

Electronic Supplementary Information

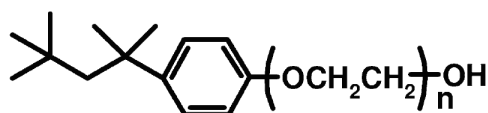
CO₂ capture by hydrocarbon surfactant liquids

Jianling Zhang*, Buxing Han*, Yueju Zhao, Jianshen Li, Minqiang Hou and Guanying Yang
Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and
Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences

*Corresponding authors: zhangjl@iccas.ac.cn; hanbx@iccas.ac.cn

1. Experimental

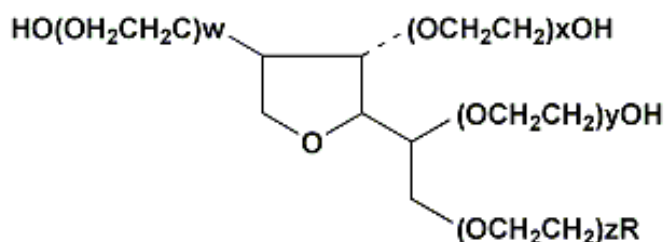
Materials TX-45 and TX-100 were provided by Sigma. TX-114, Tween 20, and Tween 80 were purchased from Shanghai ShineGene Molecular Bio-Technologies, Inc. The molecular structures of the five surfactants are shown in Fig. S1. CO₂ (>99.95% purity) was provided by Beijing Analytical Instrument Factory. CH₄ was purchased from Liuling Chemical Factory. N₂ was provided by Beijing Tailong Electronic Tech. Co., Ltd.



TX-45: n=5

TX-114: n=7.5

TX-100: n=10



Tween 20: w+x+y+z=20, R=-OCO(C₁₁H₃₃)

Tween 80: w+x+y+z=20, R=-OCO(C₁₇H₃₃)

Fig. S1 Molecular structures of the Triton surfactants and Tween surfactants used in this work.

Determination of the solubility of gas in surfactants The gas solubility measurements were made using a gravimetric microbalance (Mettler MP1200). A detailed description of the apparatus and the experimental procedures were given elsewhere.^{S1} The apparatus was composed mainly of a gas cylinder, a constant-temperature water bath, a pressure gauge, a volume-variable view cell, a sample bomb, and a magnetic stirrer. The temperature of the constant-temperature water bath was controlled by a Haake-D8 temperature controller. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT model 93) and an indicator. Its accuracy was ± 0.25 bar in the pressure range of 0-200 bar.

In a typical experiment, the desired amount of surfactant was loaded into the view cell, and the air in the system was replaced by gas. The cell was placed in the constant temperature water bath, and then gas was charged into the cell until a suitable pressure was reached, and the stirrer was started. After equilibrium had been reached, the liquid was sampled into the sample bomb. During the sampling, the volume of the view cell was adjusted to keep the pressure unchanged. The gas solubility was calculated from the masses of the liquid and the gas in the sample bomb. The mass of the liquid was known from the masses of the sample bomb before and after sampling; the mass of gas was known from the masses of the sample bomb before and after releasing the gas in the sample.

Henry's constant Henry's constant (H) at different temperatures can be obtained from Equation 1, where x is the limiting mole fraction of CO₂ absorbed in the surfactant and p is the pressure of CO₂ in the gas phase.^{S2} The gas phase is assumed to be pure and ideal, both of which are excellent assumptions under the conditions investigated. Equation 1 implies that the solubility of the gas is large as the Henry's constant is small. The estimated uncertainty of Henry's constant is 2.0 %.

$$H = \lim_{x \rightarrow 0} \frac{p}{x} \quad (1)$$

Enthalpy and entropy of CO₂ dissolution The enthalpy (ΔH_1) and entropy (ΔS_1) of absorption can be obtained by Equations 2 and 3, where p is the partial pressure of the gas, T is the temperature of the system, and x_1 is the mole fraction of the gas in the liquid phase.^{S2} Information about the strength of interaction between the surfactant and CO₂ is provided by the enthalpy, while information about the degree of ordering that takes place upon dissolution of CO₂ is given by the entropy.

$$\Delta H_1 = R \left(\frac{\partial \ln p}{\partial \ln(1/T)} \right)_{x_1} \quad (2)$$

$$\Delta S_1 = -R \left(\frac{\partial \ln p}{\partial \ln T} \right)_{x_1} \quad (3)$$

FTIR spectra The apparatus and procedures to determine the FT-IR spectra were the same as those used previously.^{S3} The apparatus consisted mainly of a gas cylinder, an IR spectrometer (Bruker TENSOR 27), and a high-pressure IR sample cell. The sample cell was composed mainly of a stainless steel body and two zinc sulfide (ZnS) windows (2.25 cm in diameter and 0.60 cm in thick), which was thermostated to ± 0.1 °C of the desired temperature by an electric heater and temperature controller. The internal volume and the path length of the cell were 1.48 cm³ and 1.56 cm, respectively.

