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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A R T I C L E   I N F O

A B S T R A C T

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 H₂S 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:

Table 1
Solubility of sulfur in sour gas mixture 1.

| Temperature (K)	Pressure (MPa)	Gas density (kg/m³)	Sulfur content	
			Solubility (g/m³)	Mass/mass (%)
373.15	20	164	0.208	0.202
	20	164	0.253	0.246
	40	282	0.789	0.0767
	52	327	1.4	0.136
	52	327	1.42	0.138
	60	350	1.99	0.194
393.15	10	74	0.115	0.0112
	10	74	0.115	0.0112
	30	213	0.749	0.0729
	45	282	1.79	0.174
	60	331	3.14	0.305
413.15	10	69	0.22	0.0214
	30	198	1.1	0.107
	45	264	2.67	0.26
	60	313	4.45	0.433
433.15	10	65	0.352	0.0342
	30	185	1.65	0.16
	40	231	2.65	0.258
	50	267	4.29	0.416

Table 2
k value at different temperatures when the system pressure is greater than 30 MPa (Method one).

Temperature (K)	373.15	393.15	413.15	433.15
k value	4.2231	3.2381	3.0553	2.6059

From Table 3, the values of k that we use the Chrastil's solubility model to fit are between 2 and 5 by using method two. The higher the temperature is, the smaller the value k is.

Seen from Fig. 2, we can calculate the parameters of Chrastil's model, A = −5322.7218 and B = −11.3005. Here the value of density what we adopt for calculation is $\rho = 253$ g/m³.
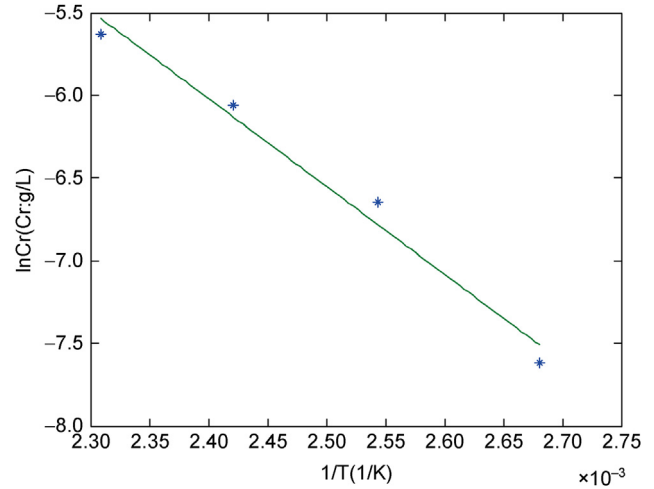
In the same way, when system pressure is less than 30 MPa, we can adopt the first fitting method and obtain straight lines about the logarithm of elemental sulfur solubility in sour gas vs the logarithm the density of sour gas under different temperatures, of which the slope is k. Calculation result are shown in Table 4 and Fig. 3 below:
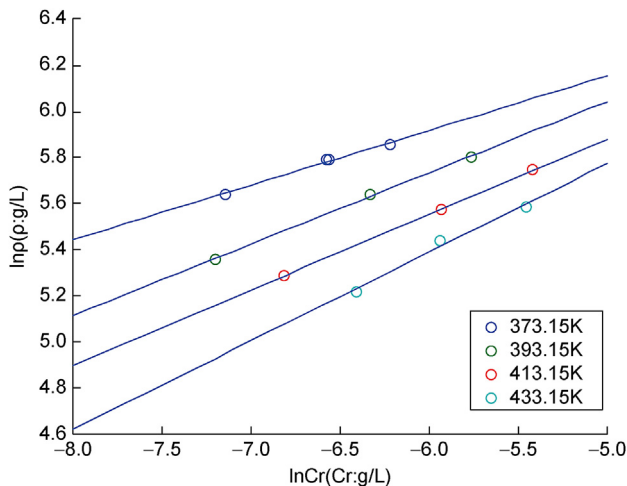
Fig. 1. Fitting line at different temperatures when the system pressure is greater than 30 MPa (Method one).

Table 3
k value at different temperatures when the system pressure is greater than 30 MPa (Method two).

Temperature (K)	373.15	393.15	413.15	433.15
k	4.1966	3.2347	3.0551	2.5649

Fig. 2. Fitting line about lnr over 1/T When the system pressure is greater than 30 MPa (Method two).

From Table 4, the values of k that we use the Chrastil's solubility model to fit are between 1 and 2 by using the 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 = −2737.2293 and B = −8.8977.

When system pressure is less than 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 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 5 and Fig. 4:

From Table 5, the values of k that we use the Chrastil's solubility model to fit are between 1 and 2 by using the method two. The higher the temperature is, the smaller the value k is.

Seen from Fig. 4 above, we can calculate the parameters of Chrastil's model (A = −4026.3084 and B = −5.4736). Here the value of density what we adopt for calculation is $\rho = 253$ g/m³.

Through the two fitting methods above, we can use the data of Mixture 1 to fit correlation coefficients of Chrastil's model and the whole result is shown in Table 6:

From Table 6, regardless of range of the system pressure, we can clearly see that the average value of k calculated by two kinds of methods is the same, while the values of A, B are not and they have a great gap. Using coefficients above to predict solubility, we can get the results in Figs. 5 and 6 and Tables 7 and 8 as follows:

Red lines are for the predicted data from Chrastil's model and the blue lines are for experimental data in Fig. 5. As shown in

Table 4
k value at different temperatures when the system pressure is less than 30 MPa (Method one).

