



Short communication

Addition of the sulfhydryl group (—SH) to the PPR78 model: Estimation of missing group–interaction parameters for systems containing mercaptans and carbon dioxide or nitrogen or methane, from newly published data

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ABSTRACT

In 2008, the PPR78 model (Predictive Peng–Robinson 1978) was extended to mercaptan-containing systems by adding the sulfhydryl group (—SH), that is, by determining the values of the group–interaction parameters between the group —SH and the fourteen other groups already present in the PPR78 model. Unfortunately, due to a lack of experimental data reported in the open literature, it was not possible to characterize interactions between the group —SH and the three groups: ethane, CO₂ and N₂. Very recently, vapor–liquid equilibrium data for three binary systems containing methanethiol and respectively methane, nitrogen and carbon dioxide were however measured. It was thus decided to use these data to estimate two of the missing group–interaction parameters (—SH/CO₂ and —SH/N₂). For such systems, deviations observed with the PPR78 model are compared to those obtained with the CPA equation of state.

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1. Introduction

The PPR78 model (Predictive Peng–Robinson 1978) is a well-established model able to predict with accuracy the phase behavior of natural gases, gas condensates and crude oils explaining why it is today integrated in famous process-simulation softwares like *ProSimPlus* or *PRO/II*. Any mixture containing alkanes, aromatics, naphthenes, CO₂, N₂, H₂S, and mercaptans can be predicted with such a model which combines the Peng–Robinson equation of state in its 1978 version, classical mixing rules and a group-contribution method for the estimation of the temperature-dependent binary interaction parameters $k_{ij}(T)$. In 2008, Privat et al. [1] decided to add the sulfhydryl group (—SH) to the PPR78 model, briefly presented hereafter. By considering – as far as possible – all the data sets available in the open literature, Privat et al. were able to estimate group–interaction parameters between group —SH and eleven

other elementary groups: alkanes groups (CH₃, CH₂, CH, C and methane), aromatic groups (C_{aro}, CH_{aro}, C_{fused aromatic rings}), naphthenic groups (CH_{2 cyclic}, CH_{cyclic} ⇌ C_{cyclic}) and group H₂S (hydrogen sulfide). In spite of a thorough bibliographic study, it was however not possible to find data allowing estimation of interactions {group ethane/group —SH}, {group CO₂/group —SH} and {group N₂/group —SH}.

In a very recent paper, Awan et al. published vapor–liquid equilibrium (VLE) data on three binary systems containing methanethiol (a mercaptan) and methane, nitrogen or carbon dioxide [2]. To the best of our knowledge, it is the very first time that experimental VLE data are reported for systems containing carbon dioxide or nitrogen and a mercaptan. These measurements clearly offer the opportunity to estimate two of the three missing sets of PPR78 group–interaction parameters mentioned above (between group CO₂ and group —SH and between group N₂ and group —SH). This is the main goal of the present paper.

Although already estimated in 2008 [1], group–interaction parameters between groups —SH and methane were re-determined using the new data on the binary system methanethiol + methane measured by Awan et al. [2].

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Table 1
Nomenclature used for the six PPR78 groups considered in this study.

Group chemical structure	Group number
—CH ₃	1
—CH ₂	2
Methane (CH ₄)	5
Carbon dioxide (CO ₂)	12
Nitrogen (N ₂)	13
—SH	15

In the last part of this paper, the performances of the PPR78 model and the Cubic-Plus-Association (CPA) EoS are evaluated and compared.

2. A short presentation of the PPR78 model

The PPR78 model relies on the Peng–Robinson equation of state (EoS) [3] with classical Van der Waals mixing rules [1,4–10]. In the PPR78 model, the binary-interaction parameters $k_{ij}(T)$, depend on temperature and are calculated by a group-contribution method through the following expression:

$$k_{ij}(T) = \frac{-(1/2) \left[\sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \cdot (298.15/(T/K))^{(B_{kl}/A_{kl})-1} \right] - [(\sqrt{a_i(T)}/b_i) - (\sqrt{a_j(T)}/b_j)]^2}{2[(\sqrt{a_i(T)} \cdot a_j(T))/(b_i \cdot b_j)]} \quad (1)$$

In Eq. (1), a_i and b_i are pure-component Peng–Robinson parameters [1,3–10]. N_g is the number of different groups defined by the method (for the time being, fifteen groups are defined and $N_g = 15$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant group-interaction parameters determined in our previous papers [1,4–10].

According to the PPR78 group-decomposition scheme, six groups (—SH, —CH₃, —CH₂, methane, CO₂, N₂) are necessary to build the five molecules (methanethiol, ethanethiol, methane, CO₂, N₂) involved in this work. These groups are numbered as mentioned in Table 1, following the nomenclature previously adopted [1,4–10].

