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Hydrolysis of Carbonyl Sulfide in Binary Mixture of Ethylene Glycol and Water

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The solubility and hydrolysis properties of carbonyl sulfide in binary mixture of ethylene glycol and water were studied as a function of composition. The use of an ethylene glycol aqueous solution can enhance the solubility and hydrolysis rate of carbonyl sulfide compared with that in pure water. The composition of the mixture with maximum hydrolysis rate varies with temperatures. The physicochemical properties including density, viscosity and surface tension as a function of composition at 308.15 K under atmospheric pressure as well as liquid-liquid equilibrium data on the temperature range from 308.15 to 318.15 K were also measured for the binary mixture.

Key Words: Carbonyl sulfide, Solubility, Hydrolysis, Ethylene glycol.

INTRODUCTION

Carbonyl sulfide (COS) is called the sulfur oxidation carbon, under the normal temperature and atmospheric pressure. It is a colourless and tasteless gas, slightly soluble with water (at 1 atm, 286.65 K, 1 mL water can dissolve 0.8 mL COS) and toluene (at 1 atm, 295.15 K, 1 mL toluene can dissolve 15.0 mL COS), easily to dissolve in the potassium hydroxide solution and mellow. The COS molecules are polar molecules sharing many characteristics with CO_2 and CS_2 molecules[1]. Different solvents have different solubility to COS. Carbonyl sulfide can not only corrode equipment and pipeline, but also hurt the skin, the eyes, the nose, the throat and the lungs, therefore, it must be removed. In the gas treating processes removing COS is tedious and in the usual condition COS does not easily separate with other components. It is difficult to transform and absorb COS so all the conventional desulfurization methods got their own difficulties. Therefore, it is very important to develop highly effective COS removing technology. At present the most common COS removing methods are hydrogenation conversion[2], the hydrolysis conversion method, organic amines solvent absorption law[3], as well as oxidized conversion method[4]. These

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methods have their own bottle-necks in the desulfurization processes. Recently, some have tried to translate COS to elemental sulfur by using photodissociation dynamics adsorbed on water ice surface[5], but the method is proved quite difficult to use in an industrial environment.

Ethylene glycol is the simplest alcohol with multi-hydroxyl groups. For its high flash point, high boiling point, low vapour pressure, low toxicity, non-corrosiveness and the character of dropping the solidification point of aqueous, ethylene glycol became an important raw material for industry. There are many reports that the solubility of COS in water can be enhanced by adding ethylene glycol[6]. It is also reported to be advantageous to the liquid phase helping absorb the COS gas, It also helps the mass transfer in the absorption process[6].

We chose ethylene glycol as the absorbent and initiated research on glycol-water system based on the patent "The DDS Desulphurization Technology"[7] with the aim on developing this technology in hydrolyzing COS for industry desulfurization. This article discusses the hydrolysis dynamics of COS in a binary ethylene glycol + water system.

EXPERIMENTAL

All of the commonly used reagents such as anhydrous ethylene glycol are analytical reagent (AR) grade. N_2 and CO_2 were purchased from Beijing Huayuan Gas Chemical Industry Co., Ltd and Beijing ZG Gases Science and Technology Co., Ltd. COS/N_2, mixtures were produced by the national standards material research center. Ethylene glycol used in this work was pretreated according to the method reported by Yang[8]. It was first dried over a molecular sieve and then fractionally distilled under reduced nitrogen gas pressure. The purity of the final samples, as determined by gas chromatograph, was higher than 99.5 %. Each density fraction of the ethylene glycol-water solution was determined using the gravimetric method. Double-distilled water was used.

Densities of the pure liquids and binary mixtures were measured using the specific gravity method. The water was degasified. A thermostatically controlled (308.15 ± 0.01K), well stirred water bath was used for all measurements of density, viscosity, surface tension and the kinetic data. Each sample was measured several times and the average value was reported as the result.

The viscosities were measured with an Ubbelohde-Viscometer which was checked by measurement of the viscosity of pure water. The flow-time was recorded by an accurate stopwatch with a precision of ± 0.01 s. The average value of three sets of data for each fluid was taken for the calculation of the viscosity.

