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VAPOR-LIQUID EQUILIBRIA OF BINARY SYSTEM CO AND Cl_2 IN MIXTURE OF GREENHOUSE GASES USING QUANTUM CALCULATION

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Abstract

The gases CO and Cl_2 presented in atmosphere and mixture of greenhouse gases cause the greenhouse effects in the stratosphere. The COSMO method was applied to calculate the physicochemical properties, quantum-optimum structures and the surface screening charges surrounding the CO and Cl_2 molecule by the DFT VWN-BP method with basis set DNP (Double Numerical basis with polarization functions). The segment activity coefficients generated by COSMO-SAC method were used to predict the vapor-liquid equilibria of binary mixture CO(1)-Cl_2(2) at different temperatures and pressures. The calculated results were also compared with those from Wilson and NTRL method. They are very close experimental data. The values of *RMSE*, the mean relative deviation at constant pressure (MRD_p) and mean deviation of vapor composition (MD_y) in Table 2 are less than 0.012, 5.735 and 0.015, respectively. So the discrepancies between models are insignificant.

Keywords. COSMO-SAC method, liquid-vapor equilibria, binary mixture CO and Cl_2.

1. INTRODUCTION

In recent years the industrial areas are being grown strongly. In particular, the chemical, pharmaceutical industry and the chemical manufacturing processes produced lots of different products. Beside the valuable products to serve the needs of people, they also generate the undesired products including the environmental pollutants. In the emitted gases, they consisted of gases SO_2, CO_2, NO_x and others such as CO and Cl_2. These gases presented in mixture of greenhouse gases cause the depletion of the ozone concentration in the stratosphere. This can lead to more harmful effects to tellurian and creature.

To implement the management and recovery for industrial emissions as well as storage and treatment, we need to have the clear knowledge of their physicochemical and thermodynamics properties. To perform the separation of the gases in the exhaust treatment, we need to have sufficient thermodynamic properties of vapor-liquid equilibria. This will facilitate the technological design of distillation techniques. The vapor-liquid equilibria of the single substances or binary and ternary systems can be determined by empirical measurements. But in many cases, the experimental measurements can not be done in many different conditions.

Nowadays the development of computational techniques has been applied in several different areas. The methods of quantum calculation are also developed in recent years, in which they have been combined the *ab initio* calculation at high level and Monte Carlo simulations [1, 2]. But this calculation is often costly. The vapor-liquid equilibria of the single molecule or the mixture can be generated by the method COSMO (Conductor-like Screening Models) [3, 4]. The COSMO-RS method (Real Solvent) proposed by group Eckert. F and Klamt in 1995 [5-7]. This method is based on the surface screening charges surrounding the molecule in the condensed phase. A sigma profile is a molecular-specific distribution of the surface-charge density, which enables the application of solvation-thermodynamic models to predict vaporliquid and solid-liquid equilibria, and other properties [7,8,9]. The method COSMO-RS (Conductor like Screening Model for Realistic Solvents) allows the prediction of many properties of pure fluids, fluid mixtures, and solutions. The method COSMO-RS assumes ideal gas behavior in the vapor phase and incompressible liquids. The COSMO method also developed by group T.S. Liu and Sandler. I.S in 2000 [10,11,12,13] using the segment activity coefficient. Liu and Sandler's group has successfully applied the method COSMO-SAC to determine the physicochemical properties of liquid-vapor equilibrium of binary systems of organic compounds and solvents [13]. This COSMO-SAC method also used Density functional theory DFT to calculate the condensed phase energy [10, 11].

In this work we report the determination of the vapor-liquid equilibria of binary mixture system consisting of CO_2(1) and Cl_2(2) by the method COSMO-SAC. To implement this method we carry out to calculate the energy information of condensed phase, quantum-optimum structures and the surface screening charges surrounding the molecule by the method DFT VWN-BP with basis set DNP. The COSMO calculation results are used to generate the segment activity coefficient and vapor-liquid equilibrium of binary mixture CO(1)-Cl_2(2) at the different temperatures and pressures. The calculated results are compared with those from Wilson and NTRL method.

