

Review

# Vapor-Liquid Equilibrium in the Acetic Acid-Ethanol-Ethyl Acetate-Water Quaternary System: Critical Literature Review and Thermodynamic Consistency of the Experimental Data

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**Abstract:** This study presents a critical review of the experimental vapor-liquid equilibrium (VLE) data for the quaternary acetic acid-ethanol-ethyl acetate-water system and its subsystems that are reported in the literature. The thermodynamic consistency of the VLE data were verified using two integral tests: the Redlich–Kister test and the direct integration of the Gibbs–Duhem equation. The VLE data were correlated using the NRTL equation for further integration. Additionally, the reliable value of the integral derived from the direct integration of the Gibbs–Duhem equation for multicomponent systems under isothermal-isobaric conditions was estimated. This integral can be used for testing the thermodynamic consistency of experimental VLE data.

**Keywords:** vapor-liquid equilibrium; ethyl acetate; thermodynamic consistency



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## 1. Introduction

The development of environmentally friendly chemical processes that should become more cost-effective, energy-efficient, and resource-saving than currently existing methods is of great current interest in light of the global trend to reduce greenhouse gas emissions and prevent global warming. This aligns with the criteria for sustainable development [1] and the Kyoto Protocol [2].

Coupled processes, where the phase transition is accompanied by a chemical reaction, are emerging as a crucial component of new energy-efficient and resource-saving industrial chemical technologies. The synergistic effect of integration into chemical production of such coupled processes as reactive distillation (RD), which combines the stages of chemical interaction and distillation separation of substances in one apparatus, includes increased reagent conversion, reduced energy costs, and minimized environmental risks [3]. The application of RD facilitates the implementation of industrial processes in which the course of a chemical reaction is limited by the chemical equilibrium between the reactants and products, necessitating the removal of products from the reaction mixture without the need for additional equipment and the generation of a significant amount of wastewater.

Detailed information on phase equilibrium in reacting systems and on the structure and topology of the phase diagrams of the systems with coupled (phase and chemical) processes is essential for the development and optimization of industrial processes involving reactive distillation.

Currently, the investigation of coupled processes, such as RD, in systems with the esterification reaction is of utmost importance in the context of industrial technologies for the production of esters, for example, ethyl acetate. This ester is highly significant in industrial applications, including the production of paints and varnishes, adhesive compositions, and artificial leather (as a solvent); pharmaceutical production (as a reagent and a reaction medium); aluminum foil production and electronic industry (as a degreasing agent); food industry (as an extracting agent of organic substances from aqueous solutions and a food

additive); explosives production (as a gelling agent); and perfumery, cosmetics, and food industry (as a component of fruit essences). Furthermore, ethyl acetate is characterized by low toxicity [4] compared to other industrially important solvents and, most importantly, is biodegradable [5,6].

Conventionally, ethyl acetate is obtained by direct acid-catalyzed esterification of acetic acid with ethanol in the liquid phase in batch or continuous reactors, and the reaction occurs at temperatures of 363.15–423.15 K [7], making it extremely energy intensive. However, employing technologies such as RD for the production of ethyl acetate at temperatures of 343.15–383.15 K can significantly increase the conversion of reagents compared to synthesis in a conventional reactor (almost complete conversion of ethanol can be achieved with a moderate height of the distillation column) and provide a high-quality target product containing almost no ethanol [8]. Therefore, incorporating ethyl acetate synthesis using RD in industrial production makes the process more environmentally friendly, energy-efficient, and resource-efficient. Significant contributions to the development of fundamental aspects of RD important for the design of industrial processes of chemical technology have been made in papers [3,9–12].

A pre-requisite for developing precise models and predictions of the behavior of complex reacting systems for the purposes of the chemical industry, including optimizing existing processes and creating new ones for the synthesis of ethyl acetate, such as RD, is the thermodynamic consistency of preliminary experimental data. This paper presents a critical review of the data on VLE for the system with ethyl acetate synthesis (including binary and ternary subsystems) available in the literature. Two rigorous thermodynamic tests of the accessible experimental VLE data array are carried out.

## 2. Thermodynamic Consistency Tests

Due to the fact that the relations of classical thermodynamics must hold true for all thermodynamic systems, regardless of their nature and the specific form of the equation of state (EoS), the thermodynamic consistency tests are a good method for verifying the reliability of the experimental VLE data [13]. The essence of all the tests is the validation of the agreement between the obtained data and the thermodynamic differential equations. The most popular tests are based on the Gibbs–Duhem equation [14–16]:

$$s dT - v dp + \sum_{i=1}^n x_i d\mu_i = 0, \quad (1)$$

where  $s$  is the molar entropy,  $T$  is the temperature,  $v$  is the molar volume,  $p$  is the pressure,  $x_i$  is the mole fraction of the component  $i$  (in terms of thermodynamics, each composition variable may be used here, i.e., mass, amount of substance, mass fraction, etc.; in this work we will use mole fractions to make further calculations more convenient),  $\mu_i$  stands for a chemical potential of the component  $i$ , and  $n$  is a number of components. Since the Gibbs–Duhem equation is the consequence of the first and second laws of thermodynamics derived by applying the Euler theorem to internal energy, it is an identical equation. The identical nature of the Gibbs–Duhem equation makes it possible to verify the reliability of different experimental data sets (isobaric VLE data and isothermal VLE data).

The chemical potential of a component of a solution can be represented in the following form [16]:

$$\mu_i = \mu_i^\circ(T, p) + RT \ln a_i = \mu_i^\circ(T, p) + RT \ln x_i \gamma_i, \quad (2)$$

where  $\mu_i^\circ(T, p)$  is the standard part of the chemical potential of the component  $i$  as a function of the temperature and pressure,  $R$  is the gas constant,  $a_i$  is the activity of the component  $i$ , and  $\gamma_i$  is the activity coefficient of the component  $i$ . Substitute Equation (2) into Equation (1) and rewrite the Gibbs–Duhem equation in the following form:

$$\frac{s}{RT} dT - \frac{v}{RT} dp + \sum_{i=1}^n x_i d \ln a_i = 0 \quad (3)$$

Given that the Gibbs–Duhem Equation (3) holds true for every state of a system, it can be integrated along with every variation of the parameters of the system:

$$\int \frac{s}{RT} dT - \int \frac{v}{RT} dp + \sum_{i=1}^n \int x_i d \ln a_i = 0 \quad (4)$$

or in the case of isothermal-isobaric conditions ( $T, p = \text{const}$ ):

$$\sum_{i=1}^n \int x_i d \ln a_i = 0 \quad (5)$$

It should be noted that such integration of a real experimental data set does not generally lead to the strong conditions (4) and (5). The values of the integrals can differ from zero due to the uncertainties of experimental methods and numerical calculations. The reliable values of integrals cannot be obtained by means of thermodynamics, which is why they should be evaluated based on the analysis of a large amount of experimental data. However, in most cases, this method is not used by researchers, so the more popular methods are applied. In our work, we will test VLE data reported by authors on the system acetic acid-ethanol-ethyl acetate-water by integrating relation (5) and estimating the reliable value of the integral for a real VLE data set.

The relations of classical thermodynamics are well known to hold true both for the thermodynamic functions themselves and for the corresponding excess functions. Thus, rewrite Equation (3) for the excess functions:

$$\frac{s^e}{RT} dT - \frac{v^e}{RT} dp + \sum_{i=1}^n x_i d \ln \gamma_i = 0, \quad (6)$$

where  $s^e$  is the molar excess entropy and  $v^e$  is the molar excess volume. The consequence of the Gibbs–Duhem equation in this form will be used for the thermodynamic consistency tests.

### 2.1. The Redlich–Kister Consistency Test

For the Redlich–Kister method (also called the Herington test), the excess Gibbs energy is used. In integral form, the following equation can be written [13,17]:

$$\frac{g^E}{RT} = \sum_{i=1}^n x_i \ln \gamma_i = 0, \quad (7)$$

where  $g^E$  is a molar excess Gibbs energy. After the differentiation of Equation (7), we have:

$$d \frac{g^E}{RT} = \sum_{i=1}^n x_i d \ln \gamma_i + \sum_{i=1}^n \ln \gamma_i dx_i. \quad (8)$$

The first term in the right part of Equation (8) can be rewritten using Equation (6), and for the second term, we can take into account the relation between mole fractions in the system (8):

$$d \frac{g^E}{RT} = -\frac{s^E}{RT} dT + \frac{v^E}{RT} dp + \sum_{i=1}^{n-1} \ln \frac{\gamma_i}{\gamma_n} dx_i. \quad (9)$$

Integrating the Equation (9), we obtained the following relation [13,17]:

$$\left. \frac{g^E}{RT} \right|_A^B = -\int_{T^A}^{T^B} \frac{s^E}{RT} dT + \int_{p^A}^{p^B} \frac{v^E}{RT} dp + \sum_{i=1}^{n-1} \int_{x_i^A}^{x_i^B} \ln \frac{\gamma_i}{\gamma_n} dx_i \quad (10)$$

or

$$\left. \frac{g^E}{RT} \right|_A^B = -\int_{T^A}^{T^B} \frac{h^E}{RT^2} dT + \int_{p^A}^{p^B} \frac{v^E}{RT} dp + \sum_{i=1}^{n-1} \int_{x_i^A}^{x_i^B} \ln \frac{\gamma_i}{\gamma_n} dx_i = 0, \quad (11)$$

where  $T^A$  and  $T^B$  are the temperatures of the system in the states A and B,  $p^A$  and  $p^B$  are the pressures of the system in the states A and B,  $x_i^A$  and  $x_i^B$  are the mole fractions of the component  $i$  of the system in the states A and B, respectively. It has been shown that the relation (10) holds true for integration under any curve in phase space; however, it seems to be the most convenient way to choose the limits so that the left part of Equations (10) and (11) equals zero. The molar excess Gibbs energy of a pure substance is known to be equal to zero; therefore, the following relation is true for a binary mixture:

$$\left. \frac{g^E}{RT} \right|_{x_1=0}^{x_1=1} = 0. \quad (12)$$

Hence, under isothermal-isobaric conditions ( $T, p = \text{const}$ ), the Redlich–Kister consistency test is based on the equation below [13,17]:

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0. \quad (13)$$

It should be noted that for a real experimental data set, the calculated value of such an integral differs from zero, which may be caused by a number of purposes, for instance, experimental uncertainties of empirical data, errors of numerical procedures during calculations, etc. The value of that integral less than 0.02 is reported to be a sufficient criterion of thermodynamic consistency.

For isothermal conditions ( $T = \text{const}$ ), the contribution of the molar excess volume should be taken into account [13,17]:

$$\int_{p_2^\circ}^{p_1^\circ} \frac{v^E}{RT} dp + \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0, \quad (14)$$

where  $p_i^\circ$  is the vapor pressure in equilibrium with the pure component  $i$ . However, for most solutions, if the pressure variation is not so high, the value of this contribution is not significant ( $\approx 0.0001$ ) and can be neglected, so that Equation (13) can be used as well [13,17].

