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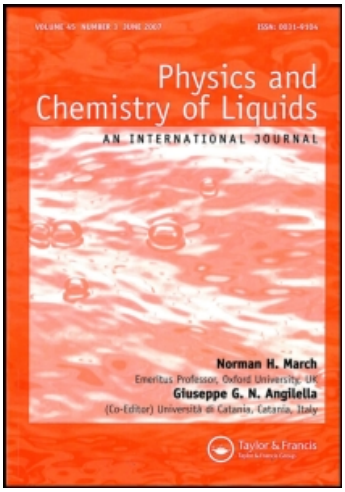

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Solubility of dilute SO_2 in DMSO Mn^2 mixture solvents and EOS Model-I

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Solubility of dilute SO_2 in DMSO + Mn^{2+} mixture solvents and EOS Model-I

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Solubility of dilute SO_2 mixture gas in dimethyl sulfoxide (DMSO) and $MnSO_4$ mixture solvent has been determined from 294.15 to 313.15 K and partial pressure of SO_2 from 0.41 to 2.70 kPa. The measured solubility data can then be used as an essential data to serve the process design of SO_2 removal from flue gas.

Keywords: Solubility; Gas–liquid equilibrium; Sulfur dioxide

1. Introduction

Removal of SO_2 and other acidic gases from flue gas is currently being addressed considerably by researchers. To this aim, various desulfurization techniques [1–4], such as activated carbon, molecular sieve, the electron-beam radiation technique, chemical method, physical solvents, etc. have been extensively studied. Compared with these methods, organic solvent absorption [4–6], to some degree, has such advantages as low investment, high SO_2 absorption efficiency, and desorption efficiency and is worthwhile of further research. At the same time, during the experiment we found that, after adding Mn^{2+} in dimethyl sulfoxide (DMSO) [6], the SO_2 absorption efficiency can be further increased, and this mixture absorbent will be used to remove SO_2 from flue gas to solve industrial problems in flue gas purification. In order to further study the absorption effect by this sort of mixture absorbent, in this article we determine the solubility of dilute SO_2 mixture gas in DMSO + $MnSO_4$ mixture absorbents to research their absorption capacity for flue gas.

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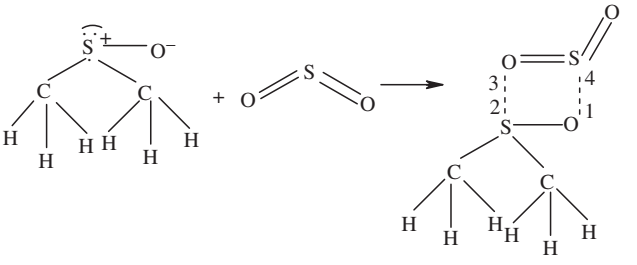

Figure 1. The absorption model of SO_2 in DMSO.

2. Experimental

2.1. *Materials and methods*

The DMSO and $MnSO_4$ used were AR grade and their purity was greater than 99%. Water was purified by vacuum distillation and deionization. Mixture solvents were obtained by mixing 0.96546 mol L^{-1} $MnSO_4$ solution in DMSO, which were mixed in 0.03 : 1 v/v. They were degassed in vacuum. The dilute SO_2 mixture was prepared by mixing sulfur dioxide, oxygen, and nitrogen. The sulfur dioxide, oxygen, and nitrogen had a purity $X_{SO_2} > 0.999$, $X_{O_2} > 0.999$ and $X_{N_2} > 0.99999$ respectively. A flue gas analyzer with SO_2 and O_2 sensor (type NTS 100, Nanjing, China) was used for the SO_2 ($\leq$0.5% SO_2) and O_2 analysis of the gas phase. The uncertainty of the SO_2 analyzer was $\pm$10 ppm, while for O_2 it was $\pm$1%. More than 0.5% SO_2 concentration was analyzed by iodometry. The two methods were calibrated before measuring SO_2 concentration. The SO_2 in the liquid was analyzed by potassium permanganate titration. The presence of sulfate ions was determined by barium chromate spectrophotometry (thermal method) [7].

