Solubility of Carbonyl Sulfide in Aqueous Solutions of Ethylene Glycol at Temperatures from (308.15 K to 323.15) K

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Solubility data were measured for carbonyl sulfide (COS) in the binary system of ethylene glycol (EG) + water at (308.15, 313.15, 318.15, and 323.15) K. Measurements were carried out by a saturation method using a glass equilibrium cell, which was controlled at constant temperatures by a thermostatic bath with a Beckmann thermometer. The solubility data were obtained with uncertainties within ± 0.02 K for temperature and ± 0.133 kPa for system pressure, and the solubility data of COS in various ethylene glycol−water solutions (EGWs) were obtained with a maximum errorr with 3.88 %. Using the calculated method, the solubility of COS is acquired in various EGWs at the same temperatures and 0.10132 MPa. The results of this work can be used to provide important solubility data for the design and operation of the absorption process for COS with potential industrial application of various EGWs.

Introduction

The removal of carbonyl sulfide (COS) from natural and synthesis gases in industrial processes is an important operation. The compound is removed because of a need to reach specifications imposed in gas transport industries and to respect strict environmental standards.[1] After hydrogen sulfide (H_2S), COS is the main sulfur compound found in coal-derived gases, and the removal of COS has been largely reported.[2−6]

Ethylene glycol (EG) is an important industrial solvent, which has been used in the absorption processes for SO_2 in previous works[7−9] because of its favorable properties, such as low vapor pressure, low toxicity, low viscosity, and low melting point. Knowledge of the solubility data for COS in various EG aqueous solutions (EGWs) is an indispensable requirement for the design of absorption and desorption processes of gases containing COS. However, solubility data are lacking in the current literature, so the determination of COS solubility data for future industrial applications is essential.

This work was mainly focused on providing solubility data for COS in various EGWs at (308.15, 313.15, 318.15, and 323.15) K and below atmospheric pressure and calculating the solubilty data of COS in various EGWs at atmospheric pressure.

Experimental Section

Materials. COS was prepared through the reaction of a potassium thiocyanate (KCNS) solution with 0.50 (mass fraction) sulfuric acid (H_2SO_4) at 303 K.[10] All gases went through a 0.30 NaOH aqueous solution (mass fraction) to remove H_2S, SO_2, and CO_2 and were dried using silica gel. A concentration of COS was found to be 0.99 (volume fraction). Analytical grade EG was purchased from Beijing Reagent Company. It was used after drying over molecular sieves (type 4A) and vacuum filtration before measurements. The purity of the sample was checked by density determination at 298.15 K. EG and water were weighed using a Sartorius BS224S balance with a precision of ± 0.0001 g to present an accurate factual mole fraction of EG. The density of EG at 298.15 K was found to be 1.1096 $g \cdot cm^{-3}$, in good agreement with the published literature.[11−13] EG (≥ 0.980 mass fraction) was purified from EG (A.R, ≥ mass fraction, made in China) dehydrated by Na_2SO_4 and refined by rectification. The purity of the final samples, as found by gas chromatography, was better than 0.994 (mass fraction). Bidistilled water was used.

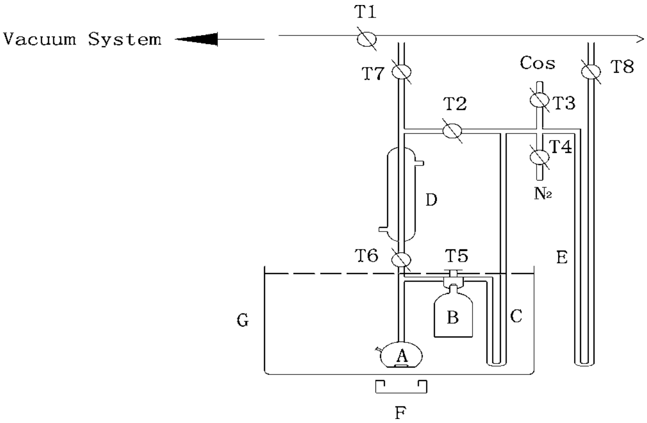

Figure 1. Schematic diagram of the experimental apparatus: A, equilibrium cell; B, gas storage cell; C, zero pressure meter; D, condensator; E, U-manometer; F, magnetic blender; G, thermol bath; T_1−T_6, valves.