3. Estimation or re-estimation of group-interaction parameters between the group sulfhydryl (—SH) and three other groups

As explained before, six groups are involved in mixtures considered in this work (groups number 1, 2, 5, 12, 13, 15). This section aims at studying and quantifying the three group interactions {group 15–group 5}, {group 15–group 12} and {group 15–group 13}.

Table 2
Pure-component properties and data sources.

Name	Source	T_c (K)	P_c (bar)	ω
Methyl mercaptan (methanethiol)	[11]	470.00	72.30	0.150
Ethyl mercaptan	[12] ^a	499.15	54.90	0.188
Methane	[11]	190.56	45.99	0.011
Carbon dioxide	[11]	304.12	73.74	0.225
Nitrogen	[11]	126.20	33.98	0.037

^a The reason for which two different data sources were considered is explained in [1].

According to Eq. (1), the six following group-interaction parameters have thus to be determined: $\left\{ \begin{matrix} A_{15-5} \\ B_{15-5} \end{matrix} \right\}$, $\left\{ \begin{matrix} A_{15-12} \\ B_{15-12} \end{matrix} \right\}$ and $\left\{ \begin{matrix} A_{15-13} \\ B_{15-13} \end{matrix} \right\}$.

Note that the three group-interaction parameters $\left\{ \begin{matrix} A_{15-1} \\ B_{15-1} \end{matrix} \right\}$, $\left\{ \begin{matrix} A_{15-2} \\ B_{15-2} \end{matrix} \right\}$ and $\left\{ \begin{matrix} A_{1-2} \\ B_{1-2} \end{matrix} \right\}$, were determined in previous works [1,4].

The regression procedure used to estimate the three sets of A_{kl} and B_{kl} parameters is similar to the one previously used [1,4–10]. It is briefly reminded hereafter.

1. Values of $T_{c,i}$, $P_{c,i}$ and ω_i (acentric factor) for each pure compound i are required to estimate parameters a_i and b_i involved in Eq. (1). These values and their sources are given in Table 2 for the six molecules considered in this study.
2. A databank containing VLE data is developed. In the present case, it contains data from [2] (for binary systems methanethiol + methane, methanethiol + CO₂ and methanethiol + N₂) and [13] (for binary systems methanethiol + methane and ethyl mercaptan + methane).
3. A_{kl} and B_{kl} parameters are fitted on VLE data using the quasi-Newton BFGS method [14]. The objective function to be minimized is defined as follows:

$$\left\{ \begin{array}{l} F_{\text{obj}} = \frac{F_{\text{obj,bubble}} + F_{\text{obj,dew}}}{n_{\text{bubble}} + n_{\text{dew}}} \\ F_{\text{obj,bubble}} = 100 \sum_{i=1}^{n_{\text{bubble}}} \frac{|\Delta x|}{2} \left(\frac{1}{x_{1,\text{exp}}} + \frac{1}{x_{2,\text{exp}}} \right)_i \quad \text{with } |\Delta x| = |x_{1,\text{exp}} - x_{1,\text{calc}}| = |x_{2,\text{exp}} - x_{2,\text{calc}}| \\ F_{\text{obj,dew}} = 100 \sum_{i=1}^{n_{\text{dew}}} \frac{|\Delta y|}{2} \left(\frac{1}{y_{1,\text{exp}}} + \frac{1}{y_{2,\text{exp}}} \right)_i \quad \text{with } |\Delta y| = |y_{1,\text{exp}} - y_{1,\text{calc}}| = |y_{2,\text{exp}} - y_{2,\text{calc}}| \end{array} \right. \quad (2)$$

n_{bubble} and n_{dew} are the number of bubble points and dew points respectively. x_i is the mole fraction of component i in the liquid phase and y_i is the mole fraction of component i in the gas phase. Subscript *exp* stands for an experimental value. $x_{i,\text{calc}}$ and $y_{i,\text{calc}}$ are the mole fractions of component i respectively in the liquid and gas phases, calculated at given experimental values of temperature and pressure using the PPR78 model.

