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Use of COSMO-SAC to Determine the Activity Coefficient and Predict Phase Equilibrium of Binary Systems Involving Methanol, Glycerol and Water

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With advances in computational chemistry, phase behavior predictions without any experimental data are becoming possible. Models based on COSMO (COnductor-like Screening MOdels) are viable alternatives to group-contribution methods. These methods may be used to determine the activity coefficient of the components in any mixtures. In this paper, the model COSMO-SAC, developed by Lin and Sandler (2002), was used to predict the activity coefficients for binary mixtures (methanol + glycerol), (methanol + water) and (glycerol + water). Prior to these calculations, the software Gaussian 03 was used to perform the structure optimization of molecules of water, methanol and glycerol, in order to find which molecule conformation has lower energy. Then, sigma profiles of the components were obtained using the software MOPAC. Data of experimental activity coefficients ($\gamma^{\exp}$) obtained from literature (Soujanya et al., 2010) were compared with calculated values (γ^{calc}) by two different methods. In the first method, the sigma profiles obtained from software MOPAC were used to calculate the activity coefficients. In the second one, they were obtained from the software known as JCOSMO, which uses the sigma profiles from VT-2005 database. The mean absolute deviation between $\gamma^{\exp}$ e γ^{calc} by the two methods analyzed were calculated. The results show that the method based on COSMO not adequately predicted the activity coefficients of the mixtures analyzed for both methods of obtaining the sigma profile. Despite the sigma profiles generated by the software MOPAC are different from those obtained by VT-2005 database, the values of the activity coefficients obtained by both methods showed no major deviations. Furthermore, COSMO-SAC model was used to calculate phase equilibrium by minimizing the Gibbs energy of the binary mixtures. These calculations were performed in the software GAMS. It was found that, although promising, the COSMO-SAC model still need refinements.

1. Introduction

Predictive thermodynamic models are being widely used, despite prediction inaccuracies, due to many advantages such as time and cost savings (Mullins et al., 2008). With advances in computational chemistry, some phase equilibrium predictions of mixtures, without any information about experimental data, are becoming possible. Although less reliable, quantum mechanical methods present a viable alternative to classical group contribution estimation methods, to estimate the phase behavior without experimental data requirements (Wang et al., 2009).
Recently Klamt (1995) proposed a new approach to describe the dependence of the activity coefficient on the mixture composition and temperature. The method, called by Klamt of COSMO-RS (Conductor-like Solvent Screening Model for Real) start from the results of quantum mechanical calculations of solvation and can

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satisfactorily describe the phase equilibrium of a mixture without the need for any experimental data. In principle, this method can be used to determine the activity coefficient of any substance in any mixture (Yang et al. 2010).
Later, Lin and Sandler (2002) developed the COSMO-SAC model (COSMO Segment Activity Coefficient), a variation of the COSMO-RS model. In this model, the authors combined the COSMO calculations with the Staverman-Guggenheim equation to calculate the activity coefficient.
In COSMO-based models, the first step to calculate the activity coefficient is to determine the “apparent” charge density distribution on the surface of the molecule in a perfect conductor. This charge distribution is called sigma profile.
The sigma profile of each substance present in the mixture must be obtained. These calculations can be computationally time-expensive, depending on the complexity of the molecule and on the package of quantum mechanics used.
The objective of this work is to calculate the phase equilibrium of binary mixtures containing water, methanol and glycerol by minimizing the Gibbs energy, formulated as a nonlinear programming, and using the GAMS (General Algebraic System Model) software with the CONOPT solver.

2. Method

Activity coefficients used in this paper were obtained using the COSMO-SAC model. Sigma profiles were obtained by a method using the MOPAC software described by Borghi et al. (2012). In that work, the researchers used quantum mechanical methods to estimate thermochemical properties of compounds present in the biodiesel production process. The method used is an alternative to classical group contribution estimation methods, as the one described by Cunico et al. (2013).
Here, the prediction power of the of the activity coefficients obtained by this method was evaluated. For this purpose, experimental data of a binary system of methanol (1) and glycerol (2) at 32.02 kPa were selected (Soujanya et al., 2010), in order to compare with the calculated values of the activity coefficients.
The mean absolute deviation (MAD) between the experimental and calculated values of activity coefficients was obtained Eq(1):

$$MAD(\%) = \frac{1}{\mathrm{NP}} \sum_{\mathrm{i=1}}^{\mathrm{NP}} \left| \gamma_{\mathrm{i}}^{\mathrm{exp}} - \gamma_{\mathrm{i}}^{\mathrm{calc}} \right| \cdot 100 \tag{1}$$