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2.2. *Reaction mechanism*

DMSO is a polar organic solvent with a rather large dipole matrix, while SO_2 is also a polar gas molecule. DMSO has a strong solubility for SO_2. The absorption model of SO_2 in DMSO is shown in figure 1.

After adding Mn^{2+} in DMSO, the chemical reaction is expressed as follows [6]:

$$SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{MnSO_4} H_2SO_4 \quad (1)$$

After adding Mn^{2+} to DMSO, SO_2 is oxidized to H_2SO_4 catalyzed by $MnSO_4$. The mixed absorbent has a good removal efficiency of SO_2 and a good regeneration. Therefore, the selected absorbent is expected to perform well in SO_2 removal.

2.3. *Solubility measurement*

The schematic diagram of the experimental setup is presented in figure 2. The essence of this method is to bring a known volume of liquid into contact with a gas in a closed

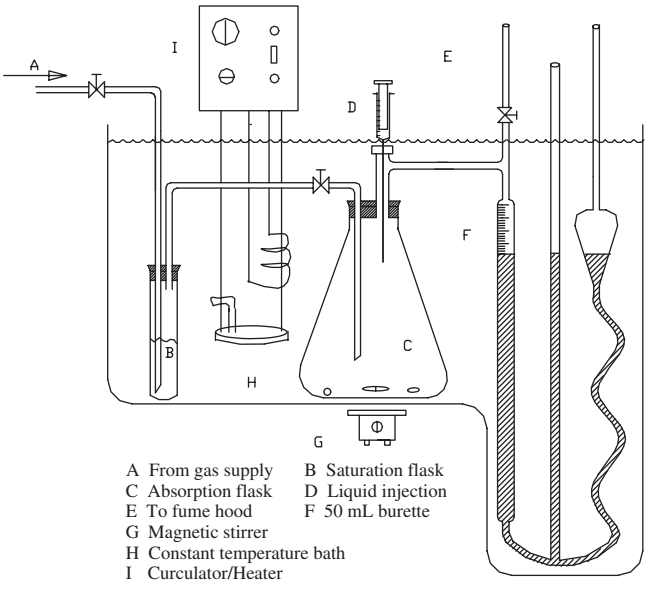

Figure 2. Solubility apparatus.

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system at a constant temperature and pressure. Equilibrium is reached by agitating the liquid for some time until no change in the volume of the gas is observed. The amount of gas changed is measured volumetrically, typical volumes ranging from 2 to 40 cm^3, with an uncertainty of $\pm 0.05\,cm^3$.

The procedure for making a solubility measurement is as follows. A gas saturated with the vapors of the absorbing liquid was passed through the system at a constant temperature long enough to completely purge the absorption flask. Then the inlet and outlet valves were closed. The height of the mercury in the three branches was leveled, ensuring that the pressure in the flask was atmospheric, and the position of the meniscus was recorded. An aliquot of a degassed mixture solvent of known composition was weighed and injected into the absorption flask. The uncertainty of the measured mass was ± 0.00001 g. The liquid sample was continuously agitated via an external magnetic stirrer. The height of the mercury in the three branches was leveled every few minutes to make sure that the gas phase was at atmospheric pressure. Equilibrium was reached when the height of the mercury in each branch was leveled and remained constant. The whole apparatus was kept at a constant temperature inside a temperature-controlled bath. The uncertainty of temperature is ± 0.05 K.

The concentration of SO_2 physical absorption in solution was analyzed by iodometry and the chemical reaction SO_2 concentration, i.e., sulfate ions, was determined by barium chromate spectrophotometry. The total '*S*' solubility can be eventually expressed as the sum of the physical SO_2 solubility plus the chemical reaction SO_2 solubility.

2.4. *Data reduction*

There are two phases in the system: (1) the gas phase which includes SO_2, O_2, N_2, and solvent vapor and (2) the liquid phase, which includes DMSO, Mn^{2+}, the dissolved SO_2, and SO_4^{2-}.

The measured volume change is equal to the volume of the gas absorbed minus the volume of liquid sample. The volume of the gas absorbed includes the volume of SO_2 (physical absorbed SO_2 and chemical reacted SO_2) and the reacted O_2 volume.

The calculation of chemical reaction SO_2 solubility ($r_{SO_2,c}$ (mol kg^{-1})) proceeds as follows.

