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Modelling of elemental mercury solubility in natural gas components

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ABSTRACT

Elemental mercury is a natural occurring trace component of fossil fuels, which poses significant health and safety risks during oil and gas processing due to its highly toxic and corrosive nature. In order to anticipate and control the distribution of mercury during industrial processes, there is a necessity for thermodynamic models, which can accurately predict its partitioning in the various phases. In this work, the UMR-PRU model is extended to systems that contain elemental mercury and is employed for predicting its solubility in hydrocarbons, compressed gases, water and methanol. A comparison is also made between UMR-PRU and the two most widely used equations of state, Soave-Redlich-Kwong and Peng-Robinson, with modified attractive terms. The results reveal that all three models can accurately describe the solubility of mercury in the aforementioned compounds, with UMR-PRU being the most accurate.

1. Introduction

Elemental mercury (Hg⁰) occurs naturally in traces in all fossil fuels, such as natural gas and crude oil [1–3]. Despite its very low concentration (a few ppb), mercury poses significant health & safety risks during oil and gas processing. Besides its highly toxic nature, mercury can cause catalyst poisoning and corrode the equipment through various mechanisms, such as Liquid Metal Embrittlement (LME) [4]. In fact, industrial accidents have been recorded in the past, which were caused by catastrophic failure of equipment due to mercury corrosion [2]. To mitigate the risks imposed by toxic volatile metals such as mercury to equipment integrity and worker health & safety [5], a tighter Hg management by the oil industry is imperative. In order to be able to predict and control its distribution during processing, it is necessary to have thermodynamic models that can accurately predict the phase equilibrium of Hg in oil & gas.

For the development of such models, reliable wide-range data on the solubility of Hg⁰ in the systems of interest are required. The systems of interest involve mainly hydrocarbons, inert gases and water, but also compounds that are used during natural gas processing, e.g. methanol used for hydrate inhibition. Unfortunately, a review of the relevant literature reveals that experimental data are scarce, while experimenters face some serious challenges when conducting Hg solubility measurements. Some of these challenges include loss of mercury through volatilization and/or adsorption on container walls, as well as mercury species interconversion due to oxidation and/or reaction with

the solvent or solvent impurities, all of which can alter the measured concentration of elemental mercury [6–9].

The main source of experimental mercury solubility data in the open literature was until recently IUPAC's Solubility Data Series [10], which is a compilation of mainly liquid-liquid equilibrium (LLE) measurements from different experimenters until 1987. Analyzing the results, the editors calculated new smoothed values for the solubility of mercury in the various compounds, which are designated as recommended by IUPAC. Despite its age, this source provides data for various solvents at a satisfactory temperature range.

More recently, Bloom & Gallup [8] presented some correlations for the solubility of Hg⁰ in various solvents, which were fitted to experimental data by the same authors. Miedaner et al. [11] also presented some Hg⁰ solubility measurements in hydrocarbons at high temperatures. Marsh et al. [12] and Gallup et al. [5] published studies on elemental mercury solubility in liquid hydrocarbons and polar solvents (i.e. water, alcohols, MEG, TEG) respectively, both covering a wide temperature range. Finally, some extra Hg⁰ solubility data in light hydrocarbons, hydrocarbon mixtures and inert gases, have been kindly provided by Equinor [13,14].

One of the challenges for any model that attempts to accurately describe the partitioning of Hg⁰ in natural gas systems is the correct prediction of its vapor pressure, which is abnormally high for its atomic weight. Also, mercury, like quantum fluids hydrogen or helium, has a negative acentric factor. For these reasons, when a cubic EoS is employed, a more complex temperature dependence for the attractive term

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Nomenclature		S	Solubility (mole fraction)
A_{nm}, B_{nm}, C_{nm}	UNIFAC binary interaction parameters between groups n and m	T	Absolute temperature (K)
AAD	Average absolute deviation	x_i	Mole fraction of component i
b	Co-volume parameter of a cubic EoS ($\text{cm}^3 \text{mol}^{-1}$)	<i>Greek letters</i>	
BIP	Binary interaction parameter	α	Attractive term parameter of a cubic EoS ($\text{bar cm}^6 \text{mol}^{-2}$)
c_1, c_2, c_3	Mathias-Copeman parameters	Ψ_{nm}	UNIFAC temperature-dependent interaction parameter between groups n and m
G	Molar Gibbs free energy (J/mol)	<i>Subscripts</i>	
k_{ij}	Binary interaction parameter for the vdW1f mixing rules	b	Boiling
L, M, N	Twu parameters	r	Reduced
MW	Molecular weight	exp	Experimental value
NDP	Number of experimental data points	calc	Calculated value
P^s	Vapor pressure (bar)		
Q_K	Relative van der Waals area		
R	Universal gas constant ($83.14 \text{ bar cm}^3 \text{mol}^{-1} \text{K}^{-1}$)		
R_K	Relative van der Waals volume		

(α) is employed or an adjusted to experimental vapor pressure data acentric factor is adopted for Hg^0 .