3.1. Interaction between group —SH and group methane

This interaction was already studied in a previous work [1]: the A_{15-5} and B_{15-5} parameters were determined from 128 bubble-point data [13] on two binary systems

(methane + methanethiol and methane + ethyl mercaptan), leading to the following values:

$$\begin{cases} A_{15-5}^{\text{old}} = 706.0 \text{ MPa} \\ B_{15-5}^{\text{old}} = 1483 \text{ MPa} \end{cases}$$

New data measured by Awan et al. [2] on the methane(1)+methanethiol(2) system offer the opportunity to incorporate 21 new bubble-point data, as well as 21 dew-point data in the databank (note that until now, only bubble-point data were present in the databank). In addition, these new data allow extending ranges of temperatures ($T \in [243.19 \text{ K}; 363.8 \text{ K}]$) and pressures ($P \in [0.98 \text{ bar}; 94.02 \text{ bar}]$) covered by the data for this system, thus increasing the PPR78 ranges of applicability. By re-adjusting the two group-interaction parameters on old and new data [2,13], one obtains:

$$\begin{cases} A_{15-5}^{\text{new}} = 704.2 \text{ MPa} \\ B_{15-5}^{\text{new}} = 1496 \text{ MPa} \end{cases}$$

The corresponding objective function defined by Eq. (2) is: $F_{\text{obj}}^{\text{new}} = 2.36\%$. Previously, using the old group-interaction parameters and the old databank (containing 128 bubble points), this function was $F_{\text{obj}}^{\text{old}} = 1.94\%$ [1]; considering the old group-interaction parameters and the new databank (containing 128 + 42 VLE data points), this function was $F_{\text{obj}}^{\text{old2}} = 2.40\%$.

Therefore, values A_{15-5} , B_{15-5} and F_{obj} are few affected by the new data.

The mean absolute errors (MAE) on the liquid- and gas-phase compositions are respectively $\Delta x_1 = \Delta x_2 = 0.0024$ and $\Delta y_1 = \Delta y_2 = 0.0177$. The corresponding mean relative errors are: $\Delta x\% = F_{\text{obj}, \text{bubble}}/n_{\text{bubble}} = 1.939\%$ and $\Delta y\% = F_{\text{obj}, \text{dew}}/n_{\text{dew}} = 5.344\%$. These results are illustrated in Fig. 1.

3.2. Interaction between group –SH and group CO_2

As explained before, due to a lack of data, it was not possible to determine the group-interaction parameters A_{15-12} and B_{15-12} when the PPR78 model was extended to mercaptan compounds [1]. Using the data by Awan et al. (9 bubble points and 9 dew points on the $\text{CO}_2(1)$ + methanethiol(2) system) and the methodology previously presented, it becomes possible to estimate these two parameters. Doing so, one obtains:

$$\begin{cases} A_{15-12} = 469.6 \text{ MPa} \\ B_{15-12} = 899.6 \text{ MPa} \end{cases}$$

The corresponding objective function defined by Eq. (2) is then: $F_{\text{obj}} = 15.9\%$, which is rather high by comparison with the rest of the data.

The MAE on the liquid- and gas-phase compositions are respectively $\Delta x_1 = \Delta x_2 = 0.0116$ and $\Delta y_1 = \Delta y_2 = 0.1178$. The

