Solubilities of Sulfur Dioxide in Aqueous Alcohol Solutions

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The solubilities of sulfur dioxide in aqueous alcohol solutions (methanol–water, ethanol–water, and *n*-propanol–water) were determined by a bubbling method at 10°, 20°, 30°, and 40°C. The solubilities are expressed as grams of sulfur dioxide dissolved per 100 grams of solute gas-free solution.

There are few data for the solubility of gases in liquid mixtures, and it is difficult to estimate the solubility of gases in mixed solutions from the solubility in pure solvents. In this work, the solubility of sulfur dioxide at 1-atm partial pressure was determined in aqueous solutions of methanol, ethanol, and *n*-propanol at concentrations from 0 to 100% and temperatures of 10°, 20°, 30°, and 40°C.

Experimental Apparatus

The solubility apparatus used in this investigation is shown schematically in Figure 1. The apparatus is similar to that used by Hudson (*4*), except that it is provided with a saturating vessel E and a sampling bulb B. The absorption chamber A, the sampling bulb B, and the gas saturating vessel E were immersed in a constant-temperature bath which maintained the temperature within ±0.01°C.

Procedure for Measuring Solubilities

Sulfur dioxide was bubbled through the solution until it was saturated with gas; then, the solution was analyzed by iodometric titration.

Introduction of solution into absorption chamber. The solution was refluxed for several hours in a degassing flask C. The absorption chamber A, the sampling bulb B, the saturating vessel E, and the glass tubing between cocks L_1 and L_{10} were evacuated with a vacuum pump. The degassed solution was transferred from the degassing flask C to the absorption chamber A and the saturating vessel E under vacuum by opening the cocks K and L_2. The saturating vessel was used to saturate the gas before it entered the absorption chamber to avoid changes in the concentration of the absorbing liquid.

Bubbling of gas. When the apparatus in the constant-temperature bath F reached the desired temperature, cocks L_1, L_3, L_4, L_5, L_6, L_7, and L_9 were opened. Sulfur dioxide was furnished directly from the cylinder through a pressure reducer. It was passed through a saturation vessel, E, into the absorption chamber A out through a mercury column, H, and released. The mercury column H was adjusted by manipulating the mercury reservoir G_2 so that the partial pressure of sulfur dioxide was about 760 mm Hg.

Absorption equilibrium. The bubbling was continued until the solution was saturated with the gas. Each equilibrium was attained after about 20 min. The final mercury level in the manometer D was recorded. Then the cock K was opened between the absorption chamber A and the mercury reservoir G_1, and it was raised so that the sampling bulb B was filled with the solution; cocks L_6 and L_7 were then closed so that the sampling bulb could be disconnected.

Determination of dissolved sulfur dioxide concentration. After being disconnected and dried, the sampling bulb was weighed together with its contents. The dissolved sulfur dioxide concentration in the solution was determined by iodometric titration.

Determination of mole fraction of alcohol in solution. About 20 cc of the aqueous alcohol solution was taken from the degassing flask, and its density was determined by means of an Ostwald-type pycnometer. The mole fraction of alcohol in the solution was determined by comparing the measured density with the density values of aqueous alcohol solutions reported in the literature.

Materials

Methanol, ethanol, and n-propanol. Each of these chemicals was fractionated in a laboratory fractionating column of about 20 theoretical plates packed with ¼-in. single-turn helices. Intermediate fractions were collected and used in making up the test solutions. The physical properties of the solvents are tabulated in Table I.

Sulfur dioxide. This gas was from a high-purity commercial cylinder. Analysis showed sulfur dioxide to be 99.96% pure.

