

Redlich–Kwong equation of state for modelling the solubility of methane in water over a wide range of pressures and temperatures



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ABSTRACT

A thorough approach to the environmental and technological issues regarding natural gas extraction from underground and underwater reserves requires a very good understanding of the phase equilibrium between hydrocarbon gas and water. In this work we present an accessible way to predict methane–water phase equilibrium. For this purpose we selected from the literature experimental data for the solubility of methane in water, covering a large range of temperature (274.35 K–627.15 K) and pressure (0.57 MPa–197.26 MPa). Mathematical modelling was performed using the online available modelling tool Phase Equilibria, 2000 (PE2000) and applying the Redlich–Kwong equation of state. To best fit the calculated solubility to the experimental values, we estimated the binary interaction coefficient by data regression, and we used the results to verify the consistency of the experimental data. The binary interaction coefficient is dependent of temperature, and this connection can be quantified and further used to estimate the phase equilibrium at the needed conditions.

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1. Introduction

Detailed information about the solubility of methane in water is important both from environmental and technological point of view. Methane may be encountered in the nature as a hydrate at conditions of high pressure and low temperature, such as in the permafrost or in the sedimentary layers of the ocean floor [1]. Once submitted to higher temperatures, the solid hydrate will separate into methane gas and water, and one challenge facing the commercial exploitation of the hydrate reserves is the technology for gas separation and recovery. Moreover, as methane is one of the primary greenhouse gases, it is imperative to minimise its accidental release into the atmosphere during exploitation of underground or underwater reserves. Another major problem is represented by groundwater contamination with hydrocarbons, following unconventional shale gas exploitation and hydraulic fracturing [2]. Waste and wastewater treatment by bacterial digestion [3] or by unconventional methods such as high pressure water reforming [4] may also generate methane–water mixtures, and the separation and recovery of methane represents an

important technological step. A thorough approach to these environmental and technological issues requires a very good understanding of the phase equilibrium between hydrocarbon gas and water, and of the effect of temperature and pressure on the behaviour of the binary mixture.

The first study of the solubility of methane in water, at atmospheric pressure, was conducted by Bunsen in 1855 [5]. In 1931 Frolich et al. [6] reported the first data for high pressure solubility of methane in water. Since then, many studies have been performed, covering a wide range of temperatures and pressures [7–15]. Moreover, the studies were extended to systems containing the solid hydrate [16], gas mixtures with other hydrocarbons [15], or solubility in salt solutions [17], in order to better simulate the conditions in which methane is usually encountered in nature.

A number of studies were also concerned with modelling the methane–water phase equilibria, in order to identify ways of predicting the behaviour of the systems without the need of expensive and time consuming laboratory measurements. Equations of state (EOS) such as Cubic Plus Association (CPA) [18,19], Perturbation Chain Statistical Association Fluid Theory (PC SAFT) [19], Soave–Redlich–Kwong (SRK) [20,21], Peng–Robinson [20], Kabadi–Danner [20], Lee–Kesler–Plocker [20], Patel–Teja [15], or Nasrifar–Bolland [22] have been successfully applied, the calculated values for the phase equilibrium being in good agreement

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with the experimental ones. However, these studies were either performed over a limited range of temperatures and pressures, or they involved a reduced number of experimental data and complex mathematical calculations. Therefore there is still a need of finding a fast and reliable method of predicting the behaviour of the gas–water system at the precise conditions encountered in a natural environment or during a technological step.

In this work we present an accessible way to predict methane–water phase equilibrium for conditions of temperature and pressure at which experimental data are not available. For this purpose we selected from the literature nine sets of experimental data for the solubility of methane in water. The selection was made with the purpose of choosing data that would cover a wide time-span (over 50 years) of investigations of the methane/water phase equilibria over a large range of temperature (274.35 K–627.15 K) and pressure (0.57 MPa–197.26 MPa), involving various measuring methods (static analytic method, pressure drop method etc.). We performed mathematical modelling for all chosen data, using the online available modelling tool Phase Equilibria, 2000 (PE2000) and applying the Redlich–Kwong EOS. We estimated the binary interaction coefficient by data regression, and we used the modelling results to verify the consistency of the experimental data. The binary interaction coefficient is dependent of temperatures, and this connection can be quantified and further used to estimate the phase equilibrium at the needed conditions.

2. Modelling the solubility of methane in water

The online available modelling tool PE2000 was employed for thermodynamic calculations. A number of equations of state and mixing rules, which can be used for describing a wide range of systems, are already implemented in the PE2000 program package [23]. For the purpose of this work we applied most built-in EOS recommended for gas–liquid phase equilibria (van der Waals, Peng–Robinson, Soave–Redlich–Kwong etc.), with the aim of obtaining the best fit with the experimental data available in the literature. Finally, we chose Redlich–Kwong EOS as the mathematical model offering the best results.

