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Vapor-Liquid-Liquid Equilibrium (VLLE) Data for the Systems Ethyl acetate + Water, Toluene + Water and Toluene + Ethyl acetate + Water at 101.3 kPa. Using Modified Equilibrium Still

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Isobaric Vapor-Liquid-Liquid equilibrium data for the binary systems ethyl acetate + water, toluene + water and the ternary system toluene + ethyl acetate + water were determined by a modified equilibrium still, the still consisted of a boiling and a condensation sections supplied with mixers that helped to correct the composition of the recycled condensed liquid and the boiling temperature readings in the condensation and boiling sections respectively. The VLLE data where predicted and correlated using the Peng-Robinson Equation of State in the vapor phase and one of the activity coefficient models Wilson, NRTL, UNIQUAC and the UNIFAC in the liquid phase and also were correlated using the Peng-Robinson Equation of State in both the vapor and liquid phases.

Introduction

Industrial distillations involve many azeotropic systems with partial miscible regions for which a few data are available. An adequate method to determine the vapor liquid equilibrium (VLE) data of such systems is of great importance. In both processes of azotropic distillation and liquid-liquid extraction, the solvent is generally removed from one or more streams by stripping columns from which the condensed overhead separates into two layers [1]. There are two major difficulties in studying partially miscible and immiscible systems in addition to those in equilibrium stills. The first is the vapor, when condensed it forms an immiscible mixture. Thus the recirculation type 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 portions. The second difficulty lies in the great difference in composition between the vapor and liquid. For example, in the miscible region of Ethyl acetate(1) + Water(2), which extends to a mole fraction of $x_1 = 0.02$. 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]. The equilibrium data of the above systems are best correlated or predicted by the aid of activity coefficient models [3]. Although attempts have been made by the Equations Of State (EOS) [4, 5] which gave good results for high pressure immiscible systems but failed for low pressure systems. The most applied activity coefficient models are the Wilson, NRTL, UNIQUAC and the UNIFAC models. All these models except the UNIFAC have adjustable parameters obtained from non linear regression of experimental equilibrium data [6]. The NRTL model has three adjustable parameters. It has one parameter more than the other models. This increases the accuracy of the correlation and the prediction of equilibrium data. The scope of this paper involves the following objectives: *Assembling* a modified equilibrium still to deal with partial miscible and immiscible systems. *Measuring* the vapor-liquid-liquid equilibrium (VLLE) data of the partial miscible binary system of ethyl acetate + water and the immiscible binary system of toluene + water and the ternary system of toluene + ethyl acetate + water in the new modified still at p = 101.325 kPa. *Correlating* and predicting the VLLE data obtained from the new modified still by applying the Peng-Robinson (EOS) in the vapor phase and applying the activity coefficient models (WILSON, NRTL, UNIQUAC and UNIFAC) in the liquid phase.

Experimental Section

Materials. The chemicals used were supplied by BDH. All Chemicals were used without further purification. Table 1 lists the specification of the chemicals used.

Equilibrium Still. The still used is a vapor circulation type similar to Othmer still [7] as shown in Figure 1. Some modifications were made to the still to allow its use with partially 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 include mechanical mixers with multi-impeller shafts for both of the boiling section (boiler) and the condensation section (condenser), two reflux lines to return the condensed vapor to the boiler. The boiling and condensing sections are glass tubes (QVF) 55 and 40 cm in diameter respectively. The sections are connected with an inclined glass tube with a thermo well. The reflux lines are 1 mm capillaries. The heads of the sections are quick-fit type with polyethylene bushing seals to prevent vapor leakage. The sections were insulated with fiber-glass insulation. The temperature in the boiling section is measured by a temperature sensor type NiCr-Ni and recorded and represented graphically via a *Cassy Module Interface* through a PC (486) by the software *Universal Data Acquisition* [8]. The speed of the mixers was also controlled through the same interface. The shafts were connected to the electric motors by rubber hoses to reduce the vibration of the motors. The shafts were operated at a speed of (1400 to 1600) rpm.

VLLE Measurements. The still is charged with (200 to 300) ml of liquid of the desired composition. The heating mantle and the mixer in the boiling section are started via the software. When the liquid mixture starts to boil after (30 to 40) min the cooling water is allowed to flow in the condenser at a rate of 2 L.min^{-1}. As vapor starts to condense the mixer of the condensing section is started at a rate below vortex formation. After the temperature of the liquid mixture in the boiling section reaches a constant value after (70 to 80) min (monitored via the software display of temperature versus time), samples are withdrawn into a 5 ml graduated test tubes with 0.1 ml graduation and a sealed cap and then the heating is stopped. After (10 to 15) min the mixers and the cooling water are stopped also.