2. COMPUTATIONAL DETAILS

2.1. Sigma profile calculation

Before the determination of the vapor-liquid equilibria, the quantum chemical calculations DFT are implemented to minimize the global energy of molecules by gradient approximation GGA [14-16]. An individual molecule in the ideal gas phase can be calculated the Hamiltonian energy using density functional theory (DFT).

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow,n_\downarrow]=\int \epsilon_{\mathrm{XC}}(n_\uparrow,n_\downarrow,\vec{\nabla} n_\uparrow,\vec{\nabla} n_\downarrow)n(\vec{r})d^3r \quad (1)$$

The use of gradient approximation GGA gives the good results for the molecular geometries and the ground state energies. The density functional theory (DFT) used in this work the theoretical level VWN-BP with basis set DNP [17,18,19]. The molecular structures are optimized at 10^{-6} precise level of Hartree energy unit. The calculated results are used for generating the surface screening charges surrounding the molecule. A molecular-specific distribution of the surface-charge density is sigma profile σ. The DFT methods generate the approximate energy in the ground state. These calculations based on the Hamiltonian operator to define the electron density. To have the full solutions of Schrödinger wave equation we should have the very strong calculability, so we can perform just an approximate solution.

2.2. Calculating activity coefficients

In this paper, the molecular profile of each sigma results was calculated by DMol3 quantum calculation, in that it combines DFT method and COSMO model. In this paper we use the COSMO-SAC model developed by Sandler and Lin [10,11,12]. The activity coefficients of binary system CO(1)-Cl_2(2) are determined from the restoring free energy and terms Staverman-Guggenheim [10,11]:

$$\ln\gamma_{i/s}=\frac{\Delta G^{*res}_{i/s}-\Delta G^{*res}_{i/i}}{RT}+\ln\gamma^{SG}_{i/s} \quad (2)$$

With $\ln\gamma^{SG}_{i/s}=\ln\left(\frac{\phi_i}{x_i}\right)+\frac{z}{2}q_i\ln\left(\frac{\theta_i}{\phi_i}\right)+l_1-\frac{\phi_i}{x_i}\sum x_j l_j$;

where ϕ_i and θ_i the volume and standard-surface area $l_1 = (z/2)(r_i - q) - r_i + 1$; $z = 10$, $q_i = A_i/q$ and $r_i = V_i/r$; with A_i and V_i the area and van der Waals volume, the two parameters derived from COSMO quantum calculation. The restoring free energy is the sum of the sigma profile times the natural logarithm of the segment activity coefficients over all surface charges, that is proposed by Liu [12]:

$$\frac{\Delta G^{*res}_{i/s}}{RT}=\sum_{\sigma_m}\left[n_i(\sigma_m)\frac{\Delta G^{*res}_{\sigma_m/s}}{RT}\right]=n_i\sum_{\sigma_m}p_i(\sigma_m)\ln\Gamma_s(\sigma_m) \quad (3)$$

Where $\Gamma_s(\sigma_m)$ is the activity coefficient for a segment *m* of charge density, σ. These segment activity coefficients derived rigorously using statistical mechanics:

$$\ln\Gamma_s(\sigma_m)=-\ln\left\{\sum_{\sigma_m}p_s(\sigma_n)\Gamma_s(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{RT}\right]\right\} \quad (4)$$

$$\ln\Gamma_i(\sigma_m)=-\ln\left\{\sum_{\sigma_m}p_i(\sigma_n)\Gamma_i(\sigma_n)\exp\left[\frac{-\Delta W(\sigma_m,\sigma_n)}{RT}\right]\right\} \quad (5)$$

The activity coefficients are calculated according to equation:

$$\ln\gamma_{i/s}=n_i\sum_{\sigma_m}p_i(\sigma_m)\left[\ln\Gamma_s(\sigma_m)-\ln\Gamma_i(\sigma_m)\right]+\ln\gamma^{SG}_{i/s} \quad (6)$$

Liu and Sandler developed the averaging algorithm for the segment surface-charge densities σ* to calculate the new surface-charge densities σ.