Apparatus and Procedure. The solubilities were measured with the apparatus shown schematically in Figure 1. The apparatus uses an improved equilibrium cell, and it consisted of an equilibrium cell, a cylinder-type gas holder, and an U-pressure gauge. The equilibrium cell was made of Pyrex glass. The volumes of the equilibrium cell and pipeline in Figure 1 were calibrated by means of pure water at 298.15 K prior to the experiment. The apparatus is similar to the previously used method in refs 14 to 16 with the following modifications. COS

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Table 1. Comparison of Measured Vapor Pressures of Several Solvents with Literature Values

	P^s/kPa					
	H_2O		ethanol		isopropyl alcohol	
T/K	exp.	lit.[17]	exp.	lit.[17]	exp.	lit.[17]
303.15	4.186	4.240	10.426	10.466	7.933	8.106
308.15	5.493	5.666			10.719	10.799
313.15	7.346	7.373	17.839	17.892		
318.15	9.493	9.586				

Table 2. Comparison of Measured Solubility of Carbon Dioxide in Water with Literature Values

T/K	exp. ($\cdot 10^4$)	lit.[17] ($\cdot 10^4$)	error, %
308.15	4.369	4.521	3.4
313.15	3.873	3.981	2.7
318.15	3.412	3.519	3.1

gas dissolution was performed with the use of a magnetic stirrer. The temperature of the whole unit was kept at a constant temperature inside a temperature-controller water bath. The uncertainties of the experimental temperature are estimated to be within ± 0.02 K.

The procedure for making a solubility measurement is as follows. The system was purged with pure COS gas into the gas storage cell. Then, the inlet and outlet valves were closed and the pressure values shown in C and E, and the room temperature was noted. After EGW was injected into the absorption equilibrium cell, the solution was degassed using the vacuum pump. After the solution was stirred for about 120 min, the levels of the mercury were made equal, and the change noted in the mercury level was measured. This measured pressure change is equal to the volume of the sample minus the volume of gas absorbed. The reliability of the apparatus was checked by measuring the saturation vapor pressures (P^s) of bidistilled water, high-performance liquid chromatography (HPLC) grade ethanol, and isopropanol and the determined results, which were in good agreement with the data reported in the literature,[17] are shown in Table 1; meanwhile, the solubilities of CO_2 in pure water at the temperatures of (308.15, 313.15, and 318.15) K were determined and shown in Table 2. The results were in good agreement with those reported in the literature.

Experiments were carried out at (308.15, 313.15, 318.15, and 323.15) K and kept at a constant temperature using a 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 ± 0.02 K, and the total pressure inspected by a pressure gauge purchased from Fuqiang Meter Factory (Hebei Province, China) with ± 0.133 kPa and the total pressure was estimated to be ± 0.11 %.

Data Processing. The mole fraction of COS in the liquid phase (x_g') and the mole fraction of COS in the liquid phase (x_g) at 0.10132 MPa were acquired by the following equations.

The total mole value of gas charged into absorption cell A is calculated according to the ideal gas law from

$$N_g = \frac{p_g V_g}{RT} \tag{1}$$

where N_g is the mole value of gas in the equilibrium cell, T is the experimental temperature, p_g is the system pressure in the gas storage cell, and V_g is the volume of the gas storage cell.