For an isobaric data set ( $p = \text{const}$ ), the contribution of the molar excess enthalpy should be taken into account [13,17]:

$$-\int_{T_2}^{T_1} \frac{h^E}{RT^2} dp + \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0. \quad (15)$$

The value of the first term in Equation (15) may reach 0.01 and usually cannot be neglected. Thus, information about the molar enthalpies of mixing, which can be obtained by means of calorimetry, is needed for testing an isobaric data set.

For multicomponent systems (ternary, quaternary, etc.), the use of isothermal-isobaric conditions is preferred to avoid the necessity of estimating the molar excess enthalpies, too. As for a binary system, the way of the composition variation could be chosen so that the limits of the integration should be pure components, therefore the integral would be equal to zero [13,17]:

$$\sum_{i=1}^{n-1} \int_{x_i^A}^{x_i^B} \ln \frac{\gamma_i}{\gamma_n} dx_i = 0. \quad (16)$$

The second convenient option is to choose the curve so that the initial and final compositions are the same and the integral around a closed curve equals zero as well [13,17]:

$$\sum_{i=1}^{n-1} \oint \ln \frac{\gamma_i}{\gamma_n} dx_i = 0. \quad (17)$$

## 2.2. The Van Ness Consistency Test

First, we will consider a binary system at constant temperature and pressure for better clarity. For a binary solution, the following relations can be written [13]:

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2, \quad (18)$$

$$\left( \frac{\partial g^E/RT}{\partial x_1} \right)_{T,p} = \ln \gamma_1 - \ln \gamma_2. \quad (19)$$

After substituting Equations (19) and (8) into Equation (18), we have [13]:

$$\ln \gamma_1 = \frac{g^E}{RT} + x_2 \left( \frac{\partial g^E/RT}{\partial x_1} \right)_{T,p}, \quad (20)$$

$$\ln \gamma_2 = \frac{g^E}{RT} - x_1 \left( \frac{\partial g^E/RT}{\partial x_1} \right)_{T,p}. \quad (21)$$

Here, we use the following notation:

$$g = \frac{g^E}{RT}, \quad (22)$$

$$g_i = \left( \frac{\partial g^E/RT}{\partial x_i} \right)_{T,p} = \left( \frac{\partial g}{\partial x_i} \right)_{T,p}. \quad (23)$$

Combine Equations (20) and (21) with Equations (22) and (23) [13]:

$$\ln \gamma_1 = g + x_2 g_1, \quad (24)$$

$$\ln \gamma_2 = g - x_1 g_1. \quad (25)$$

The main point of the van Ness method is the representation of the dependence of experimental  $g$  values on composition as a function of the composition  $g(x_1)$ , for example, a polynomial, a Margules equation, a van Laar equation, etc. Then, assume that the vapor in equilibrium with the liquid phase is the ideal gas. In this case, the vapor pressure can be calculated by means of Raoult's law in its particular statement [13]:

$$p_{calc} = x_1 \gamma_1 p_1^\circ + x_2 \gamma_2 p_2^\circ = x_1 p_1^\circ e^{g(x_1) + x_2 g_1} + x_2 p_2^\circ e^{g(x_1) - x_1 g_1}, \quad (26)$$

where  $p_{calc}$  is the calculated value of the vapor pressure. The activity coefficients can be calculated with the Equations (24) and (25). With the calculated values of pressure and activity coefficients, we can estimate the composition of the vapor:

$$y_{i,calc} = \frac{x_i \gamma_{i,calc} p_i^\circ}{p_{calc}}, \quad (27)$$

where  $y_{i,calc}$  is the calculated mole fraction of the component  $i$  in the vapor phase, and  $\gamma_{i,calc}$  is the calculated activity coefficient of the component  $i$ . The difference between calculated and experimental mole fractions of less than 1% is reported to be a sufficient criterion for the thermodynamic consistency of experimental data, according to the van Ness test.

In a general case of a multicomponent system, the molar excess Gibbs energy is presented as a function of the composition of the mixture  $g(x_1, x_2, \dots, x_{n-1})$ . The van Ness method gives the following relations for a multicomponent mixture:

$$\ln \gamma_n = g - \sum_{i=1}^{n-1} x_i g_i, \quad (28)$$

$$\ln \gamma_j = g + (1 - x_j) - \sum_{\substack{i=1 \\ i \neq j}}^{n-1} x_i g_{ij} \quad (29)$$

$$p_{calc} = \sum_{i=1}^n x_i \gamma_{i,calc} P_i^{\circ} \quad (30)$$

The vapor composition can be calculated with Equation (27) as well. The comparison of the calculated and experimental vapor compositions serves as validation of the thermodynamic consistency of an experimental data set [13].

### 2.3. Calculation of the Activity Coefficient

Both the Redlich–Kister and van Ness methods are based on the analysis of the values of the molar excess Gibbs energy or activity coefficients, which are connected with Equation (7). That is why the experimentally measured compositions of the coexisting liquid and vapor phases, pressures, and temperatures need further data processing to evaluate the activity coefficients of the components for thermodynamic consistency tests.

The way for the calculation of the activities of components in a liquid phase is through the implementation of Raoult's law, which is the consequence of the condition of the vapor-liquid phase equilibrium. The vapor-liquid phase equilibrium requires the chemical potentials of components in the equilibrium liquid and vapor phases to be equal [14–16,18]:

$$\mu_i^v = \mu_i^l, \quad (31)$$

where  $\mu_i^v$  is the chemical potential of the component  $i$  in the vapor and  $\mu_i^l$  is the chemical potential of the component  $i$  in the liquid. The chemical potential of a component in the vapor phase can be represented in the following form:

$$\mu_i^v = \mu_i^{\circ}(T) + RT \ln f_i^v, \quad (32)$$

where  $\mu_i^{\circ}(T)$  is the standard part of the chemical potential of a component  $i$  in the vapor phase as a function of the temperature, and  $f_i^v$  is the fugacity of the component  $i$  in the non-ideal vapor phase. A similar equation can be used for a liquid phase:

$$\mu_i^l = \mu_i^{\circ}(T) + RT \ln f_i^l, \quad (33)$$

where  $f_i^l$  is the fugacity of the component  $i$  in the liquid phase. Then, according to the relation (31), the VLE condition can be rewritten via the fugacity of components in the coexisting phases [18]:

$$f_i^v = f_i^l \quad (34)$$

At the same time, we can use the form (2) for the chemical potential of components in the liquid phase. The standard part  $\mu_i^{\circ}(T, p)$  can be presented with the equation similar to the relation (34):

$$\mu_i^{\circ}(T, p) = \mu_i^{\circ}(T) + RT \ln f_i^{ol}, \quad (35)$$

where  $f_i^{ol}$  is the fugacity of the component  $i$  in the pure liquid. Then, the following relation holds true for the chemical potential of the component  $i$  in the liquid phase:

$$\mu_i^l = \mu_i^{\circ}(T) + RT \ln f_i^{ol} + RT \ln a_i^l \quad (36)$$

For the fugacity of a pure liquid, the following relation can be used:

$$\frac{d \ln f_i^{ol}}{dp} = \frac{v_i^{ol}}{RT}, \quad (37)$$

where  $v_i^{ol}$  is the molar volume of the liquid  $i$ . Assuming that the pure liquids are almost incompressible, after integrating (37), we have:

$$f_i^{ol}(p) = f_i^{ol}(p_i^\circ) e^{\frac{v_i^{ol}(p-p_i^\circ)}{RT}}, \quad (38)$$

where  $f_i^{ol}(p)$  is the fugacity of the pure liquid  $i$  under the pressure  $p$ ,  $f_i^{ol}(p_i^\circ)$  is the fugacity of the pure liquid  $i$  under the saturated vapor pressure. Under the saturated vapor pressure, the fugacity of the liquid equals the fugacity of the vapor:

$$f_i^{ol}(p_i^\circ) = f_i^{ov}(p_i^\circ), \quad (39)$$

hence:

$$f_i^{ol}(p) = f_i^{ov}(p_i^\circ) e^{\frac{v_i^{ol}(p-p_i^\circ)}{RT}} \quad (40)$$

Combine relations (32), (36), and (40), so we have the following relation for the calculation of activities:

$$f_i^v(p) = f_i^{ov}(p_i^\circ) e^{\frac{v_i^{ol}(p-p_i^\circ)}{RT}} a_i^l \quad (41)$$

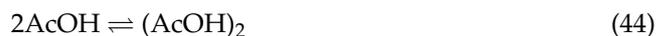
This relation (41) takes into account the non-ideal behavior of both liquid and vapor phases and may be referred to as the generalized Raoult's law, including Poynting's correction term. Assuming that the vapor phase is an ideal gas, Equation (41) can be reduced to:

$$py_i = p_i^\circ x_i \gamma_i \quad (42)$$

For an ideal solution, we have the classic form of Raoult's law:

$$py_i = p_i^\circ x_i \quad (43)$$

In the case of the system acetic acid-ethanol-ethyl acetate-water, the non-ideality of the alcohol, ester, and water in the vapor phase can be neglected in quite a wide pressure range. As for the acetic acid, due to the strong association, the deviations from an ideal gas are significant even under low pressures [17]. The non-ideal behavior of the acetic acid vapor may be taken into account by applying the relation (41); however, it is necessary to additionally use an EoS for the corresponding vapor. The alternative way is to consider the dimerization process of the acetic acid in vapor:



For the equilibrium (44) the following relation can be written:

$$K_a = \frac{p_d}{p_m^2}, \quad (45)$$

where  $K_a$  is the association constant,  $p_d$  is the vapor pressure of the dimer form of the acid, and  $p_m$  stands for the vapor pressure of the monomer form of the acid. The association constant is assumed to be independent of composition. Thus, the vapor in equilibrium with the quaternary system can be considered an ideal gas, containing five components: alcohol, ester, water, monomers, and dimers of the acid. The implementation of this approach to Equation (40) gives the relations for the calculation of activity coefficients [13,17,19]:

$$\gamma_{\text{AcOH}} = \frac{-1 + \sqrt{1 + 4K_a P y_{\text{AcOH}} (2 - y_{\text{AcOH}})}}{x_{\text{AcOH}} (2 - y_{\text{AcOH}}) (\sqrt{1 + 4K_a P_{\text{AcOH}}^\circ} - 1)}, \quad (46)$$

$$\gamma_i = y_i \frac{1 + 4K_a P (2 - y_{\text{AcOH}}) - \sqrt{1 + K_a P y_{\text{AcOH}} (2 - y_{\text{AcOH}})}}{2K_a P_i^\circ x_i (2 - y_{\text{AcOH}})^2}, \quad i \neq \text{AcOH} \quad (47)$$

For further calculations, we used the value of the association constant of  $0.375 \text{ mbar}^{-1}$  [20].

### 3. VLE Data for Binary Subsystems

#### 3.1. Ethanol-Water System

Navarro-Espinosa et al. [21] conducted a study of the VLE of nine binary mixtures at 773 mbar, focusing on the ethanol-water binary mixture. A recirculation still was used to measure the boiling temperatures of solutions at 773 mbar. The compositions of the coexisting liquid and vapor phases were determined by means of refractometry and gas chromatography. The Peng–Robinson Stryjek–Vera equation of state [22] together with the Wong–Sandler mixing rules [23] (PRSV-WS) and the NRTL model were applied to correlate the obtained VLE data for the studied systems. However, the authors did not perform any thermodynamic consistency tests.