The majority of the thermodynamic models that have been proposed so far in the literature regarding prediction of Hg^0 phase behavior in hydrocarbon systems is based on the widely used Soave-Redlich-Kwong EoS [15]. Edmonds et al. [16] proposed the use of a modified version of SRK coupled with Infochem's proprietary mixing rule in order to model the partitioning of mercury and some of its compounds between gas and condensate phases, as well as liquid mercury dropout. The authors fitted model parameters to pure component vapor pressure data and utilized binary interaction parameters (k_{ij}) fitted to experimental solubility data. Khalifa et al. [17] proposed the use of SRK coupled with a group contribution method for estimating the binary interaction parameters in order to predict the solubility of mercury in normal alkanes, aromatics, water and alcohols. The authors also used an adjusted acentric factor for Hg, which was fitted to pure component vapor pressure data. Recently, Polishuk et al. [18,19] implemented a SAFT-type model (CP-PC-SAFT) attached by a universal k_{ij} value in order to predict phase behavior of metallic mercury in liquid and compressed gaseous hydrocarbons.

The van der Waals one fluid (vdW1f) mixing rules, which are commonly used to extend cubic EoSs to multicomponent systems, have been proven to perform poorly in polar and highly asymmetric mixtures. For this reason, more advanced mixing rules have been proposed, such as those derived by combining a cubic EoS with an excess Gibbs energy model (e.g. NRTL, UNIQUAC, UNIFAC).

In this study, the UMR-PRU EoS/ G^E model, which has been proven to accurately predict the dew points and liquid dropouts of natural gases and gas condensates [20–22], is extended to mixtures that contain elemental mercury and is employed for predicting the solubility of Hg^0 in hydrocarbons, compressed gases, water and methanol in binary and multicomponent systems. A comparison is also made between UMR-PRU and the two most widely used cubic EoSs, SRK [15] and Peng-Robinson [23], both attached by modified attractive terms.

2. Thermodynamic models

All models employed in this work have been extensively presented in the literature. In order to improve the accuracy of the vapor pressure prediction of Hg^0 , two alternatives to Soave's original expression for the attractive term are compared: for SRK the expression by Twu [24] is employed (Eq. (1)), and in this work the model from now on will be called SRK-Twu, while for PR the expression proposed by Mathias-Copeman [25] is used (Eq. (2)), and the model will be hereafter referred as PR-MC.

Table 1

Van der Waals volume (R_K) and area parameters (Q_K) employed in UNIFAC model.

Group	R_K	Q_K
Hg	10.598	8.739
CO_2	1.2960	1.261
N_2	0.9340	0.985
CH_4	1.1290	1.124
C_2H_6	1.8022	1.696
CH_3	0.9011	0.848
CH_2	0.6744	0.540
CH	0.4469	0.228
C	0.2195	0
b CH_3	0.9011	0.848
c CH_2	0.6744	0.540
cCH	0.4469	0.228
cC	0.2195	0
ACH	0.5313	0.400
AC CH_3	1.2663	0.968
H_2O	0.9200	1.400
MeOH	1.4311	1.432

Table 2

Calculated parameters of pure Hg^0 for Eqs. (1) and (2) for the attractive term of SRK and PR respectively and corresponding deviations in vapor pressure.

SRK-Twu		PR-MC			
AAD% ^a in P^s		AAD% in P^s			
L	0.09245	0.57	C1	0.1491	0.40
M	0.9784		C2	-0.1652	
N	2.244		C3	0.1447	

^a $AAD\% = 100/NDP \sum_{i=1}^{NDP} \text{abs}(P_{exp}^s - P_{calc}^s)/P_{exp}^s$, where P^s is the vapor pressure of pure Hg^0 and NDP is the number of experimental data points.

$$a(T) = T_r^{N(M-1)} \exp[L(1-T_r^{NM})] \quad (1)$$

$$a(T) = \begin{cases} [1 + c_1(1-T_r^{0.5}) + c_2(1-T_r^{0.5})^2 + c_3(1-T_r^{0.5})^3]^2, & T_r \leq 1 \\ [1 + c_1(1-T_r^{0.5})]^2, & T_r > 1 \end{cases} \quad (2)$$

For SRK-Twu the L, M, N parameters for Hg^0 were estimated in this work, while for the rest of the components the generalized correlations proposed by Twu et al. [24] have been used. For PR-MC, the c_1, c_2, c_3 parameters for Hg^0 were determined in this work similarly to SRK-Twu, and for the rest of the components the values were obtained from the study by Hernández-Garduza et al. [26]. Both SRK-Twu and PR-MC utilize the vdW1f mixing rules (Eqs. (3) and (4)) with a single binary interaction parameter (k_{ij}), which is fitted to binary VLE or LLE data.

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