LLE Measurements. The same still was used for LLE measurements. After charging the still with 250 ml of liquid of the desired composition the heating mantle and the mixer in the boiling section are started via the software. When the temperature in the still reaches the desired value after (45 to 60) min, the mixer was stopped. After a period of 5 min, samples are withdrawn from each of the two liquid phases by a 0.1 ml pipette connected to a 10 ml glass syringe into a 5 ml graduated test tube with 0.1 ml graduation and a sealed cap. LLE measurements were applied to the binary system ethyl-acetate(1) + water(2) only in the temperature range t = (25 to 65) ^{o}C.

Sampling Methods. The withdrawn samples were (4 to 5) ml. Three sampling methods were employed: 1. Taking samples from condensed vapor and the boiling liquid [2], 2. Taking a sample of the condensed vapor only [9] 3. The heating and mixing was stopped and a sample of the condensed vapor was taken immediately and a sample from each phase of the liquid in the boiling section as soon as the phases separate was also taken [10]. The withdrawn samples were placed in a water bath at a temperature of t = 20 ^{o}C and left overnight for complete separation of the liquid phases in each sample. Then the volume of each phase was measured by the graduation on the test tube, with the solubility of each component at a temperature of t = 20 ^{o}C, a material balance was done to obtain the composition of the sample (two layer samples).

Sample Analysis. Most of the withdrawn samples were with two liquid phases (layers). For single layer samples, refractive indices of these samples were measured through an Abbe-Hilger Refractometer at a temperature of t = 20 ^{o}C with an uncertainty of $n_D = \pm\ 0.0001$. Two calibration curves were used to determine the mole fraction of the samples, one for the samples rich in organic component and one for rich in aqueous component below the solubility limits of the components. The curves were obtained by preparing liquid mixtures of different mole fractions for the samples and measuring the refractive index and the data obtained were best fitted. Equations 1, 2 represent the system ethyl acetate (1) + water (2).

$$n_{org.} = 1.3526\alpha^{\ 0.0038} \qquad (1)$$

$$n_{aqu.} = 0.0072\alpha + 1.3330 \qquad (2)$$

Where n_{org} and $n_{aqu.}$ are the refractive indices in the rich in organic and aqueous samples respectively and α is the mole fraction multiplied by 100 of ethyl acetate in the sample. The rich in organic sample of the system ethyl acetate (1) + toluene (2) + water (3) is given by equation 3.

$$n_{org.} = 0.0012\alpha + 1.3820 \qquad (3)$$

The aqueous rich sample of the ternary system is also given by equation 2. The assumption of water not present in the organic rich sample of the ternary system is quite reasonable due to the low solubility of water in toluene, and toluene not present in the aqueous rich sample is also due to the low solubility of toluene in water. The binary system toluene(1) + water(2) was considered as an immiscible system.

Experimental Data. The experimental data obtained from the VLLE, LEE measurements of the two binary and one ternary system are given in Tables 2, 3, 4 and 5, where l_i is the composition of the initial liquid in the still as mole fraction of component i and t is the average boiling temperature of the temperatures recorded via the software, x_i^{I}, x_i^{II} are mole fractions in top (organic) and bottom (aqueous) layers of component i, x_i, y_i are mole fractions in the liquid and vapor samples of component i.

Thermodynamic Consistency Test. The McDermont-Ellis test method [11] was used to test the experimental data given in Tables 2, 4 and 5. The experimental data are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{max} \qquad (4)$$

Where D, D_{max} are the local and the maximum deviations defined else where[11]. Table 6 lists the results of the test applied to the data in Tables 2, 4 and 5.

Results and Discussion

Temperature-Composition Diagrams. The data given in Tables 2, 3, 4 and 5 are plotted in Temperature-Composition Diagrams T,x_1^{o},y_1, T,x_1^{I},x_1^{II},y_1 and T, x_1, x_2, x_3 as shown in Figures 2, 3 and 4 [12]. $x_1^{\ o}$ is the overall mole fraction of component 1 in the liquid phase.

Prediction of Equilibrium Data. By applying equation 5 the value of the mole fraction in the vapor phase $\mathrm{y_i}$ was determined:

$$\varphi_i^{v}\ y_i\ P\ =\ \gamma_i\ x_i\ \varphi_i^{sat} P_i^{sat} \qquad (5)$$

Where φ_i^{V} is the partial molar fugasity coefficient in the vapor phase which is determined from Peng-Robinson equation of state [13] with interacting parameters

$k_{ij}=k_{ji}=0$ and n=2. γ_i is the activity coefficient determined from activity coefficient models [13] and φ_i^{sat} is the partial molar fugasity coefficient at saturation. P_i^{sat} is the vapor pressure given by Antoine equation [13]. The parameters of the activity coefficient models (Wilson, NRTL, UNIQUAC and UNIFAC) for the systems studied are taken from literature [6, 13-14]. The average absolute difference in vapor mole fraction Δy_i of component (i) is given by equation 6.

