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# Modelling of Solubility of Mercaptans in Water at Low Concentrations

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**Abstract.** Mercaptans is one of the major volatile organosulfur compounds produced in natural environments. The presence of mercaptans creates a great threat to the environmental safety and can cause health problems due to their toxicity, even at low concentrations. Knowledge on the thermodynamics properties and vapor-liquid equilibria of mercaptans-water is important for environmental impact studies and engineering design particularly when dilute aqueous systems are involved. In this work, we propose a generalized thermodynamic framework that uses Soave, Redlich and Kwong (SRK) EOS/Peng-Robinson (PR) EOS coupled with Huron-Vidal mixing rules to correlate the solubility of mercaptans- in water systems at low concentration. For this approach, the Huron-Vidal mixing rule are combined with infinite-dilution activity coefficients and the procedure is based on the reduced UNIQUAC model, suitable for infinite-pressure conditions. New binary interaction parameters are reported for studied systems for a wide range of pressure. By employing the pure component parameters with the values of infinite dilution activity coefficients, the solubility of mercaptans in water at dilute concentrations was predicted quite satisfactorily. The results of Root Mean Square Error (RMSE) illustrated good accuracy of the studied models for all systems considered in this work, with values of about 1.14-5.12%.

## INTRODUCTION

Crude Oil and raw natural gas are often produced with several contaminants from reservoirs including water, acid gases, mercaptans, etc. Mercaptans are volatile organosulfur compounds produced in natural environments (McCready and Krouse, 1979) which typically present in raw natural gas. These organic compounds are highly reactive and odiferous, and their presence creates a great threat to the environmental safety and can cause health problems due to their toxicity, even at low concentrations (Zin et al., 2017, Zin et al., 2016 and Langè et al., 2013). In practice, removing mercaptans from raw natural gas using aqueous amine based purification units has always been a challenge in oil and gas industry. Failure in removing mercaptans has led to severe effects on plants operations, equipment durability, health and environment. Knowledge of the phase behavior of systems involving mercaptans and water is therefore necessary to address these problems.

As mercaptans are found in very small quantities in crude oil or natural gas streams (very dilute), the Henry's law approach is generally used. By definition, the Henry's law coefficient is defined at infinite dilution. The approach to infinite dilution is an important state of liquid mixtures mainly for testing models in drastic conditions. For a binary mixture, the concentration of solute approach infinite dilution, and then close neighbors of solute molecules are only solvent molecules that have a mole fraction that can be considered to unity. Study at infinite dilution is a good mean to evaluate nonideality of solute-solvent mixtures. Often, the predictions of the thermodynamic models are inadequate

in the absence of consistent thermodynamic data. On the other hand, experimental measurements are expensive and time-consuming especially at extremely low concentrations. One way of working out these problems is to develop and extend a more realistic thermodynamic model which require experimental data at the minimum level and work for a wide range of temperatures and pressures and at multiple situations. In this work, we attempt to model mercaptans solubility in dilute aqueous solutions by using EOS with HV mixing rule coupled with infinite dilution activity coefficients.

## THERMODYNAMIC MODELLING

The use of infinite dilution activity coefficients in the thermodynamic modelling of the system has been shown on many occasions (Schreiber and Eckert, 1971; Feroiu and Geana, 1989; Stryjek and Vera, 1986; Twu et al., 1992, Voustas et al., 1995; Feroiu and Geana, 1996; Feroiu and Geana, 1997; Feroiu and Geana, 1998; Feroiu and Geana, 1999; Constantinescu, Klamt and Geana; 2005, Schacht et al., 2010). In these works, infinite dilution activity coefficients were used to determine adjustable parameters of activity coefficient models or to determine cubic equation of state parameters. The major advantage of this method is that the  $\gamma^\infty$  values can be measured relatively easy, conveniently and some of these data are readily available in relevant comprehensive databases. Twu et al. (1992) stated that the equation of state with the binary interaction parameters derived from the infinite dilution activity coefficients is suitable for the process design of separation processes, especially for environmental concerns, which require prediction of high purity products.