The total concentration of SO_4^{2-} in liquid ($n_{SO_4^{2-}}$) was determined by barium chromate spectrophotometry, because mixture solvents also contain $MnSO_4$. Therefore, the chemical reaction SO_2 mole number ($rt_{SO_2,c}$ (mol)) can be calculated by means of

$$rt_{SO_2,c} = n_{SO_4^{2-}} - n_{MnSO_4} \tag{2}$$

where n_{MnSO_4} (mol) represents the mole number of SO_4^{2-} in mixture solvents (DMSO + $MnSO_4$).

Then, the chemical reaction SO_2 solubility (r_{SO_2} (mol kg^{-1})) was calculated by means of

$$r_{SO_2,c} = \frac{rt_{SO_2,c} \times 1000}{m} \tag{3}$$

where 'm' represents the mass of mixture solvents injected into the absorption flask, expressed in grams.

The calculation of reacted O_2 volume (dV_{O_2} (cm^3)) proceeds as follows.

The chemical reacted O_2 mole number (rt_{O_2} (mol)) can be calculated from equation (1). It equals half of chemical reacted SO_2 mole number, and change the O_2 moles into volume. We can obtain

$$dV_{O_2} = \frac{rt_{O_2} \times 32}{\rho_{O_2}} \text{cm}^3 \tag{4}$$

where ρ_{O_2} represents the density of O_2, in g cm^{-3}.

The calculation of total SO_2 solubility ($rt_{SO_2,t}$ (mol kg^{-1})) proceeds as follows.

The decreasing SO_2 volume (dV_{SO_2}) in the gas phase in the cell, can be obtained from

$$dV_{SO_2} = \left(dV + \frac{m}{\rho_{DMSO+MnSO_4}} - dV_{O_2} \right) \text{cm}^3 \tag{5}$$

where $\rho_{DMSO+MnSO_4}$ represents the density of mixture solvents, in g cm^{-3}, and dV represents the change in the volume of the gas in the absorption flask, in cm^3.

The total SO_2 mole number (rt_{SO_2} (mol)) can be calculated from

$$rt_{SO_2} = \frac{dV_{SO_2} \times \rho_{SO_2}}{64 \times 1000} \text{mol} \tag{6}$$

where ρ_{SO_2} represents the density of SO_2, g cm^{-3}.

The total SO_2 solubility ($r_{SO_2,t}$ (mol kg^{-1})) can be obtained from

$$r_{SO_2,t} = \frac{rt_{SO_2} \times 1000}{m} \tag{7}$$

The calculation of equilibrium partial pressure of SO_2(p_{SO_2}(kPa)) proceeds as follows.

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The inlet SO_2, O_2, and N_2 moles in the gas phase in the cell, can be obtained from the SRK equation and gas analyzer.

The inlet total gas moles (n_{inlet}) can be calculated from SRK equation

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{8}$$

The inlet SO_2, O_2, and N_2 moles in the gas phase in the cell ($n_{SO_2,1}$, $n_{O_2,1}$, n_{N_2}) can be calculated respectively as:

$$n_{SO_2,1} = y_{SO_2,1} \times n_{inlet} \tag{9}$$

$$n_{O_2} = y_{O_2,1} \times n_{inlet} \tag{10}$$

$$n_{n_2,1} = y_{n_2,1} \times n_{inlet} \tag{11}$$

The equilibrium SO_2 moles in the gas phase ($n_{SO_2,2}$) is,

$$n_{SO_2,2}\ (\text{mol}) = n_{SO_2,1} - rt_{SO_2} \tag{12}$$

The equilibrium of total moles in the gas phase (n (mol)), can be calculated by equation (13)

$$n = n_{inlet} - rt_{SO_2} \tag{13}$$

Therefore, the equilibrium mole fraction of SO_2 in the gas is,

$$y_{SO_2} = \frac{n_{SO_2,2}}{n} \tag{14}$$

Since this study is concerned only with low pressures of SO_2, the fugacity coefficients for the gas equal to 1. Thus the equilibrium partial pressure of SO_2 (P_{SO_2} (kPa)) is given by

$$P_{SO_2} = y_{SO_2} P \tag{15}$$

where P represents the atmospheric pressure.

