



Investigating effects of molecular structure on the behavior of saturated liquid hydrocarbons using a novel semi-empirical equation of state



Bahador Abolpour

Department of Chemical Engineering, Sirjan University of Technology, Sirjan, Iran

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ABSTRACT

In this study, a novel equation of state has been developed to investigate the behavior of saturated liquid hydrocarbons. The developed equation was used to study the effects of molecular structure on this behavior. A set of logical rules was obtained to estimate the power of the presented equation of state. Finally, this equation and the obtained logics were validated using experimental data.

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1. Introduction

Development of various industries owes to the using of process simulation. The simulation of processes relevant to hydrocarbon industries needs accurate equations for obtaining the dependency among three key values of temperature (T), pressure (P) and molar volume (v) [1and2]. There are many simple equations of state for predicting these triple quantities for a pure substance or a mixture in a gaseous phase [3]. However, the conditions of a liquid phase are different [4]. The high molecular density makes complex the type of intermolecular forces in this phase, and hence PvT estimation is more difficult for liquids. Up to now, several equations have been presented for estimating the vT [5–8] or PvT [9–13] dependency in liquids. Attending to their focus on accurate estimation of a certain variable (for example, v), and also the complexity of the problem, these equations usually present complex relations between these parameters. Calculating other variables (for example, P or T) using these complex equations is impossible or very difficult (usually, numerical methods, such as trial and error, are necessary). A simple form of equation of state (such as $Pv=RT$) calculates each one of these triple variables, easily.

The most important characteristic of hydrocarbons is their

molecular structure (cycles or chains of carbon and hydrogen atoms with different lengths, branch's conditions and multiple bonds). This structure affects intermolecular forces in saturated liquid hydrocarbons. Therefore, for a special study of hydrocarbons, it is essential that investigate the effects of this structure on the inspected parameters. Previous studies had no tendency to investigate the effects of molecular structure on the PvT dependency [9and14]. Investigating these effects requires a theoretical base and also a simple and analyzable form of the equation of state (with a minimum number of constants depended on the type of hydrocarbon).

In this study, a semi-empirical equation is developed to investigate the behavior of saturated liquid hydrocarbons. This power equation is used to study the effects of main-chain length, branch's conditions, multiple bonds and cycles of hydrocarbons on the saturated liquid behavior. The simple form of this equation of state lets us calculate each one of unknown values of P , v or T using other two available values of these triple variables. Then, a set of logical rules is developed for estimating the power of this equation. Finally, this equation of state is validated using experimental data.

2. Methodology

2.1. Principle

Equation of state presents a relation among T , P and v of a pure

E-mail address: bahadorabolpor1364@yahoo.com.

substance or mixture. The simplest equation of state has been presented for the ideal gases. Non-ideal behaviors of gases are investigated using a definition of this equation. This investigation is based on the gas compressibility factor (Z). The value of $|Z-1|$ indicates the extent of non-ideality of gas behavior. Molecular interactions cause this non-ideal behavior in the real gases. Low-pressure real gases have no molecular interactions and, as a result, have ideal behavior ($\lim_{P \rightarrow 0} (Z) = 1$), like ideal gases [3]. At the critical point, the molecules of saturated liquid are vaporized at such a rapid rate that the densities of liquid and gas are equal [15]. On the other hand, the temperature and pressure of these phases are equal in the equilibrium condition. Therefore, $\lim_{Z \rightarrow Z_c} (Z^{Sat}) = Z_c$. Where, Z^{Sat} and Z_c are compressibility factors at equilibrium and critical point, respectively. Intermolecular forces that keep liquid molecules together are removed at this point. Ideal saturated liquid was defined as a high-compressed ideal gas, which has very low intermolecular forces for keeping the molecules together as a liquid form [14]. Therefore, saturated liquid shows an ideal behavior at its critical point (i.e. $Z_r^{Sat}|_{\text{Critical point}} = 1$).

Fig. 1 shows a brief description about the presented theory in this study. As shown in this Figure, different phases have different molecular behaviors. See the gaseous phase. The beginning of the formation of this phase is from equilibrium (saturated vapor with a high molecular interaction). Decreasing the pressure at a constant temperature (or increasing the temperature at a constant pressure) decreases the extent of interactions among the gaseous molecules ($Z \rightarrow 1$). This molecular interaction is ignorable for the ideal gas ($Z=1$). Now see the liquid phase. This phase has high intermolecular forces in its subcooled form. Increasing the temperature increases the molecular kinetic energy, as a result, decreases the intermolecular forces in this phase ($Z_r \rightarrow 1$). Saturated liquids have low intermolecular forces. Both phases have similar P and T in the equilibrium condition and similar v at the critical point [15]. Therefore, saturated liquid and gas have similar conditions of T , P and v and at the critical point (equal to T_c , P_c and v_c , respectively). It means that, $Z_r^{Sat} = 1$ for saturated liquid, like gas (with $Z=Z_c$), at this point. This dimensionless quantity, which is defined as below,