In a typical experiment, the suitable amount of surfactant was added into the cell, of which the temperature was stabilized at 25 °C, and CO₂ was charged into the cell to the desired pressure. The IR spectrum was recorded after equilibrium had been reached. Each sample was recorded with 32 scans at an effective resolution of 2 cm⁻¹.

2. Results

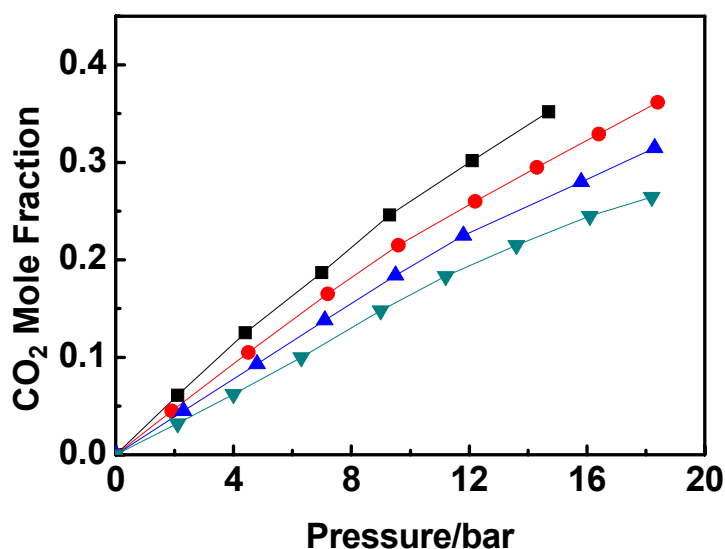


Fig. S2 Solubility of CO₂ in TX-45 at 15 °C (■), 25 °C (●), 35 °C (▲), and 45 °C (▼).

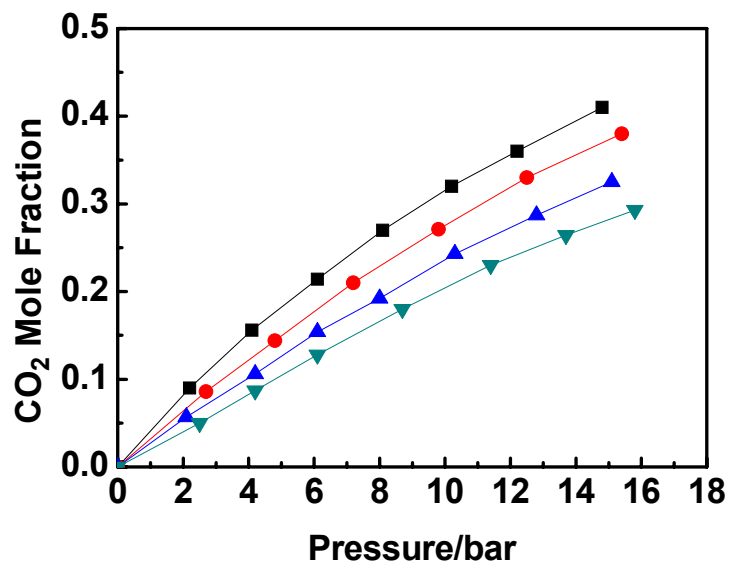


Fig. S3 Solubility of CO₂ in TX-114 at 15 °C (■), 25 °C (●), 35 °C (▲), and 45 °C (▼).

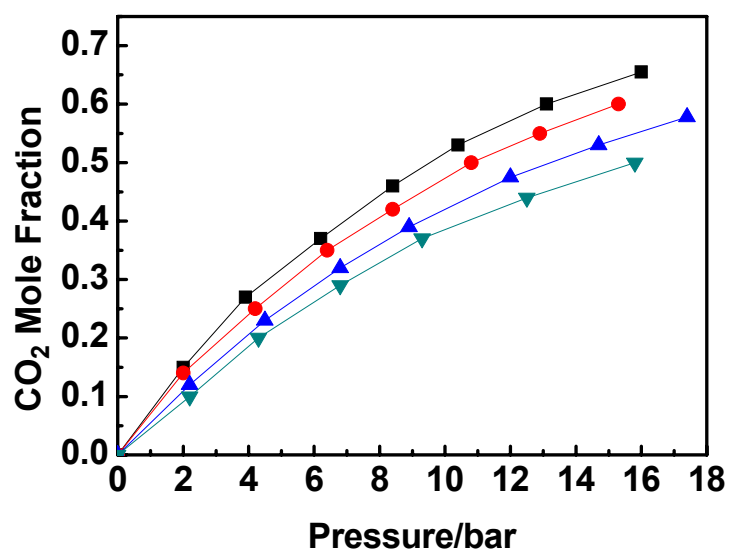


Fig. S4 Solubility of CO₂ in Tween 20 at 15 °C (■), 25 °C (●), 35 °C (▲), and 45 °C (▼).

