INVESTIGATION
OF
VAPOR-LIQUID-LIQUID
EQUILIBRIA

A Thesis
Submitted to the College of Engineering of
Al-Nahrain University in Partial Fulfillment of the
Requirements for the Degree of Doctor of
Philosophy in Chemical Engineering

by
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Certification

We certify that this thesis entitled "INVESTIGATION OF VAPOR-LIQUID-LIQUID EQUILIBRA" was prepared by GHAZWAN AHMED MOHAMMED, under our supervision at Al-Nahrain University, College of
Engineering, in partial fulfillment of the requirements for the degree of Doctor

of Philosophy in Chemical Engineering.

Certificate

We certify, as an examining committee, that we have read this thesis entitled "NVESTIGATION OF VAPOR-LIQUID-LIQUID EQUILIBRIA", examined the student GHAZWAN AHMED MOHAMMED in its content and found it meets the standard of thesis for the degree of Doctor of Philosophy in Chemical Engineering.

ABSTRACT

Vapor-Liquid-Liquid Equilibrium (VLLE) systems are complicated systems; they involve both a two phase liquid and a two phase vapor. Obtaining equilibrium data on these systems is very difficult, Vapor-LiquidEquilibrium (VLE) recirculation stills can not be used to obtain accurate VLLE data due to incorrect composition of the recycled condensed vapor to the boiler, modifications are made to these stills to obtain accurate equilibrium data for partial and immiscible liquid systems. Another difficulty when collecting the vapor & liquid samples, a modification must be made in order to collect a sample with the correct composition.

VLLE systems are non-ideal and polar systems, many Equations Of States (EOS) failed in correlating or predicting VLLE data. Activity coefficient models gave reasonable accuracy in correlating or predicting VLLE data such as T.K.Wilson and NRTL (Non-Random-Two-Liquid) and UNIQUAC (Universal-Quasi chemical-Activity-Coefficient) models while the UNIFAC (Uniquac-Functional group-Activity-Coefficient) model failed in predicting VLLE data especially for immiscible and some partial miscible liquid systems.

In this study the following was accomplished:

1- A modified recirculation still was assembled to deal with partial and immiscible liquid systems. The still consisted of 55 mm diameter boiling section and a 40 mm diameter condensing section. The modification involved supplying the still with mixers in the two mentioned sections, the speed of mixing was 1400-1600 rpm. The mixers helped in keeping the two phase liquid mixtures in the boiler and the condenser in a kind of a homogenous state.

This gave a correct composition of the recycled liquid in the condenser and a correct boiling temperature reading in the boiler.

2- Isobaric VLLE data for two binary systems; Ethyl-acetate\Water and

Toluene\Water and one ternary system Toluene\Ethyl-acetate\Water have been measured at 101.325 kPa in the modified still. All the systems are two phase mixtures were the system Ethyl-acetate\Water is a partial miscible system and the systems Toluene\Water and Toluene\Ethyl-acetate\Water are immiscible systems. No equilibrium data are available on the ternary system measured in this study. The binary systems and the ternary system forms minimum boiling point Azotropes.

3- The VLLE data where correlated and predicted by using the PengRobinson Equation Of State (EOS) in both the vapor and liquid phases and one of the activity coefficient models T.K.Wilson, NRTL, UNIQUAC and UNIFAC in the liquid phase and the Peng-Robinson (EOS) in the vapor phase. The overall average absolute deviations in vapor mole fraction for the system Ethyl-acetate \ Water measured in the present study by the prediction and correlation methods was 37.98 and 0.12 respectively and for the system Toluene \ Water it was 1.62 and 0.08 respectively and for the system Toluene \ Ethyl-acetate \ Water it was 0.16 and 0.06 respectively.

4- A modification was applied on the the UNIQUAC model by converting the

coordination number (Z / 2) which was considered as a constant = 5 into a third adjustable parameter, this helped in decreasing the average absolute deviation in vapor mole fraction from 20% to 65%.

5- liquid-liquid-Equilibrium (LLE) data of the binary system Ethylacetate\Water was measured in the Temperature range 20^{o}C to 75^{o}C by the same modified still and the overall average absolute deviation in predicted activity coefficient ratio of top and bottom layers $\Delta(\gamma_{1T}/\gamma_{1B})$ were 0.0561, 0.0112, 0.0361 and 0.1512 by using the activity coefficient models T.K.Wilson, NRTL, UNIQUAC and UNIFAC respectively.

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Abbreviations

NOMENCLATURES

ABS Absolute
24DMD 2,4-Dimethyl-1,3-dioxolane
2MD 2-Methyl-1,3-dioxolane
BDH British Drug Home
Cal. Calculated
CASSY Computer Assisted Science System
EOS Equation of State
Exp. Experimental
GRG Generalized Reduced Gradient Search method
LLE Liquid Liquid Equilibrium
M.WILSON Modified Wilson activity coefficient model
M.Wt. Molecular Weight

MEK Methyl-Ethyl-Ketone
N.V.M Non Volatile Matter
NRTL Non-Random Two Liquid activity coefficient model
O.F Objective Function
P.E Poly-ethylene
Pred. Prediction
QVF Quick-fit Visible Flow
T.K.Wilson Tsubota & Katayama modified Wilson activity coefficient model
T-X Temperature-Liquid composition
T-X-X Temperature-Liquid composition-Liquid composition
T-X-Y Temperature-Liquid composition-Vapor composition
UNIFAC UNIQUAC Functional Group Activity Coefficient model
UNIQUAC Universal Quasi-Chemical activity coefficient model
VLE Vapor Liquid Equilibrium
VLLE Vapor Liquid Liquid Equilibrium

Symbols

A
ij
, B
ij
, C
Parameters of equation 2.6.1
B
ij
ij
The second virial coefficient in equation 2.3.10
B
The second virial coefficient of the mixture in equation 2.3.9

C
1
, C
2
mix
, C
3
, C
Coefficients of equation 2.3.16
C
i0
C
, C
mix
i1
4
Coefficients of equation 2.3.17
The third virial coefficient of the mixture in equation 2.3.9
d
Derivative
E
Constant in equation 2.4.15c

i

f

Partial molar fugacity of component i
f
i
i

0
The liquid phase standard-state fugacity
f
i
L
Partial molar fugacity of component i in liquid phase
f
i
V
Partial molar fugacity of component i in vapor phase
k
Interacting parameter of Peng-Robinson (EOS)

L Liquid phase

n_{ij} Number of moles of component i

P Total pressure (kPa.)

P_i Critical pressure (kPa.)

P_C^S Saturation pressure (kPa.)

R Universal gas constant

r, q, q' Pure component molecular structures of UNIQUAC model

R Correlation coefficient (N.m / mole.K)

T Temperature (^{o}C or Kelvin)

T_{Azo} Temperature of azotrope (^{o}C or Kelvin)

T_C Critical temperature (^{o}C or Kelvin)

T_i^0 Boiling point of component i (^{o}C or Kelvin)

T_r Reduced temperature (^{o}C or Kelvin)

V Vapor phase

V Molar volume in equation 2.3.2 (cm / mole)

V_C Critical molar volume (m^3 / Kmole)

X
Composition of component i in liquid phase
X
i
i
Azo
Azotrope composition of component i
Y
Composition of component i in vapor phase
Z Compressibility factor
Z
i
Critical compressibility factor
Z
C
mix

Greek Symbols

Compressibility factor of mixture
µ Chemical potential
3
i

proportionality constant dependent on temperature and pressure
Y−
Average absolute vapor phase mole fraction difference
Parameter of UNIFAC model given by equation 2.4.32
α
ك
ij
Parameter function of temperature of equation 2.3.33
α
i
Non-randomness parameter of NRTL model
γ
γ
γ
i
ij
i
B
i
C
Activity coefficient of component i in liquid phase
Activity coefficient in Bottom liquid layer of component i
Activity coefficient in combinatorial part of UNIFAC model

γ_i^R	Activity coefficient in residual part of UNIFAC model
γ_i^T	Activity coefficient in Top liquid layer of component i

Δ	Difference
Δu	Characteristic energy of UNIQUAC model
ΔY_{ij}	Absolute vapor phase mole fraction difference of component i
θ, θ_i'	Area fractions of UNIQUAC model
λ_{ij}	Adjustable parameters of WILSON model
μ_α	Chemical potential in α phase
μ_β	Chemical potential in β phase
μ	The reduced dipole moment in equation 2.3.24
τ_R	Adjustable parameters of NRTL model
Φ_{ij}	

*
Segment fraction of UNIQUAC model
φ
Partial molar fugacity coefficient of component i
φ
i
i
L
Partial molar fugacity coefficient of component i in liquid phase
φ
i
S
Partial molar fugacity coefficient of component i at Saturation
φ
i
V
Partial molar fugacity coefficient of component i in vapor phase
ω The acentric factor

CHAPTER ONE

INTRODUCTION

Many of the azotropic systems, particularly the aqueous ones that are being used for industrial distillations involve partially miscible regions for which a few data are available. An adequate method of measuring the vapor–liquid equilibrium (VLE) data of such systems is of great importance. In both processes of azotropic distillation and liquid-liquid extraction, solvent is generally removed from one or more streams by stripping columns from which the condensed overhead separates into two layers [1]. To make accurate and economic design, an equilibrium still has to be designed which permits the determination of VLE for systems involving both a two phase liquid and a two phase vapor condensate.

There are two major difficulties in studing partially miscible and immiscible systems in addition to those in equilibrium stills. The ***first*** is the vapor when condensed will form an immiscible mixture. Thus the recirculation type of apparatus can not be used since the condensed vapor cannot be returned to the boiler of the still with the two liquid phases in proper portion. The ***second*** difficulty lies in the great difference in composition between the vapor and liquid. For example in the miscible region of Ethyl-acetate in Water, which extends to 2 mole percent Ethyl-acetate, the vapor is from 5 to 22 times as rich in Ethyl-acetate as the liquid. Therefore, if an equilibrium study is undertaken where a liquid sample is distilled, its composition will change extremely rapidly as vapor is formed, and the arrival at the desired steady state in the still becomes difficult [2].

Partially miscible and immiscible systems are non ideal and polar systems. Correlating or predicting equilibrium data of these system is best achieved by the aid of activity coefficient models [3] although attempts have been made by the aid of Equations Of State (EOS) [4, 5], this gave good results for high pressure immiscible systems but failed in low pressure systems. EOS is applied to determine the fugacity coefficients at the vapor phase and at the saturation. The most applied EOS is the Peng-Robinson EOS [4]. The fugacity coefficients can also be determined from the Virial equation [6].

The most applied activity coefficient models are the Wilson, T.K.Wilson, NRTL, UNIQUAC and the UNIFAC models. All these models except the UNIFAC have adjustable parameters which are obtained from non linear regression of experimental equilibrium data [7] or from infinite dilution activity coefficients [8], thus the UNIFAC model is not as accurate as the other models its only a predicting model and not a correlating model. The NRTL model has three adjustable parameters with one parameter more than the other models this increases the accuracy of the correlation and the prediction of equilibrium data.

The scope of this study involves the following objectives:

1- Assembling a modified equilibrium still to deal with partial miscible and immiscible systems.

2- Measuring the vapor-liquid-liquid equilibrium (VLLE) data of the partial miscible binary of Ethyl-acetate \ Water and the immiscible binary of Toluene \ Water and the ternary of Toluene \ Ethyl-acetate \ Water in the new modified still at 101.325 kPa.

3- Measuring the liquid-liquid equilibrium (LLE) data of the partial miscible binary of Ethyl-acetate \ Water in temperature range 20 ^{o}C to 65 C by the same still at 101.325 kPa.

4- Correlating and predicting the VLLE and LLE data obtained from the new modified still by applying the Peng-Robinson (EOS) in both the vapor and liquid phases and applying the activity coefficient models (T.K.WILSON, NRTL, UNIQUAC and UNIFAC) in the liquid phase and the Peng-Robinson (EOS) in the vapor phase.

5- The UNIQUAC equation is modified and converted from a two adjustable parameter model to a three adjustable parameter model.

o

CHAPTER TWO

THEORY & LITERATURE REVIEW

2.1 VLLE Phenomenon

When the binodal curve representing the liquid-liquid equilibrium (LLE) data intersects the vapor-liquid equilibrium (VLE) data curve this gives rise to the phenomenon of vapor-liquid-liquid equilibrium (VLLE) [9].

A binary system consisting of two liquid phases and a vapor phase in equilibrium has (according to the phase rule) one degree of freedom, for a given fixed pressure, temperature and composition in all three phases. On a temperature composition diagram the points representing the states of the three phases in equilibrium fall on a horizontal line at (T *) as shown in Figure 2-1. At a temperature above (T*) the system may be a single liquid phase, two phases (liquid and vapor), or a single vapor phase, depending on the overall composition.

Figure 2-1 VLLE T-X,Y diagram [9]

In region α system is a single liquid rich in species 2; in region β it’s a single liquid rich in species 1. In region α-V, liquid and vapor are in equilibrium. The states of the individual phases fall on lines *AC* and *AE*. In the region β-V, liquid and vapor phases, described by lines *BD* and *BE*, also exist at equilibrium. Finally, in the region designated V, the system is a single vapor phase. Below the three phase temperature T^*, the system is entirely liquid this is the region of LLE.

2.2 Thermodynamics of Equilibrium [3]

The fundamental equations of phase equilibrium are commonly written in terms of chemical potentials,

〈®

∝∝ =

Where ***μ*** is the chemical potential, α and β represent the phases in equilibrium, for practical engineering problem it is useful to write equation (2.2.1) in other useful form where it can be related to the chemical potential in terms of temperature, pressure and composition. To establish this relation it is convenient to introduce some auxiliary functions such as ***fugacity*** and ***activity***. These functions make the practical engineering problem easier to visualize.

When there are two phases a vapor phase (V) and a liquid phase (L), they are in equilibrium when both at the same temperature and pressure the partial molar fugacity of component i (***f***) in the vapor phase is equal to that in the liquid phase

L
i
)2.2.2(ff
i
=
i

)1.2.2(

Equation (2.2.2) is of little use unless it can be related to the fugacity with temperature (T) and pressure (P) and composition (X
i
, Yi); ***f***
i
V
must be wrote
as a function of T, P, and Y
i
(composition in vapor phase) ***f***
i
L
must be wrote
as a function of T, P, X
(composition in liquid phase). To facilitate the
desired relations, three auxiliary functions are required:

1- The vapor phase partial molar fugacity coefficient ***φ***
i
.

2- The liquid phase activity coefficient ***γ***
.

3- The liquid phase standard-state fugacity ***f***
.

Equation (2.2.2) can now be written as follows:

v
i
o
iiii
©∏ =

i
i

0
i
v

)3.2.2(fXPY

Equation (2.2.3) contains three of the variables of interest ***Xi, Yi*** and ***P***. Its no more and no less fundamental than equation (2.2.1); one is merely a mathematical transformation of the other, and any claim equation (2.2.3) may have to being more useful is only a consequence of a fortunate choice of useful auxiliary functions in the transformation.

Much of this utility comes from the concept of ideality. If mixtures are defined with certain properties as ideal mixtures, then its found that as a result of this choice of auxiliary functions, that the equation of equilibrium can be simplified further; for example, for a mixture of ideal gases φ
ideal liquid mixtures at low pressures, γ
i
= 1 when f
i
0
i
is given by the saturation pressure of pure liquid i at the temperature of interest. So its found that some of the auxiliary functions are useful because they are numerical factors, frequently of the order of unity, that establish the connection between real mixtures and those that, by judicious choice, have been defined as ideal mixtures.

V
= 1, and for

In the general case ideal behavior cannot be assumed and two relations must be established, one for φ

φ
i

V
$= F\ (T, P, Y$
1
$, Y$
2
i
V
and γ
i
:
$,\ldots)$ (2.2.4)

γ

i
$= F\ (T, P, X$
1
$, X$
2
$,\ldots)$ (2.2.5)

Equation (2.2.2) can be written in another form
V
ii
L
ii
$\prod\prod =$
$)6.2.2(XY$

Where
φ

i
L
$= F\ (T, P, X$
1
$, X$
2
$,\ldots)$ (2.2.7)

2.3 Fugacities in Gas Mixtures[3]*:*

As was shown previously equation (2.2.2) is the basic equation for equilibrium between two phases (L,V), for the gas phase mixture the fugacity
is calculated from volumetric data and the following equations:

$\prod$
$)\ln($
$\prod$
i

i
)ln(

Where
=∏

i
=
=
RT
1
RT
1
f
i
i
PY

+
P
+
⁄
′
ϒ
↕
′
≤

⌉
⌉
∈

RT
n
V

0
n,P,T
i

ϒ
↕
′
≤
′

⌉
⌉
€

V
n,V,T
i
i
RT
n
P
j
∕
∞
ƒ
∞
∞
∞
)1.3.2(dP
P
ƒ
↕
)2.3.2()Zln(dV
V

Equation (2.3.1) is used whenever the volumetric data are given in volume
explicit form; i.e.,

)3.3.2(

V = F

$$_{V}(T, P, n_1, \ldots) \qquad (2.3.4)$$

Also equation (2.3.2) is used whenever the volumetric data are expressed in pressure-explicit form, i.e.,

$$P = F_P(T, V, n_1, \ldots) \qquad (2.3.5)$$

The mathematical relation between volume, pressure, temperature, and composition is called the ***Equation Of State*** (EOS) and most forms of the equation of state are pressure-explicit. Therefore equation (2.3.2) is frequently more useful than equation (2.3.1). These equations are exact and if the information needed to evaluate the integrals is at hand, then the fugacity coefficient can be calculated exactly. The problem of calculating fugacities in the gas phase, therefore, is equivalent to the problem of estimating volumetric properties.

2.3.1 The Lewis Fugacity Rule [3]

A particularly simple and popular approximation for calculating fugacities in gas-phase mixtures is given by the ***Lewis rule***. The assumption on which the rule rests states that at constant temperature and pressure, the molar volume of the mixture is a linear function of the mole fraction. This assumption must hold not only at the pressure of interest but for all pressures up to the pressure of interest. The fugacity of component i in a gas mixture can be related to the fugacity of pure gaseous i at the same temperature and pressure by the exact relation

f
ln(RT
i
P
↕=
)6.3.2(dp)ViiV()
fY
0
ipurei
+

Equation (2.3.6) is another form of equation (2.3.1), where ***iV*** is the partial molar volume, according to Amagats law, ***ViiV*** = , and assuming validity of this equality over the entire pressure range 0-P, equation (2.3.6) becomes

=
)7.3.2(fYf
ipureii

Or in equivalent form,

∏∏ =
ipurei

Where ***f*** ***pure i*** and φ are evaluated for the pure gas at the same temperature and pressure as those of the mixture. In effect the Lewis rule assumes that at constant temperature and pressure, the fugacity coefficient of i is independent of the composition of the mixture and independent of the nature of the other components in the mixture. These are drastic assumptions, on the basis of intermolecular forces, for component i, deviations from ideal-gas behavior (as measured by

φ
i
$pure\ i$
) depend not only on temperature and pressure, but also on the relative amounts of component i and other components j, k, …; further
φ

must depend on the chemical nature of these other components that interact with component i. It is concluded that the Lewis fugacity rule for component i

1- Always a good approximation at sufficiently low pressures where the gas phase is nearly ideal.

2- Always a good approximation at any pressure whenever i is present in large excess (say, Y
i
> 0.9). The Lewis rule becomes exact in the limit as Y

approach 1.

3- Often a fair approximation over a wide range of composition and pressure whenever the physical properties of all the components are nearly the same (e.g., nitrogen-carbon monoxide or benzene-toluene).

)8.3.2(
i
i

4- Almost always a poor approximation at moderate and high pressures whenever the molecular properties of the other components are significantly different from those of i and when i not present in excess.

In summery, the Lewis fugacity rule is attractive because of convenience
but it has no general validity. However, when applied in certain limiting situations, it frequently provides a good approximation.

2.3.2 Fugacities from the Virial Equation of State [3]

To calculate with confidence fugacities in a gas mixture, it is advantageous to use an equation of state where the parameters have physical
significance, i.e. where the parameters can be related directly to intermolecular forces. One equation of state that possesses this desirable ability is the virial equation of state. The virial equation for a mixture, truncated after the third term, is given by

Z
mix
RT
PV
B
1
C
V
2
mixmix
++==
Where ***Z***
mix
)9.3.2(
V
is the compressibility factor of the mixture, ***V*** is the molar volume of the mixture, and
B
the mixture given by

=
m
ij
m
◀◀
mix
and ***C***
mix

are the second and third virial coefficient of

)10.3.2(BYYB

1j

imix

=

1i

j

==

m

◀◀ ◀

== =

1i

m

1j

m

)11.3.2(CYYYC

1k

ijkkjimix

The fugacity coefficient for any component i in a mixture of m components is obtained by substitution of equations (2.3.9, 2.3.10, 2.3.11) in equation (2.3.2) and when the indicated differentiations and integrations are preformed, yields

)ln(

∏

V

2

2

m

3

BY

m

◀◀◀

↕+=

1j

ijii
1j
mixijkk
===
m
)12.3.2()Zln(CYY
V2
1k
j

Equation (2.3.12) is one of the most useful equations for phaseequilibrium thermodynamics. It relates the partial molar fugacity of a component in the vapor phase to its partial pressure through the theoretically derived virial equation of state. It may be applied to any component in a gas mixture regardless of whether or not that component can exist as pure vapor at the temperature and pressure of the mixture, finally equation (2.3.12) is valid for many types of (no ionized) molecules, polar and no polar.

Because data for second virial coefficients are much more plentiful than those for the third virial coefficients, equation (2.3.12) is written as

2
)ln(

∏
mix
m
◀
↕=
)13.3.2()Zln(BY
V
1j
ijii
Where
Z

mix
B
1Z

=
 is given by
mix
mix
+=
)14.3.2(
V
When equation (2.3.14) and (***V = RT / P***) are substituted in equation (2.3.13), yields

mix
m
P
BBY2)ln(
∏

◄
↕=
1j
ijii
=

The viral coefficient B
€

mix
)15.3.2(
RT
 may be calculated from ***Potential Functions***
and
Corresponding-State Correlations, the first method is explained in many references [3, 8] for the second method Schreiber and Pitzer [10] have

proposed the following form to determine
B

BP
cc
c
↕↕↕
1
r21
2
r3
+++=
6
r4
mix

)16.3.2(TCTCTCC
ZRT

Where
T
r
= T / T
C
and *Z*
is the critical compressibility factor and the coefficients
C
1
, C
2
, C
3
, C
4
C
are given by the following equation

⎤+=
)17.3.2(CCC
1,i0,ii

Where
ω is the acentric factor given by

P

log1
↕↕=
⎤

And $C_{i,0}$, $C_{i,1}$

s
€

)18.3.2(
P
T
c
7.0
T
c
=
given by the following table

Table 2-1 Coefficients for Eq. (2.3.17)

i	$C_{i,0}$	$C_{i,1}$
1	0.44225900	0.725650
2	-0.98097000	0.218714
3	-0.61114200	-1.249760
4	-0.00515624	-0.189187

The previous table was determined from a large body of experimental data for polar or slightly polar fluids. Highly polar fluids such as water, nitriles, ammonia, and alcohols were not included.

For polar and hydrogen-bonded fluids, Tsonopoulos [6] gave another correlation for the second virial coefficients in the form

RT
BP
C
C

T
F
C
)0(

∈

+
=
⎤
Where

T
F
F
T
RC
)0(

∈

1445.0
T
T
F
C
)1(

T
T
C
)1(
T
330.0

€
+

T
1385.0
2
R

T
F
C
)2(

€

)19.3.2(
T
000607.0
T
0121.0
↕↕↕↕=

€
0637.0
T
T
331.0
2
R
3
R
008.0
T
423.0
↕↕+=

b
T
a
T
T
F
C
)2(

€
↕=

Where T
R
6
R
3
R
)20.3.2(
T

8
R
)21.3.2(
T
8
R
)22.3.2(
T
8
R
is the reduced temperature, Constants ***a*** and ***b*** cannot be generalized, but for polar fluids that do not have hydrogen bond, Tsonopoulos
found that
b = 0. For Ketones, Aldehydes, Alkyl Nitriles, Ethers, Carboxylic Acid Esters the constant a is given by the following equation

a = -2.14*10

Where ***μ***

μ

R
R
-4
μ
R
– 4.308*10
-21
μ
R
8
(2.3.23)
is the reduced dipole moment given by the following equation
= 0.9869*10
5
(μ
2
P
C
/ T
C
2
) ***(2.3.24)***

Where the units of μ are debye and bar for P

C
and Kelvin for T
C

The ternary expression of the fugacity coefficient of equation 2.3.15 is
given by equations 2.3.25a, 2.3.25b and 2.3.25c.

Ln

Ln

Ln
RT
P2
≤
ϒ
⁄
′

B
BYBYBY
.
()
)a25.3.2(
2
mix
1331221111
↨++=
⎞
RT
P2
⁄
′

≤
ϒ
B
BYBYBY
∞
ƒ
()

)b25.3.2(
2
mix
2332222112
↕++=
⎞
ϒ
↕++=
⎞
P2
B
∞
ƒ
()
)c25.3.2(
2
mix
3333223113

Where

2
1mix
BYBYBY
RT
′
≤
⁄
∞
ƒ
2
2233213331122111
BYBYBYY2BYY2BYY2BYB +++++=

And

)1(
12
()( )
1
V,FFFVB
)0(
11

12C12
12R
)0(
1445.0F
12
()
12R2112
0637.0F
T
33.0
T,2/
2
12R
)1(
12
12
=+=
T
331.0
T
1385.0
2
12R
T
T
423.0
T
12C
)2(
12
12
8
12R
3
12R
3
12R
T
008.0
2C
3/1
1C12C
+=++=
VV
8
000607.0
T
0121.0

↕↕↕↕=
⎤⎤⎤

Where
⎤
,
T
8
12R
a
F,
12
)2(
==↕↕+=
()
2/
6
12R
33
2
322
3
3/1
()
5.0
2C1C12C
TTT,
T
R
109869.0,10308.41014.2a
4
12
21
12R
8
12R
5
12R
┤=┤↕┤↕=
2112
12C12C
∝∝∝

+=
↕↕
∝∝∝∝

2
12

14

TV
€

The values of ***T***
C
, P
C
, V
, ω and ***μ*** of the components used in the present study are given in table 2-2 [9].

B
C

Table 2-2 Values of T
11

C , P C C , V C , ω and μ of Components Used in the Present Study.

Component	T C	P C	V C	ω	μ
Water	647.30	221.20	0.0571	0.344	1.8
Ethyl-acetate	523.20	38.30	0.2861	0.362	1.9
Toluene	591.75	41.08	0.3167	0.263	0.4

C

, B
22
, B

K bar cm
33
and B
13
3
/mol debye
are expressed the same way as ***B***
.

2.3.3 Fugacities from the Cubic Equations of State [8]

12
Cubic equations of state are another form of equation of state in which
the pressure is given by a cubic function of molar volume containing two parameters, which are functions of composition and possibly of temperature.

