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Adequacy of equation of state models for determination of adsorption of gas mixtures in a manometric set up

Elisa Battistutta *, Marcin Lutynski, Hans Bruining, Karl-Heinz Wolf, Susanne Rudolph

Faculty of Civil Engineering and Geosciences, Department of Geotechnology. Section of Geo Science, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands

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ABSTRACT

In Enhanced Coal Bed Methane (ECBM) usually CO_2 mixtures containing impurities such as NO_x, etc., are injected in the coal layer. This paper investigates the adequacy of different Equations of State (EoS) for the determination of adsorption of gas mixtures in a manometric set up.

We investigate the viability of these EoS by performing experiments in a reference cell and an empty sample cell at a constant temperature of 318.15 K. From these measurements we derive the volume ratio of these cells. We used a variety of EoS and mixing rules to validate whether they can be applied, i.e., lead to the correct volume ratio. It is shown that for a He rich mixture (98% He, 1% O_2 and 1% NO_2) it is possible to use the McCarty EoS for pure helium for this purpose but that none of the other EoS, including mixing rules, give acceptable results.

For a CO_2 rich mixture (97% CO_2, 1% He, 1% O_2 and 1% NO_2) none of the investigated EoS and mixing rules can be applied. Therefore, we present an experimental stepwise procedure based on the volume ratio measurements, to obtain correct density values with an error between 0.033% for high densities to 0.85% for low densities.

1. Introduction

A manometric set up can be used to determine sorption of gasses on coal. To obtain a sorption isotherm with a manometric set up an accurate EoS to convert pressure and temperature data to densities is required.

In our previous experiments in the Dietz Laboratory we investigated sorption of pure gasses such as CO_2, CH_4, He, N_2 on coal, for which an accurate Equation of State is usually available (Hemert et al., 2009). However impurities are always present in CO_2 streams coming from flue gas even after separation processes (Metz et al., 2005). Description of the possible post treatments of flue gas can be found in many articles (Cosam and Eiber, 2007; Li et al., 2009; Li and Yan, 2009; Liu and Shao, 2010; Sass et al., 2005). In practice usually some NO_x remains (in a ppm range) and therefore CO_2 with minor impurities is injected in the coal layer.

The sorption behavior of gas mixtures on an adsorbate using a manometric set up has been already investigated. Stevenson et al. (1991) and Zhou et al. (1994) focused on the development of an accurate EoS in combination with a mixing rule using experimental data. Other authors use conventional EoS in combination with mixing rules for the manometric set up to obtain adsorption data for binary and ternary mixtures of CO_2, N_2 and CH_4 (Arri et al., 1992; Busch et al., 2007; Chaback et al., 1996; DeGance et al., 1993; Fitzgerald et al., 2005; Hall et al., 1994; Mazumder et al., 2006). However the adequacy of these EoS needs to be validated.

Mazumder et al. (2006) studied the preferential sorption of a flue gas on coal by using a manometric set up. Here the preferential sorption of the components was quantified. However, the results based on the gas chromatographic analysis were not verified by theory using an accurate EoS.

In the storage phase, streams containing impurities have different physical properties and geochemical reactivity when compared to a pure CO_2 gas phase (Report IEA, 2005). CO_2-ECBM is an expensive technology due to the high costs of CO_2 purification. An option to reduce separation costs would be to inject the flue gas directly as an untreated mixture in deep coal seams (Wong et al., 2000). Therefore, it is important to quantify the adsorption isotherm of a gas mixture on coal at a specific temperature. The purpose of this study is to investigate the effect of NO_2 in the gas mixture on the density calculations.

The manometric set up poses an high demand on the accuracy of the EoS. There are specific EoS such as the Span and Wagner EoS for pure CO_2 (Span and Wagner, 1996) and both for pure N_2 and pure CH_2 the Wagner and Span EoS (Wagner and Span, 1993) and for He the McCarty EoS (McCarty and Arp, 1990). These equations are very accurate and precise due to the fact that they use a large experimental data set, which

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* Corresponding author. Tel.: +31 618190672; fax: +31 152783328.
E-mail address: E.Battistutta@tudelft.nl (E. Battistutta).

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make it possible to determine a large number of parameters. These equations cannot be used for mixtures. One approach to mixtures is to use a cubic EoS such as Soave Reidlich Kwong (SRK) (Soave, 1972) or Peng and Robinson (PR) (Peng and Robinson, 1976) with appropriate mixing rules. There are many mixing rules for the cubic EoS (Valderrama and Silva, 2003) all of them based on the classical van der Waals mixing rule (Kwak and Mansoori, 1986). They require extra information about the gasses used in the mixtures such as the thermodynamic properties of the critical point, the Mathias Copeman coefficients (Mathias and Copeman, 1983) and the binary interaction parameters. Equations such as SRK and PR EoS are useful for industrial purposes and for hydrocarbon recovery but may not be suitable for other purposes (Agarwal et al., 2001a, 2001b).

One of the purposes of this paper is to investigate wether the density obtained using such a specific EoS in combination with any of the mixing rule is accurate enough for manometric adsorption measurements.

