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Elemental Mercury Partitioning in High Pressure Fluids
Part 2: Model Validations and Measurements in Multicomponent Systems.

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A good understanding of the solubility of elemental mercury over wide ranges of temperature, pressure and composition is an important issue to assess the possibility of mercury dropping out in gas processing streams. In this work, new mercury solubility in three multicomponent systems with methane content varying between 89 – 26 mol% have been measured over a wide range of temperature (243.15 to 323.15 K) and pressure and up to 20 MPa. A group contribution method for the Peng-Robinson equation of state has been used to allow calculation of binary interactions between mercury and saturated hydrocarbons, aromatic hydrocarbons, nitrogen and carbon dioxide. The parameters of the group contribution have been adjusted using mercury solubility previously measured in single components. Predictions of the developed model are validated against independent experimental data and the data generated in this work. A good agreement between predictions and experimental data is observed, supporting the reliability of the developed model.

Keywords: *Mercury; Natural Gas; Phase Behaviour; Peng-Robinson Equation of State; Group Contribution Model.*

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1. INTRODUCTION

Knowledge of the maximum solubility of elemental mercury with temperature and pressure in reservoir fluids is important to avoid mercury dropping out during processing operations as mercury is intrinsically present in hydrocarbon deposits. Mercury (Hg) is highly toxic and can be a potential health danger to operators and harmful to the environment in case of accidental release [1]. Impacts of mercury on hydrocarbon processing can be highly detrimental [2]: mercury is known to attack aluminium and other metal alloy heat exchangers [3], mercury can contaminate the different streams (waste water, liquid hydrocarbons or gases) and sorbents or solvents used in processes such as triethylene glycol used in dehydration [4]. A good understanding of the solubility of Hg at low temperature is an important issue to assess the possibility of mercury dropping out during gas and hydrocarbon processing and therefore increase ability to control and ensure environmental limitations on mercury are met.

In this communication, mercury contents in three multicomponent systems were measured at (243.15, 273.15, 298.15 and 323.15) K and pressures up to 20 MPa. In this work the Enhanced Predictive Peng-Robinson (E-PPR78-EoS) [5] was updated to include the "*Hg group*". The solubility data presented by Chapoy et al. [6] were used to adjust the interaction parameters of the Hg group with 9 groups: CH_3, CH_2, C, CH_4 (methane), C_2H_6 (ethane), CH_{aro}, C_{aro}, N_2 (nitrogen) and CO_2 (carbon dioxide). To validate the new parameters, mercury solubilities in multicomponent system were compared against the predictions of the model. The predictions are in good agreement, demonstrating the reliability of experimental techniques and the modelling work used in this study. In this manuscript, all mercury content data from the literature and from this work are reported in mole fraction (ppm: part per million, i.e. 10^{-6} mole fraction / ppb: part per billion, i.e. 10^{-9} mole fraction).

2. LITERATURE REVIEW

A literature review for solubility of mercury in various alkanes, carbon dioxide and nitrogen has been described previously [6]. For multicomponent systems the data are limited. The available literature data are listed in Table 1~~Table 1~~. Koulocheris et al. [7] measured mercury solubility for a multicomponent natural gas mixture (88.10 mol% CH_4, 6.20% C_2H_6, 2.51% C_3H_8,

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1.03% N_2 and 2.16% CO_2) between 263.15 to 293.15 K at 2.8 and 6.9 MPa. For this system, the results were only published graphically and without any numerical detail.

Butala et al. [8] have reported mercury solubility in a binary mixture of propane (59.4 mole%) + 2-methylpropane (40.6 mole%) between 253.15 – 278.15 K. They also did similar measurements for a mixture of butane (32.4 mole%) + pentane (33.5 mole%) + hexane (34.1 mole%). These measurements were performed at 258.15, 273.15 and 293.15 K. Marsh et al. [9] measured the solubility of mercury in two multicomponent mixtures of hydrocarbons. However, due to the lack of information about the condition of the measured solubilities (phase and density of the fluid during the measurements) the measurements cannot be used for comparison and model validation.

Table 1. Literature data for solubility of mercury in multicomponent mixtures.

Mixture Composition*	*T*/K	*p*/MPa	X_{Hg}/ ppb	*Ref.*
0.324 (C4) + 0.335 (C5) + 0.341 (C6)	258.15	2.089	45.4	[8]
0.324 (C4) + 0.335 (C5) + 0.341 (C6)	273.15	2.068	127	[8]
0.324 (C4) + 0.335 (C5) + 0.341 (C6)	293.15	2.117	467	[8]
0.594 (C3)+0.406 (i-C4)	253.15	4.828	29.3	[8]
0.594 (C3)+0.406 (i-C4)	253.15	6.897	25.9	[8]
0.594 (C3)+0.406 (i-C4)	263.15	3.572	51.3	[8]
0.594 (C3)+0.406 (i-C4)	263.15	6.897	47.9	[8]
0.594 (C3)+0.406 (i-C4)	268.15	3.497	74.4	[8]
0.594 (C3)+0.406 (i-C4)	268.15	6.897	71.7	[8]
0.594 (C3)+0.406 (i-C4)	273.15	3.476	104	[8]
0.594 (C3)+0.406 (i-C4)	273.15	6.897	101	[8]
0.594 (C3)+0.406 (i-C4)	278.15	3.393	144	[8]
0.594 (C3)+0.406 (i-C4)	278.15	6.897	140	[8]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	263.15	6.895	3.40	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	273.15	6.895	8.42	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	283.15	6.895	24.97	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	293.15	6.895	45.05	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	263.15	2.758	4.67	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	273.15	2.758	13.36	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	283.15	2.758	43.19	[7]
0.881(C1) + 0.0620 (C5) + 0.0251(C3)+0.0103 (N2)+0.0216(CO2)†	293.15	2.758	80.24	[7]

*compositions are in mole fraction. †Data digitalised from figures.

3. EXPERIMENTAL SETUP AND PROCEDURES

3.1 Materials

The composition of gases used in this study are listed in **Table 2**, **Table 3** and **Table 4**. MIX 1 was provided by *BOC*. MIX 2 and 3 were purchased from *Air Products*. These three mixtures

were prepared gravimetrically. Mercury purchased from *Sigma-Aldrich* used in all tests was 99.9995 wt% pure (Table 5~~Table 5~~). No further purification or analysis was conducted. Measurements were only carried out in the single-phase region as seen in ***Figure 1*** ~~***Figure 1***~~.

