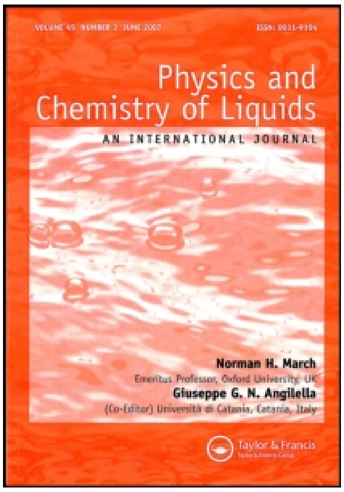

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Thermodynamic model of solubility for CO_2 in dimethyl sulfoxide

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The solubility of CO_2 in dimethyl sulfoxide has been determined from 293.15 K to 313.15 K and partial pressure of CO_2 from 5.56 kPa to 18.2 kPa. Based on the data obtained from the CO_2 solubility experiments, a gas–liquid phase equilibrium model for CO_2–DMSO system was proposed. The average relative deviation between the experimental data of equilibrium partial pressure of CO_2 in DMSO and the corresponding data predicted by the model proposed is 4.85%, it shows that the agreement is satisfactory.

Keywords: solubility; gas–liquid equilibrium; sulfur dioxide; carbon dioxide; model

1. Introduction

The environmental pollution from flue gases is becoming more and more serious, physical absorption with a polar solvent provides a convenient and economic method for removing acid gases [1–3]. But the flue gas consists of not only SO_2 but also a lot of CO_2, the absorbents used to remove the SO_2 from the flue gas should have a high absorptive selectivity for SO_2 only so as to hold its perdurability of SO_2 absorption in order to proof the high selectivity for SO_2 and CO_2 of the selected organic absorbent. In our previous work [1], dimethyl sulfoxide (DMSO) was found to be a good absorbent for SO_2 absorption. Now, in order to use the DMSO as the absorbent to remove the SO_2 from the flue gas, its good absorptive selectivity only for SO_2 should be examined by confirming that the solubility of CO_2 in DMSO is small. In this study, the solubility of CO_2 in DMSO has been determined at the temperature range of 293.15–313.15 K and the partial pressure range of CO_2 from 5.56 kPa to 18.2 kPa [4]. The result shows there is great solubility for dilute SO_2 in DMSO, and the little solubility for CO_2 in DMSO, the absorption solvent has good selectivity for SO_2 and CO_2. Based on the data obtained from the CO_2 solubility experiments, the gas–liquid equilibrium data obtained were correlated by the thermodynamic model, and comparing the correlated results with the experimental data.

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2. Experimental section

2.1. *Materials and analysis*

Dimethyl sulfoxide was AR grade and its purity was greater than 99%. It was degassed under vacuum. Water was purified by vacuum distillation and deionsation. The CO_2 mixture was prepared by mixing carbon dioxide and nitrogen. The carbon dioxide and nitrogen had a purity, $x\ (CO_2) > 0.999$ and $x\ (N_2) > 0.99999$, respectively. The solubility of CO_2 was measured using the apparatus shown in reference [1]. A CO_2 analyser (type RD-7AG, Nanjing, China) was used for the CO_2 analysis of the gas phase. The uncertainty of the CO_2 analyzer was ±3% of maximum measurement value. The measurement range of the CO_2 analyser is 0–20%.

2.2. *Solubility measurement*

The solubility of CO_2 in DMSO was measured using the previous apparatus [1].

The principle and procudure for solubility measurement used in the present study has already been described in a previous paper [1,4], hence, we are only giving hereafter the deference of solubility measurement.

The equilibrium partial pressure of CO_2 (P_{CO_2} kPa^{-1}) is given as follows:

$$p_{co_2} = y_{co_2} P_0 = \frac{n_{co_{2,2}}}{n_{co_{2,2}} + n_{N_2} + n_{DMSO}} \times P_0,$$

where

y_{CO_2} the equilibrium CO_2 mole fraction in the gas phase,
P_0 the atmospheric pressure, kPa,
$n_{CO_{2,2}}$ mol -the equilibrium CO_2 moles in the gas phase,
n_{N_2} mol -the equilibrium N_2 moles in the gas phase,
n_{DMSO} mol -the equilibrium DMSO moles in the gas phase, it can be calculated by its saturation vapour pressure.

3. Result and discussion

The solubility of CO_2 in dimethyl sulfoxide is shown in Table 1 and Figure 1.

3.1. The comparison of the experimental measurements and the reported values

The Comparison of Henry's law constant for CO_2 in DMSO at 25°C of the experimental measurements and the reported values are listed in Table 2. We can find that the experimented values and the reported values [5] are quite approximate.