Iwakabe et al. [24] introduced a recirculating still for investigating vapor-liquid-liquid equilibria (VLLE). The still was also applied for the experimental determination of the boiling temperatures and equilibrium vapor compositions in the ethanol-water binary system at 1013 mbar. The thermodynamic consistency was checked using the Herington's area test. It was found that the data were sufficiently consistent. The Equation (41) was used for calculating the activity coefficients of the components. The non-ideal behavior of the vapor phase was considered in terms of the virial equation of state. The second virial coefficient was estimated by the Tsonopoulos method [25]. The Rackett equation, modified by Spencer and Adler, was applied for the estimation of the molar volume of liquids.

Ueberfeld et al. [26] reported a variation of the static method for studying VLE in binary mixtures. The partial pressure of ethanol in the vapor phase was determined by a photoacoustic sensor. The experimental procedure included the measurement of a photoacoustic signal of the vapor phase in equilibrium with the liquid of a certain composition at a constant temperature under atmospheric pressure. The partial pressure of ethanol in the vapor phase was calculated based on the obtained values of the photoacoustic signal. Further processing of the VLE data were not conducted, and the thermodynamic consistency was not checked.

Yang and Wang [27] determined the boiling temperatures and compositions of the equilibrium liquid and vapor phases using a modified Rose still at 1013 mbar. It should be noted that the authors proposed an unusual approach for the data correlation. They did not use Equation (43) to calculate the activity coefficients of the components based on the obtained VLE data. However, the activity coefficients were calculated with two model equations (Wilson and UNIFAC). Based on the model calculations, the boiling temperatures and vapor compositions were estimated and compared with the experimental ones. The thermodynamic consistency was proven using Herington's method.

Pemberton and Mash [28] presented a new apparatus for studying VLE with the static method. Isothermal VLE data were obtained at four temperatures (303.15 K, 323.15 K, 343.15 K, and 363.15 K). The activity coefficients and, consequently, molar excess Gibbs energy were calculated by Barker's method [29]. The authors used literature information about the molar excess enthalpy for the system [30] to check the reliability of the obtained data and to calculate molar excess entropy values. However, the results of the thermodynamic consistency tests were not presented.

Cui et al. [31] studied the compositions of the equilibrium liquid and vapor phases at 323.15 K using the dynamic flow method, which were in good agreement with data measured by Pemberton and Mash [28]. The equilibrium vapor pressure was not determined; therefore, the activity coefficients could not be calculated from the obtained experimental results. The calculation was performed using the NRTL equation. The Herington's area test was used to check the thermodynamic consistency of the data.

Dalmolin et al. [32] reported equilibrium vapor pressure for five compositions of the ethanol-water system at four temperatures (288 K, 298 K, 308 K, and 323 K). However, the vapor composition was not determined, and no thermodynamic consistency tests were conducted.

Vu et al. [33] obtained isothermal VLE data at 313.15 K using the static method with a specially constructed still. Activity coefficients were calculated using the UNIQUAC equation. The Hayden-O'Connell method for the evaluation of the second virial coefficients was applied, allowing for correlation of the experimental  $P$ - $x$ - $y$  data. The thermodynamic consistency was validated using the Redlich-Kister, point-to-point Van Ness, and Fredenslund methods.

Zhang et al. [34] reported several VLE data points at 1000 mbar measured using the recirculating method with an ebulliometer. The vapor phase was considered an ideal gas for the calculation of activity coefficients. The experimental data were correlated by applying the NRTL equation. Various ways of predicting VLE were discussed. It was shown that the prediction of the equilibrium vapor compositions based on the correlation of the  $T$ - $x$  data gave significantly smaller deviations than the prediction of the boiling temperatures based on the correlation of the  $x$ - $y$  data set. The correlation of the activity coefficients was observed to give sufficient results as well. No thermodynamic consistency tests were conducted.

Orchillés et al. [35] investigated isobaric VLE at 1000 mbar using a modified Labodest model recirculating still to measure  $T$ - $x$ - $y$  data. The NRTL model was applied for modeling VLE and calculating activity coefficients. The Van Ness test in Fredenslund's modification was used to check for thermodynamic consistency.

Orjuela et al. [36] reported isobaric VLE data at 1013 mbar obtained by the static method. The obtained results were compared with those presented in other papers and were found to be in good agreement with most of them. Thermodynamic consistency was not checked. The NRTL, UNIQUAC, and Hayden-O'Connell equations were applied for VLE predictions. Good agreement between experimental and calculated values proved the reliability of the data.

### 3.2. Acetic Acid-Water System

Miyamoto and Nakamura [37] utilized a flow-type apparatus to measure isothermal VLE for the binary system of acetic acid and water at 343.2 K. Two tests (a point test and an area test) were conducted to validate the thermodynamic consistency of the obtained data. The correlation of the data were performed using the NRTL model. No azeotropes were detected. Interaction parameters for the binary system under study were used to predict VLE for ternary systems. For the correlation and prediction of VLE, the dimerization of acetic acid in the vapor phase was taken into account. The values of enthalpy and entropy change of the association were estimated to be  $-58.5$  kJ/mol and  $-136.0$  J/mol·K, respectively.

Navarro-Espinosa et al. [21] studied the VLE in the acetic acid-water system at 773 mbar, using similar experimental procedures and data processing as mentioned above for the ethanol-water system. The thermodynamic consistency test was not conducted. The NRTL and PRSV-WS equations were used for data correlation.

Vercher et al. [38] obtained isobaric VLE data for the binary systems of acetic acid and water at 1000 mbar using the Labodest model recirculating still. For further data treatment and estimation of the activity coefficients, the authors suggested applying the approach proposed by Marek [19] to take into account the dimerization process of acetic acid in both the vapor and liquid phases. The experimental apparatus was previously tested by studying pure acetic acid. The thermodynamic consistency was validated with the modified point-to-point van Ness test. Because VLE was also studied for the ternary system acetic acid-water-lithium acetate, the electrolyte NRTL model, proposed by Mock [39], was used for correlating both the binary and ternary experimental data.

Chang et al. [40] investigated VLE in the acetic acid-water binary systems at 1013 mbar using a modified Rose-type recirculating still. The experimental data showed good agreement with those obtained by Gilmont et al. [41]. The Equation (41) was utilized for the estimation of activity coefficients. The Poynting term was neglected, and the virial equation of state was applied for calculating fugacity coefficients. The second virial coefficient was calculated with the Hayden-O'Connell approach [42]. The experimental data successfully passed the Herington thermodynamic consistency test. The NRTL and

UNIQUAC equations were used for data correlation and prediction of VLE in ternary acetic acid-water-ester systems.

Bernatová et al. [43] conducted a study of isothermal VLE in the acetic acid-water system at 323.15 K using a Dvorak–Boublík recirculating still. The NRTL equation was applied to correlate activity coefficients. No thermodynamic consistency test results were reported.

Xie et al. [44] reported isobaric VLE data at 1013 mbar obtained using a modified Rose recirculating still. Equation (41) was applied for calculating activity coefficients, neglecting the Poynting term. Non-ideal behavior was accounted for by considering dimerization in the vapor phase using chemical theory, as described earlier. The virial equation of state, with the use of the Hayden–O’Connell method for the second virial coefficient evaluation, was also applied for estimating the fugacity of components in the vapor phase. The authors highlighted the significant contribution of acetic acid to deviations from ideal behavior. Thermodynamic consistency of the data was proved using the Herington and Fredenslund tests. The NRTL and UNIQUAC models were applied for correlating activity coefficients. The NRTL equation proved to be more suitable.

Garner et al. [45] determined isobaric VLE for the acetic acid-water system using the Ellis-type recirculation still. The total pressure of the experiment was not specified in the article, but it appears to be atmospheric. The boiling temperatures and the compositions of the equilibrium vapor and liquid phases were measured. Two data sets are presented: one assuming both substances in the vapor phase are ideal gases (the molecular weight of the acetic acid monomer was used in calculations), and the second considering the corrected molecular weight of the acetic acid, which takes into account its’ association in the vapor phase. The presented data indicates a significant influence of acetic acid’s association with vapor on calculating activity coefficients, as well as its considerable deviations from ideal gas behavior even at small pressures. The authors did not report any thermodynamic consistency tests.

### 3.3. Acetic Acid-Ethanol System

The isobaric VLE data at 773 mbar for the acetic acid-ethanol mixture were presented by Navarro-Espinosa et al. [21]. The data correlation were performed using the NRTL and PRSV-WS equations. The authors note the potential application of their apparatus for investigating VLE in reactive systems, depending on the rate of a chemical reaction. If the rate is too high, the continuous shift of the compositions would hinder the setting of the steady state in the recirculating still and, consequently, the VLE. That is why the possibility of the still application for VLE investigation should be checked for every reacting system. The authors did not perform any thermodynamic consistency tests. However, we will presume that in this case, the chemical reaction does not affect the VLE in the still.

The isothermal VLE data for the acetic acid-ethanol binary mixture at 323.2 K were also measured by Miyamoto and Nakamura [37]. It should be noted that the rate of esterification reaction and its possible influence on the experimental results obtained with the flow-type apparatus were not discussed by the authors. The thermodynamic consistency was checked using a point-to-point and an area test. The NRTL model was used for data correlation, and the optimized parameters were applied for VLE prediction on ternary systems. For the acetic acid-ethanol system, the presence of both the dimer of acetic acid and the heterodimer of acid and alcohol in the vapor phase was considered. The enthalpy change of the acid and alcohol association was estimated to be  $-46.0$  kJ/mol.

Reichl et al. [46] introduced a non-recycle flow still with a short equilibration time that made it possible to conduct rapid measurements for VLE investigation in reacting systems, specifically for thermally unstable compounds. The  $T$ - $x$ - $y$  VLE data were obtained for the acetic acid-ethanol reacting mixture at 500 mbar and under atmospheric pressure. The authors highlight the deviations between existent data on the system, which can be caused by the complexity of the system and difficulties in VLE studies in mixtures with chemical reactions. The experimental results were compared with the UNIFAC Dortmund calculations. It was observed that the UNIFAC data qualitatively agreed with

the experiment; however, quantitative prediction seemed to be insufficient. The results of the data correlation with the NRTL equation were presented. The Wilson and UNIQUAC equations were applied as well. These models were reported to give similar results.

Wagner et al. [47] conducted measurements of vapor pressure in equilibrium with the liquid phase for the acetic acid-ethanol system at 308.15 K and 318.15 K using the isotenoscope method. The stability of the measured pressure throughout the experiment led to the neglect of its influence on chemical reactions. Activity coefficients and excess Gibbs energy values were obtained through the integration of the Gibbs–Duhem equation. The deviations from ideal gas were accounted for by considering the dimerization of acetic acid in the vapor phase and introducing the virial equation of state. However, the association between acid and alcohol was not considered. Thermodynamic consistency tests were not performed; it should be noted that since the vapor compositions were not experimentally determined but rather calculated through the integration of the Gibbs–Duhem equation, the tests based on this equation are not applicable.

