



DIPLOMA THESIS

VAPOR – LIQUID EQUILIBRIUM MEASUREMENTS IN BINARY POLAR SYSTEMS

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Abstract

An experimental study was conducted in order to investigate the vapor – liquid equilibrium of binary mixtures of Ethanol – Butan-2-ol, Methanol – Ethanol, Methanol – Butan-2-ol, Ethanol – Water, Methanol – Water, Acetone – Ethanol and Acetone – Butan-2-ol at ambient pressure using the dynamic apparatus Labodest VLE 602.

The experimental apparatus consisted of a constant volume boiling chamber with a heating element controlled by an electrical controller for the adjustment of heating power, an equilibrium chamber ("Cottrell pump"), a pressure sensors for measuring and controlling pressure as well as options for measuring vapor and liquid temperature. Composition of vapor and liquid sample are determined via gas chromatograph and refractometer, respectively. Generated VLE data are used to Txyplots of the investigated systems, to calculate activity coefficients and to regress interaction parameters for the Van Laar activity coefficient model.

All present data are compared to the available experimental data from the literature and show good accordance in terms of Txy and xy plots for both, experimental and calculated data based on regressed Van Laar parameters. For the acetone based systems the experimental results show the highest deviations from literature of all investigated systems, most likely caused by high volatility of acetone.

Summarizing, results show that the apparatus and proposed procedure allow satisfactory determination of vapor liquid equilibrium of binary organic and aqueous systems. The Van Laar activity coefficient model – despite of its simplicity –allows a good reproduction for the description of vapor – liquid equilibrium of the investigated systems based on regressed interaction parameters.

Περίληψη

Η παρούσα μελέτη διεξήχθη με σκοπό να διερευνηθεί η ισορροπία φάσεων ατμού - υγρού των δυαδικών μειγμάτων Αιθανόλη - Βουταν-2-όλη, Μεθανόλη -Αιθανόλη, Μεθανόλη - Βουταν-2-όλη, Αιθανόλη - Νερό, Μεθανόλη - Νερό, Ακετόνη -Αιθανόλη και Ακετόνη - Βουταν-2-όλη σε πίεση περιβάλλοντος με τη χρήση της δυναμικής συσκευής Labodest VLE 602.

Η πειραματική συσκευή αποτελείται από ένα σταθερού όγκου θάλαμο βρασμού με ένα θερμαντικό στοιχείο που ελέγχεται από ένα ηλεκτρικό ελεγκτή για τη ρύθμιση της ισχύος θέρμανσης, έναν θάλαμο ισορροπίας («αντλία Cottrell»), έναν αισθητήρα πίεσης για τη μέτρηση και τον έλεγχο της πίεσης καθώς και επιλογές για τη μέτρηση θερμοκρασίας του ατμού και του υγρού. Η σύνθεση των δειγμάτων ατμού και υγρού προσδιορίζεται μέσω ενός αέριου χρωματόγραφου και ενός διαθλασίμετρου, αντίστοιχα. Τα δεδομένα που προκύπτουν από την ισορροπία φάσεων χρησιμοποιούνται για τη δημιουργία Τχγ-διαγραμμάτων για όλα τα υπό διερεύνηση συστήματα, για τον υπολογισμό των συντελεστών ενεργότητας και για τον υπολογισμό

Όλα τα παρόντα δεδομένα σε σύγκριση με τα διαθέσιμα πειραματικά από τη βιβλιογραφία παρουσιάζουν καλή συμπεριφορά, σύμφωνα με τα διαγράμματα Τχγ και χγ, καθώς και τα δεδομένα που υπολογίζονται βάσει των παραμέτρους αλληλεπίδρασης από το μοντέλο Van Laar. Για τα συστήματα με την ακετόνη, τα πειραματικά αποτελέσματα δείχνουν τις υψηλότερες αποκλίσεις από τη βιβλιογραφία σε σχέση με όλα τα συστήματα που διερευνώνται, πιθανότατα το γεγονός αυτό προκλήθηκε από την υψηλή πτητικότητα της ακετόνης.

Συνοψίζοντας, τα αποτελέσματα δείχνουν ότι η συσκευή και η προτεινόμενη διαδικασία επιτρέπει τον ικανοποιητικό προσδιορισμό της ισορροπίας φάσεων ατμού υγρού των δυαδικών οργανικών και υδατικών συστημάτων. Το μοντέλο Van Laar παρά την απλότητά του - επιτρέπει μια καλή αναπαραγωγή για την περιγραφή της ισορροπίας ατμού υγρού των συστημάτων που διερευνήθηκαν με βάση τις παραμέτρους αλληλεπίδρασης.

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1. Introduction

Vapor-liquid equilibrium (VLE) engirds the bulk of industrial separation processes, particularly in distillation processes. When the liquid mixture is heated to its boiling point, the vapor produced will, in general, have a different composition than the liquid. Thus, boiling the mixture produces a partial separation of the components. If the vapor is collected, it can be condensed and boiled again to further change the composition. Distillation columns use this principle, effectively repeating the separation process at individual trays within a column. Such columns may have over a hundred trays on which VLE is occurring.

The reason is that there are two main factors that make the vapor and liquid compositions different at equilibrium: the pure component vapor pressures and the non-idealities in the liquid phase.

In recent years, bio-based butanol has been gained more attention due to the concerns over depletion of fossil fuels. Butanol production from biomass by fermentation is considered to be a potential source of liquid fuels [1].

Despite the fact that butanol is now only used as a petrol additive (typical butanol mixtures may contain from 8 to 32% of butanol, and ethanol mixtures from 5 to 20% of ethanol) much effort is devoted to designing engines that would operate using only this compound (Durre 2008; Wackett 2008).

Nowadays, with the increase of petroleum price and shortage of petroleum resource, the utilization of renewable biomass to produce biofuel is increasing. Although the widely used biofuel is ethanol, it is found that butanol, as a new liquid fuel, has more superior properties, such as higher energy content, easy to transport, less evaporation, direct use without modification to the engine of the car. Therefore, production of butanol has received more and more attention [2].

In the course of growing interest in the production of biofuels the old process of ABE-fermentation (Acetone-Butanol-Ethanol) is back in the focus of researchers around the world. Besides optimization of the fermentation step a crucial point towards and economical process is the removal and separation of the product components from a diluted aqueous system. Additionally, there is a high interest for an in-situ removal of the produced solvents from fermentation broth to avoid product inhibition. For both tasks – in-situ removal and purification/separation of solvents – thermal separation processes could be applied.

Goal of present work was testing an apparatus for determination of VLE for ABE system. To avoid VLLE, which is formed by Butan-1-ol that is produced during ABE

process, in a first step Butan-2-ol was used. Additionally, Methanol was introduced to see the behaviour of a lower boiling component besides Acetone that is also produced by ABE fermentation. For these reasons the following binary polar systems have been under investigation:

- 1. Ethanol Water
- 2. Ethanol Butan-2-ol
- 3. Methanol Water
- 4. Methanol Ethanol
- 5. Methanol Butan-2-ol
- 6. Acetone Ethanol
- 7. Acetone Butan-2-ol

Into consideration, in present work, is taken only binary (two component) mixtures. The composition of the liquid will be designated by the mole fraction of the more volatile component (lower boiling point). The parameters determined specifically for the binary vapor liquid equilibrium systems are temperature, pressure and the compositions of the constituent phases.

2. Vapor-Liquid Equilibrium

Vapor-liquid equilibrium (VLE) relationships (as well as other interphase equilibrium relationships) are needed in the solution of many engineering problems. The required data can be found by experiment. But such measurements are seldom easy, even for binary systems. This is the incentive for application of thermodynamics to the calculation of phase-equilibrium relationships.

$$f_i^G = f_i^L \tag{1}$$

where superscripts *L* and *G* devote the liquid and vapor phases, respectively.

Considerable progress has been achieved in the application of theory to the calculation of binary mixture equilibria. Historically, the prediction of phase transitions has relied on empirical methods, but more realistic equations of state are being developed that attempt to account for the various aspects of intermolecular interactions. The unlike interaction parameter for binary mixtures are obtained by comparing experimental critical data with calculations using the equations of state. These interaction parameters and equations of state are used to predict a priori the vapor-liquid equilibria. The predicted critical properties and bimodal phase diagrams are compared with experimental data for a wide range of pressure, temperature and composition.

By using group-interaction parameters obtained from data reduction, activity coefficients in a large number of binary and multicomponent mixtures may be 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° to 400°K.

Equilibrium between phases in a multicomponent system means that temperature *T*, pressure *P* and the chemical potential μ of each component must be the same in all phases:

$$T' = T'' = T''' = \dots$$
 (2)

$$P' = P'' = P''' = ...$$
(3)

$$\mu' = \mu'' = \mu''' = \dots$$
 (4)

For the discussion of phase equilibria the conditions of equation (3) can be expressed in terms of fugacities f, e.g.

$$f'_{i} = f''_{i} = f''_{i} = \dots$$
(5)

In case of vapor-liquid equilibrium we obtain for component *i* the relation (1).

The concentration dependence of the vapor phase fugacity f_i^G is given by

$$f_i^G = y_i \cdot \Phi_i \cdot P \tag{6}$$

Since by definition the fugacity of an ideal gas is equal to its pressure, the fugacity coefficient Φ_i approaches unity for very low pressures:

$$\lim_{(P \to 0)} \Phi_i = 1 \tag{7}$$

 Φ_i is related to pressure by

$$\Phi_i = exp(\frac{1}{RT} \cdot \int_0^P \left(V_i^G - \frac{RT}{P} \right) dP)$$
(8)

This equation is the starting point for calculation of the fugacity coefficients Φ_{i} . The necessary data for the partial molar volumes V_i^G in the gas phase are determined from equations of state. For moderate pressures (up to 10-20 bars) this can be done through the second virial coefficients; a method for their calculation, also with mixtures of polar compounds, has been described by Haydn and O' Connell. For higher pressures other equations of state, such us the Redlich-Kwong equation (two parameters), are used [19].

The liquid phase fugacity f_i^L of component *i* is related to its mole fraction x_i in the liquid phase by

$$f_i^L = \mathbf{x}_i \cdot \mathbf{\gamma}_i \cdot f_i^{0\,L} \tag{9}$$

Here γ_i is the liquid phase activity coefficient of component *i*; it is a function of temperature, pressure and composition. $f_i^{0 L}$ is the fugacity of liquid component *i* at system temperature and pressure at a defined standard state. With vapor-liquid equilibrium the standard state is nearly always the pure component at the temperature and the pressure of the mixture. With this choice of standard state it follows that

For
$$x_i = 1$$
: $f_i^L = f_i^{0 L}$ (10a)

and $\gamma_i = 1$ (10b)

The fugacity $f_i^{0 L}$ of the pure liquid is related to its vapor pressure p_i^0 :

$$f_i^{0L} = p_i^0 \cdot \Phi_i^0 \cdot \exp\left(\frac{1}{RT} \cdot \int_{p_i^0}^P V_i^L dP\right)$$
(11)

Here the expression exp $(\frac{1}{RT} \cdot \int_{p_i^0}^P V_i^L dP)$ is the so-called Poynting correction which allows for the influence of the change of pressure on fugacity from *P* to p_i^0 . Φ_i^0 is the fugacity coefficient for the pure component at the pressure p_i^0 ; it is given by:

$$\Phi_i^0 = \exp\left(\frac{1}{RT} \cdot \int_0^{p_i^0} \left(V_i^G - \frac{RT}{P}\right) dP\right)$$
(12)

By combining equations (1), (5), (6) and (9) one obtains the following equation for equilibrium between vapor and liquid at the temperature T and the pressure P:

$$y_i \cdot \Phi_i \cdot P = x_i \cdot \gamma_i \cdot p_i^0 \cdot \Phi_i^0 \cdot exp\left(\frac{1}{RT} \cdot \int_{p_i^0}^P V_i^L dP\right)$$
(13)

At low pressures (up to a few bars) equation (13) can be simplified, because the fugacity coefficients tend towards 1 and Poynting corrections usually are very close to unity. Neglecting these corrections leads to:

$$y_i \cdot P = x_i \cdot \gamma_i \cdot p_i^0 \tag{14}$$

Note that for an ideal system all γ_i are equal to unity at any composition, and equation (14) then reduces to Raoult's law [19] Eq. (15).

2.1. Raoult's Law

2.1.1. Ideal mixtures

Guggenheim (1937) expressed the theoretical basis of Raoult's law [31]. Although there is no ideal mixture, however, some liquid mixtures get fairly close to being ideal. These are mixtures of two very closely similar substances.

In a pure liquid, some of the more energetic molecules have enough energy to overcome the intermolecular attractions and escape from the surface to form a vapor. The smaller the intermolecular forces, the more molecules will be able to escape at any particular temperature. If there is also a second liquid, the same thing is true. At any particular temperature a certain proportion of the molecules will have enough energy to leave the surface.

In an ideal mixture of these two liquids, the tendency of the two different sorts of molecules to escape is unchanged. If the molecules still have the same tendency to escape mixture as before, that mean that the intermolecular forces between two molecules of the same liquid must be exactly the same as the intermolecular forces between different liquids. If the forces were any different, the tendency to escape would change.

Mixtures close to ideal behavior are similarly sized molecules and so they have similarly sized van der Waals attractions between them. However, they aren't identical and so although they get close to being ideal, they aren't actually ideal.

If all these attractions are the same, there won't be any heat either evolved or absorbed when mixing. That means that an ideal mixture of two liquids will have zero enthalpy change of mixing. If the temperature rises or falls when you mix the two liquids, then the mixture isn't ideal.

Raoult's law is a law of thermodynamics established by French physicist François-Marie Raoult in 1882. It states that the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

Mathematically, Raoult's law for a single component in an ideal solution is stated as:

$$p_i = p_i^0 \cdot x_i \tag{15}$$

where p_i is the partial vapor pressure of the component *i* in the gaseous mixture (above the solution), p_i^0 is the vapor pressure of the pure component, and is the mole fraction of the component in the mixture.

In equation form, for a mixture of liquids A and B, this reads:

$$p_A = p_A^0 \cdot x_A$$
$$p_B = p_B^0 \cdot x_B \tag{16}$$

In this equation, p_A and p_B are the partial vapor pressures of the components A and B. (In any mixture of gases, each gas exerts its own pressure. This is called its partial pressure and is independent of the other gases present. Even if all the other gases are taken away, the remaining gas would still be exerting its own partial pressure.)

Also, x_A and x_B are the mole fractions of A and B.

2.1.2. Non-ideal mixtures

At sufficiently low pressures, the vapor phase may be regarded as perfect or nearly ideal, and the variation of the liquid phase fugacity with pressure may be neglected. Under these conditions, it is convenient to correlate the phase equilibrium properties of non-ideal solutions in terms of the activity coefficients γ_i of each component *i* [25]. Therefore, intermolecular interaction is taken into account which may induce minima and maxima into the T – x diagrams depending on [26]:

- Negative deviation from Raoult's law, $\gamma < 1$ and $G^{ex} < 0$
- Positive deviation from Raoult's law, $\gamma > 1$ and $G^{ex} > 0$

2.2. Vapor pressure / composition diagrams

The partial vapor pressure of A in an ideal mixture at a particular temperature is proportional to its mole fraction. In the graph, the partial vapor pressure of A against its mole fraction is a straight line.



Figure 1: Vapor pressure of pure component A [20].

The mole fraction of B falls as A increases so the line will slope down rather than up. As the mole fraction of B falls, its vapor pressure will fall at the same rate.



Figure 2: Vapor pressure of pure components A, B [20].

The vapor pressure of pure B is higher than that of pure A, which means that molecules must break away more easily from the surface of B than of A, so B is more volatile liquid.

The total vapor pressure of the mixture equals the sum of the values for A and B together at each composition. The net effect of that gives a straight line as shown in the next diagram [20].



Figure 3: Total vapor pressure of a system [20].

2.3. Dalton's Law

Based on the kinetic theory of gases, a gas will diffuse in a container to fill up the space it is in and does not have any forces of attraction between the molecules. In other words, the different molecules in a mixture of gases are so far apart that they act independently; they do not react with each other. The pressure of an ideal gas is determined by its collisions with the container, not the collisions with molecules of other substances since there are no other collisions. A gas will expand to fill the container it is in without affecting the pressure of another gas. So it can be concluded that the pressure of a certain gas is based on the number of moles of that gas and the volume and temperature of the system. Since the gases in a mixture of gases are in one container, the volume (V) and temperature (T) for the different gases are the same as well. Each gas exerts its own pressure on the system, which can be added up to find the total pressure of the mixture of gases in a container. Dalton's Law of Partial Pressure states the total pressure exerted by a mixture of gases is equal to the sum of the partial pressure of each individual gas [21].

Mathematically, this can be stated as follows:

$$P_{total} = P_1 + P_2 + P_3 \dots = \sum P_i$$
 (17)

where P_1 , P_2 and P_n represent the partial pressures of each compound. It is assumed that the gases do not react with each other. Dalton reasoned that the low density and high compressibility of gases were indicative of the fact that they consisted mostly of empty space; from this, Dalton concluded that when two or more different gases occupy the same volume, they behave entirely independently of one another.

Because it is dependent solely the number of particles and not the identity of the gas, the Ideal Gas Equation applies just as well to mixtures of gases is does to pure gases [21].