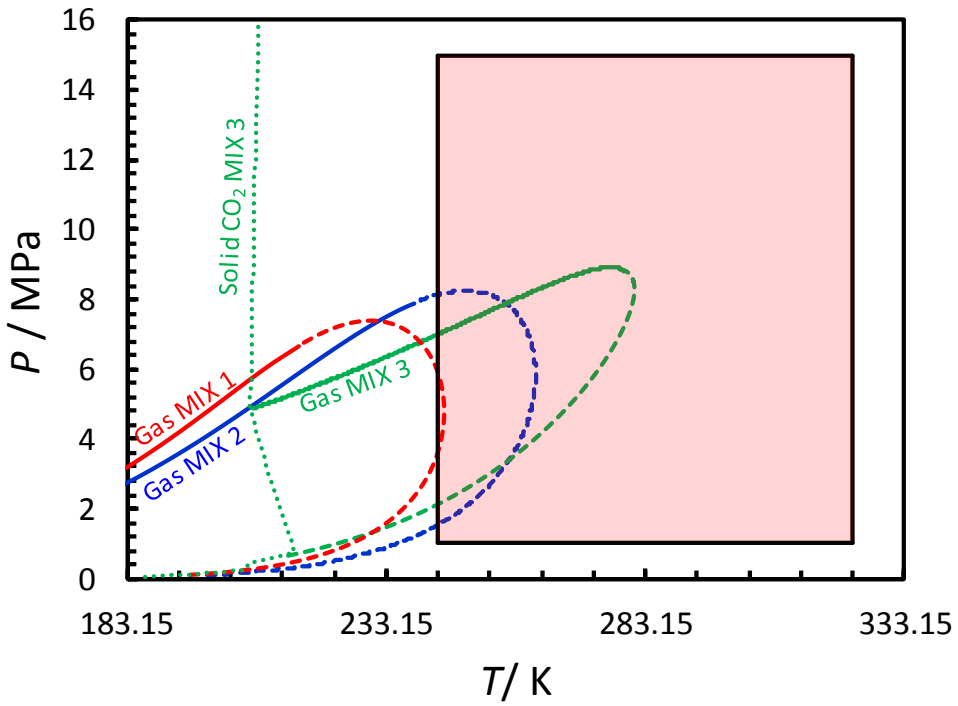

Figure 1. *Predicted phase envelopes of the multicomponent systems investigated in this work. Red boxes; experimental sampling conditions – Predictions using ePPR78-EoS* [5,10]

Table 2. Composition of *MIX 1* used in this work (M_W=18.212 g.mol^{-1} / γ_g (gas gravity)* =0.629)

COMPONENT	COMPOSITION MOL%	UNCERTAINTIES
METHANE	89.24	1.79
ETHANE	6.516	0.131
PROPANE	2.255	0.046
2-METHYLPROPANE	0.317	0.007
BUTANE	0.441	0.009
2-METHYLBUTANE	0.0442	0.0009
PENTANE	0.0299	0.0006
NITROGEN	0.390	0.008
CARBON DIOXIDE	0.771	0.016

*$\gamma_g = \frac{\sum_i z_i M_i}{28.98}$ **where z_i is the composition of component *i* and M_i its molecular weight.** *Uncertainty of the content of a specified component, is expressed as a product of the standard uncertainty and a coverage factor (k=2), providing a confidence level of +/- 95%*

Table 3. Composition of *MIX 2* used in this work (M_W=21.76 g.mol^{-1} / γ_g =0.751)

COMPONENT	COMPOSITION MOL%	UNCERTAINTIES
METHANE	74.906	0.07
ETHANE	10.397	0.01
PROPANE	3.942	0.02
2-METHYLPROPANE	0.5769	0.006
BUTANE	0.9871	0.005
NITROGEN	0.4695	0.002
CARBON DIOXIDE	8.7212	0.009

Uncertainty of the content of a specified component, is expressed as a product of the standard uncertainty and a coverage factor (k=2), providing a confidence level of +/- 95%

Table 4. Composition of *MIX 3* used in this work (M_W=36.048 g.mol^{-1} / γ_g =1.245)

COMPONENT	COMPOSITION MOL%	UNCERTAINTIES
METHANE	26.284	0.0526
ETHANE	0.931	0.019
PROPANE	0.2889	0.006
BUTANE	0.0719	0.0014
NITROGEN	3.076	0.0154
CARBON DIOXIDE	69.35	1.387

Uncertainty of the content of a specified component, is expressed as a product of the standard uncertainty and a coverage factor (k=2), providing a confidence level of +/- 95%

Table 5. Composition of mercury used in this work (used without further purification)

Chemical	Symbol	CASRN	Purity	Supplier
Mercury	Hg	7439-97-6	99.9995wt%	Sigma-Aldrich

3.2 Setup

The equipment was fully described in our previous communication [6]. The setup was used without any modification. Temperature calibration uncertainty is estimated to be 0.05 K, in the temperature range 243.15 to 323.15 K. Pressure calibration uncertainty is estimated to be 0.01 MPa. The mercury analyzer was calibrated against a MC-3000 Mercury calibrator using nitrogen. The mercury content uncertainty is $U_{cal}(y^{Hg})$=2%.

4. THERMODYNAMIC MODELLING

In this work, the PR78-EoS [4] was chosen to calculate the phase behaviour and the mercury distribution in all fluid phases. The equation is given below:

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

The co-volume *b* is given below:

$$b = 0.077796\frac{RT_C}{P_C} \quad (2)$$

The temperature dependency of the attractive term in equation (1), *a*, is defined using a Soave type temperature dependency:

$$a = a_0\alpha(T) \quad (3)$$

$$\text{Where } \begin{cases} \alpha(T) = \left[1 + m(\omega)\left(1 - \sqrt{T_r}\right)\right]^2 \\ a_0 = \frac{0.45724R^2T_c^2}{P_c} \end{cases} \quad (4)$$

where *m* is directly related to the acentric factor of the components

$$m(\omega) = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2 \; if \; \omega \leq 0.491 \\ 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 if \; \omega > 0.491 \end{cases} \quad (5)$$

To improve the calculation of the vapour pressure of mercury, the *Mathias-Copeman* (*MC*) alpha function [11] with three adjustable parameters was also used for this compound :

$$\begin{cases} if T < T_{C,} \;\; \alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_C}}\right) + c_2\left(1 - \sqrt{\frac{T}{T_C}}\right)^2 + c_3\left(1 - \sqrt{\frac{T}{T_C}}\right)^3\right]^2 \\ otherwise \;\; \alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_C}}\right)\right]^2 \end{cases} \quad (6)$$

Where c_1, c_2 and c_3 are the three adjustable parameters. These parameters are listed in Table 6~~Table 6~~.

For multicomponent systems, the van der Waals one fluid mixing rules were used:

$$a = \sum_i \sum_j x_i x_j a_{ij} \text{ where } a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_i a_j} \quad (7)$$

$$b = \sum_i x_i b_i \quad (8)$$

Where k_{ij} is the binary interaction parameters, in this work the k_{ij} is symmetrical, i.e. $k_{ij} = k_{ji}$ and equal to zero when *j=i*.