### 3.4. Acetic Acid-Ethyl Acetate System

Miyamoto and Nakamura [37] also obtained experimental isobaric VLE data for the acetic acid-ethyl acetate system at 323.2 K. The thermodynamic consistency of the data was validated with area and point consistency tests. The NRTL equation interaction parameters were estimated.

Navarro-Espinosa et al. [21] obtained the VLE data for the acetic acid-ethyl acetate system at 773 mbar as well. However, the authors did not provide any results from thermodynamic consistency tests. The experimental data were correlated with the NRTL model and the PRSV-WS equation of state.

Kato [48] used a flow-type apparatus for measuring dew-point and bubble-point temperatures in the system. The temperatures measured during the experiment were corrected to the values at 987 mbar and smoothed. The composition of the vapor phase was not determined. The Wilson equation was applied for data correlation and calculation of VLE, while the association of the acetic acid in the vapor phase was taken into account. Large deviations among experimental VLE data were observed for this system.

Garner et al. [45] applied an Ellis recirculation still to investigate isobaric VLE for the acetic acid-ethyl acetate system as well. Two data sets were presented, one taking into account the association of acetic acid in vapor and one without it. A significant discrepancy among the obtained values of activity coefficients was observed, attributed to the small deviations from ideality that led to a significant influence on the calculated activity coefficients. The Margules equation was applied for correlating activity coefficients even with small errors in determined compositions.

Macedo and Rasmussen [49] reported isothermal  $P$ - $x$ - $y$  VLE data for the binary acetic acid-ethyl acetate system at 338 K and 346 K. The measurements were carried out on a Dvorak–Boublik recirculating still. Pure substances were also studied to obtain the Antoine equation parameters for further calculation. The relation (41) was applied for estimating activity coefficients, neglecting the Poynting term. Acetic acid vapor was considered an associated ideal gas, according to (46) and (47). The obtained data were processed using the UNIQUAC equation and the two-, three-, and four-parameter Margules equation. The results of all data reduction methods were reported to yield identical results. A good correlation between experimental and calculated data was observed, with small deviations believed to be evidence of thermodynamic consistency. No classical thermodynamic consistency test based on the Gibbs–Duhem equation was conducted.

Furnas and Leighton [50] used the Othmer apparatus to measure the composition of equilibrium vapor and liquid phases in the acetic acid-ethyl acetate system at atmospheric pressure (995–1019 mbar). Boiling temperatures for the system were not measured. The  $x$ - $y$  diagram was plotted. No data reduction procedures were reported.

### 3.5. Ethanol-Ethyl Acetate System

Figurski and Malanowski [51] found significant discrepancies, reaching 100%, among the literature information on the VLE for the binary ethanol-ethyl acetate system. They measured the boiling temperatures for the ethanol-ethyl acetate system at different pressures, obtaining a total of 158 experimental points for pressures ranging from 35 mbar up to 1000 mbar, and the temperature range was from 294.15 K up to 350.15 K, both for pure substances and for several binary compositions. A van Ness ebulliometer was used for boiling temperature measurements. The refractive index of liquids was measured to determine the liquid phase composition. However, the compositions of equilibrium vapor phases were not studied. The accuracy of the experimental procedure was tested by investigating pure ethanol and comparing it with literature information reported by Ambrose and Sprake [52]. The AEOS equation [53,54] was used for data correlation. The authors assumed that the good agreement between experimental values and calculated ones proved not only the accuracy but also the thermodynamic consistency of the experimental data. However, they did not conduct any thermodynamic consistency tests using the relations of classical thermodynamics. Therefore, it can be assumed that the thermodynamic consistency of the data has not been proved by the authors, but it has not been refuted either.

Navarro-Espinosa et al. [21] studied the ethanol-ethyl acetate system (isobaric VLE at 773 mbar). The NRTL model and the PRSV-WS equation were applied to correlating the obtained VLE data for the studied system. Any thermodynamic consistency tests were not performed by the authors.

Tu et al. [55] presented isobaric data on VLE for the ethanol-ethyl acetate system at 1013 mbar. The Hunsmann equilibrium, still with recirculation, was used for this study. Gas chromatography was utilized for measuring the equilibrium liquid and vapor compositions. The activity coefficient for the liquid phase was calculated using Raoult's law. The Soave-Redlich-Kwong equation of state [56] was used to estimate the fugacity coefficients of the components in the vapor phase. The molar volumes of the liquid were calculated with the modified Racket equation [57]. However, the thermodynamic consistency tests were not provided as well.

Susial et al. [58,59] reported data on boiling temperatures and compositions of coexisting liquid and vapor phases for the binary ethanol-ethyl acetate mixtures at 3000 mbar [58], 1000 mbar [59], 5000 mbar [59], and 7000 mbar [59]. A specially constructed stainless steel ebulliometer for the high-pressure measurements was used. The activity coefficients were calculated based on the experimental data obtained with the use of Raoult's law. The fugacities of the components in the vapor phase were also calculated using the virial equation of state up to the second term. The second virial coefficients were evaluated with the Hayden-O'Connell method [42]. The thermodynamic consistency of the data was tested with the point-to-point van Ness method. Although the results of the test were not provided, it was assumed to have been successfully passed. Additionally, the experimental data were correlated with several model equations (Redlich-Kister, van Laar, Margules, Wilson, NRTL, and UNIQUAC). Two group contribution models (UNIFAC and ASOG) were applied to predict VLE in the system.

Furnas and Leighton [50] conducted research on the isobaric VLE for the ethanol-ethyl acetate system at 1013 mbar, using Othmer apparatus to obtain the  $T$ - $x$ - $y$  data set. The  $x$ - $y$  curve was plotted, and the composition of the azeotrope was estimated. No consistency tests were performed.

Kato et al. [60] proposed an apparatus for investigating isobaric VLE. The isobaric VLE data set for the binary mixture of ethanol and ethyl acetate at 1013 mbar were collected using the suggested apparatus. A substantial discrepancy was observed between their data and Furnas and Leighton's [50] results. Experimental data were smoothed and plotted on phase diagrams. Thermodynamic consistency was not verified.

Orjuela et al. [61] reported VLE data for the ethanol-ethyl acetate system at 1013 mbar. The experiment employed a recirculating apparatus (VLE 100D). The close agreement

between the obtained data and the literature was reported. The UNIQUAC and Hayden-O'Connell equations were used for data correlation with considerable accuracy.

Topphoff et al. [62] obtained isobaric VLE data for the ethanol-ethyl acetate mixture at 1013 mbar using the recirculating method with a modified Scott ebulliometer. The data were correlated and smoothed using the UNIQUAC equation to test data reliability, while thermodynamic consistency was verified with the Redlich–Kister method.

Orchillés et al. [63] performed a study of the VLE for the ethanol-ethyl acetate system at 1000 mbar using a modified Labodest model recirculating still (Pilodist). The pure substances were studied as well, and the parameters of the Antoine equations were estimated. Thermodynamic consistency was ascertained using the Van Ness test. The NRTL model was applied to reduce experimental data. The activity coefficients were derived using Raoult's law in the form of Equation (42), considering the vapor of both ethanol and ethyl acetate as ideal gases. The appropriate phase diagram and composition diagram were plotted.

Li et al. [64] utilized a modified Othmer recirculating still to obtain isobaric the  $T$ - $x$ - $y$  data set for the system ethanol-ethyl acetate at 1013 mbar. The obtained data were found to be in good agreement with measurements taken by Tu et al. [55] and Orchillés et al. [63]. The relation (42) was used to calculate activity coefficients. The NRTL model was used for data correlation. The relative volatility of ethyl acetate to ethanol was determined. The corresponding  $T$ - $x$ - $y$  phase diagram was plotted. However, the results of any thermodynamic consistency tests were not presented.

Takamatsu and Ohe [65] determined the equilibrium compositions of the liquid and vapor phases for the ethanol-ethyl acetate system at 313.15 K using the headspace gas chromatography method. Thermodynamic consistency was verified by the Herrington area test. The experimental results were correlated using the Wilson, UNIQUAC, and NRTL equations. The  $x$ - $y$  diagram was plotted, and the azeotrope composition was estimated.

Ashraf and Prasad [66] studied isothermal VLE in the ethanol-ethyl acetate system at 313.15 K. The infinite-dilution activity coefficients were evaluated. The Wilson equation was used for the calculation of activity coefficients. Thus, the vapor compositions were determined with Equation (42). Any thermodynamic consistency tests were not conducted.

### 3.6. Ethyl Acetate-Water System

Garner et al. [45] note that the experimental determination of the VLE for the binary mixture ethyl acetate-water causes significant challenges due to its wide splitting region of liquid phase. This not only results in the splitting of the liquid phase for most compositions but also causes the vapor phase condensate to be immiscible. The authors utilized two types of recirculation stills, Ellis and Gillespie, to determine the isobaric VLE for the ethyl acetate-water system. The composition of the heterogeneous azeotrope was determined. The activity coefficients of the components in the liquid phase were calculated using Raoult's law (43) assuming both the substances in the vapor phase are ideal gases. The final values of the activity coefficients of water and ethyl acetate were estimated using three methods. The authors demonstrate that the van Laar equation is unsuitable for extrapolating the activity coefficients from the homogeneous region into the immiscible region. The possibility of a hydrolysis reaction between ethyl acetate and water and its influence on the experimental data were not discussed. Any thermodynamic consistency tests were not reported.

Ellis and Garbett [67] obtained the isobaric VLE data for both homogeneous and heterogeneous compositions of the binary ethyl acetate-water system at 1013 mbar. A novel equilibrium still designed for investigating partially miscible systems was presented by the authors. The azeotrope composition was measured. The activity coefficients were calculated assuming the vapor phase behaved as an ideal gas. The possible impact of the chemical reaction on experimental results was not reported.

Reichl et al. [46] reported VLE data at atmospheric pressure obtained with a non-recirculating flow still. Good agreement with prior literature information was observed for low and medium ethyl acetate concentration. At the same time, considerable deviations

appeared for high concentrations of ethyl acetate, which were attributed to the composition determination procedure. The NRTL model was applied for data correlation. Neither the possible influence of the chemical reaction nor the thermodynamic consistency tests were discussed.

Lee et al. [68] performed a study of isobaric VLE in a modified Othmer-type recirculating still. Activity coefficients were determined with Equation (41) and molar volumes of pure liquids were estimated with the Rackett equation. In order to take into account fugacity coefficients, the virial equation of state was employed, with the second virial coefficients evaluated using the Hayden-O'Connell method. The authors reported considerable experimental difficulties when the concentration of water in the liquid phase exceeded 0.988, attributed to the partial miscibility of the systems and resulting disturbed recirculation. The authors used the van Ness and Abbot coexistence equation to predict missing data. The enthalpies of vaporization were evaluated by the Watson relation and the Viswanath–Kuloor method. The Vetere method was used to calculate the heat of vaporization at the boiling temperature. The vapor phase was considered to be an ideal gas. The NRTL and UNIQUAC models were utilized for data correlation and prediction. Two correlation methods were applied: while the correlation based on experimental VLE data showed good agreement with empirical information, the correlation based on LLE data proved unsuitable for predicting VLE. Remarkably, no thermodynamic consistency tests were performed, and the reacting nature of the system was not discussed.

