

Research Article

Extension of LIR Equation of State to Alkylamines Using Group Contribution Method

Zahra Kalantar, Hossein Nikoofard, and Faezeh Javadi

School of Chemistry, Shahrood University of Technology, P.O. Box 3619995161, Shahrood, Iran

Correspondence should be addressed to Zahra Kalantar; zahrakalantar@yahoo.com

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In this work, the modified linear isotherm regularity (LIR) equation of state parameter table is extended in order to represent volumetric behaviour of primary alkylamines. In addition, the isothermal compressibility and thermal expansion coefficient of these compounds have been predicted. To do so, we consider each of primary alkylamine as a hypothetical mixture of methyl, methylene and a primary amine functional group, in which the interaction potential of each pair is assumed to be the average effective pair potential. Then, the LIR equation of state has been extended to such a hypothetical mixture. Furthermore, three basic compounds, namely, propane, *n*-butane, and cyclohexane are used to obtain the contribution of methyl and methylene groups in the EOS parameters, and also other appropriate compounds are used to obtain the contribution of the primary amine functional groups, such as 1-pentylamine for the contribution of $-\text{CH}_2\text{NH}_2$ and 2-aminopentane for the contribution of >CHNH_2 groups. The calculated EOS parameters along with the modified EOS are then used to calculate the density and its derivatives for alkylamines at different pressures and temperatures. The obtained results for different properties are compared with the experimental values.

1. Introduction

The thermodynamic studies are important for efficient design of chemical processes, to develop correlation and prediction methods applicable over wide temperature and pressure ranges. Among others, volumetric properties such as density and its derivatives are of great interest not only for industrial applications but also for fundamental aspects. These properties can be obtained either experimentally or by thermodynamic modeling based on the equation of state (EOS). Since experimental measurements are lengthy and costly, the amount of experimental works can be reduced if efficient thermodynamic models are used to calculate the properties at different conditions of pressure and temperature. However, equations of state which are often used to predict thermodynamic properties require pure fluid parameters as inputs. The values of such parameters are, however, not only fluid specific but also temperature dependent.

To develop an EOS which is predictive, a group contribution method (GCM) can be used. This method has strong theoretical ties to statistical mechanical theory. The main idea of GCM is to reduce all the interactions existing in the system

to those pertaining to the pairs of the functional groups or segments from which the molecules are built. Therefore, properties and/or EOS parameters of corresponding chemicals may be calculated through formulae accounting for weighted contributions of the different groups present in the molecules. In the last 3 decades, this method has provided a practical and powerful tool for predicting as well as calculating the parameters of equations of state from the chemical composition and state of matter. In 1974, Nitta et al. published the first group contribution EOS [1] that is based on the cell model and is only able to deal with some pure compounds in liquid phase. In 1975, the first successful and widely applied group contribution method, UNIFAC model was published based on the lattice theory [2]. The further development of the group contribution methods proceeded through the generalization of the lattice theory to describe the gas and vapor properties and the high-pressure vapor-liquid equilibria as well [3]. Skjold-Jørgensen developed a group contribution equation of state (GC-EOS) by employing a Carnahan-Starling-van der Waals equation to calculate vapor-liquid equilibria of nonideal mixtures with low to medium molecular weight compounds [4]. Then,

Espinosa et al. [5] extended the application of this model to low-volatile high-molecular weight compounds using a unique set of parameters; a satisfactory correlation and prediction of VLE and LLE in mixtures of supercritical fluids with natural oils and derivatives could be achieved [6]. Majeed and Wagner developed the parameters of the modified Flory-Huggins theory to account for the molecular size difference [7]. Georgeton and Teja developed a GC-EOS using a modified form for the perturbed hard chain equation of state [8]. Pults et al. developed chain-of-rotator group contribution equation of state [9]. Gros et al. introduced a group contribution associating term to the original GC-EOS Helmholtz residual energy expression, extending the application of the model (so-called GC Associating EOS) to alcohols, water, gases, and their mixtures [10]. Then, GCA-EOS parameters table extended in order to represent phase equilibria behavior of carboxylic acids, alcohols, water, and gases mixtures [11] and aromatic compounds containing phenol, aromatic acid, and aromatic ether compounds [12]. Also, a few group contribution hole models and their numerous versions have been appeared [13–15].