Many cubic equations are available in the literature, the widely used are:
Van Der Waals equation of state (1873), which is the simplest. Although this
equation is never accurate for real fluids, it is based on sound theoretical approximations and predicts behavior, which is, physically, essentially correct. The form of this equation is

a
bV
RT
P
=
Where
↕
i
n
)26.3.2(
V

=
2
i
2
)RT(27

a,aXa

And

◀

1i

i

=

€

=

2c

i

)27.3.2(

P64

c

i

ii

n

RT

b,bXb

◀

==

1i

i

=

c

i

)28.3.2(

P8

c

i

And the fugacity coefficient is given by

)ln(

bV
b
RTV
aa2
ϒ

↕↕↕
b
1Zln
i
i
i
∞
=
∏
′
≤

€

ƒ
⁄
)29.3.2(
V
Where the compressibility factor Z is given by

a
bV
V
Z ↕

=
)30.3.2(
RTV

Redlich-Kwong Equation of State (1949) this equation was a considerable improvement over other available equations, Redlich states that there was no particular theoretical basis for the equation; rather it is considered as an effective empirical modification of its predecessors. The form of this equation is

a
bV
RT
P
=
+
↕
)31.3.2(
T)bV(V
Equation (2.3.31) was modified by replacing the term (***a / T***
0.5
complicated function of temperature,
aα(***T***) incorporating the acentric factor,
the resulting equation is

a
bV
RT
P

=
〈
+
↕
) with a more
)32.3.2(
)bV(V

Peng-Robinson Equation of State (1976) structurally this equation is similar
to the previous equation with better representation of PVT data in the vicinity

of the critical point, the form of this equation is

a
bV
RT
P
=
Where
n
〈
↕++
↕
)33.3.2(
)bV(b)bV(V
jjiiij
n
◀◀
〈〈〈 ↕=
)34.3.2()a)(a()k1(XXa

And
1j
i
1i
j
==
[]
)35.3.2(
P
)RT(
45724.0a,)T1(n1
i,rii
i
2
=↕+=〈

2
iii
⎤⎤ ↕+=
2c
i
c
i
)36.3.2(26992.05422.137464.0n

ii
n
RT
07780.0b,bXb
◀

==
1i
i
=
And the compressibility factor is given by
c
i
)37.3.2(
P
c
i
32223
=↨↨↨↨↨+↨

(2.3.38)

0)BBAB(Z)B2B3A(Z)B1(Z
Where

n
n
◀◀◀
=↨=
i
n
)39.3.2(BXB,AA)k1(XXA
1i
j
1j
i
1i
ijiij
===
45724.0
i
P
i

T
i,r
A ==
〈
2
i,r
i
B,
P
07780.0

And the fugacity coefficient is given by

T
i,r
i,r

)40.3.2(

∏
B
)ln(

i
=
)BZln()1Z(
B
B828.2
A
ii
≤
ϒ
′
′
B
B
a
2
jjiiij
N
◀

↕↕+↕↕↕
B414.2Z
lna)(a()k1(X
〈〈
〈
1j
j
=
ƒ
⁄
∞
∞

The binary expression of the fugacity coefficient of equation 2.3.41 is
given by equations 2.3.42a and 2.3.42b.

B
Ln
≤
ϒ
() ()( )
B
B
1
1
⎞
+↕↕↕=
a
2
BZLn1Z
B
B828.2
A

+

∈
)41.3.2(

B414.0Z
()
⁄
′
221112211111111
1
↕+↕↕
〈
B
Ln
〈〈〈〈
Lnaa)k1(Xaa)k1(X
()
()( )
B
B
2
2
a
2
BZLn1Z
B
B828.2
A
∞
ƒ

+

B414.2Z
)a42.3.2(
B414.0Z

€
()
⁄
′
≤
ϒ

⎞
+↕↕↕=
B414.2Z
Lnaa)k1(Xaa)k1(X
22222221122211
2
〈〈〈〈
〈
↕+↕↕
Where

∞
f
↕++↕+↕=+=

AA)k1(XXAA)k1(
XXAA)k1(XXAA)k1(XXA,BXBXB
2222221221
+
)b42.3.2(
B414.0Z
122112211111112211
==↕+
↕+↕+↕=
〈〈〈〈
〈〈〈〈〈
0kk,aa)k1(XXaa
)k1(XXaa)k1(XXaa)k1(XXa

211222111221111111111
2211222222221122

The ternary expression of the fugacity coefficient of equation 2.3.41 is given by equations 2.3.43a, 2.3.43b and 2.3.43c.

€

B
Ln
() ()( )
B
B
1
1
a
2
BZLn1Z
B
aa
)k1(Xaa)k1(Xaa)k1(X
B414.2Z
Ln
3311
B828.2
A
/
′
ϒ

′

≤

⎞
13322111221111111
1

↨
+↨↨↨=
〈
+

↨+↨+↨

〈〈

〈〈〈〈

∈

)a43.3.2(

B414.0Z

B

Ln

()

()( )

B

B

2

2

a

2

BZLn1Z

B

aa

)k1(Xaa)k1(Xaa)k1(X

B414.2Z

Ln

3322

B828.2

A

⁄

′

ϒ

′

≤

⎞

23322222221122211

2

↨
+↨↨↨=
+

↨+↨+↨
〈〈〈〈
〈

〈〈

€
)b43.3.2(
B414.0Z
B
Ln
()
()( )
B
B
3
3
a
2
BZLn1Z
B
aa
)k1(Xaa)k1(Xaa)k1(X
B414.2Z
Ln
3333
B828.2
A
⁄
′
ϒ

′

≤

⎞

33322333221133311

3

↕

+↕↕↕=

+

↕

〈

↕+↕+↕

〈〈

〈〈〈〈

∈

)c43.3.2(

B414.0Z

Where

∈

∞

∞

f

∈

∈

∞

∞

ƒ
∞
∞
ƒ

+↕+↕=++=
AA)k1(XXAA)k1(XXA,BXBXBXB
21122111
1111332211
↕+↕+↕++↕+↕+↕
)k1(XXAA)k1(XXAA)k1(XXAA)k1(
XXAA)k1(XXAA)k1(XXAA)k1(XX
3222222212211231133
333323322313311332223
aa)k1(XXaa)k1(XXaa)k1(XXa
,AA

33
↕+↕+↕=
〈〈〈〈〈〈〈
33111331221112211111111
===↕++↕+↕+↕+
〈〈〈〈〈〈
0kkk,aa)k1(XXaa)k1(XX
aa)k1(XXaa)k1(XXaa)k1(XX
11333113222222221122211 2
〈〈〈〈
332211333333332233322 3

The roots of equation 2.3.38 are obtained by numerical technique two of these roots are ***Z***
V
and ***Z***
which are the compressibility factor at the gas and liquid phase respectively, these values are applied in equation 2.3.41 to obtain the fugacity coefficients of the vapor and liquid phase. The interacting parameters k
ij
L
are obtained from correlation of experimental data.

2.4 Fugacities in Liquid Mixtures

[3]

Calculation of fugacities from volumetric properties was mentioned in the previous section (2.3) it can be applied to condensed phases as well as gas phase. However, it is not practical to do so because the necessary integrations require that volumetric data be available at constant temperature and constant composition over the entire density range from the ideal gas state (zero density) to the density of condensed phase, including the two-phase region. A more useful alternate method is needed for calculation of fugacities in liquid solutions. Such a method is obtained by defining an ideal liquid solution and by describing deviations from ideal behavior in terms of excess functions; these functions yield the familiar activity coefficients that give a quantitative measure of departure from ideal behavior.

The partial molar fugacity of component i in a liquid solution as was given by the left hand of equation (2.2.3)

$$f_i^L = \gamma_i X_i f_i^0 \qquad (2.4.1)$$

At any composition, the activity coefficient γ_i depends on the choice of standard state and the numerical value of γ_i

has no significance unless the
numerical value of

f

i

0

is also specified.

2.4.1 The Ideal Solution [3]

An ideal liquid solution is one where, at constant temperature and pressure, the partial molar fugacity of every component is proportional to some suitable measure of its concentration, usually the mole fraction. That is,
at some constant temperature and pressure, for any component i in an ideal
solution,

ii

Ideal

)2.4.2(Xf

i

=

Where
is proportionality constant dependent on temperature and

i

pressure but independent of X

f

i

0

= , then γ

i

composition (from X

i

i

. Its noticed from equation (2.4.1) that, if we let
=1. If equation (2.4.2) holds for the entire range of

i

= 0 to X
= 1), the solution is ideal in the sense of
Raoult’s law. In many cases, the simple proportionality between f

i

holds only over a small range of composition. If X
is near zero, it is still

possible to have an ideal solution according to equation (2.4.2) without equating
to the fugacity of pure liquid i. Such a solution is called an ideal
i

i
dilute solution leading to the familiar relation known as Henry’s law.

i
L

21
and X
i

2.4.2 Activity and Activity Coefficients [3]

The activity of component i at some temperature, pressure, and composition is defined as the ratio of the partial molar fugacity of i at these
conditions to the fugacity of i in the standard state, that is a state at the same
temperature as that of the mixture and at some specified condition of pressure
and composition:

)X,P,T(f
)X,P,T(a
i
i

Where
P
0
=
and ***X***
)3.4.2(
)X,P,T(f
oo
i
0
are an arbitrary but specified pressure and composition. The activity coefficient
γ

is the ratio of the activity of i to some convenient
measure of the concentration of i, usually the mole fraction

=©
i
a
i
i
i
)4.4.2(
X

The partial molar excess function

E
i
Ideal
ii
↕=
E
i
G
is given by
)5.4.2(GGG

Where
Ideal
ii
G,G
are the actual and standard partial molar properties
respectively, the relation between the partial molar excess function and the
fugacity is given by the following

[ ]
)6.4.2()fln()fln(RTGGG

E
i
Ideal
ii
↕=↕=
Ideal
ii
If equation (2.4.1) and (2.4.2) are substituted in equation (2.4.6) and setting

f
i
0

= we obtain
i

i
E
)7.4.2()ln(RTG

i
©=

Partial molar excess functions are defined in a manner analogous to that used for partial molar thermodynamics properties. If M is an extensive thermodynamic property, then
m
, the partial molar M of component i, is defined by

M
m
i
=

Where n

=
˥
˥
◀
i
€

i

)8.4.2(

n

n,P,T

i

j

is the number of moles of i, also from Euler’s theorem, where

)9.4.2(mnM

i

ii

If equation (2.4.9) is applied to equation (2.4.7) the following equation is obtained

E

◀

= ©

)10.4.2()ln(XRTG

i

ii

2.4.3 Activity Coefficients from Excess Functions [3]

At a fixed temperature, the molar excess Gibbs energy ***G*** depends on the composition of the mixture and, to a smaller extent, on

E

pressure. At low or moderate pressures, well removed from critical conditions, the effect of pressure is negligible. Any expression for the molar

excess Gibbs energy must obey the following condition

G

E

= 0 when X

i

of a mixture

= 0, i = 1, 2, … ***(2.4.11)***

Wohl (1946) [11] proposed a general method for expressing excess Gibbs

energies, the main advantage of his method is that rough physical significance

can be assigned to the parameters that appear in the equations; as a result, Wohl’s expansion can be extended systematically to multicomponent solutions. Many equations have been proposed for the relation between activity coefficients and mole fractions and new ones appear every year [6].

Some, but not all, of these can be derived from Wohl’s general method. In
practical, three equations that are useful for many practical calculations cannot be obtained by Wohl’s formulation.

Wilson Equation. Based on molecular considerations, Wilson (1964) [12] presented the following expression for the excess Gibbs energy of a binary solution:

G
1212221211
E
ℑℑ +↨+↨=
)12.4.2()XXln(X)XXln(X
RT

The activity coefficients for binary systems derived from this equation are:

ℑ©
+
++↨=
X)XXln()ln(

221211
ℑ©
+
↨+↨=
X)XXln()2ln(
11212

ℑ
ℑ
2121
12
1212
21
+
↕
ℑ
ℑ
€

)a13.4.2(
XXXX
ℑ
ℑ
2121
12
1212
21
+
↕
ℑ
ℑ
€

)b13.4.2(
XXXX

Equation (2.4.12) obeys the boundary condition that
G
E
vanishes as either ***X***

or
X
A
21
2

becomes zero. Wilson's equation has two adjustable parameters, ***A***
in Wilson's derivation these are related to the pure-component molar volumes by

ℑ

12
↕=
V
2
exp(
V
1
└└
1112
,)
RT
└└
ℑ
21
↕=
V
V
1
2
exp(
2221
RT
12
1
and
)c13.4.2()

Where ***V***
is the molar liquid volume of pure component i and the ***λ***'s are energies of interaction between the molecules 1, 2. To a fair approximation,
the differences in the characteristic energies are independent of temperature,
at least over modest temperature intervals. Therefore, Wilson's equation gives

not only an expression for the activity coefficients as a function of composition but also an estimate of the variation of the activity coefficients with temperature. This may provide a practical advantage in isobaric calculations where the temperature varies as the composition changes.

i

Wilson’s equation appears to provide a good representation of excess Gibbs energies for a variety of miscible mixtures. It is particularly useful for solutions of polar or associating components (e.g., alcohols) in no polar solvents. A study of Wilson’s equation by Orye (1965) [13] shows that for approximately 100 miscible binary mixtures of various chemical types, activity coefficients were well represented by Wilson’s equation. Similar conclusions were obtained by Gmehling et al.[14], who Reported Wilson parameters for many binary systems. The serious disadvantage of the Wilson’s equation lies in its inability to predict limited miscibility. When Wilson’s equation is substituted into the equations of thermodynamic stability for a binary system, no parameters A_{12} and A_{21} can be found that indicate the existence of two stable liquid phases. Wilson’s equation therefore, should be used only for liquid systems that are completely miscible or else for those limited regions of partially miscible systems where only one liquid phase is present.

For partially miscible systems, Wilson (1964) [12] suggested that the right hand side of equation (2.4.12) be multiplied by a constant greater than unity. This suggestion not only introduces a third parameter but, more important, creates difficulties when the equation is applied to ternary systems.

Also a modification has been made to Wilson equation to overcome the

problem of partial miscibility the simplest useful modification is that of Tsubota and Katayama [15] which is referred as the
T-K-Wilson model or
Modified Wilson. The excess Gibbs free energy is given by the following equation

G
E
lnX
RT

+

+
=
XX
VXX
1221
1

€
+

2
1221

VXX
lnX

+
+
2112
2112
€

)14.4.2(

XX
ℑℑ

The activity coefficients derived from this equation are:

©
)ln(

1
©
)ln(

2
=

+
+
VXX
ln

X
XX
V
X
=
2

1221
1221
2112
21
VXX
1
2112
21
XX
1
12211221
1

+
↕
€

)a15.4.2(
XXVXX
+
VXX
ln
V
X
1

€
+

+

+
𝔍𝔍

+
+

2112
2112
X
XX

1221
12

ℑ
ℑ
VXX
1
1221
12
XX
1
21122112
2
+
↕
€

€
+

)b15.4.2(
XXVXX
+
The parameters ***A***
V

V

21
i
are equal to ***V***
= *E*
i
(5.7 + 3 T
Where ***E***
i

€
+

+

$\Im$

$+$

$\Im\Im$

$_{12}$

$_{2}$

and A

$/$

$_{Ri}$

V

$_{1}$

$_{21}$

and V

$\Im$

€

$+$

are also given by equation (1.4.13c) and V

$_{1}$

$/ V$

$_{2}$

respectively. The volume **V**

$_{i}$

$_{12}$

is given by

$)$ ***(2.4.15c)***

is equal to 0.2363, 0.2121 and 0.0409 for Toluene, Ethyl-acetate and Water respectively and

T

$_{Ri}$

is the reduced temperature.

and

The ternary expressions of the activity coefficients are given by equations 2.4.16a, 2.4.16b and 2.4.16c.

$()$

LnLn

1
X
X
1
2

AXAXAX
VXVXVX
133122111
133122111

++

VXVXVX
V
133122111
11
VXVXVX
V
233222211
21
V
X
31
3
VXVXVX
333322311
AXAXAX
A
123122111
11

++

AXAXAX

A

233222211

21

++

++

=

©

()

LnLn

2

X

X

1

2

++

++

++

AXAXAX

VXVXVX

VXVXVX

V

VXVXVX

V

↕

∈

+

A

31

++

AXAXAX

333322311

A

VXVXVX
V
X
3

++
++
=
©
()
LnLn
3
X
X
X

233222211
233222211

++

133122111
12
233222211
22
333322311
32
++
AXAXAX
A
123122111
12

++

1
2
3

++
++

++
++
=
©

AXAXAX
VXVXVX
333322311
333322311
VXVXVX
V
133122111
13
VXVXVX
V
233222211
23
V
333322311
33
VXVXVX

∈
+

AXAXAX
A

233222211
22
333322311
32
++
↕

€
+

€

€
€

€
+

€

+

+

)a16.4.2(
)b16.4.2(
AXAXAX

++

AXAXAX
A
123122111
13

++

++
++
AXAXAX
A
233222211
23

++
++

€
+

A
333322311
33

€
+

€
+

€

)c16.4.2(
AXAXAX

The adjustable parameters A are obtained from correlation of experimental data.

ij

NRTL Equation. The basic idea in Wilson's derivation of equation (1.4.21) follows from the concept of local composition (Two Liquid Theory). This concept was also used by Renon (1968) [16] in his derivation of the NRTL (non random two liquid) equation; however, Renon's equation, unlike Wilson's, is applicable to partially miscible as well as completely miscible systems. The NRTL equation for the excess Gibbs energy is

21
E
RT
G

G
GXX
G
XX

1212
1212
+
=

Where

RT
gg
2212
12
| |
=
| |

2121
2121
+
+
€

)17.4.2(
GXX
=
gg
,
1121
21
)18.4.2(
RT
|⟨|⟨ ↕=↕=
)19.4.2()exp(G,)exp(G
212121121212

The significance of
g
ij
is similar to that of ***λ***
in Wilson’s equation. The
parameter
α
12
(***α***
12
= ***α***
21
ij
) is related to the non-randomness in the mixture; ***α***
is zero, the mixture is completely random and equation (2.4.17) reduces
to the
Two-Suffix Margules equation. The NTRL equation contains three
parameters, but reduction of experimental data for a large number of
binary
systems indicates that
α
α

12

12

varies from about 0.20 to 0.47; a typical choice is
= 0.3 [3]. The activity coefficients for binary systems are given by

12

∕

′

ϒ

+

G

GXX

G

X)ln(

21

2

21

=

′

≤

+

2121

21

€

2

|

|©

+

1212

)a20.4.2(

)GXX(

2
1212
/
′
ϒ
+
G
GXX
G
X)ln(
12
2
12
=
′
≤

+

1212
12

∈
2121
2
|
|©
+

∞
∞
ƒ
)b20.4.2(
)GXX(
2
2121
∞
∞
ƒ

The ternary expressions of the activity coefficients are given by equations 2.4.21a, 2.4.21b and 2.4.21c

GXGXGX
Ln

Ln

()
©
1
+
+
++
=
|||
313312122111111
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For moderately non-ideal systems, the NRTL equation offers no advantages over the Wilson and T.K.Wilson equations. However, for strongly non-ideal mixtures, and especially for partially immiscible systems, the NRTL equation often provides a good representation of experimental data if care is exercised in data reduction to obtain the adjustable parameters.

UNIQUAC Equation. An Attempt was made to derive a two parameter equation for G^E that retains at least some of the advantages of the equation of Wilson without restriction to completely miscible mixtures. Abrams [17] derived an equation that, in a sense, extends the Quasi Chemical theory of Guggenheim for nonrandom mixtures to solutions containing molecules of different size. This extension was therefore called the ***Universal QuasiChemical*** theory or, in short, ***UNIQUAC***.

The UNIQUAC equation for G^E consists of two parts, a ***combinatorial part*** that attempts to describe the dominant entropic contribution, and a ***residual part*** that is due primarily to intermolecular forces. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure-component data.

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The residual part depends also on intermolecular forces; the two adjustable binary parameters, therefore, only appear in the residual part. The UNIQUAC equation is

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Parameters r, q, and q' are pure-component molecular-structure constants depending on molecular size and external surface areas. In the original formulation, $q = q'$. To obtain better agreement for systems containing water or lower alcohols, q' values for water and alcohols were adjusted empirically by Anderson [3] to give an optimum fit to a variety of systems containing these components. For alcohols, the surface of interaction q' is smaller than the geometric external surface q, suggesting that intermolecular attraction is dominated by the OH group (hydrogen bonding). For each binary mixture, there are two adjustable parameters, τ_{12} and τ. These are given in terms of characteristic energies Δu

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Table 2-3 Structural Parameters of Components Used in the Present Study.

Component	***r***	***q***	***q***
Water	0.92	1.40	1.00
Ethyl-acetate	3.48	3.12	3.12
Toluene	3.92	2.97	2.97

The UNIQUAC equation is applicable to a wide variety of nonelectrolyte liquid mixtures containing non-polar or polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc. and water, including partially miscible mixtures.

With only two adjustable binary parameters, it cannot always represent high-quality data with high accuracy, but for many typical mixtures encountered in chemical practice, UNIQUAC provides a satisfactory description. UNIQUAC parameters for many binary systems are given by J.Gmehling [14].

The UNIFAC Method. A group contribution method for prediction of activity coefficients which combines the solution of functional groups concept with a model for activity coefficients based on an extension of the Quasi Chemical theory of liquid mixtures (UNIQUAC). The resulting UNIFAC model (UNIQUAC Functional-group Activity Coefficients) contains two adjustable parameters per pair of functional groups. By using groupinteraction parameters obtained from data reduction, activity coefficients in a large number of binary and multicomponent mixtures maybe predicted, often with good accuracy. This is demonstrated for mixtures containing water, hydrocarbons, alcohols, chlorides, nitriles, ketones, amines, and other organic fluids in the temperature range 275 ^{o} to 400 ^{o}K [18].

The equations used in the UNIFAC method will be listed in a form different from the original form mentioned in [18], the equations are [9]:

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Where ***v***
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are subgroups parameters that come from tabulations in the literature [19].

The binary expression of Activity coefficients are given by equations
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The ternary expression of the UNIFAC equation was obtained via the software (UNIFAC Activity Coefficient) programmed by the Chemical Engineering Departments at the University of Sydney Australia and Louisiana State University USA.

2.5 Equilibrium Stills

There are a large number of industrially important systems whose equilibrium relations cannot be predicted from purely theoretical considerations and which must be obtained by a direct experimental determination. The direct experimental determination of vapor-liquid equilibrium means that we separate samples of the liquid and vapor which are in true equilibrium and determine the concentrations of both phases analytically.

The determination of the equilibrium curves can be carried out either at constant temperature or at constant pressure. For distillation calculations the isobaric data are especially important and their determination is also simpler. In an accurate measurement it is necessary to have perfect control of both the temperature and pressure. From the published data it is evident however that even with the most painstaking measurements of these properties of the system certain inconsistencies in the measured equilibrium data can appear [20, 21].

The design and construction of the equilibrium stills can be a source of various errors, which need not have the same importance in all systems measured (relative volatility, heat of vaporization etc.). Even though so far it has not been possible to construct a still which would yield thermodynamically completely consistent data for all systems [21], most new units give data of adequate precision for distillation calculations.

The methods for the direct determination of equilibrium data can be classified for the most part into the following groups [22]:
1- Distillation method.
2- Circulation method.

3- Static method.
4- Dew and bubble point method.
5- Flow method.

Circulation method this method is the most widely used, it’s convenient to be used in both the region of medium and low pressures. Even though the various equilibrium stills with circulation differ significantly from one another in their construction details, they are all based on a common principle which is shown in Figure 2-2.

A
B

Figure 2-2 Diagram of Circulating Stills

The vapors evolved from the boiling mixture in the distilling flask (A) pass through the vapor conduit (   ) and after complete condensation collection in the receiver (B). After filling the receiver the condensate returns to the distilling flask through the liquid conduit (   ). If the still is started with the receiver (B) empty, at the instant when it first fills, its contents are richer in the more volatile constituent than is the vapor phase over the boiling mixture in the distilling flask. With further operation of the still, the contents of the distillation flask become richer in the more volatile component and the receiver becomes poorer. This process continues until the steady state is attained, in which the compositions in both vessels no longer change with time. Both compositions are determined analytically.

According to the manner of circulation of the phases, these stills can be classified into two groups:

(a) Stills with circulation of the vapor phase.
(b) Stills with circulation of both vapor and liquid phase.

Stills with circulation of the vapor phase the first still with circulation of the vapor phase was proposed by ***Jamaguchi*** and ***Sameshima*** [22], but the first equilibrium still which functioned satisfactory was constructed by ***Othmer*** [23] as shown in Figure 2-3.

Figure 2-3 Othmer Still

The distillation flask (A) is filled to fifth of its height which is brought to boil by a burner or electric heater. The evolved vapor fills the space above the liquid and then enters the vapor tube (P) and then flows to the condenser (CH), after complete condensation it flows into the receiver (B).

When the receiver is filled the additional condensate is returned through the weir (M) to the distilling flask (A). After a several-fold exchange of the contents of the receiver the steady state is attained in which the composition of the liquid in the boiling flask and the composition of the distillate no longer changes (30-60 min). Samples of the boiling liquid and condensed vapor can then be withdrawn from valves K1 and K2 respectively into sampling flasks for analysis.

The results obtained from this instrument may contain ***errors***, the vapor jacket around the tube carrying vapor to the cooler does not completely prevent partial condensation [21], it is recommended to insulate the upper part of the instrument or to heat it with a resistance winding. On the other hand it is necessary to avoid superheating the walls of the still, as this could lead ***to non-equilibrium total evaporation of droplets*** sprayed on the walls. The temperature measured in the vapor phase does not always correspond to the true boiling point. Because the boiling itself is not sufficient to ensure thorough mixing of the boiling liquid with the returning cold condensate, ***concentration gradients can arise*** in the distilling flask. The liquid in equilibrium with vapor ***mixes with part of the returning condensate during the withdrawal of the sample***. Othmer [24, 25, 26] proposed further modifications to remove the errors in the still. The whole instrument is made of hard glass, it is quite compact for this reason and because of its simple operation this still is very frequently used despite the cited errors. The Othmer still have been further improved by many authors [27, 28, 29, 30, 31]. None of Othmer and some of the improved stills can be used to determine vapor – liquid equilibrium in systems of limited miscibility, since the vapor after condensation and cooling usually separates into two layers and the condensate cannot be returned to the boiling flask with the liquid phases in the correct ratio.

These data are of great industrial importance, particularly in the field of azotropic and extractive distillation, a special circulation still for this purpose is needed [31] as shown in Figure 2-4.

Figure 2-4 VLE Still for Partial Miscible Systems

The boiling flask of this still is fitted with three necks; two of them (A) are for thermometers for measuring the temperature in the liquid and vapor phases and one (C) is for filling the still. The solution to be measured is placed in the flask and brought to boil with the internal heater (I). The vapor leaving through the main vapor conduit (E) condenses in the cooler and returns in the three-way valve (K) and small cooler (F) to the boiling vessel. A magnetic mixer is used. After reaching steady-state (60 min) the three way valve (K) is turned so that the condensate flows through the auxiliary cooler (F) directly into the sampling bottle. With this still it is only possible to determine the phase equilibrium for a solution that is homogeneous at the boiling point; magnetic mixing is not adequate for complete mixing of the heterogeneous mixture.

For this reason some authors propose the use of mechanical mixing [2] as shown in Figure 2-5.

