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Experimental vapor pressures and thermodynamic models of perfluorocarbons PP80 and PP90

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ABSTRACT

Complete thermodynamic models are developed for the perfluorocarbons PP80 (perfluoro-2-methyl-3-ethylpentane, C_8F_{18}, CASRN: 354-97-2) and PP90 (perfluoro-2,4-dimethyl-3-ethylpentane, C_9F_{20}, CASRN: 50285-18-2). These perfluorocarbons can be used as working fluids in energy conversion applications, like organic Rankine cycle (ORC) power systems operating at medium and high temperatures. Other areas of use of PP80 and PP90 are in the electronic industry for component testing, in the chemical industry as a hazardous reaction suppressant and as tracers in the oil and gas industry. The improved equation of state of Peng–Robinson modified by Stryjek–Vera (iPRSV) is adopted, supplemented with a third order polynomial for the ideal gas isobaric heat capacity as a function of temperature. Vapor–liquid pressures for both fluids were measured in a temperature range spanning 358–508 K. The vapor–pressure temperature range for the fitting of the equation of state is extended down to 270 K by extrapolation of the Wagner–Ambrose equation that is used for the correlation of the aforementioned measured data. Ideal gas isobaric heat capacities data are estimated with the Joback method. The obtained thermodynamic models are arguably sufficiently accurate for preliminary engineering calculations, for example for the thermodynamic design of ORC power systems.

1. Introduction

Perfluorocarbons (PFCs) are organofluorine molecules consisting of a backbone of carbon atoms, strongly bonded with only fluorine atoms. Several types of perfluorocarbons exist, from tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) up to molecules with more then twenty carbon atoms. They can have (1) a straight chain form, like tetradecafluorohexane (C_6F_{14}), (2) a branched form, e.g., perfluoro-2-methyl-3-ethylpentane (Flutec-PP80,[1] C_8F_{18}), (3) a cyclic form such as perfluorodecalin (Flutec-PP6[1], $C_{10}F_{18}$) and octafluorocyclobutane (RC318,[2] c-C_4F_8), or an aromatic form as in hexafluorobenzene (C_6F_6). All PFCs are considered to be anthropogenic, except for CF_4 and C_2F_6. Small amounts of theses gases have a lithospheric origin [1–4].

When all valences of the carbon chain are satisfied with fluorine atoms, the carbon skeleton is twisted out of its plane in the form of a helix. As a consequence, all electronegative fluorine atoms entirely surround the carbon skeleton, shielding it from chemical attack. The low polarizability and high bond energies of the carbon–fluorine bond contribute to the fact that perfluorocarbons are the most stable compounds [5]. Hence, highly fluorinated and perfluorinated compounds are thermally stable (>400 °C) and chemically inert, which make them suitable for many (high-temperature) applications for which hydrocarbons are unsuited. Experiments carried out at high temperatures confirm the exceptional thermal stability of hexafluorobenzene [13] and RC-1 (a mixture consisting of 60% pentafluorobenzene and 40% hexafluorobenzene) [14] in contact with typical metals. PFCs also feature low surface tensions and good dielectric properties and, in addition to their chemical and physical stability, they are non-flammable, non-corrosive, and characterized by a very low toxicity [5]. At room temperature conditions light perfluorocarbons CF_4, C_2F_6, and C_3F_8 are gaseous; PFCs with more than nine carbon atoms and dodecafluorocyclohexane (c-C_6F_{12}) are solid; usually other perfluorocarbons are colorless and odorless liquids.

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[1] Designation of manufacturer [20].

[2] Coding according the American Society of Heating, Refrigerating, and Air Conditioning Engineers, ASHRAE Standard 34-78.

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The high chemical and thermal stability of these molecules can also be pitfall, because it results in very long atmospheric lifetimes (more than 1000 years for $C_{10}F_{18}$ up to 50,000 years for CF_4). Perfluorodecalin ($C_{10}F_{18}$) has one of the highest radiation efficiencies[3] known so far [6] and there are strong indications that this applies for all other high molecular weight PFCs as well [7]. Although the concentrations of PFCs in the atmosphere are extremely small compared to those of the common known greenhouse gases (carbon dioxide, methane, and nitrous oxide), the combination of long atmospheric lifetimes and high radiation efficiencies yields very large global warming potentials[4] for PFCs (GWP >7000 for a 100-year time horizon) [8].

Perfluorocarbons are used, for example, in medical applications (e.g., eye surgery, treatment of lung disorders, blood substitutes) [6], as heat transfer fluids in the semiconductor industry (because of their high dielectric strengths and high insulating properties) [9], cooling of electrical and electronic applications, cosmetics (e.g., as a skin anti-aging compound) [10], fire extinguishing systems [11], and in refrigeration units as replacements for CFCs (chlorinated fluorocarbons) [12]. PFCs are also employed in organic Rankine cycle (ORC) power plants for the thermal conversion of biomass or waste heat recovery. They are especially suitable ORC working fluids because of their chemical inertness, the very high thermal stability, the non-flammability, and because they are not corrosive, nor toxic.