Value σ_m is the average surface-charge density on segment *m*, the summation is over *n* segments from COSMO results, and r_n is the radius of the actual surface segment [11, 12, 13]

$$\sigma_m=\frac{\sum_n \sigma^*_n\frac{r_n^2r_{av}^2}{r_n^2+r_{av}^2}\exp\left(-\frac{d_{mn}^2}{r_n^2+r_{av}^2}\right)}{\sum_n\frac{r_n^2r_{av}^2}{r_n^2+r_{av}^2}\exp\left(-\frac{d_{mn}^2}{r_n^2+r_{av}^2}\right)} \quad (7)$$

where σ_n^* is the segment surface-charge densities over n segments from COSMO results.

2.3. Calculation of vapor-liquid equilibria

The NRTL (Non-Random Two-Liquid) model [20] was developed from the Wilson equation [21] for the second interaction coefficients. The activity coefficients were calculated by

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ji}}{\sum_k^N G_{ki} x_k}\left(\tau_{ji} - \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k}\right) \quad (9)$$

Where second interaction coefficient is $\tau_{ji} = A_{ji} + B_{ji}/T + C_{ji}\ln(T) + D_{ji}T$; $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ and $\alpha_{ji} = \alpha_{ij}$

The optimization algorithm is used to determine the second interaction parameters by minimizing the value of the functions:

$$OF_p = \sum_i^N \left(p_{\exp,i} - p_{cal,i}\right)^2 \quad (10)$$

$$OF_\gamma = \sum_i^N \left[\left(\frac{\gamma_{\exp,i} - \gamma_{cal,i}}{\gamma_{\exp,i}}\right)^2 + \left(\frac{\gamma_{\exp,j} - \gamma_{cal,j}}{\gamma_{\exp,j}}\right)^2\right] \quad (11)$$

Since the activity coefficients γ_i, the liquid-vapor equilibria of binary systems are identified, the diagram of liquid-vapor equilibria of binary system CO(1)-Cl_2(2) can be constructed in the isothermal or isobaric condition. The molar fraction of each substance in liquid x_i and vapor phase y_i and total pressure are also fully determined by

$$\begin{aligned} y_i &= p_i^0 x_i \gamma_i / p^{tot} \quad (i = 1,2) \\ p^{tot} &= p_1^0 x_1 \gamma_1 + p_2^0 x_2 \gamma_2 \end{aligned} \quad (12)$$

With p_i^0 is the vapor pressure of the pure constituent, i; γ_i is the activity coefficient of the constituent i. RMS error values are calculated by the following formula:

$$RMS = \sqrt{\frac{1}{n}\sum_1^n (y_{\exp} - y_{\mathrm{cal}})^2} \quad (13)$$

Here n is number of observations; y_{cal} is mole fraction in vapor phase of constituent, i is determined by COSMO-SAC method, y_{exp} is mol fraction in vapor phase of constituent i, is determined by experimental measurements. The mean value of the relative deviations at the constant pressure (MRD_P), and mean value of component deviation (MD_Y) is calculated by the formula:

$$\begin{aligned} MRD_p, \% &= (100/n)\sum_i^n \left(\left|p_{i,cal} - p_{i,\exp}\right| / p_{i,\exp}\right) \\ MD_y &= (1/n)\sum_i^n \left(\left|y_{i,cal} - y_{i,\exp}\right|\right) \end{aligned} \quad (14)$$

To substantiate the reliability of the method COSMO-SAC, we should compare the obtained results with those from NRTL and Wilson method.

3. RESULTS AND DISCUSSION

3.1. Generating Sigma Profiles

The molecular structures CO and Cl_2 were carried out the geometry optimization at 10^{-6} Hartree energy unit for convergence of the self-consistent field (SCF) equations, and 0.002 Eh/Å for the convergence of the geometry-optimization calculations in the ideal gas phase by using Density functional theory (DFT) at level of theory GGA/VWN-BP with basis set DNP [17-19]. In general, the basis set DNP is very high believability [19]. The GGA method generated the gradient approximation with the method VWN-BP [18, 19].

