Full Length Article

Capillary constant and surface tension of ethane with small additions of hydrogen

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HIGHLIGHTS

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

ARTICLE INFO

ABSTRACT

One of the ways of increasing the ecological and economic performance of internal combustion engines is the addition of small amounts of hydrogen to hydrocarbon fuel. We used the differential capillary method to measure the capillary constant a^2 and to determine the surface tension σ of ethane/hydrogen mixtures. Experiments were conducted in the temperature range from 93.15 to 283.15 K at pressures from that of the phase equilibrium of pure ethane to 4 MPa. The values of a^2 and σ as functions of the temperature, pressure and concentration of hydrogen are described by analytical dependences. The effect of the nature of the substance being dissolved and the nonideality of the forming mixture on the value of its surface tension has been examined.

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1. Introduction

One possible way of improving the economic performance of transport facilities with internal combustion engines is connected with their conversion to compressed or liquefied natural gas. However, despite the sufficiently low level of toxicity of exhaust gases, an engine operating on natural gas has a reserve for a further decrease in toxicity. This is connected with the use of a mixed fuel, which is a mixture of components of natural gas and hydrogen. An addition of a small amount of hydrogen to a standard fuel, e.g. petrol, diesel or natural gas, besides the reduction of harmful emissions into the atmosphere, contributes to the increase of the engine efficiency. The saving of the main fuel in this case may reach 30% [1–3]. Besides, the enrichment with hydrogen of natural gas with a low content of methane (no more than 40 vol%) makes it

possible to use such a mixture as a fuel for gas turbine electric generators [4].

The use of hydrogen as an addition to hydrocarbon fuel requires an investigation of physicochemical properties of the forming mixtures, and also of gas-dynamic processes with their participation. The present paper shows the results of measuring the capillary constant a^2 and the surface tension σ of ethane, one of the components of natural gas with small additions of hydrogen (no more than 3 mol%). The surface tension plays an important role in processes of fuel atomization [5], boiling and condensation [6,7], determines the stability of jet flows and the development of capillary-wave processes at liquid–gas interfaces [8].

Previously the surface tension of pure ethane was investigated in references [9–12]. The results of measuring the σ of ethane saturated with helium are presented in [13]. The effect of small additions of hydrogen on the surface tension of the other component of natural gas, methane, is investigated in Ref. [14].

The paper consists of an introduction and three sections. The second section describes the experimental technique. The results

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Nomenclature

Latin letters

a^2	capillary constant, mm^2
b	radius of meniscus curvature in a capillary, mm
g	Gibbs molar free energy, J/mol
g_{22}	$= \partial^2 g/\partial x^2$
h	height of liquid rise in a capillary, mm
p	pressure, MPa
s	area per mole of the surface layer, m^2
T	temperature, K
υ	molar volume, m^3/mol
w	mixing parameter, K
x	hydrogen mole fraction in the mixture

Greek letters

μ	molecular weight, kg/kmol
ρ	density, kg/m^3
σ	surface tension, mN/m

Subscripts

c	critical state
l	liquid
v	gas
σ	surface layer
$*$	pure substance

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of measurements and their discussion are presented in the third section. The last, fourth section is a conclusion.

2. Experiment

For the measurement of the capillary constant and the ensuing determination of the surface tension use was made of the differential capillary method. The measuring cell contained three glass capillaries with internal radii: $r_1 = (0.6393 \pm 0.0005)$ mm, $r_2 = (0.2297 \pm 0.0003)$ mm, $r_1 = (0.09607 \pm 0.00008)$ mm. The radius nonuniformity along the length of the capillaries did not exceed 0.1%. At temperatures below 150 K the cell with the capillaries was cooled by liquid nitrogen. Higher temperatures in the cryostat were achieved by pumping a coolant from a low-temperature thermostat FP88-MV of Julabo firm. The temperature in the cell was measured by a platinum resistance thermometer with an error of no more than 0.02 K.