Therefore, we can obtain the SO_2 solubility ($r_{SO_2,c}$ and $r_{SO_2,t}$) and corresponding equilibrium partial pressure of SO_2 (P_{SO_2} (kPa)) by means of the procedure outlined above.

The densities of mixture solvents $DMSO + MnSO_4$ over the temperature range 294.15–313.15 K were determined using a 10 cm^3 gravity bottle with a specially made thermometer. The density was determined by mass using an analytical balance (type TG332A, China). The balance had a range of measurement up to 20 g with an accuracy of ±0.00001 g. The temperature was controlled with ±0.05 K of the test temperature. The density of the mixture solvent as a function of temperature can be expressed as

$$\rho\ (\text{g cm}^{-3}) = -0.000007\ (T(\text{K}) - 273.15)^2 - 0.0004\ (T(\text{K}) - 273.15) + 1.1111 \tag{16}$$

2.5. *Test of apparatus*

In order to ensure proper operation of the apparatus, the solubility of SO_2 in water was measured and compared with the values reported in Ref. [8]. The experimental measurements agreed with the reported values with a mean relative deviation of 2.22%. The measured values are listed in table 1.

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Table 1. Comparison of experiment data for SO_2 solubility in water and literature data.

T (K)	S/mass%	S (Ref. [10])/mass%	$(100(S - S(\text{Ref.})))/S$
293.15	10.15	9.61	5.32
298.15	8.61	8.33	3.25
303.15	7.24	7.23	0.14
308.15	6.11	6.10	0.16

Table 2. The total S solubility at different dilute SO_2 mixture gas.

	Total S solubility $r_{SO_2,t}$ (mol kg^{-1})						
T (K)	0.410% SO_2	0.570% SO_2	0.895% SO_2	1.22% SO_2	1.36% SO_2	2.03% SO_2	2.70% SO_2
294.15	0.748	1.01	1.35	1.68	2.06	2.76	3.47
298.15	0.749	1.02	1.33	1.65	2.31	2.98	3.64
303.15	0.799	1.03	1.48	1.94	2.41	3.03	3.65
308.15	0.855	1.10	1.60	2.09	2.56	3.36	4.15
313.15	0.868	1.18	1.77	2.36	2.79	3.52	4.26

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Table 3. The chemical reacted SO_2 solubility at different dilute SO_2 mixture gas.

	$r_{SO_2,c}$ (mol kg^{-1})						
T (K)	0.410% SO_2	0.570% SO_2	0.895% SO_2	1.22% SO_2	1.36% SO_2	2.03% SO_2	2.70% SO_2
294.15	0.497	0.661	0.797	0.934	1.23	1.52	1.81
298.15	0.512	0.687	0.814	0.941	1.53	1.80	2.08
303.15	0.582	0.725	1.01	1.29	1.69	1.9478	2.21
308.15	0.660	0.832	1.17	1.51	1.92	2.40	2.88
313.15	0.710	0.959	1.42	1.88	2.26	2.74	3.22

3. Results and discussion

The measured solubilities of dilute SO_2 in DMSO + Mn^{2+} mixture solvents are shown in tables 2–4, and in figures 3–5 respectively.

From table 2 and figure 3, we can find that the total S solubilities increase with the temperature, and it is different from the physical SO_2 absorption; at the same temperature, the total S solubilities increase with the SO_2 partial pressure.

From table 3 and figure 4, we can find that the chemical reacted SO_2 solubilities increase with the temperature, too; and the reacted SO_2 solubilities increase with the SO_2 partial pressure.

The SO_2 physical solubilities and the equilibrium composition are listed in table 4 and figure 5. From the table 4 and figure 5, we can find that the physical absorption SO_2 solubilities decrease with the temperature, and increase with the SO_2 partial pressure.

4. Conclusion

(1) According to the practical needs of engineering removal of sulfur dioxide from flue gas with solvent method, the solubility of dilute SO_2 in DMSO + Mn^{2+} mixture solvent

Table 4. The SO_2 solubilities in mixture absorbent and the equilibrium composition.

