



Predicting phase behavior of metallic mercury in liquid and compressed gaseous hydrocarbons



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ABSTRACT

This study presents the first predictive approach for estimating phase behavior of metallic mercury in hydrocarbons and compressed gases. This approach is based on the recently developed CP-PC-SAFT EoS attached by a universal value of $k_{12} = 0.3$. The CP method of solving SAFT parameters is not applicable for metallic mercury. Therefore it has been treated as a monoatomic substance, while σ and ϵ/k have been adjusted to the experimental vapor pressure and density data. It has been demonstrated that the proposed approach accurately predicts the solubility enhancement of metallic mercury in the compressed gases up to ~ 400 bar. The solubility data in liquid *n*-alkanes, aromatic and oxygenated hydrocarbons in wide range of temperatures have been truthfully estimated as well. The available binary diffusion coefficients of mercury in gases can also be accurately predicted by the Chapman–Enskog model when applied with the model's molecular parameters. This study also shows that the analogous implementation of the original version of PC-SAFT results in a slightly lesser over-all accuracy, which could probably be attributed to the not entirely systematic practice of evaluating its molecular parameters for various hydrocarbons. A doubtless advantage of both considered versions of PC-SAFT over Peng–Robinson EoS is demonstrated as well.

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1. Introduction

Modern fossil fuels exploration progressively involves drilling into deep Earth's layers, which increases the probability of encountering elevated amounts of mercury in natural gas and crude oil [1–4]. Mercury often appears in particulate and colloidal forms, which can be removed by filtration. In addition, some of its forms are dissolved and require advanced detection and separation methods [1,2,5–8]. Various species of mercury exhibit dissimilar chemical and physical behaviors, which are inter alia expressed by their divergent toxicity, stability and solubility in different matrices. In particular, metallic mercury has a significantly smaller solubility in hydrocarbons in comparison to its organic compounds and halides. At the same time, the metallic state is often the main form of mercury in many hydrocarbon media, such as the natural gas. Often the amount of metallic mercury absorbed by these media at the high temperatures and pressures characteristic for the deep Earth's layers [9] substantially exceeds its equilibria concentrations at the ambient conditions. This phenomenon results in

formation of metallic mercury micro-droplets, which can become the predominant state of this substance at the typical process temperatures and pressures [1]. Presence of metallic mercury leads to toxicological threats, catalysts poisoning and the corrosion produced by liquid metal embrittlement, which may result in critical damages to process equipment [10–12], and even tragic consequences [13].

The reliable information on solubility and diffusion of metallic mercury in hydrocarbons in a wide range of pressures and temperatures is crucial for appropriate design and optimization of its removal equipment. Unfortunately, the pertinent experimental data are scarce. In particular, data are unavailable for the main components of natural gas, such as methane and ethane. At the same time, some references [14–16] have reported a pressure dependence of the metallic mercury concentration in compressed propane, *n*-butane and argon above 184 °C. In addition, Jepson et al. [14] have published two values of the binary diffusion coefficient of mercury in propane and *n*-butane at $T = 256$ °C and $P \sim 12$ bar. Marceca et al. [17] have reported the equilibria ratio between the partial molar densities of metallic mercury's vapor and the densities of compressed argon at 323 and 371 K. These data might shed light on its phase behavior in compressed

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methane and ethane. Concentration enhancement of metallic mercury in additional gases, such as nitrogen, has been summarized by Haar and Levelt Sengers [18], unfortunately, without reporting the numerical values. The binary diffusion coefficients of metallic mercury in several gases at the atmospheric pressure have been published by Gardner et al. [19]. Solubility measurements of metallic mercury in heavier liquid hydrocarbons around ambient conditions performed up to 1987 have been summarized by Clever [20]. Exponential expressions fitted to the measurements performed up to 65 °C have been recently published by Bloom and Gallup [21]. Solubility data at the high temperatures relevant for deep geological formations reported by Miedaner et al. [22] present particular importance as well.

The paucity of the experimental information on phase behavior of metallic mercury in hydrocarbons outlines the prominence of development reliable methods for predicting these data in a wide range of conditions. Thus far, several companies have developed simulators for modeling the phase equilibria of mercury and its compounds in oil and gas systems. However, the underlying assumptions and the development methodology are largely proprietary information. At the same time, several attempts of modeling the data are available in the open literature. In their pioneering works, Jepson and Rowlinson [23] and Haar and Levelt Sengers [18] have discussed aspects of applying the modified virial and van der Waals Equations of State (EoS) for qualitative modeling of mercury's concentration enhancement in compressed gases. More recently, Edmonds et al. [24] and Mentzelos [25] have implemented the modified Redlich–Kwong–Soave and Peng–Robinson EoSs for correlating the solubility data in liquid hydrocarbons around the ambient conditions. It has been found that different values of the binary adjustable parameter k_{12} are required for quantitative fitting of the data for particular binary systems and even temperatures [25]. Although empirical methods for further generalizing a variety of the k_{12} values can be developed, implementation of this practice is questionable at high temperatures and pressures outside the fitting range. Moreover, doubtful results could be obtained for systems that so-far have not been investigated experimentally and for multi-compound mixtures. Consequently, quantitative and simultaneous predictions of the phase behavior of metallic mercury in liquid hydrocarbons and compressed gases in the entire range of conditions while using a single value of k_{12} for large variety of systems should doubtlessly be considered as an important progress.

