Vapor-liquid equilibrium in low pressure water+congener mixtures

Claudio Alonso Faúndez*, Felipe Andrés Urbina*, and José Omar Valderrama**,***,†

*Univ. of Concepción, Fac. of Physical and Mathematical Sciences, Casilla 160-C, Concepción, Chile
**Univ. of La Serena, Fac. of Engineering, Dept. of Mech. Eng., Casilla 554, La Serena, Chile
***Center for Technological Information (CIT), Casilla 724, La Serena, Chile

Abstract−Vapor-liquid equilibrium in binary water+congeners mixtures found in alcoholic distillation has been analyzed using the Peng-Robinson equation of state and one of the most popular modern mixing rules, the Wong-Sandler model. Accurate modeling of the concentration of congeners (substances different from ethanol and water) in the vapor phase is of special importance because these substances give some special characteristics of flavor and aroma to the final distilled spirit and also because their concentrations are regulated by law. In the Wong-Sandler mixing rules the van Laar model for the Gibbs excess energy has been used. The type of model used in this work is commonly used to correlate high pressure phase equilibrium and has not yet been used to treat complex low pressure water+congener mixtures as done in this work. Eight binary water+congeners mixtures have been considered for analysis. Comparison with available literature data is done and the accuracy of the model to correlate the pressure and the vapor phase concentration of the congeners is discussed. It is concluded that the model used is accurate enough for distillation analysis, modeling and simulation.

Key words: Vapor-liquid Equilibrium, Alcoholic Mixtures, Equations of State, Wong-Sandler Mixing Rule

INTRODUCTION

The driving force that produces separation of components in distillation processes is the difference between the actual concentration and the concentration at thermodynamic equilibrium. Therefore, accurate knowledge of the equilibrium conditions is especially important in processes such as those employed in the alcoholic beverage production. 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*, make it difficult to correlate and predict the concentration of the distilled product, considered to be the most important variable in the distilled product. Several of the congener compounds are essential part of the flavor and aroma of the spirit, and therefore their concentrations are important enological parameters [1,2]. These congener substances are usually found at very low concentrations in alcoholic beverages [3-5], a factor that imposes an additional difficulty for modeling these mixtures.

Vapor-liquid equilibrium calculations in binary mixtures consist of determining two variables of the set temperature, pressure, liquid phase concentration, and vapor phase concentration (T, P, x, y), when the other two are known. The most popular form of correlating vapor-liquid equilibrium data is the so-called bubble pressure calculations, that is, P and y are determined while T and x are given. For a vapor-liquid mixture at equilibrium conditions, 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.*" For engineering purposes, this fundamental

equation is conveniently expressed in terms of the fugacity of each component in the different phases [6].

Low pressure vapor-liquid equilibrium data is usually treated by using activity coefficient models, although the use of equations of state has also been attempted [7]. Both approaches require binary parameters to be determined from experimental data [8]. These binary parameters are considered temperature dependent although their dependency is unknown. Therefore these parameters are usually determined from isothermal data, as done in this work.

Binary mixtures containing water+congener and ethanol+congener have been studied in the literature at atmospheric pressure using several activity coefficient models [5,9-12]. However, with the proposals of modern mixing rules such as those involving the excess Gibbs free energy, the equation of state method has been used at high and low pressure mixtures. The mixing rule of Wong and Sandler [13] is one of the most popular approaches currently used and applications to correlate VLE of several mixtures have been presented in the literature [7,14,15]. Therefore, the thermodynamic model considered in this work is the Peng-Robinson equation of state with the mixing rules of Wong and Sandler, using the van Laar model for the Gibbs free energy included in the mixing rules. This is named PR/WS/VL model in the forthcoming sections.

Although other models could be applicable, the Wong-Sandler mixing rule has shown the required flexibility to represent the complex behavior of the mixtures treated in this work [7]. Ferreira et al. [16] used the group contribution with association equation of state (CGA-EoS) to represent phase equilibrium in mixtures containing acids, esters and ketones, with water, alcohols, and other inert components. Li and Englezos [17] employed the statistical associating fluid theory (SAFT) for the correlation and prediction of vapor-liquid equilibrium of eighteen binary mixtures. These include alcohols, wa-

†To whom correspondence should be addressed.
E-mail: jvalderr@userena.cl

ter, carbon dioxide and hydrocarbons. More recently, Al-Saifi et al. [18] used the dipolar perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state to predict the vapor-liquid equilibrium in water-alcohol-hydrocarbon systems. However, in none of these works are the mixtures of interest in alcoholic distillation considered in the way presented here. The only system of those included in this study (using the same experimental data), that has been treated using equations of state is methanol+water at 313 K, reported in a paper by Li and Englezos [17]. In this case the values calculated by the authors are similar to the ones found in this work.