$$\Delta y_i = \frac{\sum_{1}^{n} ABS\,(y_i - y_i^{pred})}{n} \qquad (6)$$

Where y_i^{pred} is the predicted vapor mole fraction determined from equation 5 and y_i is the experimental vapor mole fraction and n number of data points in the system. Table 7 lists the values of Δy_i for the two binary and the ternary systems using the activity coefficient models, Δy_i^{III} is the average absolute difference in the vapor mole fractions from the experimental data obtained by sampling method 3. The average absolute difference in the ratio of the activity coefficient in the top layer (γ_1^{I}) to the activity coefficient in the bottom layer (γ_1^{II}) is $\Delta(\gamma^{I}/\gamma^{II})$ for the VLLE and LLE measurements is given by equation 7.

$$\Delta\left(\frac{\gamma_1^{I}}{\gamma_1^{II}}\right) = \frac{\sum_{1}^{n} ABS\left[\left(\frac{\gamma_1^{I}}{\gamma_1^{II}}\right) - \left(\frac{\gamma_1^{I}}{\gamma_1^{II}}\right)^{pred}\right]}{n} \qquad (7)$$

Where the ratio $(\gamma_1^{I}/\gamma_1^{II})$ was determined from the experimental ratio (x_1^{II}/x_1^{I}) while the ratio $(\gamma_1^{I}/\gamma_1^{II})^{pred.}$ was determined from the activity coefficients models mentioned previously. Table 8 lists the values of $\Delta(\gamma^{I}/\gamma^{II})$ for the binary system ethyl acetate(1) + water(2).

Correlation of Equilibrium Data. The parameters of the activity coefficient equations WILSON, NRTL and UNIQUAC and the interacting parameters k_{ij}, k_{ji} and n of the Peng-Robinson equation of state were determined using a non-linear constraint optimization search. This was achieved by the aid of the software Microsoft Excel using the Solver tool. The Solver tool solves an optimization problem using the *Generalized Reduced Gradient* (GRG) search [15]. 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* or the *conjugate gradient approach.* The following objective function and constraint was used:

$$\frac{1}{c}\sum_{i=1}^{c}\frac{1}{n}\sum_{j=1}^{n} ABS(y_{ij} - y_{ij}^{pred}) = \frac{1}{c}\sum_{i=1}^{C}\Delta y_i \quad (8)$$

$$\Delta y_i - \Delta y_{i+1} = 0,\ \Delta y_i - \Delta y_{i+2} = 0 \quad (9)$$

Where c is the number of components and n is the number of data points. The aim is to minimize equation 8 subject to the constraint of equation 9. The initial values to start the search were taken from the prediction method.. Tables 9, 10 and 11 show the parameters of the activity coefficients determined from the correlation of the experimental data and Δy_1 values for the two binary and the ternary systems. Equation 5 can be written in the following form:

$$\varphi_i^{v}\, y_i \;=\; x_i\, \varphi_i^{l} \qquad (10)$$

Where φ_i^{l} is the partial molar fugasity coefficient in the liquid phase. φ_i^{l} was determined from Peng-Robinson equation of state (P.R. EOS). Table 12 lists the EOS interacting parameters k_{ij}, k_{ji} and n for the two binary and the ternary systems with Δy_1 determined by using these parameters.

Calculation of Boiling Temperature. The temperature of boiling was calculated by equation 11.

$$1 = \sum_{i=1}^{n}\gamma_i x_i P_i^{sat}/P,\ 1 = \sum_{i=1}^{n}\frac{\phi_i^{l}}{\phi_i^{v}} x_i \quad (11)$$

Table 13 lists the values of the average absolute difference in temperature ΔT of the two binary and the ternary systems by using the parameters from Tables 9, 10, 11 and 12. ΔT is defined the same as in equation 6.

Determination of Azeotropic Point. The azeotropic composition and temperature of the two binary and ternary systems were determined using the Gibbs-Konovalov theorem [16].Table 14 lists the values of the azeotropic composition x_1^{Azo} and temperature T^{Azo} of these systems.

Discussion

Systems Selected. Two binary systems 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 °C and the solubility of water in ethyl acetate is 1 ml water in 40 ml ethyl acetate at 20 °C [17]. The system toluene + water can be considered as an immiscible system where the solubility of toluene in water is 0.05 g toluene per 100 g water at 20 °C and the solubility of water in toluene is 0.03 g water per 100 g of toluene at 20 °C [17]. The mixtures of the two binary systems at boiling temperatures or above are three phase systems where two liquid phases in equilibrium with a vapor phase exist. The ternary system toluene +ethyl acetate + water consist of a miscible pair of toluene + ethyl-acetate and a partial miscible pair of ethyl-acetate + water and an immiscible pair of toluene + water. No VLLE data are available in the literature for this ternary system [12].