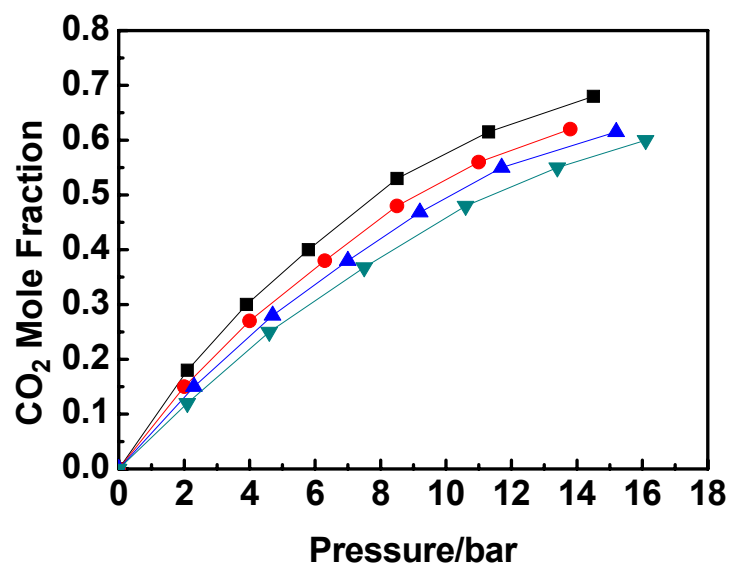


Fig. S5 Solubility of CO₂ in Tween 80 at 15 °C (■), 25 °C (●), 35 °C (▲), and 45 °C (▼).

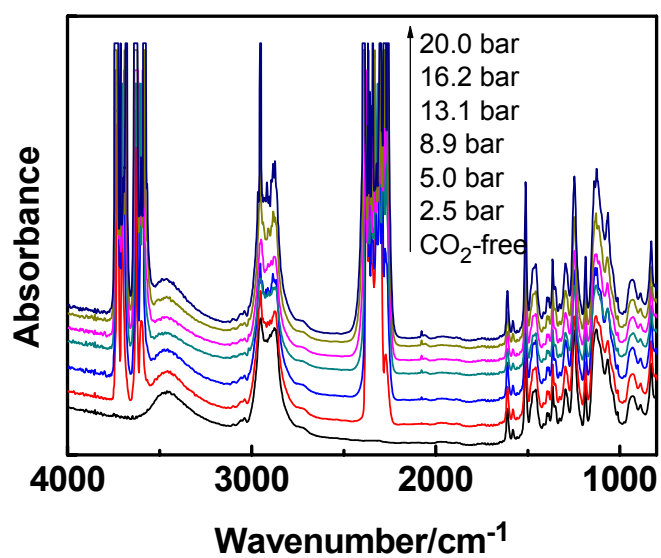


Fig. S6 FTIR spectra of TX-45/CO₂ at 25 °C and different CO₂ pressures.

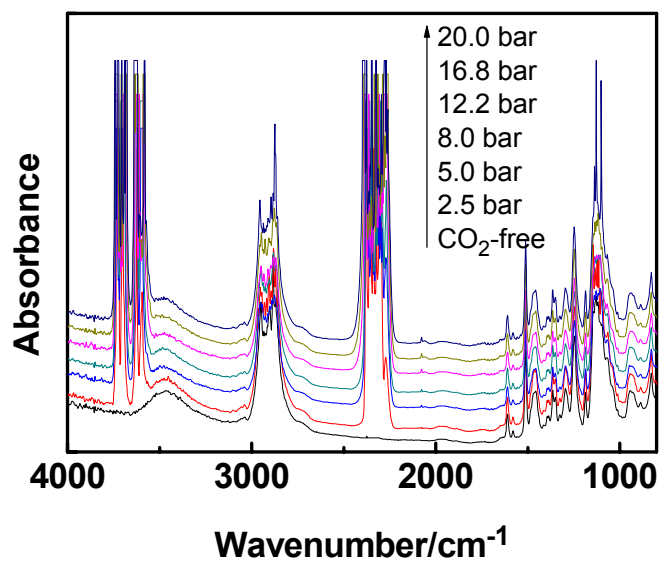


Fig. S7 FTIR spectra of TX-114/CO₂ at 25 °C and different CO₂ pressures.