Rajendran et al. [69] obtained isobaric VLE data at 1013 mbar with a Smith and Bonner type still. The heterogeneous azeotropic composition was determined. No consistency tests or correlations for this system were reported.

#### 4. VLE Data for Ternary Subsystems

The ethanol-ethyl acetate-water ternary subsystem has been most extensively studied in terms of VLE. The papers [68,70–74] include both isobaric and isothermal data.

Garner et al. [70] investigated VLE in the ternary acetic acid-ethyl acetate-water system at atmospheric pressure. Experiments were carried out using the equilibrium still. The acetic acid and water content in the samples were estimated by titration, while the ethyl acetate content was determined by saponification. The authors provided a sizable VLE data set but did not present any phase diagrams of these experimental outcomes. In addition, an appropriate method for predicting ternary data from binary data based on the Margules equation was suggested.

Griswold et al. [71] reported detailed experimental isobaric VLE data at 1013 mbar, determined using a modified glass Colburn still. The measurement of specific gravity and weight per cent of ethyl acetate by saponification was applied for sample analysis. Experimental data were represented in a detailed concentration diagram. The authors confirmed the previously obtained data [75,76] on the presence of ternary azeotrope at 343.45 K. The “low boiling zone” in the ternary phase diagram, representative of a significant region of minimum boiling temperature, was described. The authors obtained VLE data for the binary ethanol-ethyl acetate and ethyl acetate-water subsystems.

Mertl [72] presented experimental isothermal VLE data for the ternary ethanol-ethyl acetate-water system at 313.15 K, 328.15 K, and 343.15 K, and for the binary subsystems: ethyl acetate-ethanol, ethyl acetate-water, and ethanol-water. The VLE was studied using a modified Gillespie still. Samples were analyzed via refractometry (for water-rich mixtures of ethyl acetate and water) and via density measurements (for the other solutions). The author does not provide a visual interpretation of the obtained experimental data.

Van Zandijcke and Verhoeye [73] obtained a significant VLE data set at atmospheric pressure for the ethanol-ethyl acetate-water system and its binary subsystems: ethyl acetate-ethanol, ethyl acetate-water, and ethanol-water. The VLE was investigated using a modified Gillespie still and a gas chromatography method. The experimental data were represented visually, including consideration of the “low boiling zone” [71] comprising ternary azeotrope. The authors noted that the literature data regarding the ternary azeotrope

composition in the ethanol-ethyl acetate-water system were inconsistent. According to Van Zandijcke and Verhoeye [73], the boiling point of ternary azeotrope is 343.35 K. The composition of the azeotropic mixture was determined graphically. Due to accurate boiling point measurements, the authors clarified the boundaries of the «low boiling zone» and nevertheless, all previously obtained data [71,75,76] were found to fall within this region. Moreover, the ternary VLE data were predicted using the NRTL model and showed good agreement with the experimental data. However, the authors confined themselves to root mean square deviation (RMSD) values, not detailing the equilibrium data in the article.

Lee et al. [68] carried out both experimental investigation and thermodynamic modeling of VLE and vapor-liquid-liquid equilibrium (VLLE) of the ethanol-ethyl acetate-water system and its constituent binary systems: ethanol-water, ethanol-ethyl acetate, and ethyl acetate-water at atmospheric pressure. VLE and VLLE were measured using an Othmer-type recirculating still and gas chromatography analysis. The authors chose three methods to correlate experimental VLE results: UNIQUAC, NRTL, and the modified Wilson equation. Among these three models, the NRTL model provided the best estimation for the ternary VLE. It was found that the NRTL model provided the best estimation of ternary VLE. An extensive experimental data set were compared graphically with calculated data and experimental data previously obtained by other researchers [60,77] for binary subsystems.

Gomis et al. [74] studied experimentally isobaric (1000 mbar) VLLE for the ethanol-ethyl acetate-water system, utilizing a commercial all-glass dynamic recirculating still, specifically the Labodest apparatus model 602, modified with an ultrasound homogenizer. The subsequent sample analysis was carried out by GC. A comparison of the obtained VLLE data with that reported by Mertl [72], Van Zandijcke [73], and Lee [68], including phase diagrams, was presented. The authors note that their results generally agree with the data of Mertl [72] and Lee [68]. However, they found significant discrepancies between the data of Van Zandijcke [73] and the results of Lee [68] for the vapor curve. They concluded that Lee's data displayed considerable scatter, making it inadequate for constructing a smooth vapor curve. It is noteworthy that Gomis et al. [74] did not provide explanations for the discrepancies between their data and that of Van Zandijcke [73], especially considering they only obtained five experimental data points, making their data set relatively sparse compared to Van Zandijcke's much more extensive data.

## 5. VLE Data for the Quaternary System

The results of the VLE study in the quaternary acetic acid-ethanol-ethyl acetate-water system under isobaric conditions (atmospheric pressure) are presented in four works only [78–80]. Notably, no isothermal data for VLE in this quaternary system has been found in the scientific literature.

Kang [78] et al. investigated VLE in a chemically equilibrium quaternary acetic acid-ethanol-ethyl acetate-water system at atmospheric pressure. Experiments were carried out in recirculation. Samples were analyzed by the method of gas chromatography. Although there is a significant volume of experimental VLE data obtained, the article does not present a phase diagram. The phase equilibrium data were correlated using a modified UNIQUAC method, and the calculated data were in good agreement with the experimental results.

Campanella and Mandagaran [79] made a theoretical study of VLE in the quaternary system with an ethyl acetate synthesis reaction at atmospheric pressure. UNIQUAC and NRTL models and the Wilson equation were applied to calculate azeotropic points, residue curve maps, and distillation line diagrams for the conceptual design of RD. The authors highlight that the presence of a reactive azeotrope in modeling the phase behavior of the studied system depends on the value of the chemical equilibrium constant and is not influenced by phase equilibrium parameter values. Calculations were made for both reactive and non-reactive azeotropes.

Calvar et al. [80] presented detailed data on VLE in the system with the reaction of acetic acid esterification with ethanol and its constituent binary systems: ethanol-ethyl acetate, acetic acid-ethyl acetate, and acetic acid-water at 1013 mbar. The VLE study

was carried out using a glass Fischer Labodest apparatus, model 602/D. Equilibrium compositions were determined by density measurements for all binary subsystems, with the exception of the acetic acid–water system, and by gas chromatography for the quaternary system acetic acid–ethanol–ethyl acetate–water and for the binary acetic acid–water system. The UNIQUAC method was utilized to correlate the experimental VLE data with the quaternary system. Predicted and experimental data were found to be well-correlated. ASOG and UNIFAC models were used to correlate binary data with ASOG, proving better results. In addition, binary VLE data (for the ethanol–ethyl acetate and acetic acid–water systems) were graphically compared with literature data [55,67,70] and they were found to generally match well.

## 6. Thermodynamic Consistency of Experimental Data

In order to achieve the objective of our research, which is to estimate the reliable value through the direct integration of the Gibbs–Duhem equation for a real experimental data set, we applied two integral methods (the Redlich–Kister method and the direct integration of the Gibbs–Duhem equation) for the thermodynamic consistency tests. The NRTL equation was used to interpolate literature information for further processing and integration. The NRTL [81] parameters were obtained by the optimization of the following objective function (OF) to its minimum value:

$$OF = \sqrt{\frac{\sum_{i=1}^n (g_{i,exp}^E - g_{i,calc}^E)^2}{n-1}}, \quad (48)$$

where  $g_{i,exp}^E$  is the experimental value of the molar excess Gibbs energy for the composition  $i$ ,  $g_{i,calc}^E$  is the calculated value of the molar excess Gibbs energy for the composition  $i$ , and  $n$  is the number of experimental compositions. This procedure was used to estimate the NRTL parameters for every experimental data set.

For both methods, relations for isothermal-isobaric ( $T, p = \text{const}$ ) conditions (5) and (17) were used. In the case of isothermal experimental VLE data, the pressure variation, as previously mentioned, could be neglected in most cases. For the isobaric VLE data sets, the temperature dependence of activity coefficients was taken into account with the NRTL equations, and the consistency tests were conducted at a constant temperature (the mean value over the temperature range studied by the authors).

For binary systems, integration was conducted over the whole composition range (the limits of the integration are the pure components). The following integration paths were chosen for ternary and quaternary systems, respectively:

$$\begin{array}{ccc} & (0.8, 0.1, 0.1) & \\ & \swarrow \quad \nwarrow & \\ (0.1, 0.8, 0.1) & \longrightarrow & (0.1, 0.1, 0.8) \end{array}, \quad (49)$$

$$\begin{array}{ccccc} (0.2, 0.6, 0.1, 0.1) & \longleftarrow & (0.7, 0.1, 0.1, 0.1) & \longleftarrow & (0.3, 0.1, 0.1, 0.5) \\ & \searrow & & \swarrow & \\ & (0.2, 0.2, 0.5, 0.1) & \longrightarrow & (0.2, 0.2, 0.1, 0.5) & \end{array}, \quad (50)$$

where  $(x_1, x_2, x_3)$  and  $(x_1, x_2, x_3, x_4)$  represent the compositions of ternary (acetic acid (1)—ethyl acetate (2)—water (3)) and ethanol (1)—ethyl acetate (2)—water (3)) and quaternary (acetic acid (1)—ethanol (2)—ethyl acetate (3)—water (4)) mixtures; respectively. The integration was performed numerically by the rectangle method. The results of the consistency tests are summarized in Table 1.

