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Research on Thermophysical Properties of Fluids at the Grozny Petroleum Institute (USSR)

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A brief survey is presented of the thermophysical properties of petroleum, petroleum products, hydrocarbons, and their mixtures and of other working fluids that are being investigated at the Grozny Petroleum Institute in the USSR. The properties include density, specific heat, surface tension, thermal conductivity, and viscosity. A list of references with the relevant information is included.

KEY WORDS: density; hydrocarbons; petroleum products; specific heat; surface tension; thermal conductivity; viscosity.

1. INTRODUCTION

In this paper, I review the main results of the experimental work on thermophysical properties of fluids performed at the Grozny Petroleum Institute (GPI) so as to make this information more readily accessible. The thrust of the research program at GPI is the study of the thermophysical properties of hydrocarbons, petroleums, and petroleum products.

2. EXPERIMENTAL FACILITIES

More than 20 experimental apparatuses are available for measuring the density (specific volume), isobaric specific heat, surface tension, dynamic viscosity, and thermal conductivity of fluids in the vapor and liquid phases including states near the coexistence boundary and in the critical and supercritical regions. The available temperature range is 150–700 K, and the available pressure range 0.1–200 MPa.

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Mostly classical measurement methods are used. Densities are measured with the aid of a constant-volume ball piezometer yielding accuracies, henceforth designated δ, of 0.05–0.15 % and with a hydrostatic weighing technique yielding $\delta = 0.02–0.05\,\%$. Specific heats are measured with an adiabatic calorimeter with direct heating yielding $\delta = 0.5–1\,\%$ and with a highprecision adiabatic flow calorimeter yielding $\delta = 0.35\,\%$, apart from any uncertainties in the measurement of temperature and pressure. Surface tensions are measured with the capillary-rise method yielding $\delta = 0.5–0.8\,\%$. Viscosities are measured with various capillary-flow viscometers yielding $\delta = 0.2–1.2\,\%$. Thermal conductivities are measured with a hot wire and a concentric-cylinder instrument yielding $\delta = 1.1–1.6\,\%$.

To identify the petroleums and petroleum products, we also measure with standard methods the molar mass, refractive index, relative densities, kinematic viscosity, and average boiling temperatures All samples are analyzed before and after measuring the thermophysical properties.

3. PETROLEUMS AND PETROLEUM PRODUCTS

Densities (specific volumes), specific heat, surface tension, dynamic viscosities, and thermal conductivities in the fluid phase at temperatures from 230 to 520 K and pressures up to 60 MPa have been determined for (i) 35 samples of petroleums which differ markedly from each other in their physicochemical properties as well as in the hydrocarbon-group composition (ii) more than 150 samples of wide and narrow fractions from typical petroleums distilled over the temperature range from the boiling point to 550°C (iii) more than 100 samples of wide and narrow fractions and products from thermal and catalytic cracking and (iv) different oils and fuels. The results have been published in Refs. [1–63].

Using our experimental data as well as those of other authors, we have developed equations for calculating (i) the temperature corrections of the density of pertroleum products, (ii) the isobaric specific heat capacity of fluid petroleums and petroleum products at atmospheric pressure, and (iii) the thermal conductivity of fluid equations [57–60] have been adopted by Gosstandard as the recommended reference values.

Currently we are investigating the following properties: (i) *PVT* data and isobaric heat capacities of petroleum from new catalytic cracking processes and of other fuels in the liquid and vapor phases near saturation, in the two-phase region and in the critical and supercritical regions; (ii) the viscosity and thermal conductivity in the vapor phase; and (iii) the surface tension of the fractions and products from typical petroleums and processes. These measurements are made at temperatures in the range

230–650 K and at pressures in the range 0.1–30 MPa (or up to the critical pressure).

Equations are being developed for calculating the dynamic viscosity of petroleum products in the liquid phase, the isobaric specific heat of petroleum products in the vapor phase and in the supercritical region, and the surface tension of petroleum products from crude petroleum.

4. HYDROCARBONS

4.1. Specific Volume

We have investigated the specific volume of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, cyclohexane, and benzene in the liquid and vapor phases and in the critical region at temperatures from the triple-point temperature to that of the onset of dissociation and at pressures in the range 0.1–150 MPa. The data are represented by a single equation of state, which has the well-known form of a double polynomial in reduced density and temperature [2, 71, 72, 77, 83–107].

4.2. Isobaric Specific Heat

We have investigated the isobaric specific heat, C_p, at temperatures in the range 293–473 K of the following hydrocarbons in the liquid phase: the *n*-paraffins (n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, n-$C_{10}H_{22}$, n-$C_{11}H_{24}$, n-$C_{14}H_{30}$, n-$C_{15}H_{32}$, n-$C_{15}H_{34}$, n-$C_{21}H_{44}$, n-$C_{24}H_{50}$), the cycloparaffins (cyclopentane, cyclohexane, ethylcyclohexane, *trans*-1,2-dimethylcyclohexane, *cis*-1,3-dimethylcyclohexane, *trans*-1,4-dimethylcyclohexane), the aromatics (benzene, toluene, *o*-xylene, *m*-xylene, ethylbenzene, cumol, pseudocumol, buthylbenzene, mezitelen), and binary mixtures (heptane–pentadecane, benzene–cyclohexane, hexane–benzene, cyclohexane–hexane). From our data as well as from those of other investigators, we have developed equations for calculating C_p along the saturation line at temperatures from 0.35 to 0.90 T_c, where T_c is the critical temperature.