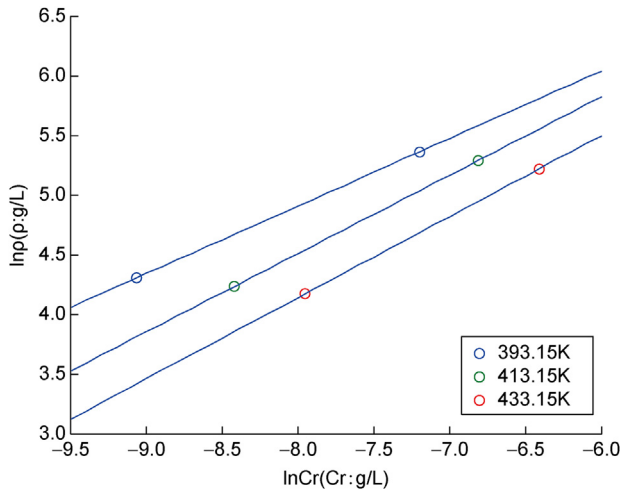| Temperature (K)	373.15	393.15	413.15	433.15
k value		1.7724	1.5267	1.4770

Fig. 3. Fitting line at different temperatures when the system pressure less than 30 MPa (Method one).

Table 5
k value at different temperatures when the system pressure is less than 30 MPa (Method two).

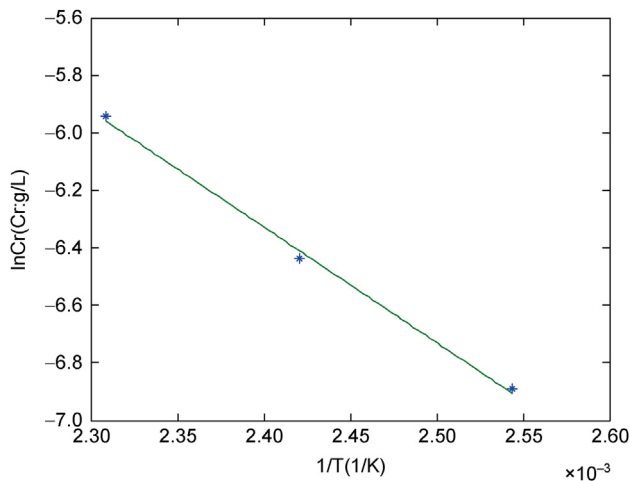| Temperature (K)	373.15	393.15	413.15	433.15
k value		1.7724	1.5267	1.4770

Fig. 4. Fitting line about lnr over 1/T when the system pressure is less than 30 MPa (Method two).

Fig. 5 and Table 7, correlation coefficients that calculated from method one cannot predict the sulfur solubility at different pressures and temperatures. The best prediction is for temperature 393.15 K and its average relative error is 9.58%. Relative error of the rest is between 30% and 110%. Obviously the accuracy

Table 6
Model coefficients calculated by the two methods.

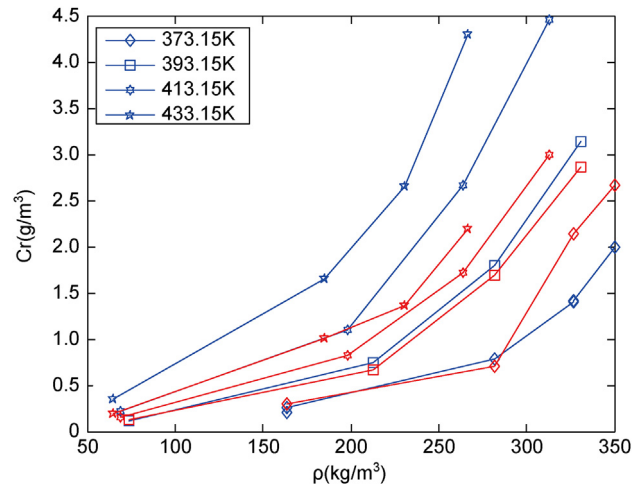| Fitting method	Correlation parameter	Pressure ≥ 30 MPa	Pressure < 30 MPa
Method one	The average value of k	3.2806	1.5920
	A	−1859.2472	−2737.2293
	B	−20.1611	−8.8977
Method two	The average value of k	3.2628	1.5920
	A	−5322.7218	−4026.3084
	B	−11.3005	−5.4736

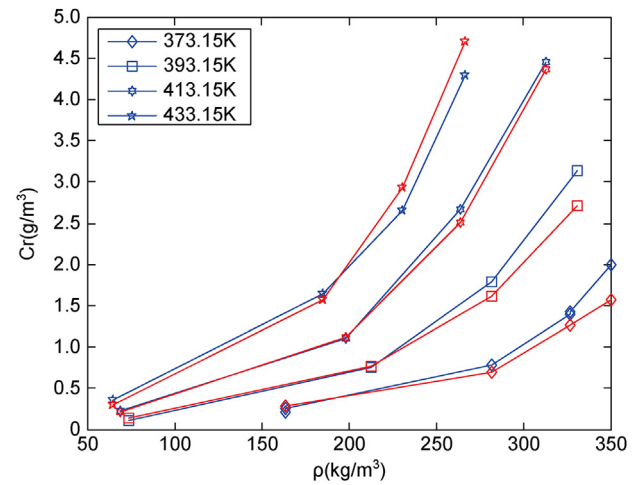**Fig. 5.** Comparison of prediction with experimental data (Method one).