Calculation of Results

The titration was carried out by adding a standard iodine solution to the solution in excess and back-titrating the iodine liberated with a thiosulfate solution. The concentration of sulfur dioxide dissolved in the aqueous alcohol solution was calculated from the equivalent amount of iodine required to oxidize SO_3^{2-} to SO_4^{2-}. The solubilities obtained from this calculation are the equilibrium values at the total pressure under investigation. The partial pressure of sulfur dioxide may be calculated from Equation 1.

$$p_{SO_2} = \pi - (p_{aq\ al} - \Delta p) \qquad (1)$$

The vapor pressure of the aqueous methanol solution was calculated as

$$p_{aq\ al} = \gamma_1 x_1 p_1^\circ + \gamma_2 x_2 p_2^\circ \qquad (2)$$

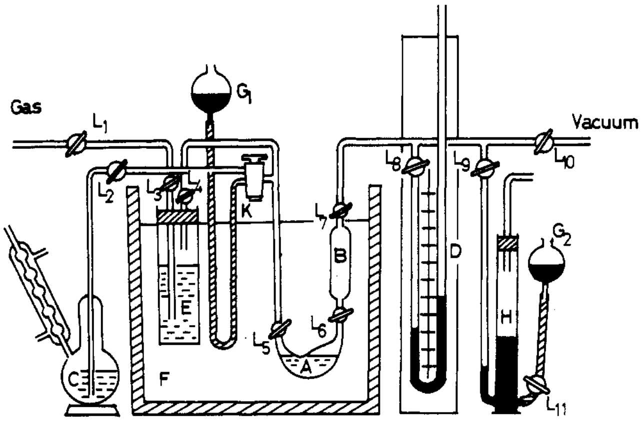

Figure 1. Apparatus for measuring gas solubilities
A, absorption chamber; B, sampling bulb; C, degassing flask; D, manometer; E, saturating vessel; F, constant-temperature bath; $G_{1,2}$, mercury reservoir; H, mercury column; K, three-way cock; L_{1-11}, two-way cock

The values of the activity coefficients of methanol and water at 20° and 40°C were taken from the literature of Katayama (*5*). The values corresponding to 10° and 30°C were estimated from γ values at 20° and 40°C by assuming that log γ is a linear function of $1/T$. Values for the vapor pressure of aqueous ethanol solutions were obtained from the International Critical Tables (*8*). The activity coefficients of the aqueous *n*-propanol solutions at each temperature were calculated from the equilibrium data of Gadwa (*3*) and the heat of mixing data of Bose (*1*).

The lowering of the vapor pressure of the aqueous alcohol solution owing to the dissolved sulfur dioxide, Δp, was calculated by assuming Raoult's law, because the

Table I. Physical Properties of Pure Solvents Used

	Density	
	Obsd	Lit
Methanol	$d_4^{25} = 0.78675$	0.78675[a]
Ethanol	$d_4^{30} = 0.78095$	0.78079[b]
n-Propanol	$d_4^{25} = 0.79991$	0.79950[c]

[a] ICT. [b] Winkler (1905). [c] Kretschmer (1951).

Table II. Solubilities of Sulfur Dioxide in Pure Solvents
Grams of sulfur dioxide per 100 grams of solvent (solute gas free)

	Water		
Temp, °C	Obsd	Hudson (*4*)	Sims (*7*)
10	15.66	15.39	15.4
20	10.90	10.64	10.4
30	7.77	7.56	7.8
40	5.76	5.54	5.8

	Methanol		Ethanol	
Temp, °C	Obsd	de Bruyn (**2**)	Obsd	de Bruyn (**2**)
10	131.56	125.3	70.50	72.7
20	86.19	68.7	46.81	44.9
30	57.53		31.62	
40	40.80		23.80	

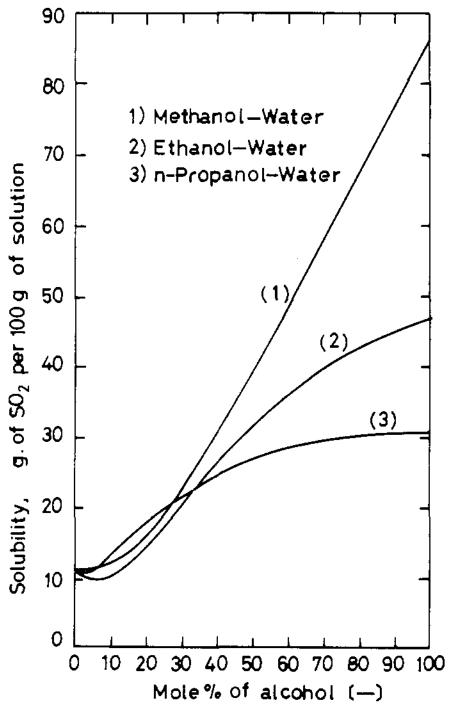

Figure 2. Solubility curves of sulfur dioxide in aqueous alcohol solutions at 20°C

