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WATER-ALCOHOL-HYDROCARBONS VLE AND VLLE: PREDICTION OF ALCOHOL PARTITION COEFFICIENT

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Abstract. *Clathrate hydrates are compounds of great interest in oil industry. They are crystalline structures formed by water and gas molecules at high pressure and/or low temperature. Formation of hydrate blockages represents both an economical loss and a safety concern in operation of a pipeline. Thermodynamic inhibitors (usually alcohols, such as methanol) change the thermodynamic equilibrium itself, avoiding the hydrate zone. Accurate results for the loss of volatile inhibitor in the gas phase (partition coefficient) are of major importance for the oil and gas industry. In this work, a flash algorithm was developed using the Cubic Plus Association (CPA) equation of state to estimate the partition coefficients of each component (water, hydrocarbon and hydrate inhibitor) in any phase over a wide range of temperature and pressure in vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE). The binary interaction coefficients were optimized as a linear function of temperature. The flash was applied to various systems with water, methane, ethane, carbon dioxide, methanol, ethanol and monoethylene glycol. The results were then compared with experimental data and satisfactory results were obtained.*

Keywords: *vapor-liquid equilibrium, vapor-liquid-liquid equilibrium, CPA, inhibitor, partition coefficient*

1. INTRODUCTION

Natural gas hydrates are a crystalline structure, composed by water and gas. They can be formed in systems that have water and a component that can act as a guest, mainly light hydrocarbons, such as methane and ethane, under high pressures and low temperatures (Sloan and Koh, 2007). Such conditions often occur in oil and gas production line. It is important to prevent hydrate formation in this scenario, because it can slow down or even stop production, which is not good economically and can cause accidents.

To prevent hydrate formation, oil and gas companies inject inhibitors, such as methanol, ethanol and MEG. Such components can dislocate the hydrate equilibrium line, making hydrate formation impossible under the flow conditions. For economic reasons, it is important to be able to calculate how much inhibitor is necessary, however different commercial softwares give different necessary inhibitors injection rates (Muhammad Riaz, et al., 2013), which can be explained by the difficulty of calculating the inhibitors partitioning in water, gas and condensate phases. A difference of 10% in the predicted inhibitors distribution may cause an increase of 50% in the inhibitor quantity injected (Tybjerg, et al., 2010).

In this work, a flash algorithm was developed in Fortran90. The algorithm uses the CPA equation of state (EoS) and the isofugacity condition to estimate the partition of each component in each phase in vapor-liquid equilibrium (VLE) and vapor-liquid liquid equilibrium (VLLE). The flash was applied to various systems with water, methane, ethane, carbon dioxide, methanol, ethanol and monoethylene glycol and then compared to literature data.

2. METHODOLOGY

This section will explain the thermodynamic modelling and the computational algorithm.

2.1 Thermodinamic modelling

To assure that a system is in equilibrium, it must have thermal equilibrium, which is the equality of temperature between all phases in the system, mechanical equilibrium, which is the equality of pressure between all phases in the system, and chemical equilibrium, which is the equality between each component's chemical potential in each phase

(Smith, *et al*., 2007). However, in certain situations, fugacity can be used instead of the chemical potential, and it also ensures chemical equilibrium.

In this work two equation of states are used, the Soave-Redlich-Kwong (SRK) and the Cubic-Plus-Association (CPA). The SRK equation is shown in Eq. (1).

$$P = \frac{RT}{v_m - b} - \frac{a(T)}{v_m \left(v_m + b\right)} \tag{1}$$

where P is pressure, R is the universal constant of the gases, T is the temperature, v_m is the molar volume, b is the co-volume parameter and $a(T)$ is the temperature-dependent energy parameter which is given by Eq. (2).

$$a = a_0 \left[1 + c_1 \left(1 - \sqrt{T / T_c}\right)\right]^2 \tag{2}$$

where a_0 and c_1 are pure component parameters and T_c is the critical temperature. However, for mixtures, it is necessary to use mixing and combining rules to calculate the parameters a and b for SRK. For this work, the traditional van der Waals mixing rules, given by Eq. (3) and Eq. (4) were applied.

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{3}$$

$$b = \sum_i b_i x_i \tag{4}$$

where x_i is the mole fraction of the component i.

And the classical combining rules, given by Eq. (5) and Eq. (6) were also used.

$$a_{ij} = \sum_{i,j} \sqrt{a_j a_i}\, x_i x_j \left(1 - k_{ij}\right) \tag{5}$$

$$b_{ij} = \frac{b_i + b_j}{2} \tag{6}$$

where k_{ij} is a binary interaction parameter, which was optimized with experimental data from the literature, assuming that it varies linearly with the temperature.

