

# Predictive models to describe VLE in ternary mixtures water + ethanol + congener for wine distillation

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## Abstract

The modeling of liquid–vapor equilibrium in ternary mixtures that include substances found in alcoholic distillation processes of wine and musts is analyzed. In particular, vapor–liquid equilibrium in ternary mixtures containing water + ethanol + congener has been modeled using parameters obtained from binary mixture data only. The congeners are substances that although present in very low concentrations, of the order of part per million,  $10^{-6}$  to  $10^{-4}$  mg/L, are important enological parameters [1,2]. In this work two predictive models, the PSRK equation of state and the UNIFAC liquid phase model and two semipredictive activity coefficient models: NRTL and UNIQUAC have been used. The results given by these different models have been compared with literature data and conclusions about the accuracy of the models studied are drawn, recommending the best models for correlating and predicting the phase equilibrium in this type of mixtures.

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**Keywords:** Wine distillation; Equations of state; Activity coefficient models; Vapor–liquid equilibrium

## 1. Introduction

Distillation is a liquid–vapor separation process that can be done in a batch or continuous manner and in which heat is used as the separating agent. In wine distillation, batch processes are very common and arrangements as that shown in Fig. 1, known as “alambiques”, are used. In this equipment, the mixture to be separated, the must contained in the pot still, is heated to its boiling temperature, at which the boiling liquid and the vapor produced are at thermodynamic equilibrium. Further addition of heat takes the system out of equilibrium and the more volatile components go into the vapor phase. The mixture reaches a new equilibrium temperature and is again taken out from equilibrium. Separation is done in the distillation column in which the vapor going to the top of the column get richer in the more volatile components, living in the pot still the heavier components. The lighter components are then converted into liquid in the condenser. Part of this liquid form the distilled product and part of

it is recycled to the column to get into contact with the raising vapor [3].

To design and simulate this type of processes, knowledge of the equilibrium conditions is of special importance. This because the driving force that produces component separation is the difference between the actual concentration and the concentration at thermodynamic equilibrium. Therefore, knowledge of vapor–liquid equilibrium data (VLE) is necessary to design and optimize distillation processes. In wine and must distillation the great amount of substances found in the mixture to be distilled and the very low concentration of many other components (different from ethanol and water), called congeners, makes it difficult to correlate and predict the concentration of the distilled product, considered to be the most important variable in the produced spirit. Several of the congener compounds are essential part of the aroma of the distilled product and therefore their concentrations are important enological parameters [4]. These congener substances are usually present in concentrations of part per million,  $10^{-6}$  to  $10^{-4}$  mg/L [5,6]. One specific example of this complex phase equilibrium problem, the production of a wine distilled liquor known as Pisco, is studied here.

As known, the problem of phase equilibrium consists of the calculation of some variables of the set  $(T, P, x, y)$ , if some of them are known. For a vapor–liquid mixture at equilibrium con-

*Abbreviations:* EoS, equation of state; NRTL, non-random-two liquid model; PSRK, predictive SRK equation of state; UNIFAC, universal functional activity coefficient model; UNIQUAC, universal-quasichemical model

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**Nomenclature**

$a_c, b$	parameter in the PSRK EoS
$a_{ij}, b_{ij}$	interaction parameters in the mixing rules
$A_1$	constant in the PSRK EoS
$B_{ij}$	NRTL parameter
$c_1, c_2, c_3$	parameters in the PSRK EoS
$g^E$	excess Gibbs free energy
$P$	pressure
$R$	ideal gas constant
$T$	temperature
$T_c$	critical temperature
$T_r$	reduced temperature ( $T_r = T/T_c$ )
$U_{ij}$	UNIQUAC parameter
$V$	volume
$x_i$	experimental mole fraction of congener in the liquid phase (component $i$ )
$y_{\text{cal}}$	calculated mole fraction of a congener in the vapor phase
$y_{\text{exp}}$	experimental mole fraction of a congener in the vapor phase
$y_1$	mole fraction of congener in the vapor phase (component 1)

*Greek letters*

$\alpha_{ij}$	NRTL parameter
$\alpha(T)$	temperature function in the PSRK EoS
$\gamma$	activity coefficient
$\% \Delta$	percent deviation
$\varphi$	fugacity coefficient
$\omega$	acentric factor

*Subscripts*

cal	calculated
exp	experimental
$i, j$	components

ditions, the temperature and the pressure are the same in both phases, and the remaining variables are defined by the material balance and the “fundamental equation of phase equilibrium”. The application of this fundamental equation requires the use of thermodynamic models which normally include binary interaction parameters.

