

Gas–Liquid Equilibrium Data for the Mixture Gas of Sulfur Dioxide + Nitrogen with Poly(ethylene glycol) Aqueous Solutions at 298.15 K and 122.61 kPa

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Isothermal gas–liquid equilibrium (GLE) data have been measured for the system SO₂ + N₂ + poly(ethylene glycol) (PEG 400) + water at 298.15 K and 122.61 kPa and SO₂ partial pressures in the range of (0 to 122) Pa. Measurements were carried out by a saturation method using a glass absorption apparatus, which was controlled at constant temperatures by a thermostatic circulation bath with Beckmann thermometer. The GLE data were obtained with relative uncertainties within $\pm 2.5\%$ for SO₂ concentration in the gas phase and $\pm 0.6\%$ for SO₂ concentration in the liquid phase. The measurement showed that the addition of water into PEG decreased the solubility of SO₂ compared with pure PEG. Compared with our previous work (Zhang, J. B.; Wei, X. H.; et al. *J. Chem. Eng. Data* 2008, 53, 2372–2374), the aqueous PEG 400 solutions present stronger solubility to SO₂ than ethylene glycol (EG) aqueous solutions. The results of this work can be used to provide important GLE data for the design and operation of the absorption and desorption process in flue gas desulfurization (FGD) with potential industrial application of PEG 400 aqueous solutions.

1. Introduction

Sulfur dioxide (SO₂) is an important atmospheric pollutant, and therefore it is severe in environmental protection. Emissions of SO₂ into the atmosphere have increased steadily with industrial development. The combustion of coal, due to its high sulfur content,¹ means it is necessary to dedicate particular attention to eliminating the resulting emission of SO₂. Among the many procedures employed to desulfurize exhaust gases, organic solvents used as absorbents have been identified as an option among the regenerative processes^{2–6} because regeneration can be done by pressure reduction, by temperature increase, and by use of a carrier gas. Of the numerous organic solvents, alcohols show favorable absorption and desorption capabilities for acid gases in industrial processes;⁷ therefore, our research group has paid great attention to the alcohol + water system for SO₂ removal for several years.^{8–12}

PEG 400 is a promising medium for flue gas desulfurization (FGD) processes because of its high absorption capacity, its low-to-moderate vapor pressure for temperatures below 373 K, and its low toxicity. This work was mainly focused on providing GLE data for SO₂ + N₂ mixtures with various PEG 400 + water solutions (PEGWs) at 298.15 K and 122.61 kPa and on optimizing the composition of PEGW for the future FGD processes.

2. Experimental Section

Materials. The SO₂ gas (99.9 %) and pure N₂ gas (> 99.9 %), purchased from the Beijing Gas Center, Peking University

(China), were employed to determine the GLE data for PEGWs with SO₂ in this work. The analytical grade PEG 400 with the number average molecular mass of 400 (380 to 420) was purchased from Beijing Reagent Company. It was used after drying over molecular sieves (type 4A) and decompression filtration before measurements. The purity of the sample was checked by density and viscosity determination at 298.15 K. The density of PEG 400 at 298.15 K was found to be 1.1218 g·cm⁻³, in good agreement with the literature.¹³ Bidistilled water was used.

Apparatus and Procedure. The apparatus used in this work was based on a dynamic analytic method and is reported in previous work.¹¹ The concentrations of SO₂ in the gas phase were determined by a gas chromatograph on a 2 × 3.2 (m × mm) Porapak Q packed column using an Agilent 6890N gas chromatograph (GC) and an FPD detector linked to an HP6890 workstation. In all cases, the injections were repeated at least seven times, and the average results were reported. To calibrate the GC FPD detector, the external standard method was used. The sulfur(IV) concentration in the liquid phase (C_{SO₂}) was determined according to ref 14. The overall relative uncertainty in the determination of the sulfur(IV) concentration was estimated to be $\pm 0.6\%$. Experiments were carried out at 298.15 K, kept at a constant temperature using a CS 501 thermostatted bath with a Beckmann thermometer purchased from Huanghua Meter Factory (Hebei province, China) with ± 0.02 K, and inspected using an accurate thermometer purchased from Fuqiang Meter Factory (Hebei province, China) with the precision of ± 0.02 K, and the total pressure of 122.61 kPa inspected by a pressure gauge purchased from Fuqiang Meter Factory (Hebei province, China) with ± 0.133 kPa, using SO₂ + N₂ mixtures in the SO₂ partial pressure range from (0 to 122) Pa.