The CPA EoS uses the SRK model and the association term from the Wertheim theory, so that it accounts for both physical and chemical interactions (Kontogeorgis, *et al*., 2006), as given by Eq. (7).

$$P = \frac{RT}{v_m - b} - \frac{a(T)}{v_m \left(v_m + b\right)} - \frac{1}{2} \frac{RT}{v_m} \left(1 + \frac{1}{v_m} \frac{\partial \ln(g)}{\partial (1/v_m)}\right) \sum_i x_i \sum_{A_i} \left(1 - X_{A_i}\right) \tag{7}$$

where g is the radial distribution function, A_i is the bonding site A of the component i , and X_{A_i} is the fraction of A-sites of the molecule i that are not bonded with other active sites. The first and second terms are identical to the SRK EoS and the third is the one that accounts for the chemical association.

The X_{A_i}, from the chemical association part, is given by Eq. (8).

$$X_{A_i} = \frac{1}{1 + \frac{1}{v_m} \sum_j x_j \sum_{Bj} X_{B_j} \Delta^{A_i B_j}} \tag{8}$$

where B_j is the summation over all sites, and $\Delta^{A_i B_j}$ is the association strength between site A on molecule i and site B on molecule j, as described by Eq. (9).

$$\Delta^{A_i B_j} = g\left(v_m\right) \left[exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1\right] b_{ij} \beta^{A_i B_j} \tag{9}$$

here, b is the co-volume parameter given by the cubic part of the equation, $\beta^{A_iB_j}$ and $\varepsilon^{A_iB_j}$ are the association volume and association energy between site A of molecule i and site B of molecule j, respectively.

2.2 Computational algorithm

The computational algorithm's flow chart is shown in Fig. 1.