The operating pressure in alcoholic distillation to produce Pisco is of the order of the atmospheric pressure and most of the substances involved are highly polar. The classical thermodynamic models commonly used in the literature to treat these mixtures at low pressure required a great amount of binary parameters to be determined from experimental data [7]. These binary parameters must be determined using experimental data for binary systems. Theoretically, once these binary parameters are known one could predict the behavior of multicomponent mixtures using standard thermodynamic relations and thermodynamics models.

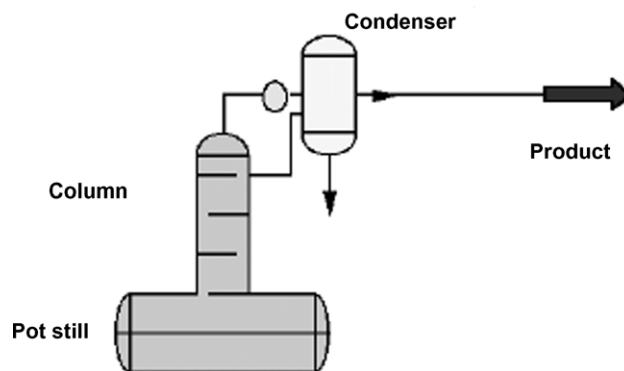


Fig. 1. Representation of a typical batch distillation equipment known as “alambique” (adapted from Chemstations [26]).

Binary mixtures containing water + congeners and ethanol + congeners have been studied in the literature [8–11] and values of the binary parameters have been provided for several models. However, the use of binary parameters to treat mixtures with more than two components in wine distillation processes has not been thoroughly analyzed. The authors have studied selected ternary mixtures water + congener + congener and ethanol + congener + congener [12], but the strong interactions between ethanol and water in ternary mixtures have been not analyzed. This paper considers the study of eight ternary mixtures containing water + ethanol + congener. The eight congeners are, methanol, 1-propanol, 2-methyl-1-propanol, 3-methyl-butanol, 1-pentanol, acetaldehyde, ethyl acetate and furfural, considered as legal compounds in the Chilean legislation for the production of a spirit called Pisco. As stated above, in wine distillation processes the congeners are present in low concentration and modeling studies should consider this aspect. However, the limited experimental data available in the open literature places an additional difficulty to more accurately correlate these mixtures in the congener infinite dilution region. Therefore in those cases in which data is not available in the low concentration range for the congeners we rely in the extrapolation capabilities of the models used.

## 2. The fundamental equation of phase equilibrium

The fundamental equation of vapor–liquid equilibrium can be expressed as the equality of fugacities of each component in the mixture in both phases (see, for instance, the book by Walas [13]):

$$\bar{f}_i^L = \bar{f}_i^V \quad (1)$$

The fugacity of a component “ $i$ ” in the vapor phase is usually expressed through the fugacity coefficient  $\bar{\phi}_i^V$ :

$$\bar{f}_i^V = y_i \bar{\phi}_i^V P \quad (2)$$

The fugacity of a component in the liquid phase is expressed through either the fugacity coefficient  $\bar{\phi}_i^L$  or the activity coefficient  $\gamma_i$ .

At low pressures the standard state fugacity  $f_i^0$  can be replaced by the vapor pressure  $P_i^{\text{sat}}$  at the temperature of the sys-

tem, Thus, the fugacity of a component “*i*” in the liquid phase can be expressed as

$$\bar{f}_i^L = x_i \gamma_i P_i^{\text{sat}} \quad (5)$$

In these equations  $y_i$  is the mole fraction of component “*i*” in the vapor phase,  $x_i$  is the mole fraction of component “*i*” in the liquid phase, and  $P$  is the pressure. The fugacity is related to the temperature, the pressure, the volume and the concentration through a standard thermodynamic relation [13]. If the fugacity coefficient is used in both phases, the method of solution of the phase equilibrium problem is known as “the equation of state method”. If the fugacity coefficient is used for the vapor phase and the activity coefficient is used for the liquid phase the equilibrium problem is known as “the gamma-phi method”.

If the equation of state method is used, an equation of state and a set of mixing rules are needed, to express the fugacity coefficient as function of the temperature, the pressure and the concentration. Modern equation of state methods include an excess Gibbs free energy model ( $g^E$ ) in the mixing rules of the equation of state, giving origin to the so-called “equation of state +  $g^E$  model” [14]. The PSRK equation used in the present study is one of these models.