The binary interaction parameter is calculated using Equation 9 as suggested in [10].

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$$k_{ij}(T) = \frac{-\frac{1}{2}\times\sum_{k=1}^{Ng}\sum_{l=1}^{Ng}(\alpha_{ik}-\alpha_{jk})(\alpha_{il}-\alpha_{jl})A_{kl}\left(\frac{298.15}{T}\right)^{\left(\frac{B_{kl}}{A_{kl}}-1\right)} - \left(\frac{\sqrt{\alpha_i(T)}}{b_i} - \frac{\sqrt{\alpha_j(T)}}{b_j}\right)^2}{2\frac{\sqrt{\alpha_i(T)\alpha_j(T)}}{b_i b_j}} \quad (9)$$

Where

$$\alpha_{ik} = \frac{number\ of\ group\ k\ in\ molecule\ i}{total\ number\ of\ groups\ in\ molecule\ i} \quad (10)$$

and A_{kl} and B_{kl} are group interaction parameters. These parameters are listed in Table 7~~Table 7~~ for the mercury group. Others group interaction parameters are directly taken from the works of Jaubert and co-workers [5,10].

The group interaction parameters between mercury and CH_3, CH_2, C, CH_4 (methane), C_2H_6 (ethane), CH_{aro}, C_{aro}, N_2 (nitrogen) and CO_2 (carbon dioxide) were adjusted using the gathered solubility data and presented by Chapoy et al. through a Simplex algorithm using the objective function, OF, displayed in equation 11:

$$OF = \frac{1}{N}\sum_{1}^{Nexp}\left|\frac{x_{exp}-x_{cal}}{x_{exp}}\right| \quad (11)$$

Where x is the solubility of mercury, N is the number of data points. The adjusted A_{kl} and B_{kl} parameters are reported in Table 7~~Table 7~~ (classical binary interaction parameters for mercury are listed in the Appendix)

Table 6. Critical parameters, acentric factor and Mathias-Copeman [11] **adjusted parameters for mercury and other compounds.**

Compound	Tc/K[a]	Pc/ MPa[a]	ω[a]	c_1[b]	c_2[b]	c_3[b]
Mercury	**1735**	160.803	-	0.14738	-0.1564	0.133982
Methane	**190.56**	4.5592	0.01142	-	-	-
Ethane	**305.32**	4.8722	0.0995	-	-	-
Propane	**369.89**	4.2512	0.1521	-	-	-
2-methylpropane	**407.81**	3.629	0.1840	-	-	-
Butane	**425.13**	3.796	0.2010	-	-	-
2-methybutane	**460.35**	3.378	0.2274	-	-	-
Pentane	**469.70**	3.370	0.2510	-	-	-
Nitrogen	**126.19**	3.3958	0.0372	-	-	-
CO_2	**304.13**	7.3773	0.22394	-	-	-

[a] DIPPR801 [b] adjusted Mathias-Copeman parameters between 234.3 and 573.15 K [6]

Table 7. Group interaction parameters for Mercury: (A_{kl} = A_{lk})/MPa and (B_{kl} = B_{lk})/MPa

Group	A_{kl} / MPa	B_{kl} / MPa
CO_2	10502	12699
N_2	11555	11233
CH_4	10288	11315
C_2H_6	9989	8883
- CH3 -	10209	8597
- CH2 -	9647	9634
- CH -	9370	12433
- C -	8359	6629
- C_{aro} -	8474	4045
- CH_{aro} -	9391	9684

5. RESULTS AND DISCUSSIONS

Measurements have been carried out at about 243.15, 273.15, 298.15 and 323.15 K and pressures up to 20 MPa for three multicomponent synthetic systems: a light natural gas (MIX 1/ Table 2~~Table 2~~), a heavier natural gas (MIX 2/ **Table 3**) and a CO_2 rich fluid (MIX 3/ Table 4~~Table 4~~). The results are tabulated in Table 8~~Table 8~~, Table 9~~Table 9~~ and **Table 10**, respectively. Predictions of models are in good agreement with these independent data (independent from the model) as seen in *Figure 2*~~*Figure 2*~~, *Figure 3*~~*Figure 3*~~ and *Figure 4*~~*Figure 4*~~. The absolute deviations between the model predictions and the obtained experimental results are 8.2% for MIX 1, 7.9% for MIX 2 and 9.3% for MIX 3.

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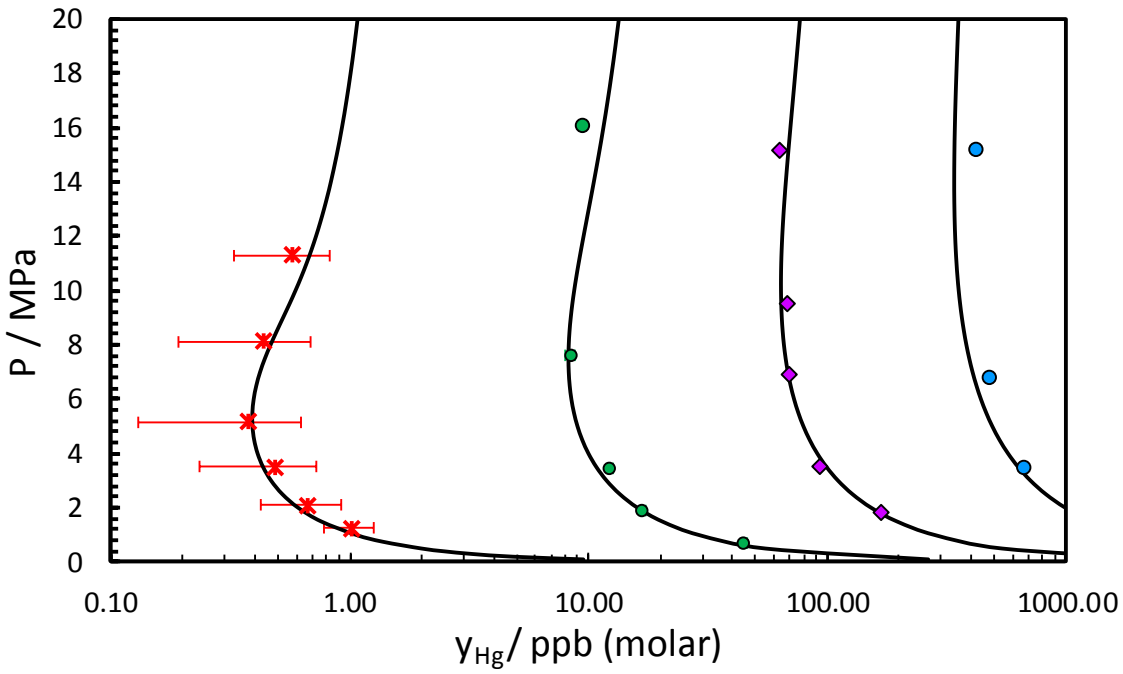

