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Interfacial tension measurements in water–methane system at temperatures from 278.15 K to 298.15 K and pressures up to 10 MPa

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ABSTRACT

This paper reports the measurements of the interfacial tension in a water–methane system at temperatures from 278.15 K to 298.15 K and pressures up to 10 MPa. The measurements using the pendant-drop method were performed at various pressures lower than or, at the highest, nearly equal to the hydrate/liquid/gas equilibrium pressure corresponding to each of the following prescribed temperatures: 278.15 K, 283.15 K, 288.15 K, 293.15 K and 298.15 K. The obtained data show that at each temperature the interfacial tension decreases almost linearly with the increasing pressure, indicating that the observed decrease in the interfacial tension results from the promotion of methane adsorption onto the interface with the increasing pressure.

1. Introduction

The development of new oil and gas fields around the world in recent years has brought about significant extension of the temperature and pressure conditions under which oil/gas recovery and transport processes are to be operated. Hydrocarbons in the liquid and/or gas (or vapor) states and water (or brine) in the liquid state constitute a multiphase flow in oil/gas pipelines, and the dynamics of such a multiphase flow strongly depends on the temperature and pressure conditions. The interfacial tension working at each liquid–gas or liquid–liquid interface is one of the most important properties controlling the multiphase-flow dynamics in such pipelines. The two-phase system consisting of liquid water and gaseous methane is the simplest model of the multiphase systems encountered not only in the oil/gas pipelines, but also in various fossil-fuel-related industrial processes, and the interfacial tension in the water–methane system is considered to be one of the fundamental properties indispensable for analyzing and/or predicting the multiphase-flow dynamics in the pipelines and designing various oil/gas processes.

Clathrate hydrates (abbreviated as hydrates), ice-like solid compounds composed of water and various types of guest substances including hydrocarbons, are known to form generally at low temperatures and/or high pressures. The hydrates of methane or methane-based hydrocarbon mixtures occasionally form in oil/gas pipelines, thereby hindering the flow in the pipelines and plugging them [1,2]. Accordingly, sufficient information is required about the interfacial tension in the water–methane and water–hydrocarbon-mixture systems at temperature–pressure conditions around the critical hydrate-forming conditions.

The technology development for recovering methane from naturally-occurring methane hydrate under the permafrost or beneath the continental shelves [3,4] also needs reliable information about the water–methane interfacial tension at high pressures. It is expected that methane gas released by artificially decomposing the hydrate under the permafrost or seabed sediment is recovered together with surrounding water in the form of a liquid–gas two-phase pipe flow. The flow characteristics must be strongly dependent on the interfacial tension which should axially change depending on the local temperature and pressure.

The technologies utilizing the artificially-formed hydrates have also been proposed. The representative of these technologies is the storage and/or transportation of natural gas in the form of hydrates [5]. The key to this technology is to develop an efficient process of

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hydrate production. Because hydrates preferentially form at the water–gas interfaces [6], the development of an efficient means for intensively mixing the two phases is needed, thereby extending the interfacial area based on accurate knowledge about the interfacial tension under hydrate-forming conditions.

The literature on the interfacial tension working at the interface separating an aqueous phase (pure liquid water or a surfactant solution) and a methane gas phase is limited. The interfacial tension data currently available in the literature were obtained only under limited pressure/temperature conditions. Massoudi & King [7] reported the variation in the interfacial tension at water–gas interfaces with an increasing gas pressure for 13 gas species including methane. Their interfacial-tension measurements using the capillary-rise method were performed only at the temperature T of 25 °C (298.15 K). The pressure p was increased to 7.6 MPa while measuring the water–methane interfacial tensions. This study was followed up by Jho et al. [8]. Using the same capillary-rise technique, they obtained interfacial tension data in six water–hydrocarbon and water–carbon-dioxide systems at three different temperatures, i.e., $T = 275.15$ K, 298.15 K and 323.15 K. The pressure p was increased to ~6.6 MPa in the water–methane system. Using the pendant-drop method, Sachs & Meyn [9] measured the interfacial tension in the water–methane system at T = 298.15 K and pressures p up to 46.8 MPa which exceeds the hydrate/liquid/gas three-phase equilibrium pressure corresponding to the system temperature, $T = 298.15$ K. The pendant-drop method was almost exclusively employed in succeeding studies dealing with water–methane and other related systems [10–13]. Ren et al. [10] measured the interfacial tension in five different systems in which pure methane and four methane/carbon-dioxide mixtures with different compositions were used to form the gas phase surrounding the pendant drops of water. Their measurements covered the temperature and pressure ranges from 298.15 K to 373.15 K and from 1.0 MPa to 30 MPa. Khosharay and Varaminian [11] measured the interfacial tension in water–methane, water–ethane, water–carbon dioxide, and water–propane systems at temperatures from 284.15 K to 312.15 K and pressures up to 6 MPa. Watanabe et al. [12] and Ando et al. [13] obtained interfacial tension data in surfactant-containing water–methane systems at $T = 275$ K and $p = 3.9$ MPa or 4.0 MPa. Although this temperature–pressure condition falls within the hydrate-forming regime, the measurements were made in the absence of any hydrate inside the pendant-drop assembly.

