SOLUBILITY OF CO_2 IN SOME PHYSICAL SOLVENTS

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Key Words: Solubility, Physical Solvents, Henry's Constant

Introduction

Gas solubility in liquids is a widely studied area, with a considerable amount of data published in the literature and used for the design of equipment such as absorption towers or scrubbers and chemical reactors. Battino and Clever[2] presented a comprehensive review of gas solubility in liquids along with solubility data treatment, various types of apparatus used, the theoretical significance of solubility study and a large number of references. Literature on the solubility of CO_2 in various solvents is also presented in this article. However, data on the solubility of CO_2 in industrially utilized physical solvents are rare.[4,5,9,11] Though chemical solvents are commonly preferred for acid gas purification, the extent of usage of physical solvents for CO_2 removal is also significant, as shown in the literature.[1,4,11] The choice of solvent for gas-treating plants is discussed by Tennyson and Schaaf.[15] An attempt is made here to study the effect of temperature on the solubility of CO_2 in four industrially important physical solvents in a low-temperature range using Morrison and Billett apparatus[8] which is suitably modified for this study. Thermodynamic considerations of the effect of temperature on solubility are limited to individual gas and liquid systems except for a study reported by Prausnitz and Shair.[10]

1. Experimental

1.1 Materials

The four physical solvents used were N-methyl 2-pyrrolidone (NMP, C_5H_9NO), propylene carbonate ($C_4H_6O_3$), sulfolane or anhydrous sulfolane (tetrahydrothiophene-1,1-dioxide, $C_4H_8SO_2$) with 3% deionised water, and methanol (CH_3OH). CO_2 gas was obtained from Dry Ice Depot (Hyderabad), India at a purity of 99.5%. The solvents were double-distilled before use. No impurity was detected in the solvents by gas chromatographic analysis (SE-30 and SE-52 columns). Source and measured physical properties of the solvents, along with comparative literature values,[7] are given in **Table 1**.

1.2 Apparatus

Solubility data were determined in a falling-film type of glass apparatus (**Fig. 1**). The principle of operation of the apparatus is identical to that of Morrison and Billett[8] and King and Al-Najjar.[6] Direct measurement of the volume of gas consumed in a known volume of liquid under experimental conditions is possible by this apparatus.

The apparatus consisted of a measuring jar, the tip (lower portion) of which was inserted into a glass tube. The middle portion of the tube was made into a helix of ten turns. The top portion of the tube was connected to the burettes and a level header bottle in series and parallel to each other. Graduations on the two burettes were at the same level. The burettes and the level header bottle contain mercury. The glass tube, measuring jar at the top and one of the burettes were jacketted and maintained at a required temperature by a cryostat. The second burette was open to the atmosphere. Standardization of the apparatus was done by measuring the solubility of O_2 in water at 25°C and atmospheric pressure (95.59 kPa). The value

Table 1. Source and Purity of Physical Solvents

Chemicals	Temperature: Density (Lit.) kg/m^3	Temperature: Refractive Index (Lit.)	Source
N-methyl 2-pyrrolidone	25°C; 1028.3 (1027.9)	25°C; 1.4637 (1.469)	SISCO, India
Propylene carbonate	25°C; 1204 (1206.9)	20°C; 1.4170 (1.4189)	BDH, England
Sulfolane	30°C; 1281.6 (1261.4)	30°C; 1.4751 (1.4821)	Spectro-Chem, India
Methanol	25°C; 781.7 (786.6)	25°C; 1.3262 (1.3263)	Loba-Chemie, Indo-Austranal Co.

* Received May 22, 1990. Correspondence concerning this article should be addressed to K. Yogish.

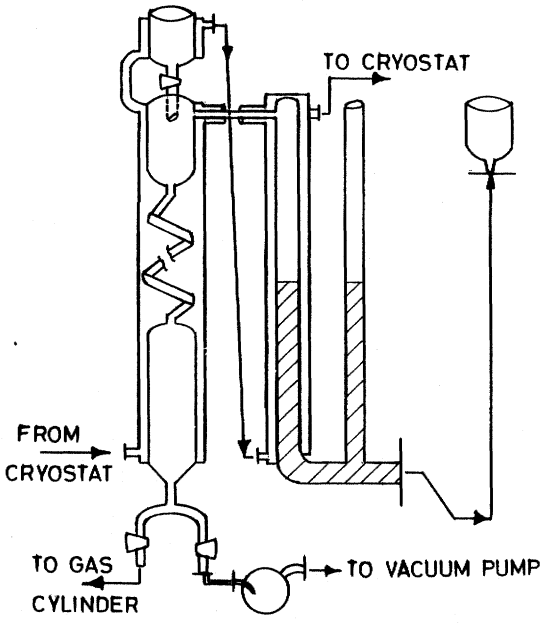

Fig. 1. Solubility Apparatus

obtained was 0.6 ml O_2/10 ml water. The literature value is 4.89 ml O_2/100 ml of water at 0°C and 101.3 kPa[12] pressure. The absolute deviation obtained was 4.1%.

1.3 Experimental procedure

The procedure adopted is given below. The glass tube and the burette were evacuated by a vacuum pump and filled with CO_2 gas. The solvent was taken in the measuring jar and a slight amount of solvent was taken in the bottom portion of the glass tube. The mercury levels in the burette were adjusted to atmospheric pressure (95.59 kPa) after maintaining the apparatus at a required temperature. This was done by using the level header bottle. The temperature was measured by a contact thermometer attached to the cryostat. Then a known amount of liquid droplets was allowed into the tube. Pressure inside the closed apparatus was decreased as the gas became absorbed in the solvent. By positioning the level header bottle again, the volume of gas dissolved in a known volume of solvent was measured as the difference between the initial and final burette readings at a constant atmospheric pressure. The volume measurements were accurate to within ± 0.1 ml and reproducibility was 98%. The volume of solvent taken was one or two ml as the case may be and each experiment was repeated three or four times. The experiments were conducted at 95.59 kPa partial pressure of the gas (in the present case total pressure was assumed, neglecting the vapour pressure of the solvents).

