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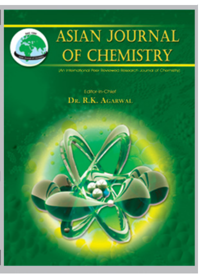

Absorption of Dilute Sulfur Dioxide in Aqueous Poly-Ethylene Glycol 200 Solutions at 298.15 K and 122.60 kPa

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In present work, isothermal gas-liquid equilibrium (GLE) data are measured for the absorption of dilute SO_2 in various aqueous poly-ethylene glycol 200 (PEG) solutions at 298.15 K and 122.60 kPa and SO_2 partial pressures in the range of (0.8-127) Pa. Measurements were carried out by a saturation method using a glass absorption apparatus, which were controlled at constant temperature using a thermostatic circulation bath with a Beckmann thermometer. The gas-liquid equilibrium data were measured with relative uncertainties within ± 0.02 K for temperature, ± 0.133 kPa for total pressures, ± 0.6 % for SO_2 concentration in the liquid phase and ± 3.5 % for SO_2 volume fraction in the gas phase. The measurement showed that the solubility of SO_2 in the system PEG (1) + water (2) increased with increasing PEG concentration in the mass fraction range of $w_1 = (0.60\text{-}1.00)$ and the solubility of SO_2 in the PEG (1) + water (2) system presented a minimum at the mass fraction of $w_1 = 0.60$ of 101 mg dm^{-3} when SO_2 in the gas phase is designed at $\Phi_{SO_2} = 5 \times 10^{-4}$. The peculiarity of this work is used to provide important gas-liquid equilibrium data for the design and operation of the absorption and desorption processes in flue gas desulfurization with potential industrial application of various aqueous solutions of poly-ethylene glycol 200.

Key Words: Absorption, Flue gas desulfurization, Phase equilibrium, Sulfur dioxide.

INTRODUCTION

Natural resources are limited, 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. 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[8-11].

This paper is a continuation of the systematic program on the absorption processes of SO_2 in the aqueous ethylene glycol solution and its silmilar solutions[12-14]. Futhermore, various aqueous ethylene glycol solutions and it's similar solutions were considered for screening better desulfurization system and finding the solubility rule of SO_2. In present work, poly-(ethylene glycol) is seen as a potential 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 data for SO_2 + N_2 mixtures with various poly-ethylene glycol 200 (PEG) + water solutions (PEGWs) at 298.15 K and 122.60 kPa to develop the various aqueous poly-ethylene glycol solutions and present the gas-liquid equilibrium data.

EXPERIMENTAL

The analytical grade PEG 200 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 PEG at 298.15 K was found to be 1.1208 g cm^{-3}, in good agreement with the literatures[15,16]. The purity of the final samples, as found by gas chromatograph, was better than 99.4 %. 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 gas-liquid equilibrium data for PEG + water with SO_2 in this work. Bidistilled water was used in this work.

The apparatus used in this work was based on a dynamic analytic method and is reported in previous work[11]. The concentrations of SO_2 in the gas phase were determined by a gas chromatograph (GC) on a 2 × 3.2 (m × 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) concentration in the liquid phase (C_{SO_2}) was determined according to ref.[17]. 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 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.

RESULTS AND DISCUSSION

The GC FPD detector was calibrated with the standard SO_2 + N_2 mixture gases. The calibrated results are shown in the Table-1.

Gas-liquid equilibrium data for DEG + water with dilute SO_2: A series of gas-liquid equilibrium experiments for the absorption of dilute SO_2 in PEG (1) + H_2O (2) binary system were performed at 298.15 K and 122.60 kPa and the data are listed in Table-1. In this table, the mass fraction of PEG in PEG + water (w_1) was used in the actual operation and PEG and water were weighed using a Sartorius BS224S balance with a precision of ± 0.0001 g to present accurate factual mass fraction of PEG. The gas-liquid equilibrium 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.

In Table-1, Φ_{SO_2} denotes the volume fraction of SO_2 in the gas phase as $\phi_{SO_2} \approx \frac{V_{SO_2}}{V_{SO_2}+V_{H_2O}+V_{N_2}+V_{PEG}} = \frac{V_{SO_2}}{V_t}$, V_{SO_2} and Vtotal denote, respectively the partial volume of SO_2 in the gas phase and the total volume of the GLE system and C_3 denotes the concentration of SO_2 in the liquid phase.