This paper considers the study of isothermal data of eight water+ ongener mixtures from 0.037 bars to 4.86 bars and the correlation of such data using an equation of state as the thermodynamic model. The eight congener substances are: acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 1-propanol, methyl acetate and 2-butanol. The PR/WS/VL model and all the equations that describe it are presented in the next section.

THE THERMODYNAMIC MODEL

One of the most commonly used methods for phase equilibrium correlation and prediction in complex systems is the application of an equation of state (EoS) and appropriate mixing and combining rules to describe the concentration dependency of the parameters of the EoS. Of the many equations of state nowadays available, the cubic equations derived from van der Waals proposal such as the Peng-Robinson EoS [19], are widely used to treat these systems. The Peng and Robinson EoS can be written in a general form as:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_R)}{V(V+b) + b(V-b)} \tag{1}$$

In this equation, a_c and b are specific parameters for each substance, determined from the critical properties, T_c and P_c. Also, $\alpha(T_R)$ is a function of the reduced temperature $T_R = T/T_c$ and of the acentric factor ω.

$$a_c = 0.457235 \left(\frac{R^2 T_c^2}{P_c} \right)$$
$$b = 0.077796 \left(\frac{RT_c}{P_c} \right)$$
$$\alpha(T_R) = [1 + F(1 - T_R^{0.5})]^2$$
$$F = 0.36646 + 1.54226\omega - 0.26992\omega^2 \tag{2}$$

During the last 30 years, efforts have been done on extending the applicability of cubic equations of state to obtain accurate representation of phase equilibria in many industrially important mixtures. An attractive way, which has been proposed to develop more accurate mixing rules, has been the combination of an EoS with a model for the excess Gibbs free energy (or activity coefficient model). Two main approaches have been used for applying these models. In the first approach, the link between the EoS and the excess Gibbs free energy model is done at infinite pressure [20,21]. In the second approach, the link between the EoS and the excess Gibbs free energy model is done at low or zero pressure [22].

In this work, the Peng-Robinson (PR) equation of state with the Wong-Sandler (WS) mixing rules has been used to correlate low pressure VLE data for water+congener mixtures. The WS mixing

rules for the Peng Robinson EoS can be summarized as follows [13]:

$$b_m = \frac{\sum_i^N \sum_j^N y_i y_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i^N \frac{y_i a_i}{b_i RT} - \frac{A_\infty^E(y)}{\Omega RT}} \tag{3}$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2}[b_i + b_j] - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \tag{4}$$

$$a_m = b_m \left(\sum_i^N \frac{y_i a_i}{b_i} + \frac{A_\infty^E(y)}{\Omega} \right) \tag{5}$$

In these equations, y represents the mole fraction of a component (i or j) in the gas phase when the mixing rule is applied to the gas phase and represents the mole fraction in the liquid phase when the mixing rule is applied to the liquid phase. Also, k_{ij} is an interaction parameter, $\Omega = 0.34657$ for the Peng-Robinson EoS, and $A_\infty^E(y)$ is calculated assuming that $A_\infty^E(y) \approx Ao^E(y) \approx g^E$. For g^E several models have been used in the literature. In this work g^E has been calculated by using the van Laar model. For a binary mixture, this model can be written as:

$$\frac{g^E}{RT} = \frac{(A_{12}/RT)y_1 y_2}{y_1(A_{12}/A_{21}) + y_2} \tag{6}$$

In this model A_{12} and A_{21} are empirical parameters for the mixture of components 1 and 2. Therefore, for a binary mixture the WS mixing rule includes one adjustable binary interaction parameter k_{12} for $(b-a/RT)_{ij}$, besides the two parameters, A_{12} and A_{21}, included in the g^E model. These three adjustable parameters for each of the mixtures are determined by using experimental phase equilibrium data at constant temperature, available in the literature. In summary, the thermodynamic model includes the Peng-Robinson equation of state, the Wong-Sandler mixing rule, and the van Laar model for g^E in the mixing rules, model designated as PR/WS/VL in the rest of the paper.