Fig. 6. Comparison of prediction and experimental data (Method two).

Table 7
Relative error between the calculated sulfur solubility and experimental results in Method one.

Temperature (K)	373.15	393.15	413.15	433.15
Relative error under different pressures	0.0913	0.0074	0.0666	0.1626
	0.0463	0.0074	0.2782	0.6485
	0.0797	0.0900	0.9558	1.2884
	0.7353	0.0972	1.4534	2.1002
	0.7153	0.2767		
	0.6788			
Average Relative Error	0.3911	0.0958	0.6885	1.0499

Table 8
Relative error between the calculated sulfur solubility and experimental results in Method two.

	Temperature (K)			
Relative error under different pressures	373.15	393.15	413.15	433.15
	0.0823	0.0266	0.0121	0.0555
	0.0373	0.0266	0.0137	0.0824
	0.1010	0.0130	0.1677	0.2840
	0.1358	0.1787	0.0890	0.4164
	0.1558	0.4224		
	0.4119			
Average relative error	0.1540	0.1335	0.0706	0.2096

Table 9
Corresponding E values calculated by model coefficients k.

k	4.1966	3.2347	3.0551	2.5649	1.7724	1.5267	1.4770
E_{min}	5.535×10^7	9.297×10^5	4.335×10^5	5.401×10^4	1.863×10^3	6.560×10^2	5.311×10^2
E_{max}	4.747×10^{10}	1.695×10^8	5.921×10^7	3.352×10^6	3.229×10^4	7.656×10^3	5.723×10^3

Table 10
Corresponding E values calculated by model coefficients average k.

	Pressure $\geq$ 30 MPa	Pressure < 30 MPa
The average value of k	3.2628	1.5920
E_{min}	1.048×10^6	8.659×10^2
E_{max}	1.999×10^8	1.123×10^4

Notes: Base numbers of density are 70 and 350 respectively in E_{min}, E_{max}.

of prediction is very bad and the coefficients of Chrastil's model that calculated from method one cannot be used to predict the solubility of elemental sulfur.

Red lines are for the predicted data from Chrastil's model and the blue lines are for experimental data in Fig. 6. As shown in Fig. 6, correlation coefficients that calculated from method two can predict the changing tendencies of the sulfur solubility under different pressures and temperatures. From Table 8, the average relative error at different temperatures is between 4% and 20%, while the total average relative error of the entire data is 14.2%. Obviously the Chrastil's model's coefficients that calculated from method two has a certain prediction ability but only the prediction results are not satisfying.

3.2. Analyzing irrationalities of Chrastil's model in numerical aspect

According to the process of two different fitting methods, the calculated coefficients and the prediction results, we can make further study on Chrastil solubility model in terms of prediction accuracy.

In order to analyze Chrastil's solubility model in prediction accuracy, this paper divides the formula (1) into two parts, which are $E = \rho^k$ and $F = exp(A/T + B)$ respectively. Both are monotone and exponential functions.

According to the value of gas density in Table 1 ($\rho = 70-350$ g/L) and the value of k from the second method, the range of E can be obtained as follows (see Tables 9 and 10).

From Table 9, we can clearly see that orders of magnitude of E are between 2 and 10 for the different values of k, while the variation range of k value is just between 1.5 and 4.2. Such a small changing range causes a great change of E value. Compared with the average k value, the gap also reaches several orders of magnitude. So in the process of predicting solubility the accuracy

of k have a great influence on the predicted solubility, and it is easy to see that for the coefficient k value of Chrastil's model, if we only adopt average k value in different temperature, there is a big error in predicting the value of E. of course, predicted value also will be Inaccurate.

For $F = exp(A/T + B)$, of which $A/T + B$ be equal to yab, we can get the value of F by calculating the value of yab under different temperatures (see Table 11).

From Table 11, we can clearly see that the value of F is extremely small and the orders of magnitude are between -7 and -12. Obviously, the value of E is very big with its orders of magnitude between 2 and 10 and is greatly influenced by the value of k. In this case, it is extremely unreasonable that utilize Chrastil's model to calculate the solubility by multiplying E that effected by k easily by F, which will cause large error.

4. The improvement of method two

To solve the problems of the second fitting method, we can use the value of k under different temperatures to calculate the values of A and B respectively and then forecast solubility and analyze error. Here the value of density what we adopt for calculation is $\rho = 253$ g/m³.

From Table 12 above, k value will affect B value, but not for A value. The A value are a fixed number under different temperatures. The smaller k value is, the bigger the B value is. The prediction is shown in Fig. 7 below:

Red lines are for the predicted data from Chrastil model by using the improved method two and the blue lines are for experimental data in Fig. 7. As shown in Fig. 7, correlation coefficients that calculated form the improved method two can predict the changing tendencies of the sulfur solubility at different pressures and temperatures. The total average relative error of the entire data is 9.29%. Compared with 14.2% that calculated by method two, its accuracy is increased by 5.4%. Therefore, correlation coefficients calculated separately in different temperatures help to improve prediction accuracy.

