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Fluid Phase Equilibria

A group contribution method for predicting the solubility of mercury

Mansour Khalifa[*], Leo Lue

Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom

ABSTRACT

Mercury is a toxic and corrosive element, and understanding its partitioning within ecosystems and industrial processes is of vital importance. The solubility of mercury in normal alkanes, aromatics, water and alcohols is predicted using widely used Soave-Redlich-Kwong equation of state in combination with a group contribution method to estimate binary interaction parameters. The interaction parameters between elemental mercury and seven other molecular groups were determined in this work by fitting available solubility data for mercury. The solubility in the studied solvents was accurately described. This work allows the prediction of the thermodynamic behavior of elemental mercury in a wide variety of solvents, solvent mixtures, and operating conditions where experimental data are unavailable.

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1. Introduction

Mercury occurs naturally in the environment and can be found in soil, air, and water. Due to its toxicity and accumulative nature, it is considered a highly dangerous element [1—3]. The sources of mercury in the biosphere can be divided into natural and anthropogenic sources. Both are considered to be equally important causes of mercury accumulation in the environment. Natural sources include volcanic activity, erosion of terrain, and dissolution of mercury minerals in the oceans, lakes and rivers [4]. Anthropogenic sources include cement manufacturing, paper milling, the combustion of coal, oil, and gas as fuel to generate power, flared gas from onshore and offshore oil and gas platforms, and produced water discharged from oil and gas processing facilities, refineries and chemical plants [5—7].

In addition to its contribution to environmental pollution, mercury has a negative impact on the production and processing of oil and gas. As mercury is present in many major oil fields, maintenance and operation teams can be exposed to this highly dangerous element on a daily basis. Activities that expose workers to mercury include equipment cleaning, oil sampling, vessel and tank inspections and hot work activities on restricted areas. The risks are proportional to the concentration of mercury in the process facilities [8]. Mercury not only poses health risks, it is also

corrosive and can cause equipment degradation and damage, catalyst poisoning, etc. [9]. It has an ability to accumulate on primary and secondary process treatment units (e.g., amine units, glycol units, cryogenic units and heat exchangers), eventually causing process failure [8].

In general, there are three ways to avoid mercury emissions from industrial sources to the environment: preventive measures, primary control measures and secondary control measures. Preventive measures can be achieved only if the source of emissions is prevented; this means fuel substitution, such as use of renewable energy or biofuels instead of mercury containing energy sources. However, this option is not popular as oil and gas are still the main source of energy. In primary control measures, Hg emissions are still generated but reduced to a certain value. In secondary control measures, Hg emissions exist but are removed later from exhaust gases [10]. The selection of the best measures requires a good understanding of the behavior of mercury and its pathways through the process and the environment. Consequently, mercury exposure risks can be mitigated by determining the concentration and understanding the exposure pathways in work locations and adopting effective health and safety policies and procedures accordingly. Understanding mercury pathways in industrial processes and the ecosystem requires knowledge of the thermodynamic behavior of mercury and its interactions with other compounds, such as process fluids (e.g., water, hydrocarbon mixtures, etc.).

Many physical properties of mercury, such as density, thermal expansion and compressibility as a function of temperature and pressure have been measured [11]. Vapor pressure is one of the

* Corresponding author.
  E-mail addresses: khalifa.manssor@strath.ac.uk (M. Khalifa), leo.lue@strath.ac.uk (L. Lue).

most important properties, as it indicates the state of mercury and its concentration in vapor, liquid, and solid phases. Several experimental measurements and correlations have been published for the calculation of mercury vapor pressure over wide range of temperatures [12,13].

Predicting the solubility of mercury in liquids and gases gives an indication of mercury pathways from one phase to another. Accurate prediction of mercury solubility plays an important role in developing a risk mitigation strategy. In general, however, the available experimental data are limited, in part, due to the difficulty in working with mercury. Experiments involving mercury can be time consuming and costly, and it is difficult to anticipate the wide range of process conditions and fluids that may be encountered.

In situations where experimental data are unavailable, predictive methods are required. A competitive model should be computationally inexpensive to evaluate and require minimal parameterization [14]. One powerful method is molecular simulation, which requires force fields to be parameterized between all species in the solution. This work has been focused particularly on systems containing elemental mercury [15] and some mercury compounds [15,16] in water. While these methods offer the possibility of predicting thermodynamic properties of system containing mercury, they are computationally intensive and not suitable for use in process scale simulations (e.g., in a refinery).