Commonly, at the conditions at which must and wine distillation processes take place, models for the activity coefficients in the “gamma-phi method” are used. This means that an activity coefficient model ( $\gamma$ ) is used to describe the complex liquid phase, and the fugacity coefficient ( $\phi$ ) is calculated using a simple equation of state. However, the “equation of state +  $g^E$  model” can also be used and has given acceptable results for some systems [15].

Most models available in the literature for the activity coefficient are of the correlating type (van Laar, Margules, Redlich-Kister, NRTL, UNIQUAC and Wilson), meaning that experimental data are needed to calculate certain empirical parameters, although some predictive models are also available (UNIFAC and ASOG). An interesting model to explore for predicting VLE in mixtures of interest in wine distillation is the predictive Soave-Redlich-Kwong (PSRK) of the group “equation of state +  $g^E$  model”, proposed by Holderbaum and Gmehling [16]. This model has been extensively used in the literature, but has not systematically applied to congener + ethanol + water mixtures as done in this work. The models NRTL, UNIFAC and UNIQUAC have been used in the literature to model binary mixtures ethanol + congener and water + congener [8].

In the study presented here, ternary mixtures congener + ethanol + water are considered. Four thermodynamic models are analyzed and result compared with experimental data available in the literature. In this work two predictive models, the PSRK equation of state and the UNIFAC liquid phase model and two semipredictive activity coefficient models: NRTL and UNIQUAC have been used. The NRTL and the UNIQUAC models are considered as semipredictive models because ternary systems have been modeled using binary data only at the same pressure. No ternary data has been used to estimate the model parameters. It is assumed in the modeling that the model parameters are concentration and temperature independent.

### 3. Model description

The main equations for the four models studied (PSRK, UNIFAC, NRTL and UNIQUAC) and the meaning of the different variables and parameters are described in what follows.

#### 3.1. The PSRK model

The idea of combining simple cubic equations of state with excess Gibbs energy ( $g^E$ ) models, to describe the intermolecular interactions derived from the behavior of the liquid and vapor phases, is well known. Since Huron and Vidal [17] published their mixing rule for the attractive EoS parameter “ $a$ ” of a cubic equation of state, numerous publications have appeared, with more or less similar approaches [14].

The excess Gibbs energy given by an equation of state is a function of pressure, whereas in the most common  $g^E$  models it is assumed that the excess volume is zero ( $V^E = 0$ ). For this reason all the approaches use limiting values for the pressure ( $P \rightarrow \infty$  or  $P \rightarrow 0$ ) to obtain a  $g^E$  mixing rule for the mixture parameter “ $a$ ”. The relation between the excess Gibbs energy and the activity or fugacity coefficients is [18]:

$$\ln \phi_i - \sum x_i \ln \phi_i^* = \sum x_i \ln \gamma_i = \frac{g^E}{RT} \quad (6)$$

The PSRK model was first proposed by Holderbaum and Gmehling [16] and considers the Soave-Redlich-Kwong equation of state [19] and the UNIFAC model for the excess free energy and for the activity coefficient in the mixing rules. This EoS belong to the so-called “equations of state + excess Gibbs free energy models”, of which several models have been proposed [14]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (7)$$

$$a_1 = 0.42748 \frac{R^2 T_c^2}{P_{c,i}} \alpha(T), \quad b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (8)$$

For polar components, the expression proposed by Mathias and Copeman [20] is used to evaluate  $\alpha(T)$  in the PSRK equation:

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3]^2, \quad \text{for } T_r < 1 \quad (9)$$

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5})]^2 \quad \text{for } T_r > 1 \quad (10)$$

In these equations,  $T_c$  is the critical temperature,  $T_r = T/T_c$  the reduced temperature and  $c_1$ ,  $c_2$  and  $c_3$  are the empirical parameters.

The mixing rules, which arise from combining the equation of state and a model for the excess Gibbs free energy [17,21] are

$$a = b \left[ \frac{g^E}{A_1} + \sum x_i \frac{a_i}{b_i} + \frac{RT}{A_1} \sum x_i \ln \frac{b}{b_i} \right] \quad (11)$$

The Eq. (6) is used together with the UNIFAC model for  $g^E$  [22] and the classical mixing and combination rule for the volume

Table 1  
Parameters for the UNIQUAC model

$$\theta_i = \frac{q_i x_i}{\sum_j r_j x_j}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\tau_{ji} = \exp\left(\frac{A_{ij} - (U_{ij} - U_{ji})}{RT}\right)$$

$$a_{ij} + \frac{b_{ij}}{T} = A_{ij} + \frac{U_{ij} - U_{ji}}{RT}$$

$$b_{ij} = -\frac{U_{ij} - U_{ji}}{R}$$

$a_{ij} = A_{ij}$ ;  $l_i = (z/2)((r_i - q_i) - r_i - 1)$ ,  $z = 10$  (coordination number);  $q_i$  is the van der Waals area parameter;  $r_i$  is the van der Waals area parameter.