To further analyze the influence of the given density value on the prediction accuracy, different density value between 200 and 700 g/m³ are respectively used to get the best value of density through the improved method two. So, we can get the relationship between the density value and relative average error, it is shown in Fig. 8:

Table 11
F values calculated by model coefficients A and B in Method one and two.

	Temperature (K)	373.15	393.15	413.15	433.15
Pressure<30 MPa					
Method one	Yab	−16.2332	−15.8600	−15.5230	−15.2171
	F	8.91×10^{-8}	1.29×10^{-7}	1.81×10^{-7}	2.46×10^{-7}
Method two	Yab	−16.2637	−15.7148	−15.2190	−14.7690
	F	8.65×10^{-8}	1.50×10^{-7}	2.46×10^{-7}	3.85×10^{-7}
Pressure $\geq$ 30 MPa					
Method one	Yab	−25.1437	−24.8902	−24.6613	−24.4535
	F	1.20×10^{-11}	1.55×10^{-11}	1.95×10^{-11}	2.40×10^{-11}
Method two	Yab	−25.5648	−24.8391	−24.1838	−23.5889
	F	7.90×10^{-12}	1.63×10^{-11}	3.14×10^{-11}	5.70×10^{-11}

Table 12
Model coefficients calculated by the improvement of Method two.

|	Temperature(K)			
	373.15	393.15	413.15	433.15
Relevant parameter	Pressure $\geq$ 30 MPa			
k	4.1966	3.2347	3.0551	2.5649
A	−5322.7218	−5322.7218	−5322.7218	−5322.7218
B	−16.467	−11.145	−10.151	−7.4387
Relevant parameter	Pressure < 30 MPa			
k	1.5920	1.7724	1.5267	1.4770
A	−4026.3084	−4026.3084	−4026.3084	−4026.3084
B	−5.4736	−6.4715	−5.1123	−4.8370

From Fig. 8, we can clearly see that the value of the given density has an influence on prediction accuracy. When the given density value is less than 450 g/m^3, the relative average error decreases with the given density value by using the above method, but it will increases when the given density value is more than 450 g/m^3. Therefor we can fine an optimal density value. When the given density value is 450 g/m^3, the total relative average error is 7.08% (see Fig. 9).
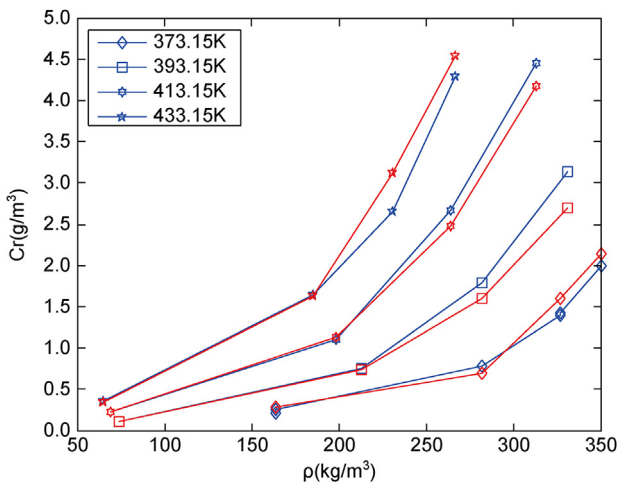
Fig. 7. Comparison of prediction with experimental data by the improvement of Method two.
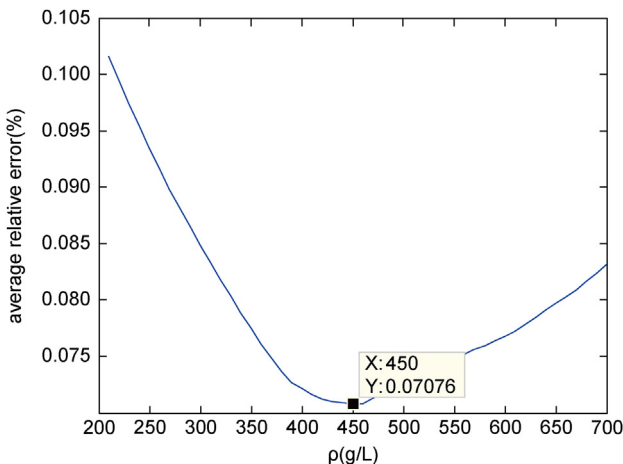
Fig. 8. Relationship between density and average relative error.
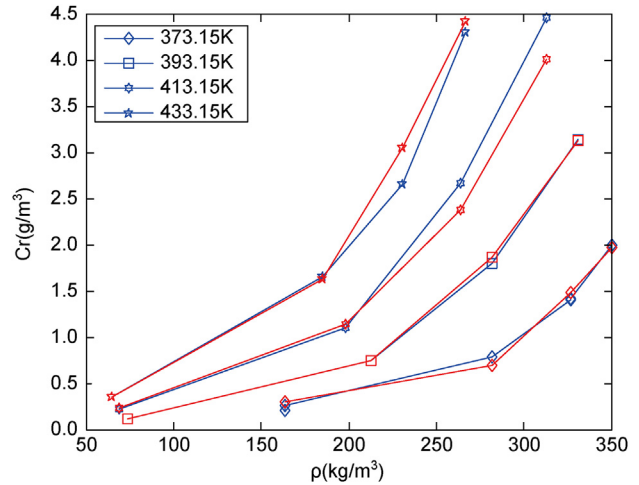
Fig. 9. Comparison of prediction with experimental data by the further improvement of methods two.

