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A semi-empirical correlation for the estimation of the second virial coefficients of refrigerants



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ABSTRACT

A new semi-empirical scaled correlation for the second virial coefficient of refrigerants, based on the corresponding states principle, is proposed. Starting from the consideration that refrigerants have different chemical structures, the considered experimental dataset, which includes 63 refrigerants and 3595 points, was split into five main subgroups: single halogenated, double halogenated, hydrocarbons, inorganics and elements. The subgroups were analyzed in detail through a factor analysis approach and the coefficients of the new equation were regressed for each group separately. When compared with the other literature models, the proposed formula is clearly simpler and easier to implement. For four of the proposed groups, the correlation adopts a minor number of constant parameters. In addition, the global RMSE is generally lower ($21.4 \text{ cm}^3 \text{ mol}^{-1}$) and the proposed mathematical expression well follows the physical constraints that the second virial coefficients must satisfy, both at low and at high reduced temperatures.

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Une corrélation semi-empirique pour l'estimation des deuxièmes coefficients du viriel de frigorigènes

Mots clés : Équation d'état du viriel ; Principe d'états correspondants ; Analyse factorielle ; Contraintes théoriques ; Sous-groupes

1. Introduction

Virial coefficients are of fundamental importance for the determination of gas densities and fugacities for VLE (vapor-liquid equilibria) assessments. The virial equation of state (in

Leiden form) shows the deviations from the perfect-gas equation as an infinite power series in the molar volume, V :

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (1)$$

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Nomenclature		calc	calculated
Latin symbols		exp	experimental
		lb	lower bound
		r	reduced
		ub	upper bound
		vp	vapor
		<i>Greek symbols</i>	
		Γ	potential energy (J)
		ε	energy parameter (J)
		μ	dipole moment (D)
		π	pi
		σ	distance parameter (m)
		ω	acentric factor
		<i>Acronyms</i>	
		ASHRAE	American Society of Heating, Refrigerating, and Air-Conditioning Engineers
		CSP	corresponding states principle
		DIISM	Department of Industrial Engineering and Mathematical Sciences
		DIPPR	Design Institute for Physical Properties
		PVT	pressure volume temperature
		RMSE	root mean square error
		VLE	vapor-liquid equilibria
		<i>Subscripts/superscripts</i>	
		B	Boyle
		c	critical
Nomenclature			
Latin symbols			
a_1	term related to the reduced dipole moment		
a	coefficient of the proposed equation		
B	second virial coefficient ($\text{cm}^3 \text{mol}^{-1}$)		
b	coefficient of the proposed equation		
b_1	term related to the reduced dipole moment		
C	third virial coefficient ($\text{cm}^3 \text{mol}^{-1}$)		
c	coefficient of the proposed equation		
card	cardinality		
D	fourth virial coefficient ($\text{cm}^3 \text{mol}^{-1}$)		
D_j	dataset		
d	coefficient of the proposed equation		
Eff	effect		
F	universal function		
f_i	terms related to Tsonopoulos' equation		
k	Boltzmann constant (J K^{-1})		
n	number of points		
P	pressure (Pa)		
R	universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)		
r	distance of separation between molecules (m)		
T	temperature (K)		
V	molar volume ($\text{cm}^3 \text{mol}^{-1}$)		
x	vector of independent variables		
y	dependent variable		
<i>Subscripts/superscripts</i>			
B	Boyle		
c	critical		

where B is the second virial coefficient, C is the third virial coefficient, D is the fourth virial coefficient, etc.

Even when truncated at the second term, the virial equation of state gives a remarkable estimate of the PVT (pressure–volume–temperature) relationship of real gases at low and moderate pressures. Two effects cause the deviation of a real gas from an ideal one: the interaction between molecules and the size and shape of the molecules themselves. The second virial coefficient represents the deviation from perfection due to interactions between pairs of molecules; thus, the virial equation represents a connection between experimental results and knowledge of molecular interactions, in particular of the forces between molecules:

$$B = 2\pi \int_0^{\infty} \left(1 - \exp\left(-\frac{\Gamma(r)}{kT}\right)\right) r^2 dr \quad (2)$$

where $\Gamma(r)$ is the intermolecular potential of the considered molecules at distance r and k is the Boltzmann constant. Equation (2) is correct only if all higher virial coefficients are set to zero.

Very frequently, the estimation of the second virial coefficient is obtained from complicate approaches based on theoretical interpretations of intermolecular interactions between molecules in the gaseous state. They are reasonably successful for simple molecules, but they generally fail when applied to more complex molecules. To overcome this draw-

back, many empirical and semi-empirical correlating models were proposed in the literature, generally based on the corresponding states principle (CSP).

The CSP indicates that all fluids have the same properties at the critical point, because the critical fluctuation is more important than the specific properties of the molecules in terms of potential of interaction or size and shape. The CSP can be extended to the region close to the critical point, leading to universal scaling laws. If the considered equation of state and, consequently, the underlying intermolecular potential have two parameters, the CSP can be expressed by a generalized intermolecular potential-energy function where the potential Γ is a universal function F of the distance of separation between molecules r (Prausnitz et al., 1998):

$$\frac{\Gamma}{\varepsilon} = F\left(\frac{r}{\sigma}\right) \quad (3)$$

where ε is an energy parameter and σ is a distance parameter for the interaction between two molecules. As this is a two-parameter model, it is limited to molecules with an energy of interaction which can be described only by a function having two parameters (Prausnitz et al., 1998). Such simple molecules are only the heavier noble gases (argon, krypton, xenon), but the properties of several others are closely approximated by the generalized potential function. In particular, a simple

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