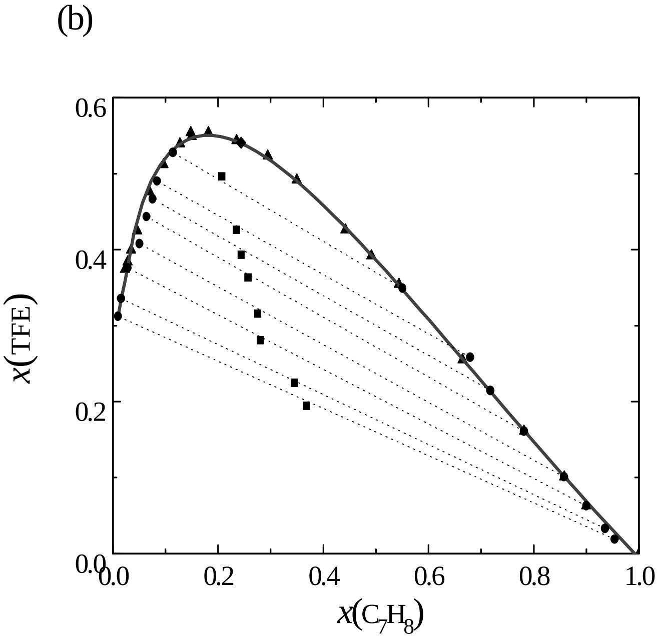


Figure (4.5.2): Solubility and liquid-liquid equilibrium data for solutions of (water + 2,2,2-trifluoroethanol + toluene) at 298.15 K: ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line: (a), ternary graph; (b), binary graph.

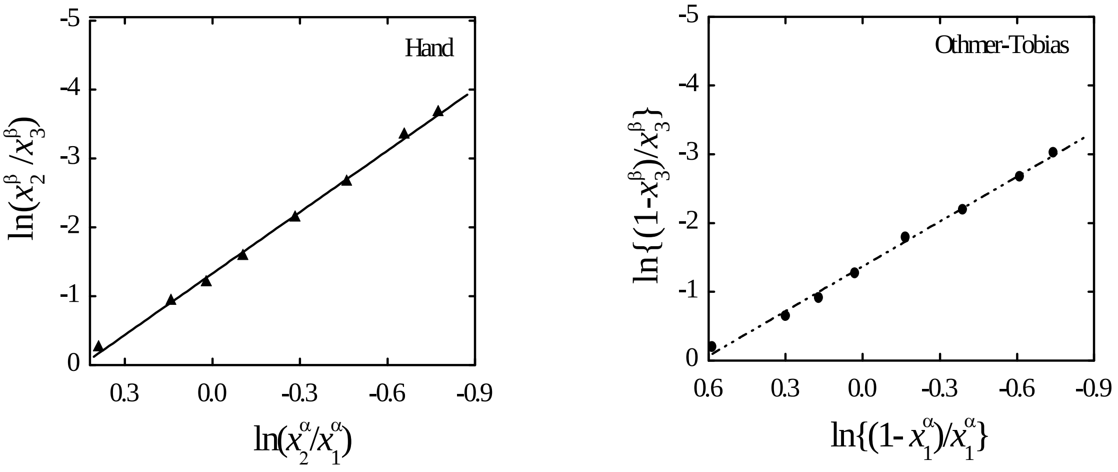


Figure (4.5.3): Correlation of the liquid-liquid equilibrium data for solutions of {(water (1) +2, 2, 2-trifluoroethanol (2) + toluene (3)} at 298.15 *K*: —, eq (2.31); …, eq (2.32).

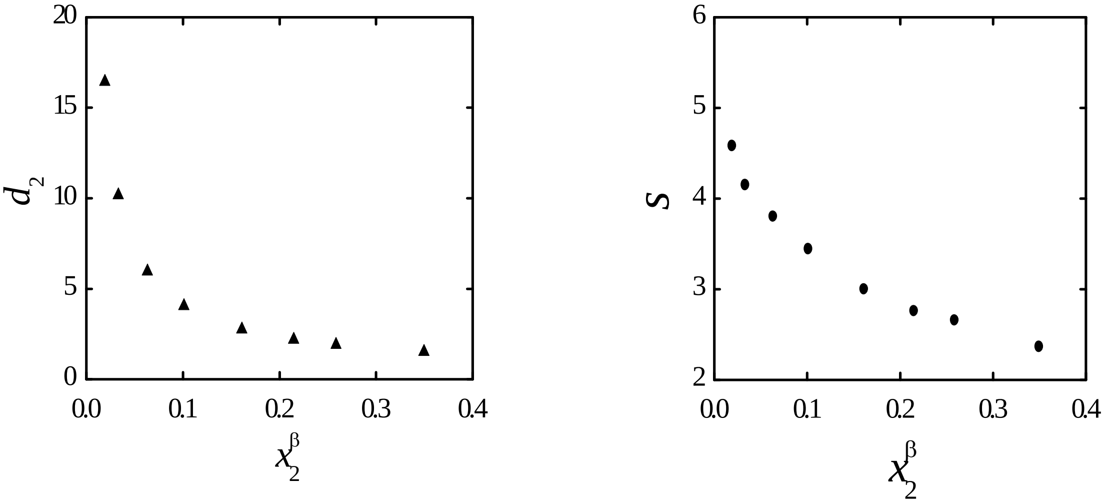


Figure (4.5.4): Distribution coefficient d_2 and selectivity S for solutions of {water (1) +2,2,2-trifluoroethanol (2) + toluene (3)} at 298.15 K.

4.6 Results for (water + 2,2,2-trifluoroethanol + α,α,α-trifluorotoluene)

The solubility and the liquid-liquid equilibrium of the (water + 2,2,2-trifluoroethanol + α,α,α-trifluorotoluene) were investigated at 298.15 K and pressure 0.1 MPa. The experimental solubility and fitting parameters are reported in Table (4.6.1) and are shown in Figure (4.6.2). For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by ethanol as standard.

The calibration points of the chromatograph are represented in Figure (4.6.1) by the fitting equations for trifluoroethanol: water-rich phase: $y_2^\alpha = 0.796 + 0.203\, x^\alpha$**,** and trifluorotoluene-rich phase: $y_2^\beta = 0.419 + 0.432\, x^\beta$

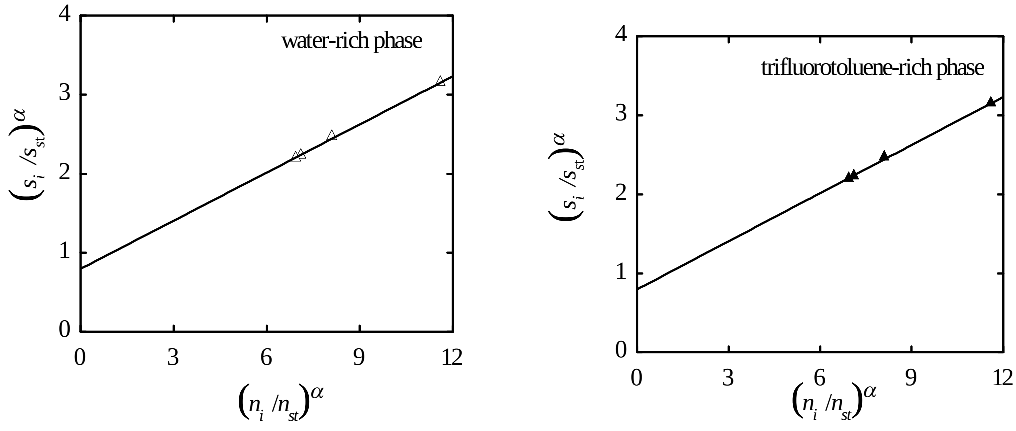


Figure (4.6.1): Chromatograph calibration for {water (1) + 2,2,2-trifluoroethanol (2)+ α,α,α-trifluorotoluene (3)} at 298.15 K: (Δ, ▲), 2,2,2-trifluoroethanol.

The liquid-liquid equilibrium values are given in Table (4.6.2). The correlations of Hand and Othmer-Tobias are given in Table (4.6.3) and shown in Figure (4.6.3). While distribution coefficient d_i, selectivity S values are outlined in Table (4.6.4) and in Figure (4.3.4). The critical solution plait point of (water + 2,2,2-trifluoroethanol + α,α,α-trifluorotoluene) at 298.15 K is: $(x_1^{cs} = 0.296,\ x_2^{cs} = 0.396)$.

Table (4.6.1): Experimental solubility data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K and 0.1 MPa

x_1	x_2	x_3
0.7755	0.2141	0.0104
0.6973	0.2808	0.0219
0.6409	0.3273	0.0318
0.5892	0.3609	0.0499
0.5224	0.3955	0.0821
0.4858	0.4089	0.1053
0.4643	0.4149	0.1208
0.4381	0.4188	0.1431
0.4234	0.4198	0.1568
0.4090	0.4185	0.1725
0.3884	0.4151	0.1965
0.3676	0.4093	0.2231
0.4796	0.4517	0.3481
0.3884	0.4151	0.1965
0.3676	0.4093	0.2231
0.3387	0.4033	0.2580
0.2998	0.3887	0.3115
0.2760	0.3763	0.3477
0.2570	0.3650	0.3780
0.2312	0.3504	0.4184
0.2058	0.3286	0.4656
0.1602	0.2833	0.5565
0.1287	0.2607	0.6106
0.0985	0.2272	0.6743

Equation: (2.31)

a	b	c	σ
0.1184	1.2884	-1.4062	0.00001

Table (4.6.2): Experimental liquid-liquid equilibrium data and plait point for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K