The Gibbs energy (G) minimization method was used to calculate the phase equilibrium for binary mixtures containing water, methanol and glycerol using global optimization techniques and GAMS 23.2.1 software.
A condition considered sufficient to thermodynamic equilibrium is given by minimizing the Gibbs energy. For the use of this methodology is necessary to obtain an expression for G which is dependent of variables such as temperature, pressure and composition. The Eq(2) is this equation:

$$\begin{aligned} \mathrm{G} = & \sum_{\mathrm{i=1}}^{\mathrm{NC}} n_i^l \cdot \mu_{\mathrm{i}}^0(\mathrm{T}) + \mathrm{R} \cdot \mathrm{T} \cdot \sum_{\mathrm{i=1}}^{\mathrm{NC}} n_i^l \cdot \ln \mathrm{P}_{\mathrm{i}}^{\mathrm{sat}} + \mathrm{R} \cdot \mathrm{T} \cdot \sum_{\mathrm{i=1}}^{\mathrm{NC}} n_i^l \cdot \ln x_i + n_t^l \cdot \mathrm{g}_i^{\mathrm{ex}} + \sum_{\mathrm{i=1}}^{\mathrm{NC}} \mathrm{n}_{\mathrm{i}}^{\mathrm{g}} \cdot \mu_{\mathrm{i}}^0(\mathrm{T}) \\ & + \mathrm{R} \cdot \mathrm{T} \cdot \sum_{\mathrm{i=1}}^{\mathrm{NC}} \mathrm{n}_{\mathrm{i}}^{\mathrm{g}} \cdot \ln \mathrm{y}_{\mathrm{i}} + \mathrm{R} \cdot \mathrm{T} \cdot \sum_{\mathrm{i=1}}^{\mathrm{NC}} \mathrm{n}_{\mathrm{i}}^{\mathrm{g}} \cdot \ln \mathrm{P} \end{aligned} \tag{2}$$

where n_i^l and n_t^l are the number of moles of component i in the liquid phase and the total number of moles of the liquid phase, respectively, T is the temperature, R is the universal gas constant, P is the pressure of the system, $\mathrm{P}_{\mathrm{i}}^{\mathrm{sat}}$ is the vapor pressure of the component i, calculated using the DIPPR correlation (Daubert and Danner, 1985), y_i and x_i are the mole fractions of the vapor and liquid phases of the component i, respectively, $\mathrm{g}_i^{\mathrm{ex}}$ is the excess molar Gibbs energy of the component i (obtained by COSMO-SAC model), NC is the number of components in the system, and $\mu_{\mathrm{i}}^0(\mathrm{T})$ is the reference chemical potential of component i, given by:

$$\begin{aligned} \mu_{\mathrm{i}}^0(\mathrm{T}) = & \frac{\mathrm{T}}{\mathrm{T}_0} \cdot \Delta \mathrm{g}_{\mathrm{f,i}}^0 + \Delta \mathrm{h}_{\mathrm{f,i}}^0 \cdot \left[1 - \frac{\mathrm{T}}{\mathrm{T}_0} \right] - \frac{\mathrm{A}_{\mathrm{i}}}{6} \cdot (\mathrm{T}^3 - 3 \cdot \mathrm{T} \cdot \mathrm{T}_0^2 + 2 \cdot \mathrm{T}_0^3) - \frac{\mathrm{B}_{\mathrm{i}}}{2} \cdot (\mathrm{T} - \mathrm{T}_0)^2 \\ & - \mathrm{C}_{\mathrm{i}} \cdot \left(\mathrm{T} \cdot \ln \left(\frac{\mathrm{T}}{\mathrm{T}_0} \right) + \mathrm{T}_0 - \mathrm{T} \right) \end{aligned} \tag{3}$$

in which T_0 is the reference temperature (298.15 K), $\Delta \mathrm{g}_{\mathrm{f,i}}^0$ is the standard molar Gibbs energy of formation, $\Delta \mathrm{h}_{\mathrm{f,i}}^0$ is the standard molar enthalpy of formation, A_{i}, B_{i} and C_{i} are the terms of the second degree polynomial to the heat capacity, previously obtained by the method described by Borghi et al. (2012):

$$Cp_i = A_i \cdot T^2 + B_i \cdot T + C_i \quad (4)$$

To solve the problem of Gibbs energy minimization using the Eq(2), certain restrictions must be satisfied as the non-negativity of the number of moles and the conservation of the number of moles. Some parameters, such as R, T and P remain constant throughout the optimization.
Finally, to quantify the deviation between the calculated and the experimental data, the mean absolute deviation was used.