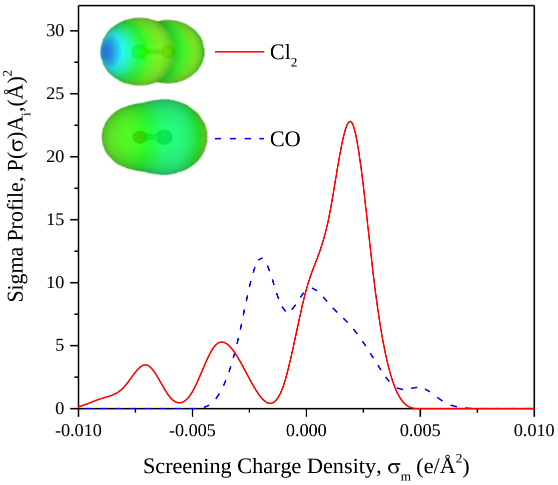

Figure 1: The sigma profiles for single molecules CO and Cl_2 resulting from COSMO calculation

The surface screening charges surrounding the molecule in the condensed phase are generated from the geometry energy calculations DFT VWN-BP/DNP. The information values and keywords for the molecular energy calculation of CO and Cl_2 used in this work for method COSMO are shown in table 1 [24]. Each of these structures produces a strongly different sigma profile, as illustrated in figure 1. The assumption is that the optimized geometry from DMol3 program [3, 24] in the vapor phase is identical to the optimal structure.

The molecules CO and Cl_2 shown in Figure 1 described that each structure to generate the clear different sigma profile. The concept of a sigma profile is introduced, which is a molecule-specific distribution of the surface-charge density. Currently there is no open source-related feasibility of each sigma profile of structures exists in this binary mixture. So the surface area of the molecular cavity can be generated from the COSMO calculation using the parameter values, as given in table 1. Each molecule-specific sigma profile was generated from the output of a series of calculations using the DMol3 module [24], which uses density functional theory DFT VWN-BP/DNP.

Table 1: The parameter values were used to generate the structural information by method COSMO [24]

Keywords	Value	Description
Cosmo	on	Turns on COSMO solvation procedure
Cosmo_Grid_Size	1082	Tells DMol3 how many basic grid points per atom to consider
Cosmo_Segments	92	The maximum number of segments on each atomic surface
Cosmo_Solvent_Radius	1.300000	Solvent probe radius
Cosmo_A-Matrix_Cutoff	7.000000	The accuracy of the electrostatic interactions on COSMO surface
Cosmo_Radius_Incr	0.000000	The increment to the atomic radii used in the construction of the COSMO cavity
Cosmo_RadCorr_Incr	0.150000	Used to construct the outer cavity for the outlying charge correction
Cosmo_A-Constraint	1.882190	Used to approximate the non-electrostatic contribution to the solvation energy within the COSMO model
Cosmo_B-Constraint	0.010140	Used to approximate the non-electrostatic contribution to the solvation energy within the COSMO model

3.2. Calculation of vapor-liquid diagram

3.2.1. Diagram P-x-y at isotherm

The COSMO-SAC model is used to predict the activity coefficients of binary mixture CO(1)-Cl_2(2). The diagram of vapor-liquid equilibria P - x - y at isotherm is predicted and constructed by using the Raoult's law. The molar fractions of the components CO(1) and Cl_2(2) in the liquid phase x and the vapor phase y in this binary mixtures were calculated by changing the total pressure P_{tot} of the system. The survey process for binary system CO(1)-Cl_2(2) was performed in the temperature range from 300.0 K to 450.0 K. The diagram of vapor-liquid equilibria of mixture CO(1)-Cl_2(2) is depicted in figure 2.