3.2. *The thermodynamic model*

According to the fundamental thermodynamic relationship that fugacities of a component in coexisting phases are equal at equilibrium, for gas–liquid equilibrium,

$$\hat{f}_i^g = \hat{f}_i^L, \tag{1}$$

Table 1. Solubility of CO_2 in DMSO at different temperatures.

					p_{CO_2}(kPa)		
T/K	$m(CO_2)\,mol\,kg^{-1}$	P_0 (kPa)	y_i	$x_i \times 10^3$	p_{exp} (kPa)	p_{cal} (kPa)	Relative deviation (%)
293.15	0.02264	100.88	0.1800	1.77	18.16	18.66	2.77
293.15	0.02123	99.98	0.1701	1.66	17.01	17.03	0.13
293.15	0.01393	100.47	0.1112	1.09	11.17	11.78	5.46
293.15	0.01204	99.29	0.09709	0.942	9.64	9.68	0.38
293.15	0.009789	100.47	0.07803	0.766	7.84	8.04	2.50
293.15	0.009150	100.27	0.07300	0.716	7.32	8.01	9.36
293.15	0.008702	99.49	0.07006	0.681	6.97	7.30	4.84
293.15	0.006951	99.52	0.05597	0.544	5.57	5.10	−8.44
298.15	0.02149	100.57	0.1799	1.68	18.09	19.61	8.39
298.15	0.02034	99.70	0.1708	1.59	17.03	17.43	2.39
298.15	0.01496	99.53	0.1263	1.17	12.57	12.13	−3.48
298.15	0.01368	99.73	0.1152	1.07	11.49	10.65	−7.28
298.15	0.01329	100.29	0.1112	1.04	11.15	10.22	−8.38
298.15	0.01146	99.19	0.09709	0.897	9.63	9.74	1.07
298.15	0.009316	100.26	0.07810	0.729	7.83	8.11	3.62
298.15	0.008702	100.18	0.07307	0.681	7.32	8.04	9.95
298.15	0.008293	99.47	0.07007	0.649	6.97	7.41	6.45
298.15	0.006631	99.54	0.05596	0.519	5.57	5.34	−4.15
303.15	0.01957	99.63	0.1707	1.53	17.01	17.74	4.30
303.15	0.01445	99.49	0.1262	1.13	12.56	12.32	−1.96
303.15	0.01317	99.73	0.1152	1.03	11.49	10.89	−5.25
303.15	0.01278	100.31	0.1112	1.00	11.15	10.47	−6.08
303.15	0.01104	99.15	0.09713	0.864	9.63	9.63	0.00
303.15	0.008958	100.08	0.07804	0.701	7.81	8.29	6.12
303.15	0.008383	100.03	0.07308	0.656	7.31	7.68	5.11
303.15	0.007961	99.25	0.07003	0.623	6.95	7.50	7.99
303.15	0.006375	99.39	0.05594	0.499	5.56	5.39	−3.10
308.15	0.01368	100.40	0.1803	1.07	18.10	18.72	3.44
308.15	0.01278	99.54	0.1708	1.00	17.00	16.67	−1.93
308.15	0.009482	99.43	0.1263	0.742	12.56	12.03	−4.16
308.15	0.008664	99.64	0.1152	0.678	11.48	10.68	−7.00
308.15	0.008434	100.38	0.1112	0.660	11.16	10.27	−8.03
308.15	0.007283	99.27	0.09711	0.570	9.64	9.68	0.35
308.15	0.005902	100.04	0.07807	0.462	7.81	8.20	4.97
308.15	0.005519	99.97	0.07302	0.432	7.30	7.88	7.88
308.15	0.005251	99.22	0.07005	0.411	6.95	7.22	3.91
308.15	0.004203	99.33	0.05598	0.329	5.56	5.35	−3.80
313.15	0.01213	100.36	0.1803	0.949	18.09	17.74	−1.91
313.15	0.01140	99.54	0.1707	0.892	16.99	16.23	−4.47
313.15	0.008421	99.51	0.1262	0.659	12.56	11.40	−9.25
313.15	0.007705	99.66	0.1152	0.603	11.48	10.45	−8.96
313.15	0.007500	100.53	0.1111	0.587	11.17	10.21	−8.63
313.15	0.006478	99.50	0.09709	0.507	9.66	8.88	−8.05
313.15	0.005238	100.01	0.07809	0.410	7.81	7.81	0.00
313.15	0.004893	99.97	0.07302	0.383	7.30	7.42	1.58
313.15	0.004650	99.09	0.07004	0.364	6.94	6.78	−2.31
313.15	0.003730	99.29	0.05600	0.292	5.56	5.08	−8.62

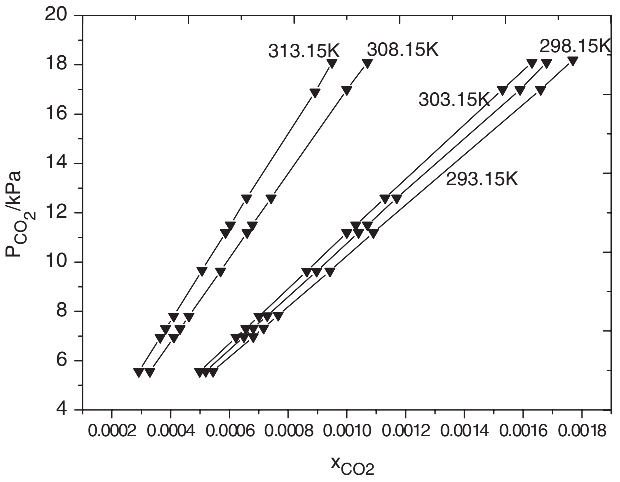

Figure 1. Phase equilibrium for (carbon dioxide + DMCO) at different temperatures.