Recently, the extension of the linear isotherm regularity equation of state to long chain organic compounds such as n -alkanes, primary, secondary, and tertiary alcohols, ketones, and 1-carboxylic acids is reported via group contribution method [16, 20]. The present paper is a fresh attempt to extend LIR equation of state to alkylamines and their mixtures and also predict the parameters of equations of state using the group contribution method.

2. Theory

2.1. Linear Isotherm Regularity Equation of State. Using the LJ (12, 6) potential for the average effective pair potential (AEPP) along with the pairwise additive approximation for the molecular interactions in the dense fluids and considering only the nearest neighbor interactions, linear isothermal regularity equation of state (LIR-EOS) have been derived from the exact thermodynamic relations as [21]

$$(Z - 1)v^2 = A + B\rho^2, \quad (1)$$

where $Z = p/\rho RT$ is the compressibility factor, $\rho = 1/v$ is the number density, and A and B are the temperature dependent parameters. AEPP was considered to be the interaction between the nearest neighbor molecules, to which all of the longer range interactions are added, and also the effect of the medium in the charge distributions of two neighboring molecules was included [22]. The temperature dependencies of the LIR parameters were found as follows:

$$\begin{aligned} A &= A_2 - \frac{A_1}{RT}, \\ B &= B_2 + \frac{B_1}{RT}, \end{aligned} \quad (2)$$

where A_1 and B_1 are related to the attraction and repulsion terms of the average effective pair potential and A_2 is related to the nonideal thermal pressure.

The LIR was experimentally found to be hold for densities greater than the Boyle density ($\rho_B \approx 1.8\rho_C$, where ρ_C is the critical density) and temperature 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].

In our previous works, we have showed that such linearity vanished for different organic compounds [16, 20]. Such a behavior is expected, because the mathematical form of the AEPP function is assumed to be the LJ (12, 6), and the potential function which is more appropriate for the spherical-symmetrical molecules than nonspherical molecules, such as chain organic compounds, show deviation from the linear behavior of the LIR. Hence, using the group contribution method, the LIR may be modified for such fluids.

2.2. Modified LIR Equation of State for Long Chain Organic Compounds. Using the GC concept, each organic compound was considered as a hypothetical mixture of their carbonic groups, in which the interaction potential of each pair is assumed to be the average effective pair potential. This potential includes both physical and chemical (bond) interactions. Then, according to the Van der Waals one-fluid approximation, the LIR-EOS would be appropriate for such a mixture, but the new EOS parameters depend on the group compositions in the mixture (the length of the chain, in this case) as well as temperature. Hence, if the molar density of the organic compound at temperature T is ρ , the total density for the hypothetical fluid is equal to $n\rho$, where n is number of carbonic groups of the molecule. Therefore, the LIR is reduced to

$$\begin{aligned} \frac{((p/n\rho RT) - 1)}{n^2\rho^2} &= A_m + B_m n^2 \rho^2 \implies \frac{((Z/n) - 1)}{\rho^2} \\ &= A' + B'\rho^2 \end{aligned} \quad (3)$$

which we were referred to it as the modified linear isotherm regularity (MLIR) [16, 20]. Like the LIR, the MLIR was found to be valid for dense fluids only for $\rho > \rho_B$. A_m and B_m are the MLIR parameters per each carbonic group and

$$\begin{aligned} A' &= A_m n^2, \\ B' &= B_m n^4. \end{aligned} \quad (4)$$

For all studied organic compounds, we found a better linearity for $(Z/n - 1)v^2$ versus ρ^2 than $(Z - 1)v^2$ versus ρ^2 for each isotherm, especially for the longer chains. Also we found that the values obtained for A_m and B_m are linear with respect to $1/T$, just the same as those for the LIR parameters [16, 20],

$$\begin{aligned} A_m &= \frac{a_1}{RT} + a_2, \\ B_m &= \frac{b_1}{RT} + b_2. \end{aligned} \quad (5)$$

2.3. Carbonic Group Contributions in A_m and B_m Parameters. To predict the MLIR parameters (A_m , B_m) for the mentioned

TABLE 1: Values of a_1/R , a_2 , b_1/R , and b_2 for 8 basic compounds, namely, Propane, *n*-Butane, Cyclohexane, 1-Pentanol, 2-Pentanol, *t*-BuOH, 2-Pentanone, and 1-Pentanoic acid taken from [16].