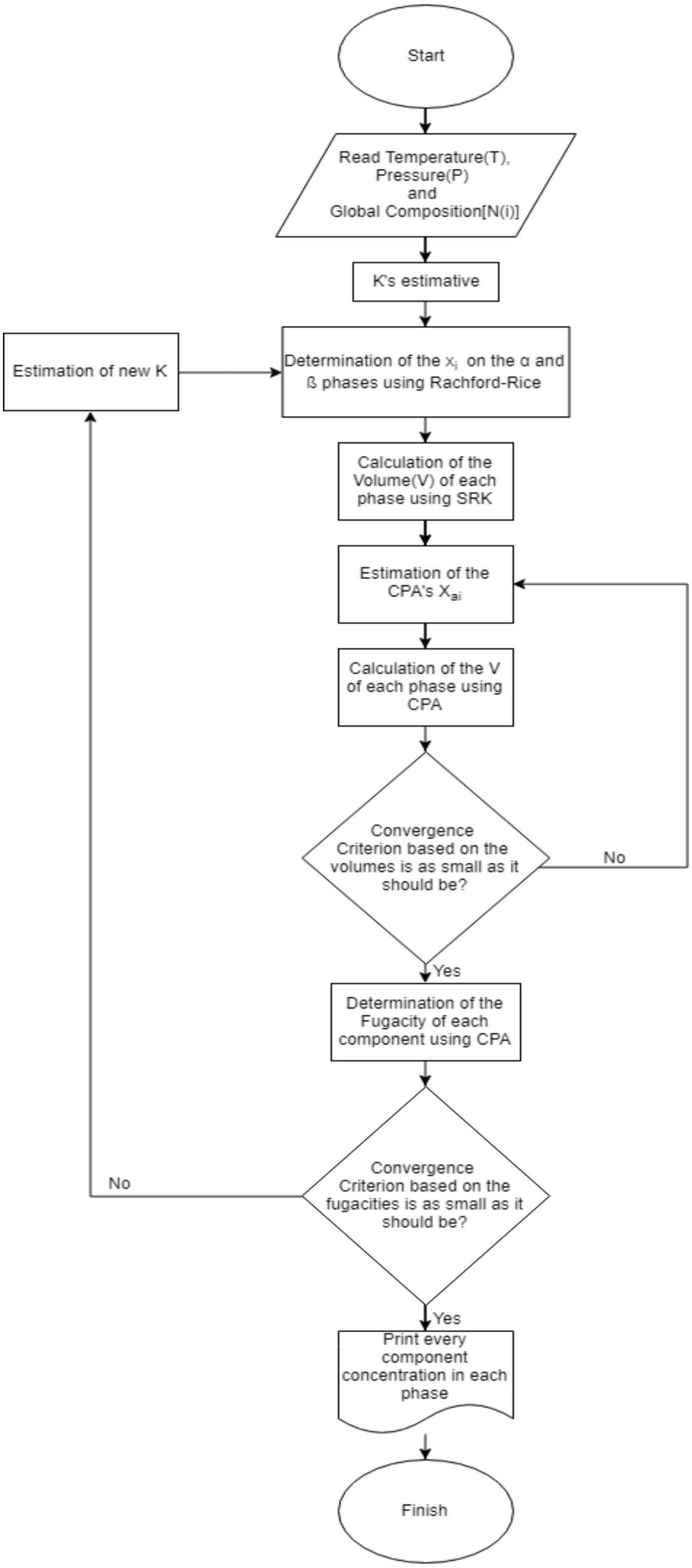

Figure 1. Computational algorithm's flow chart.

The program begins by reading the temperature, pressure and global compositions of the system, then it proceeds to estimate the *Ki*'s, which are the phase equilibrium constants. In the first interaction, it uses data that are pre inserted in the code.

The Rachford_Rice equation (Eq. (10)) is analytically solved using the *Ki*'s. Using the calculated λ's, the molar fractions of each component in each phase are calculated with Eq. (11) and Eq. (12).

$$0 = \sum_i \frac{(N_i / \sum_i N_i)(K_i - 1)}{1 + \lambda(K_i - 1)} \tag{10}$$

here N_i is the quantity of moles of the component *i*. and λ is the ratio between the total number of moles in the α and the β phases.

$$X_i^{\alpha} = \frac{(N_i / \sum_i N_i)}{1 + \lambda(K_i - 1)} \tag{11}$$

$$X_i^{\beta} = (N_i / \sum_i N_i) X_i^{\alpha} \tag{12}$$

where X_i^{α} is the molar fraction of the component *i* in the α phase and X_i^{β} is the molar fraction of the component *i* in the β phase.

The program then proceeds to calculate the total volume using the SRK EoS (Eq.(1)) as an initial estimative. Using the volume from SRK in Eq. (8) and Eq. (9), the X_{A_i} is calculated. Using the X_{A_i} and the volume from SRK in the CPA Eos (Eq. (7)), a new volume is calculated. After that, using the volume from CPA, the X_{A_i} is calculated again, and then a new volume using CPA, and this goes on until a convergence criterion based on the difference from the calculated volumes is reached.

Once the convergence criterion is reached, the fugacities of every component in each phase are calculated. Having the fugacities, the isofugacity criterion is tested, if the criterion is not reached, new *Ki*'s are estimated using the fugacities, and the program goes back to the third step. Once the volume criterion is reached, the program prints every component concentration in each phase, and then ends.

3. RESULTS

The flash algorithm was applied to various systems containing water, methane, ethane, carbon dioxide, methanol, ethanol and monoethylene glycol (MEG) in a large range of temperature and pressure.

Figure 2 and Fig. 3 shows the results for a system containing methane, water and methanol, at temperatures between 280 and 314K and pressures between 5 and 13 MPa. Experimental data came from Michal Frost, *et al*., 2014.

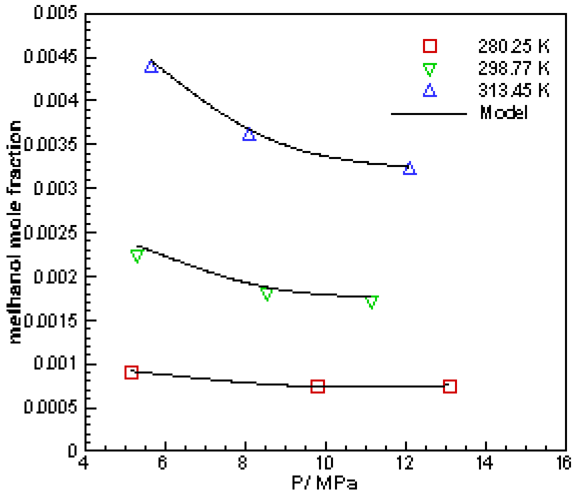

Figure 2. Prediction of the gas phase methanol content for a 25% mol methane, 46.3% water and 28.7% methanol system.

