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Gas−Liquid Equilibrium Data for Sulfur Dioxide + Nitrogen in Diethylene Glycol + Water at 298.15 K and 123.15 kPa

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Isothermal gas−liquid equilibrium (GLE) data have been measured for the system diethylene glycol (DEG) (1) + water (2) + SO_2 (3) + N_2 (4) at 298.15 K and 123.15 kPa and SO_2 partial pressures in the range of (0.7 to 100) 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 a Beckmann thermometer. The GLE compositions were obtained with relative uncertainties within ± 0.6 % for SO_2 concentration in the liquid phase and ± 3.5 % for SO_2 mole fraction in the gas phase. The measurement showed that the system DEG (1) + water (2) in the mass fraction range of $w_1 = (0.60 \text{ to } 1.00)$ decreased the solubility of SO_2 and the system DEG (1) + water (2) in the mass fraction range of $w_1 = (0.00 \text{ to } 0.60)$ increased the solubility of SO_2. Compared with our previous work (Zhang, J. B.; Wei, X. H.; et al. *J. Chem. Eng. Data* **2008**, *53*, 2372−2374; Zhang, J. B.; Wei, X. H.; et al. *J. Chem. Eng. Data* **2009**, DOI: 10.021/je900392e), the solubility of SO_2 in pure DEG is 259 $\text{mg}\cdot\text{L}^{-1}$ when SO_2 volume fraction in the gas phase is $\Phi_3 = 5\cdot10^{-4}$, which is higher than in pure ethylene glycol (EG, 128 $\text{mg}\cdot\text{L}^{-1}$) and lower than in pure poly(ethylene glycol) 400 (PEG 400, 1330 $\text{mg}\cdot\text{L}^{-1}$). 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 various PEG aqueous solutions.

Introduction

Natural resources are limited, and so coal with high sulfur content is commonly the most important consumption resource. 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 sulfur dioxide (SO_2). Emissions of SO_2 into the atmosphere have steadily increased with industrial development. SO_2 is an important atmospheric pollutant, and therefore, it is severe in environmental protection. 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 SO_2 removal for several years.[8–12]

Diethylene glycol (DEG) is a promising medium for flue gas desulfurization (FGD) processes because of its absorption capacity to acidic gases, its low-to-moderate vapor pressure for temperatures below 373 K, and its low toxicity. This work was mainly focused on providing gas−liquid equilibrium (GLE) data for SO_2 + N_2 mixtures with various DEG + water solutions at 298.15 K and 123.15 kPa to develop the various poly(ethylene glycol) (PEG) aqueous solutions and present the GLE data.

Experimental Section

Materials. The SO_2 gas (99.9 %) and pure N_2 gas (> 99.9 %), purchased from the Beijing Gas Center, Peking University (China), were employed to determine the GLE data for DEG + water with SO_2 in this work. The analytical grade DEG 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 determination at 298.15 K. The density of DEG at 298.15 K was found to be 1.1132 $\text{g}\cdot\text{cm}^{-3}$, in good agreement with the literatures.[13,14] Bidistilled water was used in this work.

Apparatus and Procedure. The apparatus used in this work was based on a dynamic analytic method and is reported in our previous work.[11] The concentrations of SO_2 in the gas phase were determined by a gas chromatograph (GC) on a 2 m × 3.2 mm Porapak Q packed column using an Agilent 6890N gas chromatograph and an FPD detector linked to an HP6890 workstation. In all cases, the injections were repeated at least seven times, and the average values were reported. To calibrate the GC FPD detector, the external standard method was used. The sulfur(IV) composition in the liquid phase (C_{SO_2}, $\text{mg}\cdot\text{L}^{-1}$) was determined according to ref 15. The overall relative uncertainty in the determination of the sulfur(IV) composition was estimated to be ± 0.6 %. Experiments were carried out at 298.15 K, kept at a constant temperature using CS 501 thermostatted bath with a Beckmann thermometer purchased from Huanghua Meter Factory (Hebei province, China) with

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Table 1. GLE for DEG (1) + H_2O (2) + SO_2 (3) + N_2 (4) at 298.15 K and 123.15 kPa[a]