Figure 2. *Experimental and calculated mercury solubilities in MIX 1 at 243.15, 273.15, 298.15 and 323.15 K (✱): 243.15 K; (●): 273.15 K; (◆): 298.15 K; (●): 323.15 K; Black lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

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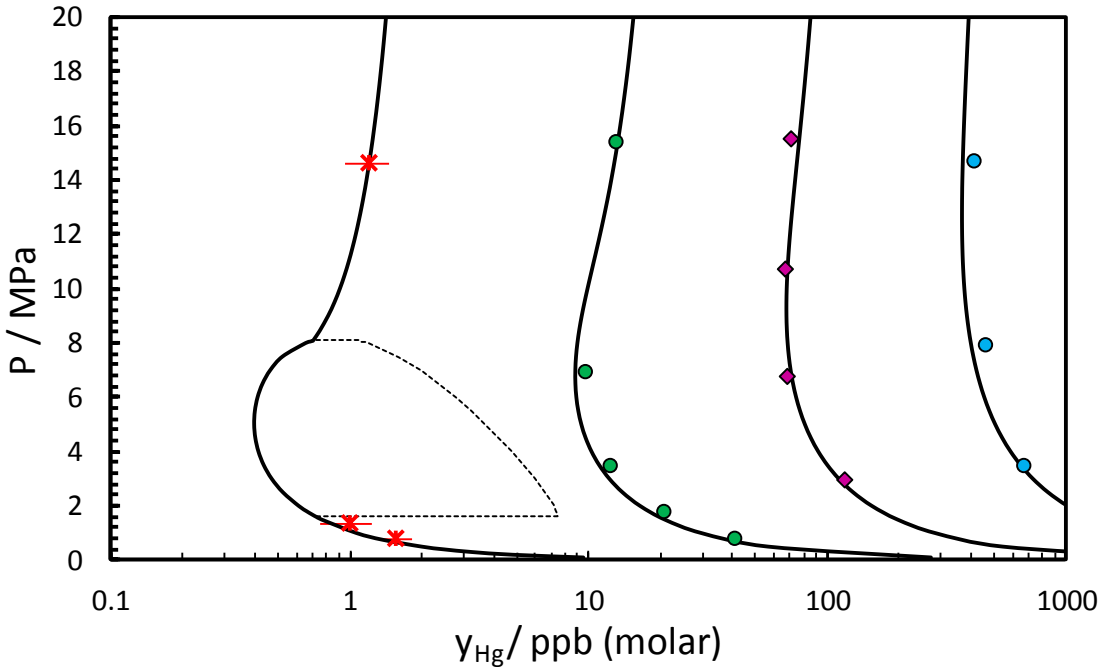

Figure 3. *Experimental and calculated mercury solubilities in MIX 2 at 243.15, 273.15, 298.15 and 323.15 K (✱): 243.15 K; (●): 273.15 K; (◆): 298.15 K; (●): 323.15 K; Black and dashed lines: PPR-78 with the k_{ij} calculated using the group contribution method (at 243.15 K between 1.6 and 8.1 MPa – 2 phases can coexist (dashed lines: mercury content in the liquid region)*

2

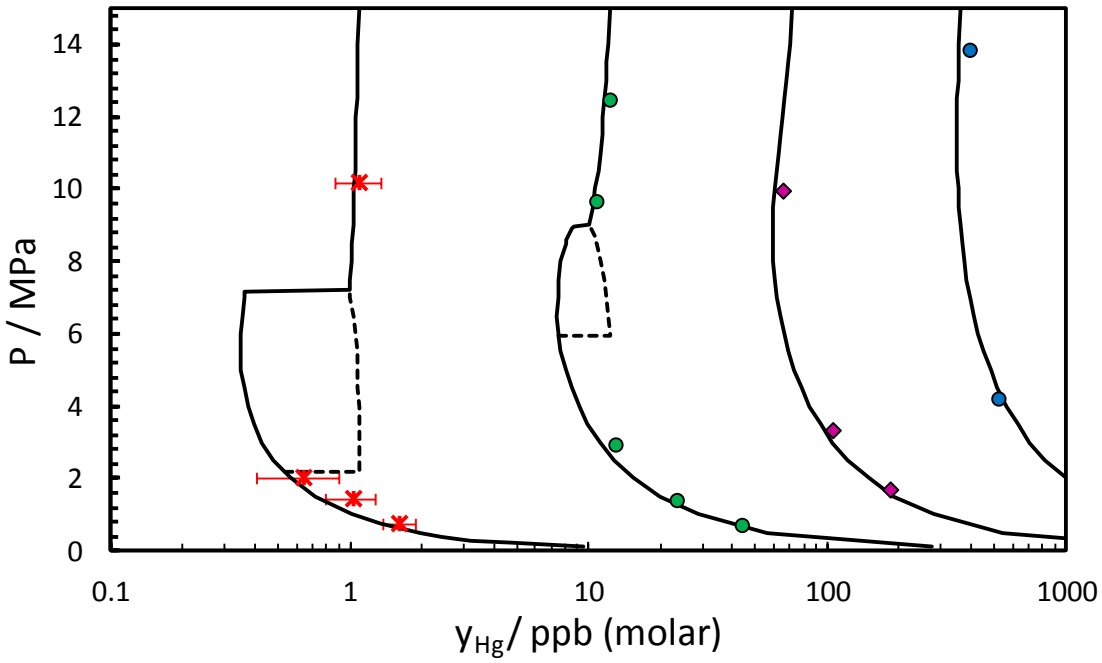

Figure 4. *Experimental and calculated mercury solubilities in MIX 3 at 243.15, 273.15, 298.15 and 323.15 (✱): 243.15 K; (●): 273.15 K; (◆): 298.15 K; (●): 323.15 K; Black and dashed lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