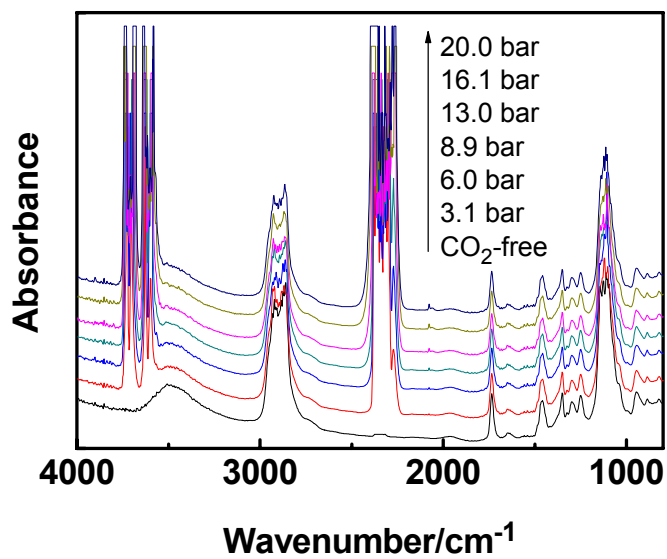


Fig. S8 FTIR spectra of Tween 20/CO₂ at 25 °C and different CO₂ pressures.

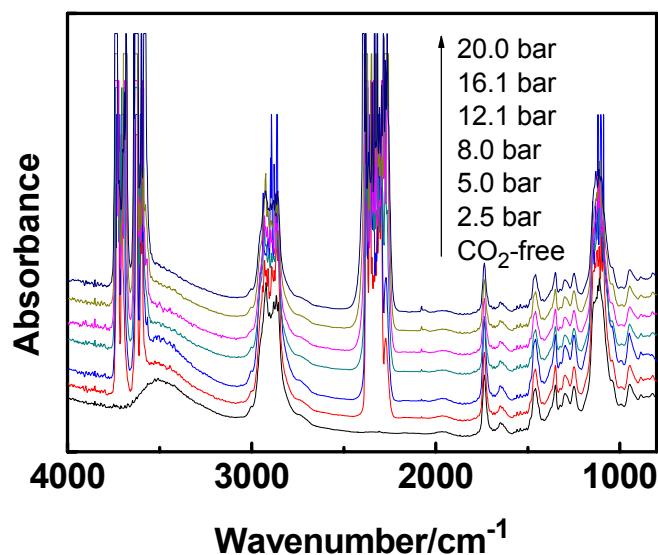


Fig. S9 FTIR spectra of Tween 80/CO₂ at 25 °C and different CO₂ pressures.

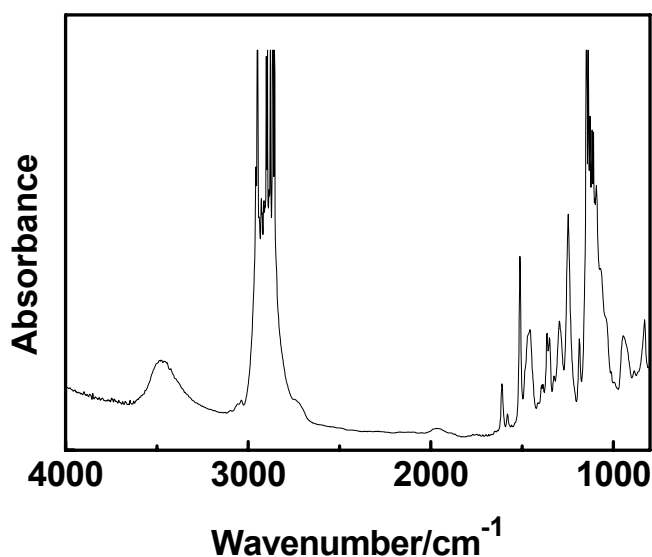


Fig. S10 FTIR spectrum of TX-100 after releasing CO₂ by depressurization from TX-100/CO₂ at 20.0 bar and 25 °C. It is nearly identical to the FTIR spectrum of the original TX-100 shown in Fig. 2.

References

- S1. X. Y. Li, M. Q. Hou, B. X. Han, X. L. Wang and L. Z. Zou, *J. Chem. Eng. Data* 2008, **53**, 548-550.
- S2. C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.* 2004, **126**, 5300-5308
- S3. Y. J. Zhao, J. L. Zhang, W. Li, C. X. Zhang and B. X. Han, *Langmuir* 2010, **17**, 2365-2367.