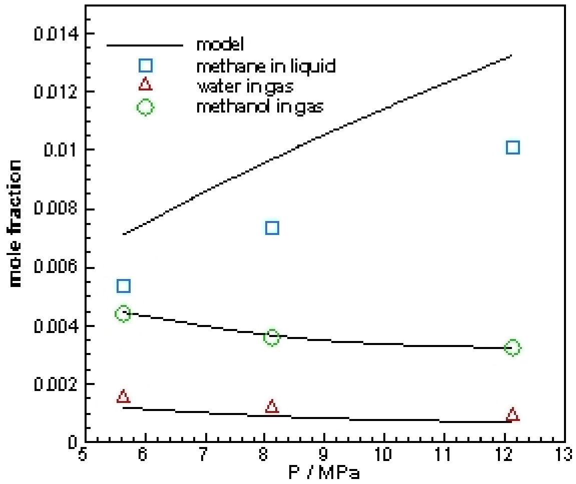

Figure 3. Prediction of methane in liquid, water in gas and methanol in gas for a 25% mol methane, 46.3% water and 28.7% methanol system at 313.45K.

Figure 2 shows that the algorithm has a good precision for estimating the methanol fraction in the gas phase, there was an mean error of 2.08%. It can be seen in Fig. 3 that the algorithm can also calculate with close results the water fraction in gas, with an error of 19.06%. The error for the methane partition in liquid was the highest, of 31.82%. The algorithm was able to follow the same trend as the experimental points.

Figure 4 shows the water and methanol fraction in liquid in a system containing water, carbon dioxide, and methanol, at the temperature of 273.15K, with pressures between 0.25 and 3.3 MPa. Experimental data came from Chang and Rousseau (1985).

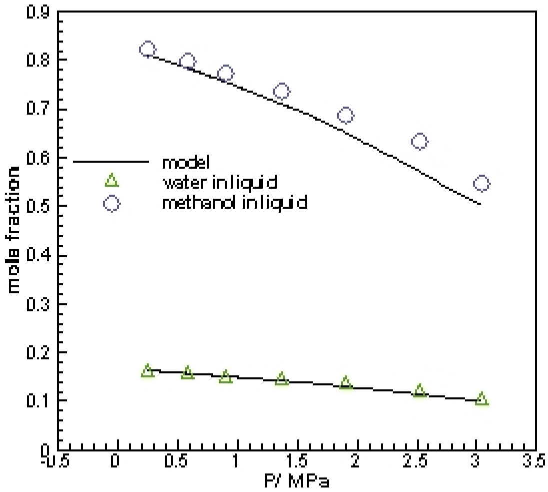

Figure 4. Prediction of methanol in liquid and water in liquid for a methanol dominant water, carbon dioxide methanol system at 273.15K.

At conditions show in Fig 4. the mean errors were 3.78% and 1.87% for methanol in liquid and water in liquid, respectively. The mean error obtained for this system, at temperatures of 243.15, 258.15 and 298.15K, for methanol in liquid was of 16.01%, and for water in liquid was of 18.53%.

Figure 5 shows the water and ethanol fraction in liquid, and the carbon dioxide fraction in gas for a water, carbon dioxide and ethanol system at the temperature of 308.15K, with pressures between 4 and 10MPa. Experimental data came from Yao, *et al*., (1994).

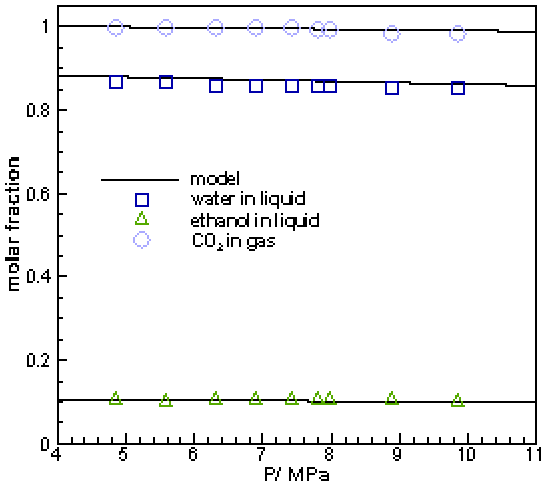

Figure 5. Prediction of water in liquid, ethanol in liquid and carbon dioxide in gas for a water, carbon dioxide and ethanol system at 308.15K.

The mean errors for the conditions show in Fig. 5 were 0.46% for carbon dioxide in gas, 2.89% for methanol in liquid and 1.89% for water in liquid. For the same system with temperatures of 313.15 and 323.15K the mean errors were of 0.61% for carbon dioxide in gas, 2.27% for ethanol in liquid and 0.27% for water in liquid.

Figure 6 shows the water and MEG content in the gas phase. And Fig. 7 shows the MEG partition in liquid for a water, methane and MEG system with pressures between 5 and 20 MPa. Experimental data came from Folas, *et al*., (2007).

