Gas−Liquid Equilibrium Data for a Mixture Gas of Sulfur Dioxide + Nitrogen with Ethylene Glycol Aqueous Solutions at 298.15 K and 123.15 kPa

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Isothermal gas−liquid equilibrium (GLE) data have been measured for the system SO_2 + N_2 + ethylene glycol (EG) + water at 298.15 K and 123.15 kPa and SO_2 partial pressures in the range of (0 to 120) Pa. Measurements were carried out by a saturation method using a glass absorption apparatus, which was controlled at constant temperature by a thermostatic circulation bath with a Beckmann thermometer. The GLE data were obtained with relative uncertainties within ± 3.5 % for SO_2 concentration in the gas phase and ± 0.6 % for SO_2 concentration in the liquid phase. The measurement showed that the addition of water to EG enhanced the solubility of SO_2 compared with pure EG and that the 80 % volume fraction of EG in ethylene glycol + water solution is a more reasonable composition used as the desulfurization solution. 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 EG aqueous solutions.

Introduction

The removal of sulfur dioxide (SO_2) from industrial waste gases is of increasing significance because emissions of SO_2 into the atmosphere have increased steadily with industrial development, and large emissions are responsible for acid rain. Its main source is flue gas from the burning of fuels with high sulfur content from 0.03 $mg \cdot m^{-3}$ in the air up to several $g \cdot m^{-3}$ in a typical flue gas.[1] The removal of SO_2 from flue gas is an increasingly important environmental challenge, on one hand, because of the lowering of the admissible emission limit and, on the other hand, due to the fact that numerous desulfurization processes, such as limestone scrubbing, produce a large volume of solid waste. In recent years, there is a growing interest in the use of organic solvents for SO_2 removal, and 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.[8−11]

In previous work,[11] we have published gas−liquid equilibrium (GLE) data for the system SO_2 + N_2 + ethylene glycol (EG), respectively, at 298.15 K, 303.15 K, 308.15 K, and 313.15 K and SO_2 partial pressures in the range of (0 to 120) Pa. The aqueous solution of EG is a promising medium for flue gas desulfurizaiton (FGD) processes because of its high absorption capacity, its low-to-moderate vapor pressure for temperatures below 373 K, and its low toxicity. Because a high EG concentration is not good for liquid transportation in the absorption and desorption processes, a suitable value must be found. This work was mainly focused on providing GLE data for SO_2 + N_2 mixtures with various EG + water solutions (EGWs) at 298.15 K and 123.15 kPa to optimize the composition of EGW for the future FGD processes.

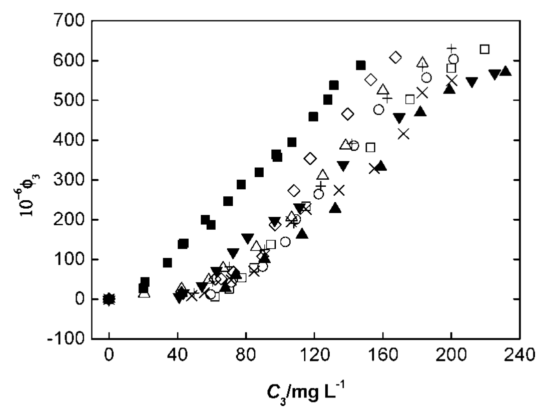

Figure 1. GLE curves for EG (1) + water (2) + SO_2 (3) + N_2 (4): □, w_1 = 0; ○, w_1 = 20 %; Δ, w_1 = 40 %; ◇, w_1 = 50 %; +, w_1 = 60 %; ×, w_1 = 70 %; ▲, w_1 = 80 %; ▼, w_1 = 90 %; ■, w_1 = 100 %.

Experimental Section

Materials. The certified standard mixture (SO_2 (1) + N_2 (2), $\Phi_{SO2} = 1.97 \cdot 10^{-3}$), purchased from the Standard Things Center (China), was employed to determine the GLE data for EGWs with SO_2 in this work. EG (≥ 99.4 %) was purified from EG (A.R, ≥ 98.0 %, made in China), dehydrated by Na_2SO_4, and distilled. The purity of the final samples, as found by gas chromatography (GC), was better than 99.4 %. Bidistilled water was used.

