MODELING OF PHASE EQUILIBRIA FOR BINARY AND TERNARY MIXTURES OF CARBON DIOXIDE, HYDROGEN AND METHANOL

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ABSTRACT

A Peng Robinson Equation of State (PREOS) with a conventional mixing rule, which is based on the two-interaction parameters k_{ij} and l_{ij}, was used to calculate the vapor-liquid phase equilibrium for the binary systems of CO_2-Methanol (MeOH), H_2-MeOH and H_2-CO_2 at temperatures between 278 and 308 K. The optimal binary interaction parameters were obtained by correlating the vapor-liquid equilibrium data of binary systems. The binary interaction parameters were then used to predict the ternary phase equilibria for the CO_2-H_2-MeOH system at pressures up to 200 bar.

It was found that both binary interaction parameters, k_{ij} and l_{ij}, were temperature dependent. The vapor-liquid equilibria calculated using the PREOS for the CO_2-MeOH, H_2-MeOH and H_2-CO_2 binary systems were found to be comparable with the experimental results. The PREOS produced satisfactory results in predicting the vapor-liquid phase behaviour for the ternary system of CO_2-H_2-MeOH in the region below the critical pressures of the CO_2-MeOH binary system. At pressures above the critical point of the CO_2-MeOH binary system, the H_2 solubility in the liquid phase predicted by PREOS was lower than the experimental data.

INTRODUCTION

Knowledge of the phase equilibria of mixtures is important for numerous industrial applications. The phase equilibria can be predicted using an appropriate model. Models are used for both correlation of existing data and to predict phase equilibria in regions where experimental results are not available. An ideal model uses measured physical properties of a mixture and theory to predict phase equilibria at all conditions. No such model currently exists.

Cubic equations of state are the most common models that are applied by many researchers to predict phase equilibria. The equations of state produce reasonable predictions for vapor-liquid equilibrium for fluids, such as polar components, using a relevant mixing rule [1]. The most widely method for predicting supercritical fluid equilibrium data is the use of cubic equations of state. Cubic equations of state are simple and can be extended to multi-component systems [2]. Many modifications have been made to improve the equation of state. Peng and Robinson developed the most successful two-parameter empirical cubic equation of state [3]. The Peng Robinson equation of state has been known to provide slightly better liquid density predictions than the Soave-Redlich-Kwong equation of state proposed by Soave [4,5]. In this study, the vapor-liquid phase equilibria calculation was performed using the following PREOS:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2 + 2Vb - b^2} \qquad (1)$$

The attractive interaction parameters a and b for a pure substance are calculated using the following equations:

$$b = 0.0778(\frac{RT_c}{P_c}) \qquad (2) \qquad\qquad a(T) = \alpha(T)a(T_c) \qquad (3)$$

$a(T_c)$ is the attractive parameter for a pure component at the critical temperature.

$$a(T_c) = 0.45724(\frac{R^2 T_c^2}{P_c}) \quad (4) \qquad\qquad \alpha(T) = 1 + m(1 - \sqrt{T_r})^2 \, (5)$$

where T_r is the reduced temperature.

The value of m is calculated using the following equations which are functions of the acentric factor (w):

for 0.2 <w<2
$$m = 0.3796 + 1.4850w - 0.1644w^2 + 0.01667w^3 \qquad\qquad (6)$$

for 0<w<0.5
$$m = 0.3746 + 1.5423w - 0.2699w^2 \qquad\qquad (7)$$

There are complexities for the prediction of mixture phase equilibria, particularly in the vicinity of the mixture critical point. Many attempts have been made to improve the accuracy of predictions by modifying the mixing rules. The introduction of a mixing rule enables calculation of the mixture parameters for an equation of state.

The quadratic mixing rules are often sufficient for the correlation of phase equilibria of mixtures where there is no specific interaction between molecules. Adachi and Sugie [6] and Iwai *et al*. [7] explained that the classical mixing rules with two parameters are adequate for mixtures that contain polar components such as alcohol–alcohol and water–lower alcohol binary systems. The most common method of expressing the adjustable parameter is a quadratic dependence on composition (also used in this study) and is as follows:

$$a_{mix} = \sum_{j=1}^{n} \sum_{i=1}^{n} x_i x_j a_{ij} \quad (8) \qquad\qquad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \qquad (9)$$

$$b_{mix} = \sum_{j=1}^{n} \sum_{i=1}^{n} x_i x_j b_{ij} \quad (10) \qquad\qquad b_{ij} = \frac{(b_{ii} + b_{jj})}{2}(1 - l_{ij}) \quad (11)$$

where l_{ij} is the binary interaction parameter.

The Absolute Average Relative Deviation (AARD) between the experimental data and those predicted by the equation of state is calculated by fitting the interaction parameters and minimisation of the Objective Function (OF) defined as follows:

$$OF = \frac{1}{2N} \sum \left| \frac{P_{\text{exp}} - P_{calc}}{P_{\text{exp}}} \right| + \left| \frac{y_{\text{exp}} - y_{calc}}{y_{\text{exp}}} \right| \tag{12}$$

RESULT AND DISCUSSION

The PREOS and a quadratic mixing rule (Equations 8, 9, 10 and 11) with two interaction parameters k_{ij} and l_{ij} were selected to correlate and predict vapor-liquid equilibria for the binary mixtures of CO_2, MeOH and H_2 and the ternary system of CO_2-H_2-MeOH at temperatures between 278 K and 308 K, and pressures up to 200 bar. The vapor-liquid equilibrium data for binary systems of MeOH-CO_2, MeOH-H_2 and H_2-CO_2 obtained previously [8] was used to optimize the interaction parameters.

The values of k_{ij} and l_{ij} for each pair of components were optimised by regression of vapor-liquid equilibrium data for the binary systems of MeOH-CO_2, MeOH-H_2 and H_2-CO_2 at various temperatures. The data in Table 1 indicate that the k_{ij} values for the binary system of MeOH-CO_2 are slightly temperature dependent. The l_{ij} values increased slightly as the temperature was raised and exhibited a maximum at 298 K. The values of k_{ij} for the H_2-MeOH binary system increased slightly with increasing temperature. An opposite trend was obtained for l_{ij}. Both interaction parameters (k_{ij} and l_{ij}) for the H_2-CO_2 binary system exhibited temperature dependency. The AARD between the experimental data and those correlated by the equation of state for each binary system was listed in Table 1.

Table 1: The binary interaction parameters for the CO_2-MeOH, H_2-MeOH and H_2-CO_2 binary systems with PREOS

System	Temp (K)	k_{ij}	l_{ij}	AARD (%)
CO_2-MeOH	308.2	0.0879	0.0271	1.3
	298.2	0.0943	0.0351	0.9
	288.2	0.0934	0.0307	1.5
	278.2	0.0708	0.0055	2.0
H_2-MeOH	308.2	-0.0879	0.0412	2.4
	298.2	-0.1006	0.0465	4.0
	288.2	-0.1058	0.0493	3.5
	278.2	-0.1195	0.0548	3.3
H_2-CO_2	298.2	0.1582	-0.0429	5.0
	290.2	0.1470	-0.0302	4.1
	288.2	0.0556	-0.0511	5.0
	278.2	0.1059	-0.0239	5.6

Correlation of Vapor-Liquid Equilibrium Data for Binary Systems

The PREOS was employed to correlate the vapor-liquid equilibrium data for the binary system of MeOH-CO_2 at various temperatures. The calculated phase behaviour for each isotherm and those obtained experimentally [8], are depicted in Figure 1(a). At low pressures, the experimental data were accurately correlated and the calculated curves passed through the experimental data. However, at higher pressures, in the vicinity of the critical point of the mixture, larger deviations were observed. As shown in Table 1, the AARD for the liquid mole fraction was higher at lower temperatures such as 288 K and 278 K.

The phase equilibrium for the binary system of H_2-MeOH at various temperatures was calculated and the results were compared with the experimental data [8]. As shown in Figure

1(b), the vapor-liquid equilibrium data in the pressure region studied were accurately correlated by the PREOS. The calculated data, as well as experimental data, for the liquid phase at each temperature followed Henry's law. The absolute average relative deviation between the experimental data and those calculated was less than 4%.

The vapor-liquid phase equilibria for the H_2-CO_2 binary system were also correlated using the PREOS and the results are presented in Figure 1(c). The phase envelope produced by the model was fitted to the experimental data at 290 K, 288 K and 278 K. As shown in Table 1, the deviation between the correlated phase behaviour and the experimental data, for all isotherms, was less than 6%. Higher accuracy was achieved as the temperature of the system increased.

At 298 K, a good agreement was obtained between the experimental data of the liquid phase of H_2-CO_2 system and the correlated phase equilibrium, whilst the concentration of H_2 in the vapor phase was slightly underestimated. The absolute average relative deviation was less than 5%.
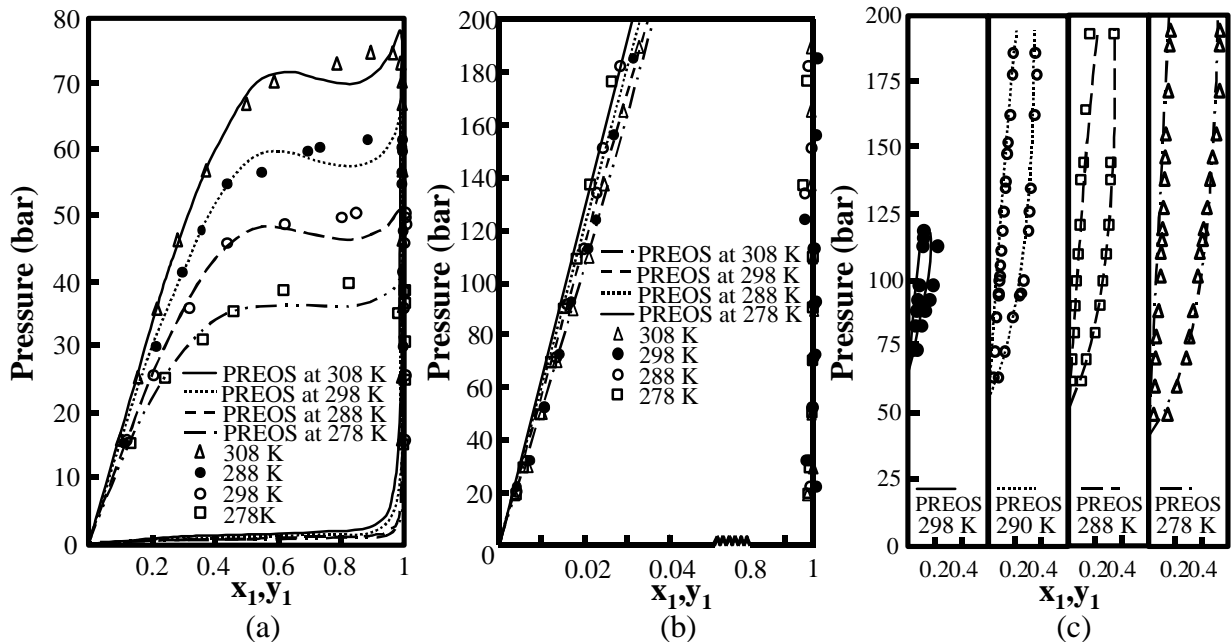

Figure 1: Correlation of experimental data for the binary systems of (a) MeOH-CO_2, (b) H_2-MeOH and (c) H_2-CO_2

Prediction of Equilibrium Data for CO₂-H₂-MeOH Ternary System

The phase equilibria for the ternary system of CO_2-H_2-MeOH was predicted at 278 K, 288 K and 298 K for various pressures up to 200 bar, using the PREOS and the binary interaction parameters obtained from the correlation of the binary vapor-liquid equilibrium data.

The liquid phase equilibria for the ternary system of CO_2-H_2-MeOH was predicted and compared with experimental data [9] in Figure 2. At each temperature, the data was predicted at pressures below the critical pressure of the CO_2-MeOH binary system. The vapor phase predicted lines are not shown in Figures 2 due to the very low solubility of MeOH in the vapor phase which resulted in parallel lines very close to the CO_2-H_2 axis. At 278 K, the predicted results were close to the experimental values (Figure 2(a)). The AARDs were found to be 7% and 2% at 20 and 30 bar, respectively. As the system approached the critical point of

the CO_2-MeOH binary mixture (39.5 bar) the predicted phase behaviours by the PREOS were lower than experimental data and the AARD for the mole fraction was 19%. At 288 K and 298 K, the predicted results for vapor-liquid equilibrium data by the PREOS were similar to experimental data. However, at 20 bar, the AARD between the predicted and experimental results were 17.8% and 21.5% for 288 K and 298 K, respectively.