We illustrate this procedure by using two different mixtures: the first one is composed of 98% He, 1% O_2 and 1% NO_2; the second mixture is composed of 97% CO_2, 1% He, 1% O_2 and 1% NO_2.

2. Theory

In the following the applied EoS and mixing rules to compute density of the gas mixtures at a given temperature and pressure are given. The cubic EoS can be represented in a general manner by (Panagiotopoulos and Reid, 1986)

$$P = \frac{RT}{v-b_m} - \frac{a_m}{v^2 + uvb_m + wb_m^2}, \tag{1}$$

where, for the Soave–Redlich Kwong (SRK) EoS, $u=1$, $w=0$ and, for the Peng and Robinson (PR) EoS, $u=2$, $w=-1$. We used T [K] to denote the absolute temperature, R is the gas constant [8.314 J/mol K], P is the pressure [Pa] and v is the specific molar volume [m^3/mol].

The cubic EoS can also be applied to mixtures by introducing mixing rules. These so-called mixing rules have been modified with respect to the van der Waals mixing rule and can be expressed as follows (Kwak and Mansoori, 1986)

$$a_m = \sum_{i=1}^{Nc}\sum_{j=1}^{Nc} x_i x_j a_{ij}, \tag{2}$$

$$b_m = \sum_{i=1}^{Nc}\sum_{j=1}^{Nc} x_i x_j b_{ij}, \tag{3}$$

where a_m accounts for the molecule–molecule interactions and b_m for the hard-core volume in the mixture. The force parameter, a_{ij}, and the volume parameter, b_{ij}, are expressed by

$$a_{ij} = a_i a_j \left(1-k_{ij}\right), \tag{4}$$

$$b_{ij} = \frac{b_i + b_j}{2}. \tag{5}$$

The binary interaction parameters k_{ij} can be obtained by fitting to phase equilibrium data of the specific mixture. For the PR EoS (Peng and Robinson, 1976) the parameter b_i is independent of temperature and can be calculated knowing the critical point of each gas component, i.e.,

$$b_i = 0.07780\frac{RT_c}{P_c}. \tag{6}$$

For the SRK EoS (Soave, 1972) b_i can be expressed as

$$b_i = 0.008644\frac{RT_c}{P_c}. \tag{7}$$

For the determination of the parameter a_i the temperature dependence is incorporated according to Mathias and Copeman (1983), i.e.,

$$a_i = a_{ci}\beta_i(T), \tag{8}$$

where for the PR EoS

$$a_{ci} = 0.45724\frac{R^2T_{ci}^2}{P_{ci}}, \tag{9}$$

and for the SRK

$$a_{ci} = 0.42188\frac{R^2T_{ci}^2}{P_{ci}}. \tag{10}$$

The effect of the temperature is described by

$$\beta_i(T) = \left[1 + c_{1i}\left(1-T_{ri}^{0.5}\right) + c_{2i}\left(1-T_{ri}^{0.5}\right)^2 + c_{3i}\left(1-T_{ri}^{0.5}\right)^3\right]^2, \tag{11}$$

where c_{1i}, c_{2i} and c_{3i} are reported in Table 1. In the case of helium and NO_2 no coefficients are available, the Mathias Copeman coefficients have been replaced by the acentric factor. In this case $c_{2i}=c_{3i}=0$ and

$$c_{1i} = 0.48 + (1.574\omega) - \left(0.176\omega^2\right), \tag{12}$$

for the SRK EoS and

$$c_{1i} = 0.37464 + (1.54226\omega) - \left(0.26992\omega^2\right), \tag{13}$$

for the PR EoS; ω is the acentric factor. The experimental temperature divided by the critical temperature T_{ci} (see Table 2) of each component i is called the reduced temperature and is denoted as T_{ri}.

To improve the description of the interactions Panagiotopoulos and Reid (1986) and Kwak and Mansoori (1986) proposed to make the interaction parameter k_{ij} composition dependent, i.e.,

$$k_{ij} = \delta_{ij}x_i - \delta_{ji}x_j. \tag{14}$$

For a number of mixtures, values of the parameter δ_{ij} can be found. If no literature data exist, the value can be estimated by the modified Chueh–Prausnitz equation (Chueh and Prausnitz, 1967)

$$\delta_{ij} = 0.018\left(1 - \frac{2V_{ci}^{\frac{1}{6}}V_{cj}^{\frac{1}{6}}}{V_{ci}^{\frac{1}{3}} + V_{cj}^{\frac{1}{3}}}\right)^6, \tag{15}$$

where V_{ci} is the critical volume of component i (see Table 2).

Peneloux et al. (1982) introduced the so-called volume shift approach to improve the performance of both the SRK and the PR EoS.

Table 1
The Mathias Copeman coefficients (c_1, c_2, c_3, the acentric factor (ω) and the parameters R_k and Q_k for each gas component.

Gas	c_1 (SRK)	c_2 (SRK)	c_2 (SRK)	ω	R_k	Q_k
CO_2	0.867	−0.674	2.471	0.2236	1.3	0.982
He	–	–	–	−0.39	0.885	0.985
O_2	0.545	−0.235	0.292	0.0222	0.733	0.849
NO_2	–	–	–	0.849	1	1.1