Phase Equilibrium in Binary Aqueous Mixtures of Interest in Alcoholic Distillation Using a Modified PSRK Equation of State

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Phase equilibrium in binary mixtures that are found in wine and must distillation processes have been modeled using the predictive Soave-Redlich-Kwong equation, with original and modified molecular parameters. In wine and must distillation, the presence of polar substances found in the mixture to be distilled and the many components (i.e., those different from ethanol and water), called congeners, makes it difficult to model these mixtures. Thus, the prediction and correlation of the concentration of the distilled product, which is the most interesting variable, become very complex, and some experimental data are needed. The cases studied considered nine binary water + congener mixtures. The congeners considered are acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 3-methylbutanol, 2-methyl-1-propanol, 1-pentanol, and 1-propanol. These are the substances that are considered to be legal compounds by the Chilean legislation governing the production of a spirit called Pisco. The work allows evaluation of the advantages, disadvantages, and expected accuracy of this model. Comparison with available literature data is done.

1. Introduction

In wine and must distillation, the great number of substances found in the mixture to be distilled called must, and the very low concentration of many other components (different from ethanol and water), called congeners, make it difficult to correlate and predict the concentration of the distilled product, which concentration is considered to be the most important variable in the produced spirit. Several of the congener compounds are an essential part of the aroma of the distilled product, and therefore their concentrations are important enological parameters [1992Lor]. These congener substances are usually present in concentrations of parts per million (10^{-6}-10^{-4} mg/L) [1975Hik]. Knowledge of the vapor-liquid equilibrium (VLE) behavior in these mixtures is necessary to design and optimize the wine and must distillation, which is one of the most frequently used separation methods [2001Val].

The problem of phase equilibrium consists of the calculation of some variables of the set (T, P, x, and y), if some of them are known. For a given mixture, the number of variables, F, to be established, so that the system is completely defined, is determined by the Gibbs phase rule: $F = c - p + 2$, with c being the number of components in the mixture and p being the number of phases. For a vapor-liquid mixture in thermodynamic equilibrium, the temperature and the pressure are the same in both phases, and the material balance and the "fundamental equation of phase equilibrium" define the remaining variables.

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The operating pressure in the alcoholic distillation that produces Pisco is of the order of the atmospheric pressure, and most of the substances involved are highly polar. The classic thermodynamic models, commonly used in the literature to described VLE in these mixtures at low pressure, require knowing binary interaction parameters, which are usually determined from experimental data [1982Gme]. These interaction parameters, which are required to solve the phase equilibrium problem in these mixtures, must be determined using experimental data for binary systems.

In this work, phase equilibrium in the binary mixtures found in wine and must distillation processes have been modeled using the predictive Soave-Redlich-Kwong (PSRK) equation with original and modified molecular parameters. In the case of this study, nine binary water + congener mixtures were considered. The congeners considered were acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 3-methylbutanol, 2-methyl-1-propanol, 1-pentanol, and 1-propanol. These are the substances that are considered to be legal compounds by Chilean legislation governing the production of the spirit called Pisco.

2. The Fundamental Equation of Phase Equilibrium

This fundamental equation can be expressed as the equality of the fugacities of each component in the mixture in both phases (see, for instance, the book by Walas [1985Wal]).