**Table 1.** Results of the thermodynamic consistency tests for VLE data of the acetic acid-ethanol-ethyl acetate-water quaternary system and its' subsystems using Redlich–Kister and Gibbs–Duhem equations.

| Reference                  | T, K            | R-K <sup>1</sup>   | G-D <sup>2</sup> |
|----------------------------|-----------------|--------------------|------------------|
| Ethanol-water system       |                 |                    |                  |
| [21]                       | 346.15          | + <sup>3</sup>     | 0.023            |
| [24]                       | 356.15          | +                  | 0.024            |
| [26]                       | NC <sup>4</sup> | NC                 | NC               |
| [27]                       | 361.85          | +                  | 0.024            |
| [28]                       | 303.15          | +                  | 0.025            |
| [28]                       | 323.15          | +                  | 0.024            |
| [28]                       | 343.15          | +                  | 0.024            |
| [28]                       | 363.15          | +                  | 0.023            |
| [31]                       | NC              | NC                 | NC               |
| [32]                       | NC              | NC                 | NC               |
| [33]                       | 313.15          | +                  | 0.024            |
| [34]                       | 351.15          | +                  | 0.024            |
| [35]                       | 356.35          | +                  | 0.025            |
| [36]                       | 359.95          | +                  | 0.026            |
| [72]                       | 343.15          | +                  | 0.022            |
| [72]                       | 328.15          | +                  | 0.024            |
| [72]                       | 313.15          | +                  | 0.026            |
| [73]                       | 354.65          | +                  | 0.024            |
| Acetic acid-water system   |                 |                    |                  |
| [37]                       | 343.15          | +                  | 0.033            |
| [21]                       | 368.15          | +                  | 0.028            |
| [38]                       | 378.65          | +                  | 0.030            |
| [40]                       | 379.15          | +                  | 0.031            |
| [41]                       | D <sup>5</sup>  | D                  | D                |
| [43]                       | 323.15          | +                  | 0.032            |
| [44]                       | 378.45          | +                  | 0.029            |
| [45]                       | 380.15          | +                  | 0.029            |
| [80]                       | 377.15          | +                  | 0.032            |
| Acetic acid-ethanol system |                 |                    |                  |
| [21]                       | 358.65          | SD(+) <sup>6</sup> | 0.045            |
| [37]                       | 323.15          | SD(+)              | 0.046            |
| [46]                       | 352.65          | SD(+)              | 0.049            |
| [47]                       | 308.15          | +                  | 0.054            |
| [47]                       | 318.15          | +                  | 0.054            |
| Acetic acid-ethyl acetate  |                 |                    |                  |
| [21]                       | 361.15          | +                  | 0.200            |
| [37]                       | 323.15          | +                  | 0.033            |
| [45]                       | 368.95          | SD(+)              | 0.040            |

Table 1. Cont.

| Reference                    | T, K   | R-K <sup>1</sup> | G-D <sup>2</sup> |
|------------------------------|--------|------------------|------------------|
| [48]                         | 367.65 | +                | 0.037            |
| [49]                         | 338.25 | +                | 0.040            |
| [49]                         | 346.15 | +                | 0.040            |
| [50]                         | NC     | NC               | NC               |
| [80]                         | 368.15 | +                | 0.042            |
| Ethanol-ethyl acetate system |        |                  |                  |
| [21]                         | 338.15 | +                | 0.028            |
| [49]                         | 313.15 | +                | 0.025            |
| [50]                         | 347.55 | +                | 0.032            |
| [51]                         | NC     | NC               | NC               |
| [55]                         | 347.55 | +                | 0.033            |
| [58]                         | 381.65 | +                | 0.036            |
| [59]                         | 347.15 | +                | 0.033            |
| [59]                         | 400.45 | +                | 0.038            |
| [59]                         | 423.15 | +                | 0.052            |
| [60]                         | 347.15 | +                | 0.031            |
| [61]                         | 347.15 | +                | 0.032            |
| [62]                         | 347.15 | +                | 0.031            |
| [63]                         | 347.15 | +                | 0.031            |
| [64]                         | 347.15 | +                | 0.033            |
| [65]                         | NC     | NC               | NC               |
| [68]                         | 347.15 | +                | 0.032            |
| [71]                         | 347.15 | +                | 0.032            |
| [72]                         | 343.15 | D                | D                |
| [72]                         | 328.15 | D                | D                |
| [72]                         | 313.15 | D                | D                |
| [73]                         | 347.15 | +                | 0.032            |
| Ethyl acetate-water system   |        |                  |                  |
| [45]                         | NC     | NC               | NC               |
| [46]                         | 351.20 | +                | 0.014            |
| [60]                         | 349.60 | +                | 0.056            |
| [67]                         | 358.85 | +                | 0.061            |
| [68]                         | 346.80 | +                | 0.013            |
| [69]                         | 344.15 | +                | 0.002            |
| [71]                         | NC     | NC               | NC               |
| [72]                         | 343.15 | +                | 0.032            |
| [72]                         | 328.15 | +                | 0.032            |
| [72]                         | 313.15 | +                | 0.024            |
| [73]                         | 344.75 | +                | 0.006            |

Table 1. Cont.

| Reference                                      | T, K   | R-K <sup>1</sup> | G-D <sup>2</sup> |
|--|--------|------------------|------------------|
| Acetic acid-ethyl acetate-water system         |        |                  |                  |
| [70]   | 361.15 | +                | 0.042            |
| Ethanol-ethyl acetate-water                    |        |                  |                  |
| [68]   | 347.15 | +                | 0.056            |
| [71]   | 346.15 | +                | 0.046            |
| [72]   | 343.15 | +                | 0.048            |
| [73]   | 347.15 | +                | 0.050            |
| [74]   | NC     | NC               | NC               |
| Acetic acid-ethanol-ethyl acetate-water system |        |                  |                  |
| [78]   | 357.15 | +                | 0.032            |
| [80]   | 352.00 | D                | 0.065            |

<sup>1</sup> The value obtained by the Redlich–Kister test (Equation (13) for binary mixtures, Equation (16) for ternary and quaternary systems); <sup>2</sup> The value obtained by the integration of the Gibbs–Duhem equation (Equation (5)); <sup>3</sup> Tests passed; <sup>4</sup> NC-Tests not conducted; <sup>5</sup> Doubtful results; <sup>6</sup> Significant dispersion of data.

## 7. Results and Discussion

As for the binary subsystems, they have been extensively studied compared to ternary and quaternary mixtures. The majority of works have focused on the study of VLE in four binary subsystems of the quaternary system: ethanol-water, acetic acid-water, ethanol-ethyl acetate, and acetic acid-ethyl acetate. Among observed mixtures, these systems are the easiest to study in terms of VLE because they are not reacting and do not have a heterogeneous area. Much less data on the VLE for the binary mixtures acetic acid-ethanol and ethyl acetate-water is available. For the acetic acid-ethanol system, the possible esterification should be taken into account during VLE studies, while the ethyl acetate-water system is not only reacting but also partially miscible, which leads to several difficulties in both experimental procedures and data analysis.

Most of the literature data sets passed the Redlich–Kister test and the point-to-point van Ness consistency test successfully (see the corresponding commentary in the above text), which makes it possible to consider the VLE information to be thermodynamically consistent. However, for the ethanol-water mixture, these tests were not performed for the data from works [26,31,32]. Ueberfeld et al. [26] did not provide a full set of parameters ( $p$ - $T$ - $x$ - $y$ ), so their results were not tested. Cui et al. [31] did not measure equilibrium vapor pressure for the isothermal data set, and vapor composition was not determined for the liquid mixtures in [32].

Isobaric VLE data were presented at 1013 mbar [24,27,36,73], 1000 mbar [34,35] and 773 mbar [21], while isothermal VLE was studied at 288.15 K [32], 298.15 K [32], 303.15 K [28], 308.15 K [32], 313.15 K [33,72], 323.15 K [28,31,32], 328.15 K [72], 343.15 K [28,72] and 363.15 K [28]. It can be observed that isobaric data were only reported for pressures close to atmospheric; thus, even isobaric VLE data for different pressures for the acetic acid-ethanol-ethyl acetate-water systems are rather limited. The temperature range for isothermal data tends to be wider, but most temperatures were studied in only one or two works, making it difficult to compare and test the reliability and reproducibility of different data.

Isobaric VLE data for the acetic acid-water system are reported at 1013 mbar [40,41,44,45,80], 1000 mbar [38], 773 mbar [21], 667 mbar [41], 333 mbar [41], and 167 mbar [41]. Data obtained by Gilmont et al. [41] are considered doubtful due to discrepancies because the dependence of the molar excess Gibbs energy  $g^E$  on composition at 1013 mbar qualitatively differs from those obtained by other researchers. Based on the data reported by Gilmont et al. [41], the  $g^E$  curve should have both positive and negative values, with one maximum

and one minimum. However, calculations according to other literature data give the  $g^E$  curve only positive values with one maximum. Isothermal data sets are presented in two works only at 343.15 K [37] and 323.15 K [43].

The reactive binary acetic acid-ethanol subsystem was studied under pressures of 773 mbar [21], 500 mbar [46], and at three temperatures: 323.15 K [37], 318.15 K [47], and 308.15 K [47]. It should be noted that the possible influence of the esterification reaction on the obtained VLE data are almost not discussed. At the same time, considerable dispersion in  $g^E$  values for this system was observed for results reported in works [21,37,46]. The consistency tests were performed for smoothed dependencies obtained using the NRTL equation. The dispersion could be caused by the temperature shift or by the influence of the chemical reactions; however, further studies are necessary to make more detailed conclusions.

For the binary acetic acid-ethyl acetate system, isobaric VLE data are presented at 1013 mbar [45,50,80], 987 mbar [48], and 773 mbar [21]. The values of the integral obtained using both the Redlich–Kister method and the integration of the Gibbs–Duhem equation for data produced by Navarro-Espinosa et al. [21] were greater than those obtained for other data sets (0.2 against 0.04 for other data sets). Such findings may be a result of the limited range of experimental compositions used for the approximation with the NRTL model. Boiling temperatures were not provided by Furnas et al. [50], hence these data were not tested. Significant dispersion of the  $g^E$  values was observed for the results reported in [45]. The isothermal VLE has been studied at 323.15 K [37], 338.15 K [49], and 346.15 K [49]. All the data satisfactorily passed the consistency test.

The ethanol-ethyl acetate system is one of the most extensively studied. Isobaric VLE data sets are available at 7000 mbar [59], 5000 mbar [59], 3000 mbar [58], 1013 mbar [50,55,60–62,64,71,73,80], 1000 mbar [59,63], and 773 mbar [21]. All these data sets passed the consistency test. The isothermal VLE data are reported at 313.15 K [49,65,72], 328.15 K [72], and 343.15 K [72]. A substantial amount of VLE data in the temperature range of 294.15–350.15 K is presented in a paper [51]. However, these data were not tested due to the omission of the vapor composition. The equilibrium vapor pressures were not measured by Takamatsu et al. [65]. Data for the ethanol-ethyl acetate system in the paper [72] are considered doubtful since the calculated curve of  $g^E$  dependence on composition has two minimums and one maximum with negative values of  $g^E$ . Meanwhile, the corresponding curve by Ashraf et al. [66] has a similar form with one maximum and positive values of  $g^E$ . This discrepancy could be attributed to a systematic error in data processing and representation.

For the ethyl acetate-water system, isobaric VLE data are solely reported at atmospheric pressure [45,46,60,67–69,71,73]. Isothermal VLE was studied at 315.15 K, 328.15 K, and 343.15 K exclusively in this work [72]. Due to the limited number of studied compositions, the results obtained by Garner et al. [45] and Griswold et al. [71] were not subjected to thermodynamic consistency tests. However, other data sets successfully passed the consistency test.

It is evident that VLE in ternary and quaternary systems is studied less extensively than that in binary ones, with only a few works focusing on the VLE investigation in ternary and quaternary mixtures. The majority of these studies were carried out at atmospheric pressure [68,70,71,73,80]. The results of the isothermal VLE study at 313.15 K, 328.15 K, and 343.15 K for the system ethanol-ethyl acetate-water are only presented in a single paper [72]. The data obtained by Calvar et al. [80] were considered doubtful due to the existence of numerous compositions with a significant mole fraction of acetic acid in the liquid phase and its absence in the vapor phase. We are not sure whether such a tendency is reliable. Moreover, the values of the integral (5) for this data set at 352.15 K were significantly higher than the mean value for all the observed systems (0.065 against the mean value of 0.03–0.04).