3. Results e Discussion

Table 1 shows the comparison between experimental and calculated activity coefficients of the binary mixture of methanol and glycerol, at the pressure of 32.02 kPa, in which x_1 is the molar fraction of methanol, T is the temperature in Kelvin and γ_1^{exp} and γ_2^{exp} are the experimental activity coefficients for methanol and glycerol, respectively (Soujanya et al., 2010), and γ_1^{calc} and γ_2^{calc} are the calculated activity coefficients.

Table 1: Comparison between experimental and calculated activity coefficients of the mixture of methanol (1) and glycerol (2).

x_1	T(K)	γ_1^{exp}	γ_2^{exp}	γ_1^{calc}(a)	γ_2^{calc}(a)	γ_2^{calc}(b)	γ_2^{calc}(b)
0	521.8	1.680324	1	0.825976	1	0.9	1
0.1	356.8	1.545155	1.004458	0.844743	0.998653	0,914	0.998
0.2	340.25	1.428468	1.018517	0.865785	0.994216	0.929	0.996
0.3	331.9	1.328211	1.043582	0.887257	0.986012	0.942	0.991
0.4	326.6	1.242749	1.08171	0.908788	0.97323	0.953	0.985
0.5	322.8	1.170837	1.135884	0.929962	0.954906	0.968	0.973
0.6	319.8	1.111608	1.210458	0.950212	0.929897	0.978	0.96
0.7	317.35	1.064599	1.311871	0.968743	0.896875	0.988	0.944
0.8	315.15	1.029809	1.449872	0.984417	0.854332	0.992	0.924
0.9	313.05	1.007817	1.63966	0.995607	0.800644	0.999	0.9
1	311	1	1.905832	1	0.734226	1	0.874

(a) Activity coefficients calculated using sigma profiles obtained from MOPAC.
(b) Activity coefficients calculated using sigma profiles from JCOSMO.

The experimental activity coefficients were compared with the values calculated using sigma profiles obtained from MOPAC software (Borghi et al., 2012) and with the values obtained from the computer program known as JCOSMO, which uses the sigma profile from VT-2005 database. This software was developed by Gerber and Soares (2010).
Analyzing the results is possible to see that COSMO-SAC model did not correctly predict the activity coefficients of the analyzed mixture, for both methods used to obtain sigma profiles. These, in turn, showed a very similar behavior.
Mean absolute deviations between γ^{calc} and γ^{exp} were calculated for both methods and, between the activity coefficients obtained by MOPAC and the JCOSMO. Table 2 shows the results.

Table 2: Mean absolute deviation between experimental and calculated activity coefficients.

MAD(%)			
	γ_1^{exp}	γ_1^{calc}(MOPAC)	γ_1^{calc}(JCOSMO)
γ_1^{exp}	-	31.3	27.7
γ_1^{calc}(MOPAC)	-	-	3.7
	γ_2^{exp}	γ_2^{calc}(MOPAC)	γ_2^{calc}(JCOSMO)
γ_2^{exp}	-	33.4	29.6
γ_2^{calc}(MOPAC)	-	-	3.8

As is possible to verify, the MAD between the experimental and calculated by both methods values, are above 27%, which is a very high deviation. The deviation shows that this methodology was not able to predict accurately the experimental data.
However, it is verified a reasonable similarity between the values of the activity coefficients calculated by the MOPAC and the JCOSMO methods, which shows that the MOPAC software can be used to obtain the sigma profile.
The method of Gibbs energy minimization was used to calculate the phase equilibrium of binary mixtures containing water, methanol and glycerol. The computational tool GAMS/CONOPT was used to implement the method of minimization of the Gibbs energy for the equilibrium calculation, and quickly converged to the solution, being very efficient.
Results of equilibrium calculation are presented in Figures 1 to 3. The COSMO-SAC method was performed using both sigma profiles obtained by MOPAC and VT-2005 database, obtained by DMol3 software. Furthermore, the equilibrium was also calculated using Raoult's Law, in order to compare with the results obtained by COSMO-SAC. In the case of Raoult's Law, it is considered that both phases are ideal, so $\gamma_i = 1$. However, it must be pointed out that Raoult's Law was used only because it is the simplest approximation possible, since it is not adequate to represent strong polar components with hydrogen bounds such as the ones considered in this study.