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Table 1. GLE for PEG (1) + H₂O (2) + SO₂ (3) + N₂ (4) at 298.15 K and 122.61 kPa

C_3				C_3			
100 w_1	$10^{-6} \Phi_3$	($\text{mg} \cdot \text{L}^{-1}$)	P_3/Pa	100 w_1	$10^{-6} \Phi_3$	($\text{mg} \cdot \text{L}^{-1}$)	P_3/Pa
0.00	6.40	61.8	0.785	60.01	775	571	95.1
0.00	25.6	70.3	3.14	60.01	829	598	102
0.00	53.8	77.6	6.59	80.02	9.19	400	1.13
0.00	79.1	84.9	9.70	80.02	53.8	554	6.59
0.00	137	94.6	16.8	80.02	55.8	561	6.84
0.00	234	115	28.6	80.02	95.1	567	11.7
0.00	381	153	46.7	80.02	210	595	25.7
0.00	502	176	61.5	80.02	254	608	31.2
0.00	580	200	71.2	80.02	354	690	43.4
0.00	627	219	76.9	80.02	502	779	61.5
20.01	23.9	132	2.93	80.02	550	786	67.4
20.01	38.2	135	4.68	80.02	695	837	85.2
20.01	82.8	153	10.2	80.02	994	933	122
20.01	128	163	15.7	85.00	19.2	265	2.35
20.01	154	170	18.9	85.00	35.3	429	4.33
20.01	170	172	20.8	85.00	139	492	17.0
20.01	258	187	31.6	85.00	237	533	29.0
20.01	384	209	47.1	85.00	424	620	52.0
20.01	425	221	52.1	85.00	549	670	67.3
20.01	536	237	65.7	85.00	709	769	86.9
20.01	603	245	74.0	85.00	858	844	105
20.01	649	253	79.6	90.01	15.0	197	1.84
20.01	692	264	84.9	90.01	32.8	408	4.02
20.01	889	295	109	90.01	52.8	550	6.47
40.39	28.2	203	3.45	90.01	149	581	18.3
40.39	34.8	224	4.27	90.01	203	690	24.9
40.39	64.9	248	7.95	90.01	361	749	44.2
40.39	84.2	253	10.3	90.01	378	793	46.3
40.39	110	273	13.5	90.01	457	824	56.1
40.39	120	277	14.7	90.01	591	901	72.5
40.39	187	294	22.9	90.01	644	950	78.9
40.39	357	304	43.8	90.01	767	998	94.0
40.39	488	325	59.8	90.01	827	1029	101
40.39	570	335	69.9	100.00	8.89	632	1.09
40.39	893	361	110	100.00	38.0	865	4.66
60.01	11.8	78.7	1.45	100.00	57.6	889	7.06
60.01	23.6	273	2.89	100.00	85.3	957	10.5
60.01	26.5	362	3.25	100.00	89.5	964	11.0
60.01	43.7	393	5.36	100.00	115	988	14.1
60.01	72.9	403	8.94	100.00	174	1022	21.4
60.01	122	431	14.9	100.00	267	1111	32.8
60.01	124	441	15.1	100.00	375	1227	45.9
60.01	218	451	26.7	100.00	450	1299	55.2
60.01	270	479	33.0	100.00	463	1306	56.7
60.01	392	499	48.1	100.00	509	1336	62.4
60.01	507	520	62.2	100.00	681	1531	83.5
60.01	541	533	66.3	100.00	695	1548	85.2
60.01	647	557	79.4	100.00	815	1658	99.9

3. Results and Discussion

GLE Data for PEGWs with Dilute SO₂. A series of GLE experiments for PEG + H₂O + SO₂ + N₂ were performed at 298.15 K and 122.61 kPa, and the GLE data are listed in Table 1. In this table, the mass fraction of PEG in PEGW (w_1) was used in the actual operation, and PEG 400 and water were weighed using a Sartorius BS224S balance with a precision of ± 0.0001 g to present accurate factual mass fraction of PEG 400. The GLE data were obtained with relative uncertainties within ± 2.5 % for SO₂ concentration in the gas phase and ± 0.6 % for SO₂ concentration in the liquid phase.

In Table 1, Φ_3 denotes the concentration of SO₂ in the gas phase as $\phi_3 \approx (p_{\text{SO}_2})/(p_{\text{SO}_2} + p_{\text{H}_2\text{O}} + p_{\text{N}_2} + p_{\text{PEG}}) = (p_{\text{SO}_2}/p_{\text{total}})$; p_3 and p_{total} denote, respectively, the partial pressure of SO₂ in the gas phase and the total pressure of the GLE system; and C_3 denotes the concentration of SO₂ in the liquid phase.