The mean value of the integral (5) across the data sets under review were calculated to be 0.04 (0.024 for the ethanol-water system, 0.031 for the acetic acid-water system, 0.050 for

the acetic acid-ethanol system, 0.039 for the acetic acid-ethyl acetate system, 0.033 for the ethanol-ethyl acetate system, 0.027 for the ethyl acetate-water system, 0.042 for the acetic acid-ethyl acetate-water system, 0.050 for the ethanol-ethyl acetate-water system, 0.032 for the quaternary system). We assume that this value can be used to test the thermodynamic consistency of VLE data in multicomponent systems through the direct integration of the Gibbs–Duhem equation.

## 8. Conclusions

A comprehensive review of both isobaric and isothermal VLE data presented in the literature for the quaternary acetic acid-ethanol-ethyl acetate-water system, along with its ternary and binary subsystems, was carried out. An analysis revealed that the majority of literature information on the VLE in this system predominantly consists of isobaric data sets obtained at pressures close to atmospheric. Compared to isobaric data, the isothermal VLE data set appeared more restricted. It was found that binary, non-reacting systems without any miscibility gaps were the most investigated. Furthermore, it was established that VLE data concerning the quaternary system and its ternary subsystems are markedly scarce. Therefore, the investigation of VLE in multicomponent reacting systems (including the system with the reaction of ethyl acetate synthesis) presents a promising direction for future research.

The thermodynamic consistency of the observed literature VLE data was examined using two integral area tests: the Redlich–Kister test and the direct integration of the Gibbs–Duhem equation. The major part of the data proved to be thermodynamically consistent. Concurrently, several works containing potentially doubtful information were found. The reliable value of the integral in condition (5) for a real experimental VLE data set was estimated to be 0.04. This value can be used for testing the thermodynamic consistency of the VLE data in multicomponent systems.

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## References

1. United Nations the Sustainable Development Goals Report. Available online: <https://unstats.un.org/sdgs/report/2022/The-Sustainable-Development-Goals-Report-2022.pdf> (accessed on 30 September 2023).
2. United Nations Kyoto Protocol to the United Nations Framework Convention on Climate Change. Available online: <https://unfccc.int/resource/docs/convkp/kpeng.pdf> (accessed on 30 September 2023).
3. Sundmacher, K.; Kienle, A. *Reactive Distillation: Status and Future Directions*; Sundmacher, K., Kienle, A., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2003; ISBN 3527305793.
4. ECHA European Chemical Agency Ethyl Acetate. Available online: <https://echa.europa.eu/brief-profile/-/briefprofile/100.005.001#collapseSeven> (accessed on 30 September 2023).
5. Waggy, G.T.; Conway, R.A.; Hansen, J.L.; Blessing, R.L. Comparison of 20-d Bod and Oecd Closed-Bottle Biodegradation Tests. *Environ. Toxicol. Chem.* **1994**, *13*, 1277–1280. [[CrossRef](#)]
6. Mormile, M.R.; Liu, S.; Sufliata, J.M. Anaerobic Biodegradation of Gasoline Oxygenates: Extrapolation of Information to Multiple Sites and Redox Conditions. *Environ. Sci. Technol.* **1994**, *28*, 1727–1732. [[CrossRef](#)]
7. *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley: Weinheim, Germany, 2011; ISBN 9783527303854.

8. Klöcker, M.; Kenig, E.Y.; Górak, A.; Markusse, A.P.; Kwant, G.; Moritz, P. Investigation of Different Column Configurations for the Ethyl Acetate Synthesis via Reactive Distillation. *Chem. Eng. Process. Process Intensif.* **2004**, *43*, 791–801. [[CrossRef](#)]
9. Grosser, J.H.; Doherty, M.F.; Malone, M.F. Modeling of Reactive Distillation Systems. *Ind. Eng. Chem. Res.* **1987**, *26*, 983–989. [[CrossRef](#)]
10. Barbosa, D.; Doherty, M.F. The Influence of Equilibrium Chemical Reactions on Vapor-Liquid Phase Diagrams. *Chem. Eng. Sci.* **1988**, *43*, 529–540. [[CrossRef](#)]
11. Barbosa, D.; Doherty, M.F. The Simple Distillation of Homogeneous Reactive Mixtures. *Chem. Eng. Sci.* **1988**, *43*, 541–550. [[CrossRef](#)]
12. Barbosa, D.; Doherty, M.F. Design and Minimum-Reflux Calculations for Single-Feed Multicomponent Reactive Distillation Columns. *Chem. Eng. Sci.* **1988**, *43*, 1523–1537. [[CrossRef](#)]
13. Morachevskiy, A.G. (Ed.) *Thermodynamics of Vapour-Liquid Equilibrium*; Himiya: Leningrad, Russia, 1989; ISBN 5-7245-0363-8. (In Russian)
14. *The Collected Works of J. Willard Gibbs*; Longmans, Green and Co.: New York, NY, USA, 1928.
15. Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Longmans, Green and Co.: Harlow, UK, 1954.
16. Münster, A. *Chemische Thermodynamik*; De Gruyter: Berlin/Heidelberg, Germany, 1969; ISBN 9783112479186.
17. Kogan, V.B. *Heterogeneous Equilibria*; Khimiya: Leningrad, Russia, 1968. (In Russian)
18. Prausnitz, J.M.; Lichtenthaler, R.N.; de Azevedo, E.G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice-Hall PTR: Upper Saddle River, NJ, USA, 1999; ISBN 13-977745-8.
19. Marek, J. Vapor-Liquid Equilibria in Mixtures Containing an Associating Substance. II. Binary Mixtures of Acetic Acid at Atmospheric Pressure. *Collect. Czechoslov. Chem. Commun.* **1954**, *20*, 1490–1502. [[CrossRef](#)]
20. Kocherbitov, V.V.; Toikka, A.M. Vapour-Liquid Equilibrium in the System Acetic Acid-n-Propanol-Water at 313.15 K. *Russ. J. Appl. Chem.* **1997**, *70*, 1777–1781. (In Russian)
21. Navarro-Espinosa, I.R.; Cardona, C.A.; López, J.A. Experimental Measurements of Vapor-Liquid Equilibria at Low Pressure: Systems Containing Alcohols, Esters and Organic Acids. *Fluid Phase Equilibria* **2010**, *287*, 141–145. [[CrossRef](#)]
22. Stryjek, R.; Vera, J.H. PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures. *Can. J. Chem. Eng.* **1986**, *64*, 323–333. [[CrossRef](#)]
23. Wong, D.S.H.; Sandler, S.I. A Theoretically Correct Mixing Rule for Cubic Equations of State. *AIChE J.* **1992**, *38*, 671–680. [[CrossRef](#)]
24. Iwakabe, K.; Kosuge, H. Isobaric Vapor-Liquid-Liquid Equilibria with a Newly Developed Still. *Fluid Phase Equilibria* **2001**, *192*, 171–186. [[CrossRef](#)]
25. Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J.* **1974**, *20*, 263–272. [[CrossRef](#)]
26. Ueberfeld, J.; Zbinden, H.; Gisin, N.; Pellaux, J.P. Determination of Henry's Constant Using a Photoacoustic Sensor. *J. Chem. Thermodyn.* **2001**, *33*, 755–764. [[CrossRef](#)]
27. Yang, B.; Wang, H. Vapor-Liquid Equilibrium for Mixtures of Water, Alcohols, and Ethers. *J. Chem. Eng. Data* **2002**, *47*, 1324–1329. [[CrossRef](#)]
28. Pemberton, R.C.; Mash, C.J. Thermodynamic Properties of Aqueous Non-Electrolyte Mixtures II. Vapour Pressures and Excess Gibbs Energies for Water + Ethanol at 303.15 to 363.15 K Determined by an Accurate Static Method. *J. Chem. Thermodyn.* **1978**, *10*, 867–888. [[CrossRef](#)]
29. Islam, A.W.; Rahman, M.H. A Review of Barker's Activity Coefficient Method and VLE Data Reduction. *J. Chem. Thermodyn.* **2012**, *44*, 31–37. [[CrossRef](#)]
30. Larkin, J.A. Thermodynamic Properties of Aqueous Non-Electrolyte Mixtures I. Excess Enthalpy for Water + Ethanol at 298.15 to 383.15 K. *J. Chem. Thermodyn.* **1975**, *7*, 137–148. [[CrossRef](#)]
31. Cui, Z.; Qian, R.; Yun, Z.; Shi, M. Vapor-Liquid Equilibria in Alcohol + Cyclohexane + Water Systems. *J. Chem. Eng. Data* **2004**, *49*, 212–217. [[CrossRef](#)]
32. Dalmolin, I.; Skovroinski, E.; Biasi, A.; Corazza, M.L.; Dariva, C.; Oliveira, J.V. Solubility of Carbon Dioxide in Binary and Ternary Mixtures with Ethanol and Water. *Fluid Phase Equilibria* **2006**, *245*, 193–200. [[CrossRef](#)]
33. Vu, D.T.; Lira, C.T.; Asthana, N.S.; Kolah, A.K.; Miller, D.J. Vapor-Liquid Equilibria in the Systems Ethyl Lactate + Ethanol and Ethyl Lactate + Water. *J. Chem. Eng. Data* **2006**, *51*, 1220–1225. [[CrossRef](#)]
34. Zhang, L.; Ge, Y.; Ji, D.; Ji, J. Experimental Measurement and Modeling of Vapor-Liquid Equilibrium for Ternary Systems Containing Ionic Liquids: A Case Study for the System Water + Ethanol + 1-Hexyl-3-Methylimidazolium Chloride. *J. Chem. Eng. Data* **2009**, *54*, 2322–2329. [[CrossRef](#)]
35. Orchillés, A.V.; Miguel, P.J.; Vercher, E.; Martínez-Andreu, A. Using 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate as an Entrainer for the Extractive Distillation of Ethanol + Water Mixtures. *J. Chem. Eng. Data* **2010**, *55*, 1669–1674. [[CrossRef](#)]
36. Orjuela, A.; Yanez, A.J.; Vu, D.T.; Bernard-Brunel, D.; Miller, D.J.; Lira, C.T. Phase Equilibria for Reactive Distillation of Diethyl Succinate. Part I. System Diethyl Succinate + Ethanol + Water. *Fluid Phase Equilibria* **2010**, *290*, 63–67. [[CrossRef](#)]
37. Miyamoto, S.; Nakamura, S.; Iwai, Y.; Arai, Y. Measurement of Isothermal Vapor–Liquid Equilibria for Binary and Ternary Systems Containing Monocarboxylic Acid. *J. Chem. Eng. Data* **2001**, *46*, 1225–1230. [[CrossRef](#)]
38. Vercher, E.; Vázquez, M.I.; Martínez-Andreu, A. Isobaric Vapor-Liquid Equilibria for Water + Acetic Acid + Lithium Acetate. *J. Chem. Eng. Data* **2001**, *46*, 1584–1588. [[CrossRef](#)]
39. Mock, B.; Evans, L.B.; Chen, C.-C. Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems. *AIChE J.* **1986**, *32*, 1655–1664. [[CrossRef](#)]