The focus of this paper emphasizes on the coupling of the Huron-Vidal mixing rule with infinite-dilution activity coefficients. The procedure is based on the reduced UNIQUAC model, suitable for low pressure and infinite-pressure conditions, coupled to SRK EOS or PR EOS. The experimental values of infinite-dilution activity coefficients of systems containing mercaptans are taken from our previous studies in Zin et al. (2017) and Zin et al. (2016).

### Principle of Thermodynamic Modelling and Model Development

In this work, we use Soave, Redlich and Kwong (SRK) and Peng-Robinson (PR) equation of state (EOS). Basically, the PR equation of state (EOS) is given by the following equation:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (1)$$

where  $P$  is pressure,  $T$  is temperature,  $R$  is universal gas constant. Parameter  $a$  accounts for interactions between the species in the mixture and  $b$  accounts for the excluded volume of the species of the mixture.  $a$  and  $b$  are calculated from the following relations:

$$a = 0.45724 \frac{(R^2 T_c^2)}{P_c} \alpha(T_r, \omega) \quad (2)$$

$$\alpha(T_r, \omega) = [1 + K(1 - \sqrt{T_r})]^2 \quad (3)$$

$$K = 0.37464 + 1.54226\omega - 0.2699\omega^2 \quad (4)$$

$$b = 0.07780(RT_c) / P_c \quad (5)$$

The equation in terms of the compressibility factor  $Z$  takes the following form:

$$Z^3 - (1-B)Z^2 + (A-2B-3B^2)Z - (AB-B^2-B^3) = 0 \quad (6)$$

where;

$$A = \frac{aP}{(RT)^2}, \quad B = \frac{bP}{RT} \quad (7)$$

Likewise, the SRK equation of state is expressed as follows;

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (8)$$

where  $a$  and  $b$  are calculated from the following relations:

$$a = 0.42747 \frac{(R^2 T_c^2)}{P_c} \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2) (1 - \sqrt{T_r}) \right]^2 \quad (9)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (10)$$

In terms of the compressibility factor  $Z$ , the equation takes the following form:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (11)$$

where the definitions of  $A$  and  $B$  are given in Equation (7). In Equation (2)-(5) and (9)-(10),  $T_r$  is reduced temperature,  $\omega$  is acentric factor,  $T_c$  and  $P_c$  are critical temperature and pressure, respectively.

In this work, for the mixtures, the Huron–Vidal mixing rules are used and  $a$  and  $b$  parameters are calculated as follows;

$$b = \sum_i x_i b_i \quad (12)$$

$$\frac{a}{bRT} = \sum_i x_i \left( \frac{a_i}{b_i RT} - \frac{\ln \gamma_i(P \rightarrow \infty)}{C^*} \right) \quad (13)$$

where  $C^*$  is 0.69314 for SRK EOS and -0.62323 for PR EOS while  $\ln \gamma_i(P \rightarrow \infty)$  is the activity coefficient of the component in the mixture at infinite pressure.

For this work, the activity coefficients in Equation (13) are given by a reduced UNIQUAC model (only to its residual part, with the original values of  $q_i$  parameters) suitable for infinite pressure conditions;

$$\ln \gamma_i(P \rightarrow \infty) = q_i \left[ 1 - \ln \left( \sum_i \theta_i \tau_{ij} \right) - \frac{\sum_j \theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (14)$$

The interaction parameters are related to the infinite dilution activity coefficient at infinite pressure for a binary system are given as (Feroiu and Geana, 1996):

$$\tau_{12} = \exp[k_2 - \exp(k_1 - \tau_{12})]; \tau_{21} = \exp(k_2 - \tau_{12}) \quad (15)$$

$$k_1 = 1 - \frac{1}{q_1} \ln \gamma_{1(2)}^\infty(P \rightarrow \infty); k_2 = 1 - \frac{1}{q_2} \ln \gamma_{2(1)}^\infty(P \rightarrow \infty) \quad (16)$$

