Fuel 200 (2017) 107–112

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Capillary constant and surface tension of methane/hydrogen mixtures

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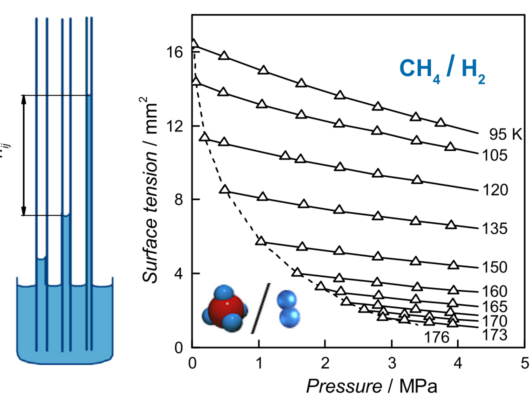
HIGHLIGHTS

- The capillary constant of methane/hydrogen mixtures has been measured.
- The surface tension of methane/hydrogen mixtures has been calculated.
- The measurements were made by the differential capillary method.
- Equations for the capillary constant and surface tension have been offered.
- Methane/hydrogen mixtures are a promising kind of fuel for transport.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 February 2017
Received in revised form 9 March 2017
Accepted 13 March 2017
Available online 27 March 2017

Keywords:
Methane/hydrogen mixtures
Capillary constant
Surface tension
Differential capillary method
Adsorption

ABSTRACT

Methane/hydrogen mixtures are a promising kind of fuel for automobile, water and railway transport, supersonic aircraft, and rocket engineering. We have used the differential capillary method to measure the capillary constant a^2 and calculate the surface tension σ in the temperature range from 95 to 176 K and the pressure range from that of the saturated vapors of pure methane to 4 MPa. Equations have been derived which describe the temperature, baric and concentration dependences of a^2 and σ. The adsorption has been determined. The results of measurements are discussed in the framework of thermodynamic models of the theory of surface phenomena.

1. Introduction

Natural gas, which mainly consists of methane, is an alternative to products of petroleum refinement, namely, gasoline and diesel fuel [1–3]. At present, this is the most economical, environmentally clean and safe kind of fuel, which may be used in both compressed and liquefied form. Liquefied natural gas is a promising fuel for automobile, railway and water transport [4], supersonic aircraft and rocket engineering [5]. As compared with traditional hydrocarbon kinds of fuels, methane has a lower normal rate of combustion. Small additions of hydrogen to natural gas make it possible to eliminate this disadvantage completely [6,7]. Enriched with hydrogen (up to 6 vol%), natural gas with a low content of methane (up to 40 vol%) may be used as a fuel for gas-turbine electric generations [8]. Small amounts of hydrogen in gasoline or diesel fuel are capable of saving up to 30% of the main fuel [9].

The use of hydrogen as an additional component of a standard fuel requires reliable data on the properties of hydrogenous mixtures. The present paper shows the results of experimental investigations of the capillary constant and surface tension of methane/hydrogen mixtures with a hydrogen content in the liquid phase of methane up to 4.5 mol%.

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http://dx.doi.org/10.1016/j.fuel.2017.03.043
0016-2361/

Surface tension plays a significant role at phase transitions determining the tearing-off bubble size and the heat-transfer coefficient during liquid boiling, the characteristic size of condensation centers and the heat-transfer coefficient during drop wise condensation. Under the action of capillary forces, a drop of a liquid jet flowing out of a nozzle breaks up, and one can observe the development of capillary waves at the free surface of the liquid.

2. Experiment

2.1. Materials

To prepare methane/hydrogen mixtures, use was made of methane produced by the Moscow gas processing plant and hydrogen produced by UralCryoGas, Russia. The rated purity of methane is 99.99%, and that of hydrogen, 99.999%. The main impurities in methane were oxygen and nitrogen (no more than 0.006%) and in hydrogen it was oxygen (no more than 0.0008%). The gases did not undergo any additional purification.

2.2. Method

To determine the surface tension of methane/hydrogen mixtures, use was made of the differential capillary method [10–12]. The measuring cell contained three glass capillaries. The internal radii of the capillaries r were determined by calibration with mercury and were as follows: $r_1 = (0.6393 \pm 0.0005)$ mm, $r_2 = (0.2297 \pm 0.0003)$ mm, and $r_3 = (0.09607 \pm 0.00008)$ mm. The cell was thermostatted (±0.005 K) in an aluminum block, which was mounted in the vacuum chamber of a cryostat. The temperature in the block was measured by a platinum resistance thermometer with an error that did not exceed ±0.02 K. Before the beginning of measurements, methane was condensed into the cell. The pressure in the cell was measured by a spring-type pressure gauge. The accuracy of determination of the phase-equilibrium pressure was no worse than ± 0.007 MPa. The methane/hydrogen mixture was prepared right in the cell with liquefied methane by letting in hydrogen. After the achievement of phase equilibrium, which was controlled by the displacement of the menisci of a liquid–gas interface, measurements were made of the difference of the heights of liquid rise in the capillaries h_{ij}. The values of h_{ij} obtained were used to calculate the capillary constant

$$a^2 = h_{ij}/(b_i^{-1} - b_j^{-1}), \tag{1}$$

where b_i and b_j are the radii of curvature of the menisci in the i-th and j-th capillaries, which were determined with the supposition of a complete wetting of the capillary walls by the liquid from the Lane equation [13] by data on the capillary radii r_i and r_j.