The GLE curves of the SO_2 absorption in various PEGWs at 298.15 K and 122.60 kPa are plotted in Fig. 1 and SO_2 partial pressure is in the range of (0.8-127) Pa. Solubilities of SO_2 in PEG + water when SO_2 volume fraction in the gas phase is designed at $\Phi_{SO_2} = 5 \times 10^{-4}$ are shown in Fig. 2.

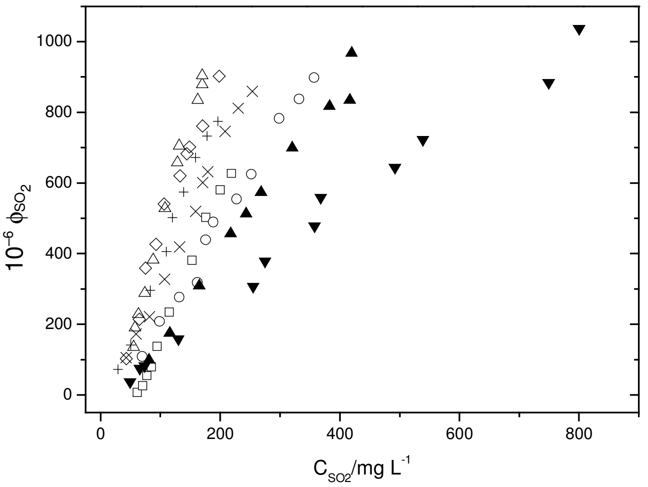

Fig. 1. GLE curves for PEG (1) + H_2O (2) + SO_2 (3) + N_2 (4): □, $w_1 = 0$; ○, $w_1 = 0.20$; D, $w_1 = 0.40$; ●, $w_1 = 0.60$; +, $w_1 = 0.70$; ×, $w_1 = 0.80$; ▲, w1 = 0.90; ▼, 1.00

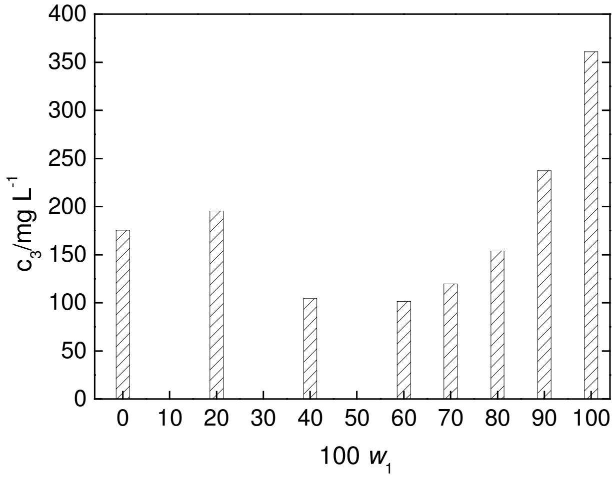

Fig. 2. Solubility of SO_2 in PEG + water when SO_2 concentration in the gas phase is designed at $\Phi_{SO_2} = 5 \times 10^{-4}$

Figs. 1 and 2 show that the solubility of SO_2 in the system PEG (1) + water (2) increased with increasing PEG concentration in the mass fraction range of w_1 = (0.60-1.00) and the solubility of SO_2 in the system PEG (1) + water (2) presented an extreme minimum at the mass fraction of $w_1 = 0.60$ of 101 mg L^{-1} when SO_2 in the gas phase is designed at $\Phi_3 = 5 \times 10^{-4}$. In the entire composition range, the pure PEG shows the strongest capabilities to dissolve SO_2 and the solubility is 361 mg L^{-1} when SO_2 concentration in the gas phase is designed at $\Phi_3 = 5 \times 10^{-4}$. The above results may be related to the excess properties of aqueous PEG solutions and the hydrogen bonding and interactions among PEG, H_2O and SO_2 and the similar hydrogen bonding and interactions among EG and PEG 400, H_2O and SO_2 had been published in the previous work[18,19]. Compared with the previous work[12-14], the solubility of SO_2 in pure PEG 200 is 361 mg L^{-1} when SO_2 volume fraction in the gas phase is $\Phi_3 = 5 \times 10^{-4}$, which is higher than in pure ethylene glycol (EG, 128 mg L^{-1}) and in pure diethylene glycol (DEG, 259 mg L^{-1}), however, which is lower than in pure polyethylene glycol 400 (PEG 400, 1330 mg L^{-1}). The comparation of the solubilities of SO_2 in various aqueous ethylene glycol solutions and its similar solutions shows that the solubility of