Table 8. Mercury solubility in MIX 1

Npts	T/ K	P/ MPa	yHg/ ppb	stdev	u_c(y)	*Phases*
1	243.15	1.23	1.02	0.01	0.25	V-L_{Hg}
2	243.15	2.06	0.67	0.01	0.25	V-L_{Hg}
3	243.15	3.49	0.48	0.01	0.25	V-L_{Hg}
4	243.15	5.17	0.38	0.00	0.25	V-L_{Hg}
5	243.15	8.14	0.44	0.01	0.25	V-L_{Hg}
6	243.17	11.31	0.57	0.01	0.25	V-L_{Hg}
7	273.15	0.68	44.89	0.18	0.95	V-L_{Hg}
8	273.19	1.90	16.86	0.31	0.52	V-L_{Hg}
9	273.19	3.46	12.30	0.14	0.38	V-L_{Hg}
10	273.19	7.63	8.38	0.28	0.41	V-L_{Hg}
11	273.18	16.06	9.49	0.07	0.32	V-L_{Hg}
12	298.28	1.83	168.53	0.84	3.84	V-L_{Hg}
13	298.28	3.54	94.07	0.65	2.20	V-L_{Hg}
14	298.28	6.88	69.57	0.18	1.57	V-L_{Hg}
15	298.28	9.54	67.78	0.67	1.66	V-L_{Hg}
16	298.28	15.17	62.93	0.11	1.42	V-L_{Hg}
17	323.14	3.45	674.45	0.83	13.52	V-L_{Hg}
18	323.14	6.77	479.54	0.48	9.61	V-L_{Hg}
19	323.14	15.17	420.33	2.90	8.90	V-L_{Hg}

Standard uncertainties are u(T) = 0.005K and u(P)=0.01 MPa; V: vapour; L: Liquid; L_{Hg}: liquid mercury
Stdev is the standard deviation.

u_c(y) is the combined standard uncertainty and defined as $u_c(y) = \sqrt{{u_{sys}}^2 + {u_{ca}}^2 + {u_{repeat}}^2}$
where u_{sys}, u_{ca}, and u_{repeat} stand for standard uncertainties of the system (device), the calibration procedure and reproducibility of the results, respectively.

Table 9. Mercury solubility in MIX 2

Npts	T/ K	P/ MPa	yHg/ ppb	stdev	u_c(y)	*Phases*
1	243.16	0.76	1.57	0.02	0.25	V-L_{Hg}
2	243.16	1.35	1.00	0.01	0.25	V-L_{Hg}
3	243.24	14.62	1.21	0.03	0.25	L-L_{Hg}
4	273.16	0.73	41.55	0.22	0.89	V-L_{Hg}
5	273.16	1.72	20.85	0.38	0.62	V-L_{Hg}
6	273.16	3.46	12.44	0.25	0.43	V-L_{Hg}
7	273.16	6.89	9.81	0.18	0.36	V-L_{Hg}
8	273.17	15.38	13.08	0.03	0.36	V-L_{Hg}
9	298.15	2.94	119.64	0.48	2.66	V-L_{Hg}
10	298.15	6.79	68.05	0.80	1.50	V-L_{Hg}

11	298.15	10.69	66.99	1.17	1.80	V-L_{Hg}
12	298.15	15.54	70.86	0.20	1.45	V-L_{Hg}
13	323.15	3.45	677.44	1.00	13.59	V-L_{Hg}
14	323.15	7.86	463.57	2.46	9.60	V-L_{Hg}
15	323.15	14.67	413.30	1.72	8.45	V-L_{Hg}

Standard uncertainties are u(T) = 0.005K and u(P)=0.01 MPa; V: vapour; L: Liquid; L_{Hg}: liquid mercury

Table 10. Mercury solubility in MIX 3

Npts	T/ K	P/ MPa	yHg/ ppb	stdev	u_c(y)	*Phases*
1	243.16	0.74	1.62	0.06	0.25	V-L_{Hg}
2	243.16	1.39	1.04	0.02	0.25	V-L_{Hg}
3	243.16	2.01	0.65	0.02	0.25	V-L_{Hg}
4	243.45	10.17	1.12	0.03	0.25	L-L_{Hg}
5	273.15	12.41	12.47	0.35	0.50	L-L_{Hg}
6	273.15	9.65	10.97	0.34	0.49	L-L_{Hg}
7	273.55	0.66	44.52	0.26	0.96	V-L_{Hg}
8	273.55	1.37	23.63	0.44	0.69	V-L_{Hg}
9	273.55	2.91	13.08	0.06	0.36	V-L_{Hg}
10	298.15	1.70	184.04	1.06	3.84	V-L_{Hg}
11	298.15	3.30	106.85	1.32	2.54	V-L_{Hg}
12	298.15	9.93	66.17	1.96	2.38	V-L_{Hg}
13	323.15	4.19	531.82	1.24	10.71	V-L_{Hg}
14	323.15	13.79	401.52	0.80	8.07	V-L_{Hg}

Standard uncertainties are u(T) = 0.005K and u(P)=0.01 MPa; V: vapour; L: Liquid; L_{Hg}: liquid mercury

Comparison

As seen in **Figures 5 to 8**, mercury solubility at the same pressure and temperature conditions is higher in liquid hydrocarbon than in vapour hydrocarbon and non-hydrocarbon gases. The following ranking in term of solubility can be established C_3H_8>C_2H_6>Natural Gas>CH_4>N_2 and with the solubility in CO_2 very close to N_2 in the vapour region and higher in the liquid region but significantly lower than in ethane. In general, for liquid hydrocarbons it can be observed that the mercury content is increasing with the carbon number. For the tested natural gas, at high pressure, the mercury content is the lowest for MIX 1, followed by the CO_2 rich fluid (MIX 3) and then heavier natural gas (MIX 2).

Predictions of the model were also compared to the only reference [7] in the open literature presenting solubility data in natural gas. Good agreement (***Figure 9*** ~~***Figure 9***~~) is observed at 268.15, 273.15 and 293.15 K between the model and the experimental data, however rather curiously deviations greater than 40% are observed at 283.15 K. Solubility data in mixtures of liquid hydrocarbon are limited to the data presented by Butala et al. [8] for a mixture of butane, pentane and hexane and a binary mixture of propane with 2-methylpropane. As seen in ***Figure 10*** ~~***Figure 10***~~, a close agreement between the model and the experimental results is observed.