The GLE curves of PEGWs for SO₂ absorption at 298.15 K and 122.61 kPa are plotted in Figure 1. Solubility of SO₂ in PEGWs when SO₂ volume fraction in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$ is shown in Figure 2.

Figures 1 and 2 show that the addition of H₂O into PEG 400 decreased the solubilities of SO₂ in PEG 400; meanwhile, w_1

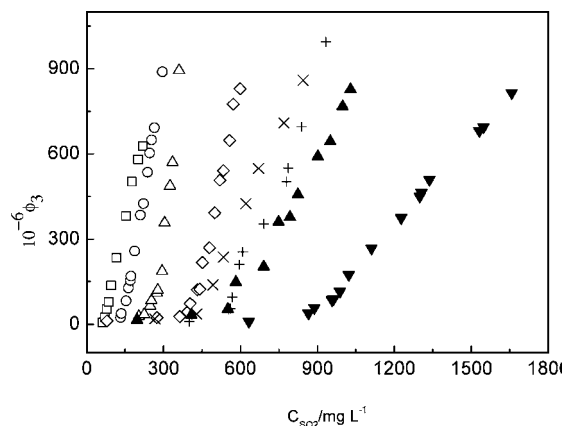


Figure 1. GLE curves for PEG 400 (1) + H₂O (2) + SO₂ (3) + N₂ (4): □, $w_1 = 0$; ○, $w_1 = 0.20$; △, $w_1 = 0.40$; ◇, $w_1 = 0.60$; +, $w_1 = 0.80$; ×, $w_1 = 0.85$; ▲, $w_1 = 0.90$; ▼, $w_1 = 1.00$.

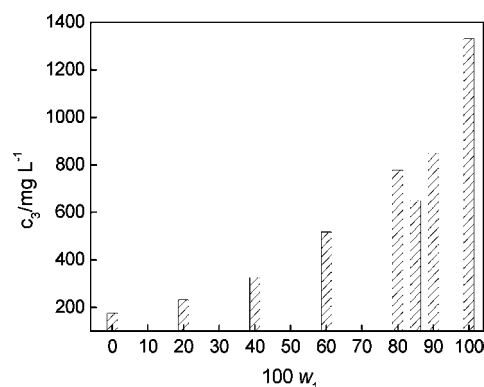


Figure 2. Solubility of SO₂ in PEGWs when SO₂ concentration in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$.

$w_1 = 0.85$ exhibits an extreme minimum value to dissolve SO₂, and the solubility is $651 \text{ mg} \cdot \text{L}^{-1}$ when SO₂ concentration in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$; $w_1 = 0.80$ PEGW shows a higher capability to dissolve SO₂, and the solubility is $778 \text{ mg} \cdot \text{L}^{-1}$ when SO₂ concentration in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$. In the entire composition range, the pure PEG 400 shows the strongest capability to dissolve SO₂, and the solubility is $1330 \text{ mg} \cdot \text{L}^{-1}$ when SO₂ concentration in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$. The above results may be related to the excess properties of aqueous PEG 400 solutions¹⁵ and the hydrogen bonding and interactions among PEG 400, H₂O, and SO₂, and the similar hydrogen bonding and interactions among EG, H₂O, and SO₂ have been published in our previous work.¹⁶ Compared with our previous work,¹² the PEG 400 aqueous solutions present stronger solubility to SO₂ than ethylene glycol (EG) aqueous solutions in the entire composition range. The result gives us important information to optimize the composition of PEGWs for the SO₂ absorption processes.

4. Conclusion

This paper presents the results of fundamental investigations on isothermal GLE data of various aqueous solutions of PEG 400 with SO₂, which were determined as a function of composition at 298.15 K and 122.61 kPa. The GLE data show that the addition of water into PEG 400 decreased the solubility of SO₂ compared with pure PEG 400. The experimental results showed that the $w_1 = 0.85$ PEG 400 presents the extreme minimum value solubility of $651 \text{ mg} \cdot \text{L}^{-1}$ to SO₂ when the SO₂ concentration in the gas phase was set at $\Phi_{\text{SO}_2} = 5 \cdot 10^{-4}$; the

solubility of SO₂ in $w_1 = 0.80$ PEGW is presented at 778 mg·L⁻¹; and the solubility of SO₂ in pure PEG 400 is 1330 mg·L⁻¹ at the same gas phase composition.

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