Already in 1966, among others, hexafluorobenzene (C_6F_6) and perfluorodecalin (Flutec-PP5[1], $C_{10}F_{18}$) were subject of study for ORC power systems [15]. Some years later, perfluoro-1,3-dimethylcyclohexane (Flutec-PP3[1], C_8F_{16}) and again hexafluorobenzene (C_6F_6) were taken into consideration [16,17]. In 1980 and 1981 perfluoro-1,3-dimethylcyclohexane and perfluorodecalin were adopted as working fluids in an experimental solar ORC power plant, and in a thermal heat pump system, respectively [18]. An exemplary application of a perfluorocarbon working fluid at present is a 1 MW ORC power system using perfluoro-2-methylpentane (Flutec-PP1[1], C_6F_{14}) as a working medium [19].

Two other PFCs, perfluoro-2-methyl-3-ethylpentane (C_8F_{18}) and perfluoro-2,4-dimethyl-3-ethylpentane (C_9F_{20}), are both good candidates as ORC working fluids, due to their high molecular complexity and high molecular weight. They also feature melting points far below 0 °C. Instead of the full chemical names, namely perfluoro-2-methyl-3-ethylpentane and perfluoro-2,4-dimethyl-3-ethylpentane, here the acronyms PP80 and PP90, respectively, are employed. These are the names proposed by the manufacturer [20]. PP80 and PP90 are heavily branched molecules. Schemes of the chemical structure of the molecules are shown in Fig. 1.

Here, complete thermodynamic models of PP80 and PP90 are documented. The models are suitable for typical engineering calculations, like the preliminary design of the thermodynamic cycle of energy conversion systems or other processes. If attention is paid to the limitations in accuracy, the fluid models could also be used for the preliminary fluid dynamic design of components.

The iPRSV equation of state (EoS), which is an improved cubic equation of state (CEoS) based on the Peng–Robinson CEoS [22] modified by Stryjek–Vera [23], has been selected for the development of the thermodynamic models. CEoS are attractive because of their simplicity and because they are widely adopted in scientific and engineering applications. In addition, the iPRSV CEoS allows for accurate estimations of vapor–liquid pressures, performs well for thermodynamic conditions other than saturation, and for other thermodynamic properties of state, like densities, enthalpies, entropies, speeds of sound, etc. Moreover, it is not affected by discontinuities [21] of the calculated thermodynamic properties all over its range of applicability, and it provides a good trade-off between simplicity of the model and its accuracy.

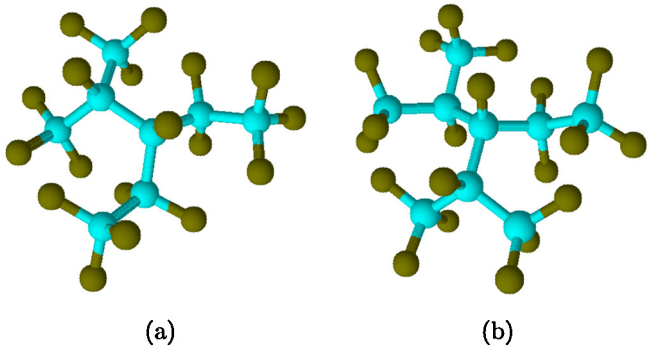

Fig. 1. Molecular structure of the perfluorocarbons PP80 (a) and PP90 (b).

Except for some limited data from the manufacturer of PP80 and PP90, like melting and boiling point temperatures, and some other data at ambient temperature and pressure, no extensive experimental data for these fluids have been published so far. In order to be able to develop sufficiently accurate thermodynamic models for these fluids, experiments were carried out in order to measure the vapor–liquid pressures. Estimation techniques are used to extend the temperature range, such that complete datasets cover the range from room temperature up to the critical points. The vapor–liquid pressures are used to fit the iPRSV component specific κ_1-factor and to calculate the acentric factor ω. For the estimation of enthalpy and entropy (and of all other calorimetric properties), the volumetric equation of state is complemented by a third degree polynomial function for the calculation of the ideal gas isobaric heat capacity as a function of temperature. Such function is fitted to isobaric heat capacities generated with the help of group contribution methods.

Section 2 presents the measurement method, and the equipment used for the experiments. Thereafter, the development of the complete thermodynamic models is described in detail. The last section discusses the capability and consistency of the thermodynamic models when used in order to calculate thermodynamic properties of technical interest over its range of validity, and exemplary results are shown in exemplary thermodynamic diagrams.

2. Measurements of vapor–liquid pressures

2.1. Materials and experimental method

Table 1 reports data on the purity of the batches of PP80 and PP90 that were used for the measurements of the vapor–liquid pressures. The data were provided by F2 Chemicals Ltd., the manufacturer of the fluids, and come from gas chromatography data analysis. The experiments were carried out with the fluids as received, i.e., without further purification.

The vapor–liquid pressures were measured with a Cailletet apparatus. For a description of this apparatus and measurement method of the vapor–liquid pressures the reader is referred to Refs. [24,25]. The maximum uncertainty is less than ±3 kPa for the pressures, and less than ±0.02 K for the temperatures. The accuracy of the data related to the critical point measurements is considered the same as the accuracy of the experimental vapor pressures, as it is measured in the same way, at the same time, and with the same equipment. Starting from a two-phase fluid (liquid and vapor), the critical point is clearly perceptible during experiments. The temperature is raised and the volume is kept such that the meniscus is in

[3] The radiation efficiency is the amount of infrared radiation that a substance can absorb in parts per billion volume.

[4] The global warming potential (GWP) is the time integrated amount of heat a substance traps in the Earth's atmosphere with respect to carbon dioxide.