The values of infinite dilution activity coefficient at infinite pressure  $\ln \gamma_i(P \rightarrow \infty)$  can be determined from its value at zero pressure  $\ln \gamma_i(P \rightarrow 0)$  through this equation;

$$\ln \gamma_{i(j)}^\infty(P \rightarrow 0) = \left( 1 - \frac{b_i}{b_j} + \ln \frac{b_i}{b_j} \right) - \ln \left( \frac{V_j/b_j - 1}{V_i/b_i - 1} \right) - \frac{a_i}{b_i RT} \ln \left( \frac{1+b_j/V_j}{1+b_i/V_i} \right) + \ln \gamma_{i(j)}^\infty(P \rightarrow \infty) \ln \left( 1 + \frac{b_j}{V_j} \right) \quad (17)$$

where the volumes ( $V_i, V_j$ ) are the solutions of Eq. (1) and (8) at  $P \rightarrow 0$ :

$$\frac{V}{b} = \frac{1}{2} \left[ \frac{a}{bRT} - 1 \pm \left( \frac{a^2}{(bRT)^2} - 6 \frac{a}{bRT} + 1 \right)^{\frac{1}{2}} \right] \quad (18)$$

Since the liquid molar volume is needed, the smallest root is used in equation (18).

The fugacity coefficient of  $i$  in the mixture can be calculated as

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln \left( Z - \frac{bP}{RT} \right) - \left[ \frac{a_i}{b_i RT} - \frac{\ln \gamma_i^\infty (P \rightarrow \infty)}{C^*} \right] \ln \left( 1 + \frac{b}{V} \right) \quad (19)$$

and the fugacity for the pure component (Soave, 1994 and Feriou, 1996) is given as

$$\ln \phi_i^o = (Z_i - 1) - \ln \left( Z_i - \frac{b_i P}{RT} \right) - \frac{a_i}{b_i RT} \ln \left( 1 + \frac{b_i}{V_i} \right) \quad (20)$$

The corresponding fugacity coefficient in a binary mixture, at infinite dilution conditions ( $x_i \rightarrow 0$ ) is given as

$$\ln \phi_{i(j)}^\infty = \frac{b_i}{b_j} (Z_j - 1) - \ln \left( Z_j - \frac{b_j P}{RT} \right) - \left[ \frac{a_i}{b_i RT} - \frac{\ln \gamma_{i(j)}^\infty (P \rightarrow \infty)}{C^*} \right] \ln \left( 1 + \frac{b_j}{V_j} \right) \quad (21)$$

The equilibrium ratio for all components involved in the system (for liquid and vapor phase) is evaluated by using the following equation

$$K_i = \frac{\phi_i^L}{\phi_i^V} \quad (22)$$

In this approach, the prediction of high pressure VLE is predicted based on available information at low temperature/low pressure condition. Figure 1 shows the flowchart of calculations designed for this study based on proposed models and available data.

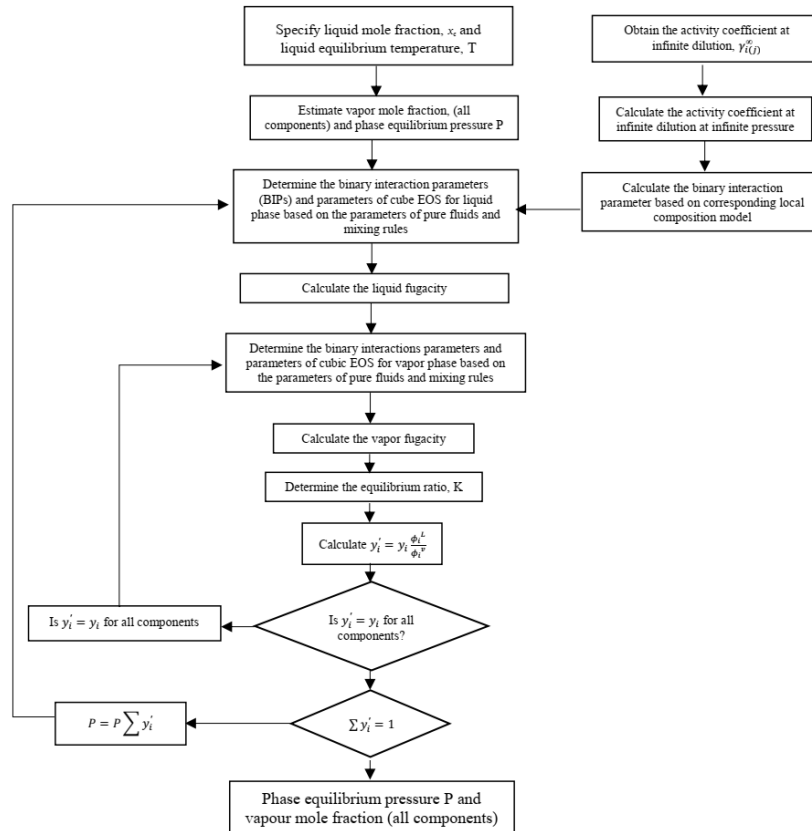


Figure 1. Flowchart of the predictive model

## RESULTS AND DISCUSSION

The properties of components and UNIQUAC parameters used in the modelling in this work, for all components are tabulated in Table 1.

