A modified perturbed hard-sphere-chain equation of state for pure halogenated organic compounds

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Abstract

Our previously reported modified perturbed hard-sphere-chain equation of state has been employed to calculate the PVT properties of pure halogenated organic compounds. Knowing the critical constants of fluids as well as one adjustable substance-dependent parameter as input data is sufficient for this purpose. We have tested the proposed equation of state against the experimental data for a large number of pure halogenated organic compounds both in saturation and compressed states. Comparison of the calculated results with the experimental data shows that from 734 data points for saturation state and 1450 data points for compressed state the average absolute deviations in calculated densities are 0.51 and 0.61%, respectively.
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Keywords: Refrigerant; Equation of state; Density

Une équation d'état des sphères et des chaînes dures modifiée pour des composés organiques halogénés

Mots clés : Frigorigéne ; Équation d'état ; Masse volumique

1. Introduction

In recent years restriction on the use of chloro-fluorocarbons (CFCs) caused the development of a wide variety of alternative refrigerants and refrigerant mixtures. Hydro-fluorocarbons (HFCs) and their mixtures are considered as alternative refrigerants for the high ozone-depleting ones as the working fluids in refrigerators and heat pumps. The availability of a reliable set of experimental thermophysical data for these refrigerants is essential in the design of effective and efficient refrigerating and air-conditioning equipments. However, the amounts of reliable and consistent experimental data on these refrigerants are still incomplete. In these circumstances prediction of thermodynamic properties using theoretical models or corresponding-states correlations is another alternative.

There are a large number of correlations in the literature, such as the corresponding-states liquid densities [1], the modified Racket correlation by Spencer and Danner [2], and a recent correlation by Iglesias-Silva and Hall [3], to predict the liquid density of refrigerants. A review on the comparison of fourteen correlations is given by Nasrifar and Moshfeghian [4]. In spite of this fact that the

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Nomenclature

a	a temperature-dependent parameter (m^3 mol^{-1})	q_{1a}–q_{3a}	coefficients in Eq. (10)
a_1–a_4	coefficients in Eq. (8)	q_{1b}–q_{3b}	coefficients in Eq. (11)
AAD	average absolute deviation (%)	r	the number of segments per chain
b	hard-sphere covolume (m^3 mol^{-1})	T	temperature (K)
b_1–b_4	coefficients in Eq. (9)	V	molar volume (m^3 mol^{-1})
d	hard sphere diameter per segment (m)		
F	a universal function of the reduced temperature in Eq. (6)	*Greek letters*	
		ρ	molar density (mol m^{-3})
$g(d^+)$	pair distribution function for hard spheres at contact	ε	potential well-depth (J)
		η	packing fraction
G	a universal function of the reduced temperature in Eq. (7)	σ	position of minimum in the potential energy function (m)
k	Boltzmann's constant (J K^{-1})		
NP	number of data points	*Subscripts*	
P	pressure (bar)	C	critical point
q_a	a constant for each chain defined in Eq. (10)	ref	reference system
q_b	a constant for each chain defined in Eq. (11)	pert	perturbed system

corresponding-states correlations are not based on a fundamental theory, their applicability is limited to only prediction of liquid densities; they cannot give information about the vapor density or vapor–pressure. However, accurate equations of state can be developed, base on fundamental theory, to calculate the thermodynamic properties of fluids over a wide range of temperatures and pressures. Although in the early pioneering days the development of fundamental equations of state was limited to a few number of fluids with small size, recently a great attention has been given toward the development of equations of state for chain-like molecules. There are numerous studies based on the modification of lattice theory [5,6], but in most recent works free-space models base on perturbation theory and integral theory of fluids [7–11] or based on the generalized Flory theory coupled with the concept of the insertion probability are developed [12–14].

In the hard-sphere chain theory, a chain molecule is modeled by a series of freely jointed tangent hard spheres. This hard-sphere term then replaces for much simpler hard-sphere reference system in the statistical-mechanical perturbation theories, and the influence of attractive forces is taken into account by adding a van der Waals attractive term. Recently, a perturbed hard-sphere-chain equation of state has been proposed by Song et al. [15–17] to predict the PVT properties of chains of small size or even large size. The two assumptions that the molecular segment is a sphere of unchangeable diameter and chain molecule is a series of hard spheres simplify the mathematical modeling of both simple (spherical) and complex (chain-like) molecules. This equation of state has been modified by Kim and Bae [18] in both attractive and repulsive contributions and is shown that the resulting modified equation of state is in a better agreement with experimental data than that of the original

one. The equation of state needs three input parameters; two scaling constant and the number of segments per chain, which can be determined by fitting with experimental PVT data. Recently we have shown [19] that using the critical constants of fluids it is sufficient to determine only one parameter, the chain length, to predict the equation of state for chain molecules. It is the purpose of this work to apply this equation of state to pure halogenated organic compounds.

2. Theory

Song et al. [15–17] started from the modified Chiew equation of state [11] for hard sphere chains as the reference system and added a van der Waals attractive term, to present a perturbed hard-sphere-chain equation of state. Due to the temperature-dependence of the volume of hard sphere and the attractive energy term this equation of state is applicable to fluids containing small or even large molecules. Kim and Bae [20,21] showed that on comparison with Monte Carlo simulation data for compressibility factors of hard spheres this equation of state slightly underestimates the pressure especially at high density region. They introduced the form of radial distribution function proposed by Chapman et al. [22] into the reference system to modify the equation of state for this effect as:

$$\left(\frac{P}{\rho kT}\right)_{\text{ref}} = 1 + r^2 b\rho g(d^+) - (r-1)\rho \frac{\partial \ln g(d^+)}{\partial \rho} \qquad (1)$$

where P is the pressure, r is the number of segments per molecule, b is the van der Waals covolume per segment, ρ is the number (molar) density, d is the hard-sphere diameter, kT is the thermal energy per one molecule, and $g(d^+)$ is the pair radial distribution function of hard spheres at contact, proposed by Carnahan and Starling as [23]: