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Original Article

In-depth study on the solubility of elemental sulfur in sour gas mixtures based on the Chrastil's association model

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ABSTRACT

Accurately predicting the solubility of elemental sulfur in sour gas mixtures is a primary task. As a current and widely-used model on the solubility of elemental sulfur in sour gas mixtures, Chrastil's association model has a big error in the process of predicting experimental data based on different fitting methods. This paper combined with experimental data reported by relevant scholars about elemental sulfur solubility in sour gases and selected density, temperature and pressure as three important influential factors. According to different fitting methods, we can calculate the correlation parameters in Chrastil's model. Then different solubility formulas can be used to predict the solubility of elemental sulfur in sour gas mixtures. Through in-depth research and analysis of Chrastil's solubility model from numerical aspects, it's easy to find the irrationality about Chrastil's solubility model and fitting methods. Especially in fitting methods, further improvement of the fitting method is proposed and used to predict the solubility of elemental sulfur in sour gas mixtures. The calculation results show that some improvements of the predicting precision have been achieved by using the improved fitting method in Chrastil's association model.

1. Introduction

High sulfur gas reservoirs have been widely distributed both in china and worldwide countries. Most of the world major oil-producing countries possess high sulfur gas reservoirs. High sulfur gas reservoirs discovered in China are mainly distributed in Bohai Bay Basin, Ordos Basin and Szechuan Basin and so on, especially in Szechuan Basin the proportion of development of gas field containing hydrogen sulfide has reached 2/3. The mining measure of high sulfur gas reservoirs is different from that in the conventional natural gas reservoirs due to the strong corrosivity and toxicity of H_2S and the deposition of sulfur. In the process of mining, the solubility of elemental sulfur in sour gas will decrease with the decline of reservoir pressure. The deposition of sulfur will block the pore and throat in the reservoirs resulting from the further reduction of pressure and temperature when the reservoir fluid reach a sulfur-saturated state and then the porosity and permeability of reservoir will reduce. It is more serious that the deposition would cause plugging of the formation, tubing, and surface equipment. The precondition of controlling the deposition of elemental sulfur is to predict the solubility and its variation characteristics of elemental Sulfur in the sour gases under the different temperatures and pressures [1]. Therefore, it is of significance to accurately predict the changing of the solubility of sulfur in sour gas reservoirs in real time.

As early as 1960, Scholars had begun to study the solubility of elemental sulfur. For example Kennedy and Wielend [2], Roof [3], Swift [4], Brunner E and Woll W [5,6], Chrastil [7], Tomxej R A [8], Roberts B E [9] and Adel M Elsharkawy [10], they analyzed the solubility of elemental sulfur through theory, experiment method and experimental data respectively. Since 1990 in China, Gu Mingxin [11], Zeng Ping [12], Yang Xuefeng [13], Bian Xiaoqiang [14], Sun Changyu [15] and Hu Jinghong [16] also

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researched the elemental sulfur solubility. Since Roberts fitted and obtained a set of coefficients, Chrastil's model was widely used to predict the solubility of elemental sulfur in sour gas mixtures by researchers at home and abroad. In recent years, on the basis of the theory of Chrastil's model, they made further research and utilized four groups of experimental data reported by Brunner and Woll to establish Piecewise Function by adopting the pressure or density nodes and fitting relevant coefficients in Chrastil's model respectively. Compared with Roberts' empirical equation, it achieved some improvements but the accuracy is still not ideal.

From the theoretical analysis of Chrastil's model, component density, temperature and pressure are necessary to calculate the solubility of elemental sulfur in the sour gas mixtures when using Chrastil's model. And the density of the sour gas mixtures contained different components varies under different temperatures and pressures. They interact with each other and are three important factors that affect the solubility of elemental sulfur in sour gases. Therefore this paper selected component density, temperature and pressure as three factors. Combined with experimental data on the solubility of elemental sulfur in sour gases published by relevant scholars, coefficients of Chrastil's model are calculated according to different fitting methods and then are used to predict the solubility. Through in-depth research and analysis of Chrastil's solubility model from numerical aspect, the irrationality about Chrastil's solubility model and fitting methods has been analyzed. The further improvement of the fitting method is proposed and used to predict elemental sulfur solubility in the sour gas mixtures.