**TABLE 1.** Pure Components Parameters, UNIQUAC q and r parameters and  $\gamma^\infty$  (P $\rightarrow$ 0) for components used in the modelling

Component	Molar Mass (g.mol <sup>-1</sup> )	Critical Temp (K)	Critical Press (atm)	Acentric Factor ( $\omega$ )	q (volume)	r (surface area)	$\gamma^\infty$ (P $\rightarrow$ 0) at 323 K (Zin et al, 2017)
Methyl Mercaptan	48.11	469.95	7.23	0.1581	1.67560	1.876700	77
Ethyl Mercaptan	62.13	499.15	54.92	0.1877	3.39830	3.928190	322
Propyl Mercaptan	76.16	536.60	4.63	0.2317	3.93893	4.60337	988
Water	18.02	647.30	220.48	0.3440	1.39970	0.920000	-

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Table 2 shows the results obtained for each of the system considered. The experimental data and relevant literature data are used to fit the mentioned parameters. The Root Mean Square Error (RMSE), was minimized to obtain the values of the binary interaction parameters and it was calculated from the objective function (*OF*) according to the following equation;

$$RMSE = \sqrt{\frac{OF}{n}} \quad (23)$$

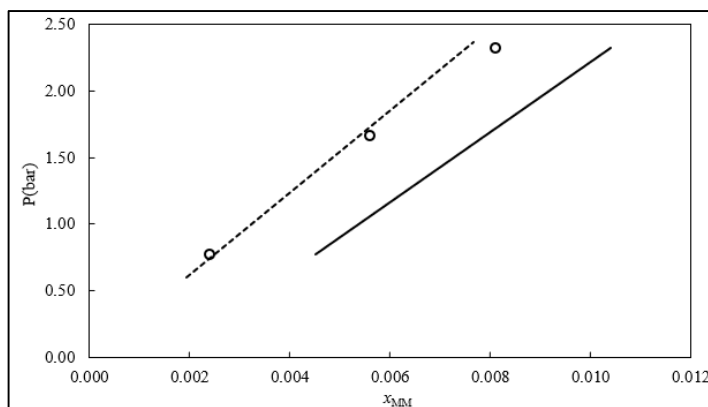
The RMSE is a measure of the difference between values predicted by our model and the experimental value, where, *n* is the number of experimental points. The adjustable parameters for the binary interaction parameter  $k_{ij}$  is adjusted to fit the experimental data for each of the systems mentioned

**TABLE 2.** Results obtained for each of the system considered in this work.

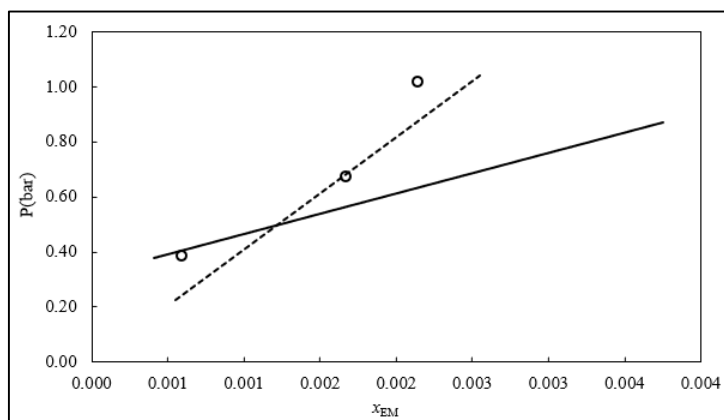
System	Model	No. of Points	T(K)	P(bar)	Data Ref.	$k_{12}$	RMSE
Methyl Mercaptan-Water	PR-UNIQUAC-HV	3	323	0.77-2.3	a	-0.3914	2.75
Methyl Mercaptan-Water	SRK-UNIQUAC-HV	3	323	0.77-2.3	a	-0.2768	1.14
Ethyl Mercaptan-Water	PR-UNIQUAC-HV	3	323	0.39-1.02	a	-0.3441	5.12
Ethyl Mercaptan-Water	SRK-UNIQUAC-HV	3	323	0.39-1.02	a	-0.6284	2.84
Propyl Mercaptan-Water	PR-UNIQUAC-HV	4	323	0.18-0.43	a	-0.5220	2.19
Propyl Mercaptan-Water	SRK-UNIQUAC-HV	4	323	0.18-0.43	a	-0.6501	1.28