parameter “ $b$ ” is assumed:

$$b = \sum_{i=1}^N \sum_{j=1}^N x_i x_j b_{ij}, \quad b_{ij} = \frac{b_i + b_j}{2} \quad (12)$$

In these equations,  $a_i$  and  $b_i$  are the pure component constants in the equation of state as defined by Eq. (8) and  $A_1$  is a constant equals to  $-0.64663$ . A survey about the current status and potential of the PSRK equation of state has been recently presented by Horstmann et al. [23]. Different fields of application are discussed by the authors but applications to mixtures such as those discussed in this paper were not included.

### 3.2. The UNIQUAC model

The universal-quasichemical theory, from which the UNIQUAC model is derived can be expressed in terms of the activity coefficients as [24]:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \quad (13)$$

with the combinatorial part  $\ln \gamma_i^c$  and residual part  $\ln \gamma_i^R$  given by

$$\ln \gamma_i^c = \ln \frac{\phi}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (14)$$

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (15)$$

The variables and parameters  $z$ ,  $\theta_i$ ,  $\phi_i$ ,  $\tau_{ij}$ ,  $q_i$  and  $l_i$  in the above equation are detailed in Table 1.

### 3.3. The UNIFAC model

The UNIFAC model [22] is the group contribution version of the UNIQUAC model. When using the UNIFAC model one needs to identify the functional subgroups present in each molecule by means of the UNIFAC group table. Next, similar to the UNIQUAC model, the activity coefficient for each species is written as Eqs. (13)–(15), except for the residual term, which is evaluated by a group contribution method in UNIFAC. Details on how to calculate the different contributions and parameters in the UNIFAC model are given in Tables 2 and 3.

Table 2  
Parameters for the UNIFAC model

$$l_i = \frac{z}{2} (r_i - q_i) - r_i - 1, \quad z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j r_j x_j}$$

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\tau_{ji} = \exp\left(\frac{U_{ij} - U_{ji}}{RT}\right)$$

$$r_i = \sum_k v_k^{(i)} R_K$$

$$q_i = \sum_k v_k^{(i)} Q_K$$

$$R_k = \frac{V_{wk}}{15.17}$$

$$Q_k = \frac{A_{wk}}{2.5 \times 10^9}$$

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \tau_k - \ln \tau_k^{(i)})$$

All groups

$$\ln \tau_k = Q_k \left[ 1 - \ln \left( \sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\psi_{nm}} \right]$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

$$\psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nm}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$

Table 3  
UNIFAC group data and contribution parameters  $r$  and  $q$  [26]

Components	Sub-group	Contribution	$r$	$q$
Acetaldehyde	1	1	1.8991	1.7960
	21	1		
Ethyl acetate	1	2	3.4786	3.1160
	23	1		
Furfural	62	1	3.1680	2.4810
Methanol	16	1	1.4311	1.4320
3-Methylbutanol	1	2	4.5979	4.2040
	2	2		
	3	1		
	15	1		
2-Methyl-1-propanol	1	2	3.9235	3.6640
	2	1		
	3	1		
	15	1		
1-Pentanol	1	1	4.5987	4.2080
	2	4		
	15	1		
1-Propanol	1	1	3.2499	3.1280
	2	2		
	15	1		
Ethanol	1	1	1.9720	2.1054
	2	1		
	15	1		
Water	17	1	0.9200	1.4000

Table 4  
Properties for all substances involved in this study [25]

Components	$M$ (Da)	$T_b$ (K)	$T_c$ (K)	$P_c$ (MPa)	$V_c$ (m <sup>3</sup> /kmol)	$\omega$
Water	18.0	373.15	647.35	22.12	0.063	0.3480
Ethanol	46.1	351.45	513.95	6.15	0.167	0.6452
Methanol	32.0	337.85	512.65	8.10	0.118	0.5640
1-Propanol	60.1	370.35	536.75	5.18	0.219	0.6218
2-Methyl-1-propanol	74.1	380.85	547.75	4.30	0.273	0.5848
3-Methyl-butanol	88.1	404.35	579.45	3.88	0.327	0.5558
1-Pentanol	88.2	410.95	586.15	3.88	0.326	0.5938
Acetaldehyde	44.1	294.05	465.95	5.50	0.154	0.2907
Ethyl acetate	88.1	350.25	523.35	3.88	0.286	0.3664
Furfural	96.1	434.85	670.15	5.66	0.252	0.3678

