Fluid Phase Equilibria 433 (2017) 79–96

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Prediction of properties of new halogenated olefins using two group contribution approaches

Maria E. Mondejar [a, *], Stefano Cignitti [b], Jens Abildskov [b], John M. Woodley [b], Fredrik Haglind [a]

[a] Department of Mechanical Engineering, Technical University of Denmark, Building 403, 2800 Kongens Lyngby, Denmark
[b] Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 227, 2800 Kongens Lyngby, Denmark

ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form
17 September 2016
Accepted 18 October 2016
Available online 20 October 2016

Keywords:
Olefins
Group contribution method
Neural network
Critical temperature
Critical pressure
Normal boiling temperature
Acentric factor
Ideal gas heat capacity

ABSTRACT

The increasingly restrictive regulations for substances with high ozone depletion and global warming potentials are driving the search for new sustainable fluids with low environmental impact. Recent research works have pointed out the great potential of fluorine- and chlorine-based olefins as refrigerants and solvents, due to their environmentally-friendly features. However there is a lack of experimental data of their thermophysical properties. In this work we present two models based on a group contribution method, using a classical approach and neural networks, to predict the critical temperature, critical pressure, normal boiling temperature, acentric factor, and ideal gas heat capacity of organic fluids containing chlorine and/or fluorine. The accuracy of the prediction capacity of the two models is analyzed, and compared with equivalent methods in the literature. The models showed an average reduction of the absolute relative deviation for all the studied properties of more than 50%, compared to other methods. In addition, it was observed that the neural-network-based model yielded a better accuracy than the classical approach in the prediction of all the properties, except for the acentric factor, due to the lack of experimental data for this property.

1. Introduction

The recent regulation of the European Parliament for the limitation of the use of fluorinated gases, which entered into force in January 2015 [1], has imposed new requirements on the environmental characteristics of a number of industrial fluids, which sum up to those of the Montreal Protocol [2]. While the latter, which was approved in 1989, governs the phase out of those substances with high ozone depletion potential (ODP) (i.e. alkanes containing chlorine or bromine), the former, also known as F-gas regulation, targets the fluids with global warming potentials (GWP) greater than 150 (i.e. hydrocarbons containing fluorine).

Many halogenated alkanes are used as refrigerants, or working fluids for organic Rankine cycles. Also, these compounds are utilized as foaming agents, or solvents. The phasing-out schedule of both regulations will have a great impact on many of these applications as a great part of the fluids currently used will soon have to be replaced. The main consequence of the Montreal Protocol is that it will phase out the use of hydrofluorocarbons (HFC), (i.e. fluorinated alkanes), which are widely used today in refrigeration systems since they were introduced as sustainable replacements of chlorofluorocarbons (CFC) (i.e. alkanes containing only fluorine and chlorine) and hydrochlorofluorocarbons (HCFC) (i.e. fluorochlorinated alkanes), given their lower GWP and ODP. Regarding the F-gas regulation, it aims initially at limiting the use of substances with high or moderate GWP, but no definitive schedule for phasing out is yet set. It is also important to mention that, although the F-gas regulation applies within the European Union, a proposal has been submitted in a recent amendment in order to extend the F-gas regulation worldwide, under the scope of the Montreal Protocol. This, if approved, will extend the application of this regulation to the United Nations.

The potential of hydrofluoroolefins (HFOs) as replacement fluids of organic compounds with high ODP and GWP in heat pumps and power cycles has been recently suggested by Brown [3]. These compounds, also known as fluoroalkenes, contain at least one double carbon bond, which is susceptible of degradation in the troposphere, and thus reduces the atmospheric lifetime of the molecule. In addition, part of the hydrogen atoms of the alkene molecule are replaced by fluorine atoms, which confers stability

* Corresponding author.
E-mail address: maemmo@mek.dtu.dk (M.E. Mondejar).

http://dx.doi.org/10.1016/j.fluid.2016.10.020

Nomenclature

ANN	artificial neural network
cEoS	cubic equation of state
CFC	chlorofluorocarbons
GCM	group contribution method
GWP	global warming potential
HCFO	hydrochlorofluoroolefins
HFC	hydrofluorocarbons
HFO	hydrofluoroolefins
ODP	ozone depletion potential
ω	acentric factor
$c_{p,0}$	ideal gas heat capacity, kJ/kmol K
p	pressure, bar
T	temperature, K
b	boiling
c	critical
est	estimated
exp	experimental

and reduces the flammability of the compound. Another feature derived from the presence of a double carbon bond is the different arrangement of fluorine and chlorine atoms around it, which results in different structural and spatial isomer configurations. Because the thermophysical properties of different isomers can vary significantly, it is important to be able to distinguish their behavior.