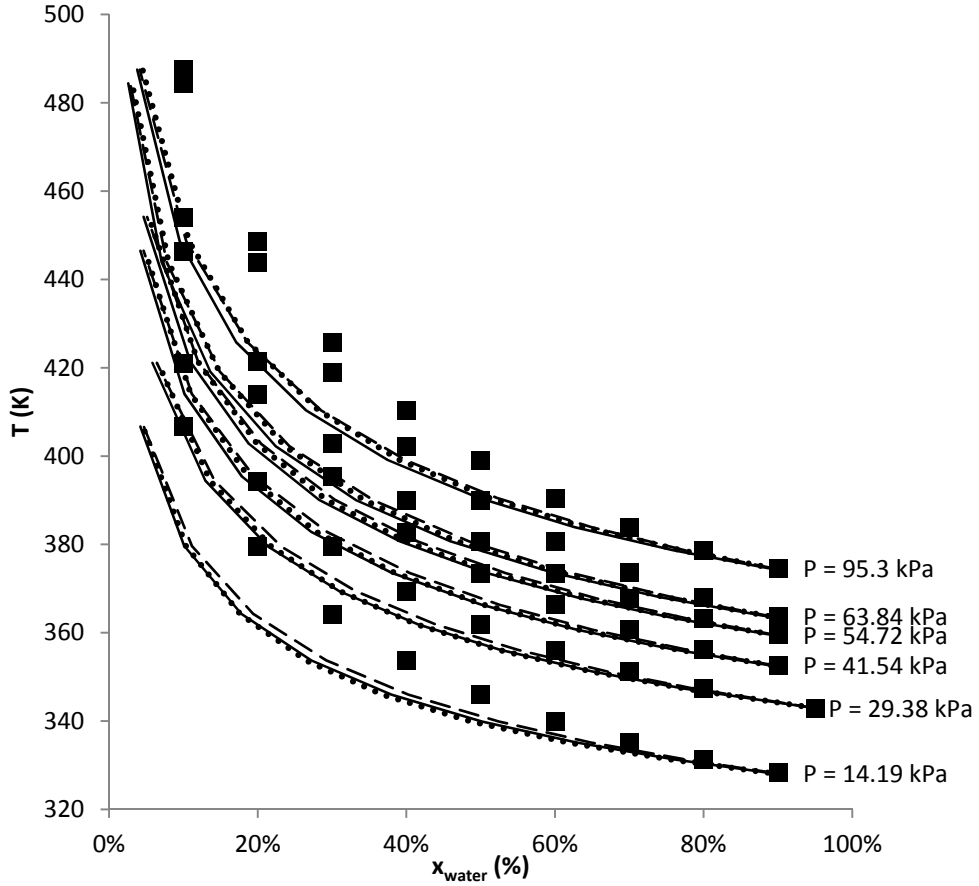

Figure 1: Vapor-liquid equilibrium to binary mixture of water + glycerol. Experimental data (■) (Soujanya et al., 2010), Raoult´s Law (— —), MOPAC (·····) and VT-2005 (——).

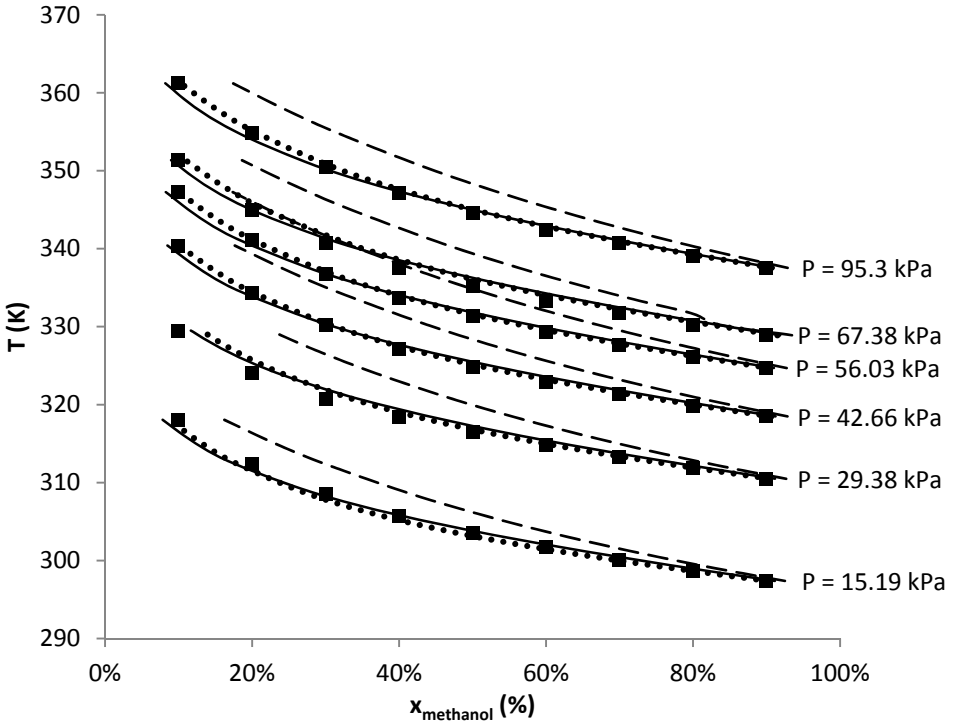

Figure 2: Vapor-liquid equilibrium to binary mixture of methanol + water. Experimental data (■) (Soujanya et al., 2010), Raoult´s Law (— —), MOPAC (·····) and VT-2005 (——).