$$\bar{f}_i^{\,L} = \bar{f}_i^{\,V} \tag{Eq 1}$$

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

$$\bar{f}_i^V = y_i \bar{\phi}_i^V P \tag{Eq 2}$$

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

Nomenclature	
Symbols	
A_1	constant in the PSRK EoS (-0.64663)
a_c, b	parameter in the PSRK EoS
a_{ij}, b_{ij}	cross-parameters in the mixing rules of the EoS
g^E	excess Gibbs free energy
g_0^E	excess Gibbs free energy at low pressure
k	UNIFAC subgroup
m	function of the acentric factor in the PSRK equation
P	pressure
P_c	critical pressure
R	ideal gas constant
R_k	UNIFAC volume contribution parameter for a subgroup
r	UNIFAC volume contribution parameter for a component
Q_k	UNIFAC surface contribution parameter for a subgroup
q	UNIFAC surface contribution parameter for a component
T	temperature
T_c	critical temperature
T_r	reduced temperature ($T_r = T/T_c$)
V	volume
v_k	number of times that a subgroup k appears in a molecule
y_1	mole fraction of a congener in the vapor phase (component 1)
y_1^{cal}	calculated mole fraction of a congener in the vapor phase
y_1^{exp}	experimental mole fraction of a congener in the vapor phase
x_i	mole fraction of component i in the liquid phase
Abbreviations	
ASOG	analytical solution of groups
EoS	equation of state
NRTL	nonrandom two liquids
PSRK	predictive Soave-Redlich-Kwong EoS
UNIFAC	universal functional activity coefficient model
$\lvert\%\Delta T\rvert$	absolute percent deviation of temperature
$\lvert\%\Delta y_1\rvert$	absolute percent deviation for the vapor mole fraction of a congener
Greek Letters	
α	temperature function in the PSRK EoS
γ_i	activity coefficient of component i
γ_i^C	activity coefficient of component i, combinatorial part
γ_i^R	activity coefficient of component i, residual part
φ_i	fugacity coefficient of component i
Δ	interval (for temperature, pressure, and mole fraction)
ω	acentric factor

$$\bar{f}_i^L = x_i \bar{\phi}_i^L P \tag{Eq 3}$$

$$\bar{f}_i^L = x_i \gamma_i f_i^o \tag{Eq 4}$$

At low pressures, the standard state fugacity f_i^o can be replaced by the vapor pressure at the temperature of the system, P_i^{sat}. Thus,

$$\bar{f}_i^L = x_i \gamma_i P_i^{sat} \tag{Eq 5}$$

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 [1985Wal]. 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 (EoS) method. If the fugacity coefficient is used for the vapor phase and the activity coefficient is used for the liquid phase, the method of solution of the phase equilibrium problem is known as "the gamma-phi method."

If the EoS method is used, an EoS and a set of mixing rules are needed to express the fugacity coefficient as a function of the temperature, the pressure, and the concentration. Modern EoS methods include an excess Gibbs free energy model (g^E) in the mixing rules of the EoS, giving origin to the so-called EoS + g^E model [2003aVal].

Commonly, for the conditions under 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 (γ) is used to describe the complex liquid phase, and a fugacity coefficient model (ϕ) is used to describe the low-pressure vapor phase [1982Gme]. However, the EoS + g^E model can be used with success [1998Orb]. The PSRK equation used in the current study is one of these models.

Most models available in the literature for the activity coefficient are of the correlating type (i.e., van Laar, Margules, Redlich-Kister, nonrandom two liquids, and Wilson), meaning that experimental data are needed to calculate certain empirical parameters, although some predictive models are also available (i.e., universal functional activity coefficient model (UNIFAC) and analytical solution of groups). An interesting model to explore for predicting VLE in mixtures of interest in wine distillation is the PSRK, which was proposed by Holderbaum and Gmehling [1991Hol]. This model has been extensively used in the literature but has not been systematically applied to water + congener mixtures, as was done in this work.

3. The PSRK Model

The idea of combining simple cubic EoS values with excess 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 [1978Hur] published their analytical mixing rule for the attractive EoS parameter

a of a cubic EoS, numerous publications have appeared using more or less similar approaches.

The excess g^E given by an EoS 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 of 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:

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

The PSRK model was first proposed by Holderbaum and Gmehling [1991Hol] and considers the Soave-Redlich-Kwong EoS [1972Soa] and the UNIFAC model for the excess free energy and the activity coefficient in the mixing rules. The PSRK model can be described as follows:

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

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T) \qquad b = 0.08664 \frac{RT_c}{P_c} \quad \text{(Eq 8)}$$

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \quad \text{(Eq 9)}$$

$$m = 0.48 + 1.574\,\omega - 0.176\,\omega^2 \quad \text{(Eq 10)}$$

In these equations, T_c is the critical temperature, $T_r = T/T_c$ is the reduced temperature and ω is the acentric factor.