Basic compound	$(b_1/R) \times 10^4, \text{L}^4 \text{mol}^{-4} \text{K}$	$b_2 \times 10^7, \text{L}^4 \text{mol}^{-4}$	$(a_1/R), \text{L}^2 \text{mol}^{-2} \text{K}$	$a_2 \times 10^4, \text{L}^2 \text{mol}^{-2}$
propane	3.330	4.677	-0.982	6.057
<i>n</i> -butane	2.830	1.810	-0.911	6.570
cyclohexane	1.006	1.323	-0.532	0.2458
1-pentanol	3.559	1.605	-1.139	4.759
2-pentanol	4.914	-3.473	-1.582	21.24
<i>t</i> -BuOH	3.285	5.264	-1.098	2.289
2-pentanone	3.549	-0.329	-1.207	10.624
1-pentanoic acid	3.860	-0.0648	-1.191	8.182

organic compounds using the group contribution method, each of these fluids has been considered as a hypothetical mixture of their carbonic groups, namely, methyl, terminal methylene, middle methylene, $-\text{CH}_2\text{OH}$, >CHOH , $-\overset{|}{\underset{|}{\text{C}}}\text{OH}$, >C=O , and $-\text{COOH}$ groups.

If A_{11} and B_{11} are the contributions of methyl groups in A_m and B_m , and A_{22} and B_{22} are those for the terminal methylene groups, respectively, the contributions of methyl and terminal methylene groups in A_m and B_m parameters will be obtained from two basic compounds, namely, propane and *n*-butane, from the following expressions:

$$\begin{aligned}
 (B_m)_{\text{propane}} &= \left(\frac{2}{3} \sqrt{B_{11}} + \frac{1}{3} \sqrt{B_{22}} \right)^2, \\
 (B_m)_{n\text{-butane}} &= \left(\frac{2}{4} \sqrt{B_{11}} + \frac{2}{4} \sqrt{B_{22}} \right)^2, \\
 \left(\frac{A_m}{B_m} \right)_{\text{propane}} &= \left(\frac{2}{3} \sqrt{\frac{A_{11}}{B_{11}}} + \frac{1}{3} \sqrt{\frac{A_{22}}{B_{22}}} \right)^2, \\
 \left(\frac{A_m}{B_m} \right)_{n\text{-butane}} &= \left(\frac{2}{4} \sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{4} \sqrt{\frac{A_{22}}{B_{22}}} \right)^2.
 \end{aligned} \tag{6}$$

The unlike parameters are taken as the mean geometric of the like parameters; that is, $B_{12} = \sqrt{B_{11}B_{22}}$ and $A_{12}/B_{12} = \sqrt{(A_{11}/B_{11})(A_{22}/B_{22})}$. Note that the 2/3 and 1/3 coefficients in the former expressions are the fraction of carbonic groups (1) and (2) in propane, respectively, and 2/4 in the others are for *n*-butane. The contributions of a middle methylene group in A_m and B_m parameters are related to those of CH_2 in cyclohexane. If A_{33} and B_{33} are the contributions of the middle methylene groups to the A_m and B_m , then the values of A_m and B_m for cyclohexane are the same as A_{33} and B_{33} for linear alkanes [20]. Other appropriate compounds were also used to obtain the contributions of the five functional groups to the MLIR-EOS parameters in the same approach: 1-pentanol for the contribution of $-\text{CH}_2\text{OH}$ (A_{44}, B_{44}), 2-pentanol for >CHOH (A_{55}, B_{55}), 2-methyl-2-propanol (*t*-BuOH) for $-\overset{|}{\underset{|}{\text{C}}}\text{OH}$ (A_{66}, B_{66}), 2-pentanone for >C=O (A_{77}, B_{77}), and 1-pentanoic acid for $-\text{COOH}$ (A_{88}, B_{88}).

We may use the values for a_1/R , a_2 , b_1/R , and b_2 for the basic compounds given in Table 1 along with (5) to obtain values of A_m and B_m for them at any temperature [16].