2. Results and Discussion

Solubility data in terms of volume of CO_2 per volume of solvent (Ostwald Coefficient) for a temperature range of 0–25°C and a gas partial pressure of 95.59 kPa are shown in **Table 2**. These values are Ostwald (original) coefficients.[3] It can be seen that in all four solvents, solubility decreased with increase in temperature. Henry's Constant (H) values were calculated using Henry's law for dilute solutions, $H=p/x$. These values are plotted against the temperature in **Fig. 2**, from which it can be seen that there is a definite relationship between the molecular weights of the solvents and the gas and the solubility values. As the molecular weights of the solvents increased, H values also increased. This phenomenon is valid if the molecular weight of the solvent is more than that of the gas. However, if the solvent molecular weight is less than that of the gas, as in the case of the CO_2-methanol system, then the H values increased. In other words, Ostwald Coefficients decreased as the molecular weight of the solvents increased when $M_s > Mg$ whereas the Ostwald Coefficient increased when $Mg > M_s$ (Table 2). This

Table 2. Solubility Data of CO_2 in Physical Solvents

Solvents		Temperature °C					
		0	5	10	15	20	25
Solubility, m^3 gas/m^3 solvent (Ostwalds Coefficient)	N-methyl 2-pyrrolidone	4.75	4.45	4.2	4.0	3.8	3.5
	Propylene carbonate	4.8	4.5	4.2	4.0	3.7	3.1
	Sulfolane	3.5	3.1	2.8	2.6	2.3	2.1
	Methanol	5.6	5.3	5.0	4.7	4.2	3.8

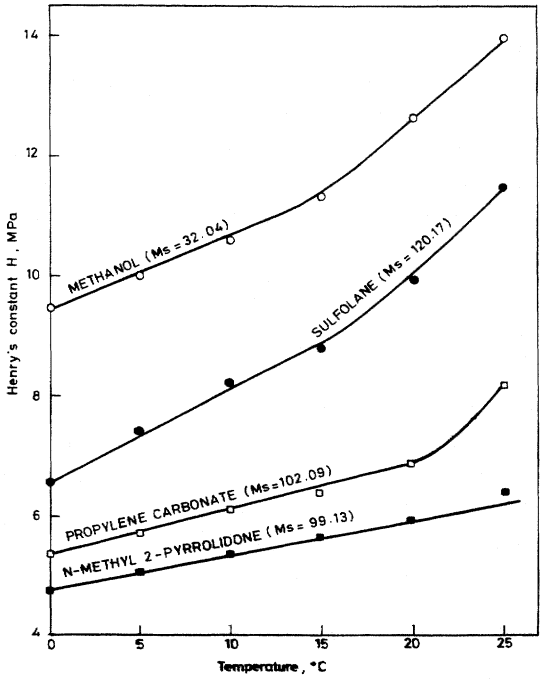

Fig. 2. Effect of Temperature on Solubility of CO_2 in Physical Solvents

Table 3. Comparative Solubility Data of CO_2

CO_2-propylene carbonate system	Pressure, kPa		Temperature, °C 25	20	15	10	5	0
Rivas and Prausnitz[11] study	101.325	H, MPa	8.3876	6.9063	6.3895	6.0977	5.6813	5.3459
this study	95.59		8.2420	6.8869	6.3723	6.0808	5.6831	5.3313
Murrieta-Guevara and Rodriguez[9]	93.928	x_{CO_2}	0.012					
this study	95.59		0.0116					

CO_2-NMP system	Pressure, kPa	Temperature, °C	x_{CO_2}
Murrieta-Guevara and Rodriguez[9]	99.197	25	0.014
this study	95.59	25	0.01492
Sweeney *et al.*[14]	101.325	25	0.0145

CO_2-Methanol system	Pressure, kPa	Temperature, °C	x_{CO_2}
Sweeney *et al.*[14]	101.325	25	0.00558
this study	95.59	25	0.006862
Stephen and Stephen[13]	101.325	20	0.006452
this study	95.59	20	0.007581

shows that physical solubility is a molecular phenomenon. However, this observation cannot be generalised since the gas solubility in liquids is not influenced by molecular weight alone.

A comparative study is presented in **Table 3** of the experimental and rare data available in the literature. Issacs *et al.*[5] determined the solubility of H_2S and CO_2 in propylene carbonate solvent but their range of parameters employed is beyond that of the present study. Data on the CO_2-sulfolane system is not available in the literature and hence no comparative study was made. An increase in solubility value compared to that reported in the literature for the CO_2-methanol system was observed. This is due to the different pressures employed, and the effect of the vapour pressure of methanol may not be significant due to the shorter experimental time (less than one minute) for each experiment in the closed apparatus.

Conclusions

Solubility data of CO_2 for four industrially important physical solvents were presented. The solubility measurements were done in a new modified apparatus. The experimental data agreed satisfactorily with available existing data in the literature. The Ostwald Coefficient values were decreased with increase in temperature. It is also observed that the solubility data also depend on gas and liquid molecular weights.

Nomenclature

H	=	Henry's Constant	[Mpa]
M_g	=	Molecular weight of gas	[—]
M_s	=	Molecular weight of solvent	[—]
p	=	partial pressure of gas	[kPa]
x	=	mole fraction of gas	[—]

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