The surface tension of the pure liquids and the binary mixtures of ethylene glycol + water were measured using the drop-volume method[9]. All samples were equilibrated at (308.0 ± 0.1) K. The outer diameter of the capillary tube was 4.451 mm. Five sets of data for each sample were measured and the average value was taken for the calculation of surface tension.

Hydrolysis of carbonyl sulfur in the ethylene glycol + water system: Sample bottles with shock insulation were used in these hydrolysis experiments. After acid pickling, water scrubbing and drying, sample bottles were vacuum-pumped and filled with binary mixtures of ethylene glycol + water and adequate supplementary COS gas. They were then set aside in a constant temperature water bath. When the equilibrium of COS and the binary mixtures were achieved, a sample injector was used to discrete sample through the shock insulation at set time intervals. The COS was analyzed with an Agilent Gas Chromatograph, Type 6890N, equipped with thermal Flame Photometric Detector (FPD). A curve of concentration-time was drawn with the data record on the 6890 N.

Hydrolysis mechanism

The reaction for hydrolysis can be represented by the following equation:

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad (1)$$

The kinetic equation can be expressed as:

$$-\frac{\partial[COS]}{\partial t} = k[COS][H_2O][catalyst] \qquad (2)$$

The kinetics of the reaction of COS in water was a pseudo first order reaction[10], when the water and addition (or with no addition) were in excess. So eqn. 3 can be simplified as:

$$-\frac{\partial[COS]}{dt} \approx k'[COS] \qquad (3)$$

where k' in eqn. 3 was the constant of this pseudo first order reaction, while [COS] was the concentration of the COS gas, $[COS]_0$ was the initial concentration of COS gas. Based on this equation, the relationship between ln $[COS]_0/[COS])$ and the time can be expressed with a line whose slope coefficient represents the kinetic parameter k'.

Analysis method chromatograph condition: The gas chromatographic column P (3 mm × 2 m) was used for the analysis of COS gas. The column was specially treated to detect sulfur compounds and the detector was supplied with a glass filter which had a maximum transmission of 394 nm. The column temperature rose up to 393.15 K from 313.15 K at 30 K/min after a 1 min step at 313.15 K. The temperature of the injection port and detector respectively was 473.15 K and 523.15 K. The carrier gas (high purity N_2) flow-rate was 30 mL/min, the hydrogen flow-rate was 75 mL/min and the air flow-rate was 100 mL/min. For the calibration of the gas chromatograph, external standard methods were used[9].

RESULTS AND DISCUSSION

Physical-chemical properties and liquid-liquid equilibrium for binary mixture of ethylene glycol + water: Table-1 represents the measured value and the literature value of density, viscosity and surface tension of the pure glycol and showed that the methods employed in this studies is appreciable.

TABLE-1
COMPARISON OF MEASURED DENSITY AND VISCOSITY WITH THE LITERATURE VALUES AT 308.15 K AND THE SURFACE TENSION AT 313.15 K

Temp. (K)	ρ (g cm^{-3})		η (m Pa s)		γ (m N m^{-1})	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
308.15	1.1030	1.1054[11]	9.2122	10.473[11]	–	–
313.15	–	–	–	–	48.732	48.07[12]

Fig. 1a shows that the viscosity had a positive deviation over the entire range of the composition. Along with the ethylene glycol concentration increase in the mix system, the density of the mix system had a sharp growth and while the concentration of the ethylene glycol rose the rise rate of the density of the mix system tended to decrease.