2.4. Antoine Equation

It is important to know the vapor pressure of the pure substance i. Various equations have been published for that purpose, e.g. the Clausius-Clapeyron Equation (C-C eq.), which has an often use of estimating the vapor pressures of pure liquids or solids:

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$
(18)

Most usually, the Antoine equation is used for describing the vapor pressures of pure components of the measurements.

The equation fails at high pressure and near the critical point, and under those conditions the equation gives inaccurate results. However, the most prominent and frequently used 3-parameter equation is the Antoine equation for more reliable vapor pressure estimates. The Antoine equation describes more accurate the relation between vapor pressure and temperature for pure components.

$$\log_{10} p^0 = A - \frac{B}{C+T}$$
(19)

where p^0 is the vapor pressure, *T* is temperature and *A*, *B* and *C* are component-specific constants.

The simplified form with *C* set to zero:

$$\log_{10} p^0 = A - \frac{B}{T}$$
 (20)

is named the August equation, after the German physicist Ernst Ferdinand August (1795–1870). The August equation describes a linear relation between the logarithm of the pressure and the reciprocal temperature. This assumes a temperature-independent heat of vaporization. The Antoine equation allows an improved, but still inexact description of the change of the heat of vaporization with the temperature [22].

The Antoine equation can also be transformed in a temperature-explicit form with simple algebraic manipulations from equation (19):

$$T = \frac{B}{A - \log_{10} p^0} - C$$
 (21)

2.5. Deviations from Raoult's Law – Non-ideal Systems

In representing binary VLE and VLLE it has to be appreciated that the nature of the plots differs according to the type and extent of variations from Raoult's Law. Thus, if pressure is held constant for a binary system a typical plot of VLE for a system close to obeying Raoult's law is shown in Figure 4-A.

A non-ideal polar system start to show positive deviations and as the deviations increase it is possible to get the formation of a minimum boiling azeotrope; a typical plot will have a phase diagram as shown in Figure 4-B. If the binary system exhibits negative deviations from Raoult's law it is possible to get a maximum boiling azeotrope (Figure 4-C). If the positive deviations from Raoult's law are very large it is possible to get a heterogeneous azeotrope e.g. systems having immiscible liquid phases (Figure 4-D) and systems having partially miscible liquid phases (Figure 4-E) [4].





Figure 4: Types of binary systems showing T-x-y & P-x-y phase diagram [4].

The fact that the vapor pressure is higher than ideal in mixtures showing positive deviations from Raoult's law means that molecules are breaking away more easily than they do in the pure liquids.

That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids. Mixing the liquids, less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

When observing negative deviations from Raoult's law the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

Also, heat is evolved when mixing the liquids; more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones. Many examples, but not all, of this involve actual reaction between the two liquids.

A large positive deviation from Raoult's Law produces a vapor pressure curve with a maximum value at some composition other than pure A or B. If a mixture has a high vapor pressure it means that it will have a low boiling point. The molecules are escaping easily have to heat the mixture much to overcome the intermolecular attractions completely.

At ambient pressure the implication of this is that the boiling point/composition curve will have a minimum value lower than the boiling points of either A or B. In the case of mixtures of ethanol and water, this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C, compared with the boiling point of pure ethanol at 78.5°C, and water at 100°C.

Figure 5 shows the boiling point/composition curve for ethanol - water mixtures. In the same diagram, a vapor composition curve included.



Figure 5: The boiling point – composition diagram for EtOH – H2O system [20].

There is though a barrier. It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point, and the vapor composition is exactly the same as the liquid. It is known as a *constant boiling mixture* or an *azeotropic mixture* or an *azeotrope*.

3. Activity Coefficients

or

Liquid phase models were developed to determine the departure of a real mixture from the ideal behavior of low pressure VLE and LLE systems. These models are capable of representing adequately the excess Gibbs energy for a mixture through calculation of the activity coefficient γ_{ℓ} of each component [4]. The activity coefficient can be found from the excess Gibbs free energy G^{ℓ} defined as [24]:

$$\frac{G^{E}}{RT} = \sum n_{i} \ln \gamma_{i}$$
$$\frac{g^{E}}{RT} = \sum x_{i} \ln \gamma_{i}$$
(22)

where $g^E = \frac{G^E}{n_T}$ is the excess Gibbs free energy per mole of mixture (the molar excess Gibbs free energy), n_T is the total number of mole in the mixture.

3.1. Activity Coefficient Models

Wohl (1959) expressed the excess of free energy by Gibbs in a two-component solution by a power series of 'active' volume fractions of the two components, z_1 and z_2 :

$$\frac{G^E}{RT(q_1x_1+q_2x_2)} = 2 a_{12}z_1z_2 + 3 a_{112}z_1^2z_2 + 3 a_{122}z_1z_2^2 + \cdots$$
(23)

where:

$$Z_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \qquad \qquad Z_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$
(24)

qi: a measure of the size of the molecule i or the "sphere of influence" of the solution. *a*: interaction parameter with physical meaning similar to that of Virial rates. For example a_{12} illustrates interaction between two molecules, one of the substance 1 and one of substance 2, while the a_{122} illustrates the interaction of three molecules, one of substance 1 and two of substance 2.

The following two expressions, the van Laar and Margules equation, may be considered special cases of Eq. 23 although they were developed earlier.

3.1.1. Van Laar equation

For a binary system, which have different molar volumes, may be assumed that the interaction coefficients of more than two molecules are negligible. Then the expression of Wohl becomes:

$$\frac{G^E}{RT} = \frac{2 a_{12} \cdot x_1 \cdot x_2 \cdot q_1 \cdot q_2}{x_1 q_1 + x_2 q_2}$$
(25)

From this equation, the following expressions derive for activity coefficients:

$$ln\gamma_1 = \frac{A_{12}}{[1 + \frac{A_{12}x_1}{A_{21}x_2}]^2}$$
(26)

$$ln\gamma_2 = \frac{A_{12}}{[1 + \frac{A_{21}x_2}{A_{12}x_1}]^2}$$
(27)

where $A_{12} = 2 \cdot q_1 \cdot a_{12}$ and $A_{21} = 2 \cdot q_2 \cdot a_{12}$.

The binary interaction parameters can be calculated by using expressions (28) and (29).

$$A_{12} = \ln \gamma_1 \cdot \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right)^2$$
(28)

$$A_{21} = \ln \gamma_2 \cdot \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 \tag{29}$$

Expressions (30) and (31) are used for calculating the binary interaction parameters from the principle of infinite dilution.

$$\lim_{x_1 \to 0} \ln \gamma_1 = A_{12} \tag{30}$$

$$\lim_{x_2 \to 0} \ln \gamma_2 = A_{21} \tag{31}$$

3.1.2. Margules equation

If the sizes of the molecules of the components of a binary mixture are not very different, it may be assumed that $q_1 = q_2 = q$, and by neglecting interactions between more than three molecules, the following expressions are being derived for the coefficients activity:

$$ln\gamma_1 = A' x_2^2 + B' x_2^3$$
(32)

$$ln\gamma_2 = (A' + \frac{3}{2}B') x_1^2 + B' x_1^3$$
(33)

where $A' = q(2 a_{12} + 6a_{112} - 3a_{122})$ and $B' = q(6a_{122} - 6a_{112})$.

The estimation of the parameters in the equations of van Laar and Margules naturally requires experimental activity coefficients for the given binary system.

For this purpose, regression analysis is made for all data to get the values of the parameters that are giving better adaptation. It is of course possible the values of the parameters to result from a pair of experimental activity coefficients, by solving a system of two equations with two unknowns. Thus, for a given concentration x_1 , if the activity coefficients γ_1 and γ_2 are known, the following expressions derive for the parameters of the van Laar equation:

$$A = \left(1 + \frac{x_2}{x_1} \frac{ln\gamma_2}{ln\gamma_1}\right)^2 ln\gamma_1 \tag{34}$$

$$B = (1 + \frac{x_1}{x_2} \frac{ln\gamma_1}{ln\gamma_2})^2 ln\gamma_2$$
(35)

In a similar way, may be developed the expressions for Margules equation.

The two equations, although they are derived from the Wohl equation by different assumptions, they give very close results, because of their purely empirical characters and of the fact that they contain the same number of customizable parameters [3].

Margules and Van Laar equations fit to multiple points, which require regression of the parameters to optimize the fit. An advantage of these models is that they can be linearized for fitting of parameters. Also, their primary role is to provide semi-empirical models which have a greater degree of flexibility than equation of state models, owing to the greater number of adjustable parameters and their judicious choice such as both magnitude and skewness of the free energy curves can be accurately tuned [32]. On the other hand, an important disadvantage of Van Laar equation is that it is not easy extension to multicomponent systems and in its theoretical formulation predicts only positive deviation from Raoult's law [33].

Besides the easier procedures for evaluating the parameters, polynomial correlations have two advantages over other equations [34]:

- One or both of the parameters may be negative. Both Van Laar parameters must be of the same sign if data over the full concentration range are to be presented, and both parameters must be positive in equations that involve logarithms of composition.
- 2. Data that exhibit a maximum or minimum activity coefficient can be represented.

3.1.3. Wilson equation

Based on molecular considerations, Wilson (1964) presented the expression for the excess Gibbs energy of a binary solution:

$$\frac{g^E}{RT} = -x_1 ln(x_1 + \Lambda_{12} x_2) - x_2 ln(x_2 + \Lambda_{21} x_1)$$
(36)

The activity coefficients derived from equation (33) are:

$$ln\gamma_1 = -ln(x_1 + \Lambda_{12}x_2) + x_2(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2})$$
(37)

$$ln\gamma_{2} = -ln(x_{2} + \Lambda_{21}x_{1}) - x_{1}(\frac{\Lambda_{12}}{x_{1} + \Lambda_{12}x_{2}} - \frac{\Lambda_{21}}{\Lambda_{21}x_{1} + x_{2}})$$
(38)

In equation (36) the excess Gibbs energy is defined with the reference to an ideal solution in the sense of Raoult's law; Eq. (36) obeys the boundary condition that g^{E} vanishes as either x_1 or x_2 becomes zero.

Wilson's equation has two adjustable parameters Λ_{12} and Λ_{21} . In Wilson's derivation, these are related to the pure component molar volumes and to characteristic energy differences.

Wilson's equation has two disadvantages that are not serious for many applications. First, Eqs. (37) and (38) are not useful for systems where the logarithms of the activity coefficients, when plotted against x, exhibit maxima or minima. Such systems, however, are not common. The second and more serious disadvantage of Wilson's equation is substituted into the equations of thermodynamic stability for a binary system. No parameters Λ_{12} and Λ_{21} can be found that indicate the existence of two stable liquid phases. Therefore, the equation 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 [27].

3.1.4. NRTL equation

The nonrandom two-liquid (NRTL) model is utilized widely in phase equilibria calculations and employs three adjustable parameters (two interaction parameters and the non-randomness factor) that are determined through regression of experimental data for a specific binary vapor—liquid equilibrium (VLE) system. The two interaction parameters (A_{12} and A_{21}) account for the difference between the pure-component liquid interactions (A_{11} and A_{22}) and mixed-component liquid interactions (A_{12} and A_{21}). The main disadvantage of the NRTL model is the strong correlation between the two parameters of the model [27].

The NRTL equation for the excess Gibbs energy is:

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$$
(39)

Where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$
$$G_{12} = exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = exp(-\alpha_{12}\tau_{21}) \qquad (40)$$

The g_{ij} is an energy parameter characteristic of the *i-j* interactions. Parameter α_{12} is related to the nonrandomness in the mixture; when α_{12} is zero, the mixture is completely random and Eq. (39) reduces to the two suffix Margules equation.

From Eq. (39) the activity coefficients are:

$$ln\gamma_1 = x_2^2 [\tau_{21} (\frac{G_{21}}{x_2 + G_{12} x_2})^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}]$$
(41)

$$ln\gamma_{2} = x_{1}^{2} \left[\tau_{12} \left(\frac{G_{12}}{x_{2} + G_{12} x_{1}} \right)^{2} + \frac{\tau_{12} G_{21}}{\left(x_{2} + x_{1} G_{21} \right)^{2}} \right]$$
(42)

For moderately nonideal systems, the NRTL equation offers no advantages over the simpler van Laar and three-suffix Margules equation [27].

3.1.5. UNIQUAC equation

A critical examination of the derivation of the NRTL equation shows that this equation, like those obtained from Wohl's expansion is more suitable for h^{E} than g^{E} [28]. Further, because experimental data for typical binary mixtures are usually not sufficiently plentiful or precise to yield three meaningful binary parameters, attempts were 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 derived an equation that, in a sense, extends the quasichemical theory of Guggenheim for nonrandom mixtures to solutions containing molecules of different size. This extension was therefore called the universal quasi-chemical 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 that are responsible for the enthalpy of mixing. The combinatorial part is determined only by the composition and by the sizes and shapes of the molecules; it requires only pure component data. The residual part, however, depends also on intermolecular forces; the two adjustable binary parameters, therefore, appear only the residual part [28].

The UNIQUAC equation is:

$$\frac{g^{E}}{RT} = \left(\frac{g^{E}}{RT}\right)_{combinatorial} + \left(\frac{g^{E}}{RT}\right)_{residual} \tag{43}$$

3.1.6. UNIFAC equation

This is an extension of UNIQUAC with no adjustable parameters for the user to input or fit to experimental data. Instead, all of the adjustable parameters have been characterized by the developers of the model based on group contributions that correlate the data in a very large data base. The assumptions regarding coordination numbers, etc., are similar to the assumptions in UNIQUAC. The same strategy is applied,

$$\ln \gamma_k = \ln \gamma_k^{COMB} + \ln \gamma_k^{RES} \tag{44}$$

The combinatorial term is therefore identical and given by Eq. (44). The major difference between UNIFAC (short for UNIversal Functional Activity Coefficient model) and UNIQUAC is that, for the residual term, UNIFAC considers interaction energies between Functional groups (rather than the whole molecule). Interactions of functional groups are added to predict relative interaction energies of molecules. Full implementations of the UNIFAC method with large numbers of functional groups are typically available in chemical engineering process design software.

Although UNIFAC is closely related to UNIQUAC, there is no direct extension to a correlative equation like UNIQUAC. Also, fitting of experimental data cannot be done within the defined framework of UNIFAC; UNIQUAC is the preferred choice when adjustable parameters are desired [35].

3.2. Effect of temperature on Vapor-Liquid Equilibria

When *x-y* data are available at atmospheric pressure and an estimate of the *x-y* curve at reduced pressure is desired, the effect of temperature on the activity coefficients needs to be considered. There is a similar problem in the fitting of a van Laar or Margules equation to isopiestic data covering a big range of temperature, because the Gibbs-Duhem equation [24] and its integrated forms are valid only at constant temperature. The change of the activity coefficient with temperature is related to the relative partial molar enthalpy, *L*, by the thermodynamic equation:

$$\frac{d\ln\gamma_1}{dT} = -\frac{L_1}{RT^2}$$
(45)

 L_1 is the partial molar enthalpy of component 1 in solution minus the enthalpy of the pure liquid at the same temperature, and may be visualized as the heat absorbed on adding a mole of component 1 to an infinite quantity of solution. When heat is evolved on mixing two liquids, L is negative and the activity coefficient rises with the temperature.

The labor of calculating the effect of temperature on the x-y diagram is considerably reduced when the activity coefficient curves can be fitted with van Laar or Margules equations. These equations have been written in the form so that the constants are terminal values of log γ . Thus, the change of A and B with temperature may be related to L at $x_1 = 0$ and $x_1 = 1.0$, respectively.

An inspection of the values of *L* at infinite dilution calculated from heats of mixing liquids in the International Critical Tables reveals values as high as 2000 calories/mole for mixtures of organic liquids. For mixtures of alcohols with water, the partial molar enthalpy may reach 5000 calories/mole. Activity coefficients for systems of organic liquids, having either positive or negative deviations from Raoult's law, approach unity as the temperature rises and thus approach Raoult's law as a limit. For aqueous solutions the change is not so simple. Activity coefficients for immiscible systems with an upper critical solution temperature must decrease with rise in temperature.

To give an idea of the order of magnitude of the change in the activity coefficient with temperature, *a* change of 6 per cent in the activity coefficient results from a 30 °C temperature change with L = 500 calories/mole. If the left-hand side of the various equations had been written *RT* In γ instead of log γ , and the resulting parameters had been regarded as independent of temperature, the activity coefficients would approach unity as the temperature increased, agreeing with the general rule for organic liquids. Unfortunately, most of the available data on *L* have been measured only at room temperature, and there are indications that *L* changes rapidly with temperature [17].

3.3. Activity Coefficients at Infinite Dilution

The infinite dilution activity coefficient, also referred to as limiting activity coefficient is the limiting value of the activity coefficient of a solute when its concentration tends towards zero. Alessi et al. (1991) defined the infinite dilution region as one where each molecule of the solute is surrounded by molecules of the solvent only. Only solute-solvent interactions take place. This can be assumed for mole fractions ranging between 10^{-7} and 10^{-4} , depending on components under investigation. The infinite dilution region of solutions attracted much interest for couple of reasons underlining its great importance [23]:

- a) The system behavior in the very dilute regions is instrumental in obtaining high purity products;
- b) The most difficult and costly stage of a separation process is the removal of the last traces of impurity;
- c) The greatest departure from ideality occurs in the very dilute regions;

d) Environmental concerns are based on the very dilute regions in the gas phase which is air.