40. Chang, W.; Guan, G.; Li, X.; Yao, H. Isobaric Vapor–Liquid Equilibria for Water + Acetic Acid + (n-Pentyl Acetate or Isopropyl Acetate). *J. Chem. Eng. Data* **2005**, *50*, 1129–1133. [[CrossRef](#)]
41. Gilmont, R.; Othmer, D.F. Composition of Vapors from Boiling Binary Solutions Water—Acetic Acid System at Atmospheric and Subatmospheric Pressures. *Ind. Eng. Chem.* **1944**, *36*, 1061–1064. [[CrossRef](#)]
42. Hayden, J.G.; O’Connell, J.P. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–216. [[CrossRef](#)]
43. Bernatová, S.; Aim, K.; Wichterle, I. Isothermal Vapour-Liquid Equilibrium with Chemical Reaction in the Quaternary Water + Methanol + Acetic Acid + Methyl Acetate System, and in Five Binary Subsystems. *Fluid Phase Equilibria* **2006**, *247*, 96–101. [[CrossRef](#)]
44. Xie, Q.; Wan, H.; Han, M.; Guan, G. Investigation on Isobaric Vapor–Liquid Equilibrium for Acetic Acid+water+methyl Ethyl Ketone+isopropyl Acetate. *Fluid Phase Equilibria* **2009**, *280*, 120–128. [[CrossRef](#)]
45. Garner, F.H.; Ellis, S.R.M.; Pearce, C.J. Extraction of Acetic Acid from Water. *Chem. Eng. Sci.* **1954**, *3*, 48–54. [[CrossRef](#)]
46. Reichl, A.; Daiminger, U.; Schmidt, A.; Davies, M.; Hoffmann, U.; Brinkmeier, C.; Reder, C.; Marquardt, W. A Non-Recycle Flow Still for the Experimental Determination of Vapor-Liquid Equilibria in Reactive Systems. *Fluid Phase Equilibria* **1998**, *153*, 113–134. [[CrossRef](#)]
47. Wagner, M.; Apelblat, A.; Tamir, A. Excess Gibbs Free Energy in Methanol + Acetic Acid and Ethanol + Acetic Acid. *J. Chem. Thermodyn.* **1980**, *12*, 181–186. [[CrossRef](#)]
48. Kato, M. Vapor-Liquid Equilibrium Measurements for Binary Systems of Acetic Acid with Ethyl Acetate and Vinyl Acetate by the Dew-Bubble Point Temperature Method. *J. Chem. Eng. Data* **1988**, *33*, 499–501. [[CrossRef](#)]
49. Macedo, E.A.; Rasmussen, P.; Macedo, E.A. Vapor-Liquid Equilibrium for the Binary Systems Ethyl Acetate-Acetic Acid and Ethyl Propionate-Propionic Acid. *J. Chem. Eng. Data* **1982**, *27*, 463–465. [[CrossRef](#)]
50. Furnas, C.C.; Leighton, W.B. Ethyl Alcohol-Ethyl Acetate and Acetic Acid–Ethyl Acetate Systems. *Ind. Eng. Chem.* **1937**, *29*, 709–710. [[CrossRef](#)]
51. Figurski, G.; Malanowski, S.K. Vapor-Liquid Equilibrium Studies of the Ethanol + Ethyl Acetate System. *Fluid Phase Equilibria* **1998**, *148*, 161–169. [[CrossRef](#)]
52. Ambrose, D.; Sprake, C.H.S. Thermodynamic Properties of Organic Oxygen Compounds XXV. Vapour Pressures and Normal Boiling Temperatures of Aliphatic Alcohols. *J. Chem. Thermodyn.* **1970**, *2*, 631–645. [[CrossRef](#)]
53. Anderko, A.; Malanowski, S. Calculation of Solid-Liquid, Liquid-Liquid and Vapor-Liquid Equilibria by Means of an Equation of State Incorporating Association. *Fluid Phase Equilibria* **1989**, *48*, 223–241. [[CrossRef](#)]
54. Anderko, A. Modeling Phase Equilibria Using an Equation of State Incorporating Association. *Fluid Phase Equilibria* **1992**, *75*, 89–103. [[CrossRef](#)]
55. Tu, C.H.; Wu, Y.S.; Ou, F.C. Effect of 1,2-Propanediol on the Vapor-Liquid Equilibria of the Ethyl Acetate + Ethanol System at 101.3 kPa. *Fluid Phase Equilibria* **1997**, *130*, 243–252. [[CrossRef](#)]
56. Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203. [[CrossRef](#)]
57. Spencer, C.F.; Danner, R.P. Improved Equation for Prediction of Saturated Liquid Density. *J. Chem. Eng. Data* **1972**, *17*, 236–241. [[CrossRef](#)]
58. Susial, P.; Rodriguez-Henriquez, J.J.; Sosa-Rosario, A.; Rios-Santana, R. Vapor-Liquid Equilibrium of Ethyl Acetate + C<sub>n</sub>H<sub>2n</sub> + 1OH (N = 1,2,3) Binary Systems at 0.3 MPa. *Chin. J. Chem. Eng.* **2012**, *20*, 723–730. [[CrossRef](#)]
59. Susial, P.; Sosa-Rosario, A.; Rodríguez-Henríquez, J.J.; Rios-Santana, R. Vapor Pressure and VLE Data Measurements on Ethyl Acetate/Ethanol Binary System at 0.1, 0.5, and 0.7 MPa. *J. Chem. Eng. Jpn.* **2011**, *44*, 155–163. [[CrossRef](#)]
60. Kato, M.; Konishi, H.; Hirata, M. New Apparatus for Isobaric Dew and Bubble Point Method. Methanol-Water, Ethyl Acetate-Ethanol, Water-1-Butanol, and Ethyl Acetate-Water Systems. *J. Chem. Eng. Data* **1970**, *15*, 435–439. [[CrossRef](#)]
61. Orjuela, A.; Yanez, A.J.; Rossman, P.K.; Vu, D.T.; Bernard-Brunel, D.; Miller, D.J.; Lira, C.T. Phase Equilibria for Reactive Distillation of Diethyl Succinate. Part II: Systems Diethyl Succinate + Ethyl Acetate + Water and Diethyl Succinate + Acetic Acid + Water. *Fluid Phase Equilibria* **2010**, *290*, 68–74. [[CrossRef](#)]
62. Topphoff, M.; Kiepe, J.; Gmehling, J. Effects of Lithium Nitrate on the Vapor-Liquid Equilibria of Methyl Acetate + Methanol and Ethyl Acetate + Ethanol. *J. Chem. Eng. Data* **2001**, *46*, 1333–1337. [[CrossRef](#)]
63. Orchillés, A.V.; Miguel, P.J.; Vercher, E.; Martínez-Andreu, A. Isobaric Vapor-Liquid Equilibria for Ethyl Acetate + Ethanol + 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate at 100 kPa. *J. Chem. Eng. Data* **2007**, *52*, 2325–2330. [[CrossRef](#)]
64. Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Xing, F. Isobaric Vapor-Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Ethyl-3-Methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2009**, *54*, 193–197. [[CrossRef](#)]
65. Takamatsu, H.; Ohe, S. Measurement of the Effect of Salt on Vapor-Liquid Equilibria by Using Headspace Gas Chromatography. *J. Chem. Eng. Data* **2003**, *48*, 277–279. [[CrossRef](#)]
66. Ashraf, S.M.; Prasad, D.H.L. Isothermal Phase Equilibria in the Binary Mixtures of Some Polar Compounds. *Phys. Chem. Liq.* **1999**, *37*, 333–343. [[CrossRef](#)]
67. Ellis, S.R.M.; Garbett, R.D. A New Equilibrium Still for the Study of Partially Miscible Systems. *Ind. Eng. Chem.* **1960**, *52*, 385–388. [[CrossRef](#)]

68. Lee, L.-S.; Chen, W.-C.; Huang, J.-F. Experiments and Correlations of Phase Equilibria of Ethanol-Ethyl Acetate-Water Ternary Mixture. *J. Chem. Eng. Jpn.* **1996**, *29*, 427–438. [[CrossRef](#)]
69. Rajendran, M.; Renganarayanan, S.; Srinivasan, D. Salt Effect in Phase Equilibria and Heat of Mixing: Effect of Dissolved Inorganic Salts on the Liquid-Liquid Equilibria of Ethyl Acetate-2-Propanol-Water System and the Vapor-Liquid Equilibria and Heat of Mixing of Its Constituent Binaries. *Fluid Phase Equilibria* **1991**, *70*, 65–106. [[CrossRef](#)]
70. Garner, F.H.; Ellis, S.R.M.; Pearce, C.J. Extraction of Acetic Acid from Water. 4. Ternary-Vapour-Liquid Equilibrium Data. *Chem. Eng. Sci.* **1955**, *4*, 273–278. [[CrossRef](#)]
71. Griswold, J.; Chu, P.L.; Winsauer, W.O. Phase Equilibria in Ethyl Alcohol–Ethyl Acetate–Water System. *Ind. Eng. Chem.* **1949**, *41*, 2352–2358. [[CrossRef](#)]
72. Mertl, I. Liquid-Vapour Equilibrium. II. Phase Equilibria in the Ternary System Ethyl Acetate-Ethanol-Water. *Collect. Czechoslov. Chem. Commun.* **1972**, *37*, 366–374. [[CrossRef](#)]
73. Van Zandijcke, F.; Verhoeve, L. The Vapour-Liquid Equilibrium of Ternary Systems with Limited Miscibility at Atmospheric Pressure. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 709–729. [[CrossRef](#)]
74. Gomis, V.; Ruiz, F.; Asensi, J.C. The Application of Ultrasound in the Determination of Isobaric Vapour–Liquid–Liquid Equilibrium Data. *Fluid Phase Equilibria* **2000**, *172*, 245–259. [[CrossRef](#)]
75. Merriman, R.W. CXCIV.—The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures above and below the Atmospheric Pressure. Part I. *J. Chem. Soc. Trans.* **1913**, *103*, 1790–1801. [[CrossRef](#)]
76. Washburn, E.W. (Ed.) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill Book Company, Inc.: New York, NY, USA; London, UK, 1928; Volume III.
77. Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection, Aqueous Organic Systems (Supplement 1)*; Chemical Data Series; DECHEMA: Frankfurt, Germany, 1981; Volume I.
78. Kang, Y.W.; Lee, Y.Y.; Lee, W.K. Vapor-Liquid Equilibria with Chemical Reaction Equilibrium. Systems Containing Acetic Acid, Ethyl Alcohol, Water, and Ethyl Acetate. *J. Chem. Eng. Jpn.* **1992**, *25*, 649–655. [[CrossRef](#)]
79. Campanella, E.A.; Mandagaran, B.A. Phase Equilibria for Quaternary Mixtures in Esterification Reaction Systems. *Lat. Am. Appl. Res.* **2003**, *33*, 313–321.
80. Calvar, N.; Domínguez, A.; Tojo, J. Vapor–Liquid Equilibria for the Quaternary Reactive System Ethyl Acetate + ethanol + water + acetic Acid and Some of the Constituent Binary Systems at 101.3 kPa. *Fluid Phase Equilibria* **2005**, *235*, 215–222, Corrigendum in *Fluid Phase Equilibria* **2007**, *254*, 225–226. [[CrossRef](#)]
81. Renon, H.; Prausnitz, J.M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144. [[CrossRef](#)]

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