The mixing rules, which arise from combining the EoS and a model for the excess g^E [1978Hur, 1981Mol], are:

$$a = b\left[\frac{g_0^E}{A_1} + \sum x_1 \frac{a_i}{b_i} + \frac{RT}{A_1} \sum x_i \ln \frac{b}{b_i} \right] \quad \text{(Eq 11)}$$

Equation 6 is used together with the UNIFAC model for g_0^E [1977Fre] and the classic mixing and combination rule for the volume parameter b:

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

In these equations, a_i and b_i are the pure component EoS constants defined by Eq 8, A_1 is a constant equal to -0.64663 for the PSRK equation, and g_0^E is the excess Gibbs free energy calculated using UNIFAC.

In the UNIFAC model, the liquid phase activity coefficients for each species are calculated from group contributions, as follows [1997Smi]:

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^R \quad \text{(Eq 13)}$$

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

Table 1   Parameters for the UNIFAC Model Used in the PSRK EoS

UNIFAC Model	
$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$	(Eq 1.1)
$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right)$	(Eq 1.2)
$\ln\gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ij}}{s_k} - e_{ki}\ln\frac{\beta_{ij}}{s_k}\right)\right]$	(Eq 1.3)
$r_i = \sum_k v_k^{(i)} R_K$	(Eq 1.4)
$q_i = \sum_k v_k^{(i)} Q_K$	(Eq 1.5)
$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i}$	(Eq 1.6)
$B_{ik} = \sum_m e_{mi}\tau_{mk}$	(Eq 1.7)
$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j}$	(Eq 1.8)
$s_k = \sum_m \theta_m\tau_{mk}$	(Eq 1.9)
$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T}\right)$	(Eq 1.10)
$J_i = \frac{r_i}{\sum_j r_j x_j}$	(Eq 1.11)
$L_i = \frac{q_i}{\sum_j q_j x_j}$	(Eq 1.12)

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \quad \text{(Eq 14)}$$

$$\ln\gamma_i^R = q_i\left[1 - \sum_k\left(\theta_k\frac{\beta_{ij}}{s_k} - e_{ki}\ln\frac{\beta_{ij}}{s_k}\right)\right] \quad \text{(Eq 15)}$$

Details on how to calculate the different contributions and parameters in the UNIFAC model are given in Table 1-4 and in the Appendix.

The PSRK model has all the advantages of an EoS. It can be applied to systems at low and high pressure, and allows the calculation of densities, enthalpies, and VLE in systems with polar components. Also important to mention is the fact that the PSRK model can be tuned in different forms to give more accurate results. This model is quite useful for preliminary design of chemical systems at high and low pressures. Among the disadvantages of the PSRK model that should be mentioned is that the PSRK equation does not accurately handle systems with strong association in the gas phase and highly asymmetric mixtures. For mixtures containing highly polar fluids, such as those considered in this study, predictions give high deviations in some cases. However, simple modifications can improve results and keep the predictive capabilities of the PSRK equation, as is shown below.

Table 2   Selected UNIFAC Contribution Parameters, R_k and Q_k

Sub-group	Main Group	Molecular Mass	Q_k	R_k
1	1	1.50E + 01	8.48E − 01	9.01E − 01
2	1	1.40E + 01	5.40E − 01	6.74E − 01
3	1	1.30E + 01	2.28E − 01	4.47E − 01
15	5	1.70E + 01	1.20E + 00	1.00E + 00
16	6	3.20E + 01	1.43E + 00	1.43E + 00
17	7	1.80E + 01	1.40E + 00	9.20E − 01
21	10	2.90E + 01	9.48E − 01	9.98E − 01
23	11	5.80E + 01	1.42E + 00	1.68E + 00
43	20	4.50E + 01	1.22E + 00	1.30E + 00
62	30	9.61E + 01	2.48E + 00	3.17E + 00