As surveyed above, the pressure dependence of the interfacial tension in the water–methane system at temperatures below 298.15 K has not yet been reported except that Jho et al. [8] showed a Π (surface pressure) versus p curve based on their interfacial-tension data obtained at $T = 275.15$ K and that Khosharay and Varaminian [11] provided interfacial-tension data in the pressure range from 1 MPa to 6 MPa at each of the two temperatures, $T = 284.15$ K and 291.15 K. As hydrate formation in industrial processes [1–5] generally occurs in the temperature range from 275.15 K to 298.15 K, the interfacial tension data in this temperature range should be more comprehensive.

Besides the experimental interfacial-tension measurements, a thermodynamics-based theoretical approach to the nature of interfacial tension in water–methane and other related systems has been attempted by several research groups. For example, Schmidt et al. [14] demonstrated the calculation of the water–methane interfacial tension using the linear gradient theory combined with the Soave–Redlich–Kwong or the Peng–Robinson equation of state. Khosharay and Varaminian [11] applied the gradient theory combined with the Chene–Kreglewski equation to calculate the interfacial tension in the water–methane and three other systems. An alternative molecular-dynamics-based approach has also been reported. Sakamaki et al. [15] performed molecular dynamics simulations to evaluate the interfacial properties including the interfacial tension in the water–methane system. These non-experimental methods will possibly be effective tools for estimating the interfacial-tension values in temperature/pressure regions lacking experimental interfacial-tension data. However, for validating and/or further improving such non-experimental methods, reference experimental data of the interfacial-tension over a wide temperature range are indispensable.

Based on the literature survey and our consideration outlined above, we planned and performed this study aimed at measuring the interfacial tension in the water–methane system at temperatures from 278.15 K to 298.15 K and pressures up to 10 MPa or the critical hydrate-forming pressure. The pendant-drop method was used for the technical convenience in dealing with a closed, and pressurized measuring system.

2. Experimental section

2.1. Materials

The sample fluids used in the experiments were research-grade methane gas supplied from Takachiho Chemical Industrial Co., Ltd., and distilled water prepared in our laboratory. The former having certified purity of 0.9999 in mole fraction was used as received from the supplier. The latter was produced by treating tap water with a laboratory water distiller (Yamato Scientific Co., Ltd., model WG222) which was comprised of an ion-exchange device and an all-glass distillation unit. The distilled water thus prepared was directly used with no further purification by a second distillation for forming pendant drops for the interfacial tension measurements. The suitability of this water sample for use in the measurements was evaluated by comparing the values of the surface tension of water (in contact only with its own vapor) obtained with this water sample to the corresponding surface-tension value obtained with doubly distilled water as well as to the IAPWS-recommended correlation for the water surface tension.

2.2. Apparatus and procedure

A schematic diagram of the experimental setup used in the present study is shown in Fig. 1. The main part of the setup was a cylindrical pendant-drop cell made of stainless steel. The inside volume of the cell was 25 cm^3. The cell was equipped with a pair of glass windows to allow visual observation and recording of the shape of each pendant drop using a CMOS camera (model EOS 50D, Canon, Inc.). The temperature inside the cell was controlled by circulating temperature-controlled water through the stainless-steel jacket of the cell during each experiment. A stainless-steel tube, 1.583 mm o.d., was vertically inserted into the cell such that each pendant drop of water suspended from the tip was located at the midpoint inside the cell. The other end of the tube was connected to a 15 cm^3 stainless-steel tank. A platinum-wire resistance thermometer (Class B, Ichimura Metal Co., Ltd.) was inserted into the cell from its bottom. The thermometer was so located that its tip was only ~1 mm away from the bottom of the pendant drop. The uncertainty of the temperature measurement using this thermometer was estimated to be ±0.2 K. The inside pressure of the cell was measured by a strain-gauge pressure transducer (model FP101, Yokogawa Electric Corporation) with an estimated uncertainty of ±0.03 MPa.

Each experiment for measuring the interfacial tension was commenced by charging the tank connected to the pendant-drop cell with water. Subsequently, the pendant-drop cell was evacuated and then charged with methane such that its inside pressure

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