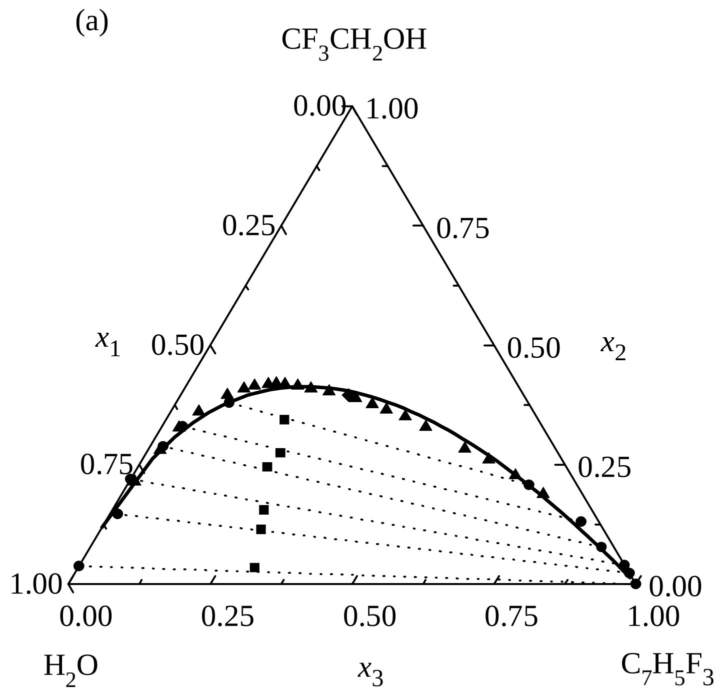
Feed Solution		Water-Rich Phase		Trifluorotoluene-Rich Phase	
x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
0.447	0.344	0.358	0.380	0.085	0.208
0.488	0.275	0.425	0.330	0.031	0.131
0.578	0.155	0.457	0.288	0.022	0.077
0.527	0.245	0.492	0.220	0.010	0.040
0.654	0.034	0.541	0.147	0.009	0.023
0.603	0.114	0.596	0.038	0.007	0.001
x^{cs}		0.296	0.396	0.296	0.396

Table (4.6.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K

Hand: eq (2.32)			Othmer-Tobias: eq (2.33)		
A	B	R^2	A_1	B_1	R^2
-0.7451	1.7984	0.995	-0.6718	1.9022	0.996

Table (4.6.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K

d_1	d_2	S
6.23	1.83	3.41
20.50	2.53	8.10
38.61	3.73	10.35
78.05	5.50	14.19
93.27	6.41	14.55



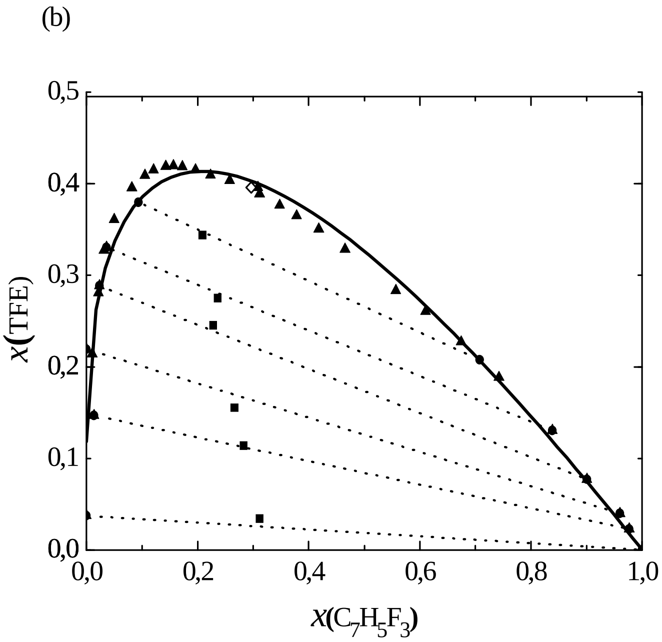


Figure (4.6.2): Solubility and liquid-liquid equilibrium data for solutions of (water + 2,2,2-trifluoroethanol + α,α,α-trifluorotoluene) at 298.15 K: ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line: (a), ternary graph; (b), binary graph.

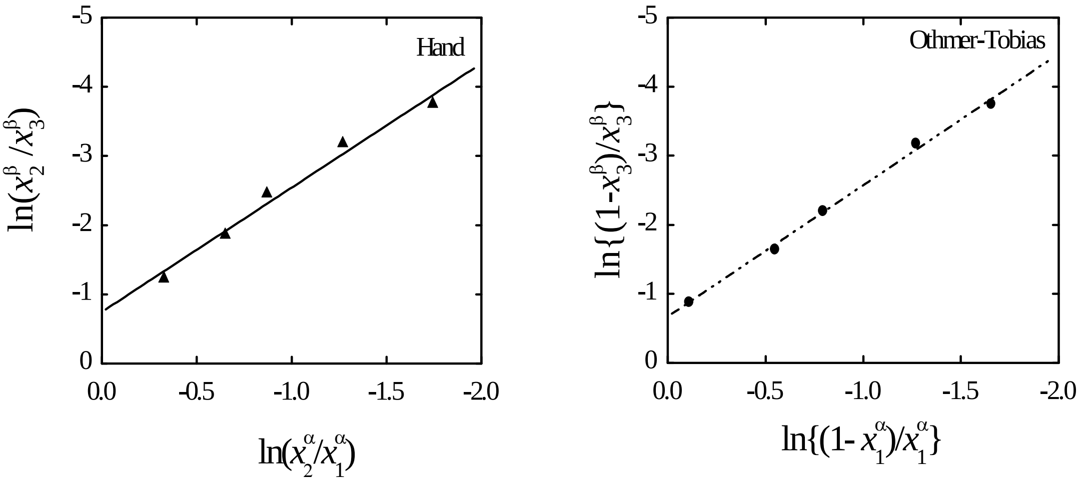


Figure (4.6.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K: —, eq (2.31); .., eq (2.32).

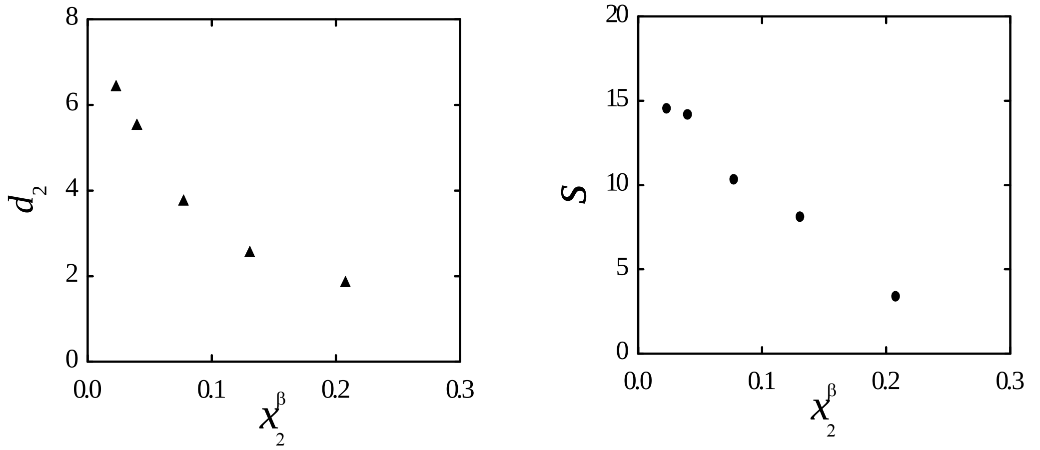


Figure (4.6.4): Distribution coefficient d_2 and selectivity S for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + α,α,α-trifluorotoluene (3)} at 298.15 K.

4.7 Results for (water + ethanol + 1,4-difluorobenzene)

The solubility and the liquid-liquid equilibrium of the water (1) + ethanol (2) + 1,4-difluorobenzene (3) were investigated at 318.15 K and pressure 0.1 MPa. The experimental solubility and fitting parameters are reported in Table (4.7.1) and are shown in Figure (4.7.2). For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by 2-propanol as standard.

The calibration points of the chromatograph are represented in Figure (4.7.1) by the fitting equations for ethanol:

water-rich phase: $y_2^{\alpha} = 0.291 + 0.250\,x^{\alpha}$, difluorobenzene-rich phase: $y_2^{\beta} = 0.936 + 0.241\,x^{\beta}$

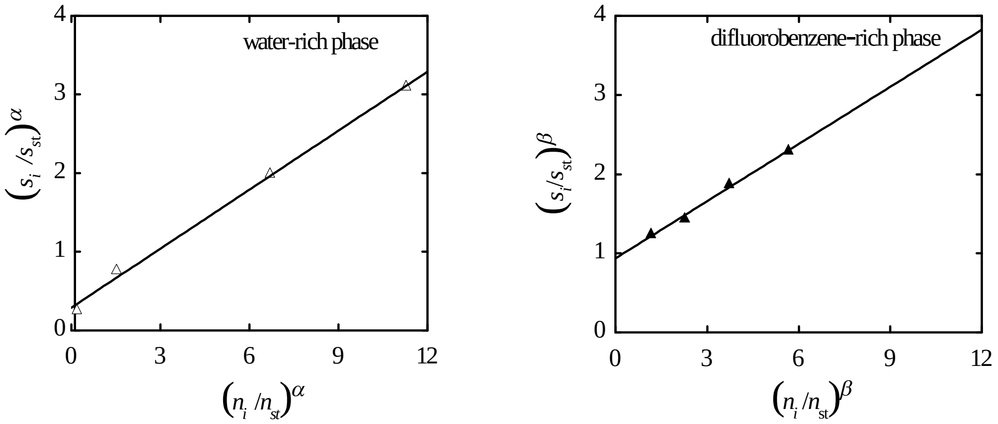


Figure (4.7.1): Chromatograph calibration for {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 318.15 K: (Δ, ▲), ethanol.

The liquid-liquid equilibrium values are given in Table (4.7.2). The correlations of Hand and Othmer-Tobias are given in Table (4.7.3) and are shown in Figure (4.7.3). While distribution coefficient d_i, selectivity S values are outlined in Table (4.7.4), and are shown in Figure (4.7.4). The plait point of water (1) + ethanol (2) + 1,4-difluorobenzene (3) at 298.15 K is: $(x_1^{cs} = 0.352,\ x_2^{cs} = 0.372)$.