Table 3   Selected UNIFAC Contribution Parameters for V-L

Main Groups		Interaction Parameter V-L	
i	j	a_{ij}	a_{ji}
1	5	9.87E + 02	1.56E + 02
1	6	6.97E + 02	1.65E + 01
1	7	1.32E + 03	3.00E + 02
1	10	6.77E + 02	5.06E + 02
1	11	2.32E + 02	1.15E + 02
1	20	6.64E + 02	3.15E + 02
1	30	3.55E + 02	−2.53E + 01
5	6	−1.37E + 02	2.49E + 02
5	7	3.54E + 02	−2.29E + 02
5	10	−2.04E + 02	5.29E + 02
5	11	1.01E + 02	2.45E + 02
5	20	1.99E + 02	−1.51E + 02
5	30	−1.21E + 02	5.22E + 02
6	7	−1.81E + 02	2.90E + 02
6	10	3.06E + 02	−3.40E + 02
6	11	−1.07E + 01	2.50E + 02
6	20	−2.02E + 02	3.40E + 02
7	10	−1.16E + 02	4.81E + 02
7	11	7.29E + 01	2.01E + 02
7	20	−1.41E + 01	−6.62E + 01
7	30	1.88E + 02	2.35E + 01
10	11	−1.10E + 02	1.85E + 02
10	20	4.98E + 02	−1.66E + 02
11	20	6.60E + 02	−2.56E + 02
11	30	2.02E + 02	−1.46E + 02
20	30	−2.09E + 02	5.71E + 02

4. Modified PSRK Model

The PSRK model includes two molecular parameters, a volume parameter, r, and a surface area parameter, q, which are available in the literature for many groups [1977Fre]. Here, we proposed to modify these parameters for water, assuming them to be adjustable parameters. Data for binary water + congener mixtures were used to obtain optimum values of r and q.

Table 4   UNIFAC Group Data for the Components

Components	Sub-group (k)	Contribution (v_k)	r	q
Acetic acid	1	1	2.2024	2.0720
	43	1		
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		
Water	17	1	0.9200	1.4000

The mixtures in this investigation considered nine binary water + congener mixtures. The congeners that were considered were acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 3-methylbutanol, 2-methyl-1-propanol, 1-pentanol, and 1-propanol. These substances are considered to be legal compounds by Chilean legislation governing the production of a spirit called Pisco and are controlled by the Chilean Health Ministry.

Table 5 shows the pure component properties for all the substances involved in this study. In the table, M is the molecular weight, T_c is the critical temperature, T_b is the normal boiling temperature, P_c is the critical pressure, V_c is the critical volume, and ω is the acentric factor. Data were obtained from Daubert et al. [1996Dau] and Chemstations [2001Che]. Table 6 gives some details on the experimental data used in the study. In this table, ΔT (°C) is the temperature range in the data set, Δx_1 is the liquid mole fraction range for the congener in the data set, and Δy_1 is the vapor mole fraction range for the congener in the data set.

The VLE data were analyzed using the PSRK model leaving the molecular parameters r and q as adjustable parameters. To evaluate these parameters, a numerical optimization procedure was implemented on the computer. The program utilizes a modified Marquardt method [1972Rei] as the basic numerical algorithm. It has been demonstrated that for cases such as those containing supercritical carbon dioxide multiple solutions (local optimum values) are found in a range that seem to be "acceptable" for correlation purposes. The optimum value of the interaction parameters depends on the searching interval and on the initial value of

Table 5 Properties for all Pure Substances Involved in This Study

Components	M	T_c (°C)	T_b (°C)	P_c (MPa)	V_c (m³/Kmol)	ω
Acetic acid	60.0	318.8	117.9	5.79	0.180	0.4665
Acetaldehyde	44.0	192.9	20.9	5.50	0.154	0.2907
Ethyl acetate	88.1	250.2	77.1	3.88	0.286	0.3664
Furfural	96.1	397.0	161.7	5.66	0.252	0.3678
Methanol	32.0	239.5	64.7	8.10	0.118	0.5640
3-Methylbutanol	88.2	306.3	131.2	3.88	0.327	0.5558
2-Methyl-1-propanol	74.1	274.6	107.7	4.30	0.273	0.5848
1-Pentanol	88.2	313.0	137.8	3.88	0.326	0.5938
1-Propanol	60.1	263.6	97.2	5.18	0.219	0.6218
Water	18.0	374.2	100.0	22.12	0.063	0.3480