This study evaluates the likelihood of achieving this progress by implementing three models. The first one is the recently developed Critical Point-based Perturbed-Chain Statistical Association Fluid

[38], and their mixtures. A second model considered in this study is the original version of PC-SAFT [39]. A third model is the EoS of Peng–Robinson attached by a Mathias–Copeman temperature dependence, as proposed by Mentzelos [25]. In addition, this study assesses the possibility of predicting another practically important property, namely the binary diffusion coefficients of elementary mercury in gases on the basis of the molecular parameters of CP-PC-SAFT and PC-SAFT. The details of CP-PC-SAFT EoS are given below.

2. Theory

Similarly to other SAFT approaches, CP-PC-SAFT [26] is expressed as a sum of hard sphere, chain and dispersion contributions to the residual Helmholtz energy:

$$A^{res} = A^{HS} + A^{chain} + A^{disp} \quad (1)$$

The hard sphere contribution is:

$$A^{HS} = RT \frac{m}{\zeta_0} \left(\frac{3\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3} - \zeta_0 \right) \ln[1 - \zeta_3] \right) \times \sqrt{\frac{d^3(\zeta_3 - 1)}{\zeta_3 \sigma^3 - d^3}} \quad (2)$$

where m is the number of segments, σ is the segment diameter (Å), ε/k segment energy parameter divided by Boltzmann's constant (K), $d = \sigma\theta$, and θ (dimensionless) is:

$$\theta = \frac{1 + 0.2977(k/\varepsilon)T}{1 + 0.33163(k/\varepsilon)T + 0.0010477(k/\varepsilon)^2 T^2} \quad (3)$$

ζ_k are given by:

$$\zeta_k = \frac{\pi N_{av}}{6v} \sum_i x_i m_{ii} d_{ii}^k \quad (4)$$

where N_{av} is the Avogadro's number and x is the mole fraction. The chain contribution is:

$$A^{chain} = RT \sum_{ij} x_i x_j (1 - m_{ij}) \ln [g_{ij}(d_{ij})^{hs}] \quad (5)$$

where $g_{ij}(d_{ij})^{hs}$ is the segment radial distribution function given as:

$$g_{ij}(d_{ij})^{hs} = \frac{1}{1 - \zeta_3} + \frac{3d_{ii}d_{jj}\zeta_2}{(d_{ii} + d_{jj})(1 - \zeta_3)^2} + 2 \left(\frac{d_{ii}d_{jj}}{d_{ii} + d_{jj}} \right)^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3} \quad (6)$$

The dispersion contribution is:

$$A^{disp} = -RN_{av} \left(\frac{2\pi(\varepsilon/k)m^2\sigma^3}{v} I_1 + \frac{\pi(\varepsilon/k)^2 m^3 \sigma^3}{vT \left(1 + m \frac{8\zeta_3 - 2\zeta_3^2}{(1 - \zeta_3)^4} + (1 - m) \frac{20\zeta_3 - 27\zeta_3^2 + 12\zeta_3^3 - 2\zeta_3^4}{((1 - \zeta_3)(2 - \zeta_3))^2} \right)} I_2 \right) \quad (7)$$

Theory (CP-PC-SAFT) [26]. The rationale of this approach is replacing the non-transparent fitting procedures of the SAFT's substance-dependent parameters by their standardized numerical solution at the characteristic states, namely the pure compound critical and triple points. Additionally, it has aimed at removal of undesired numerical problems affecting several versions of SAFT [27–33]. So far, CP-PC-SAFT has been implemented for predicting various thermodynamic properties of light compounds, n -alkanes and 1-alkenes [26], 1-alkanols [34], aromatic and haloaromatic compounds [35], some haloalkanes [36,37], oxygenated compounds

In Eq. (7) I_1 and I_2 are the analytical functions representing the integrals of the radial distribution function in 1st and 2nd order perturbation terms:

$$I_1 = \sum_{i=0}^{i=6} \left(a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m} \frac{m-2}{m} a_{2i} \right) \zeta_3^i \quad (8)$$

$$I_2 = \sum_{i=0}^{i=6} \left(b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m} \frac{m-2}{m} b_{2i} \right) \zeta_3^i \quad (9)$$

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