Figure 2-5 VLE for Partial Miscible Systems with Mechanical Stirrers.

The above still consists of a liquid chamber (A) provided with a heater, a 20 mm diameter vapor space containing a saucer –shaped baffle (C) which eliminates entrainment by deflecting the liquid spray from condenser (D), a condensate chamber (E) and a line back from the liquid chamber. The two phase liquid is boiled in the liquid chamber where it is completely emulsified by the stirrer. The vibration of the stirrer pumps the liquid up between the inside of the stirrer and the wall of the heating surface. The vapor condenses into a two phase liquid which collects in the condensate chamber (E), the condensate stirrer is powered by the same vibrating unit as the main stirrer.

The returning condensate leaves the condensate chamber (E) via a sloping tube of 1 mm bore which has a very fine construction over the half of its length next to the chamber. This ensures that a minimum of separation occurs in the return tube and that the condensate leaving is reprehensive of the dispersed two phase mixture in the condensate chamber.

2.6 Azeotropic Predictions

The term ***Azeotrope*** means “non-boiling by any means” (Greek: a- non, zeo- boil, tropos – way/mean), and denotes a mixture of two or more components where the equilibrium vapor and liquid compositions are equal at a given pressure and temperature. Systems which do not form Azeotropes are called Zeotropic. Azeotropes occur frequently between compounds whose boiling points differ by less than about 30 ^{o}C. If the vapor and liquid are of the same composition, the two-phase mixture is called a ***Homogenous Azeotrope***. The constant-boiling mixtures that occur with a vapor and two or more dense phases are called ***Heterogeneous Azeotrope***. Figure 2.1 represents a VLLE system with minimum-boiling Heterozeotrope.

The ability to predict Azotropic behavior becomes more and more important and complex when the number of components in the mixture increases. The prediction is tested successfully by applying the Gibbs-Konovalov theorem [32]. They developed correlation equations for expressing boiling temperature of the vapor-liquid equilibrium data, isobaric conditions, as a function of liquid composition, where

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Where T_i^0 is the boiling temperature of the pure component (i) in C, and N the number of components in the mixture. The coefficients A_{ij}, B are binary or ternary parameters which are determined directly from the binary or ternary data. The increase in the number of parameters increases the prediction accuracy.

The Gibbs-Konovalov theorem for multicomponent systems states that the following conditions are fulfilled at the azeotropic point at constant pressure:

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Equation 2.6.4 is solved numerically for the value of X
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value is inserted in equation 2.6.3 and the temperature of the binary Azeotrope is determined.

For a ternary mixture equation 2.6.1 and 2.6.2 are written as in Table 2-4.
Equations 2.6.6 and 2.6.7 are solved numerically for the values of X
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then the values are inserted in equation 2.6.5 and the temperature of the ternary Azeotrope is determined. The parameters of equations 2.6.3 and 2.6.5
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Table 2-4 The Gibbs-Konovalov theorem for Ternary systems**.**

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T
)6.6.2(])X2X1(C)X2X1(BA[X

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321232121232
BA[X)]X2X1(C2B[X)XX1(
])XX21(C)XX21(BA)[XX21(
13133321313332
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)7.6.2(])XX(C)XX(BA[X
)]XX(C2B[XX])X2X1(C)X2X1(
321332
2

32233223233
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2.7 Previous Studies of VLLE Systems

The previous studies did not use the term VLLE systems, where the term partial miscible systems [1, 31, 2] or systems of limited miscibility [33, 34] was used, then authors started using the term VLLE of three phase systems [35, 36, 37]. Most of the studies that involved experimental work used a modified equilibrium still to deal with partial miscible systems. Some of the most important studies of binary system are:

1- One of the first studies was the determination of VLE of the systems nButanol \ Water and Isobutanol \ Water at 760 mmHg [38]. The equilibrium still used consists of a flask closely connected to a condenser by a flexible connection. The condenser could be tilted so that the condensate either refluxed totally or was wholly collected in the receiver. Only a vapor sample could be collected by this still. The VLE data collected for the system

Isobutanol \ Water showed a constant vapor composition of 67 mole % Isobutanol for a liquid charge of 2 to 43 mole % Isobutanol also for the system of n-Butanol \ Water showed a constant vapor composition of 25 mole

% n-Butanol for a liquid charge 1.5 to 50 mole % n-Butanol.

2- A study on the system Isobutanol \ Water at 758-762 mmHg [1] was achieved using equilibrium still specially constructed for partial miscible systems, the still was a circulation type of both the vapor and liquid. The data obtained did show a constant vapor composition, the initial charges in the still where a single phase liquid charge only one charge was a two phase liquid charge. Thus the system studied could not be considered as a VLLE system.

3- The system 1-Butanol \ Water at 760 mmHg [31] was studied in a modified Othmer still as shown in Fig.2.5.3. The data obtained showed a constant vapor composition of 75 mole % 1-Butanol for a liquid charge of 54 to 97 mole % 1-Butanol. The data was correlated by the aid of Van Larr equation.

4- A study on the systems Ethyl-acetate \ Water, Methyl Ethyl Ketone \ Water, n-Butyl Alcohol \ Water and Isobutyl Alcohol \ Water at 760 mmHg [2] were accomplished with a modified Othmer still with mechanical stirrers. The data collected showed a constant vapor composition of 70.9 mole % Ethyl-acetate for a liquid charge 35 to 69 mole % Ethyl-acetate, a constant vapor composition of 64 mole % Methyl Ethyl Ketone for a liquid charge of 20 to 56 mole % Methyl Ethyl Ketone, a constant vapor composition of 26 mole % n-Butyl -Alcohol for a liquid charge of 6.4 to 24 mole % n-Butyl Alcohol and a constant vapor composition of 33.5 mole % Isobutyl Alcohol for a liquid charge of 6.4 to 22.4 mole % Isobutyl Alcohol. The data was correlated by the aid of Van Larr three suffix equation.

5- The system Water \ Methyl Isobutyl Ketone at 760 mmHg [34] was studied in the same still in (3) above. The data collected showed a constant vapor composition of 64.1 mole % Methyl Isobutyl Ketone for a liquid charge of 30 to 90 mole % Methyl Isobutyl Ketone. The data was correlated by the aid of the Modified WILSON Equation.

6- The systems 2-Methyl-1,3-dioxolane (2MD) \ Water and 2,4-Dimethyl-1,3dioxolane (24DMD) \ Water at 760 mmHg [39] were studied in a modified

Othmer still with mechanical

mixing.
The data showed a constant vapor composition of 67 mole % 2MD for a liquid charge of 33 to 57 mole % 2MD.
The data was correlated by the aid of the UNIQUAC Equation.

And some of the most important studies of ternary systems are:

1- A study on the system MEK \ Benzene \ Water at 760 mmHg [40] was accomplished in an Othmer still, only homogenous liquid charges were studied (single phase liquid charge), the condensed vapor formed a two phase liquid.

2- The system Cyclohexane \ 2-Propanol \ Water at 760 mmHg [41] was studied in a modified Othmer still, both homogenous and heterogeneous liquid charges were studied. The data were correlated by the aid of both Van Larr and Redlich-Kister Equations.

3.1 Chemicals

CHAPTER THREE

EXPERIMENTAL WORK

The chemicals used in this study were fine chemicals of high purity and known brand tables 3-1 and 3-2 lists the specification of the chemicals used in this study.

Table 3-1 Specification of Chemicals Used in the Present Study

Chemical	Assay	N.V.M*	Water	Manufacturer
Ethyl-acetate	99.7%	0.0005%	0.03%	Riedel-de Haen
Toluene	99.9%	0.001%	0.03%	BDH
Distilled Water	100 %			Triple distilled
Acetone	99%	0.005%	0.5%	BDH

* Non volatile mater.

Table 3-2 M.Wt. and density of chemicals used in present study.

	Toluene	Ethyl-acetate	Water
M.Wt.	92.14	88.11	18.016
Density (g/L) 20 ©	0.8669	0.901	0.998

3.2 Equilibrium Still

The equilibrium still used in this study is a circulation type still with circulation of the vapor; it’s similar to Othmer still [23]. Some modifications were applied to the still so it can be used for partial miscible systems. The modifications helped in giving a steady temperature reading in the boiling section and helped in keeping the condensed vapor in the condensing section in a semi homogenous state. The modifications were:

1- The still was supplied with mechanical mixers for both the boiling section (boiler) and the condensation section (condenser).

2- The still was supplied with multi-impeller shafts for both mixers of the boiling section and the mixing section.

3- The still was supplied with two reflux lines for the reflux of the condensed vapor to the boiler.

The assembled still as shown in Figure 3-1 consists of the following parts:

12
5
9
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Figure 3-1 Assembled Still of the Present Study.

1- A 55 mm diameter glass cylinder type QVF (Length = 325mm).
2- Quick-fit head with two P.E bushing rings.
3- Thermometer well.
4- Multi-impeller shaft (Length = 400 mm).
5- Sampling valve.
6- Inclined pipe with thermo well (Length = 50 mm).
7- Capillary pipes (1 mm diameter) with spherical bulb.
8- A 40 mm diameter glass cylinder type QVF (Length = 250 mm).
9- Quick-fit head with two P.E bushing rings.

8
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10- Multi-impeller shaft.
11- Glass condenser connection with flange (Length = 90 mm).
12- Vapor conduct (prevents condensation of vapor on walls of boiling section.

The multi-impeller shafts were driven by electric motors type Parvalux electric motor LTD with a max. Speed of 2500 rpm. The speeds of the motors were controlled by a volt Regulator (0 – 300 volts), at all the runs the speed of the motors were from 1400 to 1600 rpm.The shafts were connected to the motor by rubber pipes to reduce the vibration. The P.E bushing rings in the Quick-fit heads helped in preventing vapor leakage and also reduces the vibrations from the motor (see Appendix A.1). The still was heated by a heating mental with grades from 0 – 10 grades. The vapor was condensed by a glass condenser connected at the condenser connection (11); the connection was accomplished by two stainless steel flanges with a Teflon cascade. The cooling fluid in the condenser was a once through tap water at 17-23 C, when the tap water temperature exceeded this range (Runs performed in the summer) the condenser was connected to a water bath with refrigeration unit (-10 to 150 ^{o}C) type Julabo. The whole still is insulated with fiber glass insulation except the condensing section. A picture of the whole unit used in the present study is shown in Figure 3-2.

When the still was used to determine LLE data the heating mantle was replaced by a water bath with temperature control type Memmert, where the still was partially immersed in the water bath as shown in Figure 3-3. The condenser is not needed in the LLE data measurement, and the mixer in the condenser section is also not needed, the quick fit head (2) is replaced by a rubber cork with three holes the middle one for the multi-impeller shaft and the other two for the pipettes for sampling the two liquid layers.

o

Figure 3-2 Picture of the whole unit used in the present study.

Figure3-3 Still used for LLE data measurement.

3.3 Temperature Sensor

The temperature was measured by a NiCr-Ni sensor which is able of temperature measurements of liquids and gases in the range -200 to +1200 C, the temperature was recorded and represented graphically via a ***CASSY Module Interface*** in conjunction with a personal computer (486) and the software "***Universal Data Acquisition***", more details are given in appendix (A.2). A schematic of the unit with the control is shown in Figure 3-4.

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Figure3-4 Schematic of the Unit with the Control Used in the Present Study.

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4

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8
3
9
9
1- Computer
2- Interface
8
12
3- Temperature sensor

4- Heating mantle
5- Modified Still
6- Condenser
7- Electric motor
8- Voltage regulator
9- Cooling water inlet and outlet
10- Thermometer
11- Condensing section
12- Boiling section
13- Vapor path

3.4 Preparation of Liquid Mixtures

The liquid mixtures were prepared by measuring a volume of each chemical by a graduated cylinder (100 ml). The chemicals were not mixed before charged in the still.

The mole percent of each chemical in the liquid mixtures measured in present study are given in table 3-3.

Table 3-3 Composition of liquid mixtures measured in the present study.

	Mole percent		
Mixture No.	Toluene	Ethyl-acetate	Water
1	0.266	99.734	
2	0.986	99.014	
3	1.555	98.445	
4	2.416	97.584	
5	4.341	95.659	
6	10.180	89.820	
7	26.535	73.465	
8	33.837	66.163	
9	40.571	59.429	
10	47.233	52.767	
11	55.739	44.261	
12	66.891	33.109	
13	71.315	28.685	
14	79.644	20.356	

15	82.450	17.550
16	88.782	11.218
17	95.000	5.000
18	98.400	1.600
19	1.670	98.330
30	2.369	97.631
21	5.358	94.642
22	8.622	91.378
23	14.519	85.481
24	21.318	78.682
25	29.398	70.602
26	36.909	63.091
27	44.215	55.785

Table 3-3 (cont/d) Composition of liquid mixtures measured in the present study.

	Mole percent		
Mixture No.	Toluene	Ethyl-acetate	Water
28	54.315	45.685	
29	61.737	38.263	
30	75.956	24.044	
31	76.151	23.849	
32	86.883	13.117	
33	89.465	10.535	
34	91.772	8.228	
35	94.941	5.059	
36	12.603	64.209	23.188
37	19.469	42.321	38.210
38	22.778	38.904	38.318
39	26.106	35.467	38.427
40	29.453	32.011	38.536
41	32.819	28.536	38.645
42	38.957	38.107	22.936
43	39.608	21.525	38.867
44	41.318	19.759	38.923
45	46.476	14.432	39.092
46	53.424	7.258	39.318
47	55.227	21.711	23.062
48	61.528	15.100	23.372

49 67.540 9.068 23.392
50 72.327 14.769 12.904

The total volume of each mixture measured in the present study is 200-300 ml.

3.5 Operating the equilibrium still for VLLE measurements

The measurements by the modified equilibrium still of the present study are begun by inserting the liquid mixture one chemical at a time in the boiling section and the following procedure is followed:

1- Running the software “***Universal Data Acquisition***”, that measures and records the temperature of the liquid mixture with time via the personal computer.

2- Starting the heating mantle from the above software via the Interface (***CASSY Module Interface***) and starting the mixer of the boiling section at a rate below vortex formation.
3- When the liquid mixture starts boiling after 25-40 min the cooling water is allowed to flow in the condenser at a rate of about 2 liter / min.
4- As vapor starts to condense the mixer of the condensation section is started at a rate below vortex formation.

5- After the temperature of the liquid mixture reaches steady state (constant value) usually after 70-80 min samples are withdrawn from both the boiling and the condensation sections.

6- After samples are withdrawn the software is turned off by saving the recorded data in the personal computer under a certain name e.g. VLLE

.

7- The mixers are turned off and the cooling water to the condenser is stopped after 10-15 min.

3.6 Sampling Methods

The samples are withdrawn from the still from both the condensation and the boiling section into a graduated test tube (0-5 ml) with 0.1 ml graduation; the samples withdrawn are 4-5 ml for each of the boiling liquid and the condensed vapor. Three methods of sampling were employed:

1- Taking samples of both the condensed vapor and the boiling liquid [2].
2- Stopping the mixer of the boiling section then after 2-5 min the heating mantle is turned off and a sample of the condensed vapor is withdrawn and then a sample from each layer of the boiling liquid is withdrawn separately [39].
3- Taking sample of the condensed vapor only [38].

The withdrawn samples are placed in a water bath at a temperature of 20 ^{o}C and are left over night for complete separation of the two liquid layers in each sample. Then the volume of each layer is measured by the graduation on the test tube.

3.7 Sample Analysis

Most of the samples of the measured liquid mixtures in the present study were with two liquid layers, a sample was taken from each layer by a 0.1 ml pipette with 0.01 ml graduation then the refractive index of these samples were measured at 20 ^{o}C by a Refractometer, details of the measuring procedure is given in appendix B.1.

Two calibration curves were used to determine the mole fraction of the samples one for the top layer (Organic layer) and one for the bottom layer (Aqueous layer). The curves were obtained by preparing liquid mixtures of different mole composition for each layer and measuring the refractive index and the data obtained were represented graphically. Figures 3-5 and 3-6 represent the calibration curve of the aqueous and organic layer respectively of the system Ethyl-acetate \ Water.

R.I (refractive index)
1.3370
1.3380
1.3390
1.3330
1.3340
1.3350
1.3360

Aqueous layer(20 C)

$$R.I = 0.0023X1^3 - 0.0068X1^2 + 0.0072X1 + 1.333$$

$$R^2 = 1$$

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
Mole% Ethyl-acetate

Figure 3-5 Calibration curve of the aqueous layer of the system Ethyl-acetate \ Water.

R.I (refractive index)
1.3758
1.3759
1.3760
1.3761
1.3762
1.3763
1.3757

Organic layer(20 C)

R.I = 1.3526X1
R^{2} = 0.9998
0.0038
88.0 90.0 92.0 94.0 96.0 98.0 100.0
Mole % Ethyl-acetate (X1)

Figure 3-6 Calibration curve of the organic layer of the system Ethyl-acetate \ Water.

The system Toluene \ Water was considered as an immiscible system were the solubility of Toluene in Water is 0.05% at 20 ^{o}C and the solubility of Water in Toluene is 0.03% at 20 ^{o}C. As for the system Toluene \ Ethyl-acetate \ Water Fig.3.7.1 was used for the bottom layer of the samples withdrawn, for the top layer of the withdrawn samples a calibration curve was obtained by preparing liquid mixtures of different compositions of Toluene and Ethylacetate

and measuring the refractive indices
of these mixtures and the data
obtained
were represented graphically. Figure
3-7 represents the calibration
curve
of the organic layer for the system
Toluene \ Ethyl-acetate \ Water.

R.I (refractive index)

1.4400
1.4700
1.5000
1.5300
1.3500
1.3800
1.4100
O
rganic layer(20 ©
Organic layer (20
R.I = 0.0012x + 1.382
R
2
= 0.9934
o
C)
)
0.0 20.0 40.0 60.0 80.0 100.0
Mole % Toluene (X1)

Figure 3-7 Calibration curve of the organic layer of the system Toluene \ Ethyl-acetate \
Water.

The assumption of Water is not present in the top layer of the withdrawn
samples of the system Toluene \ Ethyl-acetate \ Water is quite reasonable due
to the low solubility of Water in Toluene, and Toluene not present in the
bottom layer of the withdrawn samples also due to the low solubility of
Toluene in Water.

3.8 Operating the equilibrium still for LLE measurements

The same equilibrium still was used for LLE measurements of the system Ethyl-acetate \ Water in the temperature range 25-65 ^{o}C. The measurements are begun by inserting the liquid mixture one chemical at a time in the boiling section and the following procedure is followed:

1- Running the software “***Universal Data Acquisition***”, that measures and records the temperature of the liquid mixture with time via the personal computer.

2- Setting the water bath temperature at the desired value and starting the mixer of the boiling section at a rate below vortex formation.

3- After the temperature in the still reaches a steady state value (constant value) usually after 45-60 min the mixer is stopped.

4- After a period of 5 min samples are withdrawn from each layer by a 0.1 ml pipette with 0.01 ml graduation into a graduated test tube (0-5 ml) with 0.1 ml graduation.

5- After samples are withdrawn the software is turned off by saving the recorded data in the personal computer under a certain name e.g. LLE1.

The withdrawn samples are treated and analyzed as in VLLE measurements. All the measured liquid feed mixtures were 15.585 mole % Ethyl-acetate.

3.9 Cleaning the equilibrium still

The equilibrium still is disconnected from the whole unit after each measurement and drained from the remaining liquid mixture and rinsed with
acetone and allowed to dry. The same thing is applied to the test tubes and
pipettes used in the analysis of the withdrawn samples.

3.10 Experimental data

The experimental data obtained from VLLE measurements of the binary
system Ethyl-acetate \ Water is given in table 3-5.

Table 3-5 VLLE measurements of the binary system Ethyl-acetate \ Water.

Mole % Average Mole % Mole % Mole % Mole %
Run # L
VLLE
18
1
T
0
1
T
C X
X
1
B
X
1
O
0.266 98.478 0.029 7.793
VLLE
0.986 96.920 0.059 8.127
VLLE
17
1.555 92.374 0.651 9.566
VLLE
16

2.416 84.529 1.508 44.675

VLLE

15

4.341 70.882 3.038 44.675

VLLE

2

10.180 71.383 77.782 78.060

VLLE

5

26.535 70.407 55.313 71.916

VLLE

1

33.837 72.960 58.956 1.662 31.812 50.861

VLLE

10

40.571 71.862 78.687 3.007 38.800 63.273

VLLE

8

47.233 71.258 77.357 1.204 45.139 66.801

VLLE

3

55.739 71.753 78.981 0.676 54.128 68.133

VLLE

6

66.891 71.283 67.195 73.685

VLLE

4

71.315 71.850 73.096 75.010

VLLE

VLLE

7

11

12

79.644 73.419 95.000 32.573 79.263 78.984

82.450 73.763 95.000 73.989 82.391 85.062

VLLE

88.782 74.800 90.153 85.097 88.509 85.279

VLLE

13

95.000 72.125 95.000 91.261

VLLE

Where L

9

98.400 76.370 98.400 42.673

Sampling method 2 1

14

1

is the initial mole % of Ethyl-acetate charged in the still and T the average boiling point of the mixture from the time the temperature reaches a steady state value to the time of sampling.

61
Y_{1O}
C is

X_{1T} and X_{1B} are the mole % of Ethyl-acetate in the top layer (organic layer) and the bottom layer (aqueous layer) respectively in the boiling liquid. X is the mole of Ethyl-acetate in both layers of the withdrawn sample of the boiling liquid.Y is the mole % of Ethyl-acetate in the condensed vapor.

Samples of the VLLE measurements 3, 6, 8 and 10-13 were withdrawn by sampling method 2 and the rest of the VLLE measurements were by sampling method 1.

1

The numerical values of X_{1T}, X_{1B}, X_{1O} and Y were determined by measuring the refractive index of the withdrawn samples and substituting their values in the calibration curves of Figure 3-5 and 3-6 and by material

balance as shown in appendix C.1.1. The experimental data obtained from
VLLE measurements of the binary system Toluene \ Water is given in table 36.

1
Table 3-6 VLLE measurements of the binary system Toluene \ Water.

Mole % Average Mole % Mole %
Run # L
VLLE
35
1
T
O
1
O
C X
1.670 98.083 1.592 5.642
VLLE
2.369 97.901 2.143 9.873
VLLE
34
5.358 96.948 5.188 14.347
VLLE
33
8.622 96.121 8.097 21.372
VLLE
19
14.519 94.601 14.443 27.764
VLLE
20
21.318 93.497 20.582 33.746
VLLE
21
29.398 92.610 28.316 36.746
VLLE
VLLE
22
23
24
Y
36.909 92.474 36.978 40.437
44.215 92.487 43.648 48.064
VLLE
54.315 93.730 54.779 53.623
VLLE
25
61.737 94.966 61.300 57.692

VLLE
26
75.956 99.151 76.141 62.548
VLLE
27
76.151 99.336 76.673 64.372
VLLE
VLLE
28
29
31
86.883 103.890 88.129 71.343
89.465 107.255 95.229 78.557
VLLE
91.772 106.098 92.883 74.491
VLLE
30
32
94.941 108.543 95.310 83.012
Sampling method 3
1

1
O

Where L
1
is the initial mole % of Toluene charged in the still and T
C is the
average boiling point of the mixture from the time the temperature reaches a
steady state value to the time of sampling. X
1
O
is the mole % of Toluene in
both layers of the boiling liquid.Y
is the mole % of Toluene in the condensed
vapor. Samples of the VLLE measurements 19-35 were withdrawn by
sampling method 3. The numerical values of X
1
1
O
and Y
were determined by

the solubility of Toluene in Water and the solubility of Water in Toluene at 20 °C and by material balance.[1]

The experimental data obtained from VLLE measurements of the Ternary system Toluene \ Ethyl-acetate \ Water is given in table 3-7.

Table 3-7 VLLE measurements of the ternary system Toluene \ Ethyl-acetate \ Water.

Run #	L	Mole %	Mole %	Average	Mole %	Mole %	Mole %	Mole %
		L_1	L_2*	T °C	X	X		
42	VLLE	**12.603**	**64.209**	**72.889**	**13.181**	**64.221**	**1.789**	**43.538**
	VLLE	**19.469**	**42.321**	**74.157**	**19.951**	**41.648**	**7.024**	**41.534**
41	VLLE	**22.778**	**38.904**	**75.680**	**23.593**	**38.041**	**6.996**	**42.935**
46	VLLE	**26.106**	**35.467**	**76.882**	**26.685**	**34.939**	**10.037**	**33.323**
45	VLLE	29.453	32.011	79.361	30.312	31.119	10.097	40.054
36	VLLE	32.819	28.536	77.495	33.826	27.853	11.897	32.783
37	VLLE	38.957	38.107	80.178	40.260	37.365	9.469	39.927
43	VLLE	39.608	21.525	79.887	40.621	20.806	15.173	30.198

VLLE
38
41.318 19.759 83.247 42.344 19.078 12.221 29.776
VLLE
47
46.476 14.432 83.652 47.900 13.668 18.136 24.831
VLLE
39
53.424 7.258 87.081 55.113 6.760 22.563 14.123
VLLE
VLLE
40
44
48
Y
55.227 21.711 89.263 56.658 21.071 19.611 27.862
61.528 15.100 90.520 62.852 14.408 21.915 28.349
VLLE
67.540 9.068 93.766 69.306 8.662 15.846 20.632
VLLE
49
50

Where L
72.327 14.769 93.288 74.482 14.478 15.846 20.632
Sampling method 3
1
, L
are the initial mole % of Toluene and Ethyl-acetate charged
in the still respectively and T
2
o
C is the average boiling point of the mixture
from the time the temperature reaches a steady state value to the time of
sampling.
1
o

Y
2

X
1
O
, X

2
O
are the mole % of Toluene and Ethyl-acetate in both layers of the boiling liquid respectively.Y
, Y2 are the mole % of Toluene and Ethylacetate
in the condensed vapor respectively.
Samples
of the VLLE
measurements
36-50 were withdrawn by sampling
method
3.

The numerical values of X
1
1
O
and Y
were determined by measuring the
refractive index of the withdrawn samples and substituting their values in the
calibration curves of Figures 3-5 and 3-7 and by material balance as shown in
appendix C.1.1.

1

The experimental data obtained from LLE measurements of the binary
system Ethyl-acetate \ Water is given in table 3-8.

Table 3-8 LLE measurements of the binary system Ethyl-acetate \ Water.

Mole % Average Mole % Mole %
Run # L1 T
LLE
1
o
C X
1
T
15.585 24.804 95.000 1.873
LLE
15.585 30.774 95.000 1.761
LLE
2
15.585 34.272 93.565 1.724

LLE_3
15.585 41.610 91.645 1.683
LLE_4
15.585 49.675 88.492 1.704
LLE_5
15.585 57.903 82.910 1.589
LLE_6
7
15.585 65.331 82.109 1.724
Sampling method 2

Where L T °C … X_1^o is the initial mole % of Ethyl-acetate charged in the still and T °C is the average boiling point of the mixture from the time the temperature reaches a steady state value to the time of sampling. X_{1T} and X_{1B} are the mole % of Ethyl-acetate in the top layer (organic layer) and the bottom layer (aqueous layer) respectively in the boiling liquid. Samples of the LLE measurements were withdrawn by sampling method 2.