Sandler (1996) [36] discusses theoretical and practical applications of infinite dilution activity coefficient (IDAC) values in chemical and environmental engineering. The most important that is related to chemical engineering is the synthesis, design and optimization of separation processes [7].

Activity coefficients at infinite dilution ($\gamma \infty$) are important for:

- characterizing the behavior of liquid mixtures
- fitting g^E-model parameters (e.g. Margules, van Laar, Wilson, NRTL, UNIQUAC)
- predicting the existence of an azeotrope
- the estimation of mutual solubilities
- providing concise information for the statistical thermodynamics (no solutesolute interactions)
- analytical chromatographers
- screening solvents for extraction and extractive distillation processes
- the calculation of limiting separation factors necessary for the reliable design of distillation processes
- the calculation of Henry constants and partition coefficients
- the development of predictive methods (e.g. mod. UNIFAC (Do))

Several methods were developed for the measurement of γ^{∞} . The most important methods are: gas chromatography (GC), non-steady-state gas-liquid chromatography, differential ebulliometry, static methods and the dilutor method. Chromatographic methods allow the determination of γ^{∞} of volatile solutes in high and low boiling solvents. The dilutor method permits the determination of γ^{∞} in solvent mixtures. The addition of water to selective solvents (e.g. NMP + water) often increases the selectivity of the solvents used [5].

4. Methods for Determination of VLE

For a binary mixture, pressure and temperature fix the equilibrium vapor and liquid compositions. Thus, experimental data are frequently presented in the form of tables of vapor mole fractions y and liquid mole fraction x for one constituent over a range of temperature T and fixed pressure P or over a range of pressure for a fixed temperature.

For a nearly isobaric process, binary mixture data are frequently potted, for a fixed pressure, as y versus x, with a line of 45° slop included for reference, and as T versus y and x [2].

In all VLE measurements the system component must be of the highest possible purity. In the very dilute composition range, for example, any impurity in the component of high concentration competes with the added component is influencing system behavior. Some chemicals are difficult to purify to very high levels and thus, or for other reasons, may be very expensive. To cover the full composition range may require large amounts of the two components in either static or dynamic VLE apparatus, more so in the latter. Surprisingly, very few static or dynamic equipment types have been developed specifically to reduce chemical volume to a minimum [23].

Recirculation methods involve the closed-loop mechanically driven recirculation of one or more phases from one section of the equilibrium cell to another. Two different phase recirculation methods have been reported: single-phase and two-phase recirculation [24]. Schematic illustration of a typical phase recirculation method is shown in Figure 6.



Figure 6: Schematic illustration of the phase recirculation methods [19].

In principle VLE data can be determined with the dynamic or static method.

4.1. Dynamic equilibrium stills

In the dynamic equilibrium stills the mixture is brought to boil under controlled pressure. The vapor and liquid mixture is separated in the equilibrium chamber and the vapor phase is condensed and returned to the boiling chamber. The liquid phase formed in the equilibrium chamber is also circulated. The composition of the boiling liquid and the vapor change with time until a steady state is achieved [17]. The steady state represents the true equilibrium values or, in other words, one equilibrium step. The principle of a dynamic equilibrium still is presented in Figure 7 [19].



Figure 7: The principle of a dynamic equilibrium still [19].

The development of the dynamic still type apparatus can be considered to have reached the mature stage of progress [18]. The instrumentation can be purchased from a multitude of companies and assembling the apparatus is fast and easy. With these kinds of apparatuses it is possible to begin the experimental work quickly. The automation of these apparatuses also demands the automation of the sampling system, which can be achieved by circulating the samples. Pressure-regulation systems are commercially available at a reasonable price. With these apparatuses conditions are favorable for measuring one total composition at several pressures, though there is the difficulty to keep composition constant throughout sampling. In the end, follows the analysis of vapor and liquid samples. Adding and removing the components to change the total composition in the still are most easily done manually. One challenge that should be mentioned in the use of the automated apparatus is the possible need to adjust the heat input to the Cottrell pump. That happens for stabilizing the system temperature and obtaining a stable drop rate for liquid and condensate, indicating an appropriate circulation rate [19].

4.2. Static VLE apparatus

In the static method, the degassed components are fed to the equilibrium cell. The volume of the cell can either be controlled or uncontrolled. The temperature and pressure are regulated to assure that two phases are present. The runs carried out with this type of apparatus are most often isothermal. The content of the cell is agitated in order to shorten the equilibration time.

Samples are drawn from the liquid and vapor phases and analyzed, for example, with gas chromatography. These samples can also be drawn from sample circulation lines. The principles of the static method are presented in Figure 8.



Figure 8: The principles of a static VLE measurement apparatuses [19].

The challenging task is to ensure that the samples analyzed represent the equilibrium state. The problems that arise are associated with the partial condensation of the vapor phase and the partial vaporization of the liquid phase, during sampling and sample transfer. Another drawback of this type of apparatus is the time needed for producing one isotherm and the calibration of the analyzer. An advantage is that the results obtained can be tested with consistency tests [19]. It is possible to use a data consistency test, which holds at wide temperatures and pressure ranges. The data consistency test uses an empirical linear relationship holding between the logarithm the polarity exclusion factor, $In\beta$, and the logarithm of pressure, InP [29].

Static equilibrium cells in a variety of configurations have been widely used for VLE measurement. The static method can be subdivided into analytical methods, in which both vapor and liquid compositions are sampled and analyzed, and the synthetic method, for which no sampling of the phases is required.

The static analytical method is the most common of the static methods for VLE measurements. The solutions components are charged into the equilibrium cell. The liquid components may be flushed into the equilibrium cell by the volatile component or pumped in. The volatile component is usually supplied directly from its storage cylinder. High-boiling volatile components may have to be heated and pumped in by some compressor-type device (Mühlbauer, 1990 [37]). The content of the equilibrium cell is agitated to promote contact between the phases, thereby shortening the time taken to reach equilibrium. After equilibrium has been obtained, the temperature and pressure are recorded and samples of either the liquid or vapor or both are withdrawn from the equilibrium cell and their compositions analyzed. The equilibrium cell temperature and pressure are regulated to generate the required vapor-liquid equilibrium isothermal or isobaric phase diagrams [24].

4.3. Composition determination

The determination of composition is the most complex task: the devices needed are often expensive and there is no universal analytical device that is suitable for all components. Gas chromatography is used most often for the determination of the composition of phases. Other methods for composition determination, although seldom applied in VLE measurements, include mass spectrometry, various spectroscopic methods, and density and refractive measurement.

Calibration procedures for the analyzers are required for accurate analysis. Accurate gas chromatograph detector calibration remains a considerable problem for gas mixtures or for gas-liquid mixtures when reliable commercial standards are not available. For many systems the response-factor ratios are not constant over the entire mole fraction range, and their variation with concentration must be determined. However, in case of a use of standard solutions with different composition over the whole range of concentration, the response factor ratios should be correct. Overall, the calibration of the analyzers is being succeeded with the preparation of standard solution at the same conditions as the ones that the experiments are taking place.

4.4. Thermodynamic Consistency Test

One of the greatest arguments in favor of obtaining redundant data is the ability to assess the validity of the data by means of a thermodynamic consistency test. The consistency of the experimental data was examined to provide information on the thermodynamic plausibility or inconsistency and to recognize any deviations from ideality (by Raoult's Law) of the measured values [11].

4.4.1. The Interdependence of Activity Coefficients

All partial molar properties must satisfy the equation Gibbs-Duhem equation, which when is applied to the excess Gibbs free energy gives:

$$RT\sum x_i dln\gamma_i = V^E dP - S^E dT$$
(45)

where V^E, S^E is the excess molar volume and entropy of the mixture respectively, at a given temperature, pressure and composition. So the activity coefficients of the components of a mixture, that balances cannot be changed independently; they must verify Eq. (45) in order to be accepted thermodynamically. Subsequently it is examined how this correlation is used for the control of binary data.

By the integration of Eq. (45) for a binary system from $x_1 = 0.0$ till $x_1 = 1.0$ the following equations come up:

$$\int_{0}^{1} ln \frac{\gamma_{1}}{\gamma_{2}} dx_{1} = \int_{0}^{1} \frac{H^{E}}{RT^{2}} \frac{dT}{dx_{1}} dx_{1} \quad (P: \text{ constant})$$
(46)

$$\int_{0}^{1} ln \frac{\gamma_{1}}{\gamma_{2}} dx_{1} = \int_{0}^{1} \frac{V^{E}}{RT} \frac{dT}{dx_{1}} dx_{1} \quad (T: \text{ constant})$$
(47)

The estimation of the thermodynamic consistency of binary VLE data at constant temperature (isothermally) or pressure (isobaric) requires knowledge of the corresponding excess properties as a function of the composition. However, in the typical case, where such experimental information is not available, the second part of Eq. (46), (47) is set equal to zero. While this is an acceptable assumption for Eq. (47), it may not always apply to Eq. (46), especially for highly non-ideal mixtures [3].

4.4.2. Area Consistency Test

The method for estimating the thermodynamic consistency of binary data is referred as areas control (area test). For isothermally data, the consistency index (CI) is defined by the following equation:

$$CI = |\frac{A_p - A_n}{A_p + A_n}| \times 100$$
 (48)

where A_p , A_n are the areas over and below the $ln(\gamma 1/\gamma 2)$ plot, respectively, as shown in Figure 9, and is a measure of data quality. For isobaric data, a factor of their quality is the amount (CI-J), where J is given by:

$$J = 150 \frac{\Delta T}{T_{min}}, \qquad \Delta T = T_{max} - T_{min}$$
(49)

 T_{max} and T_{min} are the extremes of temperature for the binary system, including boiling points of the pure components and the azeotrope, if any, whereas the multiplier 150 is empirical and proposed by Herington based on typical data of heats of mixing (Prausnitz) [3].



Figure 9: Thermodynamic consistency check for a binary system [3].

CI values of less than 5, for isothermally conditions, and (CI-J) of less than 10, for isobaric conditions, indicate reliable data [3].

| Table 1: Ranking of typical VLE data for binary systems from literature according to |
|--|
| Thermodynamic Consistency Test (Silverman) [3]. |

| Data | Isothermally (CI) | lsobaric (Cl-J) |
|---------------|----------------------|--------------------|
| Good | <5 | <10 |
| Satisfactory | 5 - 15 | 10 - 20 |
| Low Precision | >15 | >20 |

5. Experimental Measurement of VLE

The following chapter describes the experimental setup as well as procedure used to determine the VLE of binary mixtures practically. Furthermore, the procedure is discussed in terms of calibration and reproducibility.

5.1. Setup for the determination of VLE

The measurements of vapor-liquid-equilibrium are performed with the apparatus VLE 602 (Figure 10) of the company i-Fischer Engineering GmbH, Waltbüttelbrunn (Germany). The VLE 602 can be used at atmospheric pressure,

1013.25 mbar abs., vacuum and overpressure conditions up to 4 bar abs. The operation procedure is based on the principle of the Circulation Method (Dynamic VLE Still).

- A part of the liquid mixture is evaporated by an electrical immersion heater (7) installed in the glass apparatus.
- The rising vapors transport also some part of boiling liquid (drops), and there is a very intensive phase exchange in a "contact tube", which is called "COTTRELL"-pump. The vapor-liquid mixture is separated in liquid and vapor in separation chamber (3). The design of the separation chamber prevents a transport of liquid in the vapor phase, which is condensed in a separate condenser (4).
- The status of equilibrium is reached by constant recycling of liquid phase and condensed vapor phase at simultaneous mixing of recirculated flow in the mixing chamber (6).
- The concentrations of recycled liquid phase and condensed vapor phase are measured at stationary conditions.



Figure 10: Scheme of the apparatus VLE 602 and the controller.
Apparatus

Controller

| 1 | Feed Vessel | 8 | Switch activating the sample |
|---|--------------------------|----|------------------------------|
| 2 | Vapor Temperature Sensor | | valves for liquid and vapor |
| | Pt-100 | | sampling |
| 3 | Condenser | 9 | Data input / Data selection |
| 4 | Sample Liquid Phase | | (push-turn-knob) |
| 5 | Sample Vapor Phase | 10 | Display: Heating power, |
| 6 | Mixing Chamber | | Vapor-Liquid Temperature, |
| 7 | Heater | | Pressure |

The circulation method requires relatively high solvent masses (large operation volume) compared to the static method, and the concentrations of both phases have to be measured. The advantage of the circulation method is the quick appearance of phase equilibrium with simultaneously exact measurement of the boiling temperature, measured by the Pt-100 for the vapor temperature.

5.2. Procedure for measuring a binary system at ambient pressure

A VLE apparatus is used to obtain samples for determining the composition of the vapor and liquid phases of binary mixtures that coexist at equilibrium. The composition of the mixtures is obtained from the refractive indices of the samples or from GC analysis.

The procedure followed for measuring a binary system is divided in three steps:

1. <u>Calibration of refractometer and gas chromatograph</u>

The two analyzers have some advantages and disadvantages when they are in use.

• Both analyzers need to be calibrated. Though, the refractometer is giving as a result, after the introduction of the sample, a refractive index and a calibration correlation needs to be done manually earlier. In comparison, the GC, after being calibrated, gives automatically the concentration that is found in the sample.

- For VLE procedure, the less volume of sample that is gathered, the most accurate the values would be and the procedure will be less disturbed. For the GC analysis a larger volume of samples than the suggested one must be collected. This fact may lead to inaccuracy at the reading of the sample. This inaccuracy is avoided with the analysis by a refractometer, because only 1-2 mL are enough to give the refractive index of the sample each time a measurement is taking place.
- For the measurement of phase equilibrium data (vapor-liquid equilibria, gas solubilities, dew points, critical data, etc.) at higher pressures an equilibrium cell with direct GC sampling data can be used.
- a. <u>Refractometer</u>

The models of the two different refractometers that were used during the experimental work are:

- i. DRG100T, A. Krüss Optronic GmbH, Germany
- ii. DRG301-95, A. Krüss Optronic GmbH, Germany

The refractive index is a function of temperature, the wavelength of the light source, and the substance which is being investigated. The refractometer is thermostated and uses an appropriate light source. Mixtures with known concentrations are being prepared for the binary system of interest and their refractive indices are measured as long as the ones of the pure components. (Usually, a few droplets are sufficient).

b. Gas Chromatograph

The GC that was used for current work is the Shimadzu GC-2010 Plus with AOC-5000 Auto-Injector, FID + TCD.

For each mixture that was under investigation, standard solutions were being created and injected in the GC and a method file for all samples was used loptimized for ABE solutions.

- Split: 20
- Sample Volume: 1 μL
- Line 1: DB1, Lenght: 30m, Inner Diameter: 0,32 mm, Film Thickness: 3,0 μm
- Line 2: Elite WAX ETR, Lenght: 30m, Inner Diameter: 0,32 mm, Film Thickness: 0,5 μm



Table 2: Temperature profile used for GC analysis.

2. <u>Operation of VLE apparatus</u>

In the beginning the ventilation of the apparatus is being checked by opening valves 17, 18, 19 and 20. After ventilation valves 17 and 18 are kept open during the whole experiment, for operation in ambient pressure. Afterwards the valve for the cooling water opens.

The VLE apparatus is first filled with approximately 110 ml of the lower boiling substance (via the feed opening). The liquid level in the reboiler has a major effect on the operation of the apparatus, and it has to be approximately 2 cm above the immersion heater. If the level is too high, the boiling mixture is raising up into the liquid and vapor phase chambers. The measured compositions of the liquid and vapor chamber are equal and do not represent the equilibrium. If the level is too low, almost no liquid is entering into the liquid phase chamber. In this case, the composition of the liquid phase chamber will stay the same all the time and does not represent the equilibrium.

After filling the apparatus correctly, the magnetic stirrer has to be started (usually to full operation). The electrical heater is turned on (set at 35%). To achieve equilibrium a time about 20-25 minutes is needed, for a complete liquid exchange in vapor and liquid phase chamber. Samples can be taken, if the vapor temperature remains constant (does not deviate more than 0.1). The boiling temperature is noted. Finally, samples from both

the liquid and vapor chamber are collected by using the sample valves and the refractive indices are measured.

Then an amount of the liquid through the bleed valve of the boiler (v. 21) has to be removed. This liquid is replaced with the same volume of the higher boiling substance. The system is left to operate until the boiling temperature reaches a constant value. Again the procedure for taking samples is taking place. Then the addition of higher boiling substances is repeated as many times as needed in order to cover a suitable concentration range for the binary system. The ambient pressure is measured by using a barometer at the beginning of the experiment.

3. <u>Shutdown procedure</u>

The heating power is reset to 0% and the electrical heater is turned off. After boiling has stopped, the magnetic stirrer is also turned off and the cooling water valve is closed. The apparatus is cooling down for approximately 20-30 minutes. Then the liquid from the boiler is removed.

5.3. Calibration for the operation of the apparatus

Initially, the binary system of Ethanol-Water is being measured for the determination of the operation conditions of the VLE 602 apparatus. The mixture is being tested in three different heating power sets:

- 1. At 15% of power of heating and the liquid level (in the evaporator) is located approximately 3-4 cm above the immersion heater.
- 2. At 20% of power of heating and the liquid level is located approximately in the half distance of the immersion heater and the column.
- 3. At 35% of power of heating and the liquid level is located approximately 3-4 cm above the immersion heater.