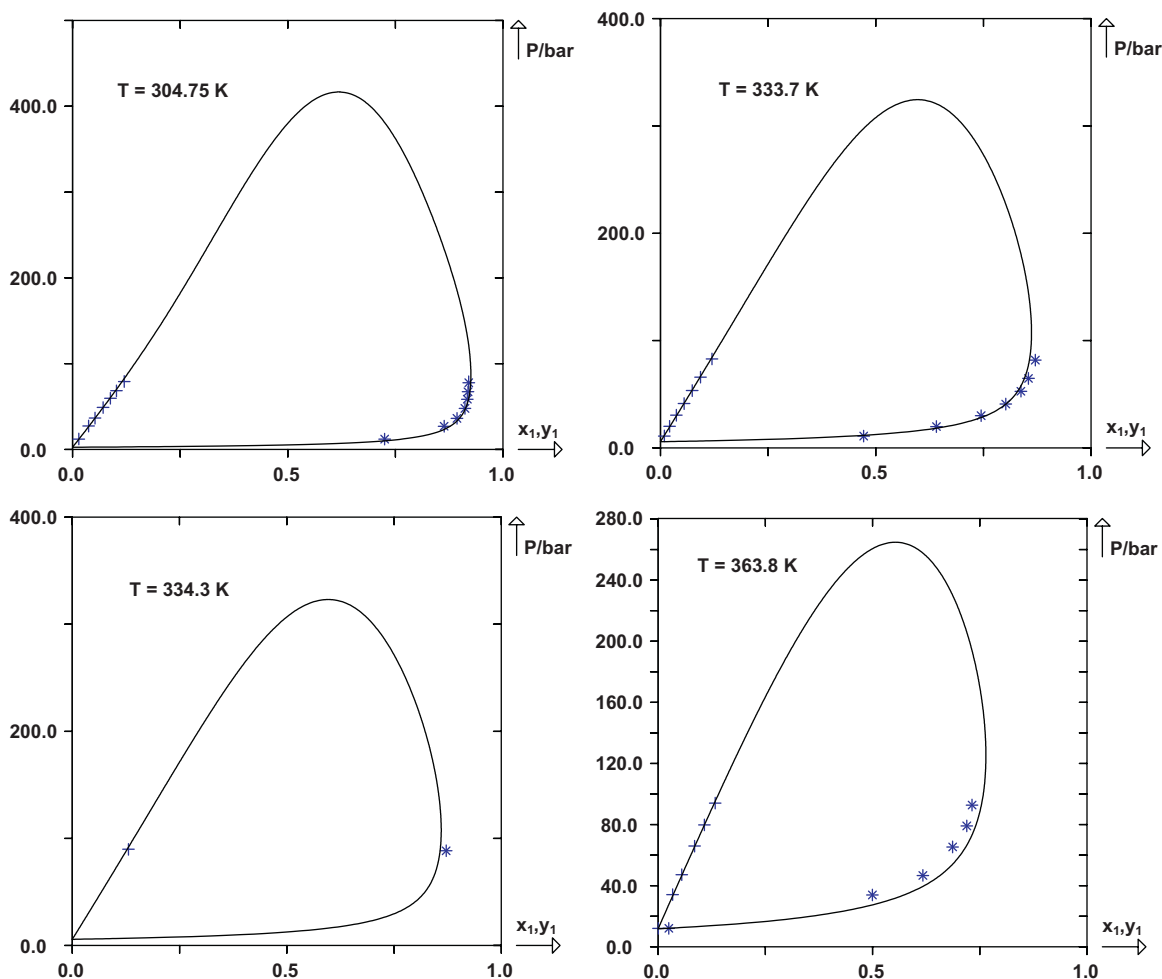


Fig. 1. Prediction of isothermal dew and bubble curves for the methane(1)+methanethiol(2) system using the PPR78 model. (+) Experimental bubble points measured by Awan et al. [2], (*) experimental dew points measured by Awan et al. [2]. Solid lines: prediction from the PPR78 model.