The Peng-Robinson EoS with the Wong-Sandler mixing rules has been used in several applications, mainly vapor-liquid equilibria at high pressure and liquid-liquid equilibrium at low and high pressure [7,13]. Lee and Lin [23], recently employed the PR EoS and COSMO-SAC including the Wong-Sandler mixing rules to predict vapor-liquid equilibrium of highly nonideal binary mixtures over a wide range of pressure (0.1-19 MPa). To the best of the author's knowledge there is no application of this combined PR/WS/VL model to correlate low-pressure vapor-equilibrium data of water+congener mixtures. Therefore, the analysis done in this study represents a new application of modern mixing rules combined with equations of state to treat low pressure alcoholic mixtures for simulation and design.

MIXTURES STUDIED

Eight binary water+congener mixtures were considered for the study. The congeners included in these mixtures are: acetic acid, acetaldehyde, ethyl acetate, furfural, methanol, 1-propanol, methyl acetate and 2-butanol. Table 1 shows pure component properties for all the substances involved in this study. In the table, M is the molecular weight, T_b is the normal boiling temperature, T_c is the critical temperature, P_c is the critical pressure, V_c is the critical volume and w is the acentric factor. The values for these properties were obtained

Table 1. Properties for all substances involved in this study

Components	M (Da)	Tb (K)	Tc (K)	Pc (bar)	Vc (m³/kmol)	ω
Water	18.0	273.16	647.13	220.55	0.056	0.3449
Acetic acid	60.1	391.05	591.95	57.86	0.180	0.4665
Acetaldehyde	44.0	294.00	466.0	55.50	0.154	0.29073
Ethyl acetate	88.1	350.25	523.35	38.80	0.286	0.3664
Furfural	96.1	434.85	670.15	56.60	0.252	0.3678
Methanol	32.0	337.85	512.65	80.84	0.117	0.5659
1-Propanol	60.1	370.35	536.75	51.69	0.218	0.6204
Methyl acetate	74.1	330.09	506.55	47.50	0.228	0.3313
2-Butanol	74.1	372.70	536.20	42.02	0.269	0.5768

Table 2. Details on the phase equilibrium data for the systems considered in this study. In the table the temperature values have been rounded to the closest integer

Systems water (2)+	Ref.	T (K)	N	Range of date		
				P (bar)	Δx_1	Δy_1
Acetic acid	[25]	333	10	0.1414-0.1939	0.0300-0.8507	0.0220-0.7824
		343	11	0.1957-0.3045	0.0500-0.9500	0.0420-0.9083
		353	11	0.2974-0.4664	0.0500-0.9500	0.0415-0.9060
		363	11	0.4297-0.6908	0.0500-0.9500	0.0410-0.9010
Acetaldehyde	[25]	348	5	1.2156-4.0520	0.0250-0.2600	0.6850-0.9300
		373	5	1.7728-4.8624	0.0100-0.1500	0.4800-0.7950
Ethyl acetate	[26]	313	19	0.1710-0.2770	0.0500-0.9500	0.5860-0.8960
		328	19	0.2610-0.5250	0.0500-0.9500	0.4250-0.8730
		343	19	0.4750-0.9270	0.0500-0.9500	0.3740-0.8600
Furfural	[25]	323	7	0.0373-0.1399	0.0038-0.9488	0.0190-0.3039
		338	7	0.0680-0.2559	0.0038-0.9488	0.0200-0.3360
		353	7	0.1400-0.5065	0.0038-0.9488	0.0209-0.3600
Methanol	[26]	308	19	0.0770-0.2700	0.0500-0.9500	0.2920-0.9850
		313	19	0.0960-0.3400	0.0500-0.9500	0.2750-0.9810
		323	19	0.1670-0.5380	0.0500-0.9500	0.2960-0.9810
		333	19	0.2695-0.8130	0.0500-0.9500	0.2920-0.9800
		338	19	0.3482-1.000	0.0500-0.9500	0.2340-0.9800
		373	19	1.3216-3.3630	0.0500-0.9500	0.2360-0.9770
1-Propanol	[26]	333	19	0.2260-0.3098	0.0500-0.9500	0.3210-0.8500
		363	19	0.8090-1.0303	0.0500-0.9500	0.3850-0.8740
Methyl acetate	[25]	333	8	0.3945-1.1009	0.0095-0.9636	0.5121-0.9497
		343	8	0.5692-1.7248	0.0095-0.9636	0.4913-0.9420
		353	8	0.8304-2.1833	0.0095-0.9636	0.4740-0.9320
2-Butanol	[25]	333	13	0.2439-0.3146	0.0130-0.8500	0.2550-0.6550
		353	10	0.5705-0.7478	0.0130-0.8500	0.2730-0.7020

from [24].