Having the contributions of the groups from which the molecules are built in the EOS parameters, along with dependencies of the LIR parameters to system composition, the MLIR parameters for each of the compounds mentioned were predicted using the following expressions:

$$(B_m) = \left(\sum_{i=1}^8 x_i \sqrt{B_{ii}} \right)^2, \tag{7}$$

$$\left(\frac{A_m}{B_m} \right) = \left(\sum_{i=1}^8 x_i \sqrt{\frac{A_{ii}}{B_{ii}}} \right)^2,$$

where

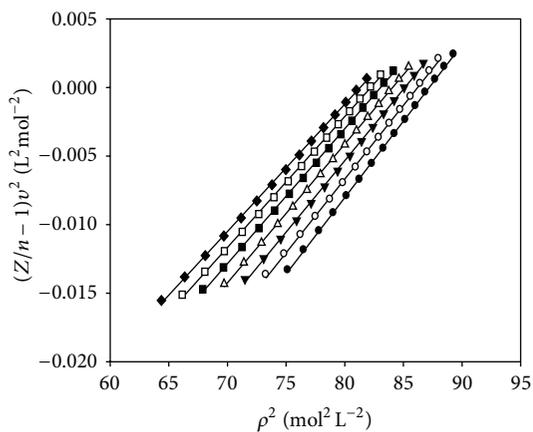
$$x_i = \frac{\text{number of group } i}{\text{total number of groups } (n)}. \tag{8}$$

Then using the calculated A_m and B_m parameters along with (3), densities of these compounds and their binary mixtures at different pressures and temperatures were calculated.

3. Results and Discussion

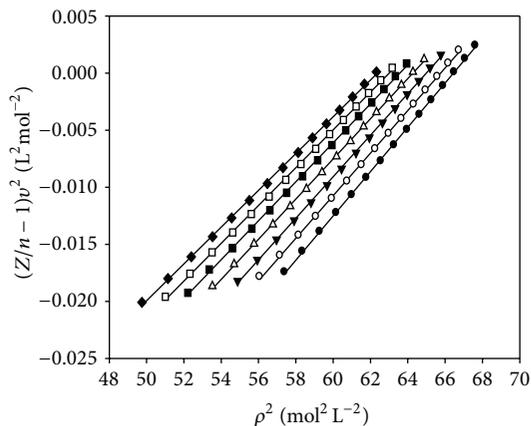
3.1. Extension of MLIR Equation of State to Primary Alkylamines. The main purpose in this section is to investigate the accuracy of the MLIR-EOS for primary alkylamines. According to MLIR-EOS, plot of $(Z/n - 1)v^2$ must be linear against ρ^2 for each isotherm of these dense fluids. To do so, we may use the experimental pVT data for these compounds to plot $(Z/n - 1)v^2$ against ρ^2 for each isotherm. As shown in Figure 1 the linearity holds quite well for each isotherm of these fluids with the correlation coefficient, $R^2 \geq 0.9994$, for all chains.

The line for each isotherm given in Figure 1 for different alkylamines were used to determine A' (from the intercept) and B' (from the slope) in order to calculate the parameters A_m and B_m for that isotherm using (4). Then the calculated values for the parameters were plotted versus $1/T$ to obtain the values for a_1/R , a_2 , b_1/R , and b_2 . These values and



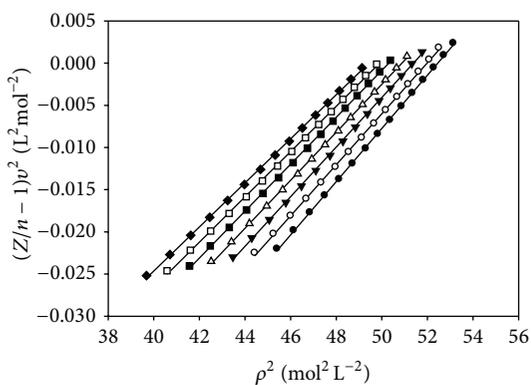
- $T = 293.15 \text{ K}, R^2 = 0.9997$ ■ $T = 333.15 \text{ K}, R^2 = 0.9996$
- $T = 303.15 \text{ K}, R^2 = 0.9994$ □ $T = 343.15 \text{ K}, R^2 = 0.9995$
- ▼ $T = 313.15 \text{ K}, R^2 = 0.9996$ ◆ $T = 353.15 \text{ K}, R^2 = 0.9996$
- ▲ $T = 323.15 \text{ K}, R^2 = 0.9997$