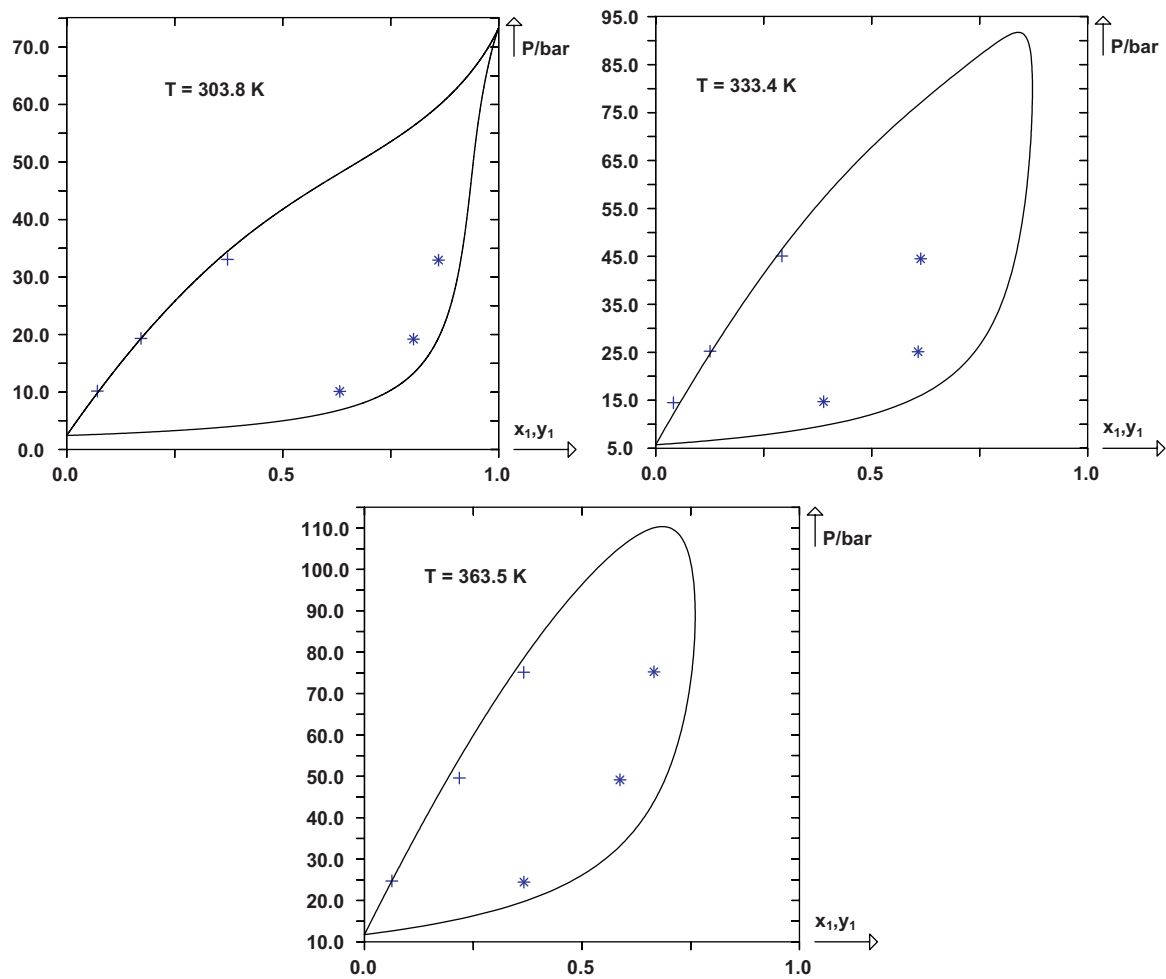


Fig. 2. Prediction of isothermal dew and bubble curves for the CO₂(1) + methanethiol(2) system using the PPR78 model. (+) Experimental bubble points measured by Awan et al. [2], (*) experimental dew points measured by Awan et al. [2]. Solid lines: prediction from the PPR78 model.

corresponding mean relative errors are: $\overline{\Delta x\%} = 4.870\%$ and $\overline{\Delta y\%} = 26.84\%$. Results are illustrated in Fig. 2.

It could be objected that the two group-interaction parameters A_{15-12} and B_{15-12} – which were adjusted on solely 18 data points – are probably not highly reliable. No doubt the confidence in those parameters could be improved if more appropriate VLE data were available, but this is not the case. These parameters however lead to k_{ij} values close to 0.1 at ambient temperature and we know by experience that such values are correct. Moreover, the VLE phase diagrams predicted with the proposed A_{15-12} and B_{15-12} values are much more accurate than those obtained with null k_{ij} .

3.3. Interaction between group –SH and group N₂

Using the data by Awan et al. (14 bubble points and 14 dew points on the N₂(1) + methanethiol(2) system) and the

methodology previously presented, it becomes also possible to estimate these two parameters. One gets:

$$\begin{cases} A_{15-13} = 1044 \text{ MPa} \\ B_{15-13} = 1872 \text{ MPa} \end{cases}$$

The corresponding objective function defined by Eq. (2) is then: $F_{\text{obj}} = 6.38\%$.

The MAE on the liquid- and gas-phase compositions are respectively $\overline{\Delta x_1} = \overline{\Delta x_2} = 0.0005$ and $\overline{\Delta y_1} = \overline{\Delta y_2} = 0.0434$. The corresponding mean relative errors are: $\overline{\Delta x\%} = 1.696\%$ and $\overline{\Delta y\%} = 11.06\%$. Results are illustrated in Fig. 3.

Similarly to results obtained with the CO₂(1) + methanethiol(2) system, it is observed that the prediction of the bubble curve is much more accurate than the prediction of the dew curve. In addition, as classically encountered with nitrogen-containing systems, the N₂(1) + methanethiol(2) mixture exhibits at a fixed

Table 3
Comparison between the PPR78 and the CPA models in terms of mean average errors $\overline{\Delta x_1}$ and $\overline{\Delta y_1}$.

	PPR78		CPA	
	$100 \times \overline{\Delta x_1}$	$100 \times \overline{\Delta y_1}$	$100 \times \overline{\Delta x_1}$	$100 \times \overline{\Delta y_1}$
Methane(1) + methanethiol(2)	0.12	1.77	2.06	1.89
CO ₂ (1) + methanethiol(2)	1.16	11.8	4.24	9.32
N ₂ (1) + methanethiol(2)	0.05	4.34	4.01	3.53

Table 4Group interaction parameters: $(A_{kl} = A_{lk})/\text{MPa}$ and $(B_{kl} = B_{lk})/\text{MPa}$ of the PPR78 model.