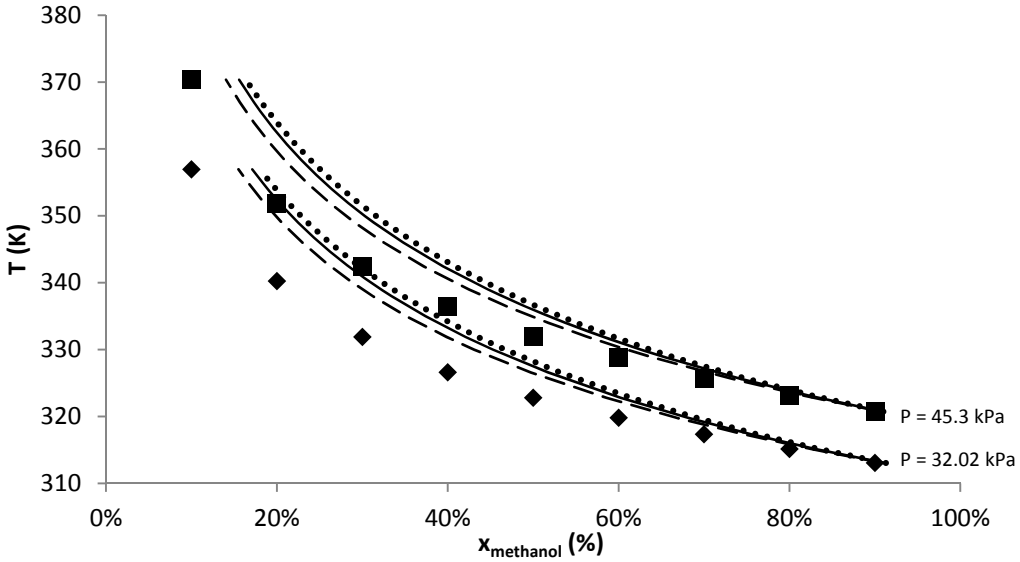

Figure 3: Vapor-liquid equilibrium to binary mixture of methanol + glycerol. Experimental data (■) (Soujanya et al., 2010), Raoult´s Law (— —), MOPAC (·····) and VT-2005 (——).

Analyzing Figures 1 to 3 is possible to see that the curves of the COSMO-SAC model have similar behavior to the experimental data, however, the deviations obtained are high in most of the studied systems.
The mean absolute deviations between the experimental and calculated mole fractions using the method COSMO-SAC with sigma profiles obtained by MOPAC and VT-2005 database, and the molar fractions obtained using Raoult's Law were calculated. Table 3 shows these values.

Table 3: Mean absolute deviation obtained by Gibbs energy minimization.

	MAD(%)		
	MOPAC	VT-2005	Raoult
Methanol + water	1.55	2.22	10.00
Water + glycerol	7.96	8.48	6.92
Methanol + glycerol	7.79	6.84	5.42

Analyzing Table 3, it is possible to see that the mean absolute deviations obtained for the mixture methanol + water using the COSMO-SAC model are satisfactory, but for water + glycerol and methanol + glycerol the deviations are higher, for all models. This may be due to the higher boiling point of glycerol compared to the others and the values used for the saturation pressure of glycerol, but the results for COSMO-SAC were even worse than using the simplest model (Raoult).

4. Conclusions

This paper uses a new approach to phase equilibrium calculation, which is very promising, the COSMO-SAC method. While very promising, it needs refinements, as it was not found to be completely accurate in predicting the activity coefficient of components present in a binary mixture and deviations presented in vapor-liquid equilibrium calculations were relatively high in some cases.

The methodology used to obtain sigma profiles to be used in the COSMO-SAC model, using MOPAC software, proved to be a viable alternative to methods that use quantum chemistry software, whose calculations are much slower. The differences obtained between the sigma profiles generated by MOPAC and those obtained with DMol3, present in VT-2005 database and in the JCOSMO, were relatively low.

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