Table 2 gives some details on the experimental data used in the study including the literature source for each data set [25,26]. In this table, T is the temperature (expressed in Kelvin), N is the number of experimental data for each data set, P is the pressure (expressed in bar), Δx_1 is the liquid mole fraction range for component 1 and Δy_1 is the vapor mole fraction range for component 1. As seen in Table 3, data for 25 isotherms with a total of 330 data points were considered. The temperature ranges from 308 to 373 K and the pressure from 0.037 to 4.86 bar.

Bubble pressure calculations for binary mixtures were performed by using the PR/WS/VL model. The adjustable parameters (k_{12}, A_{12}, A_{21}) of the model were determined by optimization of the objective function given by Eq. (7). The program designed considers the use of the Levenberg-Marquardt algorithm [27] as the optimization method. The objective function was defined as the relative error between calculated and experimental values for the pressure:

$$F = \sum_{i=1}^{N} \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| \tag{7}$$

Table 3. Optimum binary interaction parameter and van Laar constants in the Wong-Sandler mixing rules at all temperatures studied

Systems water (2)+	T (K)	A_{12}	A_{21}	K_{12}
Acetic acid	333	0.149356	3.850412	0.187405
	343	0.206863	3.100079	0.258107
	353	0.226129	3.100327	0.281257
	363	0.358435	1.011737	0.230928
Acetaldehyde	348	0.984857	0.019106	0.536528
	373	1.425242	0.120431	0.371703
Ethyl acetate	313	2.080384	2.747955	0.220820
	328	1.926172	2.962098	0.145635
	343	1.760662	3.284445	0.156905
Furfural	323	3.020996	1.834339	0.448047
	338	0.580705	1.596488	0.854729
	353	3.294394	1.673120	0.395367
Methanol	308	0.147043	2.098819	0.177939
	313	0.173217	1.097426	0.175602
	323	0.136436	1.100679	0.203432
	333	0.006764	1.084072	0.290486
	338	0.118867	0.026956	0.279183
	373	0.153688	0.045698	0.157689
1-Propanol	333	2.104775	0.542814	0.412399
	363	3.114559	1.272395	0.222554
Methyl acetate	333	1.077894	1.376839	0.631593
	343	0.925441	2.602629	0.689210
	353	1.896379	1.567343	0.487906
2-Butanol	333	1.329271	0.534729	0.631364
	353	2.266891	0.974472	0.485387

Table 4. Average deviations for the pressure and vapor mole fraction of component (1) using the PR/WS/VL model

Systems water (2)+	T (K)	% ΔP	$|\%\Delta y_1|$	$\%\Delta y_1$
Acetic acid	333.15	9.0	8.2	−0.6
	342.85	6.0	10.2	−10.2
	353.05	2.5	11.7	1.3
	363.05	1.9	11.8	0.6
Acetaldehyde	348.15	4.5	3.3	3.0
	373.15	2.2	4.9	1.6
Ethyl acetate	313.15	1.6	3.6	3.6
	328.15	1.9	3.0	3.0
	343.15	1.0	2.7	2.7
Furfural	323.15	6.7	7.0	3.1
	338.15	7.3	8.8	−2.1
	353.15	4.1	7.7	3.2
Methanol	308.15	3.6	4.0	3.9
	312.95	2.8	3.5	3.5
	323.15	1.6	3.1	3.1
	333.15	0.6	3.1	3.1
	338.15	0.6	5.0	5.0
	373.15	3.7	2.9	2.4
1-Propanol	333.15	5.5	6.1	4.7
	363.15	1.5	4.4	3.8
Methyl acetate	333.15	3.4	1.6	1.5
	343.15	3.5	2.2	1.4
	353.15	5.3	1.8	1.0
2-Butanol	333.15	2.2	7.1	6.4
	353.15	3.5	3.3	2.2

In this equation N is the number of points in the experimental data set and P is the bubble pressure.

