VAPOR-LIQUID EQUILIBRIUM CALCULATIONS FOR ALCOHOL AND HYDROCARBON MIXTURES USING COSMO-SAC, NRTL, AND UNIQUAC MODELS

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ABSTRACT

Vapor-Liquid equilibrium (VLE) data involving alcohols and hydrocarbons are relevant to the gas and oil industry. Under certain circumstances, for instance, in the determination of the distribution of components between phases in equilibrium, and physical properties of the fluids in reservoirs, the predictions from the available models for hydrocarbon systems in the presence of flow-assurance additives, such as alcohols, are, at times, insufficient. This study used the Conductor-like Screening Model-Segment Activity Coefficient (COSMO-SAC) to predict liquid phase activity coefficients for the description of VLE of seven binary systems containing alcohols and hydrocarbons, at low and high pressures (10-2500kPa), and under temperatures ranging from 298-400K. The COSMO-SAC has a relatively simple mathematical form and can be easily incorporated into a process simulation software. COSMO-SAC model predictions in this work showed average absolute relative deviation (AARD) values ranging from 5.0% to 13.8%.

KEYWORDS

COSMO-SAC; VLE; alcohol; hydrocarbon

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1. INTRODUCTION

Thermodynamic modeling of phase equilibrium is of fundamental importance in the development of the oil and gas industry. Experimental data of vapor-liquid equilibrium in binary systems involving alcohol and hydrocarbons at low pressure are usually required for the design of separation processes. Therefore, novel thermodynamic models that are able to predict mixtures phase equilibrium may significantly reduce design time and cost.

Despite the relevance of studying systems containing hydrocarbons and alcohols for the oil and gas industry, literature reports few works involving the topic. There is a lack of attention to the study of thermodynamic models that describe the behavior of these systems. Thermodynamic modeling is of fundamental importance in the determination of reservoir composition, distribution of components between phases in equilibrium, and physical properties of the fluids through numerical simulations. In such simulations, equations of state are often applied and have demonstrated good results. Nevertheless, with the increasing complexity of new reservoirs – i.e. higher pressure, porous media effect, and injection flow assurance additives such as alcohols – the predictions from the available models aren't always satisfactory (Pires et al., 2001).

In recent years, the scientific community has studied a class of thermodynamic models for phase equilibrium prediction, the COSMO-based methods. These methods include the COSMO-RS (Klamt & Schuurmann, 1993; Klamt, 1995; Klamt et al., 1998) and its variants such as the COSMO-SAC (Lin & Sandler, 2002; Lin et al., 2004; Wang et al., 2007) and the COSMO-RS (OI) (Grensemann & Gmehling, 2005). Essentially, these methods consider the liquid phase solution non-ideality using molecular interactions derived from solvation calculations based on quantum chemistry (*ab initio*). The COSMO-SAC model does not require estimation of parameters from experimental data, therefore, it is a predictive model. It has been used to provide acceptable predictions of vapor-liquid equilibrium (VLE) of mixtures. However, Hsieh and Lin (2010) recently reported poor accuracy of the COSMO-SAC for the description of liquid-liquid equilibrium (LLE).

The main objective of this study is to predict the data from vapor-liquid equilibrium of systems containing alcohols and hydrocarbons gathered from the literature (decane/butanol, butanol/hexane, heptane/1-pentanol, ethanol/cyclohexane, isobutene/ethanol, pentane/ethanol, pentane/methanol) using COSMO-SAC. Calculations using the commercial simulator Aspen Hysys v7.3 were also performed for comparison. Calculations in this software used Peng-Robinson (PR) equation of state for the vapor and liquid phases. NRTL and UNIQUAC activity models were tested using the available set of parameters from the simulator. The seven binary VLE systems were studied at low and high pressures (10-2500 kPa), and at temperatures in the range of 298-400 K.

2. METHODOLOGY

2.1 The fundamental equation of phase equilibrium

A necessary condition for phase equilibrium is the equality of fugacity of each component in the present phases.

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

Where $\hat{f}_i^V$ and $\hat{f}_i^L$ are the fugacity of component i at vapor and liquid mixtures, respectively.