Apparatus and Procedure. The apparatus used in this work was based on a dynamic analytic method and is reported in a previous work.[11] The concentrations of SO_2 in the gas phase were determined by gas chromatography on a 2 × 3.2 (m ×

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Table 1. GLE for EG (1) + Water (2) + SO_2 (3) + N_2 (4) at 298.15 K and 123.15 kPa

$100\ w_1$	$10^{-6}\ \Phi_3$	C_3/(mg·L^{-1})	P_3/Pa	$100\ w_1$	$10^{-6}\ \Phi_3$	C_3/(mg·L^{-1})	P_3/Pa
0.00	6.4	61.8	0.78	71.79	16.2	55.6	1.97
0.00	25.6	70.3	3.13	71.79	48.5	71.3	5.95
0.00	53.8	77.6	6.60	71.79	70.5	84.7	8.63
0.00	79.1	84.9	9.71	71.79	110	90.7	13.4
0.00	137	94.6	16.8	71.79	194	106	23.7
0.00	234	115	28.6	71.79	226	115	27.7
0.00	381	153	46.6	71.79	274	134	33.6
0.00	502	176	61.6	71.79	329	155	40.4
0.00	580	200	71.1	71.79	416	172	50.9
0.00	627	219	76.8	71.79	520	183	63.6
21.74	12.1	59.4	1.48	71.79	550	200	67.5
21.74	41.8	71.5	5.13	81.33	15.4	42.4	1.89
21.74	82.0	89.7	10.1	81.33	27.3	67.9	3.34
21.74	144	103	17.7	81.33	60.5	74.0	7.43
21.74	200	109	24.5	81.33	99.3	90.9	12.2
21.74	264	122	32.4	81.33	161	113	19.8
21.74	386	143	47.3	81.33	227	132	27.7
21.74	476	158	58.4	81.33	332	159	40.7
21.74	557	185	68.3	81.33	469	182	57.5
21.74	603	201	74.1	81.33	525	199	64.3
42.21	13.4	20.6	1.64	81.33	570	232	70.0
42.21	25.8	42.4	3.17	90.75	5.9	41.0	0.72
42.21	48.1	58.2	5.91	90.75	16.1	43.5	1.98
42.21	78.4	66.7	9.60	90.75	33.8	54.4	4.15
42.21	130.4	86.1	16.0	90.75	72.0	62.8	8.84
42.21	205	107	25.2	90.75	118	72.5	14.5
42.21	310	125	37.9	90.75	155	81.0	19.1
42.21	386	138	47.3	90.75	198	96.8	24.3
42.21	525	160	64.2	90.75	232	111	28.4
42.21	593	183	72.5	90.75	338	137	41.4
52.24	51.6	65.5	6.32	90.75	458	170	56.2
52.24	50.7	61.8	6.22	90.75	549	212	67.2
52.24	67.8	72.7	8.31	90.75	568	225	69.6
52.24	108	89.7	13.2	100.00	27.6	20.1	3.37
52.24	187	97.0	23.0	100.00	42.8	21.1	5.20
52.24	272	108	33.4	100.00	91.6	34.2	11.2
52.24	353	116	43.4	100.00	138	43.0	16.8
52.24	465	139	57.0	100.00	141	43.8	17.23
52.24	552	153	67.6	100.00	186	59.6	22.7
52.24	608	167	74.6	100.00	199	56.2	24.3
62.15	15.5	49.7	1.90	100.00	246	69.6	30.2
62.15	44.5	60.6	5.46	100.00	288	77.3	35.2
62.15	81.5	70.3	10.0	100.00	319	87.8	39.1
62.15	125	90.9	15.3	100.00	357	98.3	43.3
62.15	191	108	23.4	100.00	363	97.6	44.3
62.15	284	124	34.8	100.00	394	107	48.2
62.15	392	142	48.0	100.00	458	119	55.9
62.15	505	162	62.0	100.00	501	128	60.9
62.15	584	183	71.5	100.00	538	131	65.6
62.15	630	200	77.3	100.00	587	147	71.7
71.79	8.6	48.3	1.1				

mm) Porapak Q packed column using an Agilent 6890N gas chromatograph (GC) and a FPD detector linked to an HP6890 workstation. In all case, 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, once equilibrium was reached, by adding a known volume of solution from the vessel to a known volume of standard iodine solution. The excess iodine solution was back-titrated with a standard sodium thiosulfate solution.[12] The overall relative uncertainty in the determination of the sulfur(IV) concentration was estimated to be ± 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 123.15 kPa inspected by a pressure gauge purchased from Fuqiang Meter Factory (Hebei province, China) with ± 0.133 kPa, using $SO_2 + N_2$ mixtures ($\Phi_{SO2} = 1.97 \cdot 10^{-3}$) in the SO_2 partial pressure range from (0 to 120) Pa.