Assembled Equilibrium Still. An Equilibrium Still was assembled to deal with partial miscible and immiscible systems. The Still was provided with mechanical mixers in both the boiling and condensing sections. The system ethyl acetate(1) + water(2) was studied by Ellis et.al.[12] using an equilibrium still with mechanical agitation in both the boiling and condensing sections the equilibrium data obtained showed a constant vapor composition with a mole fraction of y_1= 0.70 and a constant boiling liquid temperature of t = 70.5 °C in the boiling liquid composition with mole fraction range of x_1= (0.05 to 0.78). Also the data obtained by Kato.M et.al.[6] showed a constant vapor composition with mole fraction of y_1= 0.701 in the boiling liquid composition with mole fraction range of x_1= (0.08 to 0.71) where an equilibrium still is similar to the Othmer still with no mechanical agitation or mixing 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.

Prediction Method. The activity coefficient equations WILSON, NRTL, UNIQUAC and UNIFAC and the Peng-Robinson (EOS) were used to determine the value of Y_i theoretically by using the Peng-Robinson (EOS) for vapor phase and by using one of the activity coefficient equations in liquid phase. The adjustable parameters of the first three activity coefficient equations were obtained from previous studies specially the two binary systems and for the ternary system 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 et.al.[6]. The NRTL activity coefficient equation gave the lowest Δy and $\Delta(\gamma^I / \gamma^{II})$ as seen in Tables 13 and 14; the NRTL equation has three adjustable parameters which give a better representation of the equilibrium data. The UNIFAC method gave high Δy values; it has no adjustable parameters. The predicted parameters of the binary system toluene + water were in the temperature range t = (10 to 60) °C; very high average Δy values were obtained using these parameters as seen in Table 13.

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 8 subjected to the constraint given by equation 9. The adjustable and interacting parameters used in the prediction method where used as initial values to start the search. The activity coefficient equations and the P.R.(EOS) were used to determine the value of y_i theoretically by using the later for the vapor and liquid phases the partial molar fugacity coefficients for both phases were determined with interacting parameters obtained by the correlation of the equilibrium data. And by using the P.R (EOS) for vapor phase and using the activity coefficient equations in liquid phase, the adjustable parameters of the activity coefficient equations were obtained from correlation of equilibrium data. The parameters of the ternary system were obtained by using the adjustable and interacting parameters of the binary systems as initial values to start the search. The UNIQUAC and the NRTL equations gave the lowest average Δy 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 P.R (EOS) gave high average Δy values, according to the ***Lattice Model*** [3] which considers the liquid phase as a dense and highly non-ideal-gas whose properties can be described by some (EOS); this is not correct in VLLE systems (Partial-miscible and immiscible) were the liquid phases in equilibrium are highly non ideal systems. The average boiling temperature was determined theoretically by solving equation 11 for T where the Newton-Raphson method [18] was used with $T^{exp.}$ as the initial value to start the calculations. The UNIQUAC equation gave low ΔT values as shown in Table 13.

Azeotropic Point. The determination of the azeotrope point (x^{Azo}, T^{Azo}) of partial and immiscible systems is very complex. 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(1) + water(2) showed a minimum boiling behavior at certain compositions as can be noticed from Table 2 and Figure 2 the data points T,y_1 and T,x_1 appear to meet in a straight line in the mole fraction range of $x_1, y_1 =$ (0.50 to 0.80). The binary system toluene(1) + water(2) also showed a minimum boiling behavior as can be noticed from Table 4 and in Figure 3 the data points T-y_1 and T-x_1 appear to meet in a straight line in the mole fraction range of $x_1, y_1 =$ (0.35 to 0.53).

The ternary system toluene + ethyl-acetate + water showed a minimum boiling temperature as can be noticed in Table 5 and Figure 4. Below the temperature contour of $t = 79.81\,^{o}$C lies mixtures with minimum boiling temperature especially the temperature contour of $t = 76.35\,^{o}$C.

Conclusions

The modified still with mechanical mixing in both the boiling and condensation sections appeared to be suitable for VLLE measurements of the binary systems ethyl acetate + water and toluene + water and the ternary system toluene + ethyl acetate + water. The same still was used for LLE measurements of the binary system ethyl acetate + water. Using equation 5 to predict or correlate VLLE data gave the lowest Δy values than equation 6. The UNIQUAC and NRTL models agreed better with the experimental VLLE data than the other models. The NRTL model agreed well with the experimental LLE data.