Table 2. Comparison of Henry's law constant for CO_2 in polar solvent DMSO at 25°C.

	H (atm)	
Solvent	Experimental value	Literature value
DMSO	107	106 ([5])

Note: $H = P_{co_2}/x_{co_2}$, where p_{co_2} is in atm and x_{co_2} is the CO_2 mole fraction.

in the low pressure,

$$\hat{\phi}_i^g y_i p = \gamma_i x_i \phi_i^s p_i^s. \tag{2}$$

Equation (2) is the basic thermodynamic relationship equation, where p_i^s is calculated by the equation of Reid[6] x_i, y^i, p are the mole fraction of the liquid, gas and the total pressure. So the key of the model is the calculation of $\hat{\phi}_i^g$, ϕ_i^s and γ_i. Critical properties and acentric factors see Table 3 [6,7].

3.2.1. *Fugacity coefficient* $\hat{\phi}_i^s$ *of pure component i at the system temperature T and* p_i^s

Fugacity coefficient ϕ_i^s may be obtained from equation of the modification of Redlich–Kwong equation of state by Soave for this study [6].

Fugacity coefficient ϕ_i^s of pure component following the SRK equation of State are given by:

$$\ln \hat{\phi}_i^s = Z - 1 - \ln(Z - B) - \frac{A}{B}\ln\left(1 + \frac{B}{Z}\right), \tag{3}$$

Table 3. Critical properties and acentric factors.

Component	T_c (K)	P_c (10^5 Pa)	ω	V_c ($cm^3 mol^{-1}$)
CO_2	304.1 ([6])	73.8 ([6])	0.239 ([6])	93.9 ([6])
N_2	126.2 ([6])	33.9 ([6])	0.039 ([6])	89.8 ([6])
DMSO	707 ([7])	58.5 ([7])	0.025 ([7])	276 ([7])

where

$$A = \frac{aP}{R^2T^2}. \tag{4}$$

$$B = \frac{bP}{RT}. \tag{5}$$

$$Z = \frac{PV}{RT}. \tag{6}$$

Pure component constants required in Equation 3 are given in Table 3.

3.2.2. *Fugacity coefficient $\hat{\phi}_i^g$ for constituents i of a gas mixture*

Fugacity coefficient $\hat{\phi}_i^g$ for constituents i of a gas mixture following the SRK equation of State are given by

$$\text{In } \hat{\phi}_i^g = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B}\left[\frac{2\sum_{j=1}^{N} y_j \mathrm{a}_{ij}}{\mathrm{a}} - \frac{b_i}{b}\right]\ln\left(1+\frac{B}{Z}\right). \tag{7}$$

For a gas mixture, the following mixing rules apply:

$$a = \sum_i \sum_j y_i y_j a_{ij}, \tag{8}$$

$$b = \sum_i y_i b_i, \tag{9}$$

where y_i, y_j is the mole fraction of component i and j, a_{ij} is given as follows:

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1-k_{ij}), \tag{10}$$

where k_{ij} is the interaction coefficient. k_{ij} is given as following [8]:

$$k_{ij} = \frac{1-2(T_{ci}T_{cj})^{1/2}}{T_{ci}+T_{cj}}. \tag{11}$$

Table 4. Binary interaction constants.

Components	τ_{ij}
CO_2 –DMSO	–3.11
DMSO – CO_2	11.2

3.2.3. *Activity coefficient γ_i of component i*

Activity coefficient γ_i of component i in a liquid solution can be calculated by NRTL equation [9]. According the experimental system, and the recommendation of literature [9], $\alpha_{12} = 0.3$. For a Binary system, adjustable parameters τ_{ij} can be obtained from simplex optimization.

Object function $F = \min \sum |\gamma_{\exp} - \gamma_{\text{cal}}|^2$, the result of τ_{ij} is listed in Table 4.

3.2.4. *The test of experimental data*

The calculated solubility result with binary interaction coefficient are listed in Table 1. The comparison with diagonal chart is listed in Figure 1. From Table 1 and Figure 1, we can know the solubilities calculated by the model showing good agreement with the experimental data.

4. Conclusion

(1) According to the measured solubilities of CO_2 in DMSO from 293.15 K to 313.15 K and partial pressure of CO_2 from 5 kPa to 18 kPa, a suitable solubility model based on gas–liquid phase equilibrium principles is proposed, and the solubilities calculated by the model show good agreement with the experimental data.

(2) From Figure 1 and Table 1, we can find that the solubilities calculated by the model show good agreement with experimental data.

(3) The experimental solubility and correlation equation in this article can be used as essential data and model to serve the process design of removal SO_2 from flue gas.

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