Results and Discussions

GLE Data for EGWs with Dilute SO_2. A series of GLE experiments for EG + water + SO_2 + N_2 were performed at 298.15 K and 123.15 kPa, and the GLE data are listed in Table 1. In this table, the volume ratio was set to simplify the actual operation in future FGD processes, and EG and water were weighed using a Sartorius BS224S balance with a precision of ± 0.0001 g to present the accurate factual mass fraction of EG. The GLE data were obtained with relative uncertainties within ± 3.5 % for SO_2 concentration in the gas phase and ± 0.6 % for SO_2 concentration in the liquid phase.

In Table 1, Φ_3 denotes the concentration of SO_2 in the gas phase as $\Phi_3 \approx p_{SO_2}/(p_{SO_2} + p_{H_2}O + p_{N_2} + p_{EG}) = p_{SO_2}/p_{total}$; p_3 and p_{total} denote, respectively, the partial pressure of SO_2 in

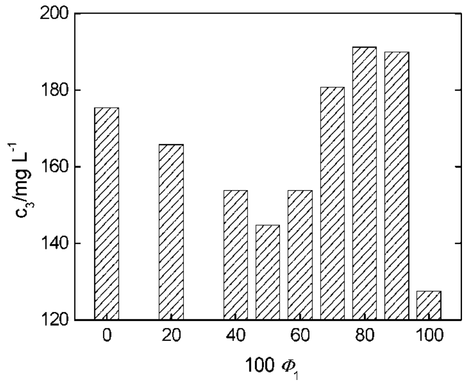

Figure 2. Solubility of SO_2 in EGWs when SO_2 concentration in the gas phase is designed at $\Phi_1 = 5 \cdot 10^{-4}$. Φ_1 denotes the volume fraction of EG in EG (1) + water (2) and is defined as $\Phi_1 = v_1/(v_1 + v_2)$ and Φ_2 denotes the volume fraction of water in EG (1) + water (2) and is defined as $(1 - \Phi_1)$.

the gas phase and the total pressure of the GLE system; and C_3 denotes the concentration of SO_2 in the liquid phase.

The GLE curves of EGWs for SO_2 absorption at 298.15 K and 123.15 kPa are plotted in Figure 1. Solubility of SO_2 in EGWs when SO_2 volume fraction in the gas phase is designed at $\Phi_1 = 5 \cdot 10^{-4}$ is shown in Figure 2.

Figures 1 and 2 show that $\Phi_1 = (70 \text{ to } 90)$ % exhibit strong capabilities to dissolve SO_2: for $\Phi_1 = 80$ %, EGW shows a higher capability to dissolve SO_2. The solubility of SO_2 is 191 $mg \cdot L^{-1}$ when the SO_2 volume fraction in the gas phase was set at $\Phi_3 = 5 \cdot 10^{-4}$. The result gives us important information to optimize the composition of EGWs for the SO_2 absorption processes.

In industrial operations, flue gas has a large quantity of energy as well as high relative humidity. If $\Phi_1 = 80$ % is used in the industrial processes, the high energy in the flue gas will gasify part of water from EGW so that the Φ_1 moves toward 90 %. The process does not affect the EGW's absorption and desorption properties toward SO_2 because the Φ_1 of 90 % has a strong capacity to absorb and release SO_2. On the contrary, the high relative humidity of the flue gas will make the Φ_1 move toward 70 %, which still has a high capacity to absorb and release SO_2.

The result analyses of the absorption processes, the desorption processes, surface tension properties, and viscosities (see Supporting Information) show that $\Phi_1 = 80$ % can be used as the optimum composition of solution for the absorption and desorption processes of SO_2.

Conclusion

This paper presents the results of fundamental investigations on isothermal GLE data of various aqueous solutions of EG with SO_2, which were determined as a function of composition at 298.15 K and 123.15 kPa. The GLE data show that the addition of water in EG enhanced the solubility of SO_2 compared with pure EG. The experimental results showed that the EG volume fraction is specified as 80 %; the corresponding solubility of SO_2 is 191.18 $mg \cdot L^{-1}$ when the SO_2 concentration in the gas phase was set at $\Phi_{SO2} = 500 \cdot 10^{-6}$; the desorption efficiency is 90 %; and the composition presents lower viscosity than pure EG and more reasonable surface tension (see Supporting Information).

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Supporting Information Available:

Desorption data of various EGWs dissolving SO_2 at 333.15 K, surface tension properties of EGWs, and viscosity properties of EGWs. This material is available free of charge via the Internet at http://pubs.acs.org.

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