The vapor-liquid phase equilibria for the ternary system of CO_2-H_2-MeOH at pressures above the critical point of the CO_2-MeOH binary mixture were also predicted for various temperatures. The liquid mole fraction predicted by PREOS at 278 K was less than the experimental data (Figure 3(a)) and the AARD was less than 19.7% (see Table 2). Above the critical pressure of CO_2-MeOH binary system at 288 K (P>55 bar) the mole fractions predicted were in good agreement with those measured experimentally, as demonstrated in Figure 3(b). At higher concentrations of CO_2, where the solubility of H_2 was significantly increased, the predicted mole fraction by the PREOS was lower than the experimental data. The AARD within the pressure range studied were found to be less than 16%.
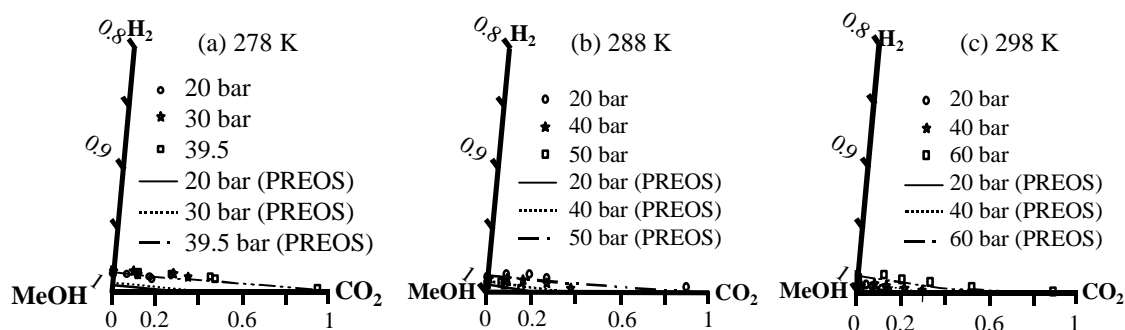

Figure 2: Comparison between the experimental data for the ternary system of CO_2-H_2-MeOH and the results predicted by the PREOS at various temperatures and pressures below the critical point of the CO_2-MeOH binary system

The predicted results for the phase equilibrium of CO_2-H_2-MeOH ternary system by PREOS at 298 K and pressures below the critical pressure of the H_2-CO_2 binary system (125 bar) were in good agreement with the experimental data, as presented in Figure 3(c). The AARDs were less than 7% in the pressure range from 70 to 110 bar. At pressures above 125 bar and 298 K, a binodal curve was formed, for each isobar, in the ternary system. However, the predicted phase equilibrium, where the CO_2 mole fraction was more than 0.6, were considerably far from the experimental data. Below 0.6 mole fraction of CO_2, the AARD was less than 3%.