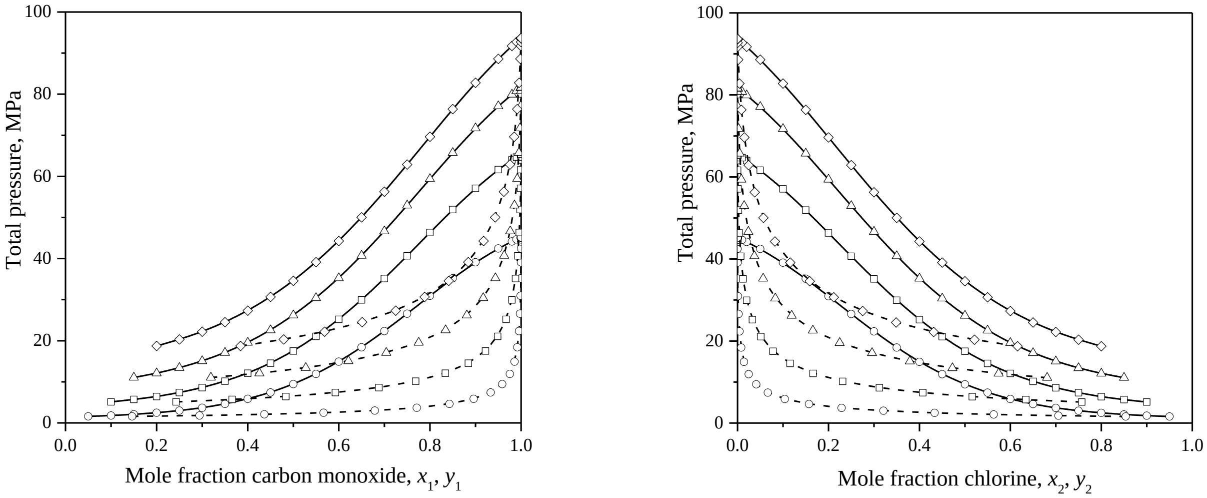

Figure 2: The diagram of vapor-liquid equilibria *P-x-y* of mixture CO(1)-Cl_2(2) at different temperatures. Symbol: ○: at 300 K; □: at 350 K; Δ: at 400 K; ◇: at 450 K; solid line: liquid phase

The diagram of vapor-liquid equilibria *P-x-y* of mixture CO(1)-Cl_2(2) was constructed from equation (12), in which the activity coefficients were determined from equations (6) and (9). The COSMO-SAC predictions have proved its efficiency. The difference between liquid component and vapor component in the cases of the increasing temperature is very clear. Thus this COSMO-SAC method presented the precise predictability. These results seem to be consistent with the NRTL and Wilson method, as given in table 2.

3.2.2. Diagram x–y at isotherm

To have the different change between liquid component *x* and vapor component *y*, the unit diagram *x* - *y* was built by using the calculated-activity coefficients, which were generated from equations (6) and (9). The molar fractions of first component CO(1) for liquid phase x_1 and vapor phase y_1, and second component Cl_2(2) with liquid phase x_2 and vapor phase y_2 were predicted in range from 300 K to 450 K, as depicted figure 3.

3.2.3. Diagram T-x-y at isobar

The COSMO-SAC method was also used to predict the vapor-liquid equilibria for binary mixture system CO(1)-Cl_2(2) at constant pressure conditions. The diagram of vapor-liquid equilibria *T-x-y* is constructed from the temperature change at each pressure value *P* (MPa). The vapor-liquid equilibrium diagram *T-x-y* is also obtained from Raoult's law, in which the molar fractions of CO(1) and Cl_2(2) constituent in the liquid and vapor phase depend on the temperature change. Assuredly, the total pressure of system was kept to be a constant P_{tot}. The diagrams *T-x-y* for CO and Cl_2 constituent also were built from the activity coefficients calculating from their sigma profiles. The diagram *T-x-y* was surveyed by the temperature change in pressure range 0.02 MPa to 0.09 MPa with increment 0.02. In this diagram *T-x-y*, the change of either liquid components *x* or vapor components *y* for each constituent at between two near pressure levels is not large. But opposite the difference between liquid component *x* and vapor component *y* for either constituent CO or constituent Cl_2 is very large as depicted in figure 4.