Table (4.7.1): Experimental solubility data for solutions of {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 318.15 K and 0.1 MPa

x_1	x_2	x_3
0.7755	0.2141	0.0104
0.6973	0.2808	0.0219
0.6409	0.3273	0.0318
0.5892	0.3609	0.0499
0.5224	0.3955	0.0821
0.4858	0.4089	0.1053
0.4643	0.4149	0.1208
0.4381	0.4188	0.1431
0.4234	0.4198	0.1568
0.4090	0.4185	0.1725
0.3884	0.4151	0.1965
0.3676	0.4093	0.2231
0.3387	0.4033	0.2580
0.2998	0.3887	0.3115
0.2760	0.3763	0.3477
0.2570	0.3650	0.3780
0.2312	0.3504	0.4184
0.2058	0.3286	0.4656
0.1602	0.2833	0.5565
0.1287	0.2607	0.6106
0.0985	0.2272	0.6743
0.0690	0.1885	0.7425
0.0534	0.1655	0.7811

Equation: (2.31)			
a	b	c	σ
0.0464	1.4136	-1.4512	0.0002

Table (4.7.2): Experimental liquid-liquid equilibrium data and plait point for solutions of {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 318.15 K

Feed Solution		Water-Rich Phase		Diflluorobenzene-Rich Phase	
x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
0.504	0.286	0.577	0.361	0.119	0.263
0.524	0.246	0.632	0.316	0.054	0.203
0.560	0.208	0.688	0.272	0.044	0.162
0.584	0.151	0.730	0.243	0.027	0.127
0.616	0.105	0.796	0.187	0.016	0.092
0.647	0.081	0.866	0.129	0.007	0.026
0.464	0.329	0.881	0.110	0.008	0.020
	x^{CS}	0.352	0.372	0.352	0.372

Table (4.7.3): Correlation liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 318.15 K

Hand: Equation (2.32)			Othmer -Tobias: Equation (2.33)		
A	B	R^2	A_1	B_1	R^2
0.066	1.892	0.995	-0.080	1.717	0.997

Table (4.7.4): Distribution coefficient d_i and selectivity S for solutions of {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 298.15 K

d_1	d_2	S
4.62	1.35	3.43
11.63	1.56	7.46
15.76	1.67	9.42
27.34	1.92	14.31
43.64	2.51	17.36
117.53	4.94	23.78
139.32	5.47	25.49

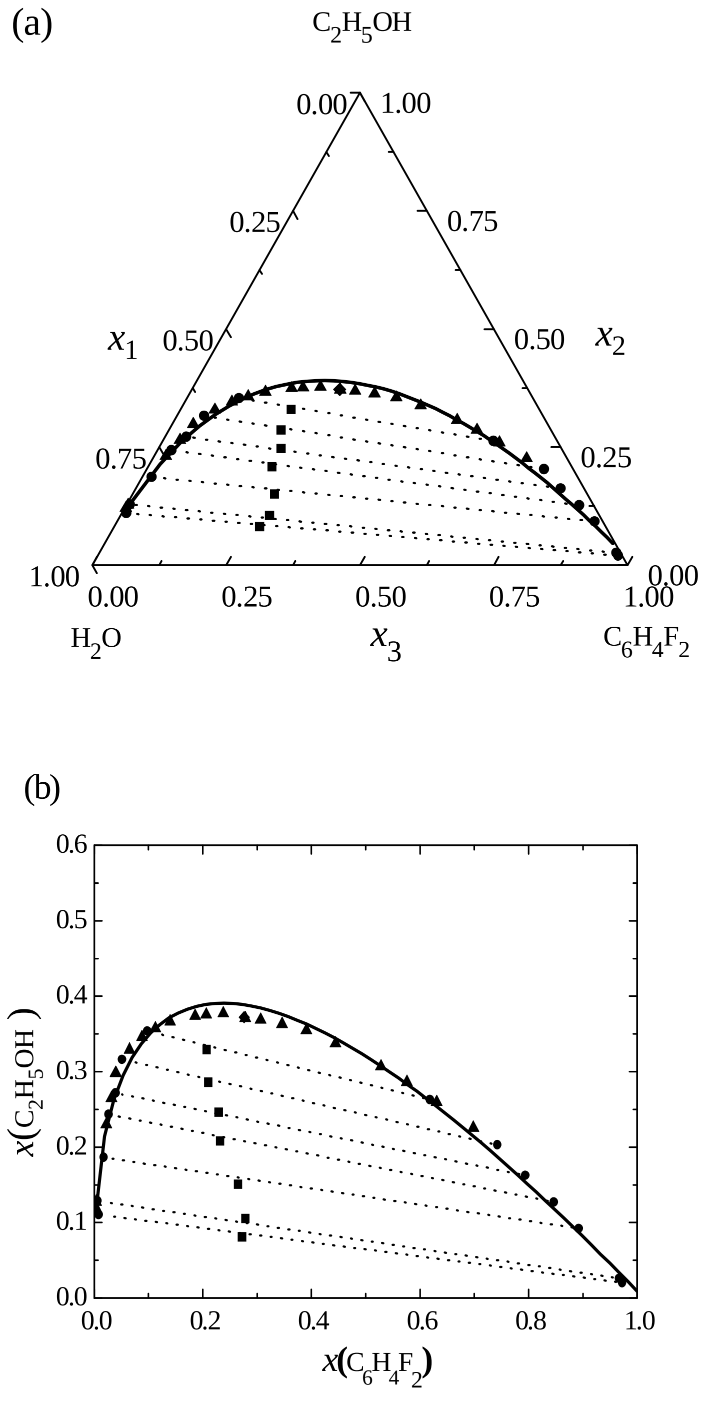


Figure (4.7.2): Solubility and liquid-liquid equilibrium data for solutions of (water + ethanol + 1,4-difluorobenzene) at 298.15 K. ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line: (a), ternary graph; (b), binary graph.

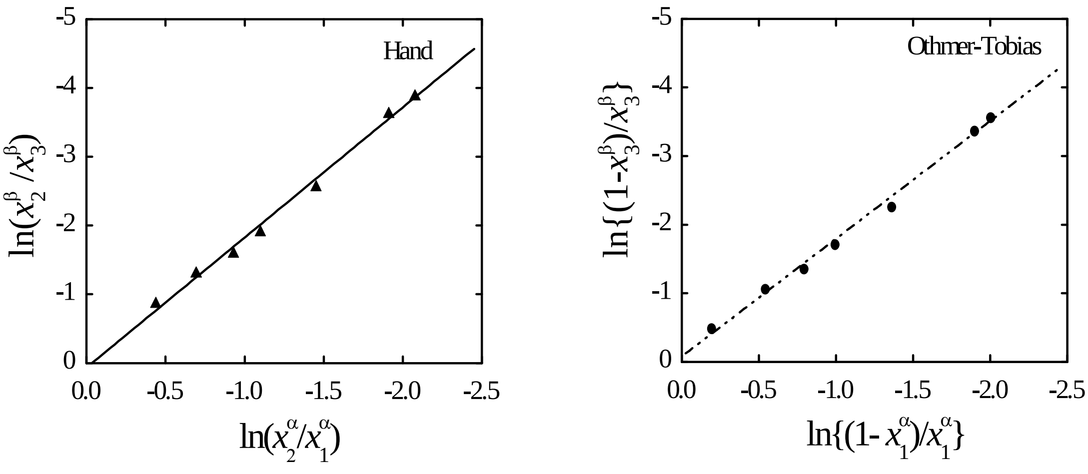


Figure (4.7.3): Correlation of liquid-liquid equilibrium data for solutions of {water (1) + ethanol (2) + 1,4-difluorobenzene (3)} at 318.15 K: —, eq (2.31); …, eq (2.32).

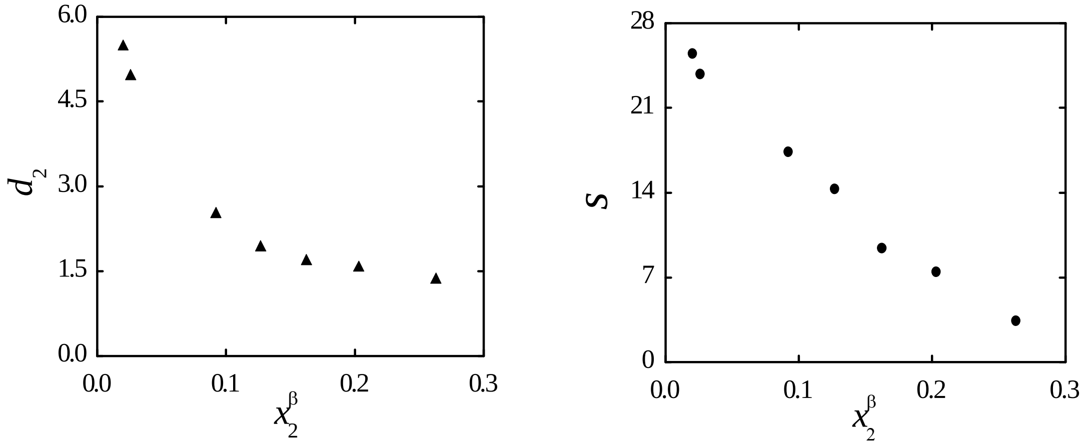


Figure (4.7.4): Distribution coefficient d_2 and selectivity S for solutions of {water (1) + ethanol (2) + 1,4-di-fluorobenzene (3)} at 318.15 K.

4.8 Results for (2,2,2-trifluoroethanol + ethanol + cyclohexane)

The solubility and the liquid-liquid equilibrium of 2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3) were investigated at three temperatures: (288.15, 298.15, 308.15)K and pressure 0.1MPa. The experimental solubility values are reported in Table (4.8.1) and are shown in Figure (4.8.2). For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by 2-propanol as standard.