For components in the vapor phase:

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

Where y_i is the molar fraction of component i in vapor mixture, $\hat{\phi}_i^V$ is fugacity coefficient and P is pressure.

For components in the liquid phase, the gamma (activity coefficient) approach may be used (Equation 3):

$$\hat{f}_i^L = x_i \cdot \gamma_i \cdot P_i^{sat} \cdot \phi_i^{sat} \cdot \exp\left(\int_{P^{sat}}^P \frac{V^L dP}{RT}\right) \quad (3)$$

Where x_i is molar fraction of component i in liquid mixture, γ_i is the activity coefficient of component i in liquid mixture, P_i^{sat} is the vapor

pressure of pure component i , ϕ_i^{sat} is the fugacity coefficient of pure component i at saturation condition, and V^L is pure component i molar volume. $\hat{\Phi}_i$ is defined as follows:

$$\hat{\Phi}_i = \frac{\phi_i^V}{\phi_i^{sat} \cdot \exp\left(\int_{P^{sat}}^P \frac{V^L dP}{RT}\right)} \quad (4)$$

The equilibrium pressure can, then, be calculated by the complete equilibrium equation (Equation 5):

$$y_i \hat{\Phi}_i P = x_i \gamma_i P_i^{sat} \quad (5)$$

The value $\hat{\Phi}_i$ was approximated to unity, which is often a good approximation for fluids at low pressure. This approximation is valid if the compressibility factor for the mixture and for pure components, as well as the system's pressure and the pure components' saturation pressures, are of comparable magnitudes (Rousseau, 1987). The activity coefficients were calculated with the COSMO-SAC model.

$$P = \sum_i x_i \gamma_i P_i^{sat} \quad (6)$$

Bubble point pressure calculations were performed for different composition and temperatures to generate pressure versus composition phase envelope diagrams at given temperatures.

Vapor pressure for the pure components were obtained from Antoine correlations available in NIST WebBook database (Lemmon et al., 2011).

2.2 COSMO-SAC

In the COSMO approach in modeling excess Gibbs energy, the distribution of charges on the surface of the cavity surrounding a molecule immersed in a perfect conductor material is used as reference. The activity coefficient is obtained based on the difference in energy for the molecule from the state of immersion in the ideal conductor and the state of immersion in the real solution condition. The calculation of this difference in energy is performed based on the charge density probability profile.

First, the tridimensional geometry of each molecule must be determined by minimization of configurational energy. These calculations were performed using the quantum chemistry software ChemBioOffice (trial version). The quantum mechanical calculations are necessary for the determination of the geometric configuration of the atoms in the molecule that presents the lowest energy, knowing which atoms compose the molecules and how they are bonded. It is desired to determine the angles and distances between the atoms nuclei in the molecule in its most stable configuration. This procedure is known as geometry optimization. The necessary calculations for the determination of these data are available in quantum chemistry software packages such as GAUSSIAN, TURBOMOLE, MOPAC, DMol3, and GAMESS (Gerber & Soares, 2010).

After, the cavity volume, the total number of segments, and the sigma profile of each substance are calculated. Solvation calculations in a perfect conductor are performed, using the equilibrium geometry, to obtain the surface charge of the desired substance. The *ab initio* parameters for the compounds of the present work were obtained following the recommendations provided by Mullins et al. (2006) and Alvarez et al. (2011). More details about the theory can be found in the work of Lin and Sandler (2002).

The activity coefficient of the present species, which are necessary for the vapor-liquid equilibrium calculations, can be determined from the COSMO-SAC model using the sum of combinatorial and residual contributions.

$$\ln \gamma_i = \ln \gamma_i^{res} + \ln \gamma_i^{com} \quad (7)$$

The residual contribution is calculated from the molecular solvation in a perfect conductor. The charge distribution of the molecular surface, called sigma profile, $p(\sigma)$, is determined from quantum mechanics calculations. Molecular interactions in the liquid phase are assumed to be the sum of contributions from the interactions of surface segment through selected charges.

$$\ln \gamma_i^{res} = n_i \sum_{\sigma_m} p_i(\sigma_m) \ln[\Gamma_S(\sigma_m) - \Gamma_i(\sigma_m)] \quad (8)$$