$_{1B}$

The numerical values of X_{1T}, X_{1B} were determined by measuring the refractive index of the withdrawn samples and substituting their values in the calibration curves of Figures 3-5 and 3-6 and by material balance.

More details are given in appendix C.1.1 on determining the numerical values of X_{1T}, X_{1B}, X_{1O} and Y_1.

3.11 Testing Experimental Data

A semi empirical test for the thermodynamic consistency of isobaric equilibrium data was proposed by Herington [42]. This proposal suggests a plot of ln (γ_1/γ_2) vs. X_1 for the range X_1=0 to X =1. From this plot calculate the percent deviation defined by equation 3.11.1.

$$D = \frac{Area\ above\ X\ axis.\ Area\ below\ X\ axis}{Area\ above\ X\ axis + Area\ below\ X\ axis} \qquad (3.11.1)$$

The quantity D is compared with another quantity J which is found from equation 3.11.2.

=

150J

|

)2.11.3(

T_{min}

Where

τ is the absolute difference between the maximum and minimum temperatures cited in the equilibrium data and T_{min} is the minimum temperature cited in the equilibrium data. The constant 150 is empirical based on analysis of typical heat-of-mixing data. If (D – J) < 10 then the data is probably consistent. Isobaric data of 24 systems taken from the third edition of Perry's ***Handbook for Chemical Engineers***, the data of 9 of these systems were inconsistent according to this method [42].

This method was applied to the two binary systems of the present study. Table 3-9 lists the value of the parameters of the Herington test.

Table 3-9 Values of the parameters of the Herington test.

P = 101.325 KPa. **Ethyl-acetate \ Water** [Present study]

D	***τ***	***T_{min} (K)***	***J***	***(D-J) < 10***	***> 10***
15.013	28.071	343.557	12.256	2.847	YES

P = 101.325 KPa. **Toluene \ Water** [Present study]

D	***τ***	***T_{min} (K)***	***J***	***(D-J) < 10***	***> 10***

12.652 16.937 365.072 6.959 5.693 YES

P = 101.325 **Ethyl-acetate \ Water** [2]

D τ T

min

(K) J (D-J) < 10 > 10

21.466 29.550 343.6 12.900 8.566 YES

For the ternary system Toluene \Ethyl-acetate \Water the McDermontEllis test method [43] was used. Two experimental points a and b are thermodynamically consistent if the following condition is fulfilled:

D < D

max

(3.11.3)

Where

D is the local deviation and is given by equation 3.11.4

N

◀

=

()()()

↕+=

)4.11.3(lnlnXXD ©©

And ***D***

1i

iaibibia

max

the max deviation is given by equation 3.11.5.

ϒ

++++=

N

◀

X

1

()
XXD
N
Y
1
N
1
T
1
()
)5.11.3(T
T
XXXlnln2
1i
iaib
1
X
1
1i
ibibiaia
ibiamax
=
′
≤
◀◀
==
Y
Y
+++↕
ƒ
⁄
+
∞
⁄
′
≤
ϒ
−
−−©©
1i
ba
iaib
∞

f

N is the number of components in the system tested. The values of the local deviation ***D*** and the maximum deviation of the ternary system were 4.387 and 9.958 respectively.

When the above test was applied to the binary systems Ethylacetate\Water and Toluene\Water and the ternary system Toluene (1) \ Ethylacetate (2) \ Water (3) the results were as given in table 3-10.

Table 3-10 Results of the McDermont-Ellis test applied to the binary and Ternary systems.

P = 101.325 kPa. **Ethyl-acetate \ Water** [Present study]

D	**D_{max}**	**$D < D_{max}$**
7.080	9.523	YES

P = 101.325 kPa. **Toluene \ Water** [Present study]

D	**D_{max}**	**$D < D_{max}$**
12.362	13.624	YES

P = 101.325 kPa. **Toluene(1) \ Ethyl-acetate(2) \ Water(3)** [Present study]

D	**D_{max}**	**$D < D_{max}$**
4.387	9.958	YES

CHAPTER FOUR

RESULTS & CALCULATIONS

The experimental data obtained from the VLLE measurements of the two binary systems (Ethyl-acetate(1)\Water(2) and Toluene(1)\Water(2)) and the ternary system (Toluene (1)\ Ethyl-acetate (2)\Water (3))and the LLE data of the binary system (Ethyl-acetate(1)\Water(2)) are plotted in TemperatureComposition Diagrams (T-X-Y, T-X, T-X-X). Then these data are predicted and correlated by the activity coefficient models and the Peng-Robinson (EOS).

4.1 Temperature-Composition Diagrams

The experimental data obtained from the VLLE measurements of the binary system Ethyl-acetate (1) \ Water (2) in columns 3, 6, 7 of table 3-5 are plotted in Figure 4-1.

T (C) A
105
100
90
95
Te t
80
ver
era ure
age Boiling

mp
85
75
65
70

Ethyl-acetate(1) \ Water(2)
0 20406080100
X1,Y1 mole% Ethyl-acetate

Figure 4-1 T-X-Y Diagram of the System Ethyl-acetate (1) \ Water (2).

Y1 Exp.
X1O

The experimental data obtained from LLE measurements of the binary system Ethyl-acetate (1) \ Water (2) in columns 3, 4, 5 of table 3-8 are plotted in Figure 4-2.

T (C) Liquid Temperature

50
55
60
65
70
40
45
35
30
20
25
Ethyl-acetate(1) \ Water(2)
0 20406080
100
X1T, X1B mole Ethyl-aetate
%

Figure 4-2 T-X-X Diagram of the System Ethyl-acetate (1) \ Water (2).

When both of the above Figures are plotted together a system similar to the one in Figure 2-1 is obtained as shown in Figure 4-3.

T (C) Average Boiling
Temperature

120
100
80
60
40

20

Ethyl-acetate(1) \ Water(2)
0 20406080100
X1O, X1T, X1B,Y1 mole% Ethyl-acetate

Figure 4-3 T-X-X-Y Diagram of the System Ethyl-acetate (1) \ Water (2).

69
X1B
X1T
Y1 Exp.
X1O
X1B
X1T

The experimental data obtained from the VLLE measurements of the binary system Toluene (1) \ Water (2) in columns 3, 4, 5 of table 3-6 are plotted in Figure 4-4.

T(C) Averag Bol
Temper ure

120
ng
e i
at
115
110
100
105
90
95
Toluene(1) \ Water(2)
0 20406080100
X1, Y1 mole% Toluene

Figure 4-4 T-X-Y Diagram of the System Toluene (1) \ Water (2).

The experimental data obtained from the VLLE measurements of the ternary system Toluene (1) \ Ethyl-acetate(2) \ Water (3) in columns 4, 5, 6 of table 37 are plotted in Figure 4-5.

Toluene (**Figur** f 1) \ ta e**e 4-5** T-X Diagram o the System Ethyl-ace te(2) \ Wat r (3).

70
X1O
Y1

4.2 Pred o a

n th o p
c e
Φ et b
on o t pa s
e values of ***Φ***
pling m thod (1). Tables 4-2 and 4-3 list the values of
S

iction f Equilibrium D ta

By applying equations 2.2.3 a d 2.2.6 e value f ***Y***
is redicted
theoreti ally wh re ***Φ***
1
v
, ***Φ***
1
S
and
1
L
are d ermined y applying PengRobins
equati n of state with in eracting rameter k
= 0, equations
2.3.42a and 2.3.42b. Table 4-1 lists th
the binary system Ethyl-acetate (1) \ Water (2) where samples are withdraw
by sam e ***Φ***
and ***Φ***
1
1
V
, ***Φ***
e a \ W) w
w m T s o iv c

r s l o
I u .15 4.
L o 2
u 4 2.4
nd 2.4.35b.
1
L
ij
, ***P***
for the binary syst m Ethyl- cetate (1) ater (2 here samples are withdra n by sa pling method (2). he value f the act ity coeffi ients γi are dete mined u ing the fo lowing m dels:
1- MOD FIED WILSON (M.W.), eq ations 2.4 a and 2. 15b.
2- NRT , equati ns 2.4.20a and 2.4. 0b.
3- UNIQUAC (UNIQ.), eq ations 2. .26a and .26b.
4- UNIFAC (UNIF.), equations 2.4.35a a

Table 4-1 Values of Φ
Run # T
VLLE
18
o
1
v
, P
i
S
and Φ
1
S
and Φ
1
L
i
i
S
and ***Φ***
1
for the binary system Ethyl-acetate (1) \
Water (2) by sampling method 1.
C P (kPa) X
1
O
Φ
1
v
P
1
S
(kPa)
Φ
98.478 101.325 0.00029 0.97834 195.104 0.98227 1958822
VLLE

17
1
S
96.920 101.325 0.00059 0.97808 186.563 0.98307 240012
VLLE
92.374 101.325 0.00651 0.97723 163.297 0.98501 140835
VLLE
16
84.529 101.325 0.01508 0.97568 128.542 0.98802 68998
VLLE
15
70.882 101.325 0.03038 0.97268 82.172 0.99211 21697
VLLE
2
72.960 101.325 0.31812 0.96951 88.206 0.98385 2.56189
VLLE
10
71.862 101.325 0.38800 0.96854 84.975 0.98266 1.63506
VLLE
VLLE
8
3
6
V
Φ
1
S
for
n
1
L S
, , ***P***
• ***Φ***
71.258 101.325 0.45139 0.96782 83.239 0.98149 1.25959
71.753 101.325 0.54128 0.96724 84.660 0.97921 1.03533
VLLE
70.407 101.325 0.55313 0.96680 80.840 0.97974 0.97315
VLLE
1
71.283 101.325 0.67195 0.96630 83.310 0.97683 0.87505
VLLE 71.850 1 .97535 0.85972
LE
4
01.325 0.73096 0.96618 84.940 0
VL 83 101.325 0.7778 83.596 0.97483 0.83032
7
71.3 2 0.96587
LLE
E
5

11
12
13
9
73.41 101.325 0.79 3 0.96637 89 0. 0.88291
V 9 26 .585 97316
VLLE 73.763 223 0.88565
101.325 0.8 3 0.96637 90.629 0.97240
74 101.325 0.8 9 0.96651 9 7 0.9705 0.90562
VLL .800 850 3.83 8
VLLE 72.125 1 9500 0.82575
01.325 0. 0 0.96569 85.740 0.97161
LLE
14
76.37 .96682 9 0.9678 0.94631
V 0 101.325 0.98400 0 8.865 5

- ***Φ***

1
S
=f
1
0
/ P
1
S
1
S
from equation
(P C.1.2)

1
L
i

Table 4-2 Values of Φ
o
1
v
, P
i
S
and Φ
1
S
and Φ
1
L
for the binary system Ethyl-acetate (1) \ Water (2) by sampling method 2.

(kPa) X

1

T

Φ

v

(kPa)

Run #

LE

10

3

T

P

1

S

C P

Φ

1

72 01.325 6 0.970 .205 01.00

VL .960 1 0.5895 22 88 0.97745 73

VLLE 71.258 1 0.77357 54 83 0.97499 817

VL .862 101.325 0.78687 756 84. 0.97435 088

VL .753 101.325 0.78981 6750 84.6 0.97437 3723

01.325 0.967 .238 0.82

LE

71 0.96 975 0 4.8

LE

VLLE

8

6

13

71 0.9 59 0.8

74.800 101.325 0.90153 0.96724 93.839 0.97032 0.90394

VLLE 1 0.97064

73.419 0.86142

LE

01.325 0.95000 0.96646 89.584

VL .763 101.325 0.95000 5

- ***Φ***

11

12

1

S

1

S

73 0.9665 90.629 0.97038 0.87110

= ***f***

1

0

/ ***P***

1

S
1
S
of Φ
f C.1.2)
(P rom equation
Table 4-3 Values P
Run # T
o
1
v
,
i
S
and Φ
S
1
L
and Φ
ry system acetate (1
by samp d 2.
1
•
for the bina Ethyl-) \
Water (2) ling metho
C P (kPa) X
1
B
Φ
1
v
P
1
S
(kPa)
Φ
1
S
• ***Φ***
VL LE
71.753 101.325 0.00676 0.97322 84.659 0.99249 302565
LE 71.258 101.325 0.01204 0.97304 83.238 0.99248 149312VL
6

VLLE
3
72.960 101.325 0.01662 0.97333 88.205 0.99188 83777
V 7 10 5 0 72 .9LLE
10
1.862 1.32 .03007 0.9 9 84 75 0.99184 22149
LLE
8
3.419 01.325 2573 0.9 55 89.5 0.983 2.4502

LLE

V 7 1 0.3 69 84 43

V 7 1 0.7 66 29 88

V 7 1 0.8 66 39 15

11

3.763 01.325 3989 0.9 65 90.6 0.973 0.9106

LLE

12

4.800 01.325 5097 0.9 58 93.8 0.971 0.91031

• Φ

13

e   Th

4

1

S

= f

1

0

/ P

1

S

qu)

(P

1

S

from e ation C.1.2

p e firs tiv ie ns

aramet rs of the t three ac ity coeffic nt equatio are given

in table -4.

Ac icie ers

tio et

Table 4-4 tivity Coeff

Param

nt Paramet

[8] .

ers

Φ

1

L

1

L

Equa n T

M.WILS (/ R λ

134

3ON λ -λ)

(λ -

= -751.71 K

12 22

NRTL (R

) \ R
= 3.3 K
21
11
α 3 g -g) /
12 11
= 671.8 K
UNIQUAC ΔU / R

= 1081.40 K
12
(g - g
22
21
63.
) / R
=12 08 K
U
2
12
33.15 K
= α =
0.4
21
22
3Δ
/ R
= - 2.02 K
1

The p r N atio n -5

UNIFAC Equatio rs
43.65 K
Z / 2 = 5 43.15 K
aramete s of the U IFAC equ n are give in tables 4 and 4-6.

Table 4-5 n Paramete [9].

CH2O
Branch CH3 CH3CO H2O
R
0.9011 1.6724 0.9183 0.90
Q
k
0.848 1.488 0.78 1.40
Group 1 9 13 7
k

IFAC Equa n Paramete [9].

a

k,m

Table 4-6 UN tio rs

) 3

(K 1 9 1 7

1 0 476.4 251.5 1318

9 26.76 0 -103.6 472.5

13 83.36 191.1 0 -314.7

7 300 -195.4 540.5 0

The value

1

ua iv es nd

s of γ for the 4 eq tions are g en in tabl 4-7, 4-8 a 4-9.

Table 4-7 Values of γ

un # T C

1

for the binary system Ethyl-acetate (1) \ Water (2) by sampling method 1.

γ

1

O

1

.WILSON RTL UNIQUAC UNIFAC

LLE

R

98.478 0.00029 5.44755 1.38311 9.54445 120.86540

LLE

18

96.920 0.00059 5.44044 1.88505 9.46096 119.04740

VLLE

17

92.374 0.00651 5.30048 63.91702 8.77798 112.27510

VLLE

16

84.529 0.01508 5.11063 54.56045 7.87525 105.31170

VLLE

15

70.882 0.03038 4.80413 41.00261 6.57662 6.51260

VLLE

2
72.960 0.31812 2.23809 2.74150 2.18071 1.13736
VLLE
10
71.862 0.38800 1.97667 2.22034 1.91031 1.02596
LLE
8
3
o
X M N
V 7
V 7
V
VLLE
6
71.258 0.45139 1.78533 1.91016 1.72265 0.97816
71.753 0.54128 1.56633 1.60702 1.51494 0.95498
VLLE
70.407 0.55313 1.54217 1.57582 1.49188 0.97967
VLLE
1
71.283 0.67195 1.32580 1.31703 1.29098 0.98426
VLLE
4
71.850 0.73096 1.23851 1.22083 1.21080 0.98475
VLLE 71.383 0.77782 1.17775 1.15691 1.15546 0.97751
VLLE
7
5
73.419 0.79263 1.15870 1.13789 1.13829 0.98040
473 1.VLLE
11
73.763 0.82233 1.12 10438 1.10777 0.98499
VLLE
12
74.800 0.88509 1.06235 1.04716 1.05266 0.99325
VLLE
13
5 0 0 71 10 .0172.12 .9500 1.015 1.0 03 1 278 0.99858
VLLE
9
14
76.370 0.98400 1.00187 1 .0 0.99989 1.00 08 1 0149

em Ethyl-a**Table** s t c samp
4-8 Value of γ for the
1
binary sys etate (1) \ Water (2) by ling
et

m hod 2.

γ

o

1

Run # S R I NIF T

C X

1

T

M.WIL ON N TL UN QUAC U AC

VLLE

72.960 5 8 .63548 0.95462 0.58956 1.467 3 1.4 357 1

VLLE 8 0 6 .20700 0.97677

10

71.25 0.77357 1.183 8 1.1 238 1

VLLE 2 4 4 .18536 0.97911

3

71.86 0.78687 1.166 6 1.1 547 1

VLLE 3 9 4 .18005 0.97955

8

71.75 0.78981 1.162 9 1.1 194 1

VLLE

VLLE

6

13

11

74.800 5 3 .04630 0.99494 0.90153 1.048 3 1.0 549 1

73.419 5 0 .01349 0.99860 0.95000 1.015 5 1.0 997 1

VLLE

12

73.763 5 0 .01346 0.99861 0.95000 1.015 1 1.0 996 1

Table s t c sa

et

4-9 Value of γ

1

for the binary sys

m

em Ethyl-a

hod 2.

γ

Run # T

o

C X

1

B

etate (1) \ Water (2) by mpling

1

M.WILS R I UON N TL UN QUAC NIFAC

VLLE

71.753 0.00676 5.07834 57.41965 21.45212 42.89405

VLLE

6

71.258 0.01204 5.17695 66.19153 22.65216 56.66427

VLLE

3

72.960 0.01662 5.29538 76.99368 24.17656 82.56744

VLLE

10

71.862 0.03007 4.80943 41.06641 18.42553 22.80326

VLLE

8

73.419 0.32573 2.20601 2.671489 3.20944 1.12219

VLLE

11

73.763 0.73989 1.17354 1.20683 1.16686 0.97488

VLLE

12

74.800 0 32 75 .0.85097 1.094 1.0 76 1 9703 0.98913

13

The

ined by using equations (2.2.3), (2.2.6)

m l e th

r o y i

values of ***Y***

1 f h s -a \ y

thod 1.

Y

1

pred

are determ

and fro the data in the tab es 4-1 to 4-9. Tabl s 4-10 to 4-12 list e values of the p edicted m le % Eth l-acetate n the gas phase (***Y***

Table 4- 0 Values o Y

Run # X

1

O

1

pred

for t e binary sy

me

1

exp

Y
1
pred

p
1
red

).
tem Ethyl cetate (1) Water (2) b sampling
Exp. M.W RTL UNIQ. UNIF. P.R.(EOS)N
VLLE
0.00029 0.07793 0.00305 0.04002 0.00535 0.00683
581
4 0.0784VLLE
18
0.00059 0.09566 0.0059 9 0.01033 0.01329
145
VLLE
17
0.00651 0.42673 0.05605 0.67594 0.0 0.11062
938
9283
LLE
16
4675 09901 .05698 .15256 .16341
1066
VLLE
V 0.01508 0.4 0. 1 0 0
15
0 0 0 1.03038 .71916 .12073 .03038 0.16527 0.15611
678
LLE
2
.31812 .66801 .62896 .77043 0.61283 .29556 .8406
LLE
V 0 0 0 0 0 0 2
V 0 0 0 0 0 1
V 0 0 0 0 0 7
10
.38800 .68133 .65257 .73301 0.63066 0.32411 .6550
LLE
8
.45139 .73685 .67139 .71833 0.64782 0.35881 .5874
VLLE
3
0 0 0 0.54128 .78067 .71715 .73578 0.69362 0.43334 0.57939
VLLE

VLLE
VLLE
6
1
4
7
0 0 0 0.55313 .68436 .68968 .70473 0.66719 0.4371 0.55676
0 0 0 0.67195 .63273 .74046 .73556 0.72101 0.53663 0.6085
0.73096 0.50861 0.76611 0.75518 0.74897 0.60085 0.65042
VLLE
0.77782 0.7501 0.7628 0.7493 0.74837 0.63413 0.66866
VLLE
5
0.79263 0.85062 0.81771 0 80302 0.8033 0.69312 0.72417 .
VLLE
V
V
11
0.82233 0.85279 0.83243 0.81737 0.81987 0.73019 0.75364
LLE
12
0.88509 0.91261 0.87446 0.86196 0.86649 0.81844 0.82933
LLE
LLE
13
9
14
0.95000 0.78984 0.82151 0.81691 0.81914 0.80746 0.81233
0.98400 0.98608 0.96293 0.96217 0.96256 0.96312
V 0.96312

Table 4-11 Values of Y

Y
Run # X
1
T
1
pred
 f ling
method 2.

1
exp
or the binary sys em Ethyl-acetate (1) \ Water (2) by sampt

Y
1
pred
Exp. M.W. UNIQ. UNIF. P.R(EOS)NRTL
0VLLE
0.58956 0.66801 0.79553 .78113 0.80720 0.49331 0.68458
VLLE
6
0.77357 0.73685 0.75713 0.74388 0.77243 0.62760 0.66330
VLLE
3
0.78687 0.68133 0.77057 .75671 0.78306 0.65281 0.68497 0
VLLE
8
0.78981 0.78067 0.72834 0.73630 0.81169 0.65313 0.60998
0.90153 0.91261 0.87885 0.86792 0.87698 0.83471 0.84319 VLLE
VLLE
10
13
1
1
0.950 0.84275 5702 0.84258 0.84711
00 0.85062 0.85876 0.8
E
12
0. 00 0.8 79 0.8 58 0.86 4 0.86 0.852 4 0.8565
VLL 950 52 67 28 583 6 5

Table 4-12 a
V lues of Y
1
pr

for the bi ry system E hyl-acetate) \ Water (y samp
method 2.

Y
n #
1
B
xp
Y
1
p d

E p. M . NRTL UNI . UNIF P.R(EO
L .E
0 676 0.7 067 0.0 13 0.43815 0.137 8 0.0554
1431
LE
10
0 204 0.7 685 0.0 57 0.65 3 0.225 3 0.086
1848
LE
3
0 662 0.6 801 0.0 31 0.82651 0.308 9 0.6019
0221
LE
6
0 007 0.6 133 0.1 41 1.03672 0.465 5 0.1536
685
LE
8
0 573 0.8 062 0.6 9 46 0.76 32 0.930 4 0.3046 0.8231
LE
11
0 989 0.8 279 0.78 61 0.80378 0.777 6 0.649 0.6969
LE
12
13
ed
na t (1 2) b ling
1
e re
Ru X x .W Q . S)
VL 00 8 30 5 6

VL .01 3 51 9 6

VL
.01 6 7 7 2

VL .03 8 21 1 6
VL .32 5 3 5 7 7
VL .73 5 1 1 3 9
VL
.85 1 65 9 5 3

0 097 0.9 261 0.8 79 0.8511 71 0.86 3 0.7828 0.8014

The ab olute dev tion or d fference (***Y***

s ia i Δ
h b n
1
) whic is given y equatio
is ulated for he binary system Et yl-acetate (1) \ Wat (2) for th
4.2.1 calc t h er e
two sampling methods. The values are listed in tables 4-13 to 4-15.

ΔY

1
= ABS (Y
1
exp
- Y
1
pred
) ***(4.2.1)***

Tab a a e (
.

T
le 4-13 V lues of ΔY

1
for the bin ry system Ethyl-acetat (1) \ Water 2) by sampling method 1

Exp.
ΔY
Y
exp
1

M.W NRTL UNIQ. UNIF. P.R(EOS)
Run #
VLLE

18

1

0.07793 0.07488 0.03791 0.07258 0.0711

581

VLLE

0.09566 0.08972 0.01717 0.08533 0.08237

145

VLLE

17

0.42673 0.37068 0.24921 0.3339 0.31611

938

0.61023

VLLE

16

0.44675 0.34774 0.29419 0.28334

1066

VLLE

15

0.50 61 036 0.09224 0.14181 8 0.2575 0.24657 0.24

LLE

7

.10283 .08828 0.0961 0.02423

VLLE

V 0.63273 0.10773 0 0

4

0.66801 0.03905 0.10242 0.05518 0.37245 0.17261

VLLE

10

0.68133 0.02876 0.05168 0.05067 0.35722 0.02632

VLLE

8

0.68436 0.00532 0.02037 0.01717 0.24726 0.1276

VLLE

1

0.71916

0.59843

0.31122

0.55389 0.56305 ***677***

VLLE

2

0.73685 0.06546 0.01852 0.08903 0.37804 0.14938

VLLE

3

0.7501 0.0127 0.0008 0.00173 0.11596 0.08144

VLLE

VLLE

VLLE

5
6
9
11
0.78067 0.06352 0.04489 0.08698 0.34732 0.20128
0.78984 0.03167 0.02707 0.0293 0.01762 0.02249
0.85062 0.03291 0.0476 0.04732 0.1575 0.12645
VLLE
0.85279 0.02036 0.03542 0.03292 0.1226 0.09915
VLLE
12
0.91261 0.03815 0.05065 0.04612 0.09417 0.08328
VLLE 0.98608 0.02315 0.02391 0.02144 0.02296 0.02296
13
14
Average 0.12265 0.11103 0.11924 0.20763 0.09838

able 4-14 Values of ΔY
1

for the binary system Ethyl-acetate (1) \ Water (2) by sampling method 2.

$\Delta \boldsymbol{Y}$
Run # X
1
T
1
M.W. NRTL UNIQ. UNIF. P.R(EOS)
VLLE
0.58956 0.12752 0.11312 0.13919 0.17471 0.01657
VLLE
6
0.77357 0.02028 0.00703 0.03558 0.10925 0.07355
VLLE
3
0.78687 0.08924 0.07538 0.10173 0.02852 0.00364
VLLE
8
0.78981 0.05233 0.04430 0.03109 0.12753 0.17069
VLLE
10
0.90153 0.03376 0.04469 0.03563 0.07790 0.06942
4 0.00787 0.00VLLE
13
11
0.9500 . 81 640 00 0 00 .00804 0.00351
VLLE 0.95000 0.01479 0.01005 0.01304
12

0.00014 0.00376

0.0 4 0.04320 05181 .07516 0.04873

Average 494 0. 0

Table 4-1 of e bin Eth (1) by
.