In the first conditions, it takes a lot of time for the system to come to equilibrium and for the boiling temperature to be stabilized. Also, the vapor sample that is being collected is not enough for the further analysis within a reasonable time frame. During the VLE procedure, there is a presence only of droplets in the exit of the bottom product and it is being observed that the boiling in the immersion heater in not smooth. In the second operating conditions, the observations are the same as above with the only difference that now there is a constant flow of the bottom product instead of droplets.

Finally, in the third operating set, the vapor sample is being condensed with the appearance of 1-2 droplets per second. There is a continuous flow of the residue, however, the boiling is not either smooth yet.

The results are shown in Figure 11. As obvious, results obtained from the third operation set also fits best to literature data. Thus, these operation conditions are selected for all further experiments.



Figure 11: Comparison of the three operating conditions for the binary system of ethanolwater at P = 0.986 bar.

5.4. Temperature calibration

After determining the operating conditions of the apparatus, the accuracy of the results is being tested by measuring the boiling temperature of the pure solvents that are going to be used. Also, we calculate a calibration line for the temperatures, because the indicator of the temperature is not calibrated by bought, and this calibration line gives us the values of $T_{b,exp}$. Results for observed boiling temperatures are given in Table 3. The values are plotted in Figure 12 to obtain a correlation for correcting measured data.

| Solvents | T _b (°C) (lit) | T _b (°C) (exp) |
|----------------|---------------------------|---------------------------|
| Butan – 2 – ol | 99.00 | 98.96 |
| Ethanol | 78.27 | 78.00 |
| Methanol | 64.65 | 64.56 |
| Water | 99.98 | 99.77 |
| Acetone | 56.20 | 56.10 |

Table 3: The literature, experimental and calculated values for pure solvents (p = 1.008 bar).

Therefore, the accuracy of the boiling temperature of each component is shown below:



Figure 12: Experimental temperature versus the one that is given by literature and calculated temperature by the equation that comes up from the data at P= 1.008 bar.

For all systems that were under investigation in current work the temperature, which was given from the controller of the apparatus at each sampling, was corrected by the linear equation that was resulted from Figure 12.

5.5. Reproducibility of Results

The analysis of the results was done, at the beginning, with the use of two refractometers, as it was referred, which are operated at in two different temperatures (at 20 °C and at 25 °C). The reason that two refractometers were used is for testing the reliability of both experimental results and instruments of analysis. After all measurements were completed, it was possible to show that the results are reproducible and equal to each other. Therefore, both analyzers are reliable for the experimental procedure.

Furthermore, the binary system of EtOH – Bu-2-OH was examined at different days and to test, if the results can be reproduced. The results from all runs are shown in Figure 13, revealing that obtained vapor liquid equilibria are all similar and close to the literature data, considering shlightly different pressure levels.





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From Figure 13, it can be safely concluded that for a binary system the combination of VLE apparatus and the refractometer gives reliable and repeatable results. Also, the boiling point for pure components matches totally to the literature given values.

6. Experimental Measurement of Phase Equilibrium Data

Measurements using the VLE procedure applying a Refractometer (R) and a Gas Chromatograph (GC) will be presented and discussed further in this chapter in terms of:

- 1. Analysis with two different instruments (refractometer and GC).
- Calculation of liquid and vapor compositions of binary mixtures in equilibrium (Refractometer = blue color, GC = orange color).
- 3. Calculation of activity coefficients.
- 4. Regression of binary interaction parameters for van Laar activity coefficient model.
- 5. Graphs and tables of the results to evaluate the accuracy of the measurements and comparison to available literature data.
- 6. Consistency tests to evaluate the results.

The interaction parameters A_{12} and A_{21} of the Van Laar activity coefficient model are computed by averaging the binary interaction parameters obtained from single equilibrium data sets are compared with those from literature and those calculated from the infinite dilution principle of Van Laar's model (see equations 29 and 30).

Afterwards the interaction parameters are used to back-calculate the vapor liquid equilibrium following equations 50 and 51. For each system under investigation the calculated values are compared to the experimental data.

$$\ln \gamma_1 = A_{12} \cdot \left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{50}$$

$$\ln \gamma_2 = A_{21} \cdot \left(\frac{A_{12}x_1}{A_{12}x_1 + A_{21}x_2}\right)^2 \tag{51}$$

All literature values for the comparison with experimental data were retrieved from:

• DECHEMA Chemistry Data Series [8]

The constants for the Antoine equation were taken from:

• Nist Chemistry WebBook [30]

The average pressure for all experiments was about 0.9946 bar.

6.1. Experimental results

6.1.1. Binary system Ethanol – Butan-2-ol

The system of only organic components is being tested based on alcohol mixtures, which are – although highly polar – expected to show lower deviations from ideal behavior. Since molecules in the binary system are similar, vapor-liquid equilibrium can be represented by Van Laar activity coefficient model. Figure 14 shows the experimental values that were obtained for the mixture of EtOH-Bu-2-OH from two different experimental days. The results from the analysis with the refractometer exhibit perfect fit to literature curves for both liquid and vapor phase. However, the data obtained from GC analysis show strong deviations at low EtOH concentration, whereas at higher EtOH content the results considerably improved.

Reason for this behavior might be the fact, that samples for the analysis with the refractometer are analyzed right after they are collected. However, samples that were collected for analyses via GC are kept in the refrigerator for a few days allowing evaporization of lower boiling component due to not tightly sealed vials.



Figure 14: T versus x,y for experimental values for the binary mixture of Ethanol – Butan-2-ol (p = 0.991 bar).

Table 4: Interaction parameters Van Laar's model for system EtOH – Bu-2-OH (R).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.277 | 0.210 | 0.1826 |
| A ₂₁ | 0.064 | 0.052 | 5.13E-02 |



Figure 15: x versus y for the binary mixture of Ethanol – Butan-2-ol. (R)

Although, they depend on the data set that is chosen, the interaction parameters (Table 4) obtained from data sets generated from measurement of refractive index are close to literature values and give good accuracy concerning the xy-plot and the literature curve (Figure 15).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.143 | 0.021 | 0.1826 |
| A ₂₁ | 0.097 | 0.008 | 5.13E-02 |

Table 5: Interaction parameters Van Laar's model for system EtOH – Bu-2-OH (GC).



Figure 16: x versus y for the binary mixture of Ethanol – Butan-2-ol. (GC)

Surprisingly, also data obtained from GC analysis give reasonable results for interaction parameters (Table 5) and the equilibrium plot (Figure 16). Just slightly deviations for middle EtOH observed. This might be caused of the problem that is mentioned, about the vaporization of the samples for the period they have remained in the refrigerator, although results fit well in face of poor experimental data from GC analysis.

6.1.2. Binary system Methanol – Ethanol

Next mixture that is being searched is the MeOH-EtOH. According to Figure 17 well-fitting results are obtained for both analyses. There are some outliers for both experimental values, but in general they fit well, although also here refractive index is determined immediately, while samples for GC analysis are stored. Obviously, in this case vials were better sealed during storage.



Figure 17: T versus x,y for the binary mixture of Methanol – Ethanol(p = 0.9987 bar).

From Figure 17 only a small deviation is observed at higher MeOH content. This may be caused by the fact that the pressure of the experiment is slightly lower than the 1.013 bar of literature data.

| Table 6: Interaction | parameters \ | Van Laar's | s model for | system | MeOH – | EtOH (R). |
|----------------------|--------------|------------|-------------|--------|--------|-----------|
| | | | | | | |

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | -0.172 | -0.026 | -0.1706 |
| A ₂₁ | 0.634 | 0.133 | 0.0845 |

According to Table 6 the interaction parameters for this system are negative. Both calculated and experimental xy data fit well to literature.



Figure 18: x versus y for the binary mixture of Ethanol – Methanol. (R)

Table 7: Interaction parameters Van Laar's model for system MeOH – EtOH (GC).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | -0.123 | -0.015 | -0.1706 |
| A ₂₁ | 0.035 | 0.184 | 0.0845 |



Figure 19: x versus y for the binary mixture of Ethanol – Methanol. (GC)

In Table 7 one of the interaction parameters is not negative as it was supposed to be according to literature and of what applies for Van Laar model indicating thermodynamic inconsistencies, although experimental VLE data fit well to literature. This fact might also lead to the outliers in the xy-plots in Figure 19.

6.1.3. Binary system Methanol – 2-Butanol

As with the data sets before, the experimental data for system methanol -2butanol are from different experimental days and as stated, the vials of samples for GC analysis were kept for some period of time.



Figure 20: T versus x,y for the binary mixture of Methanol – Butan-2-ol(p = 0.9979 bar).

There is small deviation in experimental data which may be caused again by evaporation losses for the lower boiling component due to storage.

Table 8: Interaction parameters Van Laar's model for system MeOH – Bu-2-OH (R).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | -0.257 | -0.153 | -3.75E-01 |
| A ₂₁ | -0.214 | -0.192 | -6.31E-02 |



Figure 21: x versus y for the binary mixture of Methanol – Butan-2-ol. (R)

The interaction parameters that were obtained from infinite dilution (refractive index) have big difference from literature values. This is underlined in Figure 21 since the calculated data from infinite dilution exhibit deviations. The obtained values for interaction parameters from infinite dilution based on GC data (Table 9) were calculated positive in contrast to literature data. This leads to the errors shown in Figure 22.

Table 9: Interaction parameters Van Laar's model for system MeOH – Bu-2-OH (GC).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | -0.236 | 0.467 | -3.75E-01 |
| A ₂₁ | -0.142 | 0.468 | -6.31E-02 |





6.1.4. Binary system Ethanol – Water

The aqueous system of Ethanol – Water was examined. Aqueous mixtures are expected to exhibit higher deviations from ideal behavior than binary alcohol mixtures. This is obvious from Figure 23 showing azeotropic behavior.





The liquid values from both, refractometer and GC, fit perfect to the literature data. However, deviations are observed for vapor data, especially near the azeotropic point, which cannot be exactly identified from the experimental data. For low till middle ethanol contents literature data are presented pretty well by the obtained experimental data.

| Table 10: Interaction | parameters | Van Laar's model | for system | $EtOH - H_2O$ | (R). |
|------------------------------|------------|------------------|------------|---------------|------|
|------------------------------|------------|------------------|------------|---------------|------|

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 1.3230 | 1.8290 | 1.7693 |
| A ₂₁ | 0.4710 | 0.8090 | 0.9409 |



Figure 24: x versus y for the binary mixture of Ethanol – Water. (R)

Table 11: Interaction parameters Van Laar's model for system EtOH – H₂O (GC).

| | Regression | Infinite | Literature [8] |
|------------------------|------------|----------|----------------|
| A ₁₂ | 1.1040 | 2.0750 | 1.7693 |
| A ₂₁ | 0.4790 | 0.8220 | 0.9409 |



Figure 25: x versus y for the binary mixture of Ethanol – Water. (GC)

6.1.5. Binary system Methanol – Water

Subsequently another aqueous system is being tested, this of $MeOH - H_2O$. The experimental results that were analyzed by the refractometer and the gas chromatograph came from different experimental run and once again the GC analysis was performed after storage. In Figure 26 the vapor and liquid data, which were calculated from the refractive indices, fit excellently to literature curves. Data obtained from GC measurements show higher deviations including obvious outliers at higher methanol content.



Figure 26: T versus x,y for the binary mixture of Methanol – Water (p = 0.99 bar).

One observation that was made for this mixture, during the experimental procedure, is that during measurement of refractive index at high concentration of methanol problems occurred. However, the deviations are significant only in vapor samples.

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.369 | 0.528 | 0.9141 |
| A ₂₁ | 0.219 | 0.404 | 0.5107 |



Figure 27: x versus y for the binary mixture of Methanol – Water. (R)

In Figure 27 calculated and experimental data fit almost perfectly to literature values. Although, it is an aqueous mixture the Van Laar model can predict accurately the behavior of the system.

Table 13: Interaction parameters Van Laar's model for system MeOH – H₂O (GC).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.430 | 0.974 | 0.9141 |
| A ₂₁ | 0.268 | 0.799 | 0.5107 |



Figure 28: x versus y for the binary mixture of Methanol – Water. (GC)

The results of the GC analysis do not fit as well as the refractometer's, but they exhibit deviation in medium and higher methanol contents. However, deviations only are visible with the experimental data.

6.1.6. Binary system Acetone – Ethanol

A mixture with volatile compound has been investigated to see how VLE procedure behaves when such systems are examined. In Figure 29 the experimental data of two different runs are presented and both of the samples that were collected after the experiment were analyzed immediately with refractometer and gas chromatograph, respectively.





The analysis with the refractometer gives many data which are diverged in all range of the temperatures of the mixture which are omitted from this figure. In general, the analysis with the refractometer needed more time than all the other analyses and it was hard to obtain one stable refractive index for each sample. This may results from the sensitivity of the refractometer in solvents with low refractive indices in parallel with the volatility of acetone. In contrast, GC data show an excellent fit. One reason for this fit is that the composition with gas chromatograph was determined right after the experiment. This figure show that the GC gives better results when volatile solvents are investigated since it does not have the same sensitivity as the refractometer.

Table 14: Interaction parameters Van Laar's model for system Acetone – EtOH (R).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.187 | 0.366 | 6.15E-01 |
| A ₂₁ | 0.082 | 0.068 | 4.49E-01 |



Figure 30: x versus y for the binary mixture of Acetone – Ethanol. (R)

As emphasized, the experimental values from refractive measurements did not expected to fit with literature. But it is surprising that the calculated values with Van Laar activity coefficient model predict xy data with excellent fit to literature.

Table 15: Interaction parameters Van Laar's model for system Acetone – EtOH (GC).

| | Regression | Infinite | Literature [8] |
|-----------------|------------|----------|----------------|
| A ₁₂ | 0.610 | 0.931 | 6.15E-01 |
| A ₂₁ | 0.849 | 0.329 | 4.49E-01 |





On the contrary, experimental data from GC analysis exhibit perfect fit as it was expected. Also, the calculated values from Van Laar produce perfect fitted data.

6.1.7. Binary system Acetone – Buta-2-nol

Finally, another acetone based mixture was investigated. This was due to having a variety of data and results when such mixtures are examined with VLE procedure. The results are not expected to show the best behavior since it was concluded from the results of Acetone-Ethanol system that the procedure is not accurate referring to a volatile solution. The data in Figure 32 were from the same experimental day and without storage of the samples before GC analysis.



Figure 32: T versus x,y for the binary mixture of Acetone – Butan-2-ol (p = 0.9931 bar).

The deviations that are shown in Figure 32 might be caused because of the nature of the mixture and not the procedure or the analysis. This can be explained from the similarity of results with two different analyzers. However, in case of acetone – ethanol mixtures GC analyses gives excellent results of the system composition as show via comparison with literature.

Table 16: Interaction parameters Van Laar's model for system Acetone – Bu-2-OH (R).

| | Regression | Infinite |
|-----------------|------------|----------|
| A ₁₂ | 0.648 | 0.069 |
| A ₂₁ | 0.239 | 0.027 |





| Table 17: Interaction | parameters | Van Laar's mo | odel for system | Acetone – | Bu-2-OH (| GC). |
|------------------------------|------------|---------------|-----------------|-----------|-----------|------|
|------------------------------|------------|---------------|-----------------|-----------|-----------|------|

| | Regression | Infinite |
|------------------------|------------|----------|
| A ₁₂ | 0.863 | 0.537 |
| A ₂₁ | 0.277 | 0.284 |



Figure 34: x versus y for the binary mixture of Ethanol – Water. (GC)

For the system of Acetone-Butan-2-ol there are not many literature data and the system has not been yet largely investigated. That is the reason that no literature interaction parameters for Van Laar's activity coefficient model were found. Concerning the results that are shown in Figures 33 and 34 there is a constant deviation from literature values but the experimental and calculated results seem to exhibit good behavior.

6.2. Consistency results

The value of the CI-J criteria is being calculated for all systems that have been investigated and it is shown in Tables 17 and 18:

| Binary mixtures | CI — J | Data |
|------------------------|--------|---------------------|
| ethanol – water | 4.1 | Good |
| ethanol – butan-2-ol | 9.3 | Good |
| methanol – water | 8.2 | Good |
| methanol – ethanol | 10.1 | Good – Satisfactory |
| methanol – butan-2-ol | 2.1 | Good |
| acetone – butan-2-ol | 15.5 | Satisfactory |
| acetone – ethanol | 12.9 | Satisfactory |

Table 18: Estimations for the consistency of experimental data by the analysis with therefractometer.

Table 19: Estimations for the consistency of experimental data by the analysis with the GC.

| Binary mixtures | CI — J | Data |
|------------------------|--------|---------------------|
| ethanol – water | 8.3 | Good |
| ethanol – butan-2-ol | 12.4 | Satisfactory |
| methanol – water | 11.2 | Satisfactory |
| methanol – ethanol | 6.1 | Good |
| methanol – butan-2-ol | 7.2 | Good |
| acetone – butan-2-ol | 10.0 | Good – Satisfactory |
| acetone – ethanol | 4.9 | Good |

The consistency test was made for evaluating the thermodynamic behavior of the experiments. The conclusion according to Tables 18 and 19 is that for all systems that were investigated the VLE procedure gives most of the times good or satisfactory results, but no experiment was of low precision or a total failure.

Furthermore, for acetone based systems the results from the analysis with a refractometer show satisfactory consistency as it was expected. But on the contrary, with the GC analysis in these solutions with meticulous experimental procedure and

instant analysis of the samples that will be collected, good results can be obtained. Although, the Van Laar activity coefficient model fails to calculate correctly the activity coefficients of the mixture.