The most recent research regarding the use of HFOs focuses on the study of fluoropropenes (e.g. R1233zd, R1234ze(Z) and R1234yf) [3], which are intended to be used in a temperature operating range below 450 K. However, olefins with a greater number of carbon atoms, or even containing chlorine atoms, can offer a number of possibilities as refrigerants or working fluids for medium to high temperature applications [4], and therefore must be investigated.

The evaluation of the performance of new fluids in industrial applications, such as refrigeration systems or organic Rankine cycles, requires an accurate knowledge of their thermophysical properties [5]. This knowledge, which is of particular importance for an optimal design of the mentioned technologies, is given by the use of equations of state to estimate different properties (e.g. enthalpy, vapor pressures, entropy) of the utilized fluids. The most simple way of predicting the thermophysical behavior of these compounds is by using a simple cubic equation of state (cEoS) for which only the critical parameters T_c, p_c, the acentric factor ω, and the ideal gas heat capacity $c_{p,0}$ are required. In addition, the value of the normal boiling point T_b is very useful for different generalized correlations (i.e. heat of vaporization, vapor-liquid equilibria). If these parameters are not available from experimental measurements, they can be predicted through different methods. However, a review of the available literature suggests a lack of predictive methods tailored for the property prediction of organic compounds containing chlorine and/or fluorine atoms, given that previous methods were developed based on limited information on such compounds. Developing predictive models for a specific chemical group will help to improve the accuracy of the predictions, and the distinction of different molecule structures.

In this work we present two methods to improve the prediction of the critical temperature, critical pressure, acentric factor, normal boiling temperature, and ideal gas heat capacity of organic compounds containing fluorine and/or chlorine atoms. The methods were developed by following a classical group contribution approach, and an approach based on artificial neural networks (ANNs), in order to assess the suitability of each method for the prediction of these properties. The main objectives of this paper are:

- To provide two methods based on a group contribution approach for the prediction of the aforementioned properties with a better accuracy than the available methods, tailored for fluoro-chloro-organic compounds.
- To provide a comparison of the two developed methods, in terms of accuracy and computational time, in order to assess the suitability of combining group contribution methods with neural networks for property prediction.

The main novelty of this work is the focus on the prediction of the properties of organic compounds containing chlorine and/or fluorine, which are needed for the use of cubic equations of state. Moreover, the comparative analysis of both proposed approaches provides a base for the assessment of the benefits resulting from combining group contribution methods with artificial neural networks. The developed methods will provide approximate predictions of the thermophysical behavior of new environmentally-friendly fluids, facilitating their introduction in refrigeration processes, organic Rankine cycles, and heat pumps.

2. Methods

2.1. Experimental data generation

An extensive experimental dataset of pure substances containing carbon, hydrogen, fluorine and/or chlorine was generated from several databases in order to have the maximum amount of data for the development of the methods, although not all the properties were available for some fluids. In the selection of the fluids of the dataset: i) aromatic and cyclic compounds were neglected; and ii) only molecules with a number of carbon atoms between 2 and 10 were considered. Reasons for these assumptions come from the lack of experimental data for cyclic and long-chain components, and the reduction of accuracy resulting from including too small molecules in the fitting process. The experimental data were collected from the following databases:

- The database of the Project 801 of the Design Institute for Physical Property Data (DIPPR® 801) [6].
- The Handbook of Chemical Compound Data for Process Safety [7].
- The Computer-Aided Process-Product Engineering Center (CAPEC) database [8].
- The Reference fluid thermodynamic and transport properties database (REFPROP) [9].
- Recent experimental data from Ref. [10].

The generated dataset was used for the determination of the group contributions for the critical temperature T_c (132 fluids), the critical pressure p_c (123 fluids), the acentric factor ω (96 fluids), the normal boiling temperature T_b (315 fluids), and the ideal gas heat capacity $c_{p,0}$ (89 fluids). The complete list of fluids used in the fitting, including their source database, molar weight, and property availability, is given in Table A.7 of the Appendix, and includes 334 fluids, from which 71 are fluorine compounds, 200 are chlorine compounds, and 63 are fluoro-chlorine compounds.

The experimental values of the critical temperature, the critical pressure, the normal boiling temperature, and the acentric factor were used as the targets values for the optimization of the two group contribution models (GCM), while the number of groups of