Table III. Solubilities of Sulfur Dioxide in Aqueous Methanol Solutions

x_1	π	p_{SO_2}	S	S_0
		10°C		
0	768.5	759.7	15.66	15.66
0.0608	773.2	760.3	16.06	16.06
0.0813	774.8	760.5	16.92	16.91
0.1415	783.6	764.8	20.55	20.42
0.2066	783.2	761.8	25.04	24.98
0.3428	784.6	761.9	43.60	43.50
0.4161	790.6	763.3	51.75	51.53
0.4620	793.0	764.9	56.63	56.26
0.5862	787.1	757.9	75.96	76.17
0.6792	797.8	767.9	91.79	90.85
0.7490	793.8	762.9	97.44	97.07
0.8694	800.5	768.3	112.18	110.97
0.9263	794.8	762.3	120.38	120.02
1.0000	795.4	761.7	131.85	131.56
		20°C		
0	777.5	760.5	10.90	10.90
0.0107	778.6	760.5	10.45	10.44
0.0675	786.4	761.5	11.14	11.12
0.1835	796.2	758.5	14.48	14.51
0.2659	806.2	762.3	19.05	18.99
0.3503	807.5	758.6	24.51	24.56
0.4233	812.2	760.2	31.41	31.40
0.5080	813.6	767.3	38.64	38.27
0.5798	821.9	764.8	45.87	45.58
0.6694	823.7	764.0	53.02	52.74
0.7638	823.0	761.5	63.57	63.44
0.8996	817.2	751.9	75.33	76.15
1.0000	827.3	759.3	86.11	86.19
		30°C		
0	793.6	762.5	7.79	7.77
0.0811	809.8	761.5	8.35	8.33
0.1890	827.1	759.0	10.80	10.88
0.2849	840.8	758.3	14.13	14.16
0.4193	849.9	758.1	21.18	21.23
0.4679	850.5	755.3	23.41	23.56
0.6197	861.3	757.0	32.69	32.82
0.6760	865.7	757.7	35.69	35.79
0.7506	868.7	756.8	40.36	40.53
0.8734	876.8	758.5	49.09	49.19
0.9673	877.7	755.7	56.60	56.92
1.0000	886.1	761.3	57.63	57.53
		40°C		
0	815.0	760.6	5.76	5.76
0.0830	844.4	759.0	6.26	6.26
0.1402	865.7	762.5	7.22	7.20
0.3185	901.5	759.9	11.98	11.98
0.4041	916.2	761.7	14.88	14.85
0.5332	932.5	763.4	20.94	20.85
0.5822	930.6	755.9	22.21	22.33
0.6354	924.5	758.3	24.69	24.75
0.6740	947.1	762.9	26.33	26.23
0.7957	954.3	757.9	31.96	32.05
0.8400	966.5	758.5	33.56	33.62
0.9165	968.6	760.5	37.46	37.44
1.0000	976.5	760.3	40.82	40.80