		C_3	P_3			C_3	P_3
$100\ w_1$	$10^6\ \Phi_3$	$mg \cdot L^{-1}$	Pa	$100\ w_1$	$10^6\ \Phi_3$	$mg \cdot L^{-1}$	Pa
0.00	6.40	61.8	0.78	69.95	198	27.3	23.9
0.00	25.6	70.3	3.14	69.95	232	34.7	28.2
0.00	53.8	77.6	6.59	69.95	274	46.5	81.8
0.00	79.1	84.9	9.70	69.95	287	82.1	34.9
0.00	137	94.6	16.8	69.95	356	104	43.2
0.00	234	115	28.6	69.95	476	118	57.6
0.00	381	153	46.7	69.95	588	147	71.0
0.00	502	176	61.5	69.95	673	192	81.3
0.00	580	200	71.2	69.95	722	233	87.4
0.00	627	219	76.9	69.95	783	276	94.9
20.02	23.1	31.3	2.84	79.97	34.9	3.28	4.23
20.02	70.1	43.5	8.63	79.97	49.7	4.02	6.02
20.02	111	50.1	13.7	79.97	70.9	18.1	8.59
20.02	149	63.2	18.3	79.97	96.1	21.8	11.6
20.02	198	83	23.4	79.97	176	39.1	21.3
20.02	285	121	35.1	79.97	227	53.9	27.6
20.02	337	138	41.5	79.97	289	59.9	35.0
20.02	451	149	55.5	79.97	389	92.4	47.2
20.02	534	159	65.8	79.97	423	119	52.1
20.02	603	198	74.3	79.97	604	197	84.7
39.95	54.8	15.1	6.66	79.97	659	200	79.8
39.95	96.8	25.8	11.8	89.99	5.91	41.0	0.72
39.95	117	34.7	14.1	89.99	16.1	43.5	1.98
39.95	186	45.0	22.5	89.99	33.8	54.4	4.15
39.95	278	53.9	33.6	89.99	72.0	62.8	8.84
39.95	404	82.1	49.0	89.99	118	72.5	14.5
39.95	423	103	51.4	89.99	155	81.0	19.1
39.95	493	124	59.7	89.99	198	96.8	24.3
39.95	560	161	67.9	89.99	232	111	28.4
39.95	677	230	82.1	89.99	338	137	41.4
39.95	812	319	98.3	89.99	458	170	56.2
59.98	26.1	5.50	3.18	89.99	545	212	66.7
59.98	42.7	15.5	5.18	89.99	558	225	68.3
59.98	56.8	21.8	6.92	100.00	13.9	39.1	1.71
59.98	69.2	33.6	8.39	100.00	35.8	61.7	4.41
59.98	130	43. 6	15.7	100.00	70.5	67.3	8.68
59.98	181	49.5	22.0	100.00	106	72.1	13.0
59.98	247	56.9	30.2	100.00	157	88.0	19.3
59.98	323	63.3	39.1	100.00	223	97.3	27.5
59.98	400	85.0	48.4	100.00	289	121	35.6
59.98	586	155	70.8	100.00	329	151	40.5
59.98	628	196	76.1	100.00	414	180	51.0
59.98	641	206	77.5	100.00	450	220	55.4
59.98	747	235	90.5	100.00	513	269	61.2
69.95	24.1	2.74	2.91	100.00	612	306	75.4
69.95	79.8	3.65	9.66	100.00	689	338	84.9
69.95	130	8.05	15.7				

[a] w_1 denotes the mass fraction of DEG in DEG + water system; Φ_3 denotes the volume fraction of SO_2 in the gas phase; C_3 denotes the sulfur(IV) composition in the liquid phase; and p_3 denotes the partial pressure of SO_2 in the gas phase.

an uncertainty of ± 0.02 K, and inspected using an accurate thermometer purchased from Fuqiang Meter Factory (Hebei province, China) with an uncertainty of ± 0.02 K. The total pressure of 123.15 kPa was inspected by a pressure gauge purchased from Fuqiang Meter Factory (Hebei province, China) with an uncertainty of ± 0.133 kPa and estimated to be ± 0.11 %.

Results and Discussion

GLE Data for DEG + Water with Dilute SO_2. A series of GLE experiments for DEG (1) + H_2O (2) + SO_2 (3) + N_2 (4) were performed at 298.15 K and 123.15 kPa, and the GLE data are listed in Table 1. In this table, the mass fraction of DEG in DEG + water (w_1) was used in the actual operation, and DEG and water were weighed using a Sartorius BS224S balance with a precision of ± 0.0001 g to present accurate factual mass fraction of DEG. The GLE data were obtained with relative uncertainties within ± 0.6 % for SO_2 concentration in the liquid phase and ± 3.5 % for SO_2 concentration in the gas phase.