Table 3. Solubility of COS in EG (1) + Water (2) Mixtures

x_1	P_{COS} (kPa)	x_{COS} ($\cdot 10^3$)	x_1	P_{COS} (kPa)	x_{COS} ($\cdot 10^3$)
		$T = 308.15$ K			
0.000	60.532	0.245	0.303	53.663	0.959
	30.864	0.094		27.265	0.413
	13.999	0.075		13.800	0.314
0.031	59.698	0.740	0.403	51.529	1.074
	41.730	0.478		36.197	0.890
	28.012	0.320		14.399	0.378
0.069	41.730	0.557	0.537	53.129	1.174
	30.398	0.327		27.998	0.780
	21.465	0.270		19.198	0.380
0.111	49.196	0.701	0.723	53.196	1.722
	40.263	0.497		29.531	0.829
	20.136	0.307		16.799	0.407
0.162	46.662	0.701	1.000	50.729	2.317
	31.971	0.497		29.731	1.310
	27.998	0.307		14.799	0.850
0.225	50.263	0.857			
	37.597	0.572			
	31.331	0.515			
		$T = 313.15$ K			
0.000	59.928	0.189	0.303	44.063	0.752
	53.262	0.164		29.197	0.402
	35.930	0.126		14.266	0.286
0.031	57.265	0.621	0.403	49.063	1.174
	42.130	0.405		29.664	0.680
	32.797	0.362		18.998	0.261
0.069	45.996	0.554	0.537	54.529	1.120
	27.998	0.275		33.397	0.867
	10.532	0.170		18.932	0.360
0.111	45.463	0.561	0.723	54.995	1.609
	36.797	0.407		32.531	1.022
	23.865	0.318		18.665	0.450
0.162	50.529	0.700	1.000	50.996	1.802
	38.863	0.483		32.331	1.403
	33.797	0.440		15.265	0.506
0.225	52.929	0.814			
	38.596	0.531			
	20.132	0.369			
		$T = 318.15$ K			
0.000	60.862	0.163	0.303	54.262	0.837
	53.629	0.127		36.530	0.504
	13.466	0.039		14.399	0.311
0.031	50.263	0.524	0.403	51.062	1.051
	36.330	0.303		34.197	0.659
	18.398	0.182		20.932	0.498
0.069	52.691	0.532	0.537	54.862	1.202
	31.331	0.294		37.197	0.680
	20.536	0.255		15.599	0.381
0.111	51.529	0.611	0.723	54.795	1.521
	37.197	0.353		35.997	0.878
	25.011	0.290		15.345	0.493
0.162	54.396	0.720	1.000	55.462	1.803
	43.063	0.487		35.130	1.470
	26.131	0.336		15.865	0.483
0.225	54.263	0.783			
	39.197	0.491			
	18.399	0.322			
		$T = 323.15$ K			
0.000	57.729	0.135	0.303	50.596	0.730
	45.596	0.081		31.065	0.410
	12.932	0.016		19.799	0.336
0.031	57.582	0.525	0.403	52.662	1.004
	45.596	0.326		37.730	0.676
	14.132	0.151		19.465	0.342
0.069	41.597	0.397	0.537	54.129	1.126
	39.330	0.336		31.331	0.703
	29.531	0.266		20.798	0.308
0.111	51.169	0.545	0.723	51.062	1.360
	38.264	0.345		36.730	0.852
	24.051	0.272		15.465	0.545
0.162	48.663	0.614	1.000	57.195	1.871
	36.197	0.367		34.131	1.183
	24.401	0.294		16.665	0.769
0.225	52.929	0.732			
	36.864	0.408			
	13.132	0.234			

Table 4. Solubility of COS in EG (1) + Water (2) Mixtures at 0.10132 MPa Pressure

x_1	$(\cdot 10^3)$	x_1	$(\cdot 10^3)$
	$T = 308.15$ K		
0.000	0.390	0.303	1.759
0.031	1.160	0.403	2.228
0.069	1.247	0.537	2.302
0.111	1.365	0.723	3.085
0.162	1.504	1.000	4.600
0.225	1.643		
	$T = 313.15$ K		
0.000	0.319	0.303	1.634
0.031	1.052	0.403	2.161
0.069	1.162	0.537	2.177
0.111	1.205	0.723	2.936
0.162	1.326	1.000	3.738
0.225	1.512		
	$T = 318.15$ K		
0.000	0.255	0.303	1.522
0.031	0.972	0.403	2.056
0.069	1.016	0.537	2.108
0.111	1.112	0.723	2.746
0.162	1.254	1.000	3.492
0.225	1.404		
	$T = 323.15$ K		
0.000	0.210	0.303	1.437
0.031	0.844	0.403	1.858
0.069	0.906	0.537	2.058
0.111	1.022	0.723	2.603
0.162	1.178	1.000	3.398
0.225	1.313		