(a) 1-Pentylamine



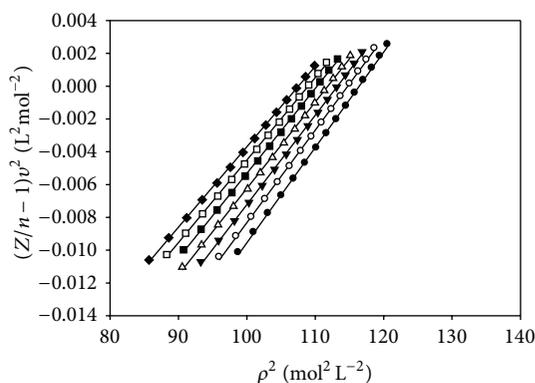
- $T = 293.15 \text{ K}, R^2 = 0.9998$ ■ $T = 333.15 \text{ K}, R^2 = 0.9996$
- $T = 303.15 \text{ K}, R^2 = 0.9996$ □ $T = 343.15 \text{ K}, R^2 = 0.9995$
- ▼ $T = 313.15 \text{ K}, R^2 = 0.9997$ ◆ $T = 353.15 \text{ K}, R^2 = 0.9996$
- ▲ $T = 323.15 \text{ K}, R^2 = 0.9997$

(b) 1-Hexylamine



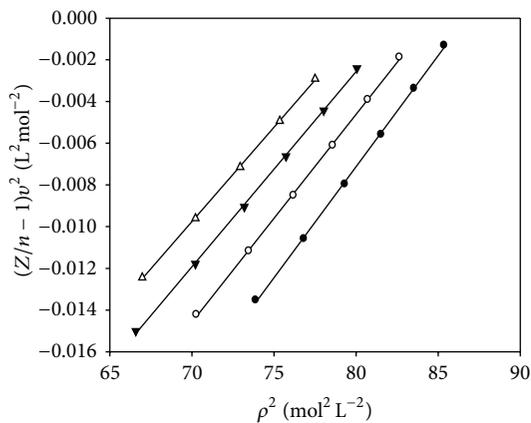
- $T = 293.15 \text{ K}, R^2 = 0.9997$ ■ $T = 333.15 \text{ K}, R^2 = 0.9997$
- $T = 303.15 \text{ K}, R^2 = 0.9995$ □ $T = 343.15 \text{ K}, R^2 = 0.9995$
- ▼ $T = 313.15 \text{ K}, R^2 = 0.9996$ ◆ $T = 353.15 \text{ K}, R^2 = 0.9996$
- ▲ $T = 323.15 \text{ K}, R^2 = 0.9997$

(c) 1-Heptylamine



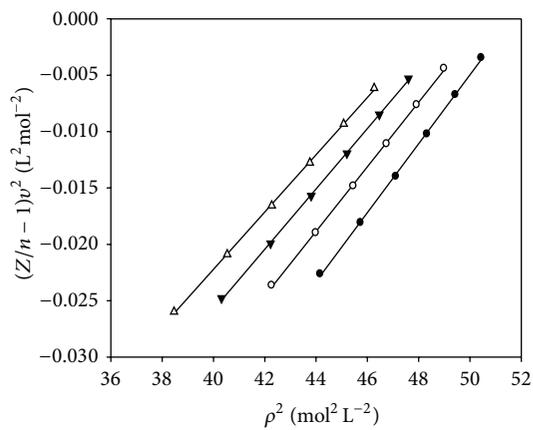
- $T = 293.15 \text{ K}, R^2 = 0.9995$ ■ $T = 333.15 \text{ K}, R^2 = 0.9996$
- $T = 303.15 \text{ K}, R^2 = 0.9995$ □ $T = 343.15 \text{ K}, R^2 = 0.9996$
- ▼ $T = 313.15 \text{ K}, R^2 = 0.9996$ ◆ $T = 353.15 \text{ K}, R^2 = 0.9997$
- ▲ $T = 323.15 \text{ K}, R^2 = 0.9995$

(d) 2-Aminobutane



- $T = 293.15 \text{ K}, R^2 = 0.9996$
- $T = 313.15 \text{ K}, R^2 = 0.9997$
- ▼ $T = 333.15 \text{ K}, R^2 = 0.9992$
- ▲ $T = 353.15 \text{ K}, R^2 = 0.9998$

(e) 2-Aminopentane



- $T = 293.15 \text{ K}, R^2 = 0.9996$
- $T = 313.15 \text{ K}, R^2 = 0.9997$
- ▼ $T = 333.15 \text{ K}, R^2 = 0.9992$
- ▲ $T = 353.15 \text{ K}, R^2 = 0.9998$

(f) 2-Aminoheptane

FIGURE I: Continued.