Where n_i is the total number of surface segments in molecule i , $p_i(\sigma_m)$ is the sigma profile for a

molecule i , $\Gamma_S(\sigma_m)$ is the activity coefficient for a segment with charge density σ_m in solution, and $\Gamma_i(\sigma_m)$ is the activity coefficient for a segment with charge density σ_m in the pure liquid.

$$\ln \Gamma_{S \text{ or } i}(\sigma_m) = -\ln \left\{ \sum_{\sigma_n} \left(\left(p_{S \text{ or } i}(\sigma_n) \Gamma_{S \text{ or } i}(\sigma_n) \right) \cdot \exp \left[\frac{-\Delta W(\sigma_m \sigma_n)}{RT} \right] \right) \right\} \quad (9)$$

Where $W(\sigma_m \sigma_n)$ is the electrostatic interaction between two segments of charge density σ_m and σ_n . The combinatorial contribution is based on the Staverman–Guggenheim model, it is calculated by considering the fraction of surface θ_i , volume fraction Φ_i , coordination number ($z=10$), area parameters (q_i), and volume parameters (r_i) of molecule i .

$$\ln \gamma_i^{com} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (10)$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (11)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (12)$$

$$l_i = (z/2)(r_i - q_i) - (r_i - 1) \quad (13)$$

2.3 The σ -profile

The COSMO-SAC modeling considers the molecule as composed of the atomic nuclei, electrons, and an external contact surface. This surface delimits the molecule from the solvent, and presents an electrical charge induced by the nuclei and electrons. For the construction of this surface, each atom is regarded as a nucleus centered on a sphere with a given radius, the surface then is constructed from the union of all spheres and a posterior smoothing procedure. This simplified approach is required for quantum mechanical calculations to obtain information on the substances, which will be used by the COSMO-SAC model. It dismisses the need for experimental data obtainment and parameter estimation procedures. The attainment of required information can be divided in two steps. First, it is necessary to determine the tridimensional apparent charge distribution induced in the molecules' surfaces. Following, this information is interpreted in a two dimensional plot, called sigma profile. The sigma profile is generated as a file which shows the probability distribution of a molecular surface segment that has a specific charge density.

Figure 1. Sigma profile (Hydrocarbons).

Figure 2. Sigma profile (Alcohols).

The sigma profiles generated for the substances studied in this work are presented in Figures 1 and 2. The horizontal axis represents the charge density induced in the molecules' surfaces, these values usually range from -0.025 to +0.025 ($e/\text{\AA}^2$). The vertical axis represents the probability of a surface segment having a specific charge density multiplied by the molecule surface area.

Figures 1 and 2 show that the sigma profiles are similar among the solvents in each group. Nevertheless, the values are very different between the two groups, as one can observe by looking at the different scales used for the chart of each group. In the same way that interactions between two molecules of different hydrocarbons or different alcohols are similar to interactions between two molecules in pure hydrocarbon or alcohol liquids. While interactions between hydrocarbons and alcohols are different from the interactions in the pure hydrocarbon or alcohol liquids. Therefore, noticeable deviations from ideal solution behavior are expected along with the occurrence of vapor-liquid azeotropes.

2.4 Calculation Analysis

The capability of the model was evaluated by comparing calculated values and experimental data for equilibrium pressures through three measures: average absolute relative deviation, linear correlation, and coefficient of determination. The use of these three different measures is important

because they are all commonly used in literature, but they have different interpretations and limitations, as explained in the following lines.

Average absolute relative deviation (AARD) is calculated by arithmetic mean of absolute values of relative deviations. These relative deviations are calculated by the difference between experimental and predicted values, and divided by the experimental values as a reference, giving a percentage value in relation to the experimental value. This kind of measure is adequate to variables expressed in absolute units, so that the result is not affected by the use of different unit systems. This measure is frequently used in phase equilibrium literature to evaluate goodness of fit of thermodynamic models (Bosse & Bart, 2005; Hsieh & Lin, 2009; Jia et al., 2012).

$$\text{AARD}[\%] = \frac{100}{n} \sum_{i=1}^n \left| \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right| \quad (14)$$

This calculation is useful in comparisons between different works, and between a model calculation accuracy and an application requirement.