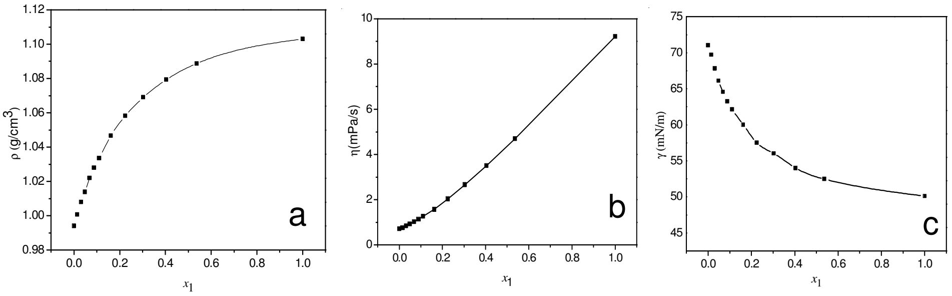


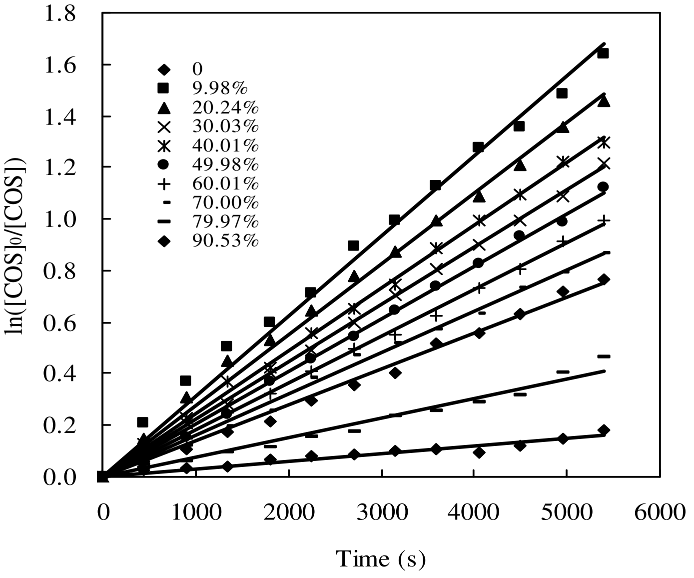
Fig. 1. Density (a), viscosity (b) and surface tension (c) for ethylene glycol (1) + water (2) at 308.15 K

The plot of viscosity against the mass fraction of ethylene glycol is given in Fig. 1b. It shows that with increasing mass fraction of ethylene glycol, the viscosity increases to the viscosity of pure ethylene glycol.

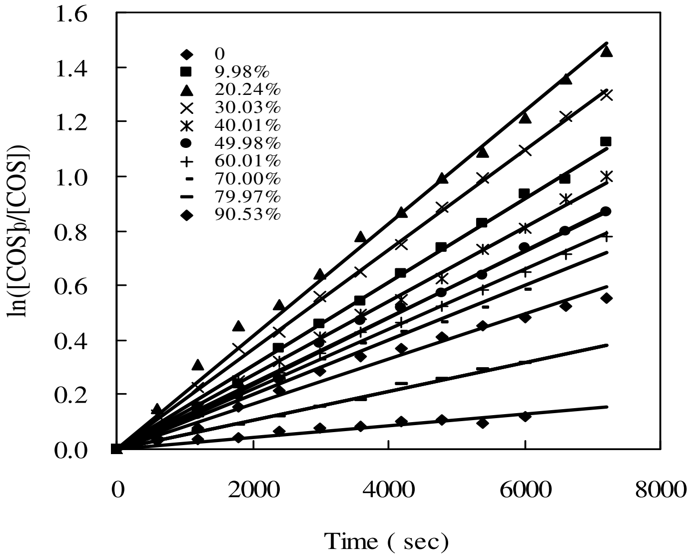
The surface tension of the ethylene glycol-water system at 308.15 K is shown in Fig. 1c. From the figure, it is observed that with the increase of the ethylene glycol, the surface tension for the system reduces obviously under the experimental temperature. That is because the ethylene glycol has a remarkable surface activity and when it is mixed with water, it can reduce the surface tension for the mixture.