TABLE-1
GAS-LIQUID EQUILIBRIUM FOR PEG (1) + H_2O (2) + SO_2 (3) + N_2 (4) AT 298.15 K AND 122.60 kPa. w_1 DENOTES THE MASS FRACTION OF PEG IN PEG + WATER SYSTEM, Φ_{SO_2} 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

100 w_1	$10^6 \times \Phi_{SO_2}$	C_3 (mg L^{-1})	P_3 (Pa)	100 w_1	$10^6 \times \Phi_{SO_2}$	C_3 (mg L^{-1})	P_3 (Pa)
0.00	6.40	61.8	0.78	20.04	108	69.8	13.2
0.00	25.6	70.3	3.14	20.05	208	98.7	25.5
0.00	53.8	77.6	6.59	20.05	276	132	33.8
0.00	79.1	84.9	9.70	20.05	318	162	39.0
0.00	137	94.6	16.8	20.05	439	176	53.8
0.00	234	115	28.6	20.05	489	189	60.0
0.00	381	153	46.7	20.05	554	227	67.9
0.00	502	176	61.5	20.05	625	252	76.6
0.00	580	200	71.2	20.05	782	298	95.9
0.00	627	219	76.9	20.05	837	332	103
–	–	–	–	20.05	898	357	110
40.02	135	55.3	16.6	60.90	103	42.9	12.6
40.02	190	57.5	23.3	60.90	214	64.8	26.2
40.02	228	63.2	28.0	60.90	359	75.3	44.0
40.02	288	74.0	35.3	60.90	426	92.7	52.2
40.02	382	88.0	46.8	60.90	540	106	66.2
40.02	528	108	64.7	60.90	620	133	76.0
40.02	658	128	80.7	60.90	682	144	83.6
40.02	705	132	86.4	60.90	702	149	86.1
40.02	835	163	102	60.90	761	171	93.3
40.02	879	170	108	60.90	902	199	110.6
40.02	904	175	111	–	–	–	–
70.00	71.9	29.2	8.81	80.10	105	42.4	12.9
70.00	141	50.5	17.3	80.10	173	59.4	21.2
70.00	296	83.2	36.3	80.10	221	81.9	27.1
70.00	405	110	49.7	80.10	328	107	40.2
70.00	502	120	61.5	80.10	419	132	51.4
70.00	574	139	70.4	80.10	519	159	63.6
70.00	672	159	82.3	80.10	601	171	73.7
70.00	733	178	89.9	80.10	632	179	77.5
70.00	774	196	94.9	80.10	746	208	91.5
–	–	–	–	80.10	812	230	99.5
–	–	–	–	80.10	859	254	105
90.20	98.2	81.0	12.0	100.00	36.5	49.2	4.47
90.20	175	116	21.5	100.00	75.0	65.7	9.20
90.20	309	165	37.9	100.00	81.8	73.7	10.0
90.20	456	218	55.9	100.00	158	130	19.4
90.20	513	243	62.9	100.00	306	255	37.5
90.20	574	268	70.4	100.00	378	275	46.3
90.20	699	320	85.7	100.00	478	358	58.6
90.20	818	383	100	100.00	558	368	68.4
90.20	834	417	102	100.00	644	492	79.0
90.20	968	420	119	100.00	722	539	88.5
–	–	–	–	100.00	884	749	108
–	–	–	–	100.00	1037	800	127

SO_2 may be related to the polymeric number of ethylene glycol molecules in the absorption system and the idea will be dicussed in the following work. In addition, the result gives us important information to optimize the composition of PEG + water for the SO_2 absorption processes.

Conclusion

This paper presents the results of fundamental investigations on isothermal gas-liquid equilibrium data of various aqueous PEG solutions with SO_2, which were determined as a function of composition at 298.15 K and 122.60 kPa. The gas-liquid equilibrium data show that the solubility of SO_2 in the system PEG (1) + water (2) increased with increasing PEG concentration in the mass fraction range of w_1 = (0.60-1.00) and the solubility of SO_2 in the system PEG (1) + water (2) presented an extreme minimum at the mass fraction of w_1 = 0.60 of 101 mg L^{-1} when SO_2 in the gas phase is designed at $\Phi_3 = 5 \times 10^{-4}$. At the same gas composition, the solubility of SO_2 in pure PEG 200 presented an extreme maximum of 361 mg L^{-1}.

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