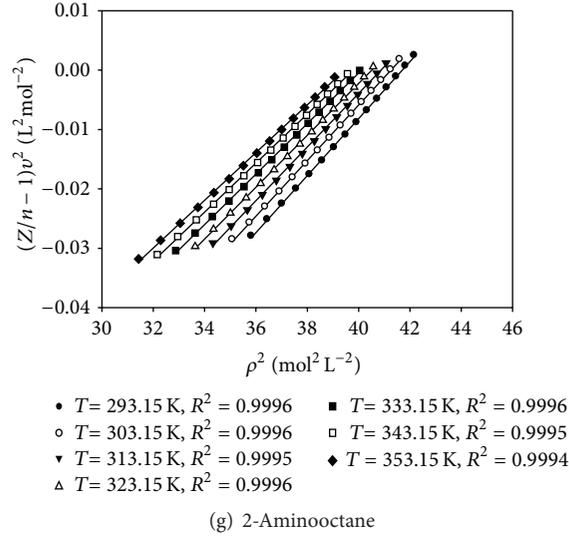


FIGURE 1: Plot of $(Z/n - 1)v^2$ versus ρ^2 for different alkylamines at given temperature.

the correlation coefficients of (5) are given in Table 2 for each alkylamine. Having these values and using (5), the values of A_m and B_m for an alkylamine may be calculated at any temperature. Then having the calculated values for the parameters and using (4) along with (3), density of the alkylamine can be calculated at different pressures and temperatures.

3.2. Prediction of MLIR Parameters for Alkylamines Using GCM. The next step is to predict MLIR parameters for alkylamines using GCM. At first, we consider the 1-alkylamines. Compared to an n -alkane, in a linear 1-alkylamine ($\text{H}_3\text{C} - \text{CH}_2 - (\text{CH}_2)_{n-4} - \text{CH}_2 - \text{CH}_2\text{NH}_2$) one methyl group is replaced with a $-\text{CH}_2\text{NH}_2$ group. Hence, in 1-alkylamine, we consider $-\text{CH}_2\text{NH}_2$ as a new functional group and use the values of A_m and B_m of 1-pentylamine, to calculate the contribution of $-\text{CH}_2\text{NH}_2$ group (A_{99}, B_{99}) from the following expressions at temperature of interest:

$$(B_m)_{1\text{-pentylamine}} = \left(\frac{1}{5} \sqrt{B_{11}} + \frac{2}{5} \sqrt{B_{22}} + \frac{1}{5} \sqrt{B_{33}} + \frac{1}{5} \sqrt{B_{99}} \right)^2,$$

$$\left(\frac{A_m}{B_m} \right)_{1\text{-pentylamine}} = \left(\frac{1}{5} \sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5} \sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5} \sqrt{\frac{A_{33}}{B_{33}}} + \frac{1}{5} \sqrt{\frac{A_{99}}{B_{99}}} \right)^2, \quad (9)$$

where the mole fractions of the methyl, terminal methylene, middle methylene, and $-\text{CH}_2\text{NH}_2$ groups in 1-pentylamine are $1/5, 2/5, 1/5,$ and $1/5,$ respectively.

Similarly, in the primary alkylamines in which an $-\text{NH}_2$ group is attached to a secondary carbon atom in alkyl group, we consider >CHNH_2 as a new functional group and use the values of A_m and B_m of 2-aminopentane to calculate

the contribution of >CHNH_2 group (A_{1010}, B_{1010}) in the MLIR parameters at each temperature from the following expressions:

$$(B_m)_{2\text{-aminopentane}} = \left(\frac{2}{5} \sqrt{B_{11}} + \frac{2}{5} \sqrt{B_{22}} + \frac{1}{5} \sqrt{B_{1010}} \right)^2,$$

$$\left(\frac{A_m}{B_m} \right)_{2\text{-aminopentane}} = \left(\frac{2}{5} \sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5} \sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5} \sqrt{\frac{A_{1010}}{B_{1010}}} \right)^2, \quad (10)$$

where the mole fractions of the methyl, terminal methylene, and >CHNH_2 groups in 2-aminopentane are $2/5, 2/5,$ and $1/5,$ respectively.