Hydrolysis of carbonyl sulfur in the ethylene glycol + water system: The hydrolysis reaction of COS in the ethylene glycol + water solution was a pseudo-first-order reaction, so the relationship of ln ($[COS]_0/[COS]$) over time can be represented by a straight line. The [COS] is the COS concentration and $[COS]_0$ is the initial concentration of COS gas. According to the equation the slope is the dynamic parameter. So we can obtain the Fig. 2 as follows:

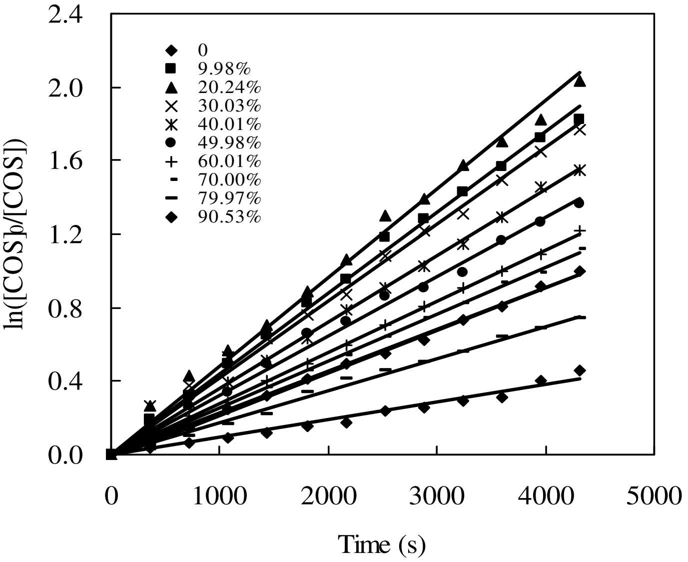
The hydrolysis behaviour of COS in the ethylene glycol + water solution over the ethylene glycol composition range was studied under 308.15, 313.15 and 318.15 K. To evaluate this hydrolysis behaviour, more than 10 experimental points for each experiment were analyzed. The slope of the kinetic equation of COS in ethylene glycol + water first increased and then decreased when the ethylene glycol concentration was increased and reaching a maximum when 20 % ethylene glycol was doped over the experimental temperature range. When 70 % ethylene glycol was doped, the kinetic was approximately of which it is in pure water and as the ethylene glycol concentration increased above 70 %, it became smaller. Both of the above were shown in Fig. 2.



(d)



(e)



(f)

Fig. 2. Dependence of the hydrolysis of COS on mass fraction of ethylene glycol at different temperatures (d) 308.15 K; (e) 313.15 K; (f) 318.15 K

The highest hydrolysis reaction dynamics results were respectively 20.7, 31.1 and 48.1 for the temperatures 308.15, 313.15 and 318.15 K when the ethylene glycol concentration was respectively controlled at 20.24, 9.98 and 20.24 % (Table-2). It is also observed that increasing the temperature enhances hydrolysis.

H_2S was not produced even if COS was in contact with pure ethylene glycol for a long time. It was slightly produced in the highly concentrated ethylene glycol in the mix system. A conclusion can be drawn from the study that the hydrolysis reaction

TABLE-2
KINETIC CONSTANTS OF COS HYDROLYSIS WITH DIFFERENT ETHYLENE GLYCOL CONCENTRATIONS AT 308.15, 313.15 AND 318.15 K

Mass fraction w_1 (%)	Kinetic constant $k' \times 10^{-5}$ (s^{-1})		
	308.15 K	313.15 K	318.15 K
0.00	8.24	13.90	22.70
9.98	15.20	31.10	43.80
20.24	20.70	27.50	48.10
30.03	18.30	22.30	41.70
40.01	13.60	24.40	35.90
49.98	12.10	20.40	32.20
60.01	11.00	18.10	27.80
70.00	10.00	16.10	25.50
79.97	5.27	7.58	17.40
90.53	2.15	2.99	9.55
100.00	0.00	0.00	0.00

of COS will only take place in the presence of water. This is because the energy of the intermolecular hydrogen bond within the water molecular could polarize the C=O bond of COS in the water, producing H_2S from COS[13], so it was easy to produce H_2S from COS with excessive water compared to pure ethylene glycol. This was verified by this experiment and we can also explain it at molecular level. As the ethylene glycol molecule is symmetric in structure and the COS is a polar molecule, it is very hard for pure ethylene glycol or a highly concentrated ethylene glycol aqueous solution to dissolve COS gas based on the theory of soluble with the same molecular polarity. The high viscosity of the ethylene glycol was also an obstacle.