The calibration points of the chromatograph are represented in Figures (4.8.1) by the fitting equations for ethanol. Trifluoroethanol-rich phase: [illegible], cyclohexane-rich phase: $y_2^{\beta} = 1.812 + 0.540\, x^{\beta}$

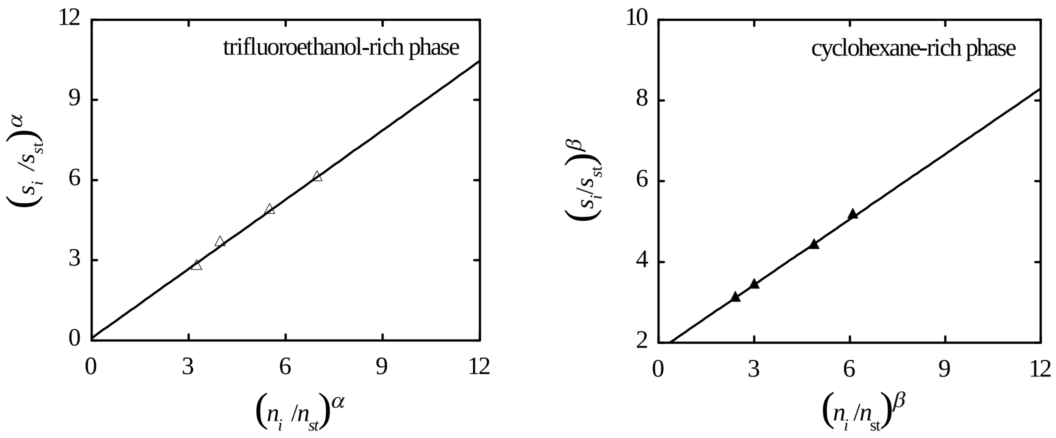


Figure (4.8.1): Chromatograph calibration for {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} at 298.15 K: (Δ, ▲), ethanol

The liquid-liquid equilibrium values as function of temperature of {2,2,2-trifluoroethanol + ethanol + cyclohexane) at three temperatures are given in Table (4.8.2), whereas Table (4.8.4) shows the effect of temperature on the plait point.

For a temperature range of (T_1→T_2), the change in the plait point is represented by: $\Delta x_i^{cs} = (x_{T_2}^{cs} - x_{T_1}^{cs})$ and the corresponding values are given in the following:

(288.15→298.15) K: $\Delta x_1^{cs} = 0.039$, $\Delta x_2^{cs} = 0.037$, $\Delta x_3^{cs} = 0.074$,

(298.15→308.15) K: $\Delta x_1^{cs} = 0.036$, $\Delta x_2^{cs} = 0.066$, $\Delta x_3^{cs} = 0.030$,

(288.15→308.15) K: $\Delta x_1^{cs} = 0.003$, $\Delta x_2^{cs} = 0.100$, $\Delta x_3^{cs} = 0.104$.

The correlations of Hand and Othmer-Tobias are given in Table (4.8.3) and are shown in Figure (4.8.3). While distribution coefficient d_i, selectivity S are plotted in Figure (4.8.4).

Table (4.8.1): Experimental solubility data for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} and p = 0.1 MPa

x_1	x_2	x_1	x_2	x_1	x_2
T = 288.15 K		T = 298.15 K		T =308.15 K	
0.116	0.329	0.037	0.173	0.172	0.255
0.142	0.394	0.060	0.223	0.201	0.294
0.168	0.424	0.081	0.279	0.220	0.310
0.200	0.452	0.111	0.342	0.248	0.334
0.249	0.472	0.146	0.382	0.274	0.355
0.284	0.475	0.184	0.420	0.296	0.368
0.309	0.473	0.216	0.437	0.326	0.372
0.337	0.472	0.265	0.441	0.368	0.376
0.392	0.444	0.305	0.436	0.402	0.369
0.459	0.413	0.342	0.430	0.448	0.356
0.532	0.370	0.386	0.407	0.563	0.294
0.587	0.333	0.453	0.367	0.607	0.271
0.644	0.283	0.508	0.338	0.655	0.238
0.746	0.205	0.593	0.281	0.712	0.194
0.785	0.165	0.662	0.261	0.764	0.158
0.819	0.148	0.720	0.213	0.832	0.102

$$T = 288.15\ \text{K}: x_2 = -0.041 + 1.346\, x_3^{1} - 2.999\, x_3^{2.5} + 1.6913\, x_3^{3.5}\ ;\ R^2 = 0.981$$

$$T = 298.15\ \text{K}: x_2 = -0.038 + 1.3294\, x_3^{0.5} - 1.668\, x_3^{1.5} + 0.3013\, x_3^{3}\ ;\ R^2 = 0.983$$

$$T = 308.15\ \text{K}: x_2 = -1.275 + 8.529\, x_3^{0.5} - 7.534\, x_3^{1.5} + 0.226\, x_3^{3}\ ;\ R^2 = 0.998$$

Table (4.8.2): Experimental liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)}

	Feed Solution		Trifluoroethanol-Rich Phase		Cyclohexane-Rich Phase	
T/K	x_1	x_2	x_1^{α}	x_2^{α}	x_1^{β}	x_2^{β}
288.15						
	0.343	0.354	0.471	0.405	0.111	0.295
	0.368	0.309	0.536	0.361	0.104	0.245
	0.390	0.275	0.573	0.336	0.095	0.208
	0.411	0.240	0.635	0.289	0.093	0.170
	0.428	0.202	0.679	0.255	0.086	0.129
	0.450	0.166	0.715	0.227	0.081	0.095
	0.469	0.132	0.777	0.176	0.077	0.070
298.15						
	0.343	0.353	0.448	0.396	0.142	0.306
	0.367	0.314	0.510	0.356	0.118	0.248
	0.389	0.280	0.581	0.312	0.108	0.195
	0.413	0.242	0.614	0.292	0.101	0.168
	0.434	0.198	0.661	0.258	0.090	0.131
	0.450	0.166	0.697	0.232	0.083	0.097
	0.471	0.130	0.749	0.198	0.072	0.066
308.15						
	0.383	0.324	0.436	0.355	0.163	0.236
	0.437	0.201	0.495	0.330	0.141	0.192
	0.422	0.234	0.549	0.298	0.131	0.136
	0.398	0.279	0.608	0.267	0.113	0.092
	0.460	0.168	0.656	0.230	0.097	0.057
	0.471	0.146	0.685	0.211	0.086	0.033

Table (4.8.3): Correlation of liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)}

T /K	Hand: Equation (2.32)			Othmer-Tobias: Equation (2.33)		
	A	B	R^2	A_1	B_1	R^2
288.15	0.311	0.709	0.992	0.464	0.944	0.992
298.15	0.195	0.611	0.996	0.370	0.812	0.997
308.15	0.123	0.418	0.992	0.481	0.648	0.991

Table (4.8.4): The effect of temperature on the plait point for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)}

T /K	x_1^{cs}	x_2^{cs}	x_3^{cs}
288.15	0.312	0.469	0.219
298.15	0.273	0.434	0.293
308.15	0.309	0.368	0.323

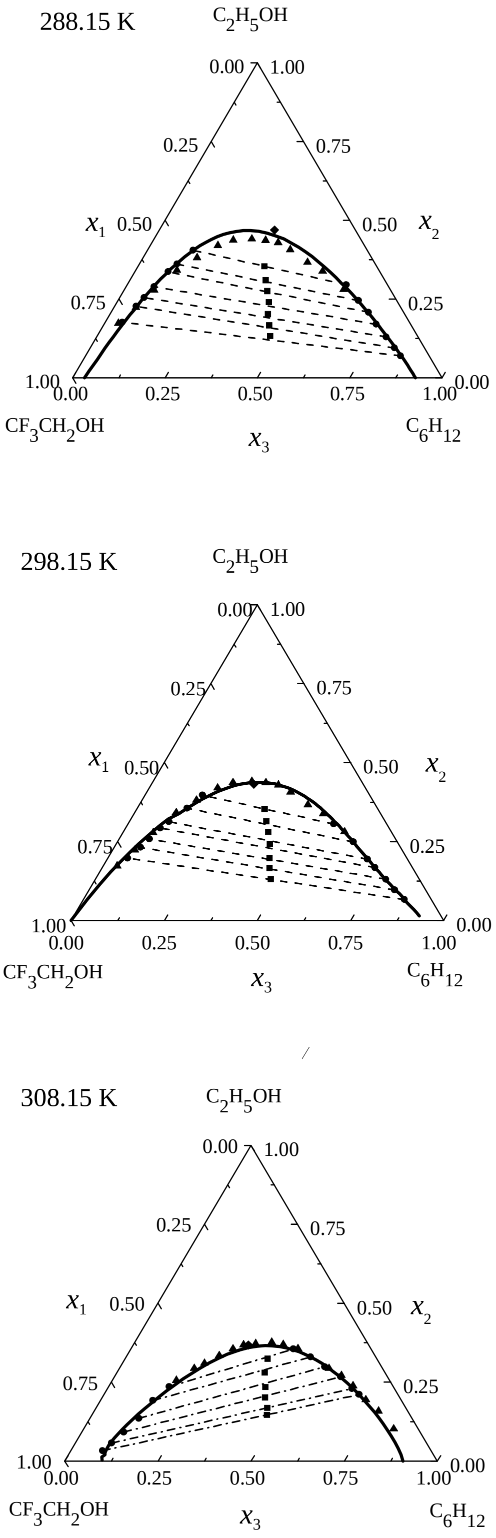


Figure (4.8.2): Solubility and liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} ▲, solubility; ■, feed solution; ●, LLE;♦, plait point; …, tie line; —, eq (2.31).