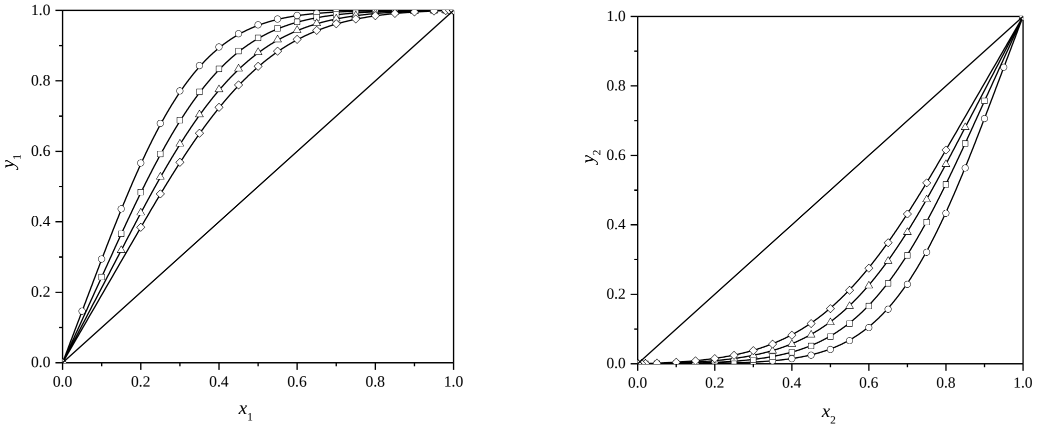

Figure 3: The unit diagram *x-y* of vapor-liquid equilibria of mixture CO(1)-Cl_2(2) at isotherm. Symbol: ○: at 300 K; □: at 350 K; Δ: at 400 K; ◇: at 450 K

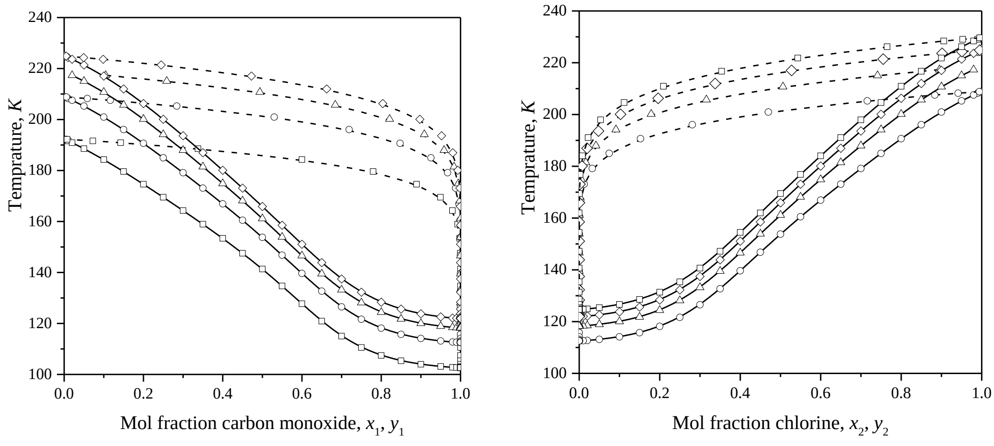

Figure 4: The diagram of vapor-liquid equilibria *T-x-y* of mixture CO(1)-Cl_2(2) at isobar. Symbol: ○: at 0.02 MPa; Δ: at 0.04MPa; ◇: at 0.06MPa ; □: at 0.08MPa; solid line: liquid phase

This diagram *T-x-y* described the temperature changes at isobaric conditions shown that the mixture of constituents CO and Cl_2 can be separated easily.