Table 2: Values of AARD% for the ternary system of CO_2-H_2-MeOH

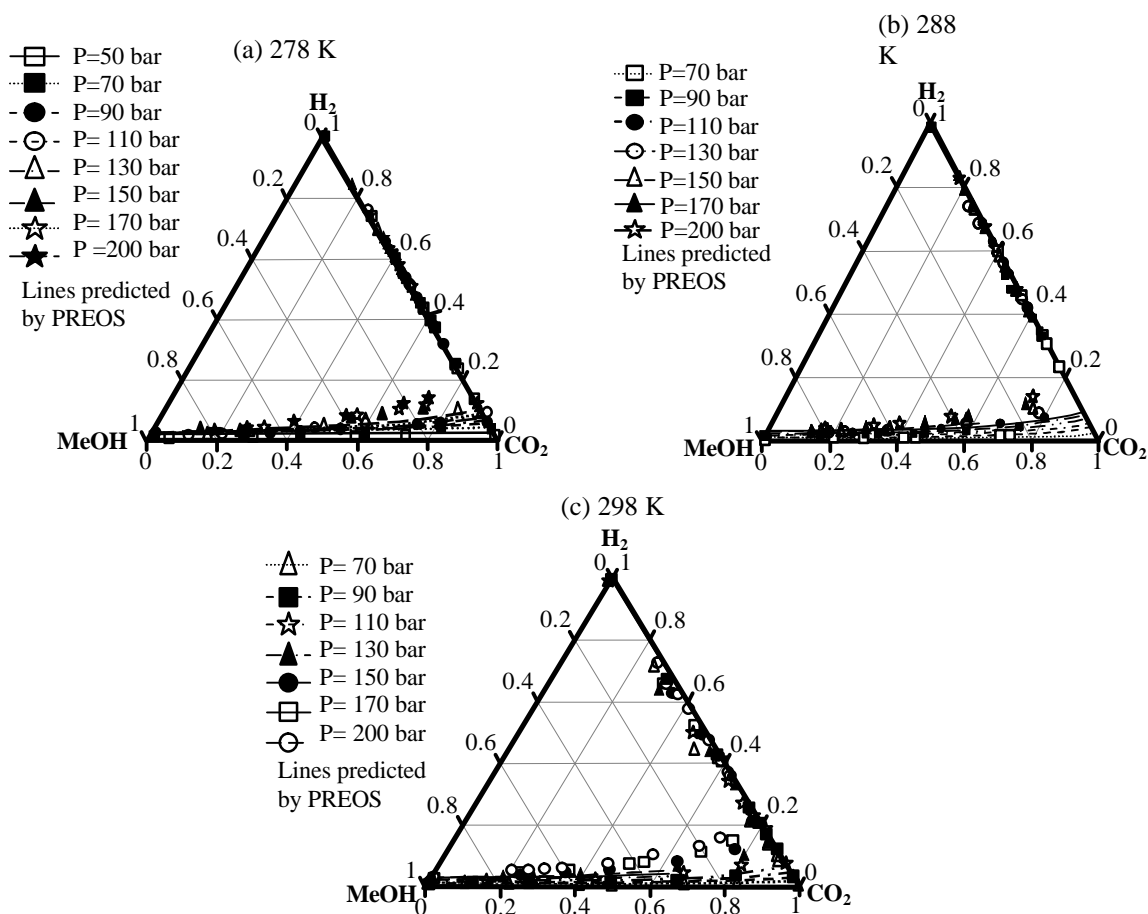| P (bar)	278 K	288 K	298 K	P (bar)	278 K	288 K	298 K
	AARD%	AARD%	AARD%		AARD%	AARD%	AARD%
20	7.3	17.8	21.5	90	16.4	11.1	7.2
30	2.1	——	——	110	16.9	8	4.1
39.5	19	——	——	130	16.7	1.5	1.8
40	——	3.6	13.9	150	17.9	9.3	2.5
50	19.6	9.7	——	170	18.4	11	2.7
60	——	——	14.6	200	13.2	4	2.7
70	19.7	16.4	6				

Figure 3: Comparison between the experimental data for the ternary system of CO_2-H_2-MeOH and the results predicted by the PREOS at various temperatures and pressures above the critical point of the CO_2-MeOH binary system

CONCLUSION

The PREOS was employed to predict the vapor-liquid equilibria for the ternary system of CO_2-H_2-MeOH. The binary interaction parameters, k_{ij} and l_{ij}, were considered to be temperature dependent. The absolute average relative deviation for the binary systems investigated did not exceed 6% in the temperature range from 278 to 308 K.

The vapor-liquid equilibria calculated using the PREOS for the CO_2-MeOH, H_2-MeOH and H_2-CO_2 binary systems were found to be comparable with the experimental data. The predicted results deviated from the experimental data in the vicinity of the critical pressure of CO_2-MeOH binary system.

The PREOS produced satisfactory results in predicting the vapor-liquid phase behaviour for the ternary system of CO_2-H_2-MeOH in the region below the critical pressures of the CO_2-MeOH binary system. At pressures above the critical point of the CO_2-MeOH binary system, the solubility of the H_2 in the liquid phase was underestimated. The maximum AARD was 20% at 278 K and 70 bar.

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