Red lines are for the predicted data from Chrastil model by using the further improvement of method two and the blue lines are for experimental data in Fig. 9. As shown in Fig. 9, the calculation of solubility are closer to experimental data and the model can better describe the way that solubility changes with the variation of temperatures and pressures. The total average relative error of the entire data is about 7%.

5. Data prediction by the further improvement of method two

On the basis of the second fitting method, using the k value under the different temperature and giving an optimal calculated

Table 13
The second group of solubility data in Brunner and Woll.

Temperature (K)	Pressure (MPa)	Gas density (kg/m^3)	Sulfur content	
			Solubility (g/m^3)	Mass/mass (%)
373.15	20	134	0.042	0.0047
	20	134	0.05	0.0055
	20	134	0.051	0.0056
	30	188	0.108	0.012
	30	188	0.136	0.0151
	40	230	0.266	0.0295
	45	247	0.476	0.0528
	50	263	0.415	0.0461
	60	289	0.687	0.0723
	60	289	0.688	0.0741
	60	289	0.879	0.0976
393.15	20	125	0.162	0.018
	20	125	0.178	0.0198
	30	176	0.39	0.0433
	30	176	0.404	0.0448
	40	215	0.615	0.0683
	40	215	0.635	0.0705
	50	247	1.074	0.119
	60	273	1.74	0.193
413.15	20	116	0.385	0.0427
	25	141	0.562	0.0624
	30	164	0.661	0.0734
	45	219	1.42	0.158
	60	260	2.41	0.267
433.15	10	56	0.304	0.0337
	25	133	0.752	0.0835
	45	207	1.98	0.22
	60	248	3.22	0.357

value of density, The corresponding parameters A and B in Chrastil's model can be calculated respectively, which can be used to predict solubility and contrast with the experimental data.

5.1. Comparison of experimental data by Brunner and Woll with predicted solubility

According to the experimental data by Brunner and Woll, two fitting methods and the further improved method are used to predict and compare with the experimental data by Chrastil association solubility model. Mixture 2 [5] (BW2):81%CH$_4$, 6% H$_2$S, 9%CO$_2$ and 4%N$_2$ (see Table 13):

Correlation coefficients in Chrastil's model are obtained from two fitting methods by fitting the data (BW2). Here the value of density what we adopt for calculation in method two is $\rho = 253$ g/m^3.

The result is shown in Table 14.

Prediction result from the method one and the analysis of error are shown in Fig. 10 and Table 15.

As seen from the Fig. 10 and Table 15, the relative average error under different temperature is between 60% and 800%. Obviously the error between predicted values and experimental data under different temperature and pressure is very big. Therefore method one cannot be used to predict the solubility.

Prediction result from method two and the analysis of error are shown in Fig. 11 and Table 16.

As seen from the Fig. 11 and Table 16, the relative average error under different temperature is between 10% and 60%. The total average relative error of the entire data is about 28.9%. Obviously the error between predicted values and experimental data under different temperature and pressure is not good.

Prediction result from the further improvement of method two and the analysis of error are shown in Fig. 11: Here the optimal calculated value of density what we adopt for calculation in method two is $\rho = 440$ g/m^3.

Compared with method one and two, we can obtain the higher prediction accuracy according the further improvement of method two. As is shown in Fig. 12, the total relative average error is 16.57%, which has increased by 12.33%.

5.2. Comparison of experimental data by Sun Changyu (2003) with predicted solubility

Likewise, two fitting methods and the further improvement of method two are used to predict and compare with the two groups of data published by Sun Changyu [15] by using Christil's association model. Here the value of density what we adopt for calculation in method two is $\rho = 300$ g/m^3. The data is shown in Table 17 and result can be obtained from Tables 18–20 and Figs. 13–18:

As seen from Figs. 13 and 14 and Table 19 obviously, the error between predicted values and experimental data (Mixture 3)
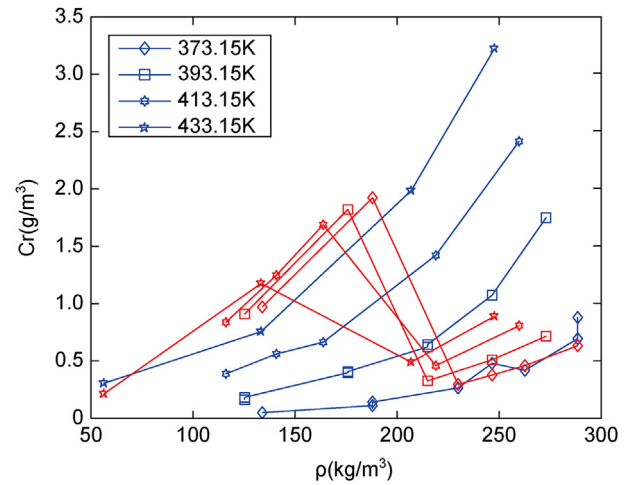

Fig. 10. Comparison of prediction with experimental data (Method one).

