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Application of the modified linear isotherm regularity equation of state to long chain amines and esters

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ABSTRACT

In this work, the linear isotherm regularity equation of state (LIR EoS) has been extended to predict the molar density of long chain primary and secondary amines, and esters and also the binary and ternary mixtures containing different functional groups. Each of these organic compounds has been assumed as a hypothetical mixture of methyl, methylene, and a functional group. Then, the LIR EoS has been modified for such a hypothetical mixture (MLIR EoS). Propane, *n*-butane, cyclohexane, 1-pentylamine, 2-aminobutane and *n*-butyl acetate have been used to investigate the contribution of the different segments in the new EoS parameters. The calculated parameters along with the MLIR EoS have been used to calculate the molar density and other thermodynamic properties of different pure compounds and their binary and ternary mixtures. A wide comparison has been made with some other EoSs and correlations. The results show that the MLIR EoS gives better results than other methods in accord with experimental data.

1. Introduction

A great number of compounds are used in chemical processes. In many cases, thermophysical experimental data are scarce or even not available. Liquid densities are needed in many engineering problems such as process calculations, simulations, equipment and pipeline designs, and liquid metering calculations. Liquid densities are usually calculated using correlations or equations of state. These equations must be simple, accurate, and also predictive so that they can be used when experimental data are not available.

Amine molecules as one of the hydrogen-bonded systems are very interesting because they play a vital role in chemical, physical, and biological processes [1]. They are often used as organic base compounds in several industrial processes. Volumetric properties such as density are important thermodynamic properties which characterize chemical behavior of these associating compounds and their binary and ternary mixtures useful for the understanding of the molecular interactions [2]. The aliphatic esters are important materials in manufacturing processes connected with flavor and fragrance industries. Esters and their widespread occurrence in nature and many practical uses make them perhaps one of the most important organic compounds. Thermophysical properties of aliphatic esters are particularly important in the pharmaceutical, food, and flavor industries. Experimental density data of pure amines and esters and their binary and ternary mixtures, in large temperature and pressure ranges, are still very scarce in literature. Thus, predictive models are needed for the calculation of the density of these liquids.

In the last decades, some fruitful attempts to develop such predictive thermodynamic models were based on the group contribution (GC) concept integrated into an equation of state (EOS). These methods generally assume that a given molecule may be divided into chemical functional groups. Properties and/or equation parameters of the corresponding chemicals are then calculated through formulae accounting for weighted contributions of the different groups present in the molecules [3]. According to this method, the properties of new materials are estimated through direct addition of additive molar quantities (AMQ) of the constituent chemical groups and the contribution of a given group is the same at different molecules. However, the definition of a functional group is a very subjective matter.

The group contribution method has been used in combination with a great variety of thermodynamic models and theories. One of the methods to apply a group contribution method to an equation of state is evaluating the EoS parameters using a built-in group contribution rule. Only a few attempts were made in this direction in the last decades [4–11]. In 1977, Nitta et al. [12] published the first group contribution EoS based on the cell model for some pure compounds in liquid phase. From then on, group contribution method has been used with different models and theories such as UNIFAC model [13], lattice theory [14], Carnahan–Starling–van der

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Waals equation [15], modified Flory–Hunggins theory [16], perturbed hard chain EoS [17], chain-of-rotator model [6], and hole models [8,18,19] by different researchers.

Recently, the linear isotherm regularity EoS [20] has been extended to the long chain n-alkanes, alcohols, ketones, nad 1-carboxylic acids via group contribution method [21,22]. In this work, the group contribution method has been applied in combination with the LIR EoS to calculate the molar density and other thermodynamic properties of some other long chain organic compounds i.e. long chain primary and secondary amines, and aliphatic esters and also their binary and ternary mixtures containing different functional groups. Since the LIR EoS is based on the average effective pair potential (AEPP) function in the form of Lennard–Jones (LJ; 12-6), it is more appropriate for spherical–symmetrical molecules. However, the non-spherical molecules such as long chain organic compounds show some deviation from the linear behavior of the LIR EoS. Thus, group contribution method has been used to modify the LIR EoS for above mentioned long chain organic compounds.