	CH ₃ (group 1)	CH ₂ (group 2)	CH (group 3)	C (group 4)	CH ₄ (group 5)	C ₂ H ₆ (group 6)	CH _{aro} (group 7)	
CH ₃ (group 1)	0	–	–	–	–	–	–	
CH ₂ (group 2)	A ₁₂ = 74.81 B ₁₂ = 165.7	0	–	–	–	–	–	
CH (group 3)	A ₁₃ = 261.5 B ₁₃ = 388.8	A ₂₃ = 51.47 B ₂₃ = 79.61	0	–	–	–	–	
C (group 4)	A ₁₄ = 396.7 B ₁₄ = 804.3	A ₂₄ = 88.53 B ₂₄ = 315.0	A ₃₄ = –305.7 B ₃₄ = –250.8	0	–	–	–	
CH ₄ (group 5)	A ₁₅ = 32.94 B ₁₅ = –35.00	A ₂₅ = 36.72 B ₂₅ = 108.4	A ₃₅ = 145.2 B ₃₅ = 301.6	A ₄₅ = 263.9 B ₄₅ = 531.5	0	–	–	
C ₂ H ₆ (group 6)	A ₁₆ = 8.579 B ₁₆ = –29.51	A ₂₆ = 31.23 B ₂₆ = 84.76	A ₃₆ = 174.3 B ₃₆ = 352.1	A ₄₆ = 333.2 B ₄₆ = 203.8	A ₅₆ = 13.04 B ₅₆ = 6.863	0	–	
CH _{aro} (group 7)	A ₁₇ = 90.25 B ₁₇ = 146.1	A ₂₇ = 29.78 B ₂₇ = 58.17	A ₃₇ = 103.3 B ₃₇ = 191.8	A ₄₇ = 158.9 B ₄₇ = 613.2	A ₅₇ = 67.26 B ₅₇ = 167.5	A ₆₇ = 41.18 B ₆₇ = 50.79	0	
C _{aro} (group 8)	A ₁₈ = 62.80 B ₁₈ = 41.86	A ₂₈ = 3.775 B ₂₈ = 144.8	A ₃₈ = 6.177 B ₃₈ = –33.97	A ₄₈ = 79.61 B ₄₈ = –326.0	A ₅₈ = 139.3 B ₅₈ = 464.3	A ₆₈ = –3.088 B ₆₈ = 13.04	A ₇₈ = –13.38 B ₇₈ = 20.25	
C _{fused aromatic rings} (group 9)	A ₁₉ = 62.80 B ₁₉ = 41.86	A ₂₉ = 3.775 B ₂₉ = 144.8	A ₃₉ = 6.177 B ₃₉ = –33.97	A ₄₉ = 79.61 B ₄₉ = –326.0	A ₅₉ = 139.3 B ₅₉ = 464.3	A ₆₉ = –3.088 B ₆₉ = 13.04	A ₇₉ = –13.38 B ₇₉ = 20.25	
CH _{2,cyclic} (group 10)	A _{1–10} = 40.38 B _{1–10} = 95.90	A _{2–10} = 12.78 B _{2–10} = 28.37	A _{3–10} = 101.9 B _{3–10} = –90.93	A _{4–10} = 177.1 B _{4–10} = 601.9	A _{5–10} = 36.37 B _{5–10} = 26.42	A _{6–10} = 8.579 B _{6–10} = 76.86	A _{7–10} = 29.17 B _{7–10} = 69.32	
CH _{cyclic} or C _{cyclic} (group 11)	A _{1–11} = 98.48 B _{1–11} = 231.6	A _{2–11} = –54.90 B _{2–11} = –319.5	A _{3–11} = –226.5 B _{3–11} = –51.47	A _{4–11} = 17.84 B _{4–11} = –109.5	A _{5–11} = 40.15 B _{5–11} = 255.3	A _{6–11} = 10.29 B _{6–11} = –52.84	A _{7–11} = –26.42 B _{7–11} = –789.2	
CO ₂ (group 12)	A _{1–12} = 164.0 B _{1–12} = 269.0	A _{2–12} = 136.9 B _{2–12} = 254.6	A _{3–12} = 184.3 B _{3–12} = 762.1	A _{4–12} = 287.9 B _{4–12} = 346.2	A _{5–12} = 137.3 B _{5–12} = 194.2	A _{6–12} = 135.5 B _{6–12} = 239.5	A _{7–12} = 102.6 B _{7–12} = 161.3	
N ₂ (group 13)	A _{1–13} = 52.74 B _{1–13} = 87.19	A _{2–13} = 82.28 B _{2–13} = 202.8	A _{3–13} = 365.4 B _{3–13} = 521.9	A _{4–13} = 263.9 B _{4–13} = 772.6	A _{5–13} = 37.90 B _{5–13} = 37.20	A _{6–13} = 61.59 B _{6–13} = 84.92	A _{7–13} = 185.2 B _{7–13} = 490.6	