Table 15
Prediction errors of model coefficients (Method one).

Temperature (K)	373.15	393.15	413.15	433.15
Relative error under different pressures	22.1324	4.6193	1.1765	0.3242
	18.4313	4.1142	1.2094	0.5609
	18.0502	3.6509	1.5470	0.7523
	16.7963	3.4898	0.6785	0.7238
	13.1324	0.4739	0.6666	
	0.1099	0.4904		
	0.2155	0.5241		
	0.1065	0.5916		
	0.0882			
	0.0895			
	0.2874			
Average relative error	8.1309	2.2443	1.0556	0.5903

under different temperature and pressure is very big (Method one), but the relative average errors under different temperatures are between 8% and 23% (Method two). The total average relative error of the entire data is 14.93% (Method two). Therefore method one cannot be used to predict the solubility, while method two has a certain prediction ability but only the prediction results are not satisfying.
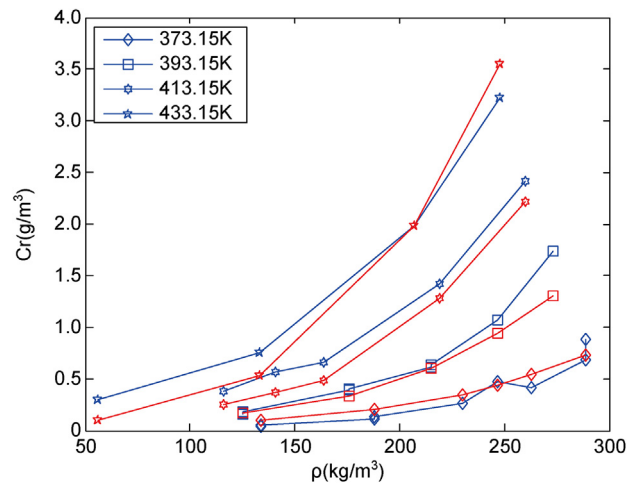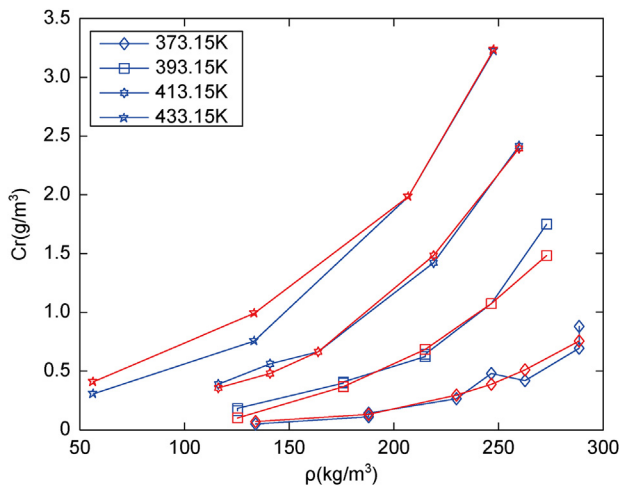
Table 14
Model coefficients calculated by Method one and two.

Fitting method	Correlation parameter	Pressure ≥ 30 MPa	Pressure < 30 MPa
Method one	The average value of k	3.2943	2.0148
	A	−2302.1526	−550.0128
	B	−19.8729	−15.3308
Method two	The average value of k	3.2247	1.9686
	A	−5584.7897	−4414.2201
	B	−10.5251	−6.9740

Fig. 11. Comparison of prediction and experimental data (Method two).

Table 16
Prediction errors of model coefficients (Method two).

Temperature (K)	373.15	393.15	413.15	433.15
Relative error under different pressures	1.4996	0.0316	0.3548	0.6809
	1.0996	0.0611	0.3509	0.2918
	1.0585	0.1596	0.2569	0.0025
	0.8931	0.1887	0.1019	0.1041
	0.5034	0.0176	0.0797	
	0.3185	0.0485		
	0.0727	0.1200		
	0.3022	0.2499		
	0.0661			
	0.0645			
	0.1668			
Average relative error	0.5495	0.1096	0.2288	0.2698

Fig. 12. Comparison of prediction and experimental data the further improvement in Method two.

Table 17
Two sets of experimental data published by Sun Changyu.

Temperature (K)	Pressure (MPa)	Density (kg m^{-3})	Solubility (g m^{-3})
Mixture 3	**H_2S** **0.1498**	**CO_2** **0.0731**	**CH_4** **0.7771**
303.2	30	287.3708	0.118
303.2	40	383.161	0.139
323.2	30	269.5879	0.142
323.2	40	359.4506	0.19
343.2	35	296.1906	0.231
343.2	40	338.5036	0.287
363.2	40	319.8635	0.497
363.2	45	359.8464	0.666
Mixture 4	**H_2S** **0.2662**	**CO_2** **0.07**	**CH_4** **0.6638**
303.2	30	328.3602	0.193
303.2	40	437.8137	0.248
323.2	30	308.0409	0.24
323.2	40	410.7212	0.368
343.2	35	338.4381	0.488
343.2	40	386.7864	0.657
363.2	40	365.4876	1.194
363.2	45	411.1736	1.455

As seen from the Figs. 15 and 16 and Table 20 obviously, the error between predicted values and experimental data (Mixture 4) under different temperature and pressure is very big (Method one). The relative average errors under different temperatures are between 9% and 22% (Method two). The total average relative

Table 18
Model coefficients calculated by Method one and two.