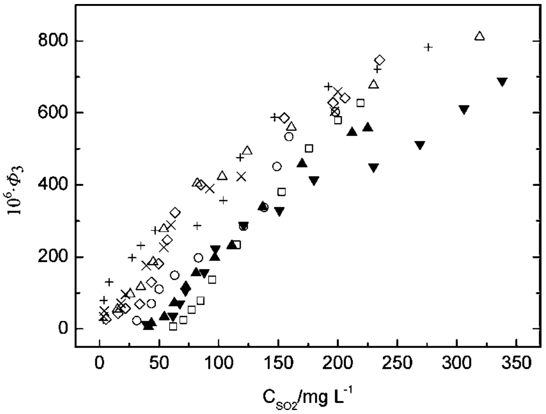

Figure 1. GLE curves for DEG (1) + H_2O (2) + SO_2 (3) + N_2 (4): ◇, $w_1 = 0$; ○, $w_1 = 0.20$; △, $w_1 = 0.40$; □, $w_1 = 0.60$; +, $w_1 = 0.70$; ×, $w_1 = 0.80$; ▲, $w_1 = 0.90$; ▼, $w_1 = 1.00$.

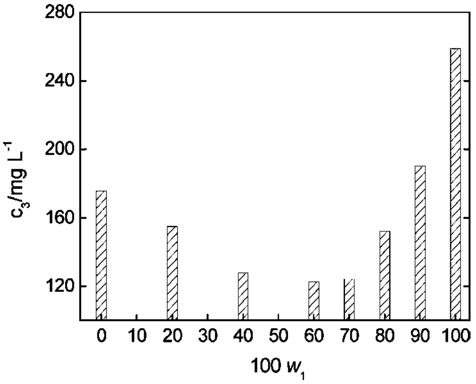

Figure 2. Solubility of SO_2 in DEG + water when the SO_2 concentration in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$.

In Table 1, Φ_3 denotes the volume fraction of SO_2 in the gas phase as $\phi_3 \approx (V_{SO_2})/(V_{SO_2} + V_{H_2O} + V_{N_2} + V_{DEG}) = (V_{SO_2})/(V_t)$, and V_{SO_2} and V_{total} denote respectively the partial volume of SO_2 in the gas phase and the total volume of the GLE system. C_3 denotes the concentration of SO_2 in the liquid phase.

The GLE curves of DEG + water for SO_2 absorption at 298.15 K and 123.15 kPa are plotted in Figure 1, and SO_2 partial pressure is in the range of (0.7 to 100) Pa. Solubilities of SO_2 in DEG + water when the SO_2 volume fraction in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$ are shown in Figure 2.

Figures 1 and 2 show that the addition of H_2O into DEG decreased the solubilities of SO_2 in DEG; meanwhile, $w_1 = 0.60$ exhibits an extreme minimum value to dissolve SO_2, and the solubility is 122 $mg \cdot L^{-1}$ when SO_2 in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$. In the entire composition range, the pure DEG shows the strongest capabilities to dissolve SO_2, and the solubility is 259 $mg \cdot L^{-1}$ when SO_2 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 DEG solutions[16] because the extreme minimum solubility value of SO_2 in DEG + water presents in between $w_1 = 0.60$ and $w_1 = 0.70$ DEG + water, and the maximum excess volume of DEG + water presents in the same range.[16] In addition, the results may be related to the hydrogen bonding and interactions among DEG, H_2O, and SO_2, and the similar hydrogen bonding and interactions among ethylene glycol (EG), H_2O, and SO_2 had been published in our previous work.[17,18] Compared with our previous work,[12,19] the solubility of SO_2 in pure DEG is 259 $mg \cdot L^{-1}$ when SO_2 volume fraction in the gas phase is designed at $\Phi_3 = 5 \cdot 10^{-4}$, which is stronger than in pure ethylene glycol (EG)

(128 mg·L^{-1}) and is lower than in pure PEG 400 (1330 mg·L^{-1}). The result gives us important information to optimize the composition of DEG + water for the SO_2 absorption processes.

Conclusion

This paper presents the results of fundamental investigations on isothermal GLE data of various aqueous DEG solutions with SO_2, which were determined as a function of composition at 298.15 K and 123.15 kPa. The GLE data show that when $w_1 = 0.60$ DEG + water presents the extreme minimum value solubility of 122 mg·L^{-1} to SO_2 when the SO_2 concentration in the gas phase was set at $\Phi_3 = 5 \cdot 10^{-4}$, and the solubility of SO_2 in pure DEG is 259 mg·L^{-1} at the same gas-phase composition. Meanwhile, the results show that the system DEG (1) + water (2) in the mass fraction range of $w_1 = (0.60$ to $1.00)$ decreased the solubility of SO_2, and the system DEG (1) + water (2) in the mass fraction range of $w_1 = (0.00$ to $0.60)$ increased the solubility of SO_2.

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