5 Values ΔY_1 for th ary system yl-acetate \ Water (2) sampling method 2

Δ

Run # X_1

B

Y_1

UNIF. M.W. NRTL UNIQ. P.R(EOS)

VLLE

0.00676 0.75053 0.34245 0.64302 0.72520

1430

VLLE

10

0.01204 0.68528 0.07755 0.51122 0.65085

1847

1 0.15850 0.35VLLE

3

0.01662 0.5949 922 0.06609

2101

VLLE

6

.030 2 0.35539 0.21 67

684

0 07 0.5599 618 0.527

VLLE

8

573 10 0 00.32 0.21 2 0.08630 .07992 .54594 0.02745

VLLE 98 18 0 0. .15

11
0.73 9 0.071 0.02218 .02662 12786 0 580
VLLE 09 82 0 0. .11
12
0.85 7 0.046 0.06150 .04468 12976 0 118
Averag 09 0 0. .09e 0.417 0.15770 .26869 39620 0 814
13

When tw pha eq 2.2 n a
there is o liquid ses (T, B) uation (2.) is writte s

f_i^T $_i^B$ $= f$ γ_i $_i$

Where f (4.2.2)

$_i^T$ $= X$, f_i $_i^B$ are the partial molar fugacities of the top and bottom liquid phases. And equation 2.2.3 is written as

$X^{T\ T\ B\ B}$

The values of (γ γ_i (4.2.3)

$_1^T$ re i us
oefficient equations and are given in tables 4-16 and 4-17
/γ
(γ $_1^B$)

pred
a pred cted ing the mentioned activity
c
Table 4-16 Values of (γ

Run # T
o
C

1
T
/γ
1
T
B
/γ
)
1
B

) for the binary system Ethyl-acetate (1) \ Water (2) by
sa

mpling method 2.
exp
1 1
(γ
T
/γ
1
B
)
pred
Exp. M N U U.WILSON RTL NIQUAC NIFAC
LLE
41.61 0 0.07211 0 0 0.01836 .01393 .04958 .13430
LLE
4
34.272 0.01843 0.07575 0 0 0.01313 .04968 .13980
LLE
3
30.774 0.01854 0.07766 0 0 0.01282 .04977 .14330
LLE
2
57.903 0.01917 0.06766 0 0 0.01672 .05143 .12410
LLE
LLE
6
5
1
49.675 0.01926 0.06981 0 0 0.01534 .05033 .13070
24.804 0.01972 0.05978 0 0 0.01893 .04964 .15130

LLE

7

65.331 0.02100 0.06640 0 0 0.01848 .05234 .12450

Table 4-17 Values of (γ

(γ

Run # T

o

C

1

T

/γ

1

T

/γ

1

B

)

1

B

exp

) for the binary system Ethyl-acetate (1) \ Water (2) by sampling method 2.

(γ

1

T

/γ

1

B

)

pred

Exp. M.WILSON NRTL UNIQUAC UNIFAC

VL 0 LE

71.753 0.00856 0.05436 0.01483 0.04647 0.0963

0.06083 0.0VLLE

10

3

6

71. 58 0 77 0.10878 2 0.01556 1756 0. 50

VLLE 72.960

0.02819 0.07756 0 .02583 0.06815 0.11670

VLLE
V
V
V
71.862 0 .03822 0.08075 0.02790 0.06318 0.15694
LLE
8
73.419 0.34287 0.48096 0.37806 0.37999 0.94887
LLE
11
73.763 0.77883 0.86330 0.83687 0.86330 1.02460
LLE
12
74.800
0.94392 0.96673 0.96256 0.97045 1.00509

13

The absolute d or [Δ
which is given by
equ tion 4.2 is c or th syst yl-ace) \ W

eviation difference ***(γ***
es o γ γ
1
B
)
ex
) for the binary system Ethyl-acetate (1) \ Water (2) by
g .

T
/γ
1 1
B
)]
a .4 alculated f e binary em Eth tate (1 ater (2)
for the sampling method 2. The values are listed in tables 4-18 and 4-19.

Δ***(γ***
1
T
/γ
1
B
) = ABS [(γ
1
T
/γ

1
B
)
exp
- (γ
1
T
/γ
1
B
)
pred
] ***(4.2.4)***

Table 4-18 Valu f Δ(

(γ
1
T
1
T
/γ
/
samplin method 2
1
B p
Δ ***(γ***
)
T
o
C Exp. M.W SON TL U IQUAC
LLE
4
1
T
/γ
1
B
Run # IL NR N UNIFAC
41.610 0.01836 5 0 0.0 400 0.00400 .03100 0.11600
LLE
34.272 0.01843 5 0 0.0 700 0.00500 .03100 0.12100
LLE
LLE
3
2
6
30.774 0.01854 5 0 0.0 900 0.00600 .03100 0.12500
57.903 0.01917 4 0 0.0 800 0.00300 .03200 0.10500
LLE
49.675 0.01926 5 0 0.0 100 0.00400 .03100 0.11100

LLE
5
24.804 0.01972 4 0 0 0.0 000 0.00100 .03000 .13200
LLE
1
65.331 0.02100 4 0 0 0.0 800 0.00200 .03200 .10500

Average 0.0 051 .004 0.031 0.116
7

Table s i a er (
4-19 Value of Δ(γ
(
1
T
/γ
1 1
p
T
1
B
) for the b nary system Ethyl-acet te (1) \ Wat 2) by
samplin
g
method 2.

γ
/γ
B
)
ex

)
Run # T
0
Δ ***(γ***
1
T B
/γ
1

C Exp. M.WILSON NRTL UNIQUAC UNIFAC
VLLE
09300 71.258 0.01556 0.04500 0.00200 0.03500 0.
VLLE
3
72.960 0.02819 0 0.04000 0.08900 0.04900 0.0020
VLLE
V
6
71.862
0 2 0.02500 0.11900 .0382 0.04300 0.01000
LLE .0085 0.04 0 0
VLLE
8
73.419 0.34287 8 03500 0.03700 0.60600 0.13 00 0.
VLLE
11
5 05800 0.08500 0.24600 73.763 0.77883 0.08 00 0.
VLLE

12
3 0 0
74.800
0.94392 0.02 00 0. 1900 .02700 0.06100

Average 60.0 1 0.019 0.041 0.186
13
The s th t b
ystem E yl-acetate (1) / Wa er (2) was studied y other researchers
. e] i g
[2, 14] The exp rimental data of [2 are pred cted usin equation 2.2.3 and
c f u a g b n
the 4 a tivity coe ficient eq ations. V lues are iven in ta les 4-20 a d 4-21.

pred
Table 4-20 Values of Y
1
for the inary syst m Ethyl-ac tate (1) \ W er
b e e at
e f
(2) experim ntal data o [2].
P 3

= 101. 25 kPa.
Y
T
o
10

71.753 0 6 60 .00600 0.03800 0.08800

C X

1

1

exp

Y

1

pred

Exp. M.W. NRTL UNIQ. UNIF. P.R(EOS)

100 0.0002 0.0017 0.0024 0.0313 0.0043 0.00551

48.53

99.9 0.0003 0.0007 0.0034 0.0439 0.006 0.00773

67.91

98.85 0.00056 0.04055 0.00594 0.07705 0.01040 0.01344

29.402

96.2 0.00114 0.12560 0.01132 0.14871 0.01957 0.02485

259.329

86.5 0.00489 0.59100 0.03540 0.46778 0.05779 0.07105

1027.154

76.2 0.00858

0.66800 0.04386 0.58388 0.06736 0.07966

26582.836

70.55 0.04590 0.71400 0.16704 1.07227 0.21644 0.17208

1296.836

70.55 0.14400 0.70250 0.38617 0.85745 0.41108 0.20955

5.924

70.5 0.26900 0.70600 0.53449 0.71817 0.52505 0.24758

1.052

70.45 0.35400 0.70900 0.60191 0.70076 0.58240 0.28844

0.70900 0.62811 0.69294 0.60605 0.32143 0.608

0.689

70.55 0.40800

70.5 0.51400 0.71000 0.68139 0.70634 0.65816 0.39406 0.557

70.5 0.60800 0.70250 0.70311 0.70746 0.68204 0.68172 0.570

70.45 0.69000 0.70700 0.72065 0.71388 0.70250 0.53716 0.601

70.5 0.77500 0.69900 0.73680 0.72379 0.72266 0.61302 0.648

73.35 0.94445 0

71.45 0.87370 0.76500 0.77760 0.76523 0.76948 0.72289 0.736

.86500 0.86796 0.86243 0.86505 0.84489 0.841

75.55 0.98070 0.94110 0.95151 0.95044 0.95099 0.93308 0.935

Table 4-21 Values of ΔY
P =101.325 kPa.
Y
1
exp
1
for the binary system Ethyl-acetate (1) \ Water
(2) experimental data of [2].

T
o
C X
1
Δ*Y*
1
Exp. M.W. NRTL UNIQ. UNIF. P.R(EOS)
100.00 0.00022 0.00171 0.00071 0.02961 0.00256 0.00380
47.847
99

.90 0.00031 0.00067 0.00273 0.04323 0.00531 0.00706
67.228
1 0.036598.85 0.00056 0.04055 0.0346 0 0.03015 0.02711
28.718
96.20 0.00114 0.12560 0. 0.02311 0.10603 0075
258.645
11428 0.1
86.50 0.00489 0.59100 0 0 0 0.55560 .12322 .53321 .51995
1026.469
76.20 0.00858 0.66800 0 0 0 0.58834
26582.152
.62414 .08412 .60064
70.55 0.04590 0.71400 0 0 0 0
1
.54696 .35827 .49756 .54192
296.151
70.55 0.14400 0.70250 0 0 0 0.31633 .15495 .29142 .49295
5.240
70.50 0.26900 0 0 0 0 0.70600 .17151 .01217 .18095 .45842 0.36800
70.45 0.35400 0 0 0 0 0.70900 .10709 .00824 .12660 .42056 0.00400

70.55 0.40800 0 0 0 0 0.70900 .08089 .01606 .10295 .38757 0.07600
70.50 0.51400 0 0 0 0 0.71000 .02861 .00366 .05184 .31594 0.12700
70.50 0.60800 0 0 0 0 0.70250 .00061 .00496 .02046 .02078 0.11500
70.45 0.69000 0 0 0 0 0.70700 .01365 .00688 .00450 .16984 0.08400
70.50 0.77500 0 0 0 0 0.69900 .03780 .02479 .02366 .08598 0.03600
71.45 0 0 0 0 0 0.87370 .76500 .01260 .00023 .00448 .04211 0.05200
73.35 0 0 0 0 0 0.94445 .86500 .00296 .00257 .00005 .02011 0.15600
75.55 0 0 0 0 0 0.98070 .94110 .01041 .00934 .00989 .00802 0.25100

A 0 0 0 0verage .14786 .05233 .14401 .23396 0.12692

The calculations in the previous tables where achieved by the aid of the
tails are give
software Microsoft Excel, more de n in appendix C.1.2.

The data of th m ater (2 also predicted
a ble e valu
btain th
ficient equations NRTL, UNIQUAC and UNIFAC and the Peng-Robinson (

The parameters of the N NIQUA en in 3 and the
parameters of the UNIFAC equation are given in tables 4-24 and 4-25.

e binary syste Toluene (1) \ W) were
s before. Ta 4-22 lists th es of Δ***Y***
o ed using e activity
coef
EOS).
1
RTL, U C are giv table 4-2

Table 4-22 for the binary system Toluene (1) \ Water (2) by sampling
Values of ΔY
1
method 3.

Y

1
exp
P = 101.325 kPa
Δ***Y***
T
o
1
o
1
C Exp. TL UNIF.
21 0.21372
8126 5 14
01 3 0.27
002 5. 3979
97 2 0.33
582 .57647
RUN X
NR UNIQ. P.R(EOS)
VLLE
96.1 0.08097
4.4 .37484 24
VLLE
19
94.6 0.1444 764
2.99 5.88894 6 1.73055
VLLE
20
93.4 0.2058 746
1.94 5.19016 2
0.52120
VLLE
21
92.610 0.28316 0.36746
1.20086 3.75540 1.29873
0.13514
LLE
22
92.474 0.36978 0.40437 0.74655
2.21773
0.87765 0.03786
LLE
V
V
V
V
V 9.151 0.76141 0.62548 0.08662 0.73402 0.07457 0.05838

VLLE

92.487 0.43648 0.48064 0.47657

1.43439

0.22940 0.10425

LLE

93.730 0.54779 0.53623 0.24968

1.02190

0.44795 0.13697

LLE

94.966 0.61300 0.57692 0.15847 0.83487 0.00917 0.14279

LLE

9

99.336 0.76673 0.64372 0.06972 0.66015 0.18343 0.07021

8129 0.71343 0.07118 0.6340VLLE

103.890 0.8 4 0.35055 0.02348

VLLE

3 0.74491 0.09 0.62848 0.12068 0.07923 106.098 0.9288 917

VLLE

255 229 8557 9670 2883 299 .086107. 0.95 0.7 0.0 0.6 0.3 1 0 48

VLLE

108.543 0.95310 0.8301 9 12 0.085 2 0.675 6 0.06872 0.07406

Averag 0 0e 0.214 6 0.685 8 0.26920 0.12250

Table 4 i e te b m 2

-23 Activ ty Coeffici nt Parame rs for the inary syste Toluene(1)\Water( )[8].

ua P s

qE tion arameter T

NR

1

)

6

(/

0

αTL (g

12

-g

/ R

= 1057. 0 K
UNIQ /
3

1
g
21
- g
) R
=1643.2 K
22
/
1
Z / 2 = 5 UAC ΔU
12

.
R
= 1371 6 K
ΔU
R
= 305.7 K

21
Table 4-24 UNI t t b e
2
12
= α
= 283.0
0.200
FAC Equa ion Parame ers for the inary syst m
Toluene (1)\Water (
A
) [9].
21
Branch ACH CCH3 H2O
R
0.5313 1.2663 0.9200
Q
k
0.4000 0.9680 1.4000
Group 10 7 12
k
Table 4-25 UNIFAC Equ
Toluen
a
k,m

a e
e)
tion Param
(1)\Water(2
(2
K) 10 1
eters for th
[9].
binary sys
7
10 0 -14 362.3
12 167 0 377.6
7 56 5 0
9903.8

81
0 K
323.00 K
tem
6 .8

T
e
he T 1 -a
P i O
data of the ternary system oluene ( ) \ Ethyl cetate (2) \ Water (3)
wer
fi
also predicted us
coef
io
t R
ing the eng-Rob nson (E S) and the activity
c a Q it a m f
u r t m
ient equ ions N TL, UNI
s
UAC w h the bin ry para eters o the
prev
e

s bina y system and he para eters of the binary system
Tolu
, Δ
n y a li a
e(1)\Eth
Y
l-acetate(2) [8]. T bles 4-26 to 4-28 st the v lues of Δ***Y***
,
Δ***Y***
2 3
.
4- es Y t u
\ Water ( ) using P.R EOS
.
26 Valu**Table** of ΔY
1
, Δ
2,
ΔY
for he Ternary system Tol ene (1) \ Ethyl-acetate (2)
3 ( ) with k
3
ij
=0
P = 101.325 kPa Exp. P.R(EOS)
o
R un # T
1
o
C X
X
2
0
Y
1
Y
2
89 0.13181 0.64221 0.01789 0.43716 0.0011 0VLLE
42
Δ***Y***
1
72.8 .1875 0.0154
VLLE
74. 57 0.199 1 1 5 0.4 6 8 0.0 02 534 0 8 81 4 7 4 0.41 .056 0.3186 0.004
VLLE
41
75.68 0.23593 0.38041 0.06996 0.42935 0 .0528 0 8 .332 0.0059
VLLE
46
76.882 0.26685 0.34939 0.10037 0.33825 0.0796 0.2427 0.0574

VLLE
45
79.361 0.30312 0.31119 0.10097 0.40054 0.0749 0.3048 0.0178
VLLE
36
77.495 0.33826 0.27853 0.11897 0.32783 0.0864 0.2233 0.0557
VLLE
37
80.178 0.4026 0.37365 0.09469 0.40495 0.0247 0.2012 0.0295
VLLE
43
79.887 0.40621 0.20806 0.15173 0.30198 0.1108 0.2262 0.0795
VLLE
38
83.247 0.42344 0.19078 0.12221 0.29776 0.0724 0.2171 0.0670
VLLE
47
83.652 0.479 0.13668 0.18136 0.24831 0.1193 0.1842 0.0764
VLLE
39
87.081 0.55113 0.0676 0.22563 0.14123 0.1345 0.1007 0.1099
VLLE
40
89.263 0.56658 0.21071 0.19611 0.28647 0.0514 0.1178 0.1059
VLLE
44
90.52 0 .62852 0.14408 0.21915 0.28349 0.0495 0.1605 0.1294

Average 0.0703 0.2167 0.0581

48

Table 4 s Y t u
s i a
-27 Value of ΔY , Δ
1
Water (2) u
2, 3
Δ***Y***
ing NRTL
ΔY for he Ternary system Tol ene (1) \ Ethyl-acetate (2)
\

equation w th binary p rameters**.**
2
P = 101.325 kPa Exp. NRTL
o
Run # T
1
o
C X
X
2
0

Y
1
Y
2
Δ***Y***
1
VL 3LE
72.889 0.13181 0.64221 0.01789 0.43716 0.0271 0.7090 0.328
LE
42
74.157 0.19951 0.41648 0.07024 0.41534VL 0.0023 0.2600 0.2578
VLLE 75.68 0.23593 0.38041 0.06996 0.42935 0.0193 0.1951 0.2166
LE
41
46
45
76.882 0.26685 0.34939 0.10037 0.33825 0.0037 0.2397 0.253
VL 6
VLLE
36
0.31119 0.1009 0054
0.0265 79.361 0.30312 7 0.4 0.1361 0.1454
VLLE
77.495 0.3 8 6 3 2 0. 3 0.1 9 83 0 4 2785 18 7 0.327 .012 0 9 0.2179.110
VLLE
37
80.178 0.4026 0.37365 0.09469 0.40495 0.0696 0.2624 0.1303
VLLE
43
79.887 0.40621 0.20806 0.15173 0.30198 0.0167 0.0295 0.1550
VLLE
38
83.247 0.42344 0.19078 0.12221 0.29776 0.0742 0.0344 0.1249
VLLE
47
83.652 0.479 0.13668 0.18136 0.24831 0.0409 0.0183 0.0899
VLLE
VLLE
39
40
44
87.081 0.55113 0.0676 0.22563 0.14123 0.0575 0.0219 0.0562
89.263 0.56658 0.21071 0.19611 0.28647 0.1092 0.1514 0.0693
VLLE
90.52 0.62852 0.14408 0.21915 0.28349 0.1315 0.0133 0.1389
Average 0.0455 0.1679 0.1680
48

ΔY
2
1
ΔY
ΔY
3
3

Table 4 s Y t u
a s
-28 Value of ΔY
1
, Δ
2,
ΔY
for he Ternary system Tol ene (1) \ Ethyl-acetate (2)
\ W

ter (2) using UNIQUAC equation with binary parameter **.**
3
. X
P = 101 325 kPa E p. UNIQUAC
Run # T
VLLE
42
o
1
o
C X
X
2
0
Y
1
Y
2
ΔY
1
72.889 0.13181 0.64221 0.01789 0.43716 0.018 0.1931 0.2608
0.41534 0.0339 0.0337 0.1582VLLE
74.157 0.19951 0.41648 0.07024
VLLE
41
75.680 0.23593 0.38041 0.06996 0.42935 0.0657 0.0297 0.1039
VLLE
46
76.882 0.26685 0.34939 0.10037 0.33825 0.0658 0.0156 0.1278
VL 0.40054 0.1159 0.0932 0.0053LE

45

79.361 0.30312 0.31119 0.10097

E 77.495 0.33826 0.27853 0.11897VL

36

0.32783 0.1017 0.0492 0.0703L

VLLE

37

80.178 0.4026 0.37365 0.09469 0.40495 0.0908 0.0681 0.0218

LE

43

79.887 0.40621 0.20806 0.15173 0.30198 0.1757 0.1662 0.0499

LE

VL

VL

VL 1 0.2782 0.1847 0.2069

VL

38

83.247 0.42344 0.19078 0.12221 0.29776 0.2671 0.1709 0.1199

LE

47

83.652 0.479 0.13668 0.18136 0.2483

LE 87.081 0.55113 0.0676 0.22563 0.1412

39

3 0.3651 0.1228 0.3719

VLLE

40

89.263 0.56658 0.21071 0.19611 0.28647 0.2132 0.1282 0.4316

VLLE

44

90.520 0.62852 0.14408 0.21915 0.28349 0.2761 0.2013 0.6208

Average 0.1474 0.1139 0.1431

48

Tables 4-29 list the values of $\Delta \boldsymbol{Y}$

th

1

, $\Delta \boldsymbol{Y}$

2

, $\Delta \boldsymbol{Y}$

using the UNIFAC equation with

e binary parameters of the previous binary systems.

Table 4-29 Values of ΔY

LE

36

1

, ΔY

2,

ΔY

3
3
ΔY
for the Ternary system Toluene (1) \ Ethyl-acetate (2)
\ Water (2) using UNIFAC equation**.**

2
P = 101.325 kPa Exp. UNIFAC
o
1
o
2
0
Run # TC XX Y Y
ΔY
ΔY ΔY
VL
VL 0.11897 0.32783 0.2523 0.1276 0.0508
VLLE
1 2
1 2 3
79.361 0.30312 0.31119 0.10097 0.40054 0.2874 0.1889 0.1125
LE
37
38
77.495 0.33826 0.27853
79.887 0.40621 0.20806 0.15173 0.30198 0.2763 0.1804 0.2963
VLLE
83.652 0.47900 0.13668 0.18136 0.24831 0.2623 0.1842 0.9224
LE
LE
39
40
41
87.081 0.55113 0.06760 0.22563 0.14123 0.9660 0.0737 0.034
VL 1
74.157 0.19951 0.41648 0.07024 0.41534 0.1322 0.0767 0.218
LE
VL 0
VL 1420
VL 4719
VLLE
72.889 0.13181 0.64221 0.01789 0.43716 0.0594 0.0016 0.
LE
42
43
44
80.178 0.40260 0.37365 0.09469 0.40495 0.1544 0.1209 0.
89.263 0.56658 0.21071 0.19611 0.28647 0.9034 0.0805 0.0531
VLLE

76.882 0.26685 0.34939 0.10037 0.33825 0.2685 0.0973 0.1148
VL 99LE
45
75.680 0.23593 0.38041 0.06996 0.42935 0.1372 0.2411 0.23
0.19078 0.12221 0.29776VLLE
46
4
7
48
83.247 0.42344 0.1532 0.1548 0.3417
90.520 2 2 0.1440 0.21915 0.28349 0.2498
VLLE 0.6 85 8 0.3210 0.1273
Aver 8 0.1
age 0.2 74 0.1889 125

ΔY
$_3$

4.3 Correlation um

of Equilibri Data

paramete ity c uatio LSON RTL
nd UNIQUAC can be determined by applying non-linear constrained
ptimization with the following objective function:
rs of the activ oefficient eq ns M.WI , N The
a
o

1
c Cn
1
1
1j
pred
ij
exp
ij
◀◀◀
=↕ −
)YY(ABS

nc
W
)1.3.4(Y
c
1i 1i
i
===
ith the following constraint:
−−***YY***
↕
==↕
−−

+
)2.3.4(0YY,0
ii
21ii
+
Wh the o ent e n dat and ere c is number f compon s and n th umber of a points
 is the de a te or . T to
Y−
min qua 1 o t aint ion ore
det ive n

ram he s M N, N
the Eth (r (2 d by tiv of
equation 4.3.1 with the constraint of equation 4.3.2 are given in table 4-30.

sired aver ge absolu deviation difference he aim is
imize e tion 4.3. subject t he constr of equat 4.3.2. M
ails are g n in appe dix D.
 The pa eters of t equation .WILSO RTL and UNIQUAC for
system yl-acetate 1) \ Wate) obtaine the objec e function
Ta ara e em te (1) ob on-

ble 4-30 P meters of th binary syst Ethyl-aceta) \ Water (2 tained by n
n Par
rain tion
linear const ed optimiza .
Equatio ameters T

(λ
M.WILSON
NRTL (g
-λ
=1911
12
12
-g
11
11
) / R
91 K
.4
(λ
) / R
= 657.643 K
UNIQUAC ΔU
/ R
= 515.041 K
12

84

21
- λ
22
) / R 343-372
K

=573.328 K
(g
R=1145.033
21
ΔU
-g
21
22
) / α
/ R
= -30.761 K
=
= 0.5
12

05
α 343-37
K
21

Z / 2
= 6.057
2
343-372
K

Table 4-31 lists the values of Δ***Y***
of the binary system Ethyl-acetate (1) \
Water (2) using the parameters of table 4-30.

Table 4-31 Values of ΔY
1
1
of the binary system Ethyl-acetate (1) \ Water (2) using the parameters of table 4-30.

Experimental
Δ***Y***
Run # X
VLLE
18
1
O

Y
1
exp
1

M.WILSON NRTL UNIQUAC
0.00029 0.07793 0.00000 0.05297 0.05279
VLLE 0.00059 0 0.04 84 0.04682
6
LLE
.09566 0.03116
V 0 51 3 0 0.00182
17
.006 0.4267 0.12567 .01467
VLLE
16

0.01508 0.44675 0.14 0.1

0

940 7959

.22692

VLLE

15

0.03038 0.71916

0.47

0.13388 0.02971

970

VLLE

VLLE

VLLE

2

10

8

3

0.31812 0.66801 0.12 0.0 0.02164 045 4495

0.38800 0.68133 0.13 0.0 0.04322 230 5300

0.45139 0.73685 0.18 0.0 0.12180 172 9477

VLLE

0.54128 0.78067 0.19 0.0 0.15415 076 9223

VLLE

6

0.55313 0.68436 0.11 0.0 0.08344 624 2179

VLLE

1

0.67195 0.63273 0.00 0.0 0.01243 499 8627

VLLE

4

0.73096 0.50861 0.15

0.2

0793

3872

.17026

VLLE

7

0.77782 0.75010 0.06 0.0 0.06118 987 0360

VLLE

5

0.79263 0.85062 0.11 0.0 0.10658 479 4936

VLLE

11

0.82233 0.85279 0.09 0.0 0.08392 026 3528

VLLE

12

0.88509 0.91261 0.07 0.0 0.07672 974 4883

VLLE 0.95000 0.78984 0.02 0.0 0.02128 069 2790
VLLE
13
9
14
0.98400 0.98608 0.02475 0.02378 0.02259
Average 0.11613 0.06936 0.07429
Correlation coefficient (R) 0.930 0.964 0.962

By applying equation 2.2.3 the value of ***Y***
w
s
is predicted theoretically
here
Φ
1
v
and ***Φ***
1
S
i
are determined by applying Peng-Robinson equation of
tate, equations 2.3.33 to 2.3.40 with k
P
i
S
ij
= 0. Table 4-32 lists the values of ***Φ***
a are
withdrawn by sampling method 3.

nd ***Φ***
1
S
for the binary system Toluene (1) \ Water (2) where samples

1
v

Table 4-32 Values of
Φ
T
1
V

, P
i
S
 and Φ
1
S

 for the binary system Toluene (1) \ Water
(2) by sampling method 3.
o O
v S S
Run # C P (kPa) X
VLLE
19
1
Φ
1
P
1
(kPa) Φ
96.121 101.325 0.08097 0.97273 66.421 0.97665
VLLE
94.601 101.325 0.14443 0.97130 63.345 0.97744
VLLE
20
93.497 101.325 0.20582 0.97004 61.184 0.97794
VLLE
21
92.610 101.325 0.28316 0.96865 59.490 0.97827
VLLE
22
92.474 101.325 0.36978 0.96737 58.864 0.97827
0.43648 0.96VLLE
23
92.487 101.325 660 59.258 0.97803
VLLE
24
93.730 101.325 0.54779 0.96574 61.635 0.97718
VLLE
25
94.966 101.325 0.6 8 1300 0.9654 64.073 0.97643
VLLE
26
10 .761 56 99.151 1.325 0 41 0.965 72.905 0.97402
VLLE
27
10 .766 58 99.336 1.325 0 73 0.965 73.317 0.97391
VLLE
28

10 .881 28 103.890 1.325 0 29 0.966 84.045 0.97134

VLLE

29

10 .928 71 106.098 1.325 0 83 0.966 89.675 0.97010

VLLE

30

10 .952 95 107.255 1.325 0 29 0.966 92.742 0.96945

VLLE

• Φ

1

S

f

31

32

1

0

10 .953 25 108.543 1.325 0 10 0.967 96.253 0.96858

= / P

1

S

(P

1

S

equation)

from C.1.2

alu he a oeff

The v es of t ctivity c icients γi are predicted by using the equations M.WILSON, NRTL and UNIQUAC, the parameters of these e are ed obje ctio ion le

4 the ter

quations determin from the ctive fun n of equat 4.3.1. Tab

-33 lists se parame s.