### 3.4. The NRTL model

The NRTL model for the activity coefficient at a given absolute temperature  $T$  in Kelvin, has the following form [18]:

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k} \left[ \tau_{ij} - \frac{\sum_k^N \tau_{ki} x_k G_{kj}}{\sum_k^N G_{kj} x_k} \right] \quad (16)$$

$$\tau_{ji} = \frac{A_{ji} + B_{ji}}{T}, \quad G_{ji} = \exp(-\alpha_{ji} \times \tau_{ji}), \quad \alpha_{ij} = \alpha_{ji} \quad (17)$$

The terms  $A_{ji}$ ,  $A_{ij}$ ,  $B_{ij}$ ,  $B_{ji}$  and  $\alpha_{ij}$  represent adjustable parameters usually calculated from experimental vapor-equilibrium data.

## 4. Ternary mixtures

Eight ternary ethanol + water + congener mixtures were considered for the study. The congeners included in these mixtures are methanol, 1-propanol, 2-methyl-1-propanol, 3-methyl-butanol, 1-pentanol, acetaldehyde, ethyl acetate and furfural. These substances are considered as legal compounds by the Chilean legislation for the production of a spirit called Pisco and are controlled by the Chilean Health Ministry.

Table 4 shows pure component properties for all the substances involved in this study. In the table,  $M$  is the molecular weight,  $T_b$  the normal boiling temperature,  $T_c$  the critical temperature,  $P_c$  the critical pressure,  $V_c$  the critical volume and  $\omega$  is the acentric factor. The data were obtained from [25,26].

Table 5  
Temperature and mol fraction ranges for the experimental data employed in the analysis

Ternary system ethanol (2) + water (3) +	Range of $T$ (K)	Range of $x_1$	Range of $x_2$	Range of $y_1$	Range of $y_2$	Reference
Acetaldehyde (1)	350.15–359.15	0.0008–0.0049	0.079–0.740	0.019–0.145	0.353–0.762	[7]
Ethyl acetate (1)	343.85–351.95	0.015–0.548	0.160–0.899	0.050–0.579	0.169–0.876	[27]
Furfural (1)	352.65–363.25	0.005–0.508	0.097–0.556	0.0003–0.054	0.350–0.773	[7]
Methanol (1)	339.95–352.35	0.157–0.781	0.202–0.831	0.236–0.882	0.110–0.754	[27]
3-Methyl-1-butanol (1)	351.65–358.65	0.0099–0.049	0.099–0.795	0.0014–0.048	0.364–0.822	[28]
2-Methyl-1-propanol (1)	353.05–360.35	0.002–0.011	0.060–0.571	0.010–0.029	0.344–0.711	[7]
1-Pentanol (1)	353.55–370.65	0.070–0.667	0.043–0.777	0.009–0.104	0.328–0.932	[29]
1-Propanol (1)	353.15–361.25	0.005–0.500	0.050–0.599	0.011–0.350	0.238–0.665	[7]

The pressure is 0.1013 MPa for the eight ternary systems.

Table 5 gives some details on the experimental data used in the study. In this table,  $\Delta T$  is the temperature range in the data set (expressed in Kelvin),  $\Delta x_i$  the liquid mole fraction range for the component “ $i$ ” and  $\Delta y_i$  is the vapor mole fraction range for the component “ $i$ ”. The experimental data used in the study were obtained from [7,27–29], as detailed in Table 4.

Although values of the interaction parameters in the models NRTL and UNIQUAC (in Eq. (17) for NRTL and Table 1 for UNIQUAC) are given in the literature for most binary pairs, in this work these parameters were obtained from available experimental binary VLE data. This was done because the range of temperature and pressure for the data presented in the literature are not necessarily the same as the data used in this work. This is the recommended way to analyze these type of systems if better results are wanted [8]. The new binary mixture parameters are shown in Table 6 for the NRTL and UNIQUAC models.

## 5. Results and discussion

According to the phase rule for a three-component mixture, three variables must be set to calculate the others, so the system is completely defined [13]. Here, the pressure ( $P$ ) and the concentration of water in both phases ( $x_3$  and  $y_3$ ) are given, while the temperature ( $T$ ) and the concentration of the other components ( $x_1$ ,  $y_1$ ,  $x_2$  and  $y_2$ ) are calculated.