Correlation coefficient (ρ) is a measure of the degree of linear dependence between two variables. In the context of evaluating goodness of fit, it is defined as follows:

$$\rho = \frac{\sum_{i=1}^n (P_{\text{exp}} - \bar{P}_{\text{exp}})(P_{\text{calc}} - \bar{P}_{\text{calc}})}{\sqrt{\sum_{i=1}^n (P_{\text{exp}} - \bar{P}_{\text{exp}})^2 \sum_{i=1}^n (P_{\text{calc}} - \bar{P}_{\text{calc}})^2}} \quad (15)$$

The correlation coefficient can be used to measure the degree of linear dependence between calculated and experimental values. If the expected value for the residuals statistical distribution is zero, i.e. the residuals are equally expected to be positive or negative, this measure can be used to analyze the goodness of fit between model and data. The correlation coefficient may assume

values between -1 and 1. Researchers usually consider a model to be satisfactory if the correlation coefficient is greater than 0.9 (Schwaab & Pinto, 2007). However, if its value is low, it may indicate poor quality of model, as well as excessive experimental variance.

The coefficient of determination, also referred to as captured variance, R^2_{adj} (Equation 16), represents the fraction of total variation among the experiments that can be explained by the model. It is calculated by comparing model calculation variance to global variance of experimental values.

Calculation variance is the sum of square residuals, SSE (Equation 17), divided by the degree of freedom of the model evaluation problem. Global variance is the sum of the squared difference between each experimental values and the mean of all experimental values, SST (Equation 18), divided by the number of experiments less one. This approach naturally penalizes models with more parameters (Montgomery & Runger, 2003).

$$R^2_{adj} = 1 - \frac{SSE / (n - p)}{SST / (n - 1)} \quad (16)$$

$$SSE = \sum (P_{\text{exp}} - P_{\text{calc}})^2 \quad (17)$$

$$SST = \sum (P_{\text{exp}} - \bar{P})^2 \quad (18)$$

The coefficient of determination value may become negative if the total variance is too low, indicating poor exploration of the controlled variables domain. In this context, having a constant value equal to the mean of the measured variable values would be better than using the models' calculation in the referred domain.

3. RESULTS AND DISCUSSION

Figures 3 to 9 describe the vapor-liquid equilibrium behavior of seven binary mixtures of alcohols and hydrocarbons, for different temperatures, as plots of equilibrium pressures versus phase composition, as predicted by the COSMO-SAC model. COSMO-SAC is a predictive

Figure 3 Pressure x composition phase diagram for the system: butanol/decane at 358.2 K, 373.2 K, 388.2 K as function of butanol molar fraction. Experimental data from Bernatová et al., (1992). Model calculation from this work.

Figure 4. Pressure x composition phase diagram for the system butanol/hexane at 298.15 K as function of butanol molar fraction. Experimental data from Rodriguez et al. (1993). Model calculation from this work.

model based on quantum chemistry calculations. It has strategic importance for it does not require parameter estimation over VLE experimental data. The necessary sigma profiles are generated from pure compounds' charge density obtained from quantum mechanical calculations. Predictions show relevant qualitative results. However, quantitative descriptions depend on type of application in use. For instance, for conceptual preliminary design of distillation operations, predictions may be considered quantitatively satisfactory for most systems. Figures 6, 8, and 9 are good examples of the model's merit. The model was able to predict azeotropic mixture formation within 0.05 molar fraction error, although the pressure was underestimated by roughly 10% along the whole concentration range. Lower than experimental pressure calculated values indicate general underprediction of the activity coefficients. The accurate prediction of the azeotropic composition indicates correct evolution of the activity coefficient values of each species in both phases with respect to the components' molar fractions.

The methodology might be refined for higher pressure systems by removing the low pressure approximation of $\hat{\Phi}_i$ to unity. This can be accomplished by using an equation of state for the gas phase correction and an accurate correlation for the liquid molar volume. That would also require an evaluation of different mixing rules, e.g. the Wong-Sandler mixing rule, and estimation of interaction parameters. The activity coefficient model might be refined by improving quantum calculation tools utilized to generate charge density profiles.