Table 6 Ranges of Temperature, Liquid Phase Mole Fraction, and Vapor Phase Mole Fraction for the Nine Binary Mixtures Studied

Major Component	Congener (a)	ΔT (°C)	Δx_1	Δy_1
Water	Acetic acid	100-118	0-1	0-1
	Acetaldehyde	33-100	0-0.2	0-0.93
	Ethyl acetate	71-76	0.124-0.988	0.693-0.917
	Furfural	98-135	0.004-0.949	0.021-0.428
	Methanol	65-100	0.0004-0.987	0.003-0.978
	3-Methylbutanol	95-130	0.001-0.988	0.015-0.939
	2-Methyl-1-propanol	90-107	0.005-0.984	0.150-0.931
	1-Pentanol	96-120	0.01-0.90	0.144-0.441
	1-Propanol	88-98	0.003-0.955	0.071-0.878

(a) The pressure is 0.1013 MPa for the nine binary systems.

Table 7 Percent Deviations for the Temperature and the Congener Vapor Phase Mole Fraction Using the PSRK With Original Parameters for Water ($r = 0.92$ and $q = 1.399$), for the Nine Binary Systems

Water (2) +	$|\%\Delta T|$	$|\%\Delta y_1|$
Acetic acid	0.4	17.9
Acetaldehyde	0.5	8.2
Ethyl acetate	0.6	7.7
Furfural	1.3	22.1
Methanol	0.6	5.0
3-Methylbutanol	0.9	32.5
2-Methyl-1-propanol	0.9	9.5
1-Pentanol	0.8	20.0
1-Propanol	1.0	11.4
Average	0.8	14.9

Table 8 Percent Deviations for the Temperature and Congener Vapor Phase Mole Fraction Using the Modified PSRK With New Parameters r and q to Water (Eq 18 and 19) for the Nine Binary Systems

Water (2) +	$|\%\Delta T|$	$|\%\Delta y_1|$
Acetic acid	0.9	2.1
Acetaldehyde	0.5	12.5
Ethyl acetate	1.9	5.6
Furfural	2.9	11.7
Methanol	1.5	3.1
3-Methylbutanol	1.8	18.8
2-Methyl-1-propanol	1.4	8.7
1-Pentanol	1.0	14.3
1-Propanol	0.9	5.4
Average	1.4	9.1

the interaction parameters used to start the iterative procedure [2003Val2, 2003Val3].

The programs developed for this study explore for multiple acceptable solutions to choose as a final solution that which gives the lowest deviation of an established objective function. This procedure consumes more computer time but guarantees the finding of an optimum parameter, which gives the lowest deviation for a given property. Thus, the non-linear regression programs developed for this study represent an important improvement in what is normally described in the literature as optimization procedures. The objective function W used in this study is

$$W = \frac{1}{N}\sum_{1}^{N}(y_1^{cal} - y_1^{exp})^2 \qquad \text{(Eq 16)}$$

In this equation, N is the number of points in the experimental data set and y_1 is the congener mole fraction in the vapor phase.

5. Results and Discussion

Tables 7 and 8 show the results for the saturation temperature and the vapor mole fraction of the congeners for the nine binary mixtures studied. In these tables, the absolute deviations for the temperature, $|\%\Delta T|$, and for the congener concentration in the vapor phase, $|\%\Delta y_1|$, for the PSRK with original parameters and with modified parameters, are given. The absolute deviations for a set of N data points, given in the tables, are defined as

$$\%|\Delta T| = 100\Sigma[|T^{exp} - T^{cal}|/T^{exp}]/N$$

$$\%|\Delta y_i| = 100\Sigma[|y_i^{exp} - y_i^{cal}|/y_i^{exp}/N \qquad \text{(Eq 17)}$$