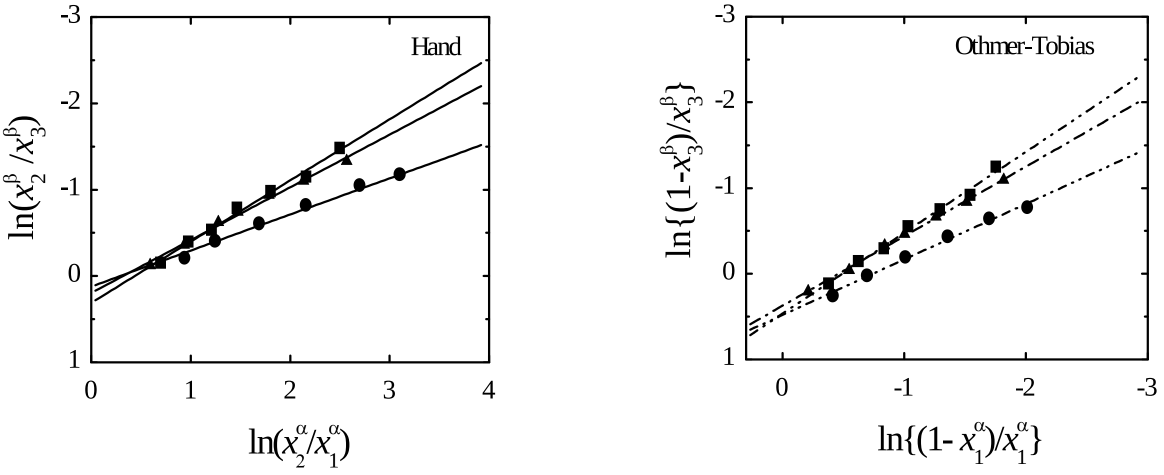


Figure (4.8.3): Correlation of liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} at T= (■, 288.15; ▲, 298.15; ●, 308.15) K: —, eq (2.32); …, eq (2.33).

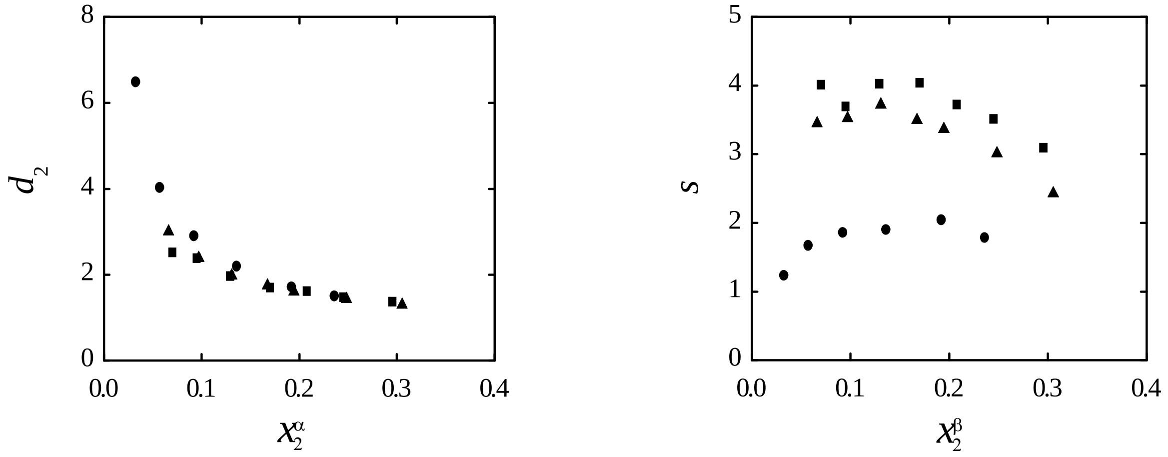


Figure (4.8.4): Distribution coefficient d_2 and selectivity S for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} at (■, 288.15; ▲, 298.15; ●, 308.15) K.

4.9 Results for (2,2,2-trifluoroethanol + 2-propanol + cyclohexane)

The solubility and the liquid-liquid equilibrium of 2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3) were investigated at three temperatures: (288.15, 298.15, 308.15) K .and pressure 0.1 MPa.. The experimental solubility are reported in Table (4.9.1) and are shown in Figure (4.9.2). For liquid-liquid equilibrium measurements, the chromatograph calibration was performed by ethanol as standard.

The calibration points of the chromatograph are represented in Figure (4.9.1) by the fitting equations for 2-propanol. 2,2,2-triluoroethanol-rich phase: $y_2^\alpha = 0.091 + 0.895\, x^\alpha$, cyclohexane-rich phase: $y_2^\beta = 0.399 + 0.532\, x^\beta$

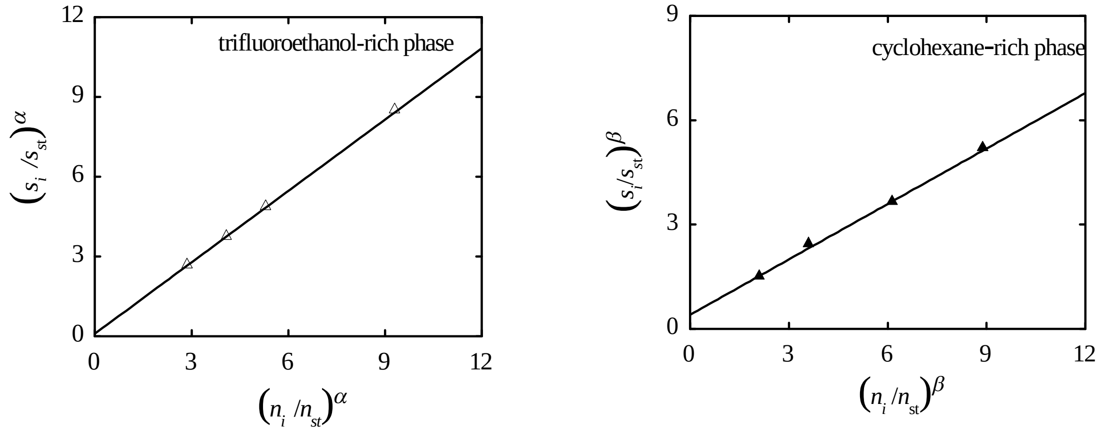


Figure (4.9.1): Chromatograph calibration for { 2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)} at 298.15 K: (Δ, ▲), 2-propanol

The liquid-liquid equilibrium values as function of temperature of {2,2,2-trifluoroethanol + 2- propanol + cyclohexane) at three temperatures are given in Table (4.9.2), whereas Table (4.9.4) shows the effect of temperature on the plait point.

For a temperature range of ($T_1 \rightarrow T_2$), the change in the plait point is represented by: $\Delta x_i^{cs} = (x_{T_2}^{cs} - x_{T_1}^{cs})$ and the corresponding values are given in the following:

(288.15 → 298.15) K: $\Delta x_1^{cs} = 0.028$, $\Delta x_2^{cs} = 0.032$, $\Delta x_3^{cs} = 0.003$,

(298.15 → 308.15) K: $\Delta x_1^{cs} = 0.026$, $\Delta x_2^{cs} = 0.069$, $\Delta x_3^{cs} = 0.041$,

(288.15 → 308.15) K: $\Delta x_1^{cs} = 0.054$, $\Delta x_2^{cs} = 0.101$, $\Delta x_3^{cs} = 0.038$.

The correlations of Hand and Othmer-Tobias are given in Table (4.9.3) and are shown in Figure (4.9.3). While distribution coefficient d_i, selectivity S are shown in Figure (4.9.4).

Table (4.9.1): Experimental solubility data for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)} and p = 0.1 MPa

x_1	x_2	x_1	x_2	x_1	x_2
T = 288.15 K		T = 298.15 K		T =308.15 K	
0.810	0.171	0.051	0.147	0.878	0.066
0.738	0.233	0.086	0.243	0.818	0.109
0.595	0.342	0.110	0.313	0.766	0.145
0.506	0.414	0.129	0.366	0.720	0.178
0.385	0.478	0.143	0.407	0.679	0.207
0.310	0.492	0.178	0.443	0.642	0.234
0.252	0.489	0.230	0.452	0.600	0.264
0.197	0.468	0.298	0.441	0.526	0.319
0.163	0.424	0.355	0.420	0.458	0.357
0.117	0.322	0.476	0.362	0.381	0.392
0.090	0.250	0.551	0.308	0.340	0.396
0.078	0.192	0.652	0.229	0.307	0.392
0.058	0.103	0.741	0.164	0.277	0.380
0.035	0.078	0.821	0.093	0.237	0.355

T = 288.15 K: $x_2 = -0.021 + 1.366\, x_3^{0.5} - 3.081\, x_3^{2} + 1.723\, x_3^{2}$; $R^2 = 0.991$

T = 298.15 K: $x_2 = -0.106 + 1.402\, x_3^{0.5} - 3.021\, x_3^{2} + 1.709 x_3^{3}$; $R^2 = 0.986$

T = 308.15 K : $x_2 = -0.133 + 0.385\, x_3^{1} - 0.799\, x_3^{2} + 0.226\, x_3^{3}$; $R^2 = 0.995$

Table (4.9.2): Experimental liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}

T/K	Feed Solution		Trifluoroethanol- Rich Phase		Cyclohexane-Rich Phase	
	x_1	x_2	x_1^α	x_2^α	x_1^β	x_2^β
288.15						
	0.303	0.323	0.865	0.119	0.040	0.016
	0.337	0.237	0.830	0.151	0.039	0.021
	0.313	0.275	0.780	0.192	0.047	0.041
	0.350	0.191	0.745	0.226	0.051	0.061
	0.363	0.168	0.702	0.253	0.059	0.042
	0.379	0.127	0.653	0.298	0.072	0.150
	0.397	0.098	0.588	0.338	0.084	0.209
	0.410	0.066	0.550	0.373	0.104	0.245
298.15						
	0.321	0.381	0.383	0.427	0.153	0.327
	0.319	0.354	0.433	0.393	0.134	0.281
	0.331	0.309	0.499	0.349	0.124	0.251
	0.346	0.261	0.572	0.303	0.110	0.202
	0.357	0.231	0.617	0.280	0.104	0.178
	0.374	0.206	0.672	0.258	0.089	0.139
	0.386	0.179	0.688	0.226	0.087	0.118
	0.394	0.145	0.733	0.192	0.085	0.090
308.15						
	0.322	0.325	0.433	0.370	0.153	0.254
	0.332	0.294	0.467	0.337	0.138	0.200
	0.346	0.261	0.535	0.306	0.137	0.151
	0.367	0.211	0.564	0.276	0.135	0.109
	0.386	0.180	0.611	0.246	0.124	0.068
	0.384	0.153	0.651	0.219	0.118	0.047
	0.394	0.126	0.703	0.191	0.109	0.024
	0.412	0.098	0.741	0.161	0.108	0.015