Table 1 presents the average absolute relative deviation (AARD), the correlation and the coefficient of determination calculated using the COSMO-SAC model. Calculated average absolute relative deviations were between 5.7% and 13.1%, which are close to values obtained for similar models in literature (COSMO-SPACE and COSMO-RS) for similar systems: from 0.2% to 20% (Bosse & Bart, 2005).

Figure 10 presents predicted values versus experimental values of equilibrium pressure for all systems studied. The three lines represents the base line for expected values, and limits of 10% relative deviation for higher or lower pressures. Correlation values were higher than 0.96 for all

Figure 5 Pressure x composition phase diagram for the system heptane/1-pentanol at 348.2 K, 358.2 K, 368.2 K as function of heptane molar fraction. Experimental data from Machova et al. (1988). Model calculation from this work.

Figure 6. Pressure x composition phase diagram for the system ethanol/cyclohexane at 298.2 K as function of ethanol molar fraction. Experimental data from Coto et al. (1995). Model calculation from this work.

Figure 7. Pressure x composition phase diagram for the system isobutane/ethanol 363.5 K as function of isobutane molar fraction. Experimental data from Zabalyo et al. (1994). Model calculation from this work.

Table 1. Quality of prediction analysis for COSMO-SAC.

Components	T [K]	Pressure range [bar]	Pressure range [bar]	AARD [%]	ρ	R^2_{adj}
Butanol/Decane	358.2	0.05 - 00.28	0.0509 - 0.2763	7.29	0.984	0.954
	373.2	0.09 - 00.52	0.0956 - 0.5215	6.34	0.991	0.968
	388.2	0.16 - 00.92	0.168 - 0.9248	5.77	0.995	0.977
Butanol/Hexane	298.2	0.17 - 00.20	0.17875 - 0.20174	4.99	0.966	0.881
	348.2	0.07 - 00.49	0.0732 - 0.4879	9.29	0.982	0.924
Heptane/1-Pentanol	358.2	0.12 - 00.68	0.1212 - 0.6807	7.31	0.989	0.958
	368.2	0.19 - 00.93	0.1937 - 0.9308	6.07	0.991	0.957
Ethanol/Ciclohexane	298.2	0.07 - 00.19	0.0791 - 0.1864	12.23	0.972	0.558
Isobutane/Ethanol	363.5	3.38 - 16.71	3.38 - 16.71	9.07	0.991	0.937
	372.7	2.24 - 06.80	2.241 - 6.843	12.73	0.973	0.733
	397.7	4.82 - 12.01	4.826 - 12.011	9.95	0.967	0.788
Pentane/Ethanol	422.6	9.64 - 19.63	9.642 - 19.629	8.46	0.985	0.794
	372.7	3.47 - 08.46	3.471 - 8.456	13.08	0.984	0.662
	397.7	7.29 - 15.18	7.295 - 15.117	11.51	0.979	0.539
Pentane/Methanol	397.7	7.29 - 15.18	7.295 - 15.117	11.51	0.979	0.539
	422.6	13.74 - 25.27	13.748 - 25.276	10.57	0.984	0.542

AARD is the average absolute relative deviation; ρ is the linear correlation; R^2_{adj} is the adjusted coefficient of determination

Table 2. Quality of calculation analysis for UNIQUAC and NRTL.

Components	T [K]	Pressure range [bar]	UNIQUAC AARD [%]	NRTL AARD [%]
Butanol/Decane	358.2	0.05 - 00.28	2.77	1.97
	373.2	0.09 - 00.52	3.08	1.32
	388.2	0.16 - 00.92	4.38	3.03
Butanol/Hexane	298.2	0.17 - 00.20	4.34	3.69
	348.2	0.07 - 00.49	6.62	6.20
Heptane/1-Pentanol	358.2	0.12 - 00.68	5.16	5.02
	368.2	0.19 - 00.93	3.98	4.08
Ethanol/Ciclohexane	298.2	0.07 - 00.19	3.76	3.56
Isobutane/Ethanol	363.5	3.38 - 16.71	32.41	8.38
	372.7	2.24 - 06.80	1.63	1.50
	397.7	4.82 - 12.01	7.66	6.39
Pentane/Ethanol	422.6	9.64 - 19.63	21.71	17.81
	372.7	3.47 - 08.46	5.16	6.09
	397.7	7.29 - 15.18	12.52	13.84
Pentane/Methanol	397.7	7.29 - 15.18	12.52	13.84
	422.6	13.74 - 25.27	68.88	72.66

AARD is the average absolute relative deviation.