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Literature Cited

(1) Colburn, A. P.; Schoenborn, E.M. ; David Shiling. Equilibrium still for partially miscible liquids. *Ind.Eng.Chem.* **1943**, *35*, 1250-1254.

(2) Ellis, S. R. M.; Garbett, R. D. A new equilibrium still for the study of partially miscible systems. *Ind.Eng.Chem.* **1960**, *52*, 385-388.

(3) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics Of Fluid-Phase Equilibria*; Prentice Hall: PTR, 1999.

(4) Peng, D. Y.; Robinson, D. B. Two and Three Phase Equilibrium Calculations for Systems Containing Water. *Canadian J. Chem. Eng.* **1976**, *54*, 595-599.

(5) Carroll, J. J. ; Mather, A. E. Phase Equilibrium in The system Water-Hydrogen Sulphide: Modelling the Phase Behavior with an Equation of State. *Canadian J. Chem. Eng.* **1989**, *67*, 999-1003.

(6) Ohe, S. *Vapor-Liquid equilibrium data*; Kodansha, 1989.

(7) Hala, E.; Pick, J;. Fried, V.; Vilim, O. *VAPOR-LIQUID EQUILIBRIUM*; Pergamon Press, 1958.

(8) Universal Data Acquisition program (525 032); Leybold Didactic GmbH,1998.

(9) Stockhardt, J. S.; Hull, C. M. Vapor-Liquid Equilibria and Boiling-Point Composition Relations for Systems n-Butanol-Water and Isobutannol-Water. *Ind. Eng. Chem.* **1931**, *23*, 1438-1440.

(10) Chopade, S. P.; Dhale, A. D.; Clark, A. M.; Kiesling, C. W.; Myrant, L. K.; Jackson, J. E.; Miller, D. J. Vapor-Liquid-Liquid Equilibrium (VLLE) and Vapor Pressure Data for the Systems 2-Methyl-1,3-dioxolane (2MD) + Water and 2,4-Dimethyl-1,3-dioxolane (24DMD) + Water. *J. Chem. Eng. Data* **2003**, *48*, 44-47.

(11) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall, 1969.

(12) Mohammed, G. A. *Investigation of Vapor-Liquid-Liquid Equilibria*; Ph.D. thesis Al-Nahrain University: Baghdad-Iraq, 2005.

(13) Assael, M. J.; Trusler, J.P.; Tsolakis, T. F. *Thermophysical Properties Of Fluids An Introduction to their Prediction*; Imperial College Press, 1996.

(14) Smith, J. M.; Van Ness, H. C.; Abbott, M. M. *Introduction to Chemical Engineering Thermodynamics*; McGraw-Hill, 1996.

(15) Edgar, T. F.; Himmelblau, D. M. *Optimization Of Chemical Processes*; McGraw-Hill, 1988.

(16) Malesinski, W. *Azeotropy and other Theoretical Problems of Vapor-Liquid Equilibrium*; Interscience, PWN:New York, 1965.

(17) Windholz, M.; Budavari, S.; Stroumtsos, L. Y.; Fertig, M. N. *THE MERCK INDEX*; MERCK & CO, 1976.

(18) Gerald, C. F.; Wheatly, P. O. *Applied Numerical Analysis*;Addison-Wesley, 1989.

TABLES

Table 1. Specifications of the Chemical Used in the Present Work.

Chemical	ethyl acetate	toluene	water
Assay (mass fraction)	0.997	0.999	1.000
Non volatile materials	0.000005	0.00001	-----
Water content	0.0003	0.0003	-----
M	88.11	92.14	18.02
ρ , g.cm^3	0.901	0.867	0.998
n_D^{20}	1.3763	1.4998	1.3334

Table 2. Experimental Vapor-Liquid-Liquid Equilibrium Data for the System Ethyl acetate(1) + Water(2) at P = 101.325 kPa. l_1 is the Initial Mole Fraction of Ethyl acetate in the Still. . x_1^I, x_2^{II} and x_1^O

are the Top, Bottom and Overall Mole Fractions of Ethyl acetate in the Liquid Phase respectively.

l_1	t_a, ^0C	x_1^I	x_1^{II}	x_1^O	y_1
0.0027	98.48			0.0003	0.0779
0.0099	96.92			0.0006	0.0813
0.0156	92.37			0.0065	0.0957
0.0242	84.53			0.0151	0.4468
0.0434	70.88			0.0304	0.4468
0.1018	71.38			0.7778	0.7806
0.2654	70.41			0.5531	0.7192
0.3384	72.96	0.5896	0.0166	0.3181	0.5086
0.4057	71.86	0.7869	0.0301	0.3880	0.6327
0.4723	71.26	0.7736	0.0120	0.4514	0.6680
0.5574	71.75	0.7898	0.0068	0.5413	0.6813
0.6689	71.28			0.6720	0.7369
0.7132	71.85			0.7310	0.7501
0.7964	73.42	0.9500	0.3257	0.7926	0.7898
0.8245	73.76	0.9500	0.7399	0.8239	0.8506
0.8878	74.80	0.9015	0.8510	0.8851	0.8528
0.9500	72.13			0.9500	0.9126
0.9840	76.37			0.9840	0.4767
Sampling method		3		1	