Redlich–Kwong EOS is an empirical equation that relates temperature, pressure and volume of gases. It was formulated by Otto Redlich and Joseph Neng Shun Kwong in 1949 [24] and is a modification of the van-der-Waals EOS. The EOS is expressed as:

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (1)$$

where P represents pressure, R is the gas constant, T is temperature, V is the molar volume, and a and b are pure component parameters.

In order to extend the Redlich–Kwong EOS to mixtures, a mixing rule has to be applied for calculation of the mixture parameters, a_m and b_m . As already mentioned, the PE2000 program package contains a range of mixing rules, which were tested in this work with the purpose of identifying the optimum EOS-mixing rule combination. Moreover, the Redlich–Kwong EOS pure component parameters a and b for methane and water are also available in the database of the software. In a previous study [25] we applied the Adachi–Sugie mixing rule during mathematical modelling of phase equilibria for the carbon monoxide–water system. The justification for our choice was the nature of the studied system. As our binary system included water which is strongly polar a conventional mixing rule would not offer reasonable results, especially under the high-pressure, high-temperature conditions employed. Likewise, in the present study we obtained the best results by combining the Redlich–Kwong EOS with the Adachi–Sugie mixing rule. Non-empirical mixing rules, such as the quadratic one, were also

tested, but they did not give satisfactory results, or the calculations did not converge. The Adachi–Sugie mixing rule was developed in 1986 by Yoshinori Adachi and Hidezumi Sugie as a modification of the Redlich–Kister mixing rule [26] and has the following expression:

$$a_m = \sum x_i a_i + \sum \sum x_i x_j [A + B(x_i - x_j) + C(x_i - x_j)^2 + D(x_i - x_j)^3] \quad (2)$$

where x_i and x_j represent the molar fraction of component i and j , respectively; A , B , C and D are parameters in Redlich–Kister mixing rule; and a_i is the pure component parameter for the chosen EOS. Therefore, Adachi–Sugie mixing rule is used for parameter a_m , while a linear mixing rule is used for parameter b_m .

Eq. (2) may be reduced to a more conventional form:

$$a_m = \sum \sum x_i x_j a_{ij} \quad (3)$$

where a_{ij} is a cohesion parameter between components i and j .

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \quad (4)$$

In Eq. (4), k_{ij} is the binary interaction parameter, which is introduced in order to compensate for the non-idealities of the system, and its value is estimated to obtain the best fit between experimental and calculated data.

3. Results and discussion

Overtime, various groups published their results for the solubility of methane in water, as obtain by applying different experimental methods. From the available literature we selected nine sets of experimental data for the aqueous solubility of methane, covering a large range of temperature (274.35 K–627.15 K) and pressure (0.57 MPa–197.26 MPa). We performed mathematical modelling for all selected data, and we estimated the binary interaction coefficient in order to obtain the best fit between calculated and experimental values. The mathematical modelling results are presented in Figs. 1 to 6, while the values of the binary interaction coefficients and the standard deviations between the experimental and calculated solubility are presented in Table 1.

In 1951 Culberson and McKetta [7] determined the solubility of methane in water at temperatures between 298.15 K and 444.26 K,

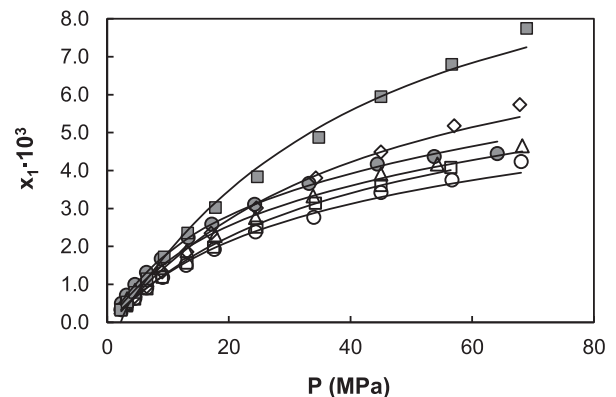


Fig. 1. The influence of pressure and temperature on the solubility (molar fraction) of methane (1) in water (2); comparison between modelling results and the experimental data obtained by Culberson and McKetta (1951) [7]. Experimental data: ●, 298.15 K; ○, 310.93 K; □, 377.59 K; ◻, 444.26 K. Modelling results: —, Redlich–Kwong equation of state.

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