RESULTS AND DISCUSSION

Table 3 shows the optimum binary interaction parameters in the Wong-Sandler mixing rules at all temperatures studied. Table 4 shows the results for the pressure and the vapor mole fraction of congeners for the nine binary mixtures studied using the PR/WS/VL model. Also given in this table are the average absolute deviations for the pressure, $|\%\Delta P|$, and the average and relative deviations for the congener concentration in the vapor phase, $|\%\Delta y_1|$ and $\%\Delta y_1$ for the PR/WS/VL model.

The average absolute deviations $|\%\Delta P|$, $|\%\Delta y_1|$, and relative deviations $\%\Delta y_1$, for a set of N data, given in the tables, are defined as:

$$|\%\Delta P| = \frac{100}{N}\sum \left| \frac{P^{cal}-P^{exp}}{P^{exp}} \right|_i \tag{8}$$

$$|\%\Delta y_1| = \frac{100}{N}\sum \left| \frac{y_1^{cal}-y_1^{exp}}{y_1^{exp}} \right|_i \tag{9}$$

$$\%\Delta y_1 = \frac{100}{N}\sum \left| \frac{y_1^{cal}-y_1^{exp}}{y_1^{exp}} \right|_i \tag{10}$$

As seen in Table 4, the PR/WS/VL model reproduces the bubble

pressures of these binary mixtures with mean absolute deviations less than 9.1% for any temperature. The pressure was calculated with deviations between 0.6% and 9.0%. In most cases, 21 out of 25 isotherms, pressure deviations are below 6%.

With respect to the congener concentration in the vapor phase y_1, this quantity is predicted in all cases studied, with mean absolute deviations from 1.6% to 11.8%. In most cases studied, the absolute average deviations of y_1 are less than 8.9%. Relative deviations vary between −10.2% and 6.4%. The maximum individual deviation in y_1 is 43%, for a single point for the system methanol (1)+water (2) at 338 K.

Figs. 1 and 2 show the bubble pressure versus concentration for the mixture methanol (1)+water (2) at 323 K, and for acetic acid (1)+water (2) at T=353 K, respectively. The symbol (●) represents the experimental data and the dashed line (---) represents the calculated values. It can be seen that there is good agreement between model estimates and experimental data, as described above.

Fig. 3 shows the predicted congener concentration in the vapor phase (y_1) versus congener concentration in the liquid phase (x_1) for the mixture acetaldehyde (1)+water (2) at 348 K. The symbol (●) represents the experimental data and the dashed line (---) represents the calculated values. Good agreement between the model results and the experimental data is observed. The individual deviations found for y_1 are less than 7.1%.

Fig. 4 shows the individual relative deviations of the predicted congener concentration in the vapor phase (y_1) in the mixture methyl acetate (1)+water (2) at three temperatures, 333, 343 and 353 K.
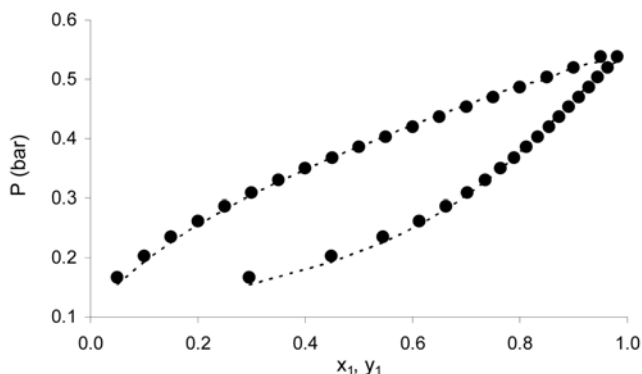
Fig. 1. Experimental (●) and calculated values (-) of bubble pressure P -vs- liquid mole fraction x_1 and vapor mole fraction y_1 for the system methanol (1)+water (2) at T=323 K.
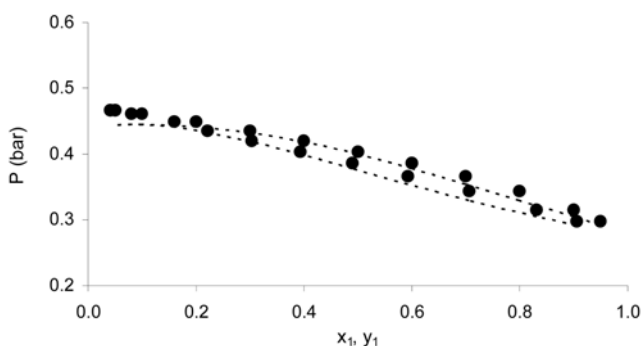