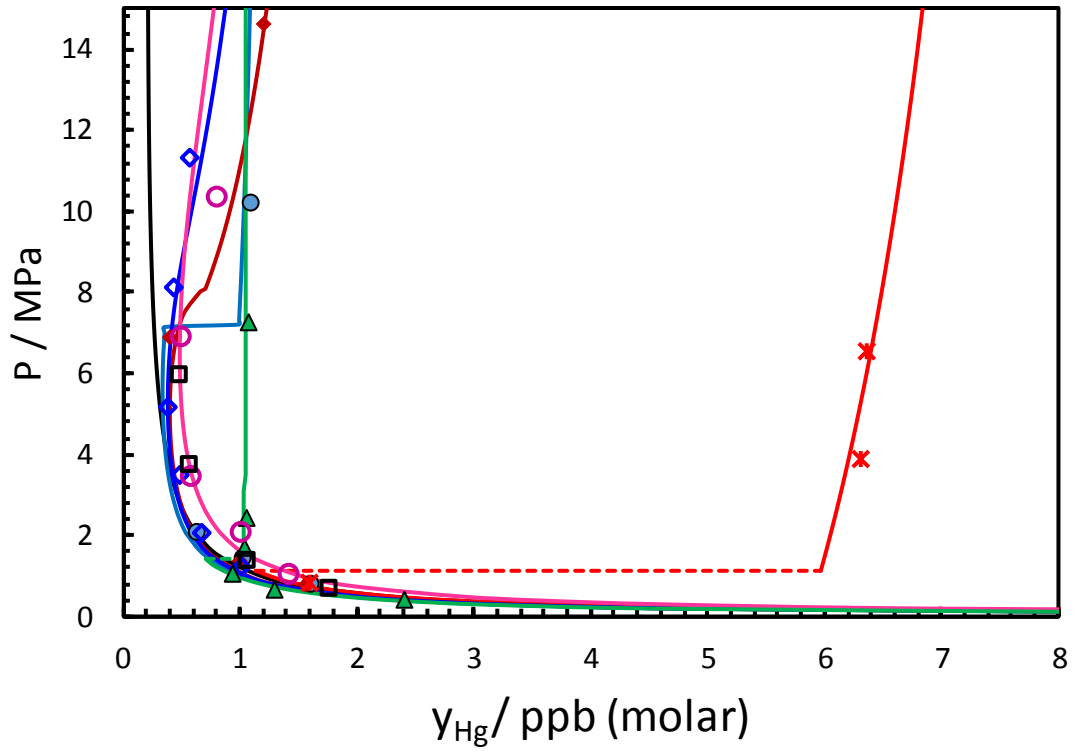

Figure 5. *Experimental and calculated mercury solubilities at 243.15 K ; Experimental data from this work and (◇): MIX 1; (◆): MIX 2; (●): MIX 3; (○): Methane ; (✱): Ethane ; (▲): Carbon dioxide ; (□): Nitrogen ; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

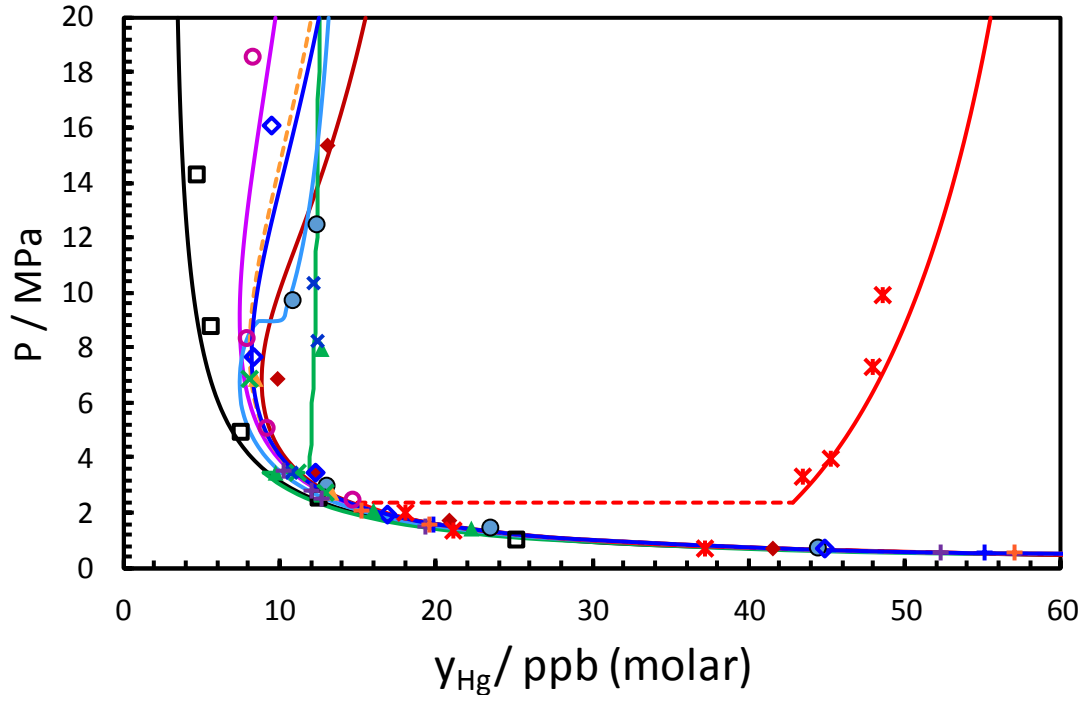

Figure 6. *Experimental and calculated mercury solubilities at 273.15 K ; Experimental data from this work and Chapoy et al.* [6]: *(◇): MIX 1; (◆): MIX 2; (●): MIX 3; (○): Methane ; (✱): Ethane ; (▲): Carbon dioxide ; (□): Nitrogen ; Experimental data from Yamada et al.* [12] *(✚): Methane; (✚): Ethane;*

(✚): Carbon dioxide; Experimental data from Butala et al. [8] *(✖): Methane; (✖): Carbon dioxide; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