Table (4.9.3): Correlation liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}

T /K	Hand: Equation (2.32)			Othmer-Tobias: Equation (2.33)		
	A	B	R^2	A_1	B_1	R^2
288.15	-0.111	2.085	0.992	-0.310	1.580	0.997
298.15	-0.543	1.201	0.987	-0.539	0.992	0.991
308.15	-0.338	2.410	0.990	-0.793	1.219	0.984

Table (4.9.4): The effect of temperature on the plait point for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}

T/K	x_1^{cs}	x_2^{cs}	x_3^{cs}
288.15	0.309	0.478	0.225
298.15	0.337	0.446	0.222
308.15	0.363	0.377	0.263

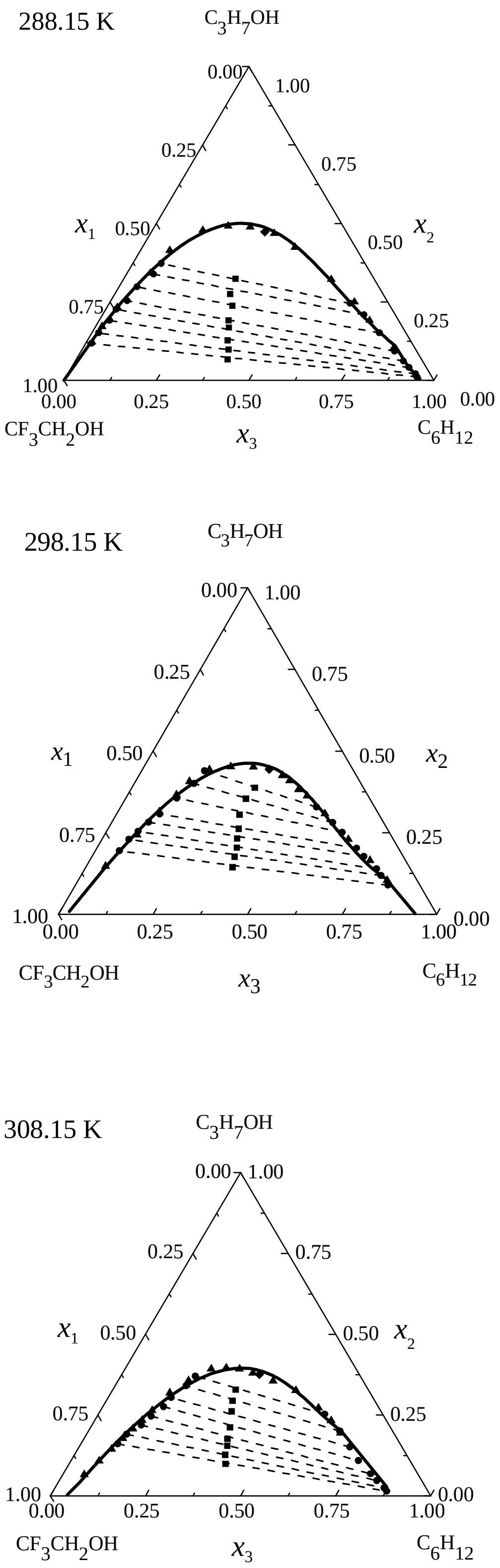


Figure (4.9.2): Solubility and liquid-liquid equilibrium data for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}: ▲, solubility; ■, feed solution; ●, LLE; ♦, plait point; …, tie line; —, eq (2.31).

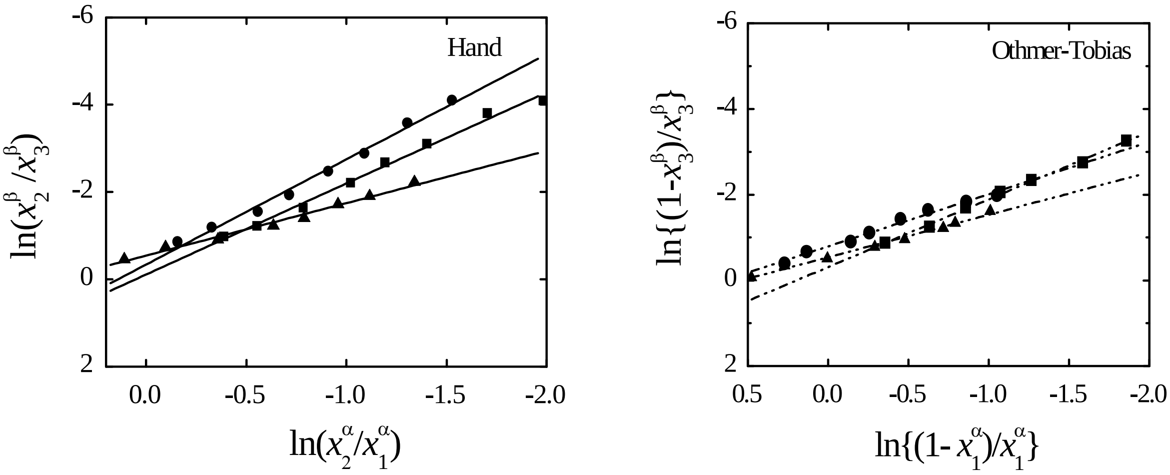


Figure (4.9.3): Correlation of liquid-liquid equilibrium data for solutions of {2, 2, 2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)} at (■, 288.15; ▲, 298.15; ●, 308.15) K: —, eq (2.31); …, eq (2.32).

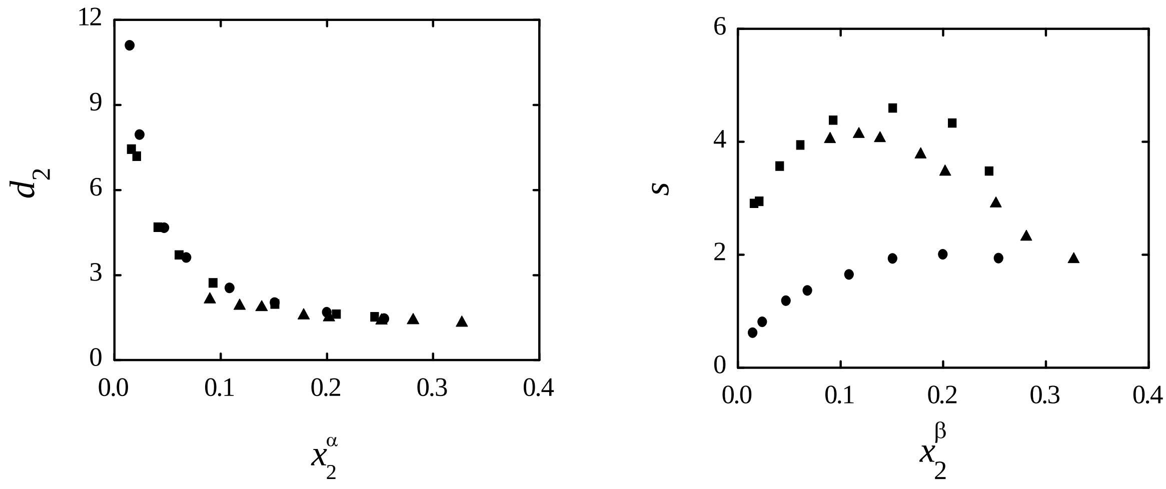


Figure (4.9.4): Distribution coefficient d_2 and selectivity S for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}at (■, 288.15; ▲, 298.15; ●, 308.15) K .

CHAPTER 5

DISCUSSION

Thermodynamic properties of mixtures reflect the physico-chemical interactions between like and unlike molecules, in particular specific interactions such as hydrogen bonding.[33]
Mixing of different components leads in general to changes in the thermodynamic properties of the formed solutions.
In solution, the intermolecular forces determine the solubility of substances in each other and the nature of the dominating phases and liquid-liquid phase separation.[47]
The mutual solubility of heterogeneous systems increases with heating them; where the region of partial miscibility becomes smaller as temperature increases.[20,48-55]

Adding an alcohol to water affects the polar characteristics of the aqueous solution formed. Water and fluorinated hydrocarbons (HFC's) are strong polar components [56], consequently, the thermodynamic properties of their multi-component solutions are diverse from large to small miscibility gaps.

Alcohols and fluoro-hydrocarbons are highly polar molecules and are strongly self-associated by means of hydrogen bonds giving different clusters formation in pure and mixed states [32] involving molecular like-like and like-unlike hydrogen bonding interactions between alcohol and 2,2,2-trifluoroethanol hydroxyl groups and fluorine atoms.[27] The capability of solvents as extractive agents is evaluated from distribution coefficients and selectivities.[57-62]

For aqueous solutions containing fluorobenzene and α,α,α-trifluorotoluene, the distribution coefficient of 2,2,2-trifluoroethanol is found of slightly larger in α,α,α-trifluorotoluene than in fluorobenzene. This makes it possible to use these solvents for an efficient extraction of 2,2,2-trifluoroethanol from aqueous solutions.[27,30-31]

The effect of the water concentration on the solute distribution coefficient in liquid phase, and on the selectivity of a solvent is important [63-68] for dilute aqueous solutions, as illustrated in Figure (5.1).