7. Summary and Outlook

The objective of present work was to develop and test a procedure to measure the vapor – liquid equilibria of binary systems with the use of a VLE 602 Labodest apparatus. The composition of liquid and vapor phase, required for calculation of all the thermophysical properties of the mixtures, was examined with two analyzers, either gas chromatograph or a refractometer), calibrated with mixtures of known concentration. Also, there was the need of temperature calibration for the correct representation of equilibrium temperature.

The results that were obtained from the experimental procedure were firstly compared to literature data to see if they are performing good behavior according to already investigated values. For this reason *T-x-y* plots were built with all obtained values. The results can be divided into three subcategories due to the mixtures that were used. The alcohol mixtures, the aqueous mixtures and the systems with acetone. During the experimental procedure the alcohol mixtures were easier to deal with, the separation were succeeded smoother and in the majority of the runs there were only a few outliers. One problem observed was with pure methanol, when the analysis with a refractometer was made, because of its low refractive index. Other problem observed was with acetone, it was difficult with the refractometer to analyze the samples and predict the correct refractive index – especially in temperatures over 343 K –. Therefore, the analyses were carried out very carefully trying to collect a large set of results.

The experimental data collected was used to calculate the interaction parameters for Van Laar activity coefficient model. Coefficients are obtained by averaging parameters (regression method) calculated for single equilibrium data points by using the principle of infinite dilution.

Van Laar coefficients obtained from infinite dilution method and regression should follow the same trend. However, both of the methods overestimate or underestimate in some cases the Van Laar coefficients when compared to the literature values. Nevertheless, both the calculated and literature parameters produced almost identical curves on the x - y diagram indicating that the obtained parameter pair is of importance to successfully model the system under investigation.

Measurements of Vapor – Liquid Equilibrium are time-consuming and need a careful operation of the apparatus. A more elaborated instrumentation may support better results, e.g. introduction of a pressure equalizer into the exchange chamber, etc. The instrumentation is dependent on the temperature of the environment of the laboratory and the cold days condenses less vapor than warmer days. Also, for better and more accurate results the apparatus should run at least one round without taking measurements the day before performing the experiment. Furthermore, small amounts of mixture should be added and extracted during the experiment for maintaining the equilibrium into the separation chamber and to collect sufficient data points.

Summarizing, results show, that the apparatus and proposed procedure allow satisfactory determination of vapor - liquid equilibrium of binary organic and aqueous systems. The Van Laar activity coefficient model – despite of its simplicity – allows a good reproduction of x-y plots of the investigated systems based on regressed interaction parameters. Thus, both – apparatus and model – are suitable to be used for education and research purposes in the chemical engineering lab at TU Wien.

8. Nomenclature

Symbols

- A Constant in Antoine and Margules equations
- *A_{ij}* Binary Interaction Parameter between substances *i* and *j* in van Laar equation
- A_p Area over the ln(γ_1/γ_2) plot
- A_n Area below the ln(γ_1/γ_2) plot
- *B* Constant in Antoine equation
- C Constant in Antoine equation
- CI Consistency Index
- CI-J Factor of quality, for isobaric data
- f Mixture fugacity (atm)
- f_i^L Liquid Phase Fugacity of pure component *I* (atm)
- f_i^G Vapor Phase Fugacity of pure component / (atm)
- g^{E} Molar excess Gibbs free energy $(\frac{J}{mole})$
- G Gibbs free energy (J)
- G^{E} Excess Gibbs free energy (J)
- H^{E} Excess Enthalpy $(\frac{kJ}{kg})$
- L_i Partial Molar Enthalpy of component *i* in solution minus the enthalpy of the pure liquid at the same temperature $(\frac{J}{mole})$
- P Pressure (bar)
- *P_i* Partial Pressure of component *i* (bar)
- p_i^0 Vapor Pressure of Pure component (bar)
- *q*_i Molecular size parameter, UNIQUAC and UNIFAC equations

g_{ij} Energy parameter characteristic of the *i-j* interactions

R Ideal gas constant
$$\left(\frac{bar \cdot cm^3}{mole \cdot K}\right)$$

- S^{E} Entropy of mixing $\left(\frac{J}{K}\right)$
- T Temperature (^oC or K)
- *T_b* Boiling temperature (°C)
- $V^{\mathcal{E}}$ Excess Molar Volume $(\frac{cm^3}{mole})$

$$V_i^G$$
 Partial Molar Volume ($\frac{cm^3}{mole}$)

 x_i Mole fraction of component *i* in liquid phase $\left(\frac{mole}{mole}\right)$ y_i Mole fraction of component *i* in vapor phase $\left(\frac{mole}{mole}\right)$

Subscripts

- exp experimental
- cal calculated
- lit literature

Greek letters

- *α*_{ij} Measure of interactions in various groups of molecules and empirical constant in Wohl equation
- *y_i* Activity Coefficient of component *i*

 ΔH_{vap} Enthalpy of vaporization $\left(\frac{J}{mole}\right)$

Λ_{ij} Constants in Wilson equation

$$\mu$$
 Partial molar free energy ($\frac{Energy}{mole}$)

- τ_{ij} Empirical constants in NRTL and UNIQUAC equations
- *Φ* Fugacity Coefficient

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Appendix

Tables of results

The red highlighted values in tables are for omitted data that were outliers.

Table 1: Experimental data for the composition of the mixture Ethanol – Butan-2-ol for reproducibility testing.

| T (°C) p = 0.981 bar | 1x (mol/mol) | 1y (mol/mol) | T (°C) p = 1.001 bar | 2x (mol/mol) | 2y (mol/mol) |
|-------------------------|-----------------|-----------------|-------------------------|-----------------|-----------------|
| 78.00 | 1.0000 | 1.0000 | 98.96 | 0 | 0.0515 |
| 78.02 | 0.9816 | 0.9799 | 98.57 | 0.1379 | 0.2569 |
| 78.40 | 0.9514 | 0.9551 | 95.17 | 0.2462 | 0.3918 |
| 79.33 | 0.8822 | 0.9365 | 92.51 | 0.4122 | 0.5756 |
| 80.43 | 0.8052 | 0.9009 | 88.21 | 0.5296 | 0.6949 |
| 82.00 | 0.7037 | 0.8380 | 85.68 | 0.6079 | 0.7556 |
| 83.71 | 0.5897 | 0.7608 | 84.05 | 0.6711 | 0.8039 |
| 85.52 | 0.5038 | 0.6824 | 82.77 | 0.7276 | 0.8561 |
| 86.79 | 0.4314 | 0.6089 | 81.72 | 0.7695 | 0.8922 |
| 88.20 | 0.3778 | 0.5371 | 80.95 | 0.8516 | 0.9169 |
| 89.38 | 0.3259 | 0.5010 | 79.88 | 0.8922 | 0.9551 |
| 90.69 | 0.2901 | 0.4286 | 79.15 | 0.9371 | 0.9820 |
| 93.27 | 0.2166 | 0.3405 | 78.67 | 0.9461 | 0.9820 |
| 92.75 | 0.2233 | 0.3491 | 78.40 | 0.9775 | 0.9843 |
| 94.25 | 0.1811 | 0.2870 | 78.20 | 1.0000 | 0.9820 |
| 95.00 | 0.1619 | 0.2654 | 78.00 | 1.0000 | 1.0000 |
| 96.12 | 0.1093 | 0.2027 | | | |
| 98.17 | 0.0631 | 0.1282 | | | |
| 98.96 | 0.0000 | 0.0000 | | | |

| T (°C) | 3x | Зу | T (°C) | 4 x | 4y |
|---------------|-----------|-----------|---------------|------------|-----------|
| p = 1.002 bar | (mol/mol) | (mol/mol) | p = 1.008 bar | (mol/mol) | (mol/mol) |
| 77.60 | 1.0000 | 1.0000 | 77.55 | 1.0000 | 1.0000 |
| 77.94 | 0.9764 | 0.9917 | 78.65 | 0.9456 | 0.9876 |
| 78.82 | 0.9190 | 0.9587 | 79.83 | 0.8564 | 0.9413 |
| 80.44 | 0.8968 | 0.9091 | 81.54 | 0.7433 | 0.8719 |
| 83.05 | 0.6636 | 0.8147 | 83.57 | 0.6311 | 0.7997 |
| 84.86 | 0.5482 | 0.7352 | 85.23 | 0.5477 | 0.7337 |
| 86.78 | 0.4565 | 0.6418 | 87.04 | 0.4697 | 0.6543 |
| 89.26 | 0.3635 | 0.5288 | 89.12 | 0.3882 | 0.5671 |
| 92.24 | 0.2559 | 0.3948 | 90.30 | 0.3409 | 0.5051 |
| 93.18 | 0.2199 | 0.3520 | 91.71 | 0.2945 | 0.4361 |
| 94.21 | 0.1619 | 0.2839 | 93.67 | 0.2039 | 0.3339 |
| 95.08 | 0.1498 | 0.2399 | 95.12 | 0.1509 | 0.2643 |
| 96.39 | 0.1189 | 0.1956 | 96.38 | 0.1076 | 0.1997 |
| 97.18 | 0.0823 | 0.1282 | 97.10 | 0.1175 | 0.1509 |
| 97.92 | 0.0392 | 0.0881 | 97.90 | 0.0655 | 0.0974 |
| 98.96 | 0.0000 | 0.0000 | 98.96 | 0.0000 | 0.0000 |

I. Ethanol – Butan-2-ol

Table 2: The molar fractions from the analysis with the refractometer for the binary systemEthanol – Butan-2-ol (p = 0.991 bar).

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 78.25 | 1.0000 | 1.0000 |
| 2 | 78.64 | 0.9868 | 0.9912 |
| 3 | 79.57 | 0.9078 | 0.9690 |
| 4 | 80.68 | 0.8274 | 0.9284 |
| 5 | 82.26 | 0.7276 | 0.8609 |
| 6 | 83.99 | 0.6155 | 0.7833 |
| 7 | 85.81 | 0.5268 | 0.7069 |
| 8 | 87.09 | 0.4478 | 0.6348 |
| 9 | 88.51 | 0.3868 | 0.5618 |
| 10 | 89.70 | 0.3260 | 0.5239 |
| 11 | 91.02 | 0.2837 | 0.4446 |
| 12 | 93.62 | 0.1978 | 0.3432 |
| 13 | 93.09 | 0.2056 | 0.3534 |

| 14 | 94.60 | 0.1582 | 0.2801 |
|----|-------|--------|--------|
| 15 | 95.36 | 0.1377 | 0.2546 |
| 16 | 96.49 | 0.0868 | 0.1821 |
| 17 | 98.55 | 0.0513 | 0.1041 |

Table 3: The molar fractions from the analysis with the GC for the binary system Ethanol –Butan-2-ol.

| Sample | T (°C) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 79.75 | 0.8656 | 0.9422 |
| 2 | 81.57 | 0.7369 | 0.8705 |
| 3 | 83.46 | 0.6223 | 0.7891 |
| 4 | 85.18 | 0.4844 | 0.7066 |
| 5 | 86.96 | 0.3804 | 0.6196 |
| 6 | 88.69 | 0.2895 | 0.5176 |
| 7 | 89.96 | 0.2255 | 0.4265 |
| 8 | 91.28 | 0.1754 | 0.3225 |
| 9 | 91.90 | 0.1542 | 0.2833 |
| 10 | 92.69 | 0.1209 | 0.2463 |
| 11 | 93.86 | 0.0827 | 0.1640 |
| 12 | 95.99 | 0.0348 | 0.0727 |
| 13 | 96.80 | 0.0201 | 0.0430 |
| 14 | 98.27 | 0.0026 | 0.0066 |

Table 4: The experimental data for binary system ethanol – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experimental | | | Calculated from Regression | Calculated from Infinite dilution |
|--------------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.0000 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.9868 | 0.9912 | 0.1 | 0.13 | 0.19 |
| 0.9078 | 0.9690 | 0.2 | 0.36 | 0.36 |
| 0.8274 | 0.9284 | 0.3 | 0.49 | 0.49 |
| 0.7276 | 0.8609 | 0.4 | 0.60 | 0.60 |

| 0.6155 | 0.7833 | 0.5 | 0.69 | 0.69 |
|--------|--------|-----|------|------|
| 0.5268 | 0.7069 | 0.6 | 0.77 | 0.77 |
| 0.4478 | 0.6348 | 0.7 | 0.84 | 0.84 |
| 0.3868 | 0.5618 | 0.8 | 0.90 | 0.90 |
| 0.3260 | 0.5239 | 0.9 | 0.95 | 0.95 |
| 0.2837 | 0.4446 | 1.0 | 1.00 | 1.00 |
| 0.1978 | 0.3432 | | | |
| 0.2056 | 0.3534 | | | |
| 0.1582 | 0.2801 | | | |
| 0.1377 | 0.2546 | | | |
| 0.0868 | 0.1821 | | | |
| 0.0513 | 0.1041 | | | |
| | | | | |

 Table 5: The experimental data for binary system ethanol – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experime | Calcu fro Regro | ılated om ession | Calculated from Infinite dilution | |
|----------|-----------------------|------------------------|--|------------|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.8656 | 0.9422 | 0 | 0.00 | 0.00 |
| 0.7369 | 0.8705 | 0.1 | 0.13 | 0.19 |
| 0.6223 | 0.7891 | 0.2 | 0.37 | 0.36 |
| 0.4844 | 0.7066 | 0.3 | 0.50 | 0.49 |
| 0.3804 | 0.6196 | 0.4 | 0.60 | 0.60 |
| 0.2895 | 0.5176 | 0.5 | 0.69 | 0.69 |
| 0.2255 | 0.4265 | 0.6 | 0.77 | 0.77 |
| 0.1754 | 0.3225 | 0.7 | 0.84 | 0.84 |
| 0.1542 | 0.2833 | 0.8 | 0.90 | 0.90 |
| 0.1209 | 0.2463 | 0.9 | 0.95 | 0.95 |
| 0.0827 | 0.1640 | 1 | 1.00 | 1.00 |
| 0.0348 | 0.0727 | | | |
| 0.0201 | 0.0430 | | | |
| 0.0026 | 0.0066 | | | |

Table 6: The experimental and the calculated activity coefficients by two different methodsfrom the analysis with the refractometer for the binary system Ethanol – Butan-2-ol.

| Experimental | | | | Calc fr Regr | ulated om ession | Calcu from I dilu | lated nfinite tion | |
|--------------|-------|-------|------------|--------------------|------------------------|-------------------------|--------------------------|--|
| X 1 | Υı | Υ2 | X 1 | Υ ₁ | Υ2 | Υ1 | Υ2 | |
| 0.9868 | 0.971 | 1.508 | 0.1 | 1.01 | 1.00 | 1.27 | 1.00 | |
| 0.9078 | 0.995 | 0.731 | 0.2 | 1.01 | 1.00 | 1.23 | 1.00 | |
| 0.8274 | 1.002 | 0.859 | 0.3 | 1.01 | 1.00 | 1.18 | 1.00 | |
| 0.7276 | 0.994 | 0.989 | 0.4 | 1.01 | 1.00 | 1.14 | 1.00 | |
| 0.6155 | 1.000 | 1.015 | 0.5 | 1.01 | 1.00 | 1.10 | 1.00 | |
| 0.5268 | 1.104 | 1.034 | 0.6 | 1.01 | 1.00 | 1.07 | 1.00 | |
| 0.4478 | 1.088 | 1.048 | 0.7 | 1.01 | 1.00 | 1.04 | 1.00 | |
| 0.3868 | 1.094 | 1.069 | 0.8 | 1.01 | 1.00 | 1.02 | 1.00 | |
| 0.3260 | 1.117 | 1.007 | 0.9 | 1.01 | 1.01 | 1.01 | 1.01 | |
| 0.2837 | 1.321 | 1.049 | | | | | | |
| 0.1978 | 0.955 | 1.001 | | | | | | |
| 0.2056 | 0.964 | 1.015 | | | | | | |
| 0.1582 | 1.005 | 1.006 | | | | | | |

0.1377

0.0868

1.022

1.115

0.988

0.981

Table 7: The experimental and the calculated activity coefficients by two different methods from the analysis with the GC for the binary system Ethanol – Butan-2-ol.

| Experimental | | | | Calculated from Regression | | Calculated from Infinite dilution | | |
|--------------|-------|-------|------------|----------------------------------|------|---|------|--|
| X 1 | ۲1 | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 | |
| 0.8656 | 1.008 | 0.927 | 0.1 | 1.11 | 1.00 | 1.01 | 1.00 | |
| 0.7369 | 1.019 | 0.981 | 0.2 | 1.08 | 1.01 | 1.01 | 1.01 | |
| 0.6223 | 1.017 | 1.028 | 0.3 | 1.06 | 1.01 | 1.00 | 1.01 | |
| 0.4844 | 1.096 | 0.975 | 0.4 | 1.04 | 1.02 | 1.00 | 1.02 | |
| 0.3804 | 1.144 | 0.977 | 0.5 | 1.02 | 1.04 | 1.00 | 1.04 | |
| 0.2895 | 1.178 | 1.008 | 0.6 | 1.01 | 1.05 | 1.00 | 1.05 | |
| 0.2255 | 1.189 | 1.045 | 0.7 | 1.01 | 1.06 | 1.00 | 1.06 | |
| 0.1754 | 1.101 | 1.100 | 0.8 | 1.00 | 1.07 | 1.00 | 1.07 | |
| 0.1542 | 1.076 | 1.107 | 0.9 | 1.00 | 1.09 | 1.00 | 1.09 | |
| 0.1209 | 1.159 | 1.086 | | | | | | |
| 0.0827 | 1.083 | 1.103 | | | | | | |
| 0.0348 | 1.057 | 1.072 | | | | | | |
| 0.0201 | 1.051 | 1.057 | | | | | | |
| 0.0026 | 1.257 | 1.020 | | | | | | |

II. Methanol – Ethanol

| Sample | T (°C) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 65.42 | 0.8562 | 0.9128 |
| 2 | 66.25 | 0.7968 | 0.8678 |
| 3 | 67.11 | 0.6547 | 0.7559 |
| 4 | 69.17 | 0.5413 | 0.6547 |
| 5 | 70.94 | 0.4851 | 0.5439 |
| 6 | 72.54 | 0.3624 | 0.4795 |
| 7 | 73.38 | 0.3222 | 0.4035 |
| 8 | 74.04 | 0.2502 | 0.3118 |
| 9 | 74.78 | 0.2234 | 0.2834 |
| 10 | 75.28 | 0.1799 | 0.2464 |
| 11 | 75.79 | 0.1266 | 0.1879 |
| 12 | 76.39 | 0.1390 | 0.1059 |
| 13 | 76.80 | 0.0000 | 0.0686 |
| 14 | 77.15 | 0.0768 | 0.0480 |
| 15 | 77.39 | 0.0645 | 0.0645 |
| 16 | 77.58 | 0.8562 | 0.9128 |

Table 8: The molar fractions from the analysis with the refractometer for the binary systemMethanol – Ethanol (p = 0.9987 bar).