We may use the values for $a_1/R, a_2, b_1/R,$ and b_2 for the basic compounds given in Table 2 along with (5) to obtain values for A_m and B_m at any temperature. We calculated the contributions of three carbonic groups and the alkylamine functional groups at different temperatures (303.15, 323.15, and 343.15 K). Having the contributions of the constituent groups to the MLIR parameters along with dependencies of the LIR parameters to system composition, the values of A_m and B_m for each alkylamine may be calculated using the following expressions:

$$(B_m)_{\text{alkylamine}} = \left(x_1 \sqrt{B_{11}} + x_2 \sqrt{B_{22}} + x_3 \sqrt{B_{33}} \right. \\ \left. + x_9 \sqrt{B_{99}} + x_{10} \sqrt{B_{1010}} \right)^2,$$

$$\left(\frac{A_m}{B_m} \right)_{\text{alkylamine}} = \left(x_1 \sqrt{\frac{A_{11}}{B_{11}}} + x_2 \sqrt{\frac{A_{22}}{B_{22}}} + x_3 \sqrt{\frac{A_{33}}{B_{33}}} \right. \\ \left. + x_9 \sqrt{\frac{A_{99}}{B_{99}}} + x_{10} \sqrt{\frac{A_{1010}}{B_{1010}}} \right)^2, \quad (11)$$

TABLE 2: The calculated values of a_1/R , a_2 , b_1/R , and b_2 and the correlation coefficients of (5) for studied alkylamines.

Fluids	$(b_1/R) \times 10^4, \text{L}^4 \text{mol}^{-4} \text{K}$	$b_2 \times 10^7, \text{L}^4 \text{mol}^{-4}$	R^2	$a_1/R, \text{L}^2 \text{mol}^{-2} \text{K}$	$a_2 \times 10^4, \text{L}^2 \text{mol}^{-2}$	R^2	References
1-Pentylamine	5.075	0.478	0.9991	-1.488	11.992	0.9994	[17]
1-Hexylamine	4.307	0.237	0.9989	-1.350	10.334	0.9993	[17]
1-Hepylamine	3.811	0.077	0.9980	-1.257	9.323	0.9987	[17]
2-Aminobutane	6.072	1.951	0.9987	-1.253	16.042	0.9986	[18]
2-Aminopentane	4.524	1.550	0.9989	-1.346	9.116	0.9991	[19]
2-Aminoheptane	3.728	0.007	0.9991	-1.201	8.808	0.9993	[19]
2-Aminooctane	3.357	0.297	0.9995	-1.138	7.492	0.9995	[18]

TABLE 3: AAD, D_{\max} , and bias of the calculated density for some alkylamines at given temperatures and for the given pressure range (Δp) using the calculated values of A_m and B_m parameters along with (3).

Fluid	T, K	$\Delta p, \text{MPa}$	AAD	D_{\max}	bias	NP
1-Butylamine	298.15	0.1-33.9	0.570	0.965	0.570	10
	303.15	0.1-140	0.703	1.05	0.703	15
1-Hexylamine	323.15	0.1-140	0.542	0.861	0.542	15
	343.15	0.1-140	0.424	0.708	0.424	15
1-Heptylamine	303.15	0.1-140	0.636	0.993	0.636	15
	323.15	0.1-140	0.459	0.677	0.459	15
	343.15	0.1-140	0.388	0.547	0.388	15
2-Aminobutane	303.15	0.1-140	1.452	1.672	1.452	15
	323.15	0.1-140	1.231	1.430	1.231	15
	343.15	10-140	1.091	1.219	1.091	14
2-Aminoheptane	293.15	0.1-100	1.17	1.48	1.17	6
	333.15	0.1-100	0.934	1.688	0.934	6
2-Aminooctane	303.15	0.1-140	1.34	1.64	1.34	15
	323.15	0.1-140	1.17	1.58	1.17	15
	343.15	0.1-140	0.939	1.25	0.939	15

where x_i could be obtained using (8). Then we may use the values calculated for A_m and B_m parameters at the temperature of interest along with (3) for a given alkylamine to obtain its density at different pressures. Some of the calculated results are given in Table 3.

The statistical parameter, namely, the absolute average percent deviation (AAD), the maximum deviation (D_{\max}), and the average deviation (bias) are defined as

$$\begin{aligned}
 \text{AAD} &= \frac{100}{N} \sum_{i=1}^N \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right|, \\
 D_{\text{Max}} &= \text{Max} \left(100 \left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \right), \\
 \text{bias} &= \frac{100}{N} \sum_{i=1}^N \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}},
 \end{aligned} \quad (12)$$

where N is the number of experimental data, and ρ_i^{exp} and ρ_i^{cal} are the experimental density values and those obtained with (3) for studied fluids, respectively. Since the values of AAD can characterize the fact that the calculated values are more or less close to experimental data, it can be claimed that MLIR EOS can predict the density of these organic

compounds with good accuracy at any temperatures and pressures.