Table 4-33 Pa ne (1) \ W) obtained by

onstra

nary system Toluerameters of the bi

Non-linea

r c

ation ara

P

ined optimization.

ater (2

1

meters Equ T

M.WILS
2
-λ
550
λ
1
-
=19
67-ON (λ
1
=35
NRTL -g
15.
) / R (
.06 K
1
21
(g
=151
21
λ) / R
3.34 K
3 384 K
22
α
= 0
65- (g
12
= 4
UNIQU U
492 K
) / R g) / R
11
694
ΔU
12
5.104 K
= α
22
= -11
Z
= 2
12
.632
3 382 K
67-AC Δ / R
= .95 K

86
21
21
1.82 K
/ R / 2 3
.700
384 K
•

The alu ***Y***
1
pr
Y
inary
W u equ .WIL TL IQ h
p s e 4 liste les 35 6
respectively.
v es of γ
1
,
1

Table ters

ed
and Δ for the b system Toluene (1) \
ater (
er
2) sing the ations M SON, NR and UN UAC wit
aramet from tabl -33 are d in tab 4-34, 4- and 4-3
4-34 Values of γ
1
for the binary system Toluene (1) \ Water (2) using parame
from table 4-33.
γ
1
M.WILSO NRT UNIQUA
E
Run T
9 0.08 273.475 3.9423 3.57617
E
19
9 0.14 2.2636 2.3492 2.8543
E 9

20

0.20 1.7610 1.8913 2.3921

E

21

9 0.28 1.4352 1.6323 1.9927

E 9

22

0.36 1.2434 1.4703 1.6865

E

E

23

24

25

E 9

26

9 0.43 1.1570 1.3806 1.5142

9 0.54 1.0740 1.2609 1.3060

0.61 1.0460 1.2014 1.2170

E

9 0.76 1.0125 1.0890 1.0790

E

27

9 0.76 1.0118 1.0856 1.0755

E

28

10 0.88 1.0024 1.0256 1.0194

E

29

10 0.92 1.0008 1.0098 1.0070

E 10

30

0.95 1.0003 1.0046 1.0031

E

31

32

o

C X

10 0.95 1.0003 1.0044 1.0030

s o**Tabl** nary luen r (2) eters
table 4-33.

e 4-35 Values of Y

1

pred

1

O

N L C

VLL 6.121 097 2

VLL 4.601 443 3 0 8

VLL 3.497 582 8 1 0
VLL 2.610 316 0 1 3
VLL 2.474 978 6 4 9
VLL 2.487 648 6 1 8
VLL 3.730 779 0 7 3
VLL 4.966 300 3 6 4
VLL 9.151 141 5 2 8
VLL 9.336 673 7 1 3
VLL 3.890 129 5 3 2
VLL 6.098 883 1 7 0
VLL 7.255 229 5 0 5
VLL 8.543 310 3 2 2
for the bi
from
ystem T e te(1) \ Wa u amsing par
Experimental
Y
Run # X
1
O
Y
1
exp
1
pred

M.WILSON NRTL UNIQUAC
VLLE
0.08097 0.21372 0.18520 0.21009 0.19058
VLLE
19
0.14443 0.27764 0.20568 0.21346 0.25936
VLLE 0.20582 .3374 0.22065 0.23697 0.29971
20
0 6
VLLE
21
22
0.28316 0.36746 0.24097 0.27406 0.33458
0.27013 0.31942 VLL 0.36978 0.40437 0.36640 E
LE
23
0.43648 0.48 64 0.2988 .39112
VL 6 1 0.42515 0 LE
VL 0 5 0.35659 0
24
0.54779 0.53 23 0.3621 .44035

VL 6 8 0.47101 0 LE
25
0.61300 0.57 92 0.4100 .47712
VL 5 8 0.60184 0 LE
26
0.76141 0.62 48 0.5595 .59635
VL 3 2 0.60748 0 LE
27
0.76673 0.64 72 0.5662 .60184
VL 3 3 0.75366 0 LE
28
29
0.88129 0.71 43 0.7366 .74909
VL 4 8 0.83306 0 LE
0.92883 0.74 91 0.8255 .83069
VL 5 8 0.87789 0 LE
30
0.95229 0.78 57 0.8741 .87663
VL
31
0 4 0.91064 0 LE 0.95310 0.83 12 0.9069 .90937
32

RUN

Table 4-3 o r y T)
r r 4
6 s Value f ΔY
fo
the pa
1
the binar
ameters f
system
om table

ΔY
Run # Y
1
exp
oluene (1
-33.
1
\ Water (2) using

% M.WIL SON NRTL UNIQUAC
VLLE
1
9
. 2
0 21372 0.0 852 0.00363 0.02314
VLLE 0.27764 0.07196 0.06418 0.01828
VLLE
20
0.33746 0.11681 0.10049 0.03775
VLLE
VLLE
21
22
23
24
0.36746 0.12649 0.09340 0.03288
VLLE 0.40437 0.13424 0.08495 0.03797
0.48064
0.18179 0.12405
0.08952
VLLE
25
0.53623 0.17412
0.11108 0.09588
VLLE
0.57692 0.16684 0.10591
0.09980
VLLE
26
0.62548 0.06590 0.02364 0.02913
VLLE 0.64372 0.07750 0.03624 0.04188
VLLE
VLLE
27
28
29
3
0
71343 02320 0. 0. 0.04023 0.03566
0.74 1 0.080 0.08815 0.08578
0.78 0.0886
0.8301 0.07682
49 67
VLLE
557 1 0.09232 0.09106
VLLE
31

2 0.08052 0.07925

Average 0.10096 0.07491 0.05700

32

ion coeffici t (R) .978 986 0 87

By applying equation 2. .3 the value of Y

Correlat en 0 0. .9

1

and Y

of t

(3) are p

ternary system

\ Ethyl-acetate

2 he

oluene (1) (2) \ Water redicted theoretically where

T

Φ

1

V S

and ***Φ***

1

ined using P.R (EOS),

2

are determ equations 2.3.43a to 2.3.43c.

As shown in table 4-37.

Table 4-37 Values of Φ

42

T

o

C X

1

o

1

V

, P

i

S

and Φ

1

S

for the ternary system Toluene (1) \ Ethyl-acetate

(2) \ Water (3) by sampling method 3.

P

1 1 1 2 2 2 2

S

S

Φ

v

Φ

S

X

0
P
s
72.889 0.131VLLE 8 30.501 0.9552 0.9677 0.6422 87.992 0.9624 0.9746
VLLE
74.157 0.1995 31.926 0.9544 0.9724 0.4165 91.838 0.9614 0.9783
VLLE
41
46
0.978575.680 0.2359 33.708 0.9547 0.9724 0.3804 96.631 0.9617
35.17 0.9549 0.9726 0.3494 1VLLE
4
5
76.88 0.266 00.552 0 619 0.9788
2 9 .9
LE
7 61 31 .348 0.9555 0.9719 0 3112 09.034 0.96 5 0.978
LLE
VL 9.3 0.30 38 . 1 2 4
V 7 . 5 1 2 8
V 0 . 9.4 7 11 64 4
V 9 . 9.0 2 11 62 9
V 3 . 3.7 2 12 63 5
V 3 4.3 2 12 63 6
36
7 .495 0 3383 3 .9 4935 0.95 0.9736 0.2785 02 96.597 0. 2 0.979
LLE
37
8 .178 0 4026 3 45 0.956 0.9713 0.3737 1.953 0.9 2 0.978
LLE 7
43
.887 0 4062 3 52 0.955 0.9746 0.2081 0.907 0.9 5 0.980
LLE 8
38
.247 0 4234 4 92 0.956 0.9727 0.1908 3.463 0.9 4 0.979
LLE 8
47
39
LLE 8
40
.652 0.479 4 95 0.956 0.9739 0.1367 5.052 0.9 5 0.980
.081 0 5511 4 57 0.957 0.9733 0.0676 9.135 0.9 5 0.980
LLE 8
V 7 . 9.7 1 13 64 5
V 9 . 3.4 2 14 66 0
V 0 . 5.6 4 15 66 1
.263 0 5666 5 34 0.959 0.9697 0.2107 8.732 0.9 6 0.978

LLE 9
44
48
.520 0 6285 5 47 0.959 0.9708 0.1441 4.487 0.9 9 0.979

88
Φ
v
Φ

Th s ac ffi dict ing
e value of the tivity coe cients γi are pre ed by us the
equat ns M.WILSON, RTL and NIQUA , the p meters o these
equa ns are etermin from the bjective function equation .3.1.
T

io N U C ara f
tio d ed o of 4
ables 4-38 and 4-42 list these parameters.

Table 4-38 Parame ate (2) \ Water (3)
ters of the ternary system Toluene (1) \ Ethyl-acet
obtained by Non-linear constra ptimization. ined o

IL R
8
M.W SON a
12
/
K
a
= 0.361
a
23
/
2.
R
= -22 72 K
21
/ R
.11 = 7
a
13

/ R
= -597.52 K
a
53
= 181 K
NR
 K 8 K
TL (g
)/R
= 33.78
 (g

l

12
)/R
=3071.211
32
1
(g
21
a
/ R
99.57 K
32
)/R
=31.3 =517
 K
α
(g
 = α
12 21
, γ , *Y*
 = α
13
1
/ R
= K 1180.72
31
T = 3 – 365 K
.

5 K
)/R
598 K
3
2

(g

)/R

=499.88 =857

31

(g

.

T 365

= α

31

=α

3

= α

= 0 649

1

32

Y te ste

l ace \ W) h ons SO

d w me ta d s 4 0 an

4 t

The va ues of γ

Table 4-39 Values of γ

1

2

, ***Y***

and γ

1

pred

2

2

pred

, Δ***Y*** and Δ

for the rnary sy m

To uene (1) \ Ethyl- tate (2) ater (3 using t e equati M.WIL N an NRTL ith para ters from ble 4-38 are liste in table -39, 4-4 d 4- 1 respec ively.

2

)/R

.35

23

8 K

= 353 – K

for the tern y system Toluene (1) \ Ethyl-acetate (2) \

ar

Water (3) using parameters from table 4-38.

γ

Run # T

o
γ
1
O
1
C .WILSON NRTL X

2
O
M.WIL NRTL X
M SON
LE
89 0 0 340 1.276 0.642 1.11000 1.1827
LLE
VL 72.8 .1318 .59 16 2 3
V 4.1 99 597 2370 5
V 5.6 35 319 8879 4
42
7 57 0.1 5 0.8 0 1.3 0.416 1.31570 1.24704
LLE
LLE
41
46
45
7 80 0.2 9 0.9 0 1.2 0.380 1.29320 1.23533
7 82 0.2 9 0.9 0 1.2 0.349 1.27220 1.22678
LLE
V 6.8 66 900 6154 4
V 9.3 03 579 3210 2
V 7.4 38 383 9343 5
V 0.1 02 442 2257 7
V 9.8 06 072 6023 1
V 3.2 23 290 4919 8
7 61 0.3 1 1.0 0 1.2 0.311 1.24690 1.21862
LLE
36
7 95 0.3 3 1.0 0 1.1 0.278 1.15980 1.20329
LLE
37
8 78 0.4 6 0.9 0 1.1 0.373 0.99480 1.15572
LLE
43
7 87 0.4 2 1.2 0 1.1 0.208 1.16070 1.20216
LLE
LLE
38
47
39
8 47 0.4 4 1.2 0 1.1 0.190 1.14220 1.20053

8 52 0. 1.2 0 1.1 0.136 1.08880 1.19751

LLE 8

V 3.6 479 842 1805 7

V 7.0 51 342 8352 6

V 9.2 66 672 6260 7

V 0.5 28 016 4598 1

81 0.5 1 1.3 0 1.0 0.067 1.01460 1.19819

LLE 8

40

63 0.5 6 1.0 0 1.0 0.210 0.88920 1.16248

LLE

44

48

9 20 0.6 5 1.1 0 1.0 0.144 0.84820 1.17153

89

2

Table 4-40 Values of Y

1

pred

and or the te ystem T (1) \ Eth tate

Y

2

pred

f rnary s oluene yl-ace

(2) \ Water (3) using parameters from table 4-38.

Y

Run # X

1

O

Y

1

exp.

1

pred

Y

M.WILSON NRTL X

2

O

Y

2

exp.

M.WILSON NRTL
VLLE
VLLE
2
0.1318 0.0179 0.0239 0.0513 0.6422 0.4354 0.6269 VLLE
424
0.1995 0.0702 0.0551 0.0848 0.4165 0.4153 0.5054 V
0 0.0745 0.1030 0.3804 0.4294 VLLE
41
46
0.2359 0.070 0.4774 VLLE
VLLE .1 934 0.349 .3 0. VLLE
VLLE
VLLE
VLLE
VLLE
VLLE
0.2669 0 004 0.0 0.1190 4 0 332 4488
0.3031 010 0.1 0.1438 0 12 0.4005 0.4244 V
4545
36
37
43
8
0.1 235 .31 LLE
0.1 0.1460 0.2785 0.3278 0.37 V64
4 947 0.15 0.1786 0 7 0.399 0.4168 V
0.3383 0.1190 270 LLE
0. 026 0.0 02 .373 3 LLE
0.1928 0.1853 0.3020 0.2694 VLLE
0.4062 0.1517 0.2081
383
7
0.4234 0.1222 0.2288 0.2139 0.1908 0.2978 0.2700 VLLE
474
VLLE LE
VLLE
0.4790 0.1814 0.2745 0.2390 0.1367 0.2483 0.1869 VL
3939
40
44
48
0.5511 0.2256 0.3672 0.2982 0.0676 0.1412 0.0957 VLLE
0.5666 0.1961 0.3224 0.3210 0.2107 0.2786 0.2783 VL
VLLE LE
0.6285 0.2192 0.3848 0.3653 0.1441 0.2835 0.1887 VLL
VLLE E

able 4-41 Values of ΔY

1

and ΔY
2

for the ternary system Toluene (1) \ Ethyl-acetate (2) \
T
Water (3) using parameters from table 4-38.

ΔY
Run #
VLLE
42
Experimental
ΔY
1
exp e
Y
2
xp
1

ON NRTL M.WILSON NRTL
Y
M.WILS
0.017 0.43
0.0700 0.429 0. 45 331 .0480
0.0702 0.415 0. 52 145 .0901
0.0947 0.399 0. 56 839 .0118
0.1004 0.333 0. 70 186 .1106
0.1010 0.400 0. 25 428 .0239
9 54 0.0060 0.0334
0.1897 0.2308
VLLE
4 00 0.0 0 0.0267
VLLE
46
3 01 0.0 0 0.0637
VLLE
41
3 05 0.0 0 0.0792
VLLE
43
2 00 0.0 0 0.0945
VLLE
VLLE
45
36
37

0.1190 0.327 0. 80 270 .0486
0.1222 0.297 0. 66 917 .0278
0.1517 0.302 0. 11 336 .0326
0.1814 0.248 0. 31 576 .0614
0.1961 0.278 0. 62 249 .0082
0.2192 0.283

0. 56 462

0.2256 0.141 0. 16 726 .0455
0. 10 600

2

5 02 0.0 0 0.0143
8 00 0.0 0 0.0627
VLLE
8 10 0.0 0 0.0140
VLLE
47
0 04 0.0 0 0.0230
VLLE
38
3 09 0.0 0 0.0427
VLLE
39
6 12 0.1 0 0.0773
VLLE
44
5

16 0.1

0.0948 0.0229
VLLE
48
40

2
pred

2 14 0.0 0 0.0282
Average 06 0.0 0.0610 0.0600
Correlation coefficient (R) 0.982 0.973 0.963 0.956

LLE
41
46
36
37
43
40

U

Table 4-42 Parameters of the ternary system Toluene (1) \ Ethyl-acetate (2) \ Water (3)
obtained by Non-linear constrained optimization.

NIQUAC ΔU
/ R =
428.815 K
ΔU
12
23
ΔU
21

/ R
= -353.542 K
/ R ΔU
32
ΔU
/ R
= 1087.34 K
13
ΔU
/ R
= -144.76 K
/ R Z / 2 T
0 – 36= 287.01 K = 604.31 K = 4.647 =35 4 K

The v f γ

Y
1
pr

, Δ nd Δ r th y system
Toluene y (er (3) using t on AC with
parameters from table 4-42 are lis ta 3, d 4-45
respectiv

alues o

1

, γ

2

,

-4 o

ed

, ***Y***

2

pred

for the ternary lu

a \ us et l

2

Y

1

a ***Y***

fo e ternar

(1) \ Eth l-acetate 2) \ Wat he equati UNIQU

2

ted in bles 4-4 4-44 an

ely.

Table 4

yl-

3 Values f γ

and γ system To ene (1) \

Eth cetate (2) Water (3) ing param ers from tab e 4-42.

1

x ta U

E perimen l UNIQ AC

Run # T C

VLLE

42

o

X

1

O

X

2

O

γ

1

72.889 0.1318 0.6422 0.6765 1.0326

VLLE

74.157 0.1995 0.4165 0.9148 1.2030

VLLE
41
75.680 0.2359 0.3804 0.9520 1.1902
VLLE
46
76.882 0.2668 0.3494 0.9862 1.1794
VLLE
45
79.361 0.3031 0.3112 1.0356 1.1704
VLLE
36
77.495 0.3383 .3147 0.9962 1.0637 0
VLLE
37
80.178 0.4026 0.3736 0.8763 0.8784
VLL 5 E
43
79.887 0.4062 0.2081 1.1701 1.129
VLLE 83.247 0.4234 1908 1.2021
38
. 1.1252
LE
0
VL 83.65 67 1 4
V 87.0 511 6
47
2 0.4790 0.13 .2906 1.10 5
LLE
LLE
39
40
44
8 0.51 0.067 1.4273 1.0987
63 0.5 0.210 1.0380 0.7114
LLE
V 89.2 666 7
V 90.5 285 1
48
20 0.6 0.144 1.1083 0.6343

91
γ
2
31

Table 4-44 Valu and the em 1) \
Ethyl-acetate (2) \ Water (3 me b
es of Y
1
pred
Y
2
pred
for ternary syst Toluene (
) using para ters from ta le 4-42.

IQU
Experimental UN AC
Run # T
VLLE
42
o
C
Y
exp
Y
exp
Y
pred
Y
1 2 1 2
72.889 0.0179 0.4354 0.02719 0.58315
VLLE
75.680 0.0700 0.4294 0.07611 0.43938
VLLE
46
74.157 0.0702 0.4153 0.05859 0.46212
VLLE
41
80.178 0.0947 0.3993 0.13943 0.36796
VLLE
43
76.882 0.1004 0.3332 0.09304 0.41609
VLLE
45
79.361 0.1010 0.4005 0.12084 0.39840
VLLE
36
77.495 0.1190 0.3278 0.12185 0.34520
VLLE
37
83.247 0.122 0.22378 0.26595

VLLE
47
38
79.887 0.1517 0.3020 0.18692 0.26215
VLLE 2 0. 275 962
39
83.65 0.1814 2483 0. 87 0.18
VLLE 3 0. 313 264
VLLE
44
48
2 .2978 0
89.26 0.1961 2786 0. 55 0.22
90.520 0.2192 0.2835 0.38712 0.14108
VLLE
87.081 0.2256 0.1412 0.39281 0.10368

40

Table 4-45 Values of ΔY
1
and ΔY
for the ternary system Tolu
Ethyl-acetate (2) \ Water (3) using parameters from table 4-42.
2

pred

ene (1) \
Experimental UNIQUAC
Run #
Y
VLLE
42
1
Δ***Y***
1
Δ***Y***
0.0179 0.4354

0.00930
0.14599
VLLE
.00.0700 0.4294 0 06 0.01003 16
VLLE
46
02 1 00.07 0.4 53 0. 1165 0.04678
VLLE

VLLE
41
43
45
4 9 00.09 7 0.3 93 0. 4475 0.03699
04 3 00.10 0.3 32 0. 0733 0.07784
VLLE
10 0 00.10 0.4 05 0. 1987 0.00213
VLLE
36
90 2 00.11 0.3 78 0. 0288 0.01736
VLLE
37
22 9 10.12 0.2 78 0. 0157 0.03181
VLLE
47
17 0 00.15 0.3 20 0. 3519 0.03982
VLLE
38
14 4 00.18 0.2 83 0. 9451 0.05869
VLLE
VLLE
VLLE
39
44
48
40
exp
Y
2
exp
61 7 10.19 0.2 86 0. 1744 0.06383
92 0.2835
0.16797
00.21 .14241

2

56 0.1412 0.10.22 6718 0.03755
Average 0.04817 0.04817
Correlation coefficient (R) 0.982 0.952

The interacti eters k
of the Peng-Robinson (EOS) for the two

binary systems Ethyl-acetate (1) \ Water (2) and Toluene (1) \ Water (2) were
obtained by non-linear constrained optimization the values of these parameters are listed in table 4-46.

ng param
ij
Table 4-46 Interacting parameters of the P.R. (EOS) for the two binary systems.
k

Ethyl-acetate(1)\Water(2) Toluene(1)\Water(2)
12
n k
21
n k
 -0.221 8 2.1 9
12
k
termined u
.42b wi the intera ting para eters f table 4- 6. The va
ط
i
L
 of th two binar systems a e listed i table 4-47
Table 4 Values of
1
v
 and Φ
1
L
21
-0.27045 4 302 -0.27683 -0.33441 1.94111
By applying equation 2.2.6 the value of Y
Φ
1
v
 and ***Φ***
1
L
using the
arameters o table 4-4
o

Ethy cetate(1)\ ene(1)\W er(2)
Φ
1
v
1
 is predicted theoretically where

is de sing the Peng-Robinson (EOS), equations 2.3.42a
and 2.3 th c m rom 4 lues of
ط

i
V

and e y r n .
-47 Φ of the two binary systems
p f 6.
l-a Water(2) T lu at
Run #
Φ
VLLE
1
1
L
Φ
1
v L
Run #
Φ
0.96347 0.96436 2.94342
0.96406 1.17861
0.63897 VLLE

VLLE
2
0.96138 19.45240 VLLE
19

VLLE
3
20
0.96338
0.96407 0.96371 0.78467
0.96434 0.96369 0.71800
0.96383
0.67556 VLLE
0.96385 0.92578
VLLE
4
0.66208 VLLE
21

VLLE
5
0.67587 VLLE
22

VLLE
VLLE
6
7
0.67014 VLLE
23
0.96378 0.69568
0.96438 0.68120 LE
0. .71699
24
VL 6414
VLLE
VLLE
8
9
0.96333 0.72225 VLLE
96485 0 VLLE
25
26
27
1
0.9 0.69286
0.96447 0.70658
0.96548 0.77409
VLLE
10
0.96337 0.82857 VLLE
0.96552 0.77747
VLLE
11
0.96496 0.72703 VLLE
28
0.96655 0.86674
VLLE
12
0.96511 0.73981 VLLE
29
0.96703 0.91399
VLLE
13
0.96551 0.77573 VLLE
30
0.96727 0.93975
VLLE
14
0.96607 0.83314 VLLE
31
0.96756 0.97319
VLLE
VLLE

15
16
0.96522 40.71559 VLLE
0.96720 63.39991 VLLE
32
33
34
0.96453 2.67112
0.96472 4.47128
VLLE
17
0.96828 84.57163 VLLE
0.96475 5.06358
VLLE
18
35
0.96865 1196.15463

The values of ΔY
o
46 are listed in table

1
f the tw e parameters of table 4
4-48.

o binary systems using th
l o n u
ters of table 4-46.