Table 7 shows results with the PSRK equation using original values for the molecular parameters r and q for water in all mixtures congener (1) + water (2) ($r = 0.92$ and $q = 1.399$ [2001Che]). As observed in Table 7, the PSRK model give good values for the saturation temperature (mean absolute deviations <1.4%). The PSRK model reproduces the congener concentration in the vapor phase of these binary systems, with mean absolute deviations ranging from 5.0-32.5%. For all systems, the average absolute deviation is 14.9%.
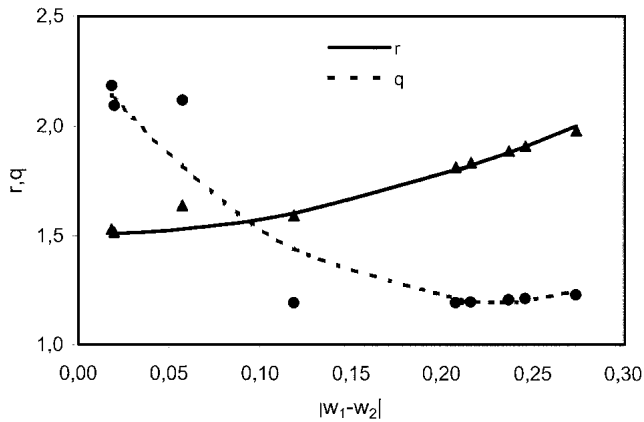
Fig. 1 Optimum parameters r and q for the congener component in the UNIFAC model in the modified PSRK EoS. The points are the values from regression, and the lines are the values from the correlation (Eq 18 and 19).

The molecular parameters for water (defined as $r = 0.92$ and $q = 1.399$) were recalculated for each binary system resulting in different values for r and q.

The optimum parameters found for each of the nine mixtures have been correlated with the acentric factors for the components in the mixture, as shown in Fig. 1. These parameters have been fitted to quadratic functions as follows:

$$r = 6.4234 \, (\omega_1 - \omega_2)^2 + 0.0555(|\omega_1 - \omega_2|) + 1.5078$$
$$\text{(Eq 18)}$$

$$q = 22.3882 \, (\omega_1 - \omega_2)^2 - 10.0445 \, (|\omega_1 - \omega_2|) + 2.3183$$
$$\text{(Eq 19)}$$

In these equations, $|\omega_1 - \omega_2|$ is the absolute value of the difference between the acentric factors of the two components (water and congener), with ω_2 being the acentric factor of water. These correlations have been used to predict T and y_1 for all mixtures studied. Table 8 shows the results obtained using the new parameters.

One should notice that with the proposed change (i.e., adjusting the parameters r and q for water), the model becomes more empirical. However, the correlation of the parameters in terms of the acentric factors of the components in the mixture (Eq 18 and 19), keeps the predictive capabilities of the model and at the same time improves its accuracy, which is demonstrated in Tables 7 and 8. In addition to this, the equations proposed here could be used to model VLE in binary water + congener mixtures of a broader class of spirits (i.e., those other than Pisco), which are aspects that might be of interest for the alcoholic beverages industry.

As seen in Table 8, the modified PSRK equation with new proposed molecular parameters for water (given by Eq 18 and 19) reproduces the saturation temperature with mean absolute deviations <3.0%. The modified PSRK equation allows for obtaining the congener concentration in the vapor phase of these systems with mean absolute deviations ranging from 2.1-18.8%. For all the systems considered, the modified PSRK equation provides considerably lower mean absolute deviations in the congener concentration in the vapor phase than the original PSRK equation. For example, for the systems acetic acid(1) + water(2), furfural(1) + water(2), and 3-methylbutanol(1) + water(2), deviations go down from 17.9%, 22.1%, and 32.5% to 2.1%, 11.7%, and 18.8%, respectively. The only exception is the deviation obtained for acetaldehyde(1) + water(2), which is somewhat higher that obtained using the original PSRK model (12.5% versus 8.2%, respectively). For all systems, the average absolute deviation is 9.1%, which is lower than the 14.9% obtained with the original universal values of the parameters r and q for water given in the literature. The deviations in the predicted temperature increase a little but are still low and reasonably accurate (original PSRK, 0.8%; modified model, 1.4%).