In Tables 7 and 8, average absolute deviations for the temperature (%  $\Delta T$ ), average relative deviations for the gas phase concentration of the three components in the mixtures (%  $\Delta y_i$ ), and average absolute deviations  $|\% \Delta y_i|$  between predicted and experimental values for all systems studied are presented. Also,



Table 6  
Parameters for the models NRTL and UNIQUAC calculated from experimental binary VLE data

Binary system	NRTL			UNIQUAC	
	$\alpha$	$B_{12}$	$B_{21}$	$U_{12}$	$U_{21}$
Ethanol (1) + water (2)	0.30407	-46.861	679.64	-23.91	328.24
Methanol (1) + water (2)	0.31072	-173.71	537.37	-403.40	685.36
1-Propanol (1) + water (2)	0.39775	115.52	997.39	97.83	440.25
2-Methyl-1-propanol (1) + water (2)	0.30409	24.947	1210.1	334.83	226.31
3-Methyl-1-butanol (1) + water (2)	0.29772	-204.55	1770.2	-198.46	787.38
1-Pentanol (1) + water (2)	0.28909	-30.155	1415.3	383.68	192.13
Acetaldehyde (1) + water (2)	0.28671	128.89	515.03	424.17	86.46
Ethyl acetate (1) + water (2)	0.39304	727.01	1881.5	1386.10	-185.17
Furfural (1) + water (2)	0.32651	120.92	1256.1	288.10	125.03
Methanol (1) + ethanol (2)	0.3020	-166.83	189.21	-79.05	107.93
1-Propanol (1) + ethanol (2)	0.3000	-85.591	112.73	-210.50	287.23
2-Methyl-1-propanol (1) + ethanol (2)	0.3092	362.21	-260.93	-68.73	102.50
3-Methyl-1-butanol (1) + ethanol (2)	0.3120	-239.47	340.58	-142.77	246.68
1-Pentanol (1) + ethanol (2)	0.3223	454.55	-274.09	532.64	-315.17
Acetaldehyde (1) + ethanol (2)	0.3733	449.60	-253.96	413.38	-247.30
Ethyl acetate (1) + ethanol (2)	0.2224	268.74	51.62	556.79	-177.69
Furfural (1) + ethanol (2)	0.3332	646.03	-34.853	955.94	-282.03

maximum and minimum deviations ( $\% \Delta y_{\max}$  and  $\% \Delta y_{\min}$ ) are shown. The average deviations and the average absolute deviations are defined as follows:

$$\begin{aligned} \% \Delta y_i &= \frac{100}{N} \sum \left[ \frac{y_{\text{cal}} - y_{\text{exp}}}{y_{\text{exp}}} \right], \\ | \% \Delta y_i | &= \frac{100}{N} \sum \left[ \frac{|y_{\text{cal}} - y_{\text{exp}}|}{y_{\text{exp}}} \right], \\ \% \Delta T &= \frac{100}{N} \sum \left[ \frac{T_{\text{cal}} - T_{\text{exp}}}{T_{\text{exp}}} \right] \end{aligned} \quad (19)$$

In these Tables, deviations for water concentration  $y_3$  are not shown because water concentrations in both phases are the data

given in the bubble temperature calculations. Since for wine distillation the congener concentration is the most interesting variable, results and discussion refer to this concentration. The temperature is, in general, well predicted by all models although the correlating models NRTL and UNIQUAC give better results.

The Table 7 shows the deviations calculated using the predictive models PSRK and UNIFAC and the experimental data obtained for the mole fractions of the congeners in the gas phase for all the mixtures studied. As observed in the Table, the predictive models PSRK and UNIFAC predict this concentration ( $y_1$ ) with relative and absolute deviations below 24% for only four of the eight systems analyzed. The highest absolute deviations, between 31 and 47%, are found for the mixtures furfural (1) + ethanol (2) + water (3), 2-methyl-1-propanol (1) + ethanol

Table 7  
Minimum, maximum, and average deviations for the vapor mole fraction of components (1) and (2) for the ternary system congener (1) + ethanol (2) + water (3), using the predictive models PSRK and UNIFAC