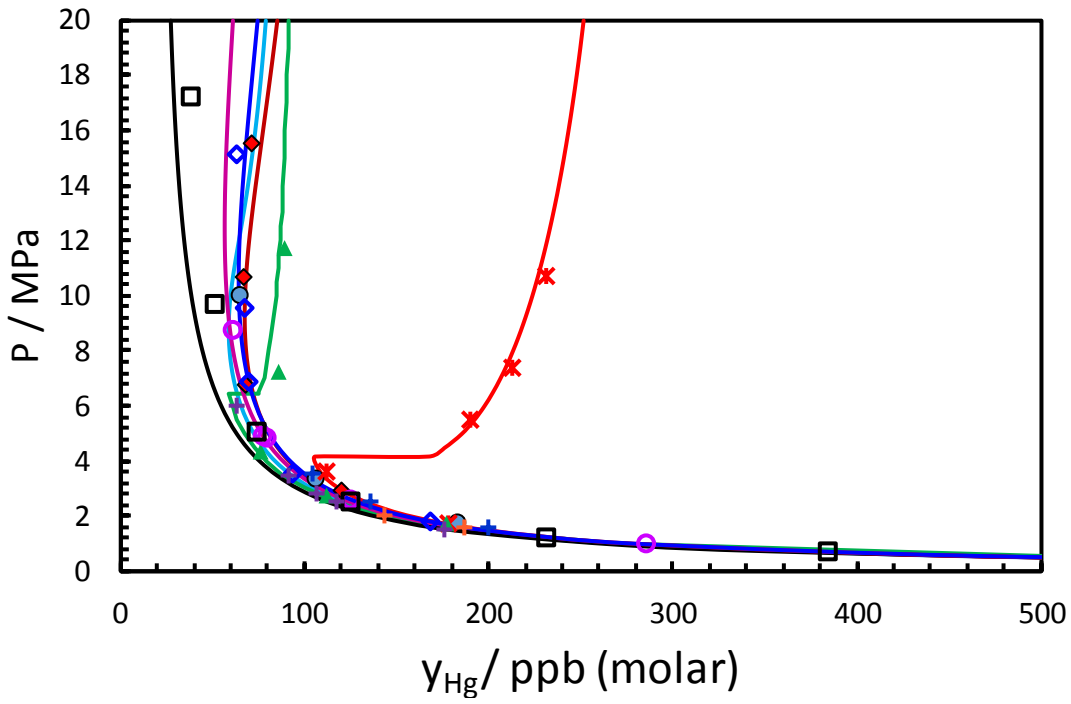

Figure 7. *Experimental and calculated mercury solubilities at 298.15 K ; Experimental data from this work and (◇): MIX 1; (◆): MIX 2; (●): MIX 3; (○): Methane ; (✱): Ethane ; (▲): Carbon dioxide ; (□): Nitrogen ; Experimental data from Yamada et al.* [12] *(✚): Methane; (✚): Ethane; (✚): Carbon dioxide; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

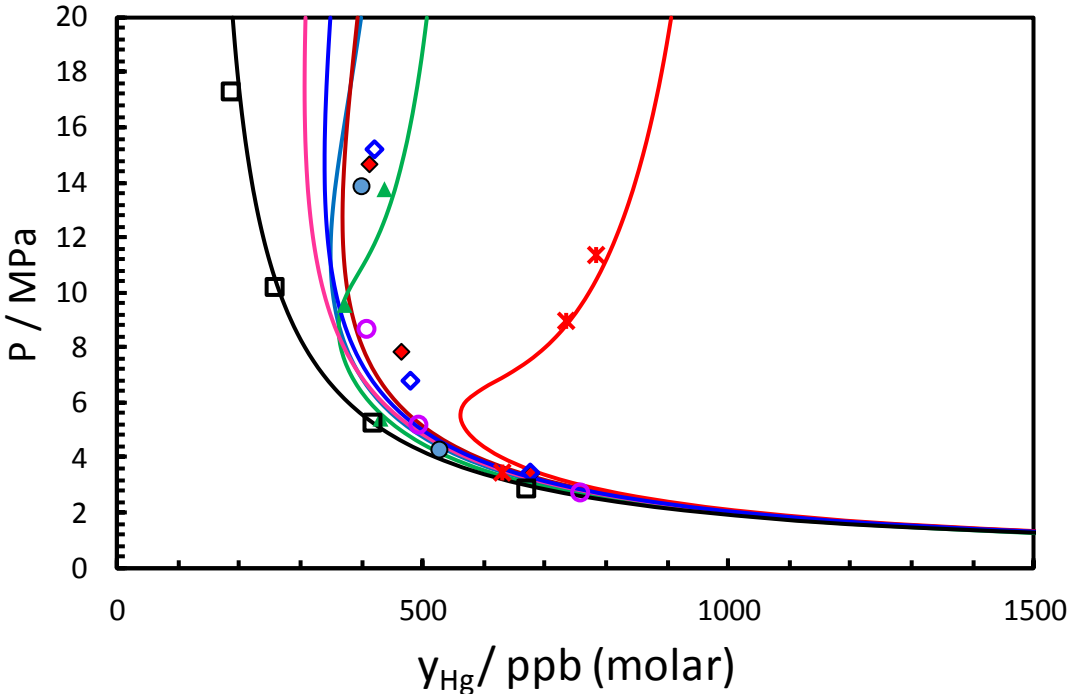

Figure 8. *Experimental and calculated mercury solubilities at 323.15 K ; Experimental data from this work and (◇): MIX 1; (○): MIX 2; (●): MIX 3; (○): Methane ; (✱): Ethane ; (▲): Carbon dioxide ; (□): Nitrogen ; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

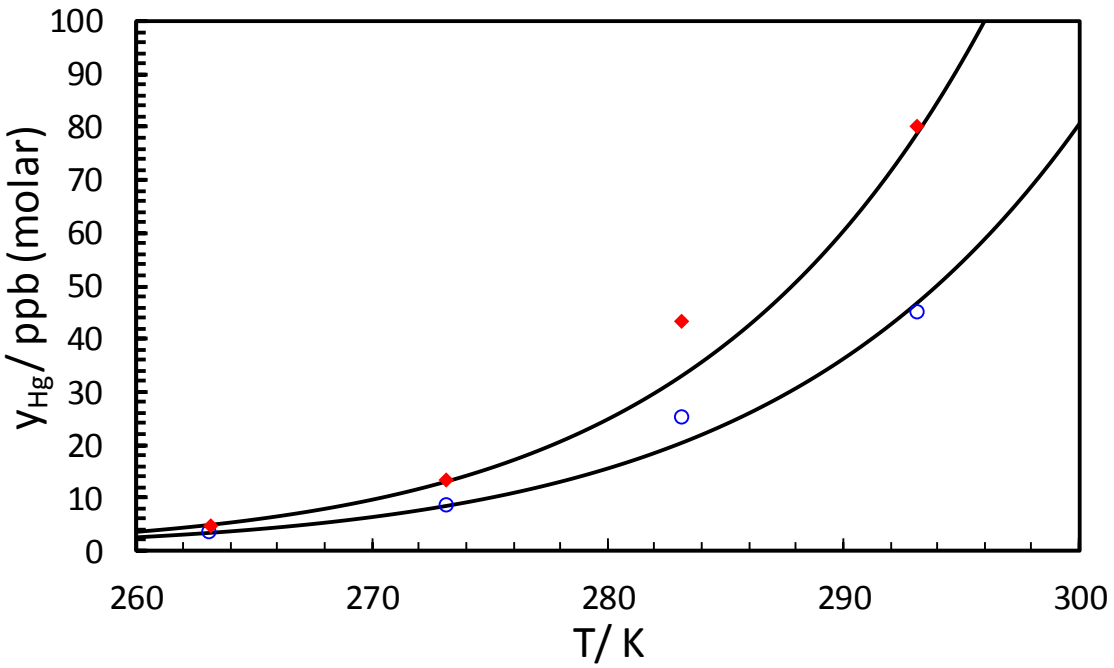

Figure 9. *Experimental and calculated mercury solubilities in a synthetic natural gas; Experimental data reported in* [7] *(◆): 2.76 MPa; (○): 6.89 MPa; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.*