The *n*-paraffin hydrocarbons from n-C_5H_{12} to $C_{11}H_{24}$ and cyclohexane have been investigated in the liquid and vapor phases at temperatures from the triple points to the onset of dissociation (~700 K) at pressures in the range 0.1–60 MPa including at saturation and in the critical and supercritical regions. Equations have been presented for calculating the caloric properties of these hydrocarbons in the ideal-gas state, along the saturation line, and in the critical and supercritical region [69, 70, 74, 80, 81, 93].

4.3 Surface Tension

We have investigated the surface tension of the *n*-paraffin hydrocarbons (from *n*-C_5H_{12} to *n*-$C_{24}H_{50}$) at temperatures from the triple point to the critical point (or to 570 K). The experimental data are approximated by an equation of the type proposed by Van der Waals [8, 126, 129].

4.4 Dynamic Viscosity

In a first series of measurements we have determined the viscosity of the *n*-paraffins from *n*-C_8H_{18} to *n*-$C_{22}H_{46}$ in the liquid phase at temperatures in the range 293–530 K at pressures up to 50 MPa. In a second series we have measured the viscosity of *n*-C_5H_{12}, *n*-C_6H_{14}, *n*-C_7H_{16}, *n*-C_8H_{18}, *n*-CC_9H_{20}, *n*-$C_{10}H_{22}$, *n*-$C_{11}H_{24}$, cyclohexane, and benzene in both the liquid and the vapor phases at temperatures from the triple-point temperature to the dissociation temperature and at pressures up to 60 MPa. The experimental viscosity data are approximated by equations in the form of polynomials [5, 79, 93, 130–139].

4.5. Thermal Conductivity

We have measured the thermal conductivity at temperatures in the range 280–473 K and at pressures up to 50 MPa of the following hydrocarbons in the liquid phase: *n*-paraffins (from *n*-C_5H_{12} to *n*-$C_{24}H_{50}$), isoparaffins (2,2,4-trimethylpentane, 2,3,5-trimethylhexane), alkenes (hexane-1,2-methylpentene-1,2-methylpentene-2,3-methylpentene-1,4-methylpentene-1), alkynes (hexyne-1, hexyne-2, hexyne-3), cycloparaffins (cyclopentane, cyclohexane, methylcyclopentane, ethylcyclohexane, *trans*-1,2-dimethylcyclohexane, *cis*-1,3-dimethylcyclohexane, *trans*-1,4-dimethylcyclohexane, cyclohexene), and aromatics (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, cumol, pseudocumol, mezithylene, tretbuthylbenzene, decalin, tetralin). In addition, we measured the viscosity of more than 30 mixtures such as iso-octane + *n*-octane, toluene + *m*-xylene, *n*-heptane + *n*-undecane, etc., at atmospheric pressure. We developed equations for calculating the thermal conductivity of hydrocarbons as a function of temperature and pressure [2–4, 64–68, 73, 75, 76, 82, 140–168].

5. WORKING FLUIDS

5.1. Water and Aqueous Solutions

The thermal conductivity of light and heavy water has been investigated at temperatures in the range 258–490 K and at pressures up to

110 MPa. We have investigated also the thermal conductivity of more than 50 aqueous solutions (electrolytes and nonelectrolytes, binary, ternary, quaternary) as a function of temperature and pressure [2, 4, 65, 67, 71, 73, 76, 148–151, 158, 159, 161–163, 166–168].

5.2. Sulfurhexafluoride

The viscosity and thermal conductivity of SF_6 in the liquid and vapor phase have been measured at temperatures in the range 245–475 K at pressures up to 112.8 MPa [73, 135, 160].

5.3. Alcohols

We have investigated the isobaric specific heat of *n*-propanol, isopropanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-octanol, *n*-nonanol, and *n*-decanol at temperatures from 293 to 473 K near the saturation line [70, 118]. We have also measured the thermal conductivity of 22 alcohols (from CH_3OH to $C_{18}H_{37}OH$) at atmospheric pressure and for ethylglycol, diethylglycol, thriethylglycol, and glycerine (up to 100 MPa) at temperatures in the range 293–473 K [67, 68, 76, 152, 154–156, 163, 167, 168].

6. TABLES OF STANDARD REFERENCE DATA

We have developed tables of standard reference data for the thermodynamic properties (density, enthalpy, entropy, isochoric specific heat, isobaric specific heat, ultrasonic velocity) of the following substances: (i) *n*-hexane for temperatures in the range 180–630 K and pressure up to 100 MPa, (ii) cyclohexane for temperatures in the range 280–680 K and pressures up to 70 MPa, and (iii) benzene for temperatures in the range 280–680 K and pressures up to 60 MPa [169, 170].

We are currently developing tables of standard reference data for the thermodynamic properties of *n*-pentane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, and toluene and for the viscosity of the *n*-paraffin hydrocarbons (from $n\text{-}C_5H_{12}$ to $n\text{-}C_{11}H_{24}$).

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Hydrocarbons and Working Fluids

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