Ternary system ethanol (2) + water (3) +	$ \% \Delta T $	$\% \Delta y_{1 \min}$	$\% \Delta y_{2 \min}$	$\% \Delta y_{1 \max}$	$\% \Delta y_{2 \max}$	$\% \Delta y_1$	$ \% \Delta y_1 $	$\% \Delta y_2$	$ \% \Delta y_2 $
<b>PSRK</b>									
Acetaldehyde (1)	1.3	0.5	-0.1	43.3	3.7	2.0	13.8	0.4	1.8
Ethyl acetate (1)	1.0	-1.0	-0.3	-21.3	17.3	-8.7	9.3	2.8	3.6
Furfural (1)	2.1	-3.9	-3.8	-76.4	11.8	-43.1	44.4	3.9	7.3
Methanol (1)	2.3	0.5	0.3	-7.0	-28.7	-1.8	3.0	-2.0	6.1
3-Methyl-1-butanol (1)	0.6	-9.1	0.0	45.3	-18.1	2.2	24.6	-3.2	3.2
2-Methyl-1-propanol (1)	1.4	-11.5	0.2	-67.4	-16.6	-40.0	40.0	-4.4	5.9
1-Pentanol (1)	0.2	-11.6	-0.6	-100.0	-13.1	-46.4	46.4	-4.0	5.1
1-Propanol (1)	0.4	-0.2	0.5	-34.3	13.1	-20.0	20.0	5.4	5.4
<b>UNIFAC</b>									
Acetaldehyde (1)	1.4	0.5	1.2	38.1	-4.8	1.6	13.1	-0.5	2.6
Ethyl acetate (1)	1.1	2.3	-0.2	-36.8	24.0	-19.1	19.6	5.8	5.8
Furfural (1)	1.9	-0.4	1.6	-76.3	9.7	-37.3	39.3	3.5	6.0
Methanol (1)	2.1	-0.2	-2.2	-9.6	-25.0	-3.7	4.3	0.7	6.8
3-Methyl-1-butanol (1)	0.3	-1.3	0.0	41.7	-22.8	10.7	16.9	-3.5	3.7
2-Methyl-1-propanol (1)	0.9	-5.9	-0.5	-65.1	-13.6	-28.8	31.8	-2.8	5.1
1-Pentanol (1)	0.1	-8.7	-0.2	-80.0	-8.0	-33.5	33.5	-1.2	2.5
1-Propanol (1)	0.4	-1.0	-0.1	-26.7	17.8	-15.8	15.8	5.9	5.9

Table 8  
Minimum, maximum, and average deviations for the vapor mole fraction of components (1) and (2) for the ternary system congener (1) + ethanol (2) + water (3), using the semipredictive models NRTL and UNIQUAC

Ternary system ethanol (2) + water (3)+	[% $\Delta T$ ]	% $\Delta y_1$ min	% $\Delta y_2$ min	% $\Delta y_1$ max	% $\Delta y_2$ max	% $\Delta y_1$	[% $\Delta y_1$ ]	% $\Delta y_2$	[% $\Delta y_2$ ]	
NRTL										
Acetaldehyde (1)	0.3	-1.6	0.2	-43.3	3.9	-5.6	12.3	0.4	1.6	
Ethyl acetate (1)	0.1	0.6	-0.3	-14.1	4.2	-0.2	5.0	-0.6	2.8	
Furfural (1)	0.3	-7.5	1.7	200.0	8.2	4.8	39.8	3.0	3.5	
Methanol (1)	0.2	0.4	0.03	4.3	17.3	0.9	2.1	-0.7	5.3	
3-Methyl-1-butanol (1)	0.4	7.1	0.2	61.7	-14.5	35.0	35.0	3.9	3.9	
2-Methyl-1-propanol (1)	0.3	-17.3	-0.2	-71.9	-14.3	-44.4	44.4	-3.0	4.9	
1-Pentanol (1)	0.3	6.3	0.2	74.7	19.2	31.2	34.0	5.5	5.5	
1-Propanol (1)	0.2	-0.5	0.1	-17.5	9.3	-2.8	6.8	3.8	4.1	
UNIQUAC										
Acetaldehyde (1)	0.3	-4.7	-0.6	-43.8	-2.0	-7.3	12.7	-0.4	1.2	
Ethyl acetate (1)	0.2	-1.7	-0.3	-30.3	12.6	-7.3	10.3	2.5	5.0	
Furfural (1)	0.3	-1.7	-0.1	233.3	8.3	10.7	42.6	2.8	3.3	
Methanol (1)	0.2	0.1	0.2	4.7	18.2	1.1	2.1	-0.7	5.3	
3-Methyl-1-butanol (1)	0.4	0.0	0.3	51.1	12.6	26.8	29.2	-3.2	3.2	
2-Methyl-1-propanol (1)	0.3	3.3	-0.2	-65.6	-14.9	-32.1	32.7	-3.5	5.0	
1-Pentanol (1)	0.2	6.7	0.1	84.7	17.1	34.9	34.9	4.0	4.0	
1-Propanol (1)	0.2	-0.8	-0.3	17.1	8.9	0.2	6.3	3.2	3.5	

(2) + water (3) and 1-pentanol (1) + ethanol (2) + water (3) and these models give lower deviations for the ethanol concentration in the gas phase (below 8%).