2. Theory

2.1. LIR equation of state

Linear isotherm regularity (LIR) was derived using the LJ (12-6) potential for the average effective pair potential along with the pairwise additive approximation for the molecular interactions in dense fluids and considering only the nearest neighbor interactions. This EoS can be written as [20]

$$(Z-1)V_m^2 = A(T) + B(T)\rho^2 \tag{1}$$

where Z, V_m, and $\rho = 1/V_m$ are compressibility factor, molar volume, and molar density, respectively. On the basis of a simple model that mimics the linearity, the intercept and slope of this equation depend on temperature via the following equations:

$$A(T) = A_2 - \frac{A_1}{RT} \tag{2}$$

$$B(T) = \frac{B_1}{RT} \tag{3}$$

where A_1 and B_1 are related to the attraction and repulsion terms of the average effective pair potential, respectively and A_2 is related to the non-ideal thermal pressure. The LIR EoS was experimentally found to be hold for all types of fluids, including nonpolar, polar, hydrogen bonded and quantum fluids, for densities greater than the Boyle density ($\rho_B \approx 1.8\rho_c$, where ρ_c is the critical density) and temperatures less than twice the Boyle temperature, the temperature at which the second virial coefficient is zero. According to the one-fluid approximation, the regularity holds for the dense fluid mixtures as well [23]. Furthermore, the LIR EoS has been used to predict many experimentally known regularities for dense pure fluids [24] and its extension to fluid mixtures [25]. To use the equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot $(Z-1)V_m^2$ versus ρ^2 for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. (2) and (3) from which A_1, A_2 and B_1 can be found, respectively.

Parsafar and Kalantar [21,22] showed that this linearity deviates for long chain alkanes, alcohols, ketones and carboxylic acids and the deviation from linearity increases with increasing the chain length of these organic compounds. Such behavior is expected, because the mathematical form of AEPP function is in the form of LJ (12-6), and it is more appropriate for spherical–symmetrical molecules. However, the non-spherical molecules such as long chain organic compounds show some deviations from the linear behavior of the LIR EoS. Therefore, group contribution method has been used to modify the LIR EoS for these fluids.

2.2. Modified LIR equation of state

Each organic compound has been assumed as a hypothetical mixture of methyl, methylene, and a functional group, in which the interaction potential of each pair is assumed to be the average effective pair potential (AEPP). Then, the LIR EoS has been modified for such a hypothetical mixture. According to the one fluid approximation, the LIR EoS can be extended to mixtures [23], but the parameters of this EoS are dependent on composition as well as temperature. In the case of long chain organic compounds, this equation of state must be modified and the parameters of the new EoS must be depended on the length of chain. Since, the total density of a hypothetical fluid is equal to $n\rho$, in which n and ρ are the number of segments of the molecule and molar density, respectively, the LIR EoS is modified to [21,22]:

$$\frac{((P/n\rho RT)-1)}{n^2\rho^2} = A_m + B_m n^2\rho^2 \tag{4}$$

or

$$\left(\frac{Z}{n}-1\right)V_m^2 = A' + B'\rho^2 \tag{5}$$

where A_m and B_m are the new EoS parameters per each segment of the molecule and

$$A' = A_m n^2 \tag{6}$$

$$B' = B_m n^4 \tag{7}$$

This new regularity was called modified LIR (MLIR) EoS. For any isotherm of each long chain organic compounds (alkanes, alcohols, ketones and 1-carboxylic acids), the linearity of $((Z/n)-1)V_m^2$ versus ρ^2 was very better than $(Z-1)V_m^2$ versus ρ^2 [22]. The values of correlation coefficients, R^2, for MLIR EoS showed very better linearity than that of for the original LIR EoS, especially for longer chain compounds. Also, the values of A_m and B_m for each isotherm were calculated using the intercept (A') and slope (B') of Eq. (5) via Eqs. (6) and (7). The temperature dependencies of the parameters of MLIR EoS were linear with respect to $1/T$ just the same as those for LIR EoS and may be shown via the following equations:

$$A_m(T) = \frac{a_1}{RT} + a_2 \tag{8}$$

$$B_m(T) = \frac{b_1}{RT} + b_2 \tag{9}$$

Each normal alkane has been assumed as a hypothetical mixture of two methyl groups at the ends of the chain, two methylene groups each attached to the methyl groups, and $n-4$ middle methylene groups. Propane, n-butane, and cyclohexane have been used as basic compounds to obtain the contribution of each carbonic (methyl and methylene) groups in the MLIR EoS parameters [21].

At first, using propane and n-butane, the contribution of two methyl groups and two terminal methylene groups in A_m and B_m parameters was obtained. Since the composition dependencies of the LIR EoS are according to the quadratic mixing rules [23], assuming the random distribution of carbonic groups, the contributions of methyl and terminal methylene groups might be obtained via the following equations:

$$(B_m)_{\text{propane}} = \left(\frac{2}{3}\sqrt{B_{11}} + \frac{1}{3}\sqrt{B_{22}}\right)^2,$$

$$(B_m)_{n\text{-butane}} = \left(\frac{1}{2}\sqrt{B_{11}} + \frac{1}{2}\sqrt{B_{22}}\right)^2 \tag{10}$$