Fig. 2. Experimental (●) and calculated values (-) of bubble pressure P -vs- liquid mole fraction x_1 and vapor mole fraction y_1 for the system acetic acid (1)+water (2) at T=353 K.
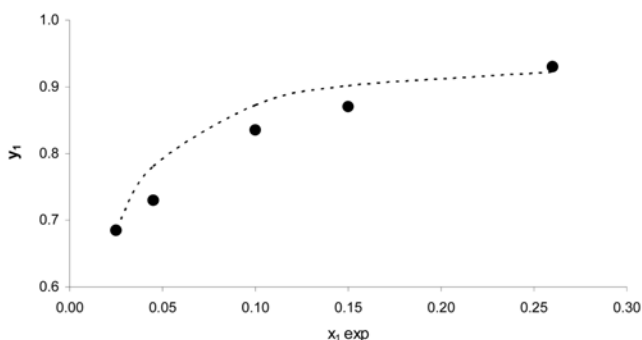

Fig. 3. Experimental (●) and calculated values (-) of congener concentration in the vapor phase (y_1) -vs- congener concentration in the liquid phase (x_1) for the mixture acetaldehyde (1)+water (2) at 348 K.

Experimental data are from the Dechema Data Base [25] and the calculated values are with the PR/WS/VL model. It can be observed that there is good agreement between correlated and experimental values. The individual deviations found for y_1 are less than 6.0%, for all temperatures considered.

CONCLUSIONS

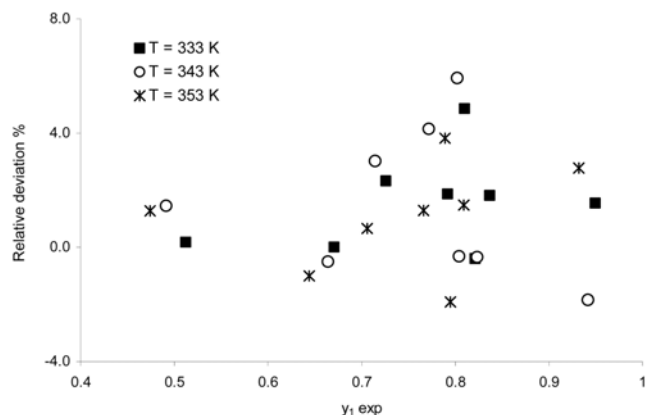Vapor-liquid equilibrium in mixtures water+congener has been

Fig. 4. Individual relative deviations of the predicted congener concentration in the vapor phase (y_1) in the mixture methyl acetate (1)+water (2) at temperatures T=333, 343 and 353 K.

modeled by using the equation of state method (Peng-Robinson+Wong-Sandler+van Laar, PR/WS/VL). The study and the results allow obtaining three main conclusions: i) the equation of state method using appropriate mixing rules such as the one of Wong and Sandler can be used to model low pressure complex mixtures; ii) bubble pressures can be obtained with good accuracy with the PR/WS/VL model, giving absolute average deviations below 9.1% for each isothermal data set and the overall absolute average deviations is 3.0%; and iii) the congener concentration in the vapor phase, y_1, can be obtained with good accuracy, giving absolute average deviations bellow 11.9% for each isothermal data set and the overall absolute average deviations and relative average deviations are 4.6% and 2.5%, respectively.