<sup>a</sup>Kilner et al. (1990)

Figure 2, Figure 3 and Figure 4 illustrate the comparisons of modeling results with literature data for methyl mercaptan, ethyl mercaptan and propyl mercaptan at temperature 323K respectively.

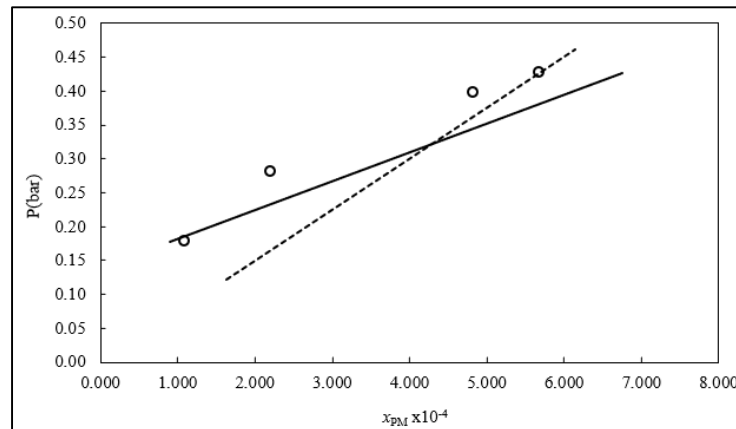


**Figure 2.** Comparison of modeling results on the solubility Methyl Mercaptan as a function of system pressure for Methyl Mercaptan-Water system: o experimental data (Kilner et al., 1990); — this work (PR-UNIQUAC -HV); this work ..... (SRK-UNIQUAC-HV) at 323K.



**Figure 3.** Comparison of modeling results on the solubility Ethyl Mercaptan as a function of system pressure for Ethyl Mercaptan-Water system: o experimental data (Kilner et al., 1990); — this work (PR-UNIQUAC -HV);..... this work (SRK-UNIQUAC-HV) at 323K.





**Figure 4.** Comparison of the modeling results on the solubility Propyl Mercaptan as a function of system pressure for Propyl Mercaptan-Water system: o experimental data (Kilner et al., 1990); — this work (PR-UNIQUAC -HV); - - - this work (SRK-UNIQUAC-HV) at 323K

As shown in these figures, SRK-UNIQUAC-Huron Vidal mixing rules provides a better estimation of the solubility of all mercaptans in water systems as compared to PR-UNIQUAC-Huron Vidal mixing rules. This probably due to the fact, the SRK equations are simpler whereas PR equations has additional term  $b(v-b)$  which can complicate the overall derivation of equation and contribute to higher deviation. The overall modelling results obtained are satisfactorily good and the presence of Huron Vidal mixing rule combined with infinite-dilution activity coefficients based on reduced UNIQUAC helps to provide good predications for VLE systems considered in the study.

## CONCLUSIONS

This modelling works attempt the approach whereby the Huron-Vidal mixing rule are combined with infinite-dilution activity coefficients and the procedure is based on the reduced UNIQUAC model. Two Equation of State are considered in the study namely PR EOS and SRK EOS. From the modelling results obtained, it appears that the presence of Huron-Vidal mixing rule combined with infinite-dilution activity coefficients (based on reduced UNIQUAC) correlates the experimental data more accurately for both EOS considered in the study. Based on the results acquired, it can be stated that in this work the PR- EOS and SRK-EOS combined with Huron and Vidal mixing rules has represented a better fit of phase behavior for the system of mercaptans-water.

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