Table 3. Experimental Liquid-Liquid Equilibrium Data for the System Ethyl acetate(1) + Water(2) at *P* = 101.325 kPa. l_1 is the Initial Mole Fraction of Ethyl acetate in the Still. x_1^I and x_2^{II} are the Top and Bottom Mole Fractions of Ethyl acetate in the Liquid Phase respectively.

l_1	t , °C	x_1^I	x_1^{II}
0.1559	24.80	0.9500	0.0187
0.1559	30.77	0.9500	0.0176
0.1559	34.27	0.9357	0.0172
0.1559	41.61	0.9165	0.0168
0.1559	49.68	0.8849	0.0170
0.1559	57.90	0.8291	0.0159
0.1559	65.33	0.8211	0.0172
Sampling method		3	

Table4. Experimental Vapor-Liquid-Liquid Equilibrium Data for the System Toluene (1) + Water(2) at *P* = 101.325 kPa. l_1 is the Initial Mole Fraction of Toluene in the Still. x_1^O is the Overall Mole Fractions of Toluene in the Liquid Phase.

l_1	t , °C	x_1^O	y_1
0.0167	98.08	0.0159	0.0564
0.0237	97.90	0.0214	0.0987
0.0536	96.95	0.0519	0.1435
0.0862	96.12	0.0810	0.2137
0.1452	94.60	0.1444	0.2776
0.2132	93.50	0.2058	0.3375
0.2940	92.61	0.2832	0.3675
0.3691	92.47	0.2698	0.4044
0.4422	92.49	0.4365	0.4806
0.5432	93.73	0.5478	0.5362
0.6174	94.97	0.6130	0.5769
0.7596	99.15	0.7614	0.6255
0.7615	99.34	0.7667	0.6437
0.8688	103.89	0.8813	0.7134
0.8947	107.26	0.9523	0.7856
0.9177	106.10	0.9288	0.7449
0.9494	108.54	0.9531	0.8301
Sampling method		2	

Table 5. Experimental Vapor-Liquid-Liquid Equilibrium Data for the System Toluene(1)+ Ethyl acetate(2) + Water(3) at P = 101.325 kPa. l_1 and l_2 are the Initial Mole Fractions of Toluene and Ethyl acetate in the Still respectively. $x_1^O$and x_2^O are the Overall Mole Fractions of Toluene and Ethyl acetate in the Liquid Phase respectively.

l_1	l_2	t ,°C	x_1^O	x_2^O	y_1	y_2
0.1260	0.6421	72.89	0.1318	0.6422	0.0179	0.4354
0.1947	0.4232	74.16	0.1995	0.4165	0.0702	0.4153
0.2278	0.3890	75.68	0.2359	0.3804	0.0670	0.4294
0.2611	0.3547	76.88	0.2669	0.3494	0.1004	0.3332
0.2945	0.3201	79.36	0.3031	0.3112	0.1010	0.4005
0.3282	0.2854	77.50	0.3383	0.2785	0.1190	0.3278
0.3896	0.3811	80.18	0.4026	0.3737	0.0947	0.3993
0.3961	0.2153	79.89	0.4062	0.2081	0.1517	0.3020
0.4132	0.1976	83.25	0.4234	0.1908	0.1222	0.2978
0.4648	0.1443	83.65	0.4790	0.1367	0.1814	0.2483
0.5342	0.0726	87.08	0.5511	0.0676	0.2256	0.1412
0.5523	0.2171	89.26	0.5666	0.2107	0.1961	0.2786
0.6153	0.1510	90.52	0.6285	0.1441	0.2192	0.2835
0.6754	0.0907	93.77	0.6931	0.0866	0.1585	0.2063
0.7233	0.1477	93.29	0.7448	0.1448	0.1585	0.2063
Sampling method	2					

Table 6. Results of the McDermont-Ellis Test Applied to the Data in Tables 2, 4, 5 and the data by Ellis,etal.[2] *D* and D_{max} are the Local and Max. Deviations defined else ware[11]

System	D	D_{max}	$D < D_{max}$
ethyl acetate(1) + water(2) [2]	10.21	10.03	NO
ethyl acetate(1) + water(2)	7.08	9.52	YES
toluene(1) + water(2)	12.36	13.62	YES
toluene(1) + ethyl acetate(2) +water(3)	4.39	9.96	YES

Table7. The Average Absolute Difference in Vapor Mole Fraction Δy of the Data in Tables 2, 4, 5 and the

data by Ellis,etal [2] Using Activity Coefficient Models with Parameters taken from Literature[6, 13-14].