Table 9: The molar fractions from the analysis with the GC for the binary system Methanol –Ethanol.

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 64.18 | 0.9396 | 1.0000 |
| 2 | 65.88 | 0.8303 | 0.9137 |
| 3 | 67.57 | 0.6978 | 0.7939 |
| 4 | 69.13 | 0.5839 | 0.7038 |
| 5 | 70.48 | 0.4958 | 0.6112 |
| 6 | 71.85 | 0.4169 | 0.5167 |
| 7 | 73.70 | 0.2924 | 0.3882 |
| 8 | 74.49 | 0.2353 | 0.3201 |
| 9 | 75.01 | 0.1963 | 0.2754 |
| 10 | 75.47 | 0.1692 | 0.2319 |

| 11 | 75.90 | 0.1380 | 0.1513 |
|----|-------|--------|--------|
| 12 | 76.25 | 0.1274 | 0.1417 |
| 13 | 76.51 | 0.0957 | 0.0390 |
| 14 | 76.92 | 0.0077 | 0.0703 |
| 15 | 77.17 | 0.0001 | 0.0534 |
| 16 | 77.60 | 0.0000 | 0.0010 |

 Table 10: The experimental data for binary system methanol – ethanol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experin | nental | | Calculated from Regression | Calculated from Infinite dilution | |
|---------|--------|------------|----------------------------------|--|--|
| Liquid | Vapor | X 1 | y 1 | y 1 | |
| 0.8562 | 0.9128 | 0.0 | 0.00 | 0.00 | |
| 0.7968 | 0.8678 | 0.1 | 0.14 | 0.16 | |
| 0.6547 | 0.7559 | 0.2 | 0.27 | 0.30 | |
| 0.5413 | 0.6547 | 0.3 | 0.39 | 0.43 | |
| 0.4851 | 0.5439 | 0.4 | 0.51 | 0.54 | |
| 0.3624 | 0.4795 | 0.5 | 0.61 | 0.64 | |
| 0.3222 | 0.4035 | 0.6 | 0.71 | 0.74 | |
| 0.2502 | 0.3118 | 0.7 | 0.81 | 0.82 | |
| 0.2234 | 0.2834 | 0.8 | 0.89 | 0.89 | |
| 0.1799 | 0.2464 | 0.9 | 0.96 | 0.96 | |
| 0.1266 | 0.1879 | 1.0 | 1.00 | 1.00 | |
| 0.1390 | 0.1059 | | | | |
| 0.0000 | 0.0686 |] | | | |
| 0.0768 | 0.0480 |] | | | |
| 0.0645 | 0.0645 |] | | | |

Table 11: The experimental data for binary system methanol – ethanol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experii | mental | | Calculate d from Regressio n | Calculated from Infinite dilution |
|---------|--------|------------|---------------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.9396 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.8303 | 0.9137 | 0.1 | 0.12 | 0.15 |
| 0.6978 | 0.7939 | 0.2 | 0.00 | 0.05 |
| 0.5839 | 0.7038 | 0.3 | 0.26 | 0.36 |
| 0.4958 | 0.6112 | 0.4 | 0.49 | 0.51 |
| 0.4169 | 0.5167 | 0.5 | 0.61 | 0.62 |
| 0.2924 | 0.3882 | 0.6 | 0.71 | 0.71 |
| 0.2353 | 0.3201 | 0.7 | 0.80 | 0.79 |
| 0.1963 | 0.2754 | 0.8 | 0.87 | 0.87 |
| 0.1692 | 0.2319 | 0.9 | 0.94 | 0.94 |
| 0.1380 | 0.1513 | 1.0 | 1.00 | 1.00 |
| 0.1274 | 0.1417 | | | |
| 0.0957 | 0.0390 | | | |
| 0.0077 | 0.0703 | | | |
| 0.0001 | 0.0534 | | | |

 Table 12: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the refractometer for the binary system Methanol – Ethanol.

0.0010

0.0000

| Experimental | | | Calco fr Regr | ulated om ession | Calcu fro Infii dilu | lated om nite tion | |
|--------------|-------|-------|---------------------|------------------------|-------------------------------|-----------------------------|------|
| X 1 | Υı | Υ2 | X 1 | Υ ₁ | Υ2 | ٢1 | Υ2 |
| 0.8562 | 0.999 | 1.143 | 0.1 | 0.85 | 1.00 | 0.85 | 1.00 |
| 0.7968 | 0.978 | 0.977 | 0.2 | 0.86 | 1.00 | 0.86 | 1.00 |
| 0.6547 | 0.966 | 1.010 | 0.3 | 0.87 | 0.99 | 0.87 | 0.99 |
| 0.5413 | 0.946 | 1.006 | 0.4 | 0.88 | 0.99 | 0.88 | 0.99 |
| 0.4851 | 0.927 | 0.994 | 0.5 | 0.90 | 0.97 | 0.90 | 0.97 |

| 0.3624 | 0.809 | 1.095 | 0.6 | 0.92 | 0.95 | 0.92 | 0.95 |
|--------|-------|-------|-----|------|------|------|------|
| 0.3222 | 0.925 | 0.975 | 0.7 | 0.94 | 0.91 | 0.94 | 0.91 |
| 0.2502 | 0.854 | 1.023 | 0.8 | 0.96 | 0.84 | 0.96 | 0.84 |
| 0.2234 | 0.827 | 1.036 | 0.9 | 0.99 | 0.73 | 0.99 | 0.73 |
| 0.1799 | 0.827 | 1.020 | | | | | |
| 0.1266 | 0.876 | 0.995 | | | | | |
| 0.1390 | 0.929 | 0.983 | | | | | |
| 0.0000 | 0.470 | 1.080 | | | | | |
| 0.0768 | | 0.956 | | | | | |
| 0.0645 | 0.377 | 1.048 | | | | | |

 Table 13: The experimental and the calculated activity coefficients by two different methods from the analysis with the GC for the binary system Methanol – Ethanol.

| Experimental | | | Calculated from Regression | | Calculated from Infinite dilution | | |
|--------------|-------|-------|----------------------------------|------|---|------|-------|
| X 1 | Υı | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 |
| 0.9396 | 1.058 | 0.000 | 0.1 | 0.71 | 1.02 | 0.99 | 1.02 |
| 0.8303 | 1.024 | 0.832 | 0.2 | 0.00 | 10.52 | 0.99 | 10.52 |
| 0.6978 | 0.991 | 1.038 | 0.3 | 0.64 | 1.33 | 0.99 | 1.33 |
| 0.5839 | 0.989 | 1.014 | 0.4 | 0.94 | 1.11 | 0.99 | 1.11 |
| 0.4958 | 0.961 | 1.038 | 0.5 | 0.98 | 1.07 | 0.99 | 1.07 |
| 0.4169 | 0.918 | 1.054 | 0.6 | 0.99 | 1.05 | 0.99 | 1.05 |
| 0.2924 | | 1.020 | 0.7 | 1.00 | 1.05 | 0.99 | 1.05 |
| 0.2353 | 1.107 | 1.015 | 0.8 | 1.00 | 1.04 | 0.99 | 1.04 |
| 0.1963 | 1.074 | 1.008 | 0.9 | 1.00 | 1.04 | 1.00 | 1.04 |
| 0.1692 | 1.053 | 1.015 | | | | | |
| 0.1380 | 1.071 | 1.062 | | | | | |
| 0.1274 | 0.747 | 1.046 | | | | | |
| 0.0957 | 0.922 | 1.119 | | | | | |
| 0.0077 | 3.121 | 0.970 | | | | | |

III. Methanol – Butan-2-ol

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 64.51 | 1.0000 | 1.0000 |
| 2 | 65.32 | 0.8546 | 0.8985 |
| 3 | 67.36 | 0.7674 | 0.8308 |
| 4 | 69.87 | 0.6327 | 0.8072 |
| 5 | 71.98 | 0.5612 | 0.7578 |
| 6 | 75.23 | 0.4042 | 0.6891 |
| 7 | 77.8 | 0.3060 | 0.6581 |
| 8 | 80.24 | 0.2742 | 0.5612 |
| 9 | 82.52 | 0.2000 | 0.4918 |
| 10 | 86.88 | 0.1547 | 0.4040 |
| 11 | 89.17 | 0.1115 | 0.4011 |
| 12 | 90.69 | 0.0825 | 0.4004 |
| 13 | 91.76 | 0.0726 | 0.4008 |
| 14 | 92.02 | 0.0559 | 0.4023 |
| 15 | 94.16 | 0.0423 | 0.2804 |
| 16 | 95.89 | 0.0334 | 0.1846 |
| 17 | 96.46 | 0.0227 | 0.1257 |
| 18 | 98.04 | 0.0185 | 0.0678 |
| 19 | 98.79 | 0.0143 | 0.0378 |
| 20 | 99.03 | 0.0143 | 0.0291 |
| 21 | 99.77 | 0.0000 | 0.0000 |

Table 14: The molar fractions from the analysis with the refractometer for the binary systemMethanol – Butan-2-ol (p = 0.9979 bar).

 Table 15: The molar fractions from the analysis with the refractometer for the binary system

 Methanol – Butan-2-ol.

| Sample | T (°C) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 64.09 | 0.8301 | 0.8241 |
| 2 | 69.92 | 0.6480 | 0.7551 |
| 3 | 73.82 | 0.5116 | 0.7303 |
| 4 | 77.00 | 0.4098 | 0.6701 |
| 5 | 79.91 | 0.3206 | 0.6241 |
| 6 | 82.71 | 0.2307 | 0.5889 |

| 7 | 85.62 | 0.1724 | 0.5429 |
|----|-------|--------|--------|
| 8 | 89.00 | 0.0982 | 0.4543 |
| 9 | 91.03 | 0.0715 | 0.4082 |
| 10 | 92.75 | 0.0482 | 0.3419 |
| 11 | 94.07 | 0.0331 | 0.2579 |
| 12 | 95.22 | 0.0197 | 0.2317 |
| 13 | 96.04 | 0.0092 | 0.1914 |
| 14 | 96.77 | 0.0031 | 0.1499 |
| 15 | 97.77 | 0.0000 | 0.0905 |
| 16 | 98.09 | 0.0000 | 0.0000 |
| 17 | 98.47 | 0.0000 | 0.8241 |
| 18 | 99.04 | 0.0000 | 0.7551 |

 Table 16: The experimental data for binary system methanol – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experim | nental | | Calculated from Regressio n | Calculated from Infinite dilution |
|---------|--------|------------|--------------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.0000 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.8546 | 0.8985 | 0.1 | 0.24 | 0.31 |
| 0.7674 | 0.8308 | 0.2 | 0.44 | 0.51 |
| 0.6327 | 0.8072 | 0.3 | 0.59 | 0.65 |
| 0.5612 | 0.7578 | 0.4 | 0.71 | 0.74 |
| 0.4042 | 0.6891 | 0.5 | 0.80 | 0.82 |
| 0.3060 | 0.6581 | 0.6 | 0.87 | 0.87 |
| 0.2742 | 0.5612 | 0.7 | 0.91 | 0.92 |
| 0.2000 | 0.4918 | 0.8 | 0.95 | 0.95 |
| 0.1547 | 0.4040 | 0.9 | 0.98 | 0.98 |
| 0.1115 | 0.4011 | 1.0 | 1.00 | 1.00 |
| 0.0825 | 0.4004 | | | |
| 0.0726 | 0.4008 | | | |
| 0.0559 | 0.4023 | | | |
| 0.0423 | 0.2804 | | | |
| 0.0334 | 0.1846 | | | |
| 0.0227 | 0.1257 | | | |
| 0.0185 | 0.0678 | | | |

| 0.0143 | 0.0378 |
|--------|--------|
| 0.0143 | 0.0291 |
| 0.0000 | 0.0000 |

 Table 17: The experimental data for binary system methanol – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experii | mental | | Calculated from Regression | Calculated from Infinite dilution |
|---------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.8301 | 0.8241 | 0.0 | 0.00 | 0.00 |
| 0.6480 | 0.7551 | 0.1 | 0.32 | 0.37 |
| 0.5116 | 0.7303 | 0.2 | 0.51 | 0.56 |
| 0.4098 | 0.6701 | 0.3 | 0.63 | 0.68 |
| 0.3206 | 0.6241 | 0.4 | 0.73 | 0.76 |
| 0.2307 | 0.5889 | 0.5 | 0.80 | 0.82 |
| 0.1724 | 0.5429 | 0.6 | 0.85 | 0.87 |
| 0.0982 | 0.4543 | 0.7 | 0.90 | 0.91 |
| 0.0715 | 0.4082 | 0.8 | 0.94 | 0.95 |
| 0.0482 | 0.3419 | 0.9 | 0.97 | 0.97 |
| 0.0331 | 0.2579 | 1.0 | 1.00 | 1.00 |
| 0.0197 | 0.2317 | | | |
| 0.0092 | 0.1914 |] | | |
| 0.0031 | 0.1499 |] | | |
| 0.0000 | 0.0905 | | | |
| 0.0000 | 0.0000 | | | |

 Table 18: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the refractometer for the binary system Methanol – Butan-2-ol.

| Experimental | | | Calculated from Regression | | Calculated from Infinite dilution | | |
|--------------|-------|-------|----------------------------------|------|---|------|------|
| X 1 | ٢ | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 |
| 1.0000 | 0.580 | 1.508 | 0.1 | 0.82 | 1.00 | 1.14 | 1.00 |
| 0.8546 | 0.596 | 0.730 | 0.2 | 0.86 | 0.99 | 1.11 | 0.99 |

| 0.7674 | 0.602 | 0.859 | 0.3 | 0.89 | 0.98 | 1.09 | 0.98 |
|--------|-------|-------|-----|------|------|------|------|
| 0.6327 | 0.600 | 0.989 | 0.4 | 0.92 | 0.96 | 1.07 | 0.96 |
| 0.5612 | 0.613 | 1.015 | 0.5 | 0.95 | 0.94 | 1.05 | 0.94 |
| 0.4042 | | 1.034 | 0.6 | 0.97 | 0.92 | 1.03 | 0.92 |
| 0.3060 | 0.684 | 1.048 | 0.7 | 0.98 | 0.89 | 1.02 | 0.89 |
| 0.2742 | 0.678 | 1.069 | 0.8 | 0.99 | 0.86 | 1.01 | 0.86 |
| 0.2000 | 0.684 | 1.007 | 0.9 | 1.00 | 0.84 | 1.00 | 0.84 |
| 0.1547 | 0.702 | 1.049 | | | | | |
| 0.1115 | 0.785 | 1.001 | | | | | |
| 0.0825 | 0.593 | 1.015 | | | | | |
| 0.0726 | 0.756 | 1.006 | | | | | |
| 0.0559 | 0.671 | 0.988 | | | | | |
| 0.0423 | 0.934 | 0.981 | | | | | |
| 0.0334 | 1.059 | 0.957 | | | | | |
| 0.0227 | 1.014 | 1.024 | | | | | |
| 0.0185 | 1.072 | 1.018 | | | | | |
| 0.0143 | 1.062 | 1.032 | | | | | |
| 0.0143 | 1.032 | 1.010 | | | | | |

 Table 19: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the refractometer for the binary system Methanol – Butan-2-ol.

| | Experime | ntal | | Calco fr Regr | ulated om ession | Calcu from I dilu | lated nfinite tion |
|------------|----------|-------|------------|---------------------|------------------------|-------------------------|--------------------------|
| X 1 | Υ1 | Υ2 | X 1 | Υ1 | Υ2 | ٢1 | Υ2 |
| 0.8301 | 0.997 | 1.625 | 0.1 | 1.18 | 1.00 | 1.46 | 1.00 |
| 0.6480 | 1.004 | 0.978 | 0.2 | 1.13 | 1.01 | 1.35 | 1.01 |
| 0.5116 | 1.005 | 0.969 | 0.3 | 1.08 | 1.02 | 1.26 | 1.02 |
| 0.4098 | 0.997 | 0.982 | 0.4 | 1.05 | 1.04 | 1.18 | 1.04 |
| 0.3206 | 1.010 | 0.973 | 0.5 | 1.03 | 1.06 | 1.12 | 1.06 |
| 0.2307 | 0.986 | 1.025 | 0.6 | 1.02 | 1.08 | 1.08 | 1.08 |
| 0.1724 | #REF! | 1.019 | 0.7 | 1.01 | 1.09 | 1.04 | 1.09 |
| 0.0982 | 1.167 | 1.007 | 0.8 | 1.00 | 1.11 | 1.02 | 1.11 |
| 0.0715 | 1.161 | 1.033 | 0.9 | 1.00 | 1.13 | 1.00 | 1.13 |
| 0.0482 | 1.187 | 1.026 | | | | | |
| 0.0331 | 1.319 | 1.045 | | | | | |
| 0.0197 | 1.305 | 1.019 | | | | | |
| 0.0092 | 2.489 | 1.032 | | | | | |
| 0.0031 | 1.308 | 1.050 | | | | | |

IV. Ethanol – Water

| Sample | T (°C) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 78.42 | 1.0000 | 1.0000 |
| 2 | 78.32 | 0.9544 | 0.9544 |
| 3 | 78.57 | 0.6342 | 0.7389 |
| 4 | 79.22 | 0.5099 | 0.5806 |
| 5 | 80.23 | 0.6959 | 0.7427 |
| 6 | 81.44 | 0.2767 | 0.7427 |
| 7 | 82.83 | 0.2129 | 0.5806 |
| 8 | 85.65 | 0.1119 | 0.3398 |
| 9 | 87.20 | 0.0749 | 0.3684 |
| 10 | 89.32 | 0.0477 | 0.3037 |
| 11 | 92.05 | 0.0271 | 0.2715 |
| 12 | 95.08 | 0.0131 | 0.2064 |
| 13 | 96.80 | 0.0089 | 0.1605 |
| 14 | 98.27 | 0.0041 | 0.0771 |
| 15 | 99.35 | 0.0015 | 0.0323 |
| 16 | 99.77 | 0.0000 | 0.0203 |

Table 20: The molar fractions from the analysis with the refractometer for the binary systemEthanol – Water (p = 0.9931 bar).