Fitting method	Correlation parameter	Mixture 3	Mixture 4
Method one	The average value of k	1.4231	1.5657
	A	−17853.1622	−6564.9237
	B	36.5912	2.5574
Method two	The average value of k	1.4231	1.5657
	A	−2265.4867	−2813.4363
	B	−9.7593	−8.4388

Table 19
Prediction errors of Mixture 3.

	Temperature (K)	303.2	323.2	343.2	363.2
Method one	Relative error under different pressures	0.9945	0.8412	1.7893	24.3634
		0.9930	0.8215	1.7137	21.3731
	Average Relative Error	0.9938	0.8314	1.7515	22.8683
Method two	Relative error under different pressures	0.1377	0.0392	0.0985	0.1809
		0.1014	0.1685	0.0688	0.2775
	Average Relative Error	0.1195	0.1038	0.0836	0.2292

Table 20
Prediction errors of Mixture 4.

	Temperature (K)	303.2	323.2	343.2	363.2
Method one	Relative error under different pressures	0.7643	0.3453	0.2193	0.6121
		0.7118	0.3292	0.1169	0.5917
	Average Relative Error	0.7381	0.3372	0.1681	0.6019
Method two	Relative error under different pressures	0.0661	0.2063	0.1422	0.1728
		0.1417	0.2359	0.0463	0.1833
	Average Relative Error	0.1039	0.2211	0.0942	0.1780

error of the entire data is 13.41% (Method two). Therefore method one cannot be used to predict the solubility, while method two has a certain prediction ability but only the prediction results are not satisfying.

Similarly, comparison of prediction result with Sun Changyu (2003) experimental data by using the further improvement of method two (see Figs. 17 and 18): Here the optimal calculated value of density what we adopt for calculation in method two are $\rho = 140$ g/m^3 and $\rho = 510$ g/m^3 respectively.

Compared with Figs. 14 and 16 above, the predicted precision of the two groups of data have greatly improved obviously. The total relative average errors between the predicted solubility and
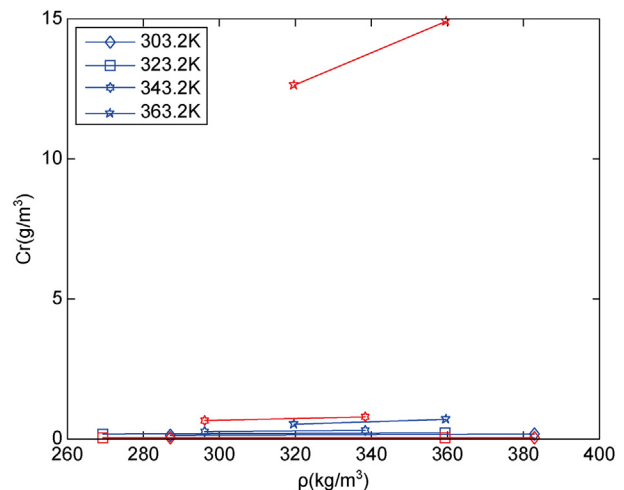
Fig. 13. Comparison of prediction with experimental data (Method one).
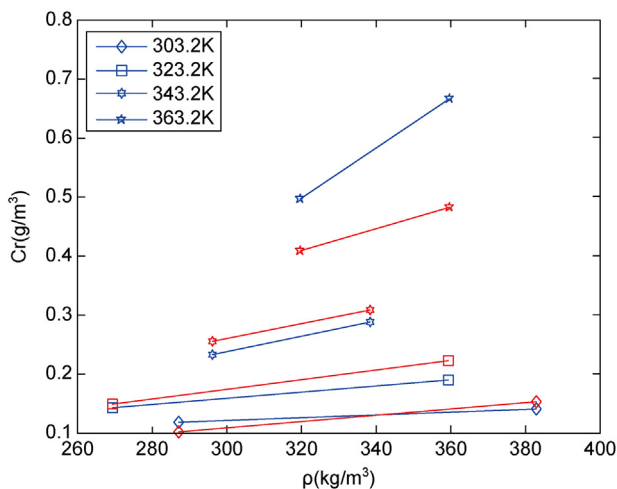
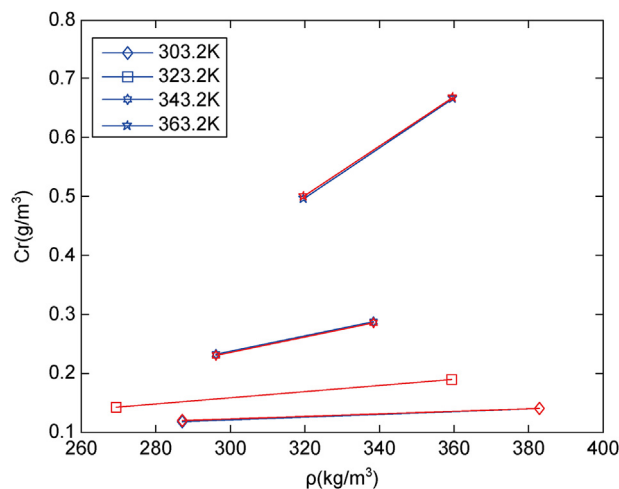**Fig. 14.** Comparison of prediction with experimental data (Method two).