Table IV. Solubilities of Sulfur Dioxide in Aqueous Ethanol Solutions

x_1	π	p_{SO_2}	S	S_0	x_1	π	p_{SO_2}	S	S_0
		10°C					30°C		
0	768.5	759.7	15.66	15.66	0	793.6	762.5	7.79	7.77
0.0628	772.5	759.4	14.44	14.45	0.0651	806.0	758.0	6.63	6.44
0.0986	776.9	762.5	14.87	14.82	0.1159	810.4	755.8	7.22	7.27
0.1722	777.3	761.3	20.18	20.15	0.1992	820.6	759.7	10.32	10.32
0.2423	778.0	761.0	26.88	26.84	0.3004	822.9	758.9	14.20	14.22
0.3325	778.3	760.7	35.76	35.73	0.3663	826.5	761.4	16.46	16.43
0.3827	779.9	762.1	39.73	39.62	0.4684	827.0	760.9	19.98	19.96
0.4728	778.9	761.2	47.06	46.98	0.5004	825.5	759.1	20.47	20.49
0.6010	778.9	761.9	57.08	56.94	0.6082	827.4	760.7	23.04	23.02
0.6650	782.8	764.8	60.83	60.46	0.7307	826.8	760.5	26.21	26.19
0.7955	777.6	761.3	65.55	65.44	0.8182	824.6	758.9	28.10	28.14
0.8730	775.8	759.9	67.60	67.61	0.8807	824.1	758.8	28.79	28.84
1.0000	776.4	760.9	70.58	70.50	0.9551	824.5	760.0	30.33	30.32
					1.0000	826.4	763.3	31.76	31.62
		20°C					40°C		
0	777.5	760.5	10.90	10.90	0	815.0	760.6	5.76	5.76
0.0563	786.8	762.1	9.21	9.19	0.0644	839.5	755.6	5.29	5.32
0.0986	782.7	754.3	9.78	9.86	0.1035	851.9	759.4	5.99	6.09
0.2168	782.9	749.0	15.08	15.30	0.1900	867.7	765.0	7.99	7.94
0.2781	798.3	763.2	19.00	18.92	0.3000	868.7	759.2	10.01	10.02
0.3399	798.5	762.9	23.09	23.00	0.3982	870.1	757.3	12.60	12.64
0.4753	795.7	760.0	30.88	30.88	0.5111	869.8	753.9	15.07	15.19
0.5923	795.0	759.4	35.73	35.76	0.6055	877.0	760.4	17.13	17.12
0.6832	796.9	761.9	39.15	39.06	0.7294	876.2	759.0	18.30	18.32
0.7927	795.1	760.8	42.37	42.33	0.8205	877.6	760.9	20.33	20.31
0.8941	794.7	761.3	44.91	44.83	0.9152	876.2	760.3	21.69	21.68
1.0000	794.8	762.3	46.95	46.81	1.0000	874.0	759.8	23.80	23.80

Table V. Solubilities of Sulfur Dioxide in Aqueous *n*-Propanol Solutions

x_1	π	p_{SO_2}	S	S_0	x_1	π	p_{SO_2}	S	S_0
		10°C					30°C		
0	768.5	759.7	15.66	15.66	0	793.6	762.5	7.79	7.77
0.0124	772.9	763.3	14.59	14.52	0.0223	798.6	760.2	7.34	7.34
0.0352	770.6	760.0	14.28	14.28	0.0516	802.2	760.8	8.04	8.03
0.0651	769.9	758.6	15.51	15.53	0.0761	803.2	759.3	8.79	8.80
0.1036	773.1	759.2	19.02	19.04	0.1964	804.9	760.6	12.78	12.77
0.2000	771.4	759.6	26.56	26.58	0.3009	793.7	750.0	15.28	15.49
0.3026	770.8	759.6	33.27	33.29	0.3976	803.0	760.3	17.67	17.66
0.3960	771.0	760.2	38.36	38.35	0.4900	801.2	759.3	18.98	18.99
0.4986	770.7	760.4	42.09	42.06	0.5984	799.6	759.4	20.43	20.45
0.5927	771.1	761.3	45.54	45.46	0.7077	798.6	760.9	21.32	21.29
0.7068	769.5	760.5	47.80	47.77	0.7732	795.5	759.9	21.53	21.53
0.8160	767.7	759.8	48.96	48.97	0.9026	789.4	759.8	21.91	21.92
0.9286	767.8	761.5	49.52	49.43	1.0000	783.0	759.6	22.05	22.06
1.0000	765.5	760.5	49.63	49.60					
		20°C					40°C		
0	777.5	760.5	10.90	10.90	0	815.0	760.6	5.76	5.76
0.0218	780.4	760.4	9.96	9.95	0.0186	821.5	756.8	5.57	5.60
0.0501	782.2	760.4	10.16	10.15	0.0355	830.3	758.7	5.59	5.60
0.0922	784.5	761.2	12.24	12.22	0.0763	836.7	762.4	6.49	6.47
0.1882	788.7	765.0	17.22	17.11	0.1043	839.6	760.7	7.21	7.20
0.2172	783.7	760.1	18.21	18.21	0.1974	839.6	760.3	9.30	9.30
0.2967	784.0	760.8	21.04	21.02	0.2992	838.4	759.8	11.22	11.22
0.3980	783.6	761.2	24.28	24.24	0.3950	837.2	759.7	12.39	12.39
0.4846	783.2	761.5	26.55	26.50	0.4994	837.1	761.0	13.60	13.58
0.5960	781.1	760.2	28.47	28.47	0.6068	834.0	760.4	14.53	14.52
0.6948	779.5	760.0	29.38	29.39	0.7108	829.8	760.4	15.15	15.14
0.7860	778.0	760.1	30.27	30.27	0.7824	823.0	757.7	15.54	15.59
0.8941	775.1	760.1	30.37	30.36	0.9112	815.7	761.5	15.69	15.66
1.0000	771.2	759.9	30.68	30.68	1.0000	803.6	759.9	15.95	15.95