System / Δy	Wilson	NRTL	UNIQUAC	UNIFAC
toluene(1) + water(2)		0.214	0.685	0.269
ethyl acetate(1) + water(2) [2]	0.166	0.054	0.162	0.263
ethyl acetate(1) + water(2)	0.123	0.111	0.119	0.208
ethyl acetate(1) + water(2)	0.233	0.100	0.160	0.236
toluene(1) + ethyl-acetate(2) + water(3)		0.127	0.135	0.196

Table 8. The Average Absolute Difference in Activity Coefficient in the Top Layer to the Activity Coefficient in the Bottom layer $\Delta(\gamma^{I}/\gamma^{II})$ for the VLLE and LLE Data of the System Ethyl acetate(1) + Water(2) Using Activity Coefficient Models with Parameters taken from Literature[6, 13-14].

System / measurement	$\Delta(\gamma^{I}/\gamma^{II})$ Wilson	NRTL	UNIQUAC	UNIFAC
ethyl acetate(1) + water(2) / VLLE	0.061	0.019	0.041	0.186
ethyl acetate(1) + water(2) / LLE	0.051	0.004	0.031	0.116

Table 9. ΔY_1 and Wilson Parameters Obtained by Appling Non-linear Constraint Optimization On the Data in Tables 2, 4 and 5.

Wilson parameter	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
λ_{12}/K	1911.5	35550.1	0.361
λ_{21}/K	573.3	193.3	- 222.9
λ_{13}/K			-597.5
λ_{23}/K			181.1
λ_{32}/K			799.6
λ_{31}/K			1180.7
ΔY_1	0.116	0.101	0.061

Table 10. ΔY_1 and NRTL Parameters Obtained by Appling Non-linear Constraint Optimization On the Data in Tables 2, 4 and 5.

NRTL parameter	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
α	0.505	0.632	0.649
g_{12}/K	657.6	415. 5	33.8
g_{21}/K	1145	1515.1	31.4
g_{13}/K			517.6
g_{23}/K			857.4
g_{32}/K			3071. 2
g_{31}/K			499. 9
ΔY_1	0.069	0.075	0.060

Table 11. ΔY_1 and UNIQUAC Parameters Obtained by Appling Non-linear Constraint Optimization On the Data in Tables 2, 4 and 5.

UNIQUAC parameter	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
Z/2	6. 06	2.7	4. 65
u_{12}/K	515	695	428. 8
u_{21}/K	- 30. 8	-111. 8	353. 5
u_{13}/K			1087. 3
u_{23}/K			287
u_{32}/K			604. 3
u_{31}/K			-144. 8
ΔY_1	0.074	0.057	0.048

Table 12. ΔY_1 and Peng Robinson (EOS) Interacting Parameters Obtained by Appling Non-linear Constraint Optimization On the Data in Tables 2, 4 and 5.

UNIQUAC parameter	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
n	2.13	1. 94	1. 96
k_{12}	- 0. 271	- 0. 277	- 0. 055
k_{21}	- 0. 222	- 0. 334	0. 083
k_{13}			0. 163
k_{23}			- 0. 049
k_{32}			- 0. 045
k_{31}			0. 025
ΔY_1	0. 213	0. 091	0. 072

Table 13. The Average Absolute Difference in Temperature ΔT of the Two Binary and the Ternary Systems by Using the Parameters from Tables 9, 10, 11 and 12.

ΔT / K	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
Wilson	2.102	2. 047	2. 120
NRTL	1. 817	1. 796	3. 455
UNIQUAC	1. 513	1. 787	1. 902
UNIFAC	9. 480	5. 105	6. 219

Table 14. Values of the Azeotropic Composition x_1^{Azo} and Temperature T^{Azo} of the Two Binary and the

Ternary systems Using the Gibbs-Konovalov Theorem [16].

