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Surface tension between CO_2 gas and tetra-*n*-butylammonium bromide aqueous solution

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ABSTRACT

This paper reports experimental values of the surface tension between CO_2 gas and tetra-*n*-butylammonium bromide (TBAB) aqueous solution measured by the pendant drop method. The experimental conditions were pressures from 1.00 MPa to 4.00 MPa, temperatures from 288.15 K to 303.15 K and w_{TBAB} from 0.10 to 0.40, where w_{TBAB} denotes the mass fraction of TBAB in the aqueous solution. These pressure–temperature-composition conditions partially fall into the stability zone of (CO_2 + TBAB) semiclathrate hydrate but all data were obtained without any hydrate in the system. Surface tension decreased with increasing w_{TBAB} and pressure but temperature dependency was not observed. Compared to the air–TBAB aqueous solution system and CO_2–water system, the values of the surface tension were smaller.

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1. Introduction

Surface tension is one of the fundamental thermodynamic properties of gas/liquid interface that reveals information about the Gibbs energy of formation at the interface, intermolecular interactions and shapes of surface. After the basic equation was reported by Young [1] and Laplace [2], the surface tension of various fluids has been studied both theoretically and experimentally. The surface tension of liquids, especially water, is affected both positively and negatively by adding electrolytes and surfactants, respectively. Although tetra-*n*-butylammonium bromide (TBAB) is classified as an electrolyte, it shows weakly surface activity in aqueous solution [3,4]. TBAB is one of the widely used phase transfer catalysts in various organic transformations [5,6]. Various properties of this salt like density [7], gas solubility [8], viscosity [9] and interfacial tension [3,4] have been reported. However, the measurement of surface tension under gas pressure was performed exclusively by Massoudi *et al.* [10] 40 years ago without a clear description of the uncertainty of the measurements. On the surface of the pressurized TBAB aqueous solution, both TBAB and CO_2 can be adsorbed. It is important to know the effect of adsorption from both the gas phase and liquid phase from the surface-thermodynamics point of view.

It is also known that TBAB aqueous solution can form an ionic semiclathrate hydrate [11]. In TBAB semiclathrate hydrates,

anions, Br^-, are incorporated to be a part of cage structures of water molecules and cations, TBA^+, occupy cages. Ionic semiclathrate hydrates have empty cages that can enclose small guest molecules, *e.g.*, H_2, CH_4, and CO_2 [12]. The technology of CO_2 capture utilizing TBAB semiclathrate hydrate has been investigated [13–15]. This technology is environmentally compatible and cost-competitive because TBAB semiclathrate hydrate is composed of a low toxic aqueous solution and guest molecules and has a high gas storage capacity [16]. It is known that hydrate first forms at the interface between solution and guest substance. Therefore, the hydrate formation method that provides a larger interface such as the spraying method [17] and the bubbling method [18] has been examined. Applying this method to chemical industry use, surface tension between CO_2 gas and TBAB aqueous solution is one of the basic thermodynamic properties that affects the process design. In this paper, measurements of the surface tension between CO_2 gas and TBAB aqueous solution were performed at temperatures, mass fractions of TBAB and pressures ranging from T = 288.15 K to T = 303.15 K, from 0.10 to 0.40 and from 1.00 MPa to 4.00 MPa, respectively.

2. Experimental

Figure 1 shows the diagram of the experimental apparatus and provenance and purity of chemical compounds used in this study are shown in table 1. The cylindrical test cell was made of stainless steel able to withstand high pressure use. Its inner diameter and height were 20 mm and 80 mm, respectively. A stainless tube of

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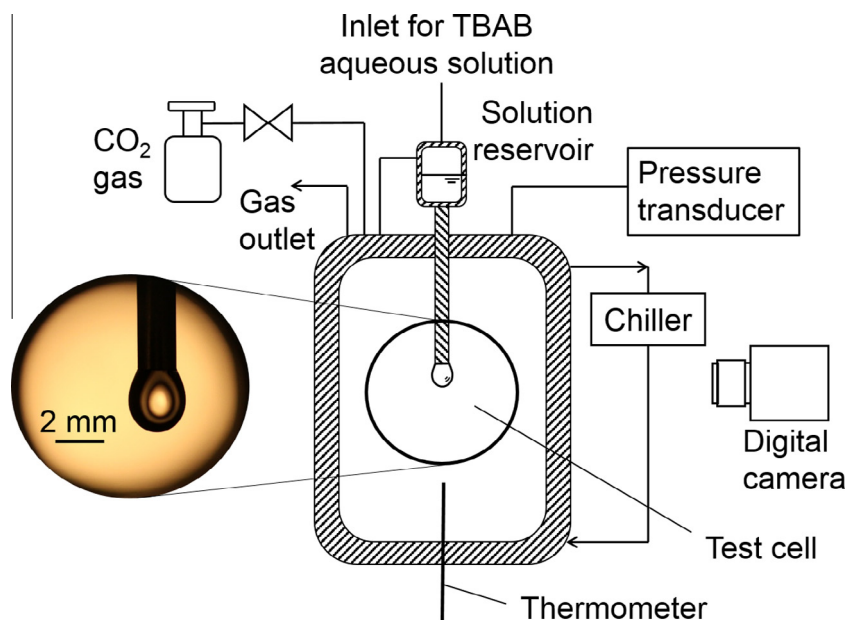 *E-mail address:* rohmura@mech.keio.ac.jp (R. Ohmura).