$$V_T = V_{T0} + Dh \cdot \Delta h \tag{2}$$

where V_T denotes the total volume of the equilibrium cell, gas storage cell, and the linking pipeline under the experimental temperature. V_{T0} denotes the total volume of the equilibrium cell, gas storage cell, and the linking pipeline under the revised temperature. $Dh \cdot \Delta h$ denotes the difference between V_T and V_{T0}.

The mole value of COS in the gas phase can be calculated from

$$N_{gL} = N_g - N_{gG} = N_g - \frac{(p_T - p^s)(V_T - V_L)}{RT} \tag{3}$$

where N_{gL} and N_{gG} denote the mole values of COS in the gas phase and the liquid phase. p_T and p^s denote the total pressure under experimental temperature and the saturated vapor pressure of the absorption solution. V_L is the volume value of the absorption solution.

The mole fraction of COS in the liquid phase under determined pressure can be acquired from

$$x_g' = \frac{N_{gL}}{N_l + N_{gL} - N_{lG}} \tag{4}$$

where N_l denotes the mole value of absorption solution and N_{lG} denotes the mole value of absorption solution in the gas phase. x_g' denotes the mole fraction of COS in the liquid phase under the experimental pressure.

The mole fraction of COS in the liquid phase under 0.10132 MPa can be acquired from

$$x_g = x_g' \cdot 0.10132/(p_T - p^s) \tag{5}$$

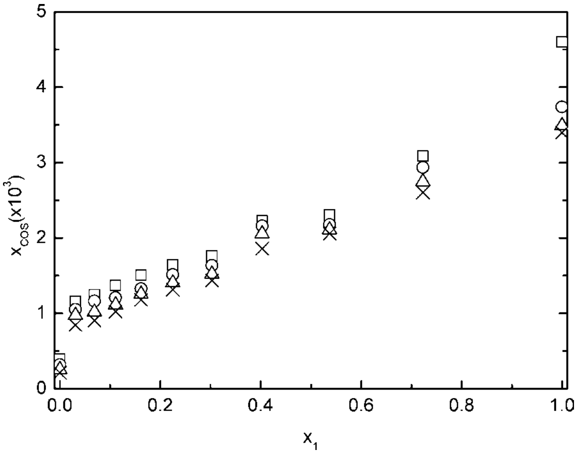

Figure 2. Solubility of COS in EG (1) + water (2) mixtures at 0.10132 MPa pressure: □, 308.15 K; ○, 313.15 K; △, 318.15 K; ×, 323.15 K.

Results and Discussion

Solubility Data of COS in Various EGWs. A series of solubility experiments for EG (1) + H_2O (2) + COS (3) were performed at (308.15, 313.15, 318.15, and 323.15) K, and the solubility data are listed in Table 3. In Table 3, the mole fraction of EG in EGW (x_1) was used in the actual operation. The solublity data were obtained with an maximum error of 3.88 %.

Using the calculated method, the solubilities of COS are in various EGWs at temperatures of (308.15 to 323.15) K and 0.10132 MPa, and the solublity data are shown in Table 4 and plotted in Figure 2.

Tables 3 and 4 and Figure 2 show that the solubility of COS in various EGWs is increased with increasing pressure at constant temperature, and the solubility in various EGWs decreases with increasing temperature under constant pressure. In addition, the solubility increases with increasing EG concentraion in EGW.

Conclusion

In this paper, solubility data for COS in the binary system of EG + water system (EGW) were determined at (308.15, 313.15, 318.15, and 323.15) K with the uncertainties within ± 0.02 K for temperature and ± 0.133 kPa for the total pressure. Furthermore, the solubility data of COS in EGW were obtained with a maximum errorr of 3.88 %. Solubility data of COS in various aqueous EG solution were acquired using the calculated method respectively at the same temperature and 0.10132 MPa.

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