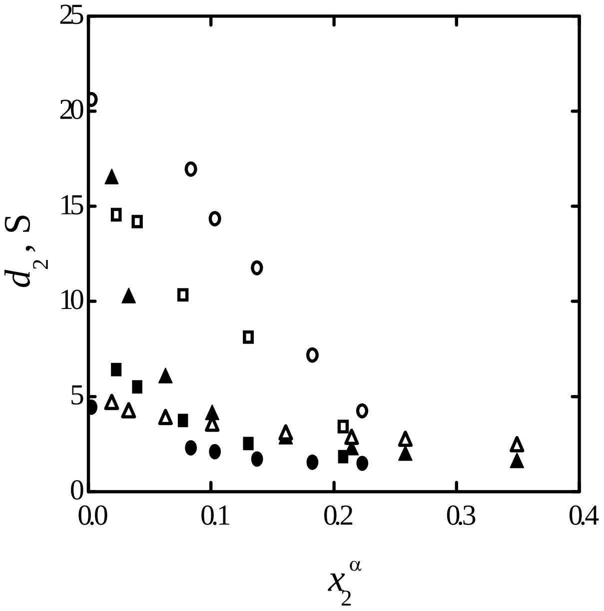


Figure (5.1): Distribution coefficient d_2 and selectivity *S* for solutions of {water (1) + 2,2,2-trifluoroethanol (2) + solvent (3)} at 298.15 K: distribution, filled symbol, selectivity, open symbol, solvent: (▲, Δ), To; (●, ○), Fb; (■, □), TFT.

From this work, it is found that the solvents fluorobenzene and α,α,α-trifluorotoluene show similar selectivity for the solute 2,2,2-trifluoroethanol;$3 \leq S \leq 20$, at ambient temperature.

The effect of temperature on the miscibility gap of the system (water + TFE/ETOH + fluorobenzene) is small and becomes moderately important at 298.15 K where the area of the two-phase region becomes smaller in which the cross associative dispersion may dominate the solution.[28] At the temperature 298.15 K, the fluorobenzene molecules are better dissolved in the presence of ethanol toward the water-rich region of the ternary solutions rather than in 2,2,2-trifluoroethanol as illustrated in Figure (5.2), and for system (water + TFE/ETOH + α,α,α-trifluorotoluene) are shown in Figure (5.3).

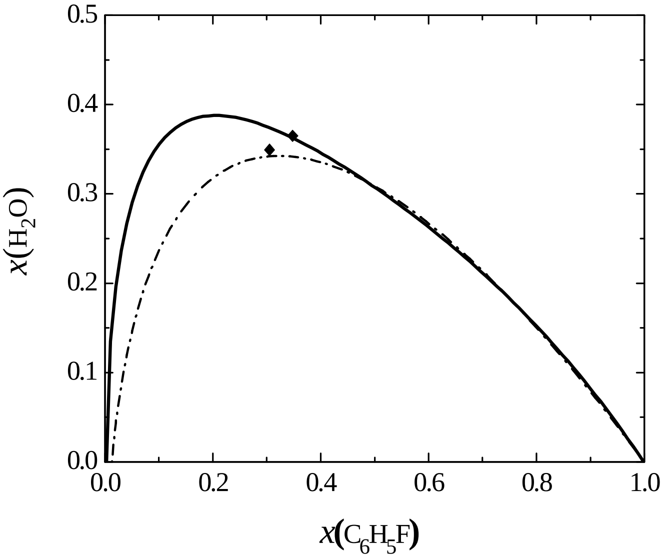


Figure (5.2): Comparison of liquid-liquid equilibrium data for {water (1) + ETOH/TFE (2) + fluorobenzene (3)} at 298.15 K: —, 2,2,2-trifluoroethanol; ---, ethanol from literature[28]; ♦, plait point.

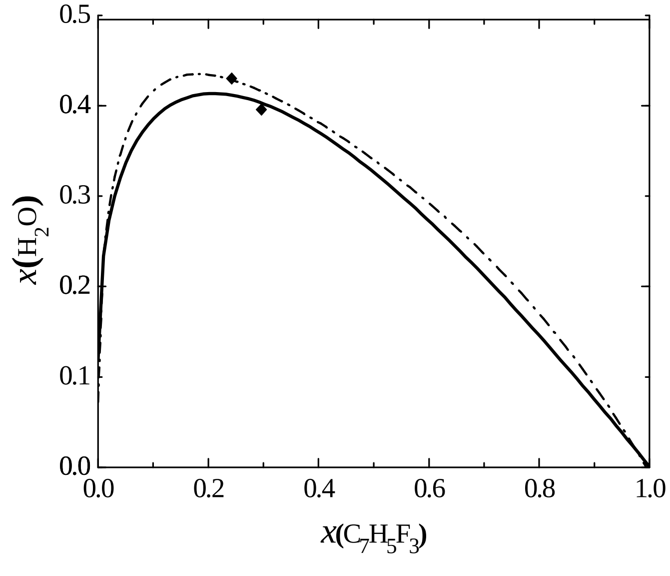


Figure (5.3): Comparison of liquid-liquid equilibrium data for {water (1) + ETOH/TFE (2) + α,α,α-trifluorotoluene (3)} at 298.15 K: —, 2,2,2-trifluoroethanol; ---, ethanol from literature [69]; ♦, plait point.

In the region of $0.10 \leq x \leq 0.70$, the immiscibility region of system {water (1) + alcohol (2) + toluene (3)} is significantly important with 2,2,2-trifluoroethanol than in ethanol as illustrated in Figure (5.4).

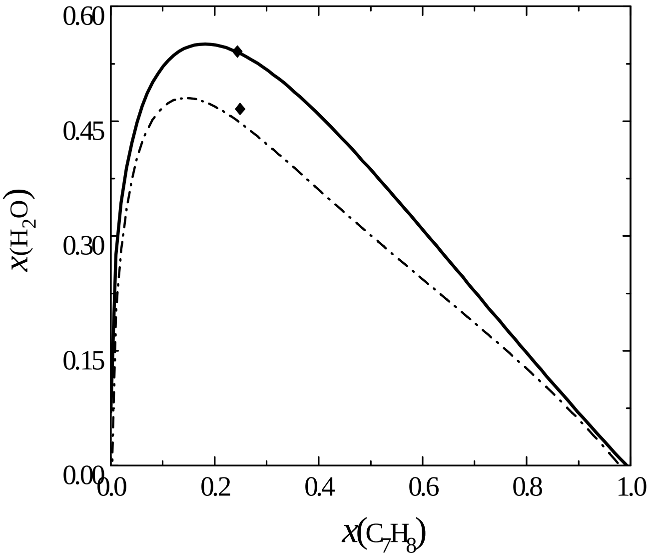


Figure (5.4): Comparison of liquid-liquid equilibrium data for {water (1) + ETOH/TFE (2) + toluene (3)} at 298.15 K: ——, 2,2,2-trifluoroethanol; ---, ethanol from literature [70]; ♦, plait point.

For the systems {water (1) + 2,2,2-trifluoroethanol (2) + solvent (3)} at 298.15 K, were solvent is toluene, or fluorobenzene, or α,α,α-trifluorotoluene, the aqueous solutions containing the fluorinated molecules have fairly stable structures due to significant dipole-dipole intermolecular interactions with water molecules giving a large immiscibility gap in the presence of toluene molecules, as illustrated in Figure (5.5).

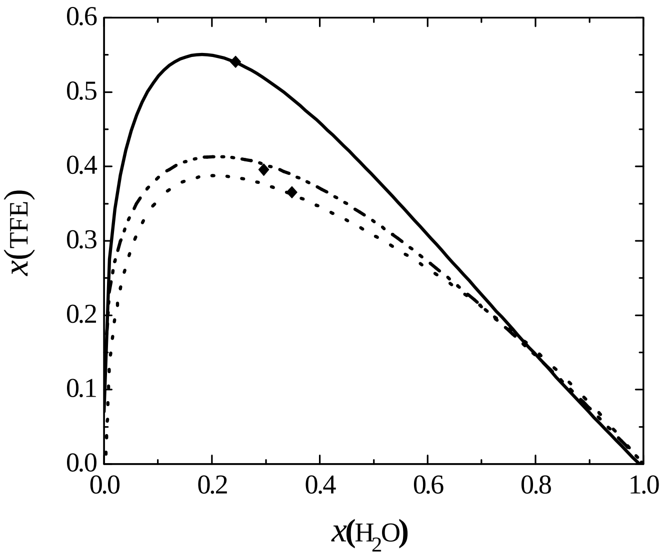


Figure (5.5): Effect of solvent molecular structure on miscibility for {water (1) + 2,2,2-trifluoroethanol (2) + solvent (3)} at 298.15 K: —, To; ---, TFT; ...., Fb; ♦, plait point.

The effect of solvent on the miscibility of a heterogeneous system is reflected in its plait point.[71] The change in the critical solution mole fractions of component *i*, x_i^{cs} in the above ternary aqueous solutions: $\Delta x_i^{cs} = x_i^{cs}(\text{TFE,expt}) - x_i^{cs}(\text{ETOH,lit})$, is illustrated in Table (5.1).

Table (5.1): Alcohol effect on critical solution point for ternary aqueous systems at 298.15 K:

Systems	Δx_1^{cs}	Δx_2^{cs}
water (1) + TFE/ETOH (2) + toluene (3)	-0.005	0.075
water (1) + TFT/ETOH (2) + fluorobenzene (3)	0.043	0.016
water (1) + TFE/ETOH (2) + α,α,α-trifluorotoluene (3)	0.053	-0.034

The miscibility gap of a heterogeneous system is affected by temperature.[72-75] For the system (2,2,2-trifluoroethanol + alcohol + cyclohexane), the miscibility gap is slightly affected by temperature in the range of (288.15 to 298.15) K, and becomes moderately significant at 308.15 K, where large miscibility areas are established in the solutions.[27, 31]

In these solutions, the plait point mole fraction of alcohols change very slightly with temperature is given in Tables (5.2) and (5.3). The temperature effect on liquid-liquid equilibrium is shown in Figures (5.6) and (5.7).