A simultaneous use of three capillaries in an experiment made it possible to obtain at a given temperature and pressure two independent values of the capillary constant, which were averaged in the course of processing. This increased the reliability of the data obtained. The total relative error of determination of a^2 at low temperatures did not exceed ±0.5% and reached (1.5–2.0)% at a temperature of 176 K. The results of measuring a^2 are presented in Table 1.

2.3. Calculations

The surface tension was calculated by the formula

$$\sigma = \frac{1}{2} g a^2 (\rho_l - \rho_v). \tag{2}$$

Here $g = 9.8162\ \mathrm{m \cdot s^2}$ is the gravitational acceleration at the measurement site, ρ_l and ρ_v are the liquid and vapor densities on the phase-equilibrium line.

The values of ρ_l and ρ_v, and also the composition of the liquid phase x_l (the molar fraction of hydrogen) were determined by data on the temperature and pressure of saturated vapors from the equation of state for a methane/hydrogen mixture [14]. The results of calculations are given in Table 1. Presented ibidem are the values of the surface tension.

3. Results and discussions

3.1. Approximations

In the whole range of state parameters investigated the capillary constant of methane/hydrogen mixtures is a monotonically decreasing function of pressure (Fig. 1) and concentration. A similar character of pressure and concentration (Fig. 2) dependence is also observed for surface tension.

The pressure dependence $z = a^2$ or σ is presented as follows:

$$z = z_* + B(\pi - \pi_*) + D(\pi - \pi_*)^2. \tag{3}$$

Here $z_* = a_*^2$ or σ_*, and $\pi_* = p_*/p_c$ are the capillary constant or surface tension and the reduced pressure of saturated vapors of pure methane, $\pi = p/p_c$, $p_c = 4.598$ MPa is the pressure at the critical point of methane. The values of a_*^2, σ_*, p_*, B and D are functions of the temperature.

As shown in Refs. [10] and [15], temperature dependences of the capillary constant and the surface tension of methane and other cryogenic liquids in the whole temperature range from the triple to the critical point within the experimental error may be approximated by the equations

$$a_*^2 = a_0^2 \varepsilon^n, \tag{4}$$

$$\sigma_* = \sigma_0 \varepsilon^\mu (1 + \sigma_1 \varepsilon), \tag{5}$$

where $\varepsilon = 1 - T/T_c$, $T_c = 190.54$ K is the temperature at the critical point of methane, $a_0^2 = 13.94\ \mathrm{mm}^2$, $n = 0.906$, $\sigma_0 = 40.92$ mN/m, $\mu = 1.258$, $\sigma_1 = -0.095$.

The pressure of saturated vapors of pure methane is adequately described by an equation in the form suggested by Wagner [16]

$$\ln \pi_* = (\alpha_1 \varepsilon + \alpha_2 \varepsilon^{1.5} + \alpha_3 \varepsilon^3 + \alpha_4 \varepsilon^6)/(1 - \varepsilon), \tag{6}$$

where $\alpha_1 = -6.005918$, $\alpha_2 = 1.193242$, $\alpha_3 = -0.844288$, $\alpha_4 = -1.180809$.

The forms of the functions $B(T)$ and $D(T)$ and the values of the free parameters included in them have been determined by the method of regressive analysis. Calculations have shown that both for the capillary constant and for the surface tension the root-mean-square deviation of experimental data from those calculated by Eq. (3) is minimum if the functions $B(T)$ and $D(T)$ look like:

$$B = b_1 + b_2 \varepsilon^2, \tag{7}$$

$$D = (d_1 + d_2 \varepsilon)\varepsilon^2. \tag{8}$$

The values of the coefficients b_1, b_2, d_1 and d_2 for a^2 and σ are given in Table 2. Fig. 3 shows the deviations of experimental values of σ from those calculated by Eq. (3). As is clear from Fig. 3, in the whole temperature and pressure range investigated they are less than 2%.

In Fig. 4 data on the surface tension of pure methane are compared with the results of some preceding papers [12,15,17–22]. The best agreement is observed with the values of σ obtained earlier in our laboratory [12,15,17,18]. We do not known of any papers on the measurement of the surface tension of methane/hydrogen mixtures.