data for calculating the Δp values were not available. When sulfur dioxide dissolves into pure methanol, the values of Δp can be calculated by referring to the literature of Katayama et al. (*6*). The values of Δp calculated at 20° and 40°C for pure methanol solution are 4.5 and 3.0 mm Hg smaller than the values by assuming Raoult's law, respectively.

Experimental Results

Solubilities of sulfur dioxide in pure solvents are shown in Table II.

About 13 solubility values were measured at each temperature. The solubilities given in Tables III–V are the experimental values. The solubilities S and S_0 in Tables III–V are grams of sulfur dioxide dissolved per 100 grams of solute gas-free solutions at total pressure π and at 1-atm partial pressure, respectively. The solubilities S_0 were calculated from the solubilities S by use of Equation 1 and assuming Henry's law.

Figure 2 indicates the smoothed solubility curves of sulfur dioxide in aqueous alcohol solutions at 20°C. The reproducibility of the solubility value was within about 1%. The error of 1 mm Hg in the pressure measurement produces the error 0.13% for the solubility. To ascertain the decrease of the alcohol concentration in the absorption chamber by the gas bubbling, sample solutions were withdrawn from the absorption chamber for the analysis at the ends of several runs. The decrease in the alcohol mole fraction by the gas bubbling did not exceed 0.002 in the most unfavorable case. For the solubility in aqueous methanol solution at 20°C, the change of 0.002 in alcohol mole fraction leads to the error of 0.5%.

Discussion of Results

The solubilities of sulfur dioxide in water obtained in this investigation agree well with Sims (*7*) at 30° and 40°C, but the values at 10° and 20°C are 1.9 and 4.8% higher than his data.

The solubilities in pure methanol and ethanol between 0° and 26°C were determined by de Bruyn (*2*). At 10° and 20°C, the percentage differences between the values observed and Bruyn's values are 5 and 25.5%, respectively, for methanol, and −3 and 4.2%, respectively, for ethanol. The results of various workers are compared in Table II.

For the solubilities of sulfur dioxide in aqueous alcohol solutions, no data are available in the literature to make a comparison of the results obtained in this work.

The solubilities of sulfur dioxide in water and pure alcohol decrease with temperature increase in the range of 10–40°C. Each solubility curve of the aqueous alcohol solutions at 10°C displays a minimum at a low alcohol concentration. At temperatures higher than 20°C, each solubility curve for the aqueous solutions of ethanol or *n*-propanol has a minimum, whereas the curve for the aqueous methanol solutions has no minimum.

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Nomenclature

p = pressure, mm Hg
Δp = lowering of pressure, mm Hg
S = grams of sulfur dioxide per 100 grams of solution (solute gas free) at total pressure, —
S_0 = grams of sulfur dioxide per 100 grams of solution (solute gas free) at 1-atm partial pressure, —
x = mole fraction, —

Greek Letters

γ = activity coefficient, —
π = total pressure, mm Hg

Superscript

° = pure component

Subscripts

1 = alcohol
2 = water
al = alcohol
aq = aqueous solution

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