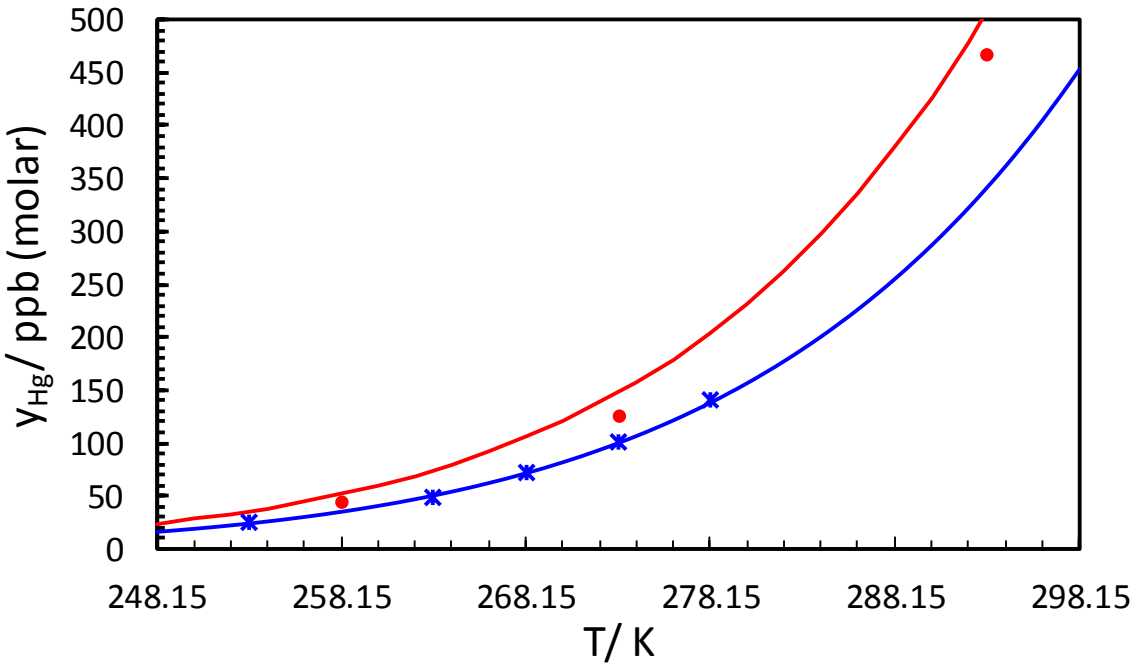

Figure 10. *Experimental and calculated mercury solubilities in mixtures of liquid hydrocarbons ; Experimental data reported in* [8] *(●): 0.324 (C4) + 0.335 (C5) + 0.341 (C6) at about 2 MPa; (✱):0.594*

(C3)+0.406 (i-C4) at 6.89 MPa; Lines: PPR-78 with the k_{ij} calculated using the group contribution method.

6. CONCLUSION

In this work, the mercury contents in three multicomponent fluids with methane content between (26 to 89) mole% have been measured over a wide range of pressure and temperature. Furthermore, the parameters of a simple group contribution model were optimized in order to predict the solubility of elemental mercury in hydrocarbon systems. The new parameters allow the calculations of binary interactions parameters between mercury and saturated hydrocarbons, aromatic compounds, nitrogen and carbon dioxide. A reasonable agreement was seen between experimental solubility measurements in multicomponent systems and model predictions.

ACKNOWLEDGMENTS

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APPENDIX

Binary Interaction Parameters for the PR-78 EoS

Table A.1. Adjusted kij and temperature range of regression for the PR78-EoS

Compound	k_0	k_1	k_2	Tmin / K	Tmax/K	Phase
CO_2	-1.2406	1.253E-02	-2.429E-05	243.15	323.15	L&SC
Nitrogen	0.2218	-	-	243.15	323.15	SC
Methane	0.1150	-	-	243.15	323.15	SC
Ethane	-0.0428	4.965E-04	-	253.15	323.15	L&SC
Propane	-0.1121	6.272E-04	-	233.15	343.15	L
n-pentane	0.0461	-	-	233.15	383.15	L
n-hexane	0.0115	-	-	273.15	336.15	L
n-heptane	-0.0088	-	-	273.15	313.15	L
n-octane	-0.0267	-	-	233.15	413.15	L
n-nonane	-0.0552	-	-	273.15	336.15	L
n-decane	-0.0771	-	-	273.15	318.15	L
n-dodecane	-0.1054	-	-	273.15	473.15	L
n-pentadecane	-0.1521	-	-	294	294	L
n-hexadecane	-0.2112	-	-	294	294	L
i-butane	0.0432	-	-	263.15	283.15	L
i-pentane	0.0356	-	-	298.15	298.15	L
Benzene	0.1024	-	-	273.15	313.15	L
Toluene	0.5031	-3.31E-03	6.6119E-06	298.15	298.15	L
Ethylbenzne	0.0279	-	-	298.15	298.15	L
o-xylene	0.0414	-	-	298.15	298.15	L
n-butane*	0.1093	-	-	258.15	293.15	L
n-butane†	0.0535	-	-	-	-	-

**Adjusted using n-butane + n-pentane + n-hexane ternary system from Butala et al.* [8]

†Estimated from Figure A.1.

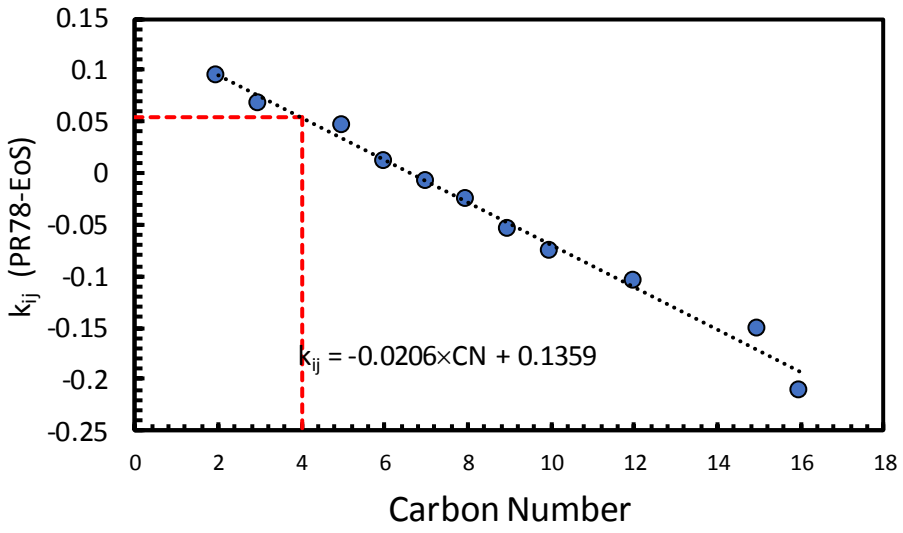

Figure A.1 Relation between k_{ij} (between mercury and n-alkanes) and carbon number (CN)