Several hydrogen bonds formed through intermolecular hydrogen bonding between the two ethylene glycol molecules and through intramolecular hydrogen bonding constituted by the two -OH in each ethylene glycol molecule as well as many hydrogen bonds within the water but this was just the intermolecular hydrogen bonding. So when the two reagents mixed together, the intermolecular hydrogen bonds between the water molecules and the ethylene glycol molecules reacted and this kind of hydrogen bond has more energy than the intermolecular hydrogen bond of two water molecules to polarize the C=O bond[14], this is why ethylene glycol can enhance the water competence to hydrolyze COS. There was a balance of the four kinds of hydrogen bonds, so there was an inflection point on the curve of the hydrolysis kinetics. This is the reason why the 20 % ethylene glycol concentration was the best proportion for hydrolyzing COS.

Energy can be easily obtained from the polarizing ability of C=O from the hydrogen bonds as the temperature was increased. The viscosity of this mixed system decreased with increasing temperature from 308.15 to 318.15 K and that was another reason for accelerating this hydrolysis.

Conclusion

(1) The physical-chemical properties were changed by adding ethylene glycol. The density increased and the viscosity also increased more quickly, while the surface tension decreased with the increasing concentration of ethylene glycol in this ethylene ethylene glycol-water system at 308.15 K. (2) All the straight slopes of the kinetic equations of COS in ethylene glycol-water system first increased and then decreased when the amount of ethylene glycol doped was increased and it reached a maximum when 20 % ethylene glycol was doped over the temperature range in this experiment. (3) Also the temperature change has a tremendous influence on the ethylene glycol-water system absorption for the hydrolysis of COS. It is advantageous for the COS hydrolysis reaction to increase the temperature in this experiment.

REFERENCES

1. P.D.N. Svoronos and T.J. Bruno, *Ind. Eng. Chem. Res.*, **41**, 5321 (2002).
2. S. Tong, I.G.D. Lana and K.T. Chuang, *Can. J. Chem. Eng.*, **71**, 392 (1993).
3. M. Liang, C. Li, H. Guo and K. Xie, *Chin. J. Catal.*, **23**, 357 (2002).
4. X. Li, X. Wei and Y. Liu, *Modern Chem. Ind.*, **8**, 19 (2004).
5. A. Ikeda, N. Kawanaka, A. Yabushita and M. Kawasaki, *J. Photochem. Photobiol. A-Chem.*,**195**, 330 (2008).
6. R.J. Littel, G.F. Versteeg and W.P.M. Van Swaaij, *J. Chem. Eng. Data*, **37**, 49 (1992).
7. X. Wei, Gas De-Sulfur Method by Catalysis of Biochemical Iron-alkali Solutions (2002).
8. C. Yang, P Ma, F Jing and D Tang, *J. Chem. Eng. Data*, **48**, 836 (2003).
9. X. Li, Y. Liu and X. Wei, *Chin. J. Chem. Eng.*, **13**, 234 (2005).
10. A. Kamyshny, A. Goifman, D. Rizkov and O. Lev, *Environ. Sci. Technol.*, **37**, 1865 (2003).
11. K.V. Reddy, S.K. Reddy and A. Krishnaiah, *J. Chem. Eng. Data*, **39**, 615 (1994).
12. N.G. Tsierkezos and I.E. Molinou, *J. Chem. Eng. Data*, **43**, 989 (1998).
13. W.C. Andersen and T.J. Bruno, *Ind. Eng. Chem. Res.*, **42**, 963 (2003).
14. X. Yang, Which Kind of Hydrogen Bond Formation in the Ethylene Glycol and Water System, Chemical Education, pp. 33-343 (1994).

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