Table (5 2): The effect of temperature on the plait point for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)}

T /K	x_1^{cs}	x_2^{cs}	x_3^{cs}
288.15	0.312	0.469	0.219
298.15	0.273	0.434	0.293
308.15	0.309	0.368	0.323

Table (5.3): The plait point for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)}

T/K	x_1^{cs}	x_2^{cs}	x_3^{cs}
288.15	0.309	0.478	0.225
298.15	0.337	0.446	0.222
308.15	0.363	0.377	0.263

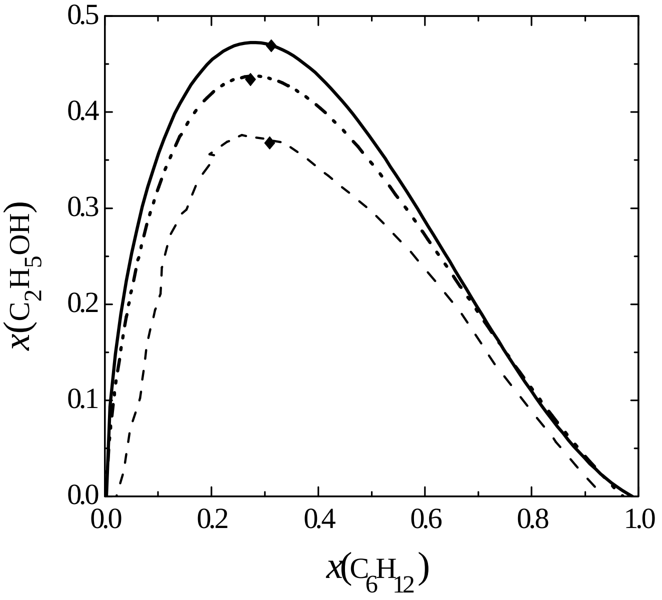


Figure (5.6): The effect of temperature on the solubility for solutions of {2,2,2-trifluoroethanol (1) + ethanol (2) + cyclohexane (3)} —, 288.15 K; ---, 298.15 K; - - -, 308.15 K; ♦, plait point.

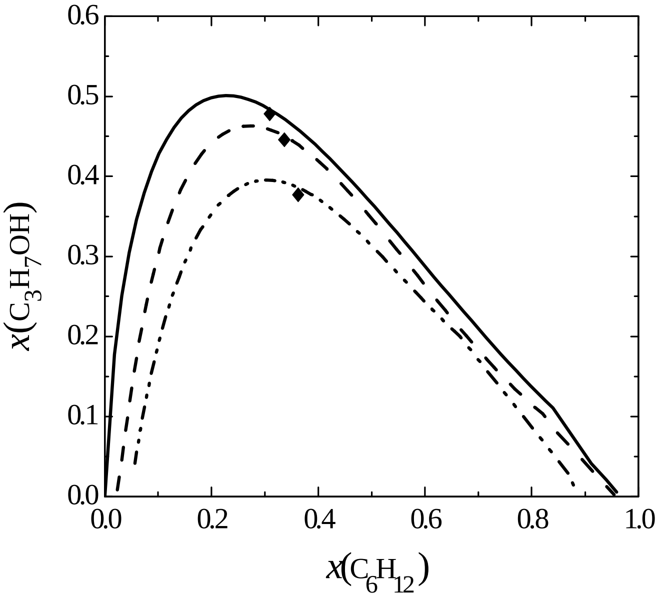


Figure (5.7): The effect of temperature on the solubility for solutions of {2,2,2-trifluoroethanol (1) + 2-propanol (2) + cyclohexane (3)} —, 288.15 K; ---, 298.15 K; - - -, 308.15 K; ♦, plait point.

The immiscibility gap decreases with the alcohol-molecular mass of (2,2,2-trifluoroethanol + alcohol + cyclohexane) as can be seen in the figure (5.8).

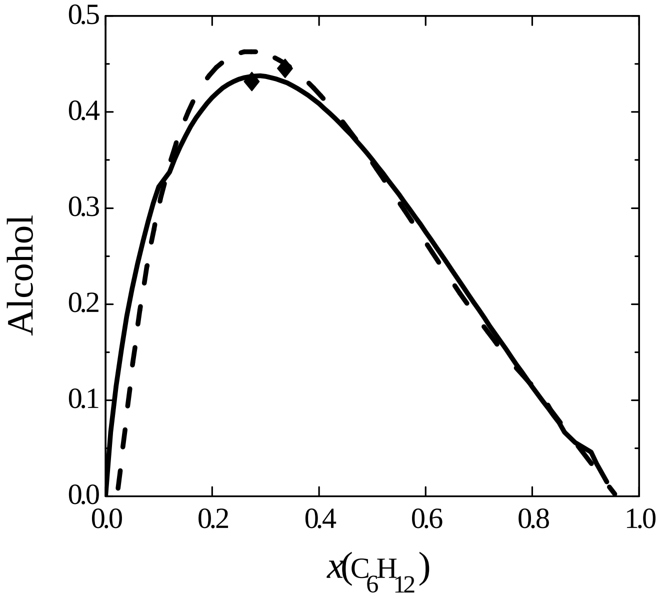


Figure (5.8): The effect of temperature on the solubility for solutions {2,2,2-trifluoroethanol (1) + alcohol (2) + cyclohexane (3)} at 298.15 K: —, ethanol; ---, 2-propanol; ♦, plait point.

For the systems (2,2,2-trifluoroethanol + alcohol + cyclohexane), the change in the critical solution mole fractions of component *i* x_i^{cs} is represented by: $\Delta x_i^{cs} = x_{i,\mathrm{Pr}OH}^{cs} - x_{i,EtOH}^{cs}$, and the corresponding values are given in the following:

(288.15 → 298.15) K: $\Delta x_1^{cs} = 0.011$, $\Delta x_2^{cs} = 0.005$, $\Delta x_3^{cs} = -0.071$,

(298.15 → 308.15) K: $\Delta x_1^{cs} = 0.010$, $\Delta x_2^{cs} = 0.003$, $\Delta x_3^{cs} = 0.011$,

(288.15 → 308.15) K: $\Delta x_1^{cs} = 0.051$, $\Delta x_2^{cs} = 0.100$, $\Delta x_3^{cs} = -0.066$.

For the systems, the immiscibility gap decreases with increasing temperature. Consequently, the effect of temperature on the miscibility of the system (cyclohexane + alcohol + 2,2,2-trifluoroethanol) is slightly more significant of alcohol. The effect of temperature of both systems on plait point is in the trend as illustrated in Figure (5.9).

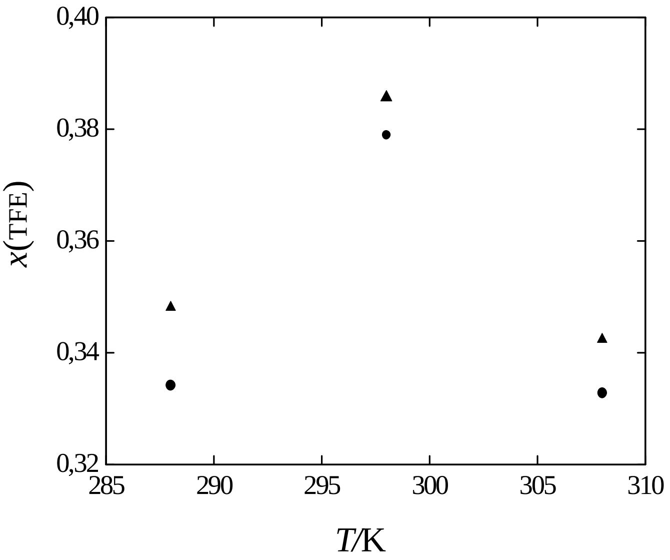


Figure (5.9): The effect of temperature on the plait point of {2,2,2-trifluoroethanol (1) + alcohol (2) + cyclohexane (3)}: ▲, ethanol; ●, 2-propanol.

Conclusion

Titration and gas chromatographic methods were used to construct the phase equilibrium diagrams of ternary systems.

The experimental solubility and tie-line data of the ternary aqueous and non-aqueous systems containing hydrocarbons: toluene, or benzene, or cyclohexane, fluorohydrocarbons: α,α,α-trifluorotoluene, 2,2,2-tifluoroethanol, or fluorobenzene, or 1,4-difluorobenzene, alcohols: 2-propanol, or ethanol, and ether: di-isopropyl ether, have been measured at different temperatures and atmospheric pressure. The binodal curve and liquid-liquid equilibrium data are well fitted to empirical equations and were correlated using the Othmer-Tobias and Hand equations with good results.

The alcohols are more readily soluble in the raffinate phase, where the separation factors are decreased by increasing of alcohol concentrations. The selectivity of fluoro-hydrocarbons for alcohols is high, which can be a practical approach to produce pure alcohols.

This study outlines experimentally that toluene, cyclohexane, α,α,α-trifluorotoluene, and fluorobenzene are suitable separating agents for alcohols.

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دراسة الانحلالية و التوازنات الثلاثية سائل ـ سائل للمحاليل المائية المحتوية مركبات فلوروعضوية

الملخص:

تحتل الانحلالية والتوازنات سائل ـ سائل مكانة هامة في تقدير و إستنباط الخواص الترموديناميكية للمكونات النقية في المزج و المحاليل.

ركزنا في هذا العمل على توفير قياسات جديدة للانحلالية والتوازنات سائل ـ سائل مرفقة بمعطيات ترموديناميكية فيما يخص التأثير الطاقي مابين الجزيئات لجمل ثلاثية مكونة من الماء ومحلات فلوروعضوية.

استعملت طريقتي المعايرة و الكروماتوغرافيا لدراسة مخططات الأطوار سائل ـ سائل لمجموع المحاليل الثلاثية المدروسة بدرجات حرارة مختلفة وضغط 0.1MPa .

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

أعطت التحاليل الترمودينامكية لقياسات الانحلالية والتوازن سائل-سائل باستعمال معادلات تجريبية لـ Hand وOthmer-Tobias توافقا جيدا مع القياسات التجريبية.

تم تقدير تأثير درجة الحرارة وكذا البنية الجزيئية للمركبات المكونة للمزج على فجوة اللامتزاج.

جامعة العلوم و التكنولوجيا هوارى بومدين

مذكرة ماجستير

دراسة الانحلالية و التوازنات الثلاثية سائل ـ سائل للمحاليل المائية المحتوية مركبات فلوروعضوية

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