Table 4-48 Va ues of ΔY
f the two bi ary systems sing the
parame
1

Ethyl-acetate(1)\Water(2) Toluene(1)\Water(2)
Run #
Y
VLLE
1
1
exp
ΔY
1
0.68436 0.31753 VLLE

Run #

Y

19

1

exp

0.21372 0.03342

VLLE

2

0.71916 0.10446 VLLE 0.27764 0.10107

20

3

685 0.42032 VLLE

0.337 77

E

VLLE 0.73

46 0.139

VLL 3

4

0.6 273 0.17127 VLLE

2

0.367 6 0.13 90

E

5

0.7 010 0.20496 VLLE

2

0.404 7 0.15 48

E

6

0.7 067

0.40425

VLLE

2

0.480 4 0.16 58

E

7

0.5 861 0.00772 VLLE

2

0.536 3

0.14 57

E

E

8

9

10

11

12

13

14

15

0.6 133 0.39043 VLLE

0.7 984 0.08388 VLLE

0.6 801 0.39440 VLLE
0.8 062 0.25343 VLLE
0.8 279 0.22243 VLLE
0.9 261 0.20149 VLLE
0.9 608 0.13540 VLLE
0.4 675 0 VLLE
2
2
2
2
2
3
3
3
3
1
4 6
VLL 5
2
3 7
VLL 8
3
6 5
VLL 0
4
2
2
VLL 8
VLL 8
VLLE 6
5
6
7
8
ΔY_1
0.576 2 0.12 83
9 7
0.625 8 0.01 01
4 5
0.643 2 0.02 33
7 6
VLLE 5
9
0.713 3 0.07 85
4 6
VLLE 5
0
0.744 1 0.13 97
9 2

VLLE 1

1

0.785 7 0.13 62

5 9

VLLE 8

2

0.830 2 0.12 52

1 8

VLLE 4 .18937

3

0.143 7 0.00 20

4 0

VLLE

16

0.42673 0.00000 VLLE

0.09873 0.00059

VLLE

17

0.09566 0.04413 VLLE

34

0.05642 0.02714

VLLE

18

35

0.07793 0.28018 Average 0.09129

Average 0.21254 R 0.971

R 0.794

By applying equatio lue of Y

is predicted theoretically

where

Φ

1

v

and ***Φ***

1

L

1

is determ ng-Robinson (EOS), equations

2.3.43a to 2.3.43c with ractin eters determine on-linear

constrained optimization which are given in table 4-49. The values of

Φ

Φ

1

L

n 2.2.6 the va

ined using the Pe

the inte g param d from n

for the ternary sy luen

listed in table 4-50.
stem To e (1) \ Ethyl-acetate (2) \ Water (3) are

Table 4-49 Values o cting rs fo ry s uene (1) \
-aceta ater (
f the intera paramete r the terna ystem Tol
Ethyl
To) \ Eth (3
luene (1
k
21
te (2) \ W
3).
yl-acetate (2) \ Water
k
 0.082 0.16287 0.04862
n k
12
13
k
23
)
k
31
1.96238 -0.05503 46 - -0.04518 0.02495

1
v
k
 and
32

4-50 Values of Φ
Table ry sy uene yl-acetate
y sampling me
RUN
VLLE

36
T
o
C X
1
v

and Φ
1
o
1
L
for
(2) \ Water (3) b
Φ
1
V
the terna stem To
thod 3.
Φ
1
L
X
2
0
l (1) \ Eth
Φ
2
V
79.361 0.3031 0.9556 0.0818 0.3112 0.9672 0.8991
VLLE
77.495 0.3383 0.9548 0.0852 0.2785 0.9669 0.9150
VLLE
37
79.887 0.4062 0.9556 0.0993 0.2081 0.9679 1.2302
VLLE
38
83.652 0.4790 0.9568 0.1340 0.1367 0.9692 1.7295
VLLE
39
87.081 0.5511 0.9580 0.1798 0.0676 0.9706 2.4010
VLLE
40
74.157 0.1995 0.9542 0.0586 0.4165 0.9656 0.5900
VLLE
41
72.889 0.1318 0.9534 0.0843 0.6422 0.9651 0.6331
VLLE
42
80.178 0.4026 0.9558 0.1364 0.3737 0.9683 1.1997
VLLE
43
89.263 0.5666 0.9590 0.2277 0.2107 0.9715 2.0872
VLLE
44
76.882 0.2669 0.9548 0.0705 0.3494 0.9665 0.7556
VLLE
45

75.680 0.2359 0.9545 0.0647 0.3804 0.9660 0.6741
VLLE
46
83.247 0.4234 0.9567 0.1173 0.1908 0.9688 1.4349
VLLE
47
48
90.520 0.62 441 0.9722 2.4339 85 0.9595 0.2545 0.1

The values of
$\Delta \boldsymbol{Y}$
, $\Delta \boldsymbol{Y}$ ted e 4

Table 4-51
1
$\Delta \boldsymbol{Y}$
2
and
3
are lis in tabl -51.

for the ternary sy ne (1)
\ Ethyl-acetate (2) \ Water (3) using parameters from table 4-49.
Values of ΔY
1
, ΔY
2
and ΔY stem Tolue
3
Experimental P.R.(EOS)
1
exp exp
Run #
Y Y
VLLE
36
2
$\Delta \boldsymbol{Y}$
1

0.1010 0 0.111
.4005 0.0750 3
VLLE
0.1190 0.3278 0.0888 0.0300
VLLE
37
0.15 0. 20
VLLE
VLLE

$\Delta \boldsymbol{Y}$

0.1814 0.2483 0.1143 4 0.004

0.2256 0 0.0260

0.01 0. 54

VLLE

0.0947 0.3993 0.0372 0 0.058

0.1961 0.2

0.1662

0.07 0. 94

VLLE

0.1222 0.2978 0.0703 2 0.015

E

17 30 0.1095 0.0375

.1412

0.1222

VLLE

VLLE

VLLE

0.0702 0.4153 0.0580 0.1608

79 43 0.0062 0.0158

786 0.0616

VLLE

0.1004 0.3332 0.0807 0.0651

VLLE

00 42 0.0540 0.1639

0.2192 0.283 0524 0.0772

VLL 5 0.

orr n coeffic nt (R) 927 .652

^{2}

Average 0.0716 0.0716

C elatio ie 0. 0

95

$\boldsymbol{\Phi}$

2
L

4.4 Modification of UNIQUAC equation

Th ation n /2) which has a value of 5 was considered as
a third adjustable parameter. This was applied on six binary systems and two
ternary systems. Table 4-52 shows the average values of
ΔY
of the binary
systems calculated using the UNIQUAC equation with the third adjustable
parameter.

e co-ordin umber (Z

Table 4-52 Average ΔY
i
i
Values of the Binary Systems using the modification
of the UNIQUAC equation.

hy 1)) a
lEt -acetate(\Water(2 Dat [2]
ΔY
Z / 2
ΔY
Z / 2
1
ΔY
2
ΔY
1 2
5 0.1440 0.1051 4.335 0.0997 0.0997
Average 0.1246 Average 0.0997
1-Butanol(1)\Water(2) Data [2]
Z / 2
ΔY
1
ΔY
2
Z / 2
ΔY

1

5 0.0290 0.0639 4.731 0.0381 0.0270

Average 0.0466 Average 0.0325

$\Delta \boldsymbol{Y}$

2

MEK(1)\Water(2) Data [2]

Z / 2

$\Delta \boldsymbol{Y}$

1

$\Delta \boldsymbol{Y}$

2

Z / 2

$\Delta \boldsymbol{Y}$

1

5 0.0899 0.0370 10.68 0.0632 0.0337

Average 63 e0.0 5 Av rage 0.0484

$\Delta \boldsymbol{Y}$

2

2M ate 9] D(1)\W r(2) Data [3

/ 2

Y

Z

$\Delta \boldsymbol{Y}$

2

/ 2

1

5 0.0450 0.0353 3.528 0.0404 .0350 8

A rage 0.0381

24DMD(1)\Wa 9] ter(2) Data [3

/ 2

$\Delta \boldsymbol{Y}$

1

Y

2

/ 2

1

5 0.0993 0.0655 5.345 0.0936 .0650 9

A rage 0.0798

Ethyl-acetate(1)\Water(2) ata t woD [Presen rk]

/ 2

$\Delta \boldsymbol{Y}$

1

Y

2

/ 2

1

5 0.1192 0.0725 6.057 0.0743 .0740 3

A rage 0.0743

Tol Wa ata t wouene(1)\ ter(2) D [Presen rk]
/ 2
ΔY
1
1
Δ
Z
ΔY
ΔY
Average 0.0402 ve
Z
Δ
Z
ΔY ΔY
Average 0.0824 ve
Z
Δ
Z
ΔY ΔY
Average 0.0959 ve
Y
2
/ 2
Z
Δ
Z
ΔY ΔY
1
5 0.0841 0.0841 2.696 0.0570 .0570 0
A rage 0.0570
Average 0.0841 ve

2
2
2
2

Table lues rnar s us difica
4-53 Average ΔY_i
Va
of the UNIQUAC equation.
of the Te y System ing the mo tion

Toluene(1)\Ethyl-acetate(2)\Water(3) Data [Present work
Z / 2
∆***Y***
Z / 2
∆***Y***
1
∆
Y ∆***Y***
3
2 1
∆***Y***
5 0.1474 0.1139 0.1431 4.647 0.0482 0.0482 0.0482
Average 0.1 r348 Ave age 0.0482
2
]
∆***Y***
EK(1)\Benzene(2) ter(3) D]
M \Wa ata [40
Z / 2
∆
Z
∆***Y*** ∆***Y***
∆***Y***
1
∆***Y***
2
Y
3
lation o boilin pera
perature of boili
 / 2
1
∆***Y***
588 98 0 0.03
0.0328
5 0.0152 0.0737 0.0812 6. 0.01 .0474 11
Average 0.0567 Average

4.5 Calcu f g tem ture

n 2.2.3.
was ca ted by ation 4 which
The tem ng lcula equ .5.1 is
derived fro o Tab 4 to st th s of T
for the two binary and the ternary systems.

m equati les 4-5 4-58 li e value T and Δ

S

P/P

iii

L

i

⎞

)1.X1

©

n

◀◀

==

V

i

⎞

X

Table 4- o the b stem etate ter (2)

rs fr es 4.3 3.17

P=101.3

54 Values f T

5.4(1,

==

1i

cal.

for

P te

inary sy Ethyl-ac (1) \ Wa Using

arame om Tabl .1 and 4.

25 kPa. T C

X

1

O

n

1i

i

o

Exp. ILSO NRTL

0.55313 70.407 72.517 72.396

0.0 38 30 74.326 71.209

.

Run # M.W N UNIQUAC P.R(EOS)

VLLE

69.961 84.042

VLLE

1

70.882 86.527 81.205

VLLE

2
0.45139 71.258 70.229 73.139 72.429 85.179
VLLE
3
0.67195 71.283 70.463 72.114 72.316 83.008
VLLE
4
0.77782 71.383 71.656 72.050 72.612 82.219
VLLE
VLLE
5
6
7
0.54128 71.753 69.958 72.577 72.409 84.189
0.73096 71.850 71.037 72.043 2.564
0.38800 71.862 70.762 73.629 6.023
0.95000 72.125 75.441 73.674 1.087
0.31812 71.746 74.197 7.080
0.79263 73.419 71.884 72.066 2.143
0.82233 73.763 72.391 72.124 1.942
0.88509 74.800 73.698 72.453 81.522
0.98400 76.370 76.544 75.511
72.411 8
VLLE
72.260 8
VLLE
8
75.272 8
VLLE
9
72.960 71.734 8
VLLE
10
72.706 8
VLLE
11
72.950 8
VLLE
12
73.776
VLLE
VLLE
13
14
15
76.441 80.912
0.01508 84.529 88.894 79.612 80.874
0.00651 92.374 90.827 87.769 92.374

0.00059 96.920 96.321 98.579
78.778
VLLE
87.705
VLLE
16
98.563 105.429
VLLE
17
18
0.00029 98.478 97.787 99.293 99.284 ------

Table the em tate (2)
ters es 4 46.
4-55 Values of ∆T for
Parame
P=101.325 kPa. T
Run # X
1
O
o
binary syst
from Tabl
Ethyl-ace
-30 and 4-
C ∆T
o
(1) \ Water

C
Exp. M.WILSON NRTL UNIQUAC P.R(EOS)
0.691 0VLLE
0.00029 98.478 .815 0.806 -----
VLLE
VLLE
VLLE
18
17
16
15
0.00059 96.92 0.599 1.659 1.643 8.509
0.00651 92.374 1.547 4.605 4.669 0.000

0.01508 84.529 .365 4.917 5.751 3.655
0.03038 0.882 0.327
0.31812 72.96 1.237 1.226
0.38800 71.862 .100 1.767 0.398
0.45139 71.258 .029 1.881 1.171
0.54128 71.753 .795 0.824 0.656
0.55313 70.407 .446 2.110 1.989
0.67195 71.283 .820 0.831 1.033
0.73096 71.85 0.193 0.561
0.77782 71.383 .273 0.667 1.229
0.79263 73.419 .535 1.353 0.713 8.724
0.82233 73.763 .372 1.639 0.813 8.179
0.88 09 5 74.8 2.347 6.722
4
VLLE
7 15.645 3.444 10.323
VLLE
2
1.214 14.120
VLLE
10
1 14.161
VLLE
8
1 13.921
VLLE
3
1 12.436
VLLE
6
0 13.635
VLLE
1
0 11.725
VLLE
4
0.813 10.714
VLLE
7
0 10.836
VLLE
5
1
VLLE
11
1

VLLE
12
1.102 1.024
VLLE
13
0.95000 72.125 3
VLLE
9
14
Using
.316 1.549 3.147 8.962
0.859 0.071 4.542
0.98400 76.37 0.174
Average 2.102 1.817 1.513 9.480
R 0.953 0.985 0.986 0.882

Table 4-56 Values of $T_{cal.}$ for the binary system Toluene (1) \ Water (2) using parameters from table 4-33 and 4-46**.**

P = 101.325 kPa. T
C
X
1
O
o
EXP. M.W SON .R(EOS)
0.0809 96.12 94 15 76.657
0.1444 94.60 93 38 95.433
0.2058 93.49 92 39 96.004
Run # IL NRTL UNIQUAC P
VLLE
7 1 .1 93.877 96.085
VLLE
19
3 1 .0 93.720 94.807
VLLE
VLLE
20
21
22
2 7 .5 93.514 94.151
0.2831 92.61 62 96.856
0.3697 92.47 92 27 98.008
0.4364 92.48 93 99.061
6 0 92.4 93.437 93.738
VLLE
8 4 .9 93.587 93.589

VLLE
23
8 7 .605 93.849 93.628
VLLE
24
25
 93.73 95 78
0.6130 94.96 96 63
0.7614 99.15 10 396
0.7667 99.33 10 560
0.8812 103.890 10 639 00.376
0.54779 0 .2 94.556 93.966 100.694
VLLE
0 6 .5 95.136 94.357 101.705
VLLE
26
1 1 0. 97.134 96.201 103.829
VLLE
27
3 6 0. 97.232 96.307 103.882
VLLE
VLLE
28
29
30
9 4. 1 99.932 105.397
0.9288 106.098 10 703 02.819
0.95229 107.255 107.821
3 6. 1 102.745 105.918
VLLE
31

98
104.567 104.659 106.158

Table 4-57 Values of ∆Y for the binary system Toluene (1) \ Water (2) using parameters
from table 4-33 and 4-46.

P = 101.325 kPa. ∆T
C
Run # X

1
O
o
EXP. M.WILSON NRTL UNIQUAC P.R(EOS)
7 96.121 2.006 2.244 0.036VLLE
0.0809 17.464
VLLE
VLLE
19
20
21
0.14443 94.601 1. 563 0.881 0.206 2.832
0.2058 93.497 958 0.017 0.654 4.507
0.2831 92.610 148 0.827
0.3697 92.474 650 1.310 7.731
0.4364 92.487 118 1.362 8.574
0.5477 93.730 548 0.826 8.964
0.6130 94.966 597 0.170 8.739
0.7614 99.151 245 2.017
0.7667 99.336 224 2.104
0.8812 103.8 0 749 3.514
0.9288 106.0 8 605 3.279
0.9522 107.2 5 566 2.688
2 0.
VLLE
6 0. 1.128 6.246
VLLE
22
8 0. 1.312
VLLE
23
8 1. 1.141
VLLE
24
9 1. 0.236
VLLE
25
0 1. 0.609
VLLE
26
1 1. 2.950 6.678
VLLE
27
3 1. 3.029 6.546
VLLE
28
9 9 0. 3.958 3.507

VLLE
29
3 9 0. 3.353 1.820
VLLE
30
9 5 0. 2.596 0.903
1. 1 5.105
31
Average 047 1.796 .787
R 0. 0.989 0.731 991 0.992
Values of T
cal

ystem T ene (1) \ l-acetate ater (3
for the ternary s olu Ethy (2) \ W)
8, 4-42 and 4-49.
Table 4-58
using parameters from tables 4-3
P = 101.325 kPa.
Run # X
42
1
O
X
2
O
T
o
C
EXP. M.W NRTL UNIQUAC P.R(EOS)
0.1318 0.6422 72.889 71.438 66.802 74.035 71.895
LLE
VLLE
V
V
VLLE 0.2669 0.3494 76.882 75.926 73.126 76.663 83.713
V .493
0.1995 0.4165 74.157 73.738 69.963 75.010 80.497
LLE
LLE
41
46
45
36
0.2359 0.3804 75.680 74.917 71.640 75.894 82.263
0.3031 0.3112 79.361 77.129 74.986 77.595 85
VLLE 0.3383 0.2785 77.495 77.732 75.797 78.299 84.328
LLE
V

VLLE
37
43
38
0.4026 0.3737 80.178 78.675 76.086 79.873 79.501
0.4062 0.2081 79.887 80.347 80.668 80.306
90.182
VLLE 0.4234 0.1908 83.247 80 80.766 91.101
.857 81.704
V .652 82
VLLE 0.5511 0.0676 87.081 84.197 90.087 84.071 99.603
VLL 666 0.2107 89.263 83.277 83.290 85.371
VLL 90.520 84

LLE
47
39
40
0.479 0.1367 83 82.399 85.166 .230 94.169
E 0.5
82.707
E
44
48
0.6285 0.1441 84.059 86.683 .408 89.148

Table 4-59 Values of ΔT for the ternary system Toluene (1) \ Ethyl-acetate (2) \ Water (3)
using parameters from tables 4-38, 4-42 and 4-49.
P = 101.325 kPa. ΔT
C
X
O
X
O
o
EXP. M.W NRTL UNIQUAC P.R(EOS)Run #
VLLE
36
1 2
0.3031 0.3112 79.361 2.232 4.375 1.766 6.132

VLLE
0.3383 0.2785 77.495 0.237 1.697 0.804 6.834
VLLE
37
0.4062 0.2081 79.887 0.460 0.781 0.418 10.295
VLLE 0.4790 0.1367 83.652 1.253 1.514 1.422 10.517
LLE
V
VLL
38
39
0.5511 0.0676 87.081 2.883 3.007 3.009 12.523
E 0.1995 0.4165 74.157 0.419 4.194 0.853 6.34
40
0
VLLE
VLLE
LLE
LE
41
42
43
44
46
0.1318 0.6422 72.889 1.45 71 6.087 1.14 0.994
0.4026 0.3737 80.178 1.504 4.092 0.306 0.677
V .56 7 89 556 5.987 5. 3.8
VLLE
45
0 66 0.210 .263 6. 973 92
0.2669 0.3494 76.882 0.956 3.757 0.219 6.831
VL 0.235 04 75 763 4.041 0.214 6.583
VLLE
47
9 0.38 .680 0.
0.4234 0.1908 83.247 2.390 1.542 2.481 7.855
VLLE

48
0.6285 0.1441 90.520 6.461 3.837 6.112 1.372
Average 2.120 3.455 1.902 6.219
R

0.973 0.960 0.983 0.830

4.6 Determination of Azeotropic Point

The Azeotropic composition and temperature of the binary mixtures

thyl-acetate\Water and Toluene\Water were determined using equations
.6.3 and 2.6.4. Table 4-60 lists the values of the parameters of equation 2.6.3
nd the Azeotropic composition and temperature of the binary systems.

E
2
a

Table 4-60 Values of the Parameters of equation 2.6.3 and the Azeotropic Composition and Temperature of the Binary Systems Ethyl-Acetate(1)\Water(2) and Toluene(1)\Water(2).

Ethyl-acetate(1) \ Water(2) Data [Present study] P = 101.325 kPa.

A_{12}	B_{12}	C_{12}	X_1	Azo
-69.366	45.157	-40.320	0.5172 mole	71.159 C

Toluene(1) \ Water(2) Data [Present study] P = 101.325 kPa.

A_{12}	B_{12}	C_{12}	X_1	Azo
-47.470	5.815	-5.892	0.3567 mole	92.180 C

T
he Azeotropic composition and temperature of the ternary mixture
oluene\Ethyl-acetate\Water were determined using equations 2.6.5, 2.6.7
nd 2.6.7.
T
a

100
T

T
Azo
Azo
o
o

Table 4-61 lists the values of the parameters of equation 2.6.5 and the Azeotropic composition and temperature of the ternary system.

Table 4-61 Values of the Parameters of equation 2.6.5 and the Azeotropic Composition and Temperature of the Ternary System Toluene(1)\Ethyl-Acetate(2)\Water(3).

Toluene(1)\Ethyl-acetate(2) \ Water(3) Data [Present study] P = 101.325 kP

A_{12}	A_{13}	A_{23}	B_{12}	B_{13}	
-28.132	-77.421	-51.398	15.718	42.614	-5.158

C_{12}	C_{13}	C_{23}	X_1 azo	X_2 azo	
6.984	18.335	-35.397	0.1532 mole	0.5543 mole	73.290 C

101
B
T
23
azo
o
a.

.7 Summery

4

The previous calculation Steps can be represented by a block diagram as shown in Figure 4-6.

Input Parameters of
Activity Coefficient

equations
From References
Calculate Φ

Prediction
Method
from
V
, Φ
i i
Peng-Robinson (EOS)
With K
ij
= 0
L
Input Equilibrium
Data
T
i
, X

i
O
, X
Calculate Φ

i
T

i
equations 2.2.3
or 2.2.6

i
, X
V
i
B
, Φ
, Y
i
S
S
from
Peng-Robinson (EOS)
and Antonie equations
Calculate Activity
Coefficients
γ
i
, γ
i
T
Calculate Y from
i
, P
/ γ
i
i
B

Figure 4-6 Block Diagram of the Calculations steps of the present study.

Correlation of equilibrium
data to obtain
Parameters of Activity
Coefficient e

quations

Correlation
Method
Calculate Φ
from
Correlation of equi
V
, Φ
i i
Peng-Robinson (EOS)
data to obtain
librium
Interacting Parameters (K
L
)
of Peng-Robinson (EOS)
ij

The calculated Y
and T by the activity coefficient equations and P.R. (EOS) for the two binary systems are plotted as T-X-Y diagrams as shown in figures 4-7, 4-8, 4-9 and 4-10.

C) Boiling Temperature
105
110
95
100
80
85
90
70
75
T (
60
65
i
Ethyl-acetate(1)\Water(2) Data [Present Study]
0 20406080100
X1, Y1 mole% Ethyl-acetate

Figure 4-7 T-X-Y Diagram of the System Ethyl-acetate (1) \ Water (2) Prediction method,

T (C) Boiling Temperature
95
100
105

110
85
90
75
80
60
65
70

Data [Present work].

Ethyl-acetate(1)\Water(2) Data [Present study]
0 20406080100
X1, Y1 mole% ethyl-acetate

Figure 4-8 T-X-Y Diagram of the System Ethyl-acetate (1) \ Water (2) Correlation method, Data [Present Study].

X1O
Y1exp.
Y1M.W
Y1NRTL
Y1UNIQUAC
Y1UNIFAC
P.R.(EOS)
X1
Y1(NRTL)
Y1(Exp.)
Y1(UNIQ.)
Y1(P.R.E)
Y1(M. W)

T (C) Boiling Temperature

120
110
100
90
80
70
60

Toluene (1) \ Water (2)
0 20406080100
X1, Y1 mole% Toluene

Figure 4-9 T-X-Y Diagram of the System Toluene (1) \ Water (2) Prediction Method, Data [present study].

T (C) Boiling Temperature
110
115
120
100
105
85
90
95
80
Toluene (1) \ Water (2)
0 20406080100
X1, Y1 mole% Toluene

Figure 4-10 T-X-Y Diagram of the System Toluene (1) \ Water (2) Correlation Method,
Data [present study].

The calculated T by the activity coefficient equations and P.R. (EOS) for the ternary system are plotted as T-X diagrams as shown in figures 4-11, 4-12, 413 and 4-14.

X1
Y1NRTL
Y1(UNIQUAC)
Y1exp.
Y1(P.R.E)
X1
Y1(M. W)
Y1(NRTL)
Y1(UNIQUAC)
Y1exp.
Y1(P.R.E)

Figure 4-11 T-X Diagram of the System Toluene (1) \ Ethyl-acetate(2) \ Water (3) using
M.WILSON equation, Correlation Method, Data [present study].

Figure 4-12 T-X Diagram of the System Toluene (1) \ Ethyl-acetate(2) \ Water (3) using
NRTL equation, Correlation Method, Data [present study].

Figure 4-13 T-X Diagram of the System Toluene (1) \ Ethyl-acetate(2) \ Water (3) using UNIQUAC equation, Correlation Method, Data [present study].

Figure 4-14 T-X Diagram of the System Toluene (1) \ Ethyl-acetate(2) \ Water (3) using P.R (EOS), Correlation Method, Data [present study].

CHAPTER FIVE

DISCUSSION & CONCLUSIONS

The present study involved measurements of VLLE data of two binary systems and one ternary system. Equilibrium still was assembled to deal with these systems. The data obtained from the new still was analyzed by two methods, prediction and correlation methods. The prediction method involved using activity coefficient equations with adjustable parameters obtained from previous studies and using the Peng-Robinson (EOS) without interacting parameters. The correlation method involved using activity coefficient equations with adjustable parameters obtained from correlation of the experimental data obtained from the assembled still and using the PengRobinson (EOS) with interacting parameters also obtained from correlation of the experimental data obtained from the same still. A modification was applied to the UNIQUAC equation to increase the accuracy of this equation to deal with VLLE systems.

5.1 Systems Selected

Two binary systems Ethyl-acetate \ Water and Toluene \ Water were selected, the system Ethyl-acetate \ Water is a system of limited miscibility where the solubility of Ethyl-acetate in water is 1 ml Ethyl-acetate in 10 ml Water at 20 ^{o}C and the solubility of Water in Ethyl-acetate is 1 ml Water in 40 ml Ethyl-acetate at 20 ^{o}C [44]. The system forms a binary Azeotrope as shown in Figures 4-3, 4-7 and 4-8.

The system Toluene \ Water can be considered as an immiscible system where the solubility of Toluene in Water is 0.05 gram Toluene per 100 gram Water at 20 ^{o}C and the solubility of Water in Toluene is 0.03 gram Water per 100 gram of Toluene at 20 ^{o}C [44]. The system forms a binary Azeotrope as shown in Figures 4-4, 4-9 and 4-10.

The mixtures of the two binary systems at temperatures of boiling or above are three phase systems where two liquid phases are in equilibrium with a vapor phase. The analysis of the withdrawn samples of the binary system Ethyl-acetate \ Water was determined by refractive index measurements (Figures 3-5 and 3-6) and solubility data of each layer of the sample and for the binary system Toluene \ Water only solubility data was used. Refractive index measurements were simple and practical and suitable for the conditions of the present study.

The ternary system Toluene \ Ethyl-acetate \ Water consists of a miscible pair of Toluene \ Ethyl-acetate and a partial miscible pair of Ethyl-acetate \ Water and an immiscible pair of Toluene \ Water. The system formed a ternary Azeotrope as shown in Figure 4-5 and Figures 4-11 to 4-14. No VLLE data are available in the literature for this ternary system.

The analysis of the withdrawn samples of the ternary system was determined by refractive index measurements (Figures 3-5 and 3-7) and solubility data. The assumption that no Water exists in the organic layer of the withdrawn samples is due to the very low solubility of Water in Toluene and the high solubility of Toluene in Ethyl-acetate, and no Toluene exists in the aqueous layer of the withdrawn samples is due to the very low solubility of Toluene in Water.

5.2 Assembled Equilibrium Still

An Equilibrium Still was assembled (Figure 3-1) to deal with partial miscible and immiscible systems. The Still was provided with mechanical mixers in both the boiling and condensing sections. The mechanical mixer in the boiling section helped in keeping the two liquid layers in the boiler in a homogenous state to get a steady temperature reading of the boiling liquid, a fluctuation in the temperature reading occurred when the still was operated with no mixing in the boiling section where a temperature difference of 3-5 C between the two liquid layers was noticed.

The mixer in the condensing section helped in correcting the composition of the recycled condensed vapor to the boiler. A constant vapor composition was obtained when the still was operated with no mechanical mixing in the condensing section even if the boiling temperature changes. The system Ethyl-acetate \ Water was studied by Ellis,etal [2] using an equilibrium still with mechanical agitation in both the boiling and condensing sections (Figure 2-5) the equilibrium data obtained showed a constant vapor composition of 70 mole % Ethyl-acetate and a constant boiling liquid temperature of 70.5 C in the boiling liquid composition range of 5-78 mole % Ethyl-acetate as noticed in table 4-20. Also the data obtained by Kato.M, etal [7] showed a constant vapor composition of 70.1 mole % Ethyl-acetate in the boiling liquid composition range 8-71 of mole % Ethyl-acetate were an equilibrium still similar to the Othmer still (Figure 2-3) with no mechanical agitation or mixing was used. This indicates that mechanical mixing is necessary in both boiling and condensing sections and even agitation is not enough. The two reflux lines in the new still assured the return of the condensed vapor to the boiler in correct composition even if vortex occurred in the condenser due to the mechanical mixing.

5.3 Prediction Method

The activity coefficient equations M.WILSON, NRTL, UNIQUAC and UNIFAC and the Peng-Robinson (EOS) were used to determine the value of Y_i theoretically as follows:

1- Using the Peng-Robinson (EOS) for the vapor and liquid phases the partial molar fugacity coefficients for both phases were determined and no interacting parameters were used.