Table 21: The molar fractions from the analysis with the GC for the binary system Ethanol –Water.

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 78.00 | 1.0000 | 1.0000 |
| 2 | 78.45 | 0.7874 | 0.9600 |
| 3 | 78.60 | 0.7524 | 0.9600 |
| 4 | 80.67 | 0.3570 | 0.7187 |
| 5 | 81.90 | 0.2316 | |
| 6 | 83.25 | 0.1317 | 0.5664 |
| 7 | 86.84 | 0.0390 | 0.4402 |
| 8 | 94.15 | 0.0000 | 0.1965 |
| 9 | 96.37 | 0.0000 | 0.0815 |
| 10 | 98.93 | 0.0000 | 0.0177 |

 Table 22: The experimental data for binary system ethanol – water and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experime | ntal | | Calculated from Regression | Calculated from Infinite dilution |
|----------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.0000 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.9544 | 0.9544 | 0.1 | 0.22 | 0.43 |
| 0.6342 | 0.7389 | 0.2 | 0.45 | 0.53 |
| 0.5099 | 0.5806 | 0.3 | 0.53 | 0.58 |
| 0.6959 | 0.7427 | 0.4 | 0.59 | 0.63 |
| 0.2767 | 0.7427 | 0.5 | 0.66 | 0.68 |
| 0.2129 | 0.5806 | 0.6 | 0.73 | 0.74 |
| 0.1119 | 0.3398 | 0.7 | 0.80 | 0.80 |
| 0.0749 | 0.3684 | 0.8 | 0.86 | 0.86 |
| 0.0477 | 0.3037 | 0.9 | 0.93 | 0.93 |
| 0.0271 | 0.2715 | 1.0 | 1.00 | 1.00 |
| 0.0131 | 0.2064 | | | |
| 0.0089 | 0.1605 |] | | |
| 0.0041 | 0.0771 |] | | |
| 0.0015 | 0.0323 |] | | |

0.0000

0.0203

 Table 23: The experimental data for binary system ethanol – water and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experin | nental | | Calculated from Regression | Calculated from Infinite dilution |
|---------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.0000 | 1.0000 | 0 | 0.00 | 0.00 |
| 0.7874 | 0.9600 | 0.1 | 0.22 | 0.45 |
| 0.7524 | 0.9600 | 0.2 | 0.45 | 0.54 |
| 0.3570 | 0.7187 | 0.3 | 0.53 | 0.58 |
| 0.2316 | | 0.4 | 0.60 | 0.63 |
| 0.1317 | 0.5664 | 0.5 | 0.67 | 0.68 |
| 0.0390 | 0.4402 | 0.6 | 0.73 | 0.74 |
| 0.0000 | 0.1965 | 0.7 | 0.80 | 0.80 |
| 0.0000 | 0.0815 | 0.8 | 0.86 | 0.86 |
| 0.0000 | 0.0177 | 0.9 | 0.93 | 0.93 |
| | | 1.0 | 1.00 | 1.00 |

Table 24: The experimental and the calculated activity coefficients by two different methodsfrom the analysis with the refractometer for the binary system Ethanol – Water.

| Experimental | | | Calculated from Regression | | Calcu fro Infi dilu | ulated om inite ition | |
|--------------|--------|--------|----------------------------------|------|------------------------------|--------------------------------|------|
| X 1 | Υ1 | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 |
| 1.0000 | 5.1301 | 0.9910 | 0.1 | 2.16 | 1.03 | 3.22 | 1.03 |
| 0.9544 | 4.3348 | 1.0065 | 0.2 | 1.58 | 1.08 | 2.11 | 1.08 |
| 0.6342 | 3.6419 | 1.0189 | 0.3 | 1.31 | 1.15 | 1.60 | 1.15 |
| 0.5099 | 2.3579 | 1.0702 | 0.4 | 1.17 | 1.22 | 1.34 | 1.22 |
| 0.6959 | 1.7785 | 1.1673 | 0.5 | 1.10 | 1.29 | 1.19 | 1.29 |
| 0.2767 | 1.6507 | 1.1985 | 0.6 | 1.05 | 1.36 | 1.10 | 1.36 |
| 0.2129 | 1.6274 | 1.2001 | 0.7 | 1.02 | 1.43 | 1.05 | 1.43 |
| 0.1119 | 1.3756 | 1.3487 | 0.8 | 1.01 | 1.49 | 1.02 | 1.49 |
| 0.0749 | 1.2308 | 1.4816 | 0.9 | 1.00 | 1.55 | 1.00 | 1.55 |
| 0.0477 | 1.1165 | 1.6873 | | | | | |

| 0.0271 | 1.0657 | 1.8439 |
|--------|--------|--------|
| 0.0131 | 1.0579 | 1.8785 |
| 0.0089 | 1.0266 | 2.0683 |
| 0.0041 | 1.0126 | 2.1822 |
| 0.0015 | 1.0113 | 2.1941 |
| 0.0000 | 1.0117 | 2.1936 |
| 0.884 | 1.0065 | 2.2625 |
| 0.908 | 1.0035 | 2.3281 |
| 0.922 | 1.0025 | 2.3621 |

 Table 25: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the GC for the binary system Ethanol – Water.

| Experimental | | | Calculated from Regression | | Calcu fro Infir dilut | ılated om nite tion | |
|--------------|--------|--------|----------------------------------|------|--------------------------------|------------------------------|------|
| X 1 | Υ1 | Υ2 | X 1 | Υ1 | Υ₂ | Υı | Υ2 |
| 0.019 | 5.1301 | 0.9910 | 0.1 | 2.16 | 1.03 | 3.22 | 1.03 |
| 0.056 | 4.3348 | 1.0065 | 0.2 | 1.58 | 1.08 | 2.11 | 1.08 |
| 0.091 | 3.6419 | 1.0189 | 0.3 | 1.31 | 1.15 | 1.60 | 1.15 |
| 0.189 | 2.3579 | 1.0702 | 0.4 | 1.17 | 1.22 | 1.34 | 1.22 |
| 0.286 | 1.7785 | 1.1673 | 0.5 | 1.10 | 1.29 | 1.19 | 1.29 |
| 0.323 | 1.6507 | 1.1985 | 0.6 | 1.05 | 1.36 | 1.10 | 1.36 |
| 0.331 | 1.6274 | 1.2001 | 0.7 | 1.02 | 1.43 | 1.05 | 1.43 |
| 0.419 | 1.3756 | 1.3487 | 0.8 | 1.01 | 1.49 | 1.02 | 1.49 |
| 0.512 | 1.2308 | 1.4816 | 0.9 | 1.00 | 1.55 | 1.00 | 1.55 |
| 0.620 | 1.1165 | 1.6873 | | | | | |

V. Methanol - Water

| Sample | T (°C) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 64.50 | 0.9712 | 0.9587 |
| 2 | 67.59 | 0.7992 | 0.8969 |
| 3 | 72.09 | 0.5244 | 0.8023 |
| 4 | 77.17 | | 0.6862 |
| 5 | 82.99 | 0.1861 | 0.4922 |
| 6 | 89.47 | 0.0897 | 0.3478 |
| 7 | 90.96 | 0.0709 | 0.3478 |
| 8 | 92.38 | 0.0550 | 0.3565 |
| 9 | 93.67 | 0.0413 | 0.3778 |
| 10 | 94.96 | 0.0301 | 0.2601 |
| 11 | 95.87 | 0.0216 | 0.1939 |
| 12 | 96.92 | 0.0157 | 0.1384 |
| 13 | 97.30 | 0.0096 | 0.1176 |
| 14 | 97.80 | 0.0096 | 0.0952 |
| 15 | 98.18 | 0.0033 | 0.0816 |
| 16 | 98.64 | 0.0000 | 0.0602 |
| 17 | 99.10 | 0 | 0.0413 |
| 18 | 99.42 | 0 | 0.0216 |
| 19 | 99.74 | 0 | 0.0064 |

Table 26: The molar fractions from the analysis with the refractometer for the binary systemMethanol – Water (p = 0.99 bar).

Table 27: The molar fractions from the analysis with the GC for the binary system Methanol –Water.

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 64.09 | 0.8301 | 0.8241 |
| 2 | 69.92 | 0.6479 | 0.7551 |
| 3 | 73.82 | 0.5116 | 0.7303 |
| 4 | 77.00 | 0.4098 | 0.6701 |
| 5 | 79.91 | 0.3206 | 0.6241 |
| 6 | 82.71 | 0.2307 | 0.5889 |
| 7 | 85.62 | 0.1724 | 0.5429 |
| 8 | 89.00 | 0.0982 | 0.4543 |

| 9 | 91.03 | 0.0715 | 0.4082 |
|----|-------|--------|--------|
| 10 | 92.75 | 0.0482 | 0.3419 |
| 11 | 94.07 | 0.0331 | 0.2579 |
| 12 | 95.22 | 0.0197 | 0.2317 |
| 13 | 96.04 | 0.0092 | 0.1914 |
| 14 | 96.77 | 0.0031 | 0.1499 |
| 15 | 97.77 | 0.0000 | 0.0905 |
| 16 | 99.04 | 0.0000 | 0.0000 |
| | | | |

 Table 28: The experimental data for binary system methanol – water and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experin | nental | Calculated from Regression | Calculated from Infinite dilution | |
|---------|--------|----------------------------------|--|------------|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.9712 | 0.9587 | 0.0 | 0.00 | 0.00 |
| 0.7992 | 0.8969 | 0.1 | 0.38 | 0.37 |
| 0.5244 | 0.8023 | 0.2 | 0.55 | 0.55 |
| | 0.6862 | 0.3 | 0.66 | 0.66 |
| 0.1861 | 0.4922 | 0.4 | 0.74 | 0.73 |
| 0.0897 | 0.3478 | 0.5 | 0.81 | 0.79 |
| 0.0709 | 0.3478 | 0.6 | 0.86 | 0.85 |
| 0.0550 | 0.3565 | 0.7 | 0.90 | 0.89 |
| 0.0413 | 0.3778 | 0.8 | 0.94 | 0.93 |
| 0.0301 | 0.2601 | 0.9 | 0.97 | 0.97 |
| 0.0216 | 0.1939 | 1.0 | 1.00 | 1.00 |
| 0.0157 | 0.1384 | | | |
| 0.0096 | 0.1176 |] | | |
| 0.0096 | 0.0952 | | | |
| 0.0033 | 0.0816 | | | |
| 0.0000 | 0.0602 | | | |
| 0 | 0.0413 | | | |
| 0 | 0.0216 | | | |

0

0.0064

Table 29: The experimental data for binary system methanol – water and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experim | nental | | Calculated from Regression | Calculated from Infinite dilution |
|---------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.8301 | 0.8241 | 0.0 | 0.00 | 0.00 |
| 0.6479 | 0.7551 | 0.1 | 0.35 | 0.47 |
| 0.5116 | 0.7303 | 0.2 | 0.53 | 0.62 |
| 0.4098 | 0.6701 | 0.3 | 0.64 | 0.71 |
| 0.3206 | 0.6241 | 0.4 | 0.73 | 0.77 |
| 0.2307 | 0.5889 | 0.5 | 0.79 | 0.81 |
| 0.1724 | 0.5429 | 0.6 | 0.84 | 0.86 |
| 0.0982 | 0.4543 | 0.7 | 0.89 | 0.90 |
| 0.0715 | 0.4082 | 0.8 | 0.93 | 0.93 |
| 0.0482 | 0.3419 | 0.9 | 0.97 | 0.97 |
| 0.0331 | 0.2579 | 1.0 | 1.00 | 1.00 |
| 0.0197 | 0.2317 | | | |
| 0.0092 | 0.1914 |] | | |
| 0.0031 | 0.1499 |] | | |
| 0.0000 | 0.0905 |] | | |

 Table 30: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the refractometer for the binary system Methanol – Water.

0.0000

0.0000

| Experimental | | | | Calculated from Regression | | Calculated from Infinite dilution | |
|--------------|-------|-------|------------|----------------------------------|----------------|--------------------------------------|------|
| X 1 | Υ1 | Υ2 | X 1 | Υ1 | Υ ₂ | Υ٦ | Υ2 |
| 0.9712 | 0.969 | 5.822 | 0.1 | 1.44 | 1.01 | 1.50 | 1.01 |
| 0.7992 | 0.977 | 1.818 | 0.2 | 1.24 | 1.04 | 1.35 | 1.04 |
| 0.5244 | 1.123 | 1.211 | 0.3 | 1.13 | 1.07 | 1.24 | 1.07 |
| 0.1861 | 1.308 | 1.160 | 0.4 | 1.08 | 1.10 | 1.16 | 1.10 |
| 0.0897 | 0.000 | 1.588 | 0.5 | 1.04 | 1.13 | 1.10 | 1.13 |
| 0.0709 | 1.848 | 0.959 | 0.6 | 1.02 | 1.16 | 1.06 | 1.16 |

| 0.0550 | 0.000 | 1.370 | 0.7 | 1.01 | 1.18 | 1.03 | 1.18 |
|--------|-------|-------|-----|------|------|------|------|
| 0.0413 | 0.000 | 1.287 | 0.8 | 1.00 | 1.20 | 1.01 | 1.20 |
| 0.0301 | 2.854 | 0.898 | 0.9 | 1.00 | 1.23 | 1.00 | 1.23 |
| 0.0216 | 2.878 | 0.924 | | | | | |
| 0.0157 | 2.732 | 0.943 | | | | | |
| 0.0096 | 3.751 | 0.946 | | | | | |
| 0.0096 | 2.989 | 0.952 | | | | | |
| 0.0033 | 7.361 | 0.947 | | | | | |

 Table 31: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the GC for the binary system Methanol – Water.

| | Experime | ntal | | Calculo fror Regres | ated n sion | Calcul from In dilut | ated finite ion |
|------------|----------|-------|------------|---------------------------|-------------------|----------------------------|-----------------------|
| X 1 | Υ1 | Υ2 | X 1 | Υ ₁ | Υ2 | ٢1 | Υ2 |
| 0.8301 | 0.991 | 4.282 | 0.1 | 1.36 | 1.01 | 2.13 | 1.01 |
| 0.6479 | 0.928 | 2.224 | 0.2 | 1.24 | 1.02 | 1.77 | 1.02 |
| 0.5116 | 0.982 | 1.495 | 0.3 | 1.16 | 1.05 | 1.52 | 1.05 |
| 0.4098 | 1.001 | 1.325 | 0.4 | 1.11 | 1.07 | 1.35 | 1.07 |
| 0.3206 | 1.073 | 1.164 | 0.5 | 1.07 | 1.11 | 1.22 | 1.11 |
| 0.2307 | 1.275 | 1.005 | 0.6 | 1.04 | 1.14 | 1.13 | 1.14 |
| 0.1724 | 1.421 | 0.926 | 0.7 | 1.02 | 1.18 | 1.07 | 1.18 |
| 0.0982 | 1.861 | 0.890 | 0.8 | 1.01 | 1.22 | 1.03 | 1.22 |
| 0.0715 | 2.146 | 0.868 | 0.9 | 1.00 | 1.26 | 1.01 | 1.26 |
| 0.0482 | 2.548 | 0.883 | | | | | |
| 0.0331 | 2.649 | 0.933 | | | | | |
| 0.0197 | 3.851 | 0.913 | | | | | |
| 0.0092 | 6.634 | 0.923 | | | | | |

VI. Acetone - Ethanol

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 55.88 | 0.8987 | 0.9737 |
| 2 | 56.87 | 0.6919 | 0.9188 |
| 3 | 60.25 | 0.4296 | 0.7798 |
| 4 | 62.66 | 0.3648 | 0.7226 |
| 5 | 65.38 | 0.2633 | 0.528 |
| 6 | 68.35 | 0.1798 | 0.7833 |
| 7 | 70.78 | 0.1032 | 0.3972 |
| 8 | 72.75 | 0.1032 | 0.2633 |
| 9 | 78.09 | 0.0000 | 0.0000 |

Table 32: The molar fractions from the analysis with the refractometer for the binary systemAcetone – Ethanol (p = 0.9982 bar).