Another approach is to use thermodynamic models, such as an equations of state (EOS) or an activity coefficient model [17]. These models have been successfully used for the estimation of physical and chemical properties of pure and multicomponent systems. The selection of a model depends on its capability of estimating the required physical and chemical properties, and predicting the phase behavior of a specific system where experimental data are unavailable. Equations of state, such as cubic equations of state or the perturbed-chain statistical associating fluid theory (PCSAFT), are characterized by their simplicity, reliability and robustness over a wide range of conditions (e.g., high pressures), and speed of computation [18]. Therefore, they are the model of choice for many multicomponent systems and are widely used for practical applications.

A recent study used PCSAFT to describe the phase behavior of elemental mercury in liquid and compressed hydrocarbon gases [19]. While this approach works well, it requires fitting binary interaction parameters k_{ij} between mercury and the specific solvents being modeled to existing experimental measurements. Properly accounting for the interactions between molecules is vital to the accurate prediction of mixture properties. Within the context of equations of state, this is typically achieved by introducing the binary interaction parameter k_{ij} between different molecular species; k_{ij} is normally used as a fitting parameter that is adjusted to minimize the differences between the calculated and experimentally measured system properties, such as VLE, LLE, density, and solubility. This limits its usage to solvents where measurements with mercury exist.

One approach developed in order to overcome this issue is the group contribution method (GCM). In the GCM, molecules are subdivided into a series of groups which consist of individual atoms or collections of atoms [20]. The binary interaction parameters between two molecules is then given as the sum of the interaction parameters between the various pairs of groups on each of the molecules. This allows the prediction of k_{ij} for a large number of compounds where experimental data are unavailable and at operating conditions outside the range of measurements.

In this work, we parameterize a group contribution method to estimate the binary mixing parameters for the Soave-Redlich-Kwong (SRK) equation of state to the estimation of the thermodynamic properties of elemental mercury in mixtures of water,

alkanes, aromatics, and alcohols. The SRK EOS is used in this work because of its simplicity, computational efficiency, and ability to predict vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) at high and low pressures. The k_{ij} of elemental mercury was predicted using the GCM developed by Peneloux and co-workers [20]. This has the advantage that the group interaction parameters already exist [21–23] for the SRK EOS for a wide range of molecular groups, and so the method can be immediately used in practical calculations. Combined with a group contribution method, the SRK EOS allows the prediction of mercury solubility and partitioning between phases.

In the next section, we briefly review the SRK EOS and its application to mixtures. We then present the group contribution method that is used to predict the binary interaction parameters required by the equation of state. In Section 3, this theory is compared against experimental measurements for the solubility of mercury in water, *n*-alkanes, aromatic solvents, and alcohols. Finally, the main points of this paper are summarized in Section 4, and directions for future work are discussed.

2. Methodology

The SRK EOS is a modification of a cubic equation of state proposed by Redlich and Kwong [24] developed by Soave [25] by studying the behavior of pure compounds:

$$p = \frac{\rho RT}{1 - \rho b} - \frac{a\rho^2}{(1 + \rho b)} \tag{1}$$

where p is the system pressure, T is the absolute temperature, and R is the universal gas constant, ρ is the molar density of the system, and a and b are parameters of the model. The first term of Eq. (1) corresponds to the repulsive force and the second term corresponds to the attraction force. The parameters a_i and b_i for a pure component i can be expressed in terms of its critical temperature T_{ci} and critical pressure p_{ci}

$$a_i = 0.42747 \frac{R^2 T_{ci}^2}{p_{ci}} \alpha_i(T) \tag{2}$$

$$\alpha_i(T) = \left[1 + \left(0.480 + 1.57\omega_i - 0.176\omega_i^2 \right) \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2 \tag{3}$$

$$b_i = 0.08664 \frac{R T_{ci}^2}{p_{ci}} \tag{4}$$

where ω_i is the acentric factor for component i, introduced by Pitzer [17].

To extend the SRK EOS to multi-component systems, mixing rules are required to obtain the parameters a and b for the solution from the a_i's and b_i's from the individual pure components. Many mixing rules have been proposed for cubic EOS [26,27]. In this work, we use the van der Waals mixing rules, which are given by

$$a = \sum_{ij} x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \tag{5}$$

$$b = \sum_i x_i b_i \tag{6}$$

where k_{ij} in Eq. (5) is the binary interaction parameter, x_i is the mole fraction of component i in the mixture, and a_i and b_i are calculated from Eqs. (2) and (4).