H ₂ S (group 14)	A _{1–14} = 158.4 B _{1–14} = 241.2	A _{2–14} = 134.6 B _{2–14} = 138.3	A _{3–14} = 193.9 B _{3–14} = 307.8	A _{4–14} = 305.1 B _{4–14} = –143.1	A _{5–14} = 181.2 B _{5–14} = 288.9	A _{6–14} = 157.2 B _{6–14} = 217.1	A _{7–14} = 21.96 B _{7–14} = 13.04	
SH (group 15)	A _{1–15} = 799.9 B _{1–15} = 2109	A _{2–15} = 459.5 B _{2–15} = 627.3	A _{3–15} = 425.5 B _{3–15} = 514.7	A _{4–15} = 682.9 B _{4–15} = 1544	A _{5–15} = 704.2 B _{5–15} = 1496	N.A. ^a	A _{7–15} = 285.5 B _{7–15} = 392.0	
	C _{aro} (group 8)	C _{fused aromatic rings} (group 9)	CH _{2,cyclic} (group 10)	CH _{cyclic} or C _{cyclic} (group 11)	CO ₂ (group 12)	N ₂ (group 13)	H ₂ S (group 14)	SH (group 15)
CH ₃ (group 1)	–	–	–	–	–	–	–	–
CH ₂ (group 2)	–	–	–	–	–	–	–	–
CH (group 3)	–	–	–	–	–	–	–	–
C (group 4)	–	–	–	–	–	–	–	–
CH ₄ (group 5)	–	–	–	–	–	–	–	–
C ₂ H ₆ (group 6)	–	–	–	–	–	–	–	–
CH _{aro} (group 7)	–	–	–	–	–	–	–	–
C _{aro} (group 8)	0	–	–	–	–	–	–	–
C _{fused aromatic rings} (group 9)	A ₈₉ = 0.0 B ₈₉ = 0.0	0	–	–	–	–	–	–
CH _{2,cyclic} (group 10)	A _{8–10} = 34.31 B _{8–10} = 95.39	A _{9–10} = 34.31 B _{9–10} = 95.39	0	–	–	–	–	–
CH _{cyclic} or C _{cyclic} (group 11)	A _{8–11} = –105.7 B _{8–11} = –286.5	A _{9–11} = –105.7 B _{9–11} = –286.5	A _{10–11} = –50.10 B _{10–11} = –891.1	0	–	–	–	–
CO ₂ (group 12)	A _{8–12} = 110.1 B _{8–12} = 637.6	A _{9–12} = 267.3 B _{9–12} = 444.4	A _{10–12} = 130.1 B _{10–12} = 225.8	A _{11–12} = 91.28 B _{11–12} = 82.01	0	–	–	–
N ₂ (group 13)	A _{8–13} = 284.0 B _{8–13} = 1892	A _{9–13} = 718.1 B _{9–13} = 1892	A _{10–13} = 179.5 B _{10–13} = 546.6	A _{11–13} = 100.9 B _{11–13} = 249.8	A _{12–13} = 98.42 B _{12–13} = 221.4	0	–	–
H ₂ S (group 14)	A _{8–14} = 1.029 B _{8–14} = –8.579	A _{9–14} = 1.029 B _{9–14} = –8.579	A _{10–14} = 120.8 B _{10–14} = 163.0	A _{11–14} = –16.13 B _{11–14} = –147.6	A _{12–14} = 134.9 B _{12–14} = 201.4	A _{13–14} = 319.5 B _{13–14} = 550.1	0	–
SH (group 15)	A _{8–15} = 1072 B _{8–15} = 1094	A _{9–15} = 1072 B _{9–15} = 1094	A _{10–15} = 446.1 B _{10–15} = 549.0	A _{11–15} = 411.8 B _{11–15} = –308.8	A _{12–15} = 469.6 B _{12–15} = 899.6	A _{13–15} = 1044 B _{13–15} = 1872	A _{14–15} = –77.21 B _{14–15} = 156.1	0