Table 33: The molar fractions from the analysis with the GC for the binary system Acetone –Ethanol.

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 56.58 | 1.0000 | 1.0000 |
| 2 | 58.87 | 0.6812 | 0.8012 |
| 3 | 61.48 | 0.5204 | 0.7272 |
| 4 | 63.79 | 0.3864 | 0.6152 |
| 5 | 65.47 | 0.3128 | 0.5670 |
| 6 | 67.15 | 0.2211 | 0.4920 |
| 7 | 68.73 | 0.1920 | 0.4332 |
| 8 | 70.36 | 0.1592 | 0.3605 |
| 9 | 71.75 | 0.1268 | 0.2934 |
| 10 | 72.93 | 0.0990 | 0.2489 |
| 11 | 73.58 | 0.0730 | 0.2176 |
| 12 | 74.25 | 0.0644 | 0.1321 |
| 13 | 74.63 | 0.0568 | 0.1567 |
| 14 | 75.99 | 0.0394 | 0.1024 |
| 15 | 77.75 | 0.0117 | 0.0179 |

Table 34: The experimental data for binary system acetone – ethanol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experim | eental | | Calculated from Regression | Calculated from Infinite dilution |
|---------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 0.8987 | 0.9737 | 0.0 | 0.00 | 0.00 |
| 0.6919 | 0.9188 | 0.1 | 0.21 | 0.21 |
| 0.4296 | 0.7798 | 0.2 | 0.37 | 0.36 |
| 0.3648 | 0.7226 | 0.3 | 0.50 | 0.49 |
| 0.2633 | 0.528 | 0.4 | 0.60 | 0.60 |
| 0.1798 | 0.7833 | 0.5 | 0.70 | 0.69 |
| 0.1032 | 0.3972 | 0.6 | 0.78 | 0.77 |
| 0.1032 | 0.2633 | 0.7 | 0.84 | 0.84 |
| 0.0000 | 0.0000 | 0.8 | 0.90 | 0.90 |
| | | 0.9 | 0.96 | 0.96 |
| | | 1.0 | 1.00 | 1.00 |

Table 35: The experimental data for binary system acetone – ethanol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experii | mental | | Calculate d from Regressio n | Calculated from Infinite dilution |
|---------|--------|------------|---------------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.0000 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.6812 | 0.8012 | 0.1 | 0.29 | 0.29 |
| 0.5204 | 0.7272 | 0.2 | 0.46 | 0.43 |
| 0.3864 | 0.6152 | 0.3 | 0.58 | 0.53 |
| 0.3128 | 0.5670 | 0.4 | 0.66 | 0.61 |
| 0.2211 | 0.4920 | 0.5 | 0.72 | 0.69 |
| 0.1920 | 0.4332 | 0.6 | 0.77 | 0.75 |
| 0.1592 | 0.3605 | 0.7 | 0.82 | 0.81 |

| 0.1268 | 0.2934 | 0.8 | 0.87 | 0.86 |
|--------|--------|-----|------|------|
| 0.0990 | 0.2489 | 0.9 | 0.93 | 0.92 |
| 0.0730 | 0.2176 | 1.0 | 1.00 | 1.00 |
| 0.0644 | 0.1321 | | | |
| 0.0568 | 0.1567 | | | |
| 0.0394 | 0.1024 | | | |
| 0.0117 | 0.0179 | | | |

 Table 36: The experimental and the calculated activity coefficients by two different methods

 from the analysis with the refractometer for the binary system Acetone – Ethanol.

| Experimental | | | | Calco fr Regr | ulated om ression | Calcu from II dilu | lated nfinite tion |
|--------------|-------|-------|------------|---------------------|-------------------------|--------------------------|--------------------------|
| X 1 | ۲1 | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 |
| 0.8987 | 1.068 | 0.663 | 0.1 | 1.13 | 1.00 | 1.15 | 1.00 |
| 0.6919 | 1.266 | 0.643 | 0.2 | 1.08 | 1.01 | 1.07 | 1.01 |
| 0.4296 | 1.544 | 0.808 | 0.3 | 1.05 | 1.02 | 1.03 | 1.02 |
| 0.3648 | 1.556 | 0.822 | 0.4 | 1.03 | 1.03 | 1.02 | 1.03 |
| 0.2633 | 1.442 | 1.071 | 0.5 | 1.02 | 1.04 | 1.01 | 1.04 |
| 0.1798 | 2.849 | 0.389 | 0.6 | 1.01 | 1.05 | 1.00 | 1.05 |
| 0.1032 | | 0.894 | 0.7 | 1.00 | 1.06 | 1.00 | 1.06 |
| | | | 0.8 | 1.00 | 1.07 | 1.00 | 1.07 |
| | | | 0.9 | 1.00 | 1.08 | 1.00 | 1.08 |

Table 37: The experimental and the calculated activity coefficients by two different methods from the analysis with the GC for the binary system Acetone – Ethanol.

| Experimental | | | | Calco fr Regr | ulated om ression | Calcu from li dilu | lated nfinite tion |
|--------------|-------|-------|------------|---------------------|-------------------------|--------------------------|--------------------------|
| X 1 | Υ1 | Υ2 | X 1 | Υ1 | Υ2 | ٢1 | Υ2 |
| 0.6812 | 1.048 | 1.389 | 0.1 | 1.69 | 1.00 | 1.71 | 1.00 |
| 0.5204 | 1.141 | 1.128 | 0.2 | 1.55 | 1.02 | 1.38 | 1.02 |
| 0.3864 | 1.205 | 1.123 | 0.3 | 1.43 | 1.05 | 1.21 | 1.05 |
| 0.3128 | 1.300 | 1.049 | 0.4 | 1.32 | 1.09 | 1.12 | 1.09 |
| 0.2211 | 1.512 | 1.011 | 0.5 | 1.23 | 1.16 | 1.07 | 1.16 |
| 0.1592 | | 1.016 | 0.6 | 1.15 | 1.26 | 1.03 | 1.26 |
| 0.1268 | 2.009 | 1.034 | 0.7 | 1.09 | 1.40 | 1.02 | 1.40 |
| 0.0990 | 2.113 | 2.435 | 0.8 | 1.04 | 1.60 | 1.01 | 1.60 |
| 0.0730 | 2.373 | 2.393 | 0.9 | 1.01 | 1.89 | 1.00 | 1.89 |
| 0.0644 | 2.295 | 2.551 | | | | | |
| 0.0568 | 1.558 | 2.417 | | | | | |
| 0.0394 | 2.536 | 2.376 | | | | | |
| 0.0117 | 5.241 | 2.338 | | | | | |

VII. Acetone – Butan-2-ol

| Sample | T (°C) | Liquid | Vapor | |
|--------|--------|--------|--------|--|
| 1 | 55.53 | 0.9983 | 1.0036 | |
| 2 | 59.84 | 0.8139 | 0.9540 | |
| 3 | 65.51 | 0.6015 | 0.9187 | |
| 4 | 67.68 | 0.5461 | 0.8544 | |
| 5 | 72.23 | 0.4063 | 0.7774 | |
| 6 | 79.36 | 0.2325 | 0.6381 | |
| 7 | 82.78 | 0.1934 | 0.5617 | |
| 8 | 86.9 | 0.2569 | 0.4442 | |
| 9 | 88.8 | 0.0931 | 0.3009 | |
| 10 | 91.05 | 0.0796 | 0.2683 | |
| 11 | 92.44 | 0.0826 | 0.2311 | |
| 12 | 93.5 | 0.0569 | 0.2109 | |
| 13 | 96.49 | 0.0251 | 0.0945 | |
| 14 | 97.02 | 0.0052 | 0.0479 | |
| 15 | 97.49 | 0.0144 | 0.0448 | |
| 16 | 98.06 | 0.0174 | 0.0281 | |

Table 38: The molar fractions from the analysis with the refractometer for the binary systemAcetone – Butan-2-ol (p = 0.9931 bar).

Table 39: The molar fractions from the analysis with the GC for the binary system Acetone –Butan-2-ol.

| Sample | Т (°С) | Liquid | Vapor |
|--------|--------|--------|--------|
| 1 | 56.25 | 1.000 | 1.0000 |
| 2 | 59.97 | 0.7779 | 0.9659 |
| 3 | 63.48 | 0.6294 | 0.8927 |
| 4 | 68.71 | 0.4286 | 0.7921 |
| 5 | 72.29 | 0.3539 | 0.7430 |
| 6 | 76.17 | 0.2882 | 0.6987 |
| 7 | 79.05 | 0.2312 | 0.6118 |
| 8 | 82.78 | 0.1122 | 0.4962 |
| 9 | 87.17 | 0.0861 | 0.3746 |
| 10 | 89.40 | 0.0930 | 0.3228 |

| 11 | 91.08 | 0.0463 | 0.2555 |
|----|-------|--------|--------|
| 12 | 92.05 | 0.0849 | 0.2219 |
| 13 | 94.25 | 0.0401 | 0.1512 |
| 14 | 95.71 | 0.0054 | 0.1206 |
| 15 | 98.06 | 0.0000 | 0.0473 |
| | | | |

Table 40: The experimental data for binary system acetone – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experim | ental | | Calculated from Regression | Calculated from Infinite dilution | |
|---------|--------|------------|----------------------------------|--|--|
| Liquid | Vapor | X 1 | y 1 | y 1 | |
| 0.9983 | 1.0036 | 0.0 | 0.00 | 0.00 | |
| 0.8139 | 0.9540 | 0.1 | 0.41 | 0.44 | |
| 0.6015 | 0.9187 | 0.2 | 0.61 | 0.60 | |
| 0.5461 | 0.8544 | 0.3 | 0.72 | 0.70 | |
| 0.4063 | 0.7774 | 0.4 | 0.80 | 0.78 | |
| 0.2325 | 0.6381 | 0.5 | 0.85 | 0.83 | |
| 0.1934 | 0.5617 | 0.6 | 0.89 | 0.88 | |
| 0.2569 | 0.4442 | 0.7 | 0.92 | 0.92 | |
| 0.0931 | 0.3009 | 0.8 | 0.95 | 0.95 | |
| 0.0796 | 0.2683 | 0.9 | 0.98 | 0.98 | |
| 0.0826 | 0.2311 | 1.0 | 1.00 | 1.00 | |
| 0.0569 | 0.2109 | | | | |
| 0.0251 | 0.0945 |] | | | |
| 0.0052 | 0.0479 |] | | | |
| 0.0144 | 0.0448 |] | | | |
| 0.0174 | 0.0281 | | | | |

 Table 41: The experimental data for binary system acetone – butan-2-ol and calculated molar fractions obtained from obtained interaction parameters (via regression and infinite dilution activity coefficient).

| Experim | ental | | Calculated from Regression | Calculated from Infinite dilution |
|---------|--------|------------|----------------------------------|--|
| Liquid | Vapor | X 1 | y 1 | y 1 |
| 1.000 | 1.0000 | 0.0 | 0.00 | 0.00 |
| 0.7779 | 0.9659 | 0.1 | 0.42 | 0.40 |
| 0.6294 | 0.8927 | 0.2 | 0.59 | 0.58 |
| 0.4286 | 0.7921 | 0.3 | 0.70 | 0.69 |
| 0.3539 | 0.7430 | 0.4 | 0.77 | 0.77 |
| 0.2882 | 0.6987 | 0.5 | 0.83 | 0.83 |
| 0.2312 | 0.6118 | 0.6 | 0.88 | 0.88 |
| 0.1122 | 0.4962 | 0.7 | 0.92 | 0.92 |
| 0.0861 | 0.3746 | 0.8 | 0.95 | 0.95 |
| 0.0930 | 0.3228 | 0.9 | 0.98 | 0.98 |
| 0.0463 | 0.2555 | 1.0 | 1.00 | 1.00 |
| 0.0849 | 0.2219 | | | |
| 0.0401 | 0.1512 | | | |
| 0.0054 | 0.1206 | | | |
| 0.0000 | 0.0473 |] | | |

Table 42: The experimental and the calculated activity coefficients by two different methods from the analysis with the refractometer for the binary system Acetone – Butan-2-ol.

| Experimental | | | | Calco fr Regr | ulated om ression | Calcu from I dilu | lated nfinite tion | |
|--------------|-------|-------|------------|---------------------|-------------------------|-------------------------|--------------------------|--|
| X 1 | Υı | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 | |
| 0.8139 | 1.018 | 1.362 | 0.1 | 1.51 | 1.01 | 1.67 | 1.01 | |
| 0.6015 | 1.101 | 0.846 | 0.2 | 1.38 | 1.02 | 1.35 | 1.02 | |
| 0.5461 | 1.052 | 1.199 | 0.3 | 1.28 | 1.05 | 1.19 | 1.05 | |
| 0.4063 | 1.116 | 1.131 | 0.4 | 1.20 | 1.08 | 1.11 | 1.08 | |
| 0.2325 | 1.291 | 1.034 | 0.5 | 1.13 | 1.13 | 1.06 | 1.13 | |
| 0.1934 | | 1.029 | 0.6 | 1.08 | 1.20 | 1.03 | 1.20 | |
| 0.2569 | 0.828 | 1.194 | 0.7 | 1.05 | 1.28 | 1.01 | 1.28 | |
| 0.0931 | 1.714 | 1.139 | 0.8 | 1.02 | 1.38 | 1.01 | 1.38 | |
| 0.0796 | 1.276 | 1.074 | 0.9 | 1.01 | 1.51 | 1.00 | 1.51 | |
| 0.0826 | 1.055 | 1.072 | | | | | | |
| 0.0569 | 1.280 | 1.027 | | | | | | |
| 0.0251 | 2.449 | 1.017 | | | | | | |
| 0.0052 | 5.218 | 1.027 | | | | | | |
| 0.0144 | 0.944 | 1.022 | | | | | | |

Table 43: The experimental and the calculated activity coefficients by two different methods from the analysis with the GC for the binary system Acetone – Butan-2-ol.

0.944

1.022

| Experimental | | | | Calculated from Regression | | Calcu from I dilu | lated nfinite tion |
|--------------|-------|-------|------------|----------------------------------|------|-------------------------|--------------------------|
| X 1 | ۲1 | Υ2 | X 1 | Υ1 | Υ2 | Υ1 | Υ2 |
| 0.7779 | 1.074 | 0.841 | 0.1 | 1.57 | 1.01 | 1.44 | 1.01 |
| 0.6294 | 1.092 | 1.328 | 0.2 | 1.33 | 1.04 | 1.28 | 1.04 |
| 0.4286 | 1.203 | 1.294 | 0.3 | 1.19 | 1.08 | 1.18 | 1.08 |
| 0.3539 | 1.222 | 1.197 | 0.4 | 1.12 | 1.12 | 1.11 | 1.12 |
| 0.2882 | 1.254 | 1.068 | 0.5 | 1.07 | 1.16 | 1.07 | 1.16 |
| 0.2312 | | 1.122 | 0.6 | 1.04 | 1.20 | 1.04 | 1.20 |
| 0.1122 | 2.322 | 1.075 | 0.7 | 1.02 | 1.24 | 1.02 | 1.24 |
| 0.0861 | 2.166 | 1.080 | 0.8 | 1.01 | 1.28 | 1.01 | 1.28 |
| 0.0930 | 1.422 | 1.077 | 0.9 | 1.00 | 1.32 | 1.00 | 1.32 |
| 0.0463 | 2.350 | 1.054 | | | | | |
| 0.0849 | 0.988 | 1.105 | | | | | |
| 0.0401 | 1.711 | 1.055 | | | | | |

Software code for consistency test

```
DISTRIBUTION_DOMAIN
```

RANGE AS (0:1) VARIABLE

y,x AS DISTRIBUTION(RANGE) OF no_type

CI, J, Ap, An, dT, Tmin, evros, Criterion AS no_type

integ AS no_type SET

RANGE:=[CFDM,2,99];

EQUATION

FOR i:=0 TO 1 DO

```
y(i) = (-0.72450839*log(x(i)+0.000001) - 0.85679554);
```

END

FOR i:=0 TO 1 DO x(i)=i; END

```
Ap = evros- An;
An = integ = INTEGRAL(r:=0:1;(ABS(y(r))));
CI * (Ap+An) = 100 * ABS(Ap-An);
J * Tmin = 150*dT;
Criterion = CI-J;
```

ASSIGN

evros := 2.18;

Tmin := 78.32;

dT := 21.45;