Fig. 17. Comparison of prediction with experimental data by using the further improvement of Method two (Mixture 3).
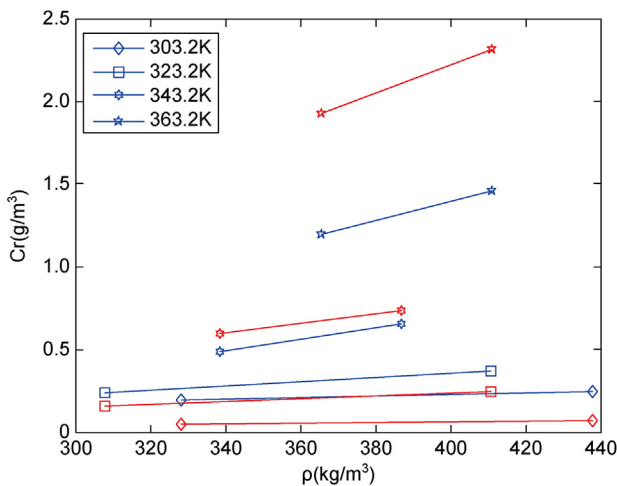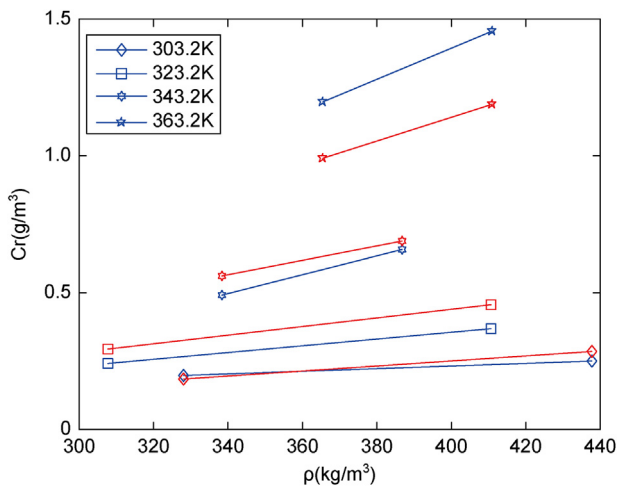
the experimental data are 0.42 and 6.47% respectively. The result shows that the sulfur solubility at different reservoir pressures and temperatures can be well fitted through the improved fitting method two.

6. Conclusions

Different fitting methods are used to analyze deeply and predict the experimental data through Chrastil's association model. The improvements of the second fitting method is proposed and combined with Chrastil's association model to predict the experimental data, we can draw the following conclusions:

(1) When Chrastil's association model was used to fit the experimental data and predict solubility, the solubility of elemental sulfur in sour gas mixtures, of which the range is $(10^{-3}-10^{-2})$g/L, can be calculated by multiplying E that affected by the k value easily by F. Usually the order of magnitude of E value range is 2−10 and the order of magnitude of F value range is −7 to −12. Therefore, it is easy to cause greater error in prediction.

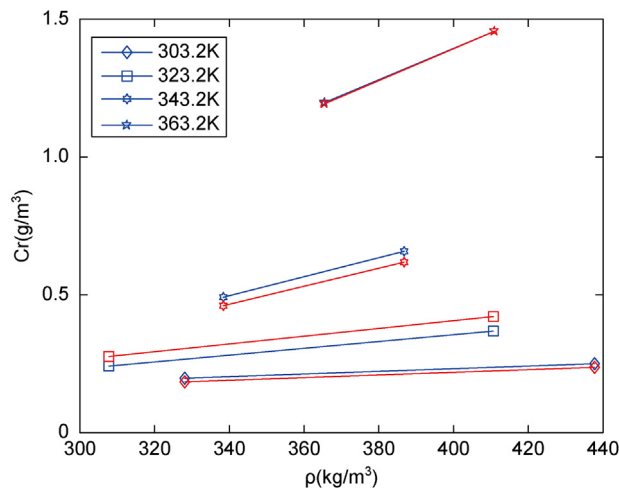(2) Through Chrastil's association model, the model co-efficients calculated from the first method cannot predict

Fig. 15. Comparison of prediction with experimental data (Method one).

Fig. 16. Comparison of prediction and experimental data (Method two).

Fig. 18. Comparison of prediction with experimental data by using the further improvement of Method two (Mixture 4).

the elemental sulfur solubility, and the error is very big. However Chrastil's model's coefficients that calculated from method two has a certain prediction ability but only the prediction results are not satisfying.

(3) On the basis of the second fitting method, the k value under different temperatures and finding the optimal density value by circulation method are respectively used to calculate the corresponding coefficients A and B of Chrastil's model. The calculation of Chrastil's model by using the further improved method two in this paper is closer to experimental data. From the above comparison of four groups of experimental data with predicted solubility in different fitting methods, the predicted accuracy increases greatly.

Acknowledgments

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