FIGURE 1. Diagram of experimental apparatus.

TABLE 1
Provenance and purity of chemical compounds.

Compound	Supplier	Purity	Purification method	Purity analysis
Carbon dioxide	Japan Fine Products	0.99995, volume fraction	Used without further purification	Measuring mass by precision balance
Tetra-n-butylammonium bromide	Sigma Aldrich	0.990, mass fraction	Used without further purification	Titration by $AgNO_3$
Water	Laboratory made	Electrical conductivity was less than 0.1 $\mu S \cdot cm^{-1}$	Distilled and deionised	Measuring electrical conductivity

1.583 mm in diameter was inserted vertically inside the test cell to hang the TBAB aqueous solution drops. The TBAB aqueous solution was made by dissolving a solid reagent of TBAB (0.990, mass fraction, Sigma Aldrich Japan, LLC.) with liquid water, which was distilled and then deionised. The electrical conductivity of the water was less than 0.1 $\mu S \cdot cm^{-1}$. The mass of TBAB and water was measured by an electronic balance (GF-3000, A and D Co., Ltd.) with 1 mg readability. The uncertainty of this balance is ±15 mg (Coverage factor $k = 2$). The evacuated test cell was filled with CO_2 (0.99995, volume fraction, Japan Fine Products Co., Ltd.) and the pressure P in the test cell was measured by a pressure transducer. A platinum resistance thermometer was used to measure the temperature inside the test cell and temperature was controlled by a water-circulating chiller. These pressure transducer and thermometer with warranted 95% uncertainty of 30 kPa and 0.2 K, respectively. The output of the thermometer was calibrated by inserting another thermometer (DS103, Tateyama Kagaku Industry Co., Ltd.) inside the droplet.

After leaving the droplet for 2 h to reach steady state, we took the images of the droplet by digital camera (EOS 50D, Canon Inc.) every 15 min for 1 h and mean values of surface tension were calculated. Although the measurements were performed under hydrate forming conditions at T = 288.15 K, w_{TBAB} > 0.20, hydrate was not visually observed.

3. Data analysis and uncertainty evaluation

A pendant drop method was used to determine the values of the surface tension. This method is capable of measuring surface tension statically and accurately. This method is independent of any contact angle unlike the Wilhelmy plate method and du Nouy ring method. The values of surface tension were deduced by using Eq. (1).

$$\gamma = \frac{\rho g d_e^2}{H},$$ (1)

where γ is the surface tension, ρ is the difference in density of two phases, g is the acceleration due to gravity and d_e is the equatorial diameter of the droplet. It is known that H is a function of the ratio of the two diameters d_s/d_e empirically, where d_s is a diameter of the droplet in a selected plane which is located d_e from the vertex vertically [19]. The density of the gas phase consisting of CO_2, TBAB and water vapour equalled that of CO_2 gas because concentrations of TBAB and water vapour were negligible. Therefore the CO_2 density was obtained from the NIST Chemistry WebBook [20]. The density values of TBAB aqueous solution range from T = 288.15 K to T = 303.15 K, from 1.0 MPa to 4.0 MPa and from w_{TBAB} = 0.10 to w_{TBAB} = 0.40 are given by Lin et al. [7] and Blendria et al. [21] measured at 298.15 K, 0.1 MPa and w_{TBAB} = 0.0697. The difference of density due to dissolving CO_2, the uncertainty of the density, was calculated on the basis of thermodynamic theory in the same way as Lin et al. [7]. The values for the mole fraction of CO_2 in the TBAB aqueous solution given by Lin et al. [7] and Muromachi et al. [8] were used to deduce the uncertainty of the density. To calculate the uncertainty of the surface tension, the uncertainty analysis scheme called combined standard uncertainty [22] was applied to the results obtained. This uncertainty was obtained by combining the individual standard uncertainties and did not exceed 1.8% in this study.

To evaluate the reliability of our experiment, we confirmed that the surface tension of water in the CO_2–water system were