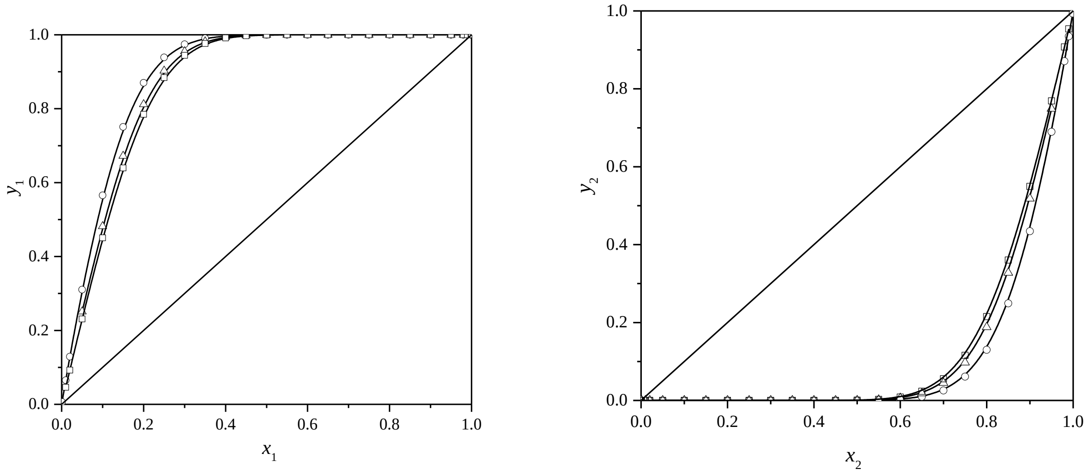

Figure 5: The unit diagram *x-y* of vapor-liquid equilibria of mixture CO(1)-Cl_2(2) at isobar.
Symbol: ○: at 0.01 MPa; Δ: at 0.05 MPa; □: at 0.09 MPa

Thereby the theoretical calculations can generate to be not only for database of vapor-liquid equilibria *P-x-y* and *T-x-y* of binary system CO(1)-Cl_2(2) at the temperatures in range 300 K to 450 K and pressures in range 0.02 MPa to 0.09 MPa. But also this way can extend to generate for the databases of several systems, respectively and these can also be referred for design of fractional distillation technology to support in processes of environmental treatment to separate the various pollutants or to reduce the industrial exhaust of the gases. For the binary system CO(1)-Cl_2(2) in this work the vapor-liquid equilibrium data resulting from COSMO-SAC calculation were compared to those from the Wilson, NRTL model and experimental data [22,23].

Table 2: Comparison between the values *RMSE*, MRD_p and MD_y of the COSMO-SAC, NRTL and Wilson model with experimental data [22, 23] for the component CO.

NRTL			Wilson			COSMO-SAC		
RMSE	MRD_p, %	MD_y	*RMSE*	MRD_p, %	MD_y	*RMSE*	MRD_p, %	MD_y
0.012	4.12	0.011	0.010	4.033	0.015	0.002	5.735	0.013

From the compared values *RMS*, MRD_p and MD_y derived from experimental data in Table 2, the COSMO-SAC model is not difficult to generate the vapor-liquid equilibrium data for component CO or Cl_2 in this binary mixture. Those generated are not only very close experimental data but also agree well with those from models Wilson and NRTL. The values of *RMS* error, the mean relative deviation of pressure (MRD_p) and mean deviation of vapor composition (MD_y) in table 2 are in range from 0.002 to 0.012 for *RMSE*, 4.033 to 5.735 for MRD_p,% and 0.011 to 0.013 for MD_y, respectively. So the discrepancies are in uncertainty interval of experimental measurements.

4. CONCLUSION

We conclude that the molecular-single sigma profiles of substances CO and Cl_2 obtained from quantum calculations DFT VWN-BP/DNP are believable. This will be the applicable way for predicting the vapor-liquid equlibria of the different systems. The molar fractions of components can be also calculated accurately from the molecular-single sigma profiles. The vapor-liquid equilibrium diagram of the binary systems CO(1)-Cl_2(2) resulting from COSMO-SAC model turns out to be in good agreement with experimental data and those from the Wilson and NRTL model.

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