NOMENCLATURE

Symbols
A_{ij} : parameter in the van Laar model
a_c, b : parameter in the Peng-Robinson equation of state
a_m, b_m: interaction parameters in the mixing rules
g^E : excess Gibbs free energy
k_{ij} : binary interaction parameter
P : pressure
P_c : critical pressure
R : ideal gas constant
T : temperature
T_c : critical temperature
T_R : reduced temperature
V : volume

y_1 : mole fraction of congener in the vapor phase (component 1)
y^{calc} : calculated mole fraction of a congener in the vapor phase
y^{exp} : experimental mole fraction of a congener in the vapor phase
x_1 : experimental mole fraction of congener in the liquid phase (component 1)

Abbreviations

EoS   : equation of state
PR   : Peng-Robinson
PR/WS/VL : Peng-Robinson+Wong-Sandler+van Laar model
VL   : van Laar
WS   : Wong-Sandler mixing rule
%D   : percent deviation

Greek Letters

α(T) : temperature function in the PR EoS
ω : acentric factor

Super/subscript

cal   : calculated
exp   : experimental
i, j   : components i and j

REFERENCES

1. A. Hikari and R. Kubo, *J. Chem. Eng. Japan*, **8**, 294 (1975).
2. M. P. Y. Lillo, E. Latrille, G. Casaubon, E. Agosin, E. Bordeu and N. Martin, *Food Quality and Preference Jan.*, **16**, 59 (2005).
3. J. Lora, M. I. Iborra, R. Perez and I. Carbonell, *Rev. Esp. Cien. Tec. Ali.*, **32**, 621 (1992).
4. C. A. Faúndez, V. H. Alvarez and J. O. Valderrama, *Thermochimica Acta*, **450**, 110 (2006).
5. V. Athès, P. Paricaud, M. Ellaite, J. Souchon and W. Fürst, *Fluid Phase Equilibria*, **265**, 139 (2008).
6. J. M. Prausnitz, R. N. Lichtenthaler and E. Gomes de Azevedo, *Molecular thermodynamics of fluid-phase equilibria*, Prentice Hall International Series, New Jersey, USA (1999).
7. J. O. Valderrama, *Ind. Eng. Chem. Research*, **42**, 1603 (2003).
8. S. M. Walas, *Phase equilibria in chemical engineering*, Butterworth Pub., Storeham (1985).
9. J. O. Valderrama, C. Pizarro and R. Rojas, *Alimentaria*, **39**, 151 (2001).
10. C. A. Faúndez and J. O. Valderrama, *J. Food Eng.*, **65**, 577 (2004).
11. C. A. Faúndez, V. H. Alvarez and J. O. Valderrama, *J. Phase Equilib. Diff.*, **25**, 230 (2004).
12. V. H. Alvarez, C. A. Faúndez and J. O. Valderrama, *Can. J. Chem. Eng.*, **83**, 485 (2005).
13. H. Orbey and S. I. Sandler, *Equations of state and their mixing rules*, Cambridge University Press, USA (1998).
14. C. Kwak, S. I. Sandler and H. S. Byun, *Korean J. Chem. Eng.*, **23**, 1016 (2006).
15. G. Seong, A. R. Kim, K. P. Yoo and J. S. Lim, *Korean J. Chem. Eng.*, **26**, 206 (2009).
16. O. Ferreira, E. A. Brignole and E. A. Macedo, *J. Chem. Thermodynamics*, **36**, 1105 (2004).
17. X. S. Li and P. Englezos, *Fluid Phase Equilibria*, **224**, 111 (2004).
18. N. M. Al-Saifi, E. Z. Hamad and P. Englezos, *Fluid Phase Equilibria*, **271**, 82 (2008).
19. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
20. M. I. Huron and J. Vidal, *Fluid Phase Equilibria*, **3**, 255 (1979).
21. D. S. Wong and S. I. Sandler, *AIChE J.*, **38**, 671 (1992).
22. S. Dahl and M. L. Michelsen, *AIChE J.*, **36**, 1829 (1990).
23. M. T. Lee and S. T. Lin, *Fluid Phase Equilibria*, **254**, 28 (2007).
24. T. E. Daubert, R. P. Danner, H. M. Sibul and C. C Stebbins, *Physical and thermodynamic properties of pure chemicals*, Data compilation, Taylor & Francis, London, UK (1996).
25. J. Gmehling, U. Onken and W. Arlt, *Vapor-liquid equilibrium data collection*, DECHEMA, Frankfurt, Germany (1982).
26. S. Ohe, *Vapor-liquid equilibrium data*, physical sciences data 37, Kodansha Ltd., Tokyo and Elsevier Science Publishers B. V. Amsterdan (1989).
27. M. Reilly, *Computer programs for chemical engineering education*, vol. 2, Sterling Swift, TX, USA (1972).