^a N.A., not available.

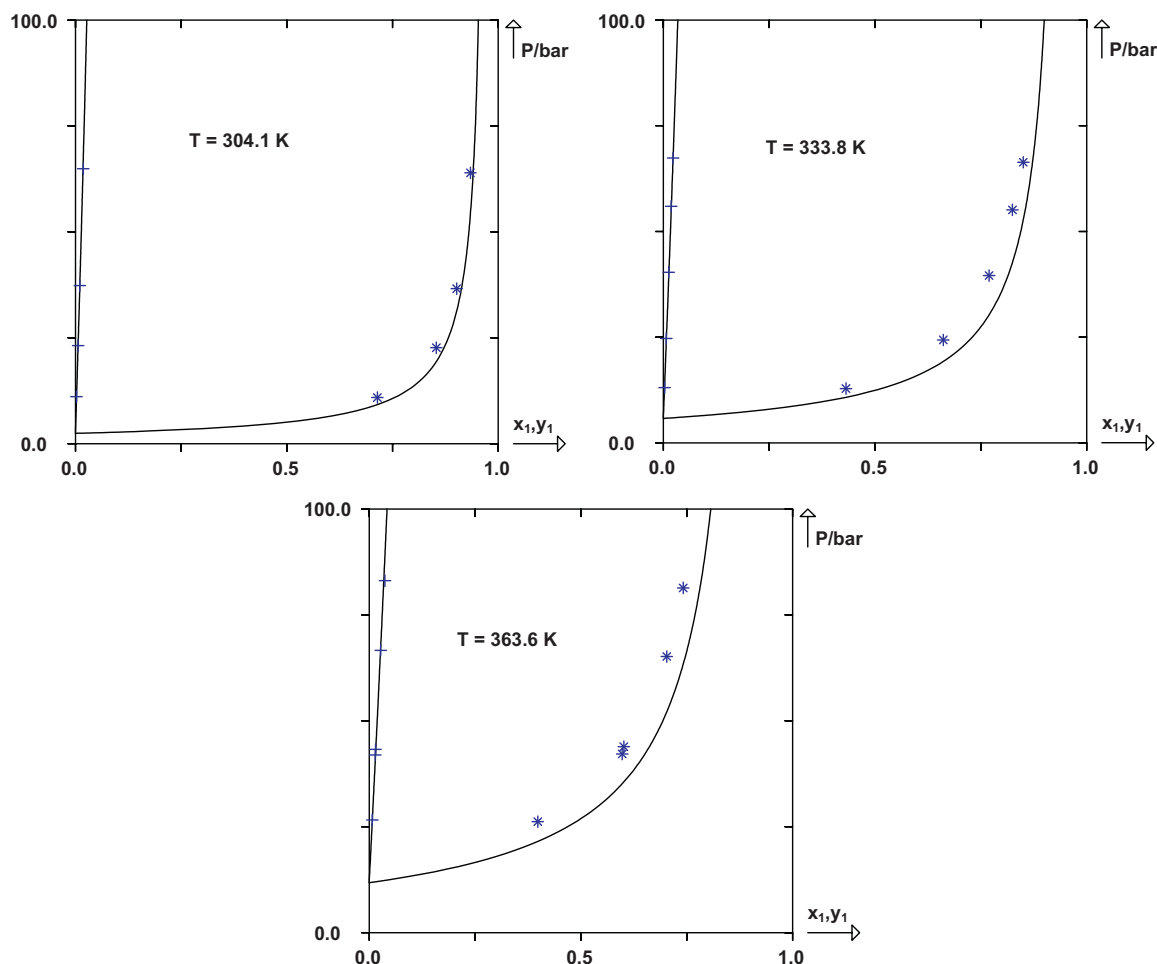


Fig. 3. Prediction of isothermal dew and bubble curves for the $N_2(1)+\text{methanethiol}(2)$ system using the PPR78 model. (+) experimental bubble points measured by Awan et al. [2], (*) experimental dew points measured by Awan et al. [2]. Solid lines: prediction from the PPR78 model.

temperature such that: $T_{c,1} < T < T_{c,2}$, a liquid–liquid equilibrium domain that runs from the vapor pressure of methanethiol $P_2^{\text{sat}}(T)$ to nearly infinite pressures.

4. Comparison between the PPR78 model and the CPA model

In their paper, Awan et al. have reported the mean average errors between the experimental mole fractions and their prediction using the CPA model (Cubic-Plus-Association) [2,15,16] respectively in the liquid phase Δx_1 and in the gas phase Δy_1 . Note that Awan et al. considered the CPA model without solvation or association effect; which becomes then equivalent to the SRK EoS.

A comparison between the PPR78 and CPA models is proposed in Table 3. It is observed that both models have a similar accuracy – with a small advantage for the PPR78 model – and are thus more or less equivalent regarding the representation of the kind of systems investigated in this paper.

5. Conclusion

This paper was dedicated to estimate four group-interaction parameters (A_{15-12} , B_{15-12} , A_{15-13} , B_{15-13}) of the PPR78 model in order to complete the PPR78 group-interaction matrix published in 2008 [1]. Therefore, thanks to the data measured by Awan et al. [2], it becomes now possible to apply this model to multicomponent

systems containing – among others – carbon dioxide, nitrogen and mercaptan compounds. In addition, two group-interaction parameters (A_{15-5} , B_{15-5}) have been re-adjusted using the new data by Awan et al.

All these results are summed up in the new group-interaction matrix, given in Table 4 (wherein the group-interaction parameters determined in this study are bolded), thus updating the one published in 2010 [17].

Unfortunately, to the best of our knowledge, due to a lack of data in the open literature, it is still not possible to estimate the interaction parameters between group –SH and group ethane (A_{15-6} and B_{15-6}).

It is also shown that the PPR78 model and the CPA model provide similar accuracy in representing the phase equilibria of the systems investigated in this study.

Finally, let us also recall that parameters given in Table 4 can not only be used to estimate the k_{ij} of the Peng–Robinson equation of state but also the binary interaction parameters of any other cubic equation of state [18].

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