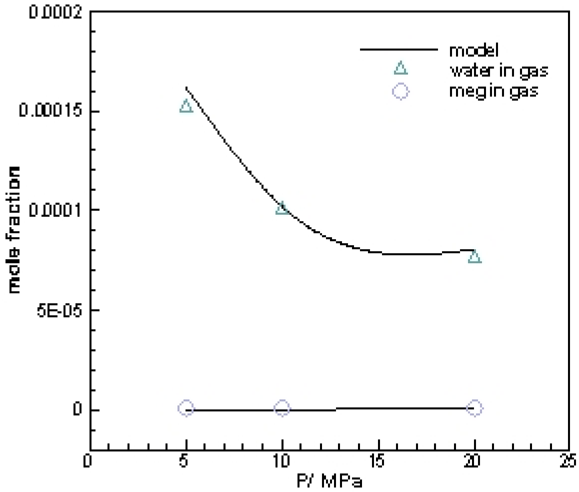

Figure 6. Prediction of water and MEG in gas for a water, methane and MEG system at 278.15K.

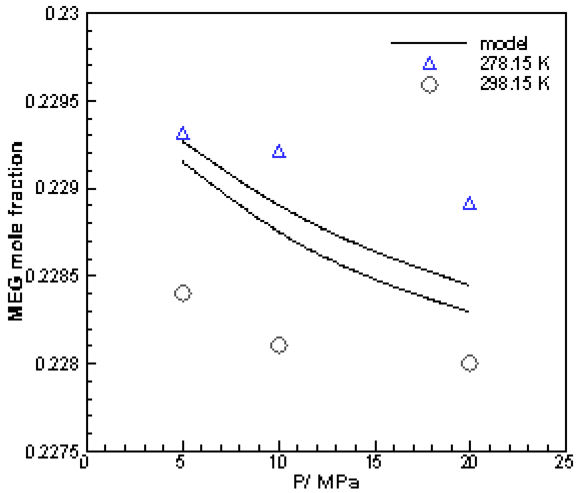

Figure 7. Prediction of the liquid phase MEG content for a 62.2% mol water, 19.25% methane and 18,55% MEG system.

The mean error for water and MEG in gas at 278.15K were of 4.97% and 46.93% respectively. The mean error for MEG in liquid was of 0.24%.

Table 1 and Table 2 show the results for a system containing water, ethane, carbon dioxide and methanol, experimental data came from Avlonitis, *et al*., (1994).

Table 1. Ethane, Carbon Dioxide, Methanol and Water partition in the liquid phase.

	Temperature [K]	Pressure [MPa]	Ethane in liquid x 10^3	%AAD	Carbon Dioxide in liquid x 10^3	%AAD	Methanol in liquid	%AAD	Water in liquid	%AAD
Exp	270.93	1.14	0.980	70.81	1.770	4.25	0.12994	5.45	0.8673	0.75
Model			1.674		1.695		0.12285		0.8738	
Exp	275.76	2.70	1.630	82.19	3.810	11.71	0.1226	0.19	0.8719	0.18
Model			2.970		4.256		0.1223		0.8704	
Exp	280.85	3.60	1.850	62.53	10.210	7.90	0.1217	0.10	0.8661	0.03
Model			3.007		9.403		0.1216		0.8659	

Table 2. Ethane, Carbon Dioxide, Methanol and Water partition in the gas phase.

	Temperature [K]	Pressure [MPa]	Ethane in gas	%AAD	Carbon Dioxide in gas	%AAD	Methanol in gas x 10^3	%AAD	Water in gas x 10^3	%AAD
Exp	270.93	1.14	0.87476	6.32	0.12393	44.53	0.620	30.08	0.720	39.25
Model			0.93001		0.06874		0.807		0.437	
Exp	275.76	2.70	0.82653	9.75	0.17286	46.72	0.570	5.79	0.410	34.95
Model			0.90708		0.09211		0.537		0.267	
Exp	280.85	3.60	0.77078	6.05	0.22668	19.84	1.560	60.61	0.780	61.75
Model			0.81738		0.18167		0.614		0.298	

In this system there was a good reliability for ethane in gas, carbon dioxide, methanol and water in liquid.

4. CONCLUSION

Using the CPA EoS and optimized binary interaction parameters, an algorithm that can predict each component concentration in each phase in VLE and VLLE was developed. It was then applied to various systems and compared with literature data. The results obtained were satisfactory.

5. ACKNOWLEDGEMENTS

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