Gases with rated purities of 99.8 (ethane) and 99.999 mol% (hydrogen) were used for preparing mixtures. The main impurities in ethane were oxygen and nitrogen (no more than 0.16 vol%) and in hydrogen, oxygen (no more than 0.0008 vol%). Solutions were prepared right in the measuring cell. An experiment began with ethane condensation into the cell. Then a hydrogen inflow was realized, on the achievement of phase equilibrium, which was controlled by the movement of liquid–gas interfaces in the capillaries, the phase equilibrium pressure was determined (with an uncertainty no more than ±0.007 MPa). The height of the liquid rise in the capillaries h_i was measured by a cathetometer with an uncertainty ±0.02 mm. The capillary constant was calculated with the assumption of complete wettability of capillary walls with the solution by the formula

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

where $\Delta h_{ij} = h_i - h_j$, b_i and b_j are the radii of curvature of the vertices of menisci in the i-th and j-th capillaries. The values of b_i and b_j were determined by the data on capillary radii r_i from Lane's equation [15]. The use of three capillaries made it possible to obtain two independent values of a^2, which were subsequently averaged. Experiments were conducted at both increasing and decreasing pressure. The coincidence of the values of a^2 for two opposite pressure courses pointed to the achievement of conditions of phase equilibrium. The design of the experimental setup and the experimental technique are described in greater detail in Refs. [13,16].

Data on the capillary constant were used to calculate the surface tension

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

where $q = 9.8162$ m/s^2 is the free fall acceleration, ρ_l and ρ_v are the densities of the liquid and vapor phases of the mixture on the phase equilibrium line.

The composition of the liquid and the vapor phase was determined from data on phase equilibrium [17–19] and the results of measuring temperature and pressure. The values of the hydrogen concentrations in the liquid x_l phase of the mixture are presented in Table 1.

Owing to the absence of experimental data on the density of the liquid and vapor phases of an ethane/hydrogen mixture, the parameters mentioned above were calculated in the following way. The molar volume of the liquid phases was assumed to be equal to its value for the pure solvent at a given pressure, and the molecular weight of the mixture $\mu_{mix} = \mu_1(1 - x_l) + \mu_2 x_l$ was used to determine the liquid density ρ_l. Since the hydrogen concentration in the liquid phase did not exceed 3 mol%, such an assumption was justified. The vapor phase density was calculated by the mixture virial equation of state, in which the second virial coefficient was taken equal to $B_{mix} = B_{11}(1 - x_v)^2 + 2B_{12}(1 - x_v)x_v + B_{22}x_v^2$, where $B_{12} = \sqrt{B_{11}B_{22}}$. In calculations use was made of the data on the liquid and vapor density and the second virial coefficient of pure ethane from Ref. [20]. The results of calculation of the densities ρ_l and ρ_v are given in Table 1.

3. Results and discussions

The capillary constant of an ethane/hydrogen mixture has been measured in the range of temperatures from 93.15 to 283.15 K and pressures from that of the phase equilibrium of pure ethane to 4.0 MPa. On 11 isotherms 79 values of the capillary constant have been obtained, among them the capillary constant of pure ethane. The error of the values of a^2 is 0.5% at low temperatures and increases to 1.0–1.5% at the approach to the critical point of ethane. The results of measurements of a^2 and σ are presented in Table 1.

In the whole temperature and pressure range under investigation the capillary constant of ethane/hydrogen mixtures at $T = const$ is a monotonically decreasing function of the pressure and the concentration of hydrogen in the liquid phase (Fig. 1). A similar character of the dependence on pressure (Fig. 2) and concentration is observed for surface tension.

3.1. Surface tension as a function of temperature, pressure and concentration

The near-linear dependence of the capillary constant and surface tension for ethane/hydrogen solution on pressure $\pi = p/p_c$, where $p_c = 4.872$ MPa is the pressure at the critical point of ethane, makes it possible to write