The Table 8 shows the results for the same ternary systems of Table 7, but found using the models NRTL and UNIQUAC. These are named “semipredictive” because ternary phase equilibrium properties are predicted using the binary parameters obtained using binary mixture data only. For example, for the mixture methanol (1) + ethanol (2) + water (3), the binary parameters  $B_{ij}$ ,  $B_{ji}$  and  $\alpha_{ij}$  required to apply the NRTL model are those shown in Table 6, in files 1, 2 and 10.

As observed in Table 8, these models predict the concentration of the congener in the gas phase ( $y_1$ ) with relative and absolute average deviations lower than 26% for only four of the eight systems analyzed. The highest absolute deviations, between 29 and 45%, are found for the mixtures furfural (1) + ethanol (2) + water (3), 3-methyl-1-butanol (1) + ethanol (2) + water (3), 2-methyl-1-propanol (1) + ethanol (2) + water (3) and 1-pentanol (1) + ethanol (2) + water (3).

The relative deviations for the concentration of the congener in the gas phase ( $y_1$ ) found for the system 1-propanol (1) + ethanol (2) + water (3) are much lower than those found using the predictive models PSRK and UNIFAC (see Table 7). The concentration of ethanol in the gas phase ( $y_2$ ) is predicted with deviations below 6% for all systems analyzed. As an example of this, Fig. 2 shows the individual relative deviations of the predicted congener concentration in the gas phase ( $y_1$ ) in the mixture 3-methyl-1-butanol (1) + ethanol (2) + water (3). Experimental data are from Hausen [28] and the calculated values are from the models NRTL (●), UNIQUAC (Δ), PSRK (+) and UNIFAC (○). As observed in the figure, the UNIFAC model gives the best estimates.

Although some models give result for some particular cases it is not possible to generalize the results and select

one of the models used as the best one for this type of complex mixtures that appear in wine distillation processes. If better result are desired, further studies are needed with data restricted to narrow ranges of temperature, pressure and concentration.

It should finally mentioned that although there are a lot of data on compositions of wine distillates [30–32], the information provided is not given in the form required for the present modeling. In the Dechema Database [7], the only multicomponent mixture ethanol+water+ congeners is the five-component mixture water + ethanol + methyl acetate + ethyl acetate + *n*-propanol. This mixture includes congeners of interest in other distillation processes but not in the production of Pisco.

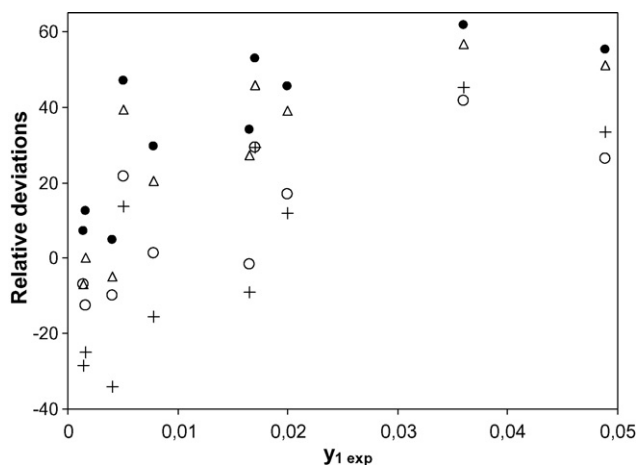


Fig. 2. Individual relative deviations of the predicted congener concentration in the gas phase ( $y_1$ ) in the mixture 3-methyl-1-butanol (1) + ethanol (2) + water (3). Experimental data are from Hausen [28] and the calculated values are from the models NRTL (●), UNIQUAC (Δ), PSRK (+) and UNIFAC (○).

## 6. Conclusions

Vapor–liquid equilibrium in ternary mixtures containing water + ethanol + cogener has been modeled using parameters obtained from binary mixture data only. The study allows obtaining the main three conclusions: (i) predictive models (PSRK and UNIFAC) that do not use empirical mixture parameters are not capable of accurately predicting the concentration of all components in the vapor phase; (ii) semi-predictive models (NRTL and UNIQUAC) that use empirical mixture parameters give similar deviations than the predictive models in estimating the concentration of the different components in the vapor phase; (iii) the temperature is better predicted by the NRTL and UNIQUAC models than by PSRK and UNIFAC.

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