2- Using the Peng-Robinson (EOS) for vapor phase and using one of the activity coefficient equations M.WILSON, NRTL, UNIQUAC and UNIFAC in liquid phase.

The adjustable parameters of the first three activity coefficient equations were obtained from previous studies specially the two binary systems Ethylacetate \ Water and Toluene \ Water and for the ternary system Toluene \

Ethyl-acetate
\ Water the same adjustable
parameters were used with the
adjustable
parameters of the binary system
Ethyl-acetate \ Toluene obtained
by
correlating the experimental
data
of Kropholler, etal [46].

The average

of the absolute deviations in mole fraction of the vapor
phase (Δ***Y***
) for the binary system Ethyl-acetate \ Water using the NRTL and
the UNIQUAC equations with predicted parameters were 0.1110 and
0.1192
respectively and 0.1227 and 0.2076 using the M.WILSON and the
UNIFAC
equations as can be noticed in table 4-13. The predicted parameters of the
binary system Toluene \ Water were in the temperature range of 10 to 60
i
C;
very high average (Δ***Y***
shown in table 4-22.
i
) values were obtained using these parameters as

o

The average of the absolute deviations in mole fraction of the vapor
phase (Δ***Y***
) for the ternary system Toluene \ Ethyl-acetate \ Water using the
NRTL, UNIQUAC and the Peng-Robinson equations and the UNIFAC
method were 0.1271, 0.1348, 0.1150 and 0.1963 respectively as shown in
tables 4-26 to 4-29.

i

The NRTL activity coefficient equation gave the lowest absolute average deviation; the NRTL equation has three adjustable parameters which gives a better representation of the equilibrium data. Both of the UNIFAC method and the Peng-Robinson (EOS) when used in both phases gave high absolute average deviation; both have no adjustable parameters. Table 5-1 summarizes the average absolute deviation in mole fraction of vapor phase values by prediction method of the two binary systems and the ternary system measured in the present study.

Table 5-1 Values of ΔY_i by Prediction method for the systems measured in the present study.

Prediction method ΔY
(Average)
System M.W
*
NRTL
*
1
UNIQ.
*
UNIF.
P.R(EOS)
Ethyl-acetate(1)\Water(2) 0.12265 0.11103 0.11924 0.20763 189.3488
Toluene(1)\Water(2)

0.86484 2.02427 1.77536 1.82154
Average NRTL UNIQ. UNIF. P.R(EOS)

Toluene(1)\Ethyl-
acetate(2)\Water(3)
ΔY
ΔY
1
*
0.0455 0.1474 0.2874 0.0703

ΔY_2	0.1679	0.1139	0.1889	0.2167
ΔY_3	0.1680	0.1431	0.1125	0.0581

* In all systems using P.R (EOS) to determine partial molar fugacities in vapor phase with no interacting parameters.

The ratio $(\gamma_{1T}/\gamma_{1B})$ of the binary system Ethyl-acetate\Water was predicted using the M.WILSON, NRTL, UNIQUAC and UNIFAC equations. The NRTL equation gave the lowest average Δ $(\gamma_{1T}/\gamma_{1B})$ values as can be noticed in tables 4-18 and 4-19.

5.4 Correlation Method

The adjustable parameters of the activity coefficient equations M.WILSON, NRTL and UNIQUAC and the interacting parameters of the Peng-Robinson (EOS) were determined by applying non-linear constrained optimization with the objective function given by equation 4.3.1 subjected to the constraint given by equation 4.3.2.

The ***Generalized Reduced Gradient*** (GRG) search [47] was used. The adjustable and interacting parameters used in the prediction method where used as initial values to start the search as shown in appendix D. The activity coefficient equations M.WILSON, NRTL, UNIQUAC and the PengRobinson (EOS) were used to determine the value of Y_i theoretically by:

1- Using the Peng-Robinson (EOS) for the vapor and liquid phases the partial molar fugacity coefficients for both phases were determined with interacting parameters obtained by correlation of the equilibrium data obtained from the assembled still.

2- Using the Peng-Robinson (EOS) for vapor phase and using the activity coefficient equations M.WILSON, NRTL and UNIQUAC in liquid phase. The adjustable parameters of the activity coefficient equations were obtained from correlation of equilibrium data. The parameters of the ternary system Toluene \ Ethyl-acetate \ Water were obtained by using the adjustable and interacting parameters of the binary systems Toluene \ Water, Ethyl-acetate \ Water and Toluene \ Ethyl-acetate as initial values to start the search, the parameters of the binary system Toluene \ Ethyl-acetate were set constant since it’s a miscible system, the average values of α in the NRTL equation and Z/2 in the UNIQUAC equation were also taken as initial values.

The average of the absolute deviations in mole fraction of the vapor phase ($\Delta \boldsymbol{Y}$) for the binary system Ethyl-acetate \ Water using the M.WILSON, NRTL and the UNIQUAC equation and the Peng-Robinson (EOS) were 0.1161, 0.0694, 0.0743 and 0.2125 respectively as shown in tables 4-31 and 4-48. And for the binary system Toluene \ Water the average values of ΔY_i using M.WILSON, NRTL and UNIQUAC equations and the Peng-Robinson (EOS) were 0.1010, 0.0749, 0.0570 and 0.0913 respectively as shown in tables 4-36 and 4-48. And for the ternary system Toluene \ Ethylacetate \ Water the average values of ΔY_i using M.WILSON, NRTL, UNIQUAC equations and the Peng-Robinson (EOS) were 0.0610, 0.0600, 0.0482 and 0.0716 respectively as shown in tables 4-41, 4-45 and 4-51.

The UNIQUAC and the NRTL equations gave the lowest average ΔY_i values for the binary systems and for the ternary system the UNIQUAC equation gave the lowest average ΔY_i values; these equations contain three adjustable parameters this gives a better representation of the equilibrium data. The Peng-Robinson (EOS) gave high average ΔY_i, according to the ***Lattice Model*** [3] which considers the liquid phase as a dense and highly nonideal-gas whose properties can be described by some (EOS); this is not correct in VLLE systems (Partialmiscible and immiscible) were the liquid phases in equilibrium are highly non ideal.

Table 5-2 summarizes the average absolute deviation in mole fraction of vapor phase values by correlation method of the two binary systems and the ternary system measured in the present study.

Table 5-2 Values of ΔY_i by Correlation method for the systems measured in the present study.

System	Correlation method ΔY (Average)			
	M.W	NRTL	UNIQ.	P.R(EOS)
Ethyl-acetate(1)\Water(2)	0.11613	0.06936	0.07429	0.21254
Toluene(1)\Water(2)	0.10096	0.07491	0.05700	0.09129

	Average	M.W	NRTL	UNIQ.	P.R(EOS)
Toluene(1)\Ethyl-acetate(2)\Water(3)	ΔY_1*	0.0610	0.0600	0.04817	0.0716
	ΔY_2	0.0610	0.0600	0.04817	0.0716
	ΔY_3	0.0610	0.0600	0.04817	0.0716

* In all systems using P.R (EOS) to determine partial molar fugacities in vapor phase with no interacting parameters.

The co-ordination number (Z/2) which has a value of 5 for typical liquids at ordinary conditions (miscible) [3] was considered as a third adjustable parameter in the UNIQUAC equation. This was applied to the two binary systems and the ternary system measured in the present study and also to four binary systems and one ternary system obtained from literature. This modification gave low average ΔY values especially for the binary systems

Toluene \ Water and MEK \ Water and the ternary systems Toluene \ Ethylacetate \ Water and MEK \ Benzene \ Water as can be noticed in tables 452and 4-53. The value of (Z/2) can reach to a value of 6 depending on the type of packing of dissimilar molecules (molecule 1, molecule 2) [3].

i

The average boiling temperature was determined theoretically by solving equation 4.5.1 for T where the Newton-Raphson method [45] was used with $T_{exp.}$ as the initial value to start the calculation. For the binary system Ethylacetate \ Water both the UNIQUAC and NRTL equations gave low average ΔT values as shown in table 4-55. And for the binary system Toluene \ Water the M.WILSON equation gave low average ΔT values as shown in table 4-57. And for the ternary system the UNIQUAC and M.WILSON equations gave low average ΔT value as shown in table 4-59.

5.5 Azeotropic Point

The determination of the Azeotrope point (X_{Azo}, T_{Azo}) of partial and immiscible systems is very complex due to the difficulties in determination of the experimental data of such systems, the fluctuations in the temperature of boiling due to the immiscible layers in the boiling section of the equilibrium still. Such systems appear to have more than one Azeotropic point especially minimum boiling mixtures where these mixtures boil at a temperature below the boiling point of any pure component in the mixture. Usually the point with the lowest boiling temperature in the equilibrium data could be considered as the Azeotropic point. In the present study two binary systems were studied, the system Ethyl-acetate \ Water showed a minimum boiling behavior at certain compositions as can be noticed from table 3-5 and figure 4-1 the data points T-Y_1 and T-X appear to meet in a straight line in the composition range 50 To 80 mole % Ethyl-acetate.

1

The Azeotropic point of the system Ethyl-acetate \ Water was determined by equation 2.6.3 where the minimum temperature was T = 71.157 = 0.5172 mole fraction Ethyl-acetate. The binary system Toluene \ Water also showed a minimum boiling behavior as can be noticed from table 3-6 and in figure 4-4 the data points T-Y_1 and T-X appear to meet in a straight line in the composition range 35 To 53 mole % Toluene. The Azeotropic point of the

1

system Toluene \ Water was determined by equation 2.6.3 where the minimum temperature was T = 92.180 ^{o}C at X = 0.3567 mole fraction

Toluene.

1

The ternary system Toluene \ Ethyl-acetate \ Water showed a minimum boiling temperature as can be noticed in table 3-7 and figure 4-5 below the temperature contour of 79.808

o

C lies mixtures with minimum boiling temperature especially the temperature contour of 76.349

o

C.

o

C at X

1

The Azeotropic point of the system Toluene \ Ethyl-acetate \ Water was determined by equation 2.6.5 where the minimum temperature was T = 73.29

o

C at X

1

= 0.1532 mole fraction Toluene and X

5.6 Conclusions

2

= 0.5543 Ethyl-acetate.

From the VLLE measurements achieved in the present study the following conclusions were observed:

1- The assembled equilibrium still with mechanical mixing in both the boiling and condensation sections appeared to be suitable for the measurements of partial and immiscible systems.

2- Using the Peng-Robinson (EOS) in both phases generally gave higher deviation in the vapor phase mole fraction than using the Peng-Robinson (EOS) in the vapor phase and one of the activity coefficient equations M.WILSON, NRTL, UNIQUAC and UNIFAC in the liquid phase in both prediction and correlation methods and shown in tables 5-1 and 5-2.

3- The prediction method gave a higher average absolute deviation in the vapor phase mole fraction than the correlation method for the two binary systems and the ternary system measured in the present study.

4- In the correlation method using the P.R (EOS) in the vapor phase and the activity coefficient equation UNIQUAC gave the lowest absolute average deviation in the vapor mole fraction for the systems measured in the present study with an overall value of ΔY 0.0552.

5- The ***Generalized Reduced Gradient*** (GRG) search approved to be more accurate and fast in determining the adjustable parameters of the activity coefficient equations and the interacting parameters of the Peng-Robinson (EOS) especially when taking the initial values of the parameters to start the search from the prediction method.

6- The increase in the number of the adjustable parameters of the activity coefficient equations gave a better representation of the equilibrium data as was noticed in the UNIQUAC equation.

5.7 Recommendations for future work

The present study was achieved in a circulating still (circulation method) under atmospheric pressure. The following is recommended for future work:

1- Studying partial and immiscible system under a pressure higher than atmospheric pressure where there is a wide application for these systems especially in the petroleum industries.

2- Studying the hydrodynamics of partial and immiscible systems on a plate of a distillation column and studying the composition and temperature distribution on this plate.

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APPENDIX A

A.1 Quick-fit heads of the Equilibrium Still

The Quick-fit heads of the equilibrium still used in the present study are shown in detail in Figure A-1.

Electric motor

Rubber tube

Multiimpeller shaft

P.E Bushing

ring
Quick-fit head
Rubber cork
Boiling or
Condensation
section
P.E Bushing
ring

Figure A-1 Quick-fit head assembly of the Equilibrium still used in the present study.

A.2 CASSY Module Interface

Experimental determination of the equilibrium data of a mixture, determination of the boiling temperature, also the measurement, recording and graphic representation of the boiling temperature and time, are all preformed via a ***CASSY interface*** in conjunction with a personal computer and the software "***Universal Data Acquisition***". The schematic diagram of the ***CASSY Module Interface*** is given in Figure A-2.

Figure A-2 CASSY Module Interface Used in the Present Study.

24- CASSY Module Interface.
25- CPS voltage supply, switch-able.
26- Cable, 25 cm, red.
27- Cable, 25 cm, blue.
28- Socket of switch-able power supply.
29- Temperature sensor, NiCr-Ni.
30- Temperature box.
31- CPS panel frame.

A.3 Universal Data Acquisition

"Universal Data Acquisition" is a software package for all purpose use in computer-supported measurement and control in the area of chemical engineering and technology. It runs on a personal computer (minimum 486 AT with 4MB RAM) under Microsoft Windows version 3.1 or Windows 95, 98 or higher.

Using the program "Universal Data Acquisition", one can observe and record the temperature curve representing the boiling point in the boiling section of the equilibrium still via the virtual instrument TA1.

After starting the software Windows, double-click the "Universal Data Acquisition" icon, one can make the following settings:

1- Temperature TA1 (boiling temperature in the boiling section):
Channels / Input / Analog Input / Input A / Quantity / Temperature TA1 / Zero point left / Range 0 to 120 ^{o}C / Mean Values / Digital Instrument / OK.

2- Controlling the housing heating mantle:
Channels / Outputs / Digital Output / Output O_{0} / Formula TA1 < 119 C and t < 2:00:00.

The formula causes the heating mantle to switch off when the temperature exceeds 119 ^{o}C or when the measurements runs longer than two hours (safety cutout).

3- Time t:
Channel / Time / Unit min / Interval 0.1 min. / Formula 1 / Digital Instrument / OK.

4- Diagram t / TA1:
Channels / Diagram / X-axis t / Y-axis TA1 / OK.

When the settings for the software “Universal Data Acquisition” program had been selected and a measurement had been taken the display on the monitor is as shown in Figure A-3.

Figure A-4 Display of “Universal Data Acquisition” in the Present Study.

A picture of the interface and the personal computer (control unit) used in the present study is shown in Figure A-4.

Figure A-4 Control Unit of the Still Used in the Present Study.

B.1 Refractometer

APPENDIX B

For measurement of the refractive index of liquid and solid objects using light at a wave length of $\lambda = 589.3$ nm. The prisms are illuminated by an illumination unit. Measurements can be made of transmitted and reflected light. The prism housing is provided with connector for a thermostat for keeping the samples at a constant temperature. The temperature of the prisms can be read from a thermometer mounted on the side of the prism housing. Complete with transformer, illumination unit, thermometer, tools for alignment, calibration object with engraved refractive index and contact liquid. The schematic diagram of the laboratory Refractometer is shown in Figure B-1.

Figure B-1 Refracometer Used in the Present Study.

Technical data on the Refractometer used in the present study are given in table B-1.

Table B-1 Technical Data of Refractometer Used in Present Study.

Measurement range (n_D)	1.3 to 1.7
Scale division (n)	0.0005
Measurement inaccuracy (n_D)	± 0.0002
Dimensions	115*222*263 mm
Weight	4.5 kg

n_D Refractive index

The refractive index is the most important optical data of a substance with which the purity, concentration and optical condition can be tested. It is necessary to keep the temperature constant for exact measurement because the refractive index of liquids alters with the temperature. First, turning the locking knob to lift up the illuminating prism, putting one or two drops of liquids on the measuring prism, then lowering the illuminating prism to its former position and locking with the knob. Looking through the ocular and sharply defining the reticle by turning to the right or left. By turning the scale adjustment knob moving along the measuring range until a light / dark division appears, the separation line must now lie on the point of intersection of the reticle, as shown in Figure B-2.

Figure B-2 The Light and Dark Divisions.

Eliminating the color round the division line with the compensation knob until a black-white division is reached. The dispersion of the light is compensated. Adjusting the light / dark line exactly on the point of intersection of the reticle and then the display will show the refractive index of the liquid sample.

B.2 Circulation Thermostat with Refrigeration Unit

Compact, silent instrument for regulating the temperature of external loads in the minus and positive range (e.g. Refractometer), simultaneous temperature regulation in the thermostat bath, is used in the experiment to control the temperature of water at 20 ^{o}C. The schematic diagram of the circulation thermostat with refrigeration is shown in Figure B-3.

Figure B-3 Circulation Thermostat with Refrigeration Unit Used in the Present Study.

Technical data on the circulation unit used in the present study is given in table B-2.

Table B-2 Technical Data of Circulation Unit Used in Present Study.

Heat capacity	2000 W
Refrigeration capacity	260 W at 20 C
Coolant	R 135 a
Range of operating temperature	-25 to 100 ^{o} ^{o}C
Constancy of temperature	± 0.03©
Pump capacity	300 hPa, 15 l / min

Volume of bath 3 to 4.5 l
Power supply 230 V Ac / 50 Hz
Weight 30 kg

C.1 Microsoft Excel

APPENDIX C

The software Microsoft Excel was used in most of the calculations of the present study its one of the tools available in the software Microsoft Office. The software consists mainly of a work book that contains work sheets (Spread sheet) which are able to form many simple and complex calculations and the software contains many statistical functions and able to plot data in many types of charts. A work book was opened for each measurement (e.g. VLLE1) which contained two work sheets.

C.1.1 Exp. Sheet

The Exp. Sheet contained the recorded temperature from the software "***Universal Data Acquisition***" and the measured refractive index of the withdrawn samples and the material balance preformed to determine the numerical values of the mole % of the boiling liquid and the mole % of the condensed vapor. A sample of this sheet is shown in Figure C-1.

Figure C-1 Exp. Sheet for Mole % Determination of Measurement VLLE

The measured volume of each layer (α, ك) of the withdrawn samples of the condensed vapor and the boiling liquid and the measured refractive index are inserted in the gray colored cells (e.g. C87, C88) then the work sheet will obtain the mole % in each layer by cells C90 and D90 which solves the calibration equations of Figures 3-5 and 3-6. Then cells G87 and H87 will give the total moles of each layer (α, ك) by material balance as shown below:

G87 = 100*C87/(C90*E5/D5 + (100-C90)*E6/D6)

H87 = 100*D87/(D90*E5/D5 + (100-D90)*E6/D6)

Where D5, D6 and E5, E6 are the cells which contain the densities and the molecular weights of the components present in the layers (α, ك) respectively. Then the amount of moles of each component in the sample (vapor) is calculated by cells I88 and I89 as shown below:

I88 = G87*C90/100 + H87*D90/100

I89 = G87 + H87 - I88

The mole % of each component in the sample (vapor) is determined by cells D100 and F100 as shown below:

D100 = 100*I88 / (I88+I89)

F100 = 100 – D100

The same is applied to the other sample (liquid). The Exp. sheets for the measurements VLLE
C-2 to Figure C-5.

12
, VLLE
23

, VLLE
46
and LLE
6
are given in Figure

Figure C-2 Exp. Sheet for Mole % Determination of Measurement VLLE

.

Figure C-3 Exp. Sheet for Mole % Determination of Measurement VLLE

12
23
.

Figure C-4 Exp. Sheet for Mole % Determination of Measurement VLLE

Figure C-5 Exp. Sheet for Mole % Determination of Measurement LLE

46
6
.
.

C.1.2 Calc. Sheet

The Calc. Sheet contained the calculations performed to obtain the values of ط$_i^V$, ط$_i^L$, P_i^S and ط$_i^S$ where the Peng-Robinson equation of state is programmed in the cells of the Calc. Sheet in connection with the cells in the Exp. Sheets. The Calc. Sheet for the VLLE measurements of the binary system Ethyl-acetate(1)\Water(2) is given in Figure C-6.

Figure C-6 Calc. Sheet for ط$_i^V$, ط$_i^L$, P_i^S and ط$_i^S$ Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Column (D) in the above figure determines the vapor pressure of Ethylacetate(1)\Water(2) as follows:

D9 = (10^(6.20229-1232.542/(-56.563+B9)))　　(C.1.2)

Column (Q) solves equation (2.3.38) by Newton-Raphson method (see appendix D) to determine the value of Z^V in column (P) as follows:

Q9 = P9^3-(1-O9)*P9^2+(N9-3*O9^2-2*O9)*P9-(N9*O9-O9^2-O9^3)

The parameters of equation (2.3.38) are determined by the hidden columns between (D) and (P). Also column (S) solves equation (2.3.38) by Newton-Raphson method to determine Z^L in column (R). Columns (W), (Y) and (AE) determine $ط_1^V$, $ط_1^L$ and $ط_1^L$ respectively by equation (2.3.42a) as follows:

W9 = EXP((L9/O9)*(P9-1)-LN(P9-O9)+(N9/(2.828*O9))*(L9/O9(2/V9)*(C9*(T9*H9*T9*H9)^0.5+E9*(1$R$6)*(T9*H9*I9*U9)^0.5))*LN((P9+2.414*O9)/(P9-0.414*O9)))

The parameters of equation (2.3.38) are determined by the hidden columns between (S) and (W).

The same is applied to the binary system Toluene(1)\Water(2) and to the Ternary System Toluene(1)\Ethyl-acetate(2)\Water(3) as shown in figures C-7 and C-8. Also column AM represents equation 2.2.6 and column AO represents equation 4.2.1.

Figure C-7 Calc. Sheet for $ط_1^V$

, ط
1
L

, P
1
S
and ط
1
S
Determination of VLLE
Measurements of the Binary system Toluene(1)\Water(2).

Figure C-8a Calc. Sheet for ط
i
V
, ط
i
L
, P
i
S
and ط
i
S
Determination of VLLE
Measurements of the Ternary system Toluene(1)\Ethyl-acetate(2)\Water(3).

Figure C-8b Calc. Sheet for ط
i
V
, ط
i
L

, P
i
S
and ط
i
S
Determination of VLLE
Measurements of the Ternary system Toluene(1)\Ethyl-acetate(2)\Water(3).

C.1.3 A.C. Sheet

The Calc. sheet is connected to A.C. sheet (Activity coefficient sheet) this sheet determines the activity coefficients **γ**
using parameters
obtained from references and also determines the values of Y
1
as
shown in figure C.1.9. Columns B, C, D and E represent the experimental values which are connected to the Calc. sheet. Column H represents equation 2.4.15a as follows:

```
H7 =
EXP(LN((B7+C7*G7/F7)/(B7+C7*(G7/F7)*EXP($I$3/(E7+0)))+B7*(1/
(B7+C7*G7/F7)-
1/(B7+C7*(G7/F7)*EXP($I$3/(E7+0))))+C7*((F7/G7)/(C7+B7*F7/G7)-
(F7/G7)*EXP($J$3/(E7+0))/(C7+B7*(F7/G7)*EXP(-$J$3/(E7+0))))))
```

Column I represents equation 2.2.3 and column J represents equation 4.2.1. Figure C-9 shows the A.C sheet of the MODIFIED WILSON (M.W) equation while figures C-10, C-11 and C-12 shows the A.C sheets for the NRTL, UNIQUAC and UNIFAC equations.

Figure C-9 A.C. Sheet for γ
1

1
and ΔY
(M.W) Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure C-10 A.C. Sheet for γ_1 (NRTL) Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure C-11 A.C. Sheet for γ_1 (UNIQUAC) Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure C-12 A.C. Sheet for γ_1 (UNIFAC) Determination of the Measurement VLLE1.

Figure C.1.12 represents the A.C sheet of the UNIFAC method to determine the activity coefficients. The data is input in the dark cells and the sheet then determines the activity coefficient and determines the value of Y_1 and ΔY.

The same is applied to the LEE measurements of the binary system Ethylacetate(1)\Water(2) and to the binary system Toluene(1)\Water(2) and the ternary system Toluene(1)\Ethyl-acetate(2)\Water(3).

APPENDIX D

D.1 Newton-Raphson Method

One of the most widely used methods of solving equations is the Newton-Raphson method [45]. The basic equation of this method is given in E.1.

ZF
XZ
i
i1i
+
()
()
=↕=

Where ***F(Z***
i
)1.D(...,3,2,1i,
ZF
i
′

) is a nonlinear equation and ***F***
with respect to ***Z***
i
`
(Z
i
) is the derivative of ***F(Z***
. Equation E.1 was used to find the value of Z in
equation 2.3.38, the calculation was stopped when ***F(Z***
the
calculations were preformed by the Cal. Sheet as shown in figure C.1.6.

i+1

D.2 Correlation of Experimental Data

The parameters of the activity coefficient equations M.WILSON,
NRTL and UNIQUAC and the interacting parameters k
of the PengRobinson
(EOS) were determined
using a non-linear constraint
optimization
search this was achieved by the aid of the soft-ware
Microsoft
Excel using the Solver tool.
The Solver tool solves an
optimization
problem
using the ***Generalized***
Reduced Gradient
(GRG)
search
[47]
were it first reduces the
problem
to an unconstrained
optimization
problem.
It does this by solving
a set of non-linear equations
for
the basic variables in terms
of
the non-basic variables. Then the
unconstrained

problem is solved using the ***quasi-Newton approach*** (BFGS) or the ***conjugate gradient approach.***

A spread sheet is preformed to correlate the experimental data similar

to the A.C. sheets shown in figures C-9 to C-11 as mentioned in appendix C. These sheets contain the objective function of equation 4.3.1 to be minimized subject to the constraint of equation 4.3.2. Figure D-1 shows part of the spread sheet performed to correlate the VLLE measurements of the binary system Ethyl-acetate(1)\Water(2) to obtain the parameters of the M.WILSON equation.

ij

) < 10

-6

i

)

Figure D-1 Part of the Sheet for M.WILSON Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

The initial values to start the determination of the parameters is taken from the A.C sheet as shown in figure D-2 below

Figure D-2 Part of the Sheet for M.WILSON Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Then the solver tool is used to search for the parameters of the M.WILSON equation as shown in figures D-3 and D-4 below:

Figure D-3 Part of the Sheet for M.WILSON Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure D-4 Part of the Sheet for M.WILSON Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

The parameters of the NRTL and UNIQUAC equations are calculated as before as shown in figures D-5 to D-8 below.

Figure D-5 Part of the Sheet for NRTL Parameters Determination of VLLE

Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure D-6 Part of the Sheet for NRTL Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure D-7 Part of the Sheet for UNIQUAC Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

Figure D-8 Part of the Sheet for UNIQUAC Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

The interacting parameters k
for the binary system Ethylacetate(1)\Water(2)
are also determined
as before as shown in figure D-9
below.

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Figure D-9 Sheet for P.R (EOS) Interacting Parameters Determination of VLLE Measurements of the Binary system Ethyl-acetate(1)\Water(2).

The same procedure is applied for the binary system Toluene(1)\Water(2) and the ternary system Toluene(1)\Ethyl-acetate(2)\Water(3) to determine the parameters of the activity coefficient equations M.WILSON, NRTL and UNIQUAC and to determine the interacting parameters of the Peng-Robinson (EOS)