T (K)	P_{SO_2} (kPa)	X_{SO_2}	$X_{H_2SO_4}$	X_{MnSO_4}	X_{DMSO}	y_{SO_2}	y_{O_2}	y_{DMSO}	y_{N_2}
294.15	0.228	0.0185	0.0366	0.00195	0.943	0.00229	0.0776	0.00183	0.918
294.15	0.306	0.0253	0.0478	0.00191	0.925	0.00307	0.116	0.00183	0.879
294.15	0.585	0.0387	0.0563	0.00187	0.903	0.00585	0.187	0.00182	0.806
294.15	0.865	0.0516	0.0644	0.00182	0.882	0.00862	0.257	0.00181	0.733
294.15	0.956	0.056	0.0824	0.00178	0.860	0.00949	0.271	0.00181	0.718
294.15	1.450	0.0798	0.0975	0.00170	0.821	0.0144	0.321	0.00180	0.663
294.15	1.945	0.101	0.111	0.00162	0.786	0.0194	0.386	0.00180	0.593
298.15	0.227	0.0175	0.0377	0.00195	0.943	0.00228	0.0775	0.00260	0.918
298.15	0.303	0.0238	0.0496	0.00191	0.925	0.00304	0.116	0.00260	0.878
298.15	0.582	0.0366	0.0575	0.00187	0.904	0.00582	0.186	0.00259	0.805
298.15	0.861	0.0488	0.0649	0.00183	0.884	0.00859	0.256	0.00258	0.733
298.15	0.902	0.0519	0.1009	0.00175	0.845	0.00859	0.270	0.00256	0.718
298.15	1.422	0.0743	0.1141	0.00167	0.810	0.0142	0.320	0.00256	0.663
298.15	1.941	0.0948	0.1261	0.00161	0.777	0.0194	0.385	0.00256	0.593
303.15	0.223	0.0159	0.0427	0.00194	0.939	0.00223	0.0774	0.00364	0.917
303.15	0.298	0.0217	0.0524	0.00191	0.924	0.00297	0.116	0.00362	0.878
303.15	0.542	0.0331	0.0705	0.00185	0.895	0.00541	0.186	0.00362	0.805
303.15	0.787	0.0437	0.0875	0.00179	0.867	0.00786	0.256	0.00362	0.733
303.15	0.900	0.0472	0.1108	0.00174	0.840	0.00893	0.270	0.00361	0.718
303.15	1.421	0.0677	0.1229	0.00167	0.808	0.0142	0.320	0.00360	0.662
303.15	1.943	0.0875	0.1340	0.00161	0.7769	0.0194	0.385	0.00365	0.592
308.15	0.186	0.0142	0.0483	0.00193	0.936	0.00186	0.0771	0.00504	0.916
308.15	0.290	0.0194	0.0597	0.00190	0.919	0.00289	0.116	0.00502	0.876
308.15	0.518	0.0294	0.0813	0.00183	0.888	0.00517	0.186	0.00503	0.804
308.15	0.746	0.0388	0.1014	0.00177	0.858	0.00745	0.256	0.00502	0.732
308.15	0.895	0.0419	0.125	0.00172	0.832	0.00889	0.270	0.00502	0.717
308.15	1.377	0.0595	0.148	0.00164	0.791	0.0137	0.319	0.00501	0.662
308.15	1.858	0.0754	0.169	0.00156	0.754	0.0185	0.384	0.00501	0.592
313.15	0.182	0.0115	0.0519	0.00193	0.935	0.00182	0.0769	0.00690	0.914
313.15	0.271	0.0159	0.0685	0.00189	0.914	0.00270	0.115	0.00689	0.875
313.15	0.509	0.0236	0.0975	0.00181	0.877	0.00507	0.185	0.00689	0.803
313.15	0.719	0.031	0.124	0.00174	0.843	0.00718	0.255	0.00689	0.731
313.15	0.798	0.0336	0.145	0.00169	0.820	0.00794	0.269	0.00687	0.716
313.15	1.34	0.0479	0.168	0.00162	0.783	0.0133	0.318	0.00686	0.662
313.15	1.88	0.0609	0.189	0.00155	0.749	0.0187	0.383	0.00686	0.591