Azeotropic conditions	ethyl acetate(1) + water(2)	toluene(1) + water(2)	toluene(1) + ethyl-acetate(2) + water(3)
x_1^{Azo}	0. 517	0. 357	0. 153
x_2^{Azo}			0. 554
T^{Azo} / K	344. 31	365. 33	346. 44

Figures

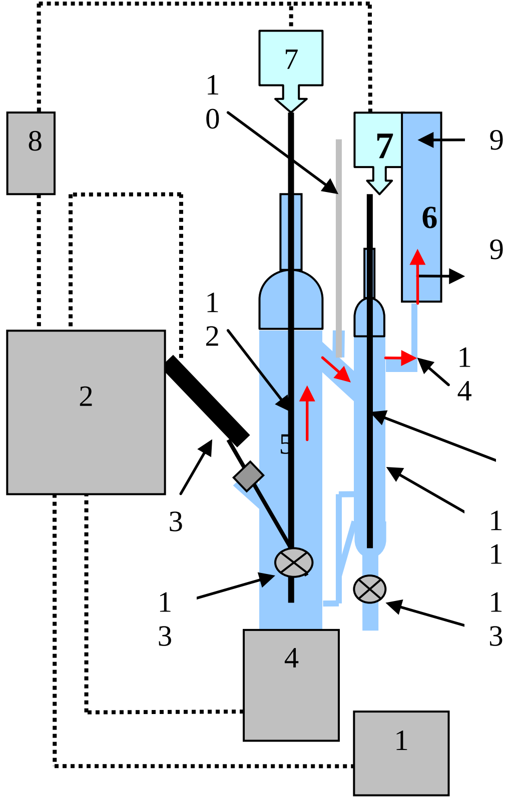

Fig. 1. Modified still with control: (1) Computer, (2) Interface, (3) Temperature sensor, (4) Heating mantle, (5) Boiling section, (6) Condenser, (7) Electric motor, (8) Voltage regulator, (9) Cooling water inlet and outlet, (10) Thermometer, (11) Condensing section, (12) Multi-impeller shaft, (13) Sampling valve, (14) Vapor path.

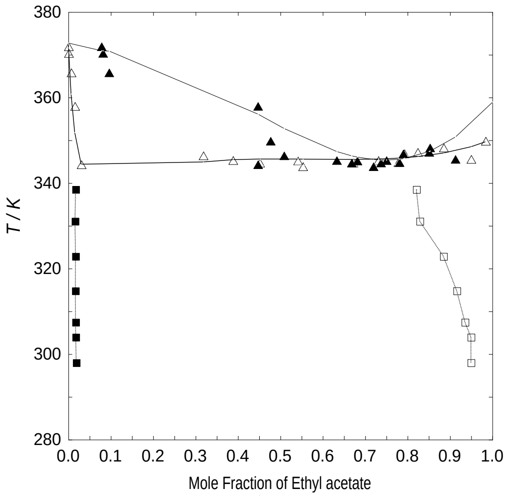

Fig. 2. Experimental data for the system ethyl acetate (1) + water (2) at P =101.325 kPa : (■, □) liquid-liquid, data from Table 3: (▲,Δ) saturated vapor and liquid, data from Table 2: (—) data correlated by Uniquac equation with parameters from Table 11.

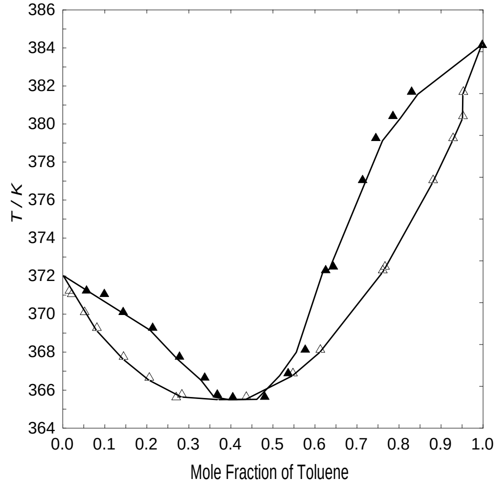

Fig. 3. Experimental data for the system toluene (1) + water (2) at P =101.325 kPa: (▲,Δ) saturated vapor and liquid, data from Table 4: (—) data correlated by Uniquac equation with parameters from Table 11.

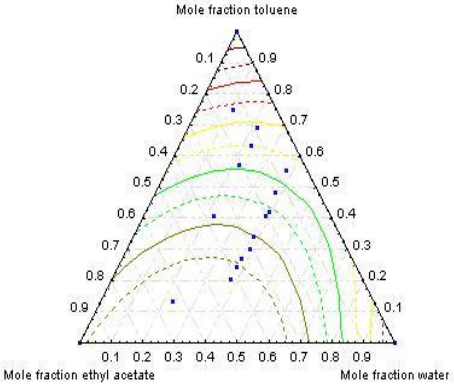

Fig. 4. Experimental data for the system toluene (1) + ethyl acetate (2) + water (3) at P =101.325 kPa: (■) T, x_1, x_2, x_3 data from Table 5: (– – –) T = 350 K contour: (—) T = 360 K contour: (—) T = 380 K contour : (—) T = 370 K contour : (—) T = 366 K [12].