6. Conclusions

VLE in binary water + congener systems has been modeled using the original PSRK model and a modification proposed in this article. Based on the results, the following conclusions can be drawn:

1) The saturation temperatures for all of the systems considered in this study can be obtained with good accuracy with both the original and modified PSRK models. The average deviation is below 3.5%.
2) The concentration of the congener in the gas phase is predicted with high deviations for some systems considered in this work when using the PSRK model with the original universal parameters of the UNIFAC model.
3) The introduction of new molecular parameters r and q into the mixing rule (Eq 13) in the UNIFAC model give more accurate predictions for the concentration of the congener in the gas phase.
4) The generalization of the parameters r and q for water, in terms of the acentric factors of the components in the mixture, keeps the predictive capabilities of the PSRK model, but gives better results with the modified parameters (Table 8) than with the unadjusted parameters (Table 7).

Acknowledgments

Appendix

This Appendix gives additional details on how the parameters "r" and "q" in the UNIFAC model, the original and the new values, are calculated. As an example of this, let's consider the binary mixture Acetic Acid (1)-Water (2) at 388.35 K for $x_1 = 0.95$. The equations mentioned in this Appendix refer to those in Table 1, numbered from 1.1 to 1.12.

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The subgroups "k" for this case, the value of the parameters R_k and Q_k (taken of the Table 2), the number of times that the subgroup is present in the molecule (v_k), and the contribution parameters r and q, are:

Components	i	k	v_k	R_k	Q_k	r (Eq 1.4)	q (Eq 1.5)
Acetic acid	1	1	1	0.92	1.399	2.2024	2.072
		43	1	1.3013	1.224		
Water	2	17	1	0.92	1.399	0.92	1.399

Replacing values in Eq 1.6, the values for e_{ki} are as follows:

	e_{ki}	
k	$i = 1$	$i = 2$
1	0.4092664	0
17	0	1
43	0.59073359	0

From Tables 2 and 3, the following interaction parameters are obtained:

$a_{1\,1}$	$a_{1\,7}$	$a_{1\,20}$	$a_{7\,1}$	$a_{7\,7}$	$a_{7\,20}$	$a_{20\,1}$	$a_{20\,7}$	$a_{20\,20}$
0	1318	663.5	300	0	−14.09	315.3	−66.17	0

The substitution of these values in Eq 1.10, with $T = 388.35$ K, gives for τ_{mk} the following:

$\tau_{1\,1}$	$\tau_{1\,7}$	$\tau_{1\,20}$	$\tau_{7\,1}$	$\tau_{7\,7}$	$\tau_{7\,20}$	$\tau_{20\,1}$	$\tau_{20\,7}$	$\tau_{20\,20}$
1	3.36E-02	0.1811	0.4618	1	1.0369	0.4440	1.1858	1

Then, Eq 1.7 is applied to obtain values for B_{ik}, giving:

	B_{ik}		
i	$k = 1$	$k = 17$	$k = 43$
1	0.6716	0.7142	0.6649
2	0.4618	1	1.0369

The substitution of these values in Eq 1.8 gives for θ_k the following: $\theta_1 = 0.3952$, $\theta_{17} = 0.0343$ and $\theta_{43} = 0.5704$. From Eq 1.9, the values of s_k are calculated as: $s_1 = 0.6644$; $s_{17} = 0.7240$ and $s_{43} = 0.6776$. The activity coefficients are directly calculated from Eqs 1.1 to 1.3 to give for this case: $\gamma_1 = 1.0007$ and $\gamma_2 = 1.7852$.

For the Proposed Modified PSRK Model the parameters r and q for the water are calculated using Eqs 18 and 19 with $\omega = 0.4665$ for acetic acid and $\omega = 0.348$ for water, $|\omega_1 - \omega_2| = 0.1185$. Finally, for water $r = 1.6046$ and $q = 3.7810$.

With these values, the procedure indicated above is repeated to obtain new values of γ_1 and γ_2 and new values for T and y. As explained, the proposed general equations for the parameters r and q for water keep the predictive capabilities of the PSRK model giving better results as shown in Table 8.

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