Available interaction parameters from simulator were used (Table 3).

systems and temperatures studied. However, most predicted values are located below the base line due to a prediction bias for equilibrium pressures lower than experimental. Due to the presence of bias, linear correlation is not a strong measure of quality of the model predictions, another measure should be analyzed as the adjusted coefficient of determination. Calculated coefficient of determination values were between 0.50 and 0.98 for all systems, except butanol/hexane, in which it was negative because of the availability of too few experimental data points, as explained before.

Table 2 presents average absolute relative deviations for the calculations with UNIQUAC and NRTL models. AARD values ranged from 4.5% to over 60%. The errors for the best calculations with UNIQUAC and NRTL were somewhat smaller than those from COSMO-SAC predictions, but for these calculations to be possible, two estimated parameters were necessary. It is important to note that the available set of parameters from the software simulator were used (summarized in Table 3), while parameters estimated by correlating the current experimental data at each

Figure 8 Pressure x composition phase diagram for the system pentane/ethanol at 372.7 K, 397.7 K, 422.6 K as function of pentane molar fraction. Experimental data from [Campbell et al. \(1987\)](#). Model calculation from this work.

Figure 9. Pressure x composition phase diagram for the system pentane/methanol at 372.7 K, 397.7 K, 422.6 K as function of pentane molar fraction. Experimental data from [Wilsak et al., \(1987\)](#). Model calculation from this work.

temperature would results in lower AARD. For the system containing methanol at the highest temperature studied (422.6K), the AARD for pressure calculation was higher than 60% for both NRTL and UNIQUAC models. This indicates a poor capability of the UNIQUAC and NRTL models to calculate activity coefficient at different temperatures with a single set of parameters. The COSMO-SAC model prediction AARD was lower than 11% for the three temperatures for this system, showing stable reliability at different temperatures.

Figure 10. Comparison of predicted values by COSMO-SAC model and experimental values for equilibrium pressure for all systems studied in this work.

Table 3. UNIQUAC and NRTL models binary interaction parameters.

Components	UNIQUAC	UNIQUAC	NRTL	NRTL
	A_{12} (J·mol ⁻¹)	A_{21} (J·mol ⁻¹)	A_{12} (J·mol ⁻¹)	A_{21} (J·mol ⁻¹)
Butanol/Decane	502.24	-91.59	1465.82	1229.06
Butanol/Hexane	968.65	-327.30	1743.44	-99.96
Heptane/1-Pentanol	-282.37	720.62	-38.41	1372.18
Ethanol/Ciclohexane	1008.92	-117.32	1253.43	545.70
Isobutane/Ethanol	1693.52	-812.51	166.69	1781.96
Pentane/Ethanol	913.58	-94.61	1143.72	477.38
Pentane/Methanol	1385.51	32.78	1053.57	1164.47

4. CONCLUSIONS

The present work evaluated vapor-liquid equilibrium data for systems involving alcohols and hydrocarbons using the COSMO-SAC model. The quality of prediction analysis showed the degree of adequacy of the model to describe the experimental data. Average absolute relative deviation values may be used as reference for the utilization of this model in applications, depending upon the required accuracy. For higher accuracy predictions, more refined quantum calculations for the sigma profile may be necessary. Calculations with NRTL and UNIQUAC were performed for comparison, using a commercial simulator. Performance results were similar. They performed better than COSMO-SAC in some temperatures due to the advantage of using regressed parameters. Nonetheless, performed poorly at some other temperatures due to low potential for extrapolation from using a single set of parameters.

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