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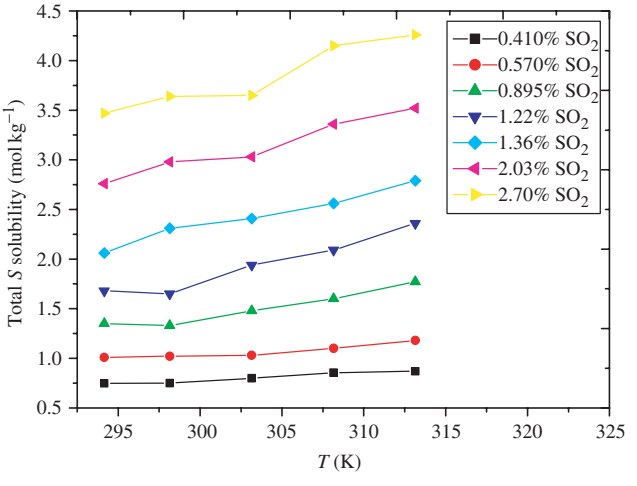

Figure 3. The relation of total S solubility with temperature at different SO_2 mixture gas.

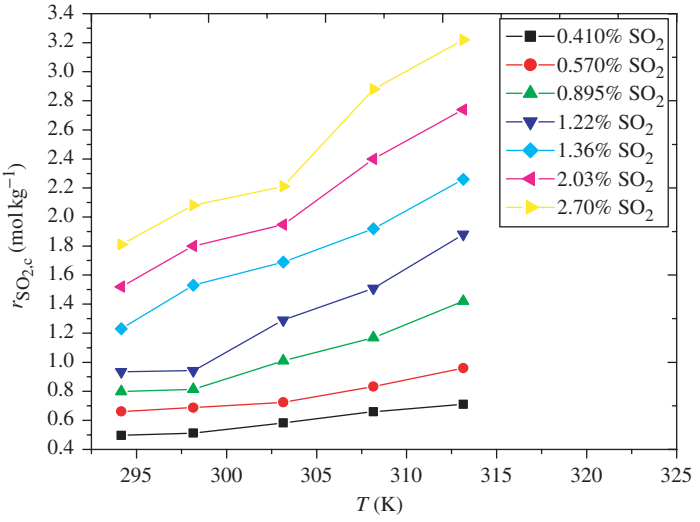

Figure 4. The relation of chemical reacted SO_2 solubility with temperature at different SO_2 mixture gas.

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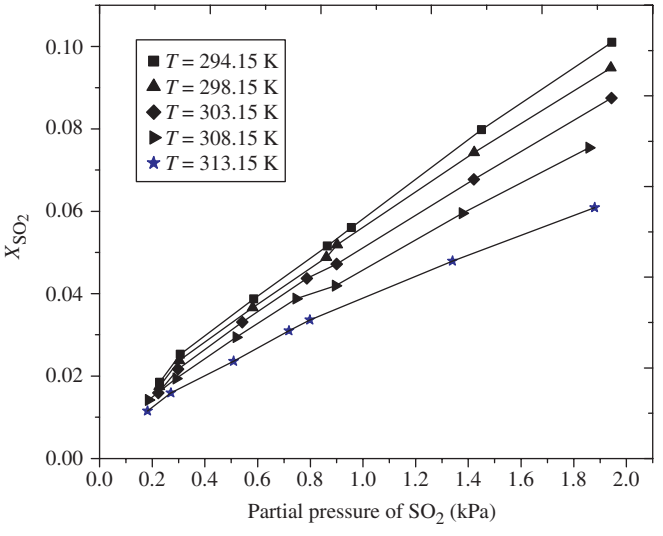

Figure 5. The relation of physical SO_2 solubility with equilibrium partial pressure of SO_2 at different temperature.

has been determined from 294.15 to 313.15 K and partial pressure of SO_2 from 0.41 to 2.70 kPa by suitable experimental method and solubility apparatus. The results show that there is a great solubility for dilute SO_2 in mixture absorbent.

(2) Compared with DMSO physical absorption [5], after adding additives of Mn^{2+}, desulfurizing efficiency is increased, and the mixture absorbent can be regenerated by this method [9]. It has stronger regeneration compared with the traditional alkali methods. Therefore, the application and development of the techniques outlined above has a promising future in SO_2 removal.

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