2. Chrastil's model and its two methods of fitting coefficients

In 1982, Chrastil [7] obtained his solubility model based on the assumption that a solvate complex is formed from the association of the solute molecules and the gas molecules and reaches the equilibrium states in the gas. We can calculate the equilibrium concentration from mass action law. Chrastil's model is shown as follows:

$$c = \rho^k \cdot \exp\left(\frac{A}{T} + B\right) \tag{1}$$

where: c is the concentration of a solute in a gas in g/L, and ρ is the density of a gas in g/L, and k is an association number, A, B- are empirical parameters which can be achieved by experiment data.

At present, for the Chrastil solubility model, there are two methods to fit the correlation coefficients through experimental data. Chrastil's model contains coefficients “k”, “A” and ”B”. Fitting method of coefficient is given as follows:

The first method [16] is shown as follow:

Taking the logarithms of left and right sides of equation (1), we can get:

$$lnc_r = kln\rho + (A/T + B) \tag{2}$$

Formula (2) can be simply changed into:

$$ln\rho = \frac{1}{k} lnc_r - \frac{1}{k}(A/T + B) \tag{3}$$

Thus, according to experimental data, at a certain temperature, a log–log plot of the solubility versus the density should yield a straight line with a slope of 1/k and an intercept of $-(A/T + B)/k$.

Due to the coefficient “A” and “B” have no relationship with T, at constant temperatures T_1 and T_2:

$$-\frac{1}{k}(A/T_1 + B) = m_1 \tag{4}$$

$$-\frac{1}{k}(A/T_2 + B) = m_2 \tag{5}$$

The coefficient “A” and “B” can be obtained by simply calculation:

$$A = \frac{kT_1T_2(m_1 - m_2)}{T_1 - T_2} \tag{6}$$

$$B = \frac{k(m_2T_2 - m_1T_1)}{T_1 - T_2} \tag{7}$$

The second method [9] is shown as follow:

Take logarithm on the sides of formula (1), we can get formula (8).

$$lnc_r = kln\rho + (A/T + B) \tag{8}$$

According to the experimental data, under a certain temperature, a log–log plot of the density versus the solubility should yield a straight line with a slope of k and an intercept of (A/T + B). After getting the numerical value of k, we can make a linear relationship diagram about the logarithm of solubility and the reciprocal of temperature with a slope of A and an intercept of ($kln\rho$ + B). Combined with the two steps above and giving a reasonable density value, we can get the relevant coefficients A and B.

3. Applying Chrastil's model to fit the experimental data and analyzing its irrationalities in numerical aspect

To calculate the correlative coefficients of Chrastil's model and analyze the validity of Chrastil's model in the aspect of numerical calculation, two groups of experimental data reported by Brunner and woll [5] and other two groups reported by Sun Changyu [15] are selected to fit the correlation coefficients and to predict solubility.

3.1. Applying Chrastil's model to fit the experimental data

Mixture 1 [5]: 66%CH_4, 20%H_2S, 10%CO_2, 4%N_2 (volume fraction), the data is shown in Table 1 below:

When system pressure is over 30 MPa, we can adopt the first fitting method and obtain straight lines about the logarithm of elemental sulfur solubility in sour gas vs the logarithm of the density of sour gas under different temperatures, of which the slope is k. Calculation result are shown in Table 2 and Fig. 1.

From Table 2, the values of k that we use the Chrastil's solubility model to fit are between 2 and 5 by using method one. The higher the temperature is, the smaller the value k is.

We can designate the temperature T_1 = 393.15 K, T_2 = 413.15 K and put it into formula (4), (5) above. The parameters of Chrastil's solubility model can be calculated easily: A = −1859.2472 and B = −20.1611.

When system pressure is over 30 MPa, we can adopt the second fitting method and obtain straight lines about the logarithm of elemental sulfur solubility in sour gas vs the logarithm of the density of sour gas under different temperature, of which the slope is k. We also obtain Fitting line about the logarithm of solubility (lnr) over the reciprocal of time (1/T). Calculation results are shown in Table 3 and Fig. 2 as follows:

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