indicates the extent of ideality of saturated liquid behavior [14]:

$$Z_r^{Sat} = \frac{Z^{Sat}}{Z_c} = \frac{P_r^{Sat} v_r^L}{T_r} \quad (1)$$

where $T_r = \frac{T}{T_c}$, $v_r^L = \frac{v^L}{v_c}$ and $P_r^{Sat} = \frac{P^{Sat}}{P_c}$ are reduced temperature, reduced molar volume and reduced pressure of saturated liquid, respectively. Empirical values of v^L and P^{Sat} were presented as functions of T [16]:

$$v^L = \left[C_1 \left(C_2 \left(1 + \left(1 - \frac{T}{T_c} \right)^{C_4} \right)^{-1} \right)^{-1} \right] \quad (2)$$

$$P^{Sat} = \exp \left(C_5 + \frac{C_6}{T} + C_7 \ln(T) + C_8 T^{C_9} \right) \quad (3)$$

Tables 1–3 present critical values and empirical constants (i.e. C_1 to C_9). In this study, eighty cases of hydrocarbons have been classified in three groups:

- Group 1: Alkanes (saturated chain hydrocarbons)
- Group 2: Alkenes and Alkynes (unsaturated chain hydrocarbons)
- Group 3: Aromatics (cyclic hydrocarbons)

2.2. Semi-empirical equation of state

Initial investigations indicated that, Z_r^{Sat} is a power function of T_r , for all studied cases. Accordance of this function was obtained using

$$R^2\text{-value} \left(R^2 = 1 - \frac{\sum (Z_r^{Sat} - Z_r^{Sat})^2}{\sum (Z_r^{Sat} - Z_r^{Sat})^2} \right) \text{ for each hydrocarbon. As seen}$$

in Fig. 2, all studied cases have $R^2 \approx 1$. It approves the accuracy of the following equation using the experimental values, which were obtained using equations (1)–(3):

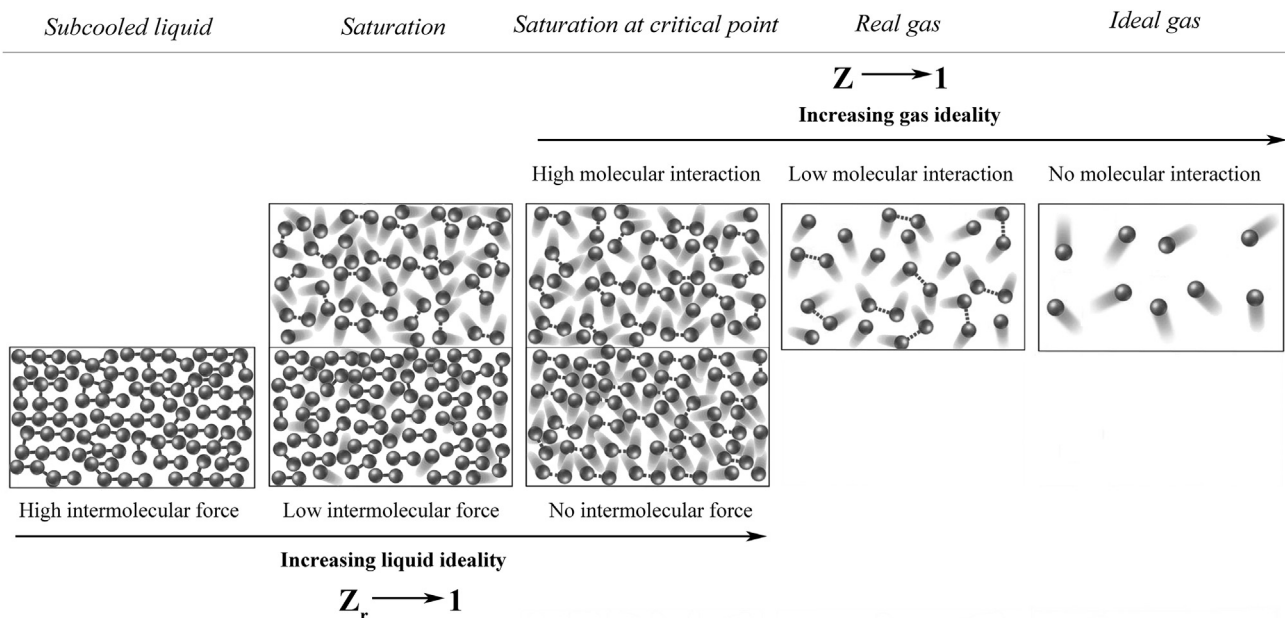


Fig. 1. A brief description about the presented theory.

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