3.3. Extension to Mixture of Alkylamines with Previously Studied Organic Compounds. The main purpose in this section is to investigate the accuracy of the MLIR-EOS for mixtures of the alkylamines with previously studied organic compounds (n -alkanes, alcohols, ketones, and carboxylic acids). To do so, we may use the experimental pVT data for binary mixture of n -butylamine with 1-alkanols [24]. These binary mixtures, besides self-association, exhibit very strong cross association due to the strong hydrogen bonding between the hydroxyl and the amine groups. This strong intermolecular association exhibits relatively large negative excess volumes [24]. Again, we have found that the linearity of $(Z/n-1)v^2$ against ρ^2 for each isotherm of a binary mixture is as good as those for its pure compounds, see Figure 2. Note that, the average value of n for a mixture may be defined as

$$n_{\text{mix}} = \sum_{\text{number of component}} x_i n_i, \quad (13)$$

where x_i and n_i refer to the mole fraction and number of carbon atom of component i in the mixture.

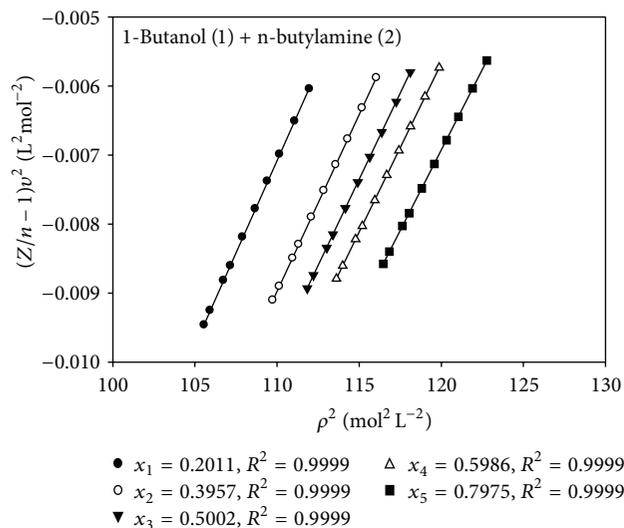


FIGURE 2: Plot of $(Z/n-1)v^2$ versus ρ^2 for binary mixture of 1-butanol (1) + *n*-butylamine (2) at 298.15 K.

We may use the group contribution method to predict the MLIR parameters for mixtures. The contributions of different groups at the temperature of interest may be calculated from the same procedure explained in the previous sections (using the values for pure compounds). Having the contributions of constituent groups in the MLIR parameters along with the dependencies of the LIR parameters to system composition, the MLIR parameters for a mixture may be calculated from the following expressions:

$$(B_m)_{\text{mixture}} = \left(\sum_{j=1}^{10} X_j \sqrt{B_{jj}} \right)^2, \quad (14)$$

$$\left(\frac{A_m}{B_m} \right)_{\text{mixture}} = \left(\sum_{j=1}^{10} X_j \sqrt{\frac{A_{jj}}{B_{jj}}} \right)^2,$$

where A_{jj} and B_{jj} are the contribution of group j in A_m and B_m and X_j is its mole fraction, in the hypothetical mixture. Note that X_j may be calculated from the following expression:

$$X_j = \frac{\text{total number of component } j}{\sum_{i=1}^{\text{total number of component}} n_i} x_i \times \frac{n_j}{n_i}, \quad (15)$$

where x_i and n_i are the mole fraction and number of carbon atoms of component i in the mixture and n_j is the number of group j in component i .

Using the calculated values of A_m and B_m parameters along with (3), the density of a mixture at any pressure, temperature, and mole fraction may be calculated. We have used this approach to calculate the density of binary mixture of *n*-butylamine with ethanol, 1-propanol, and 1-butanol at different pressures and mole fractions. Some of the results are given in Table 4. An inspection of Table 4 indicates that the strength of the intermolecular hydrogen bonding (between

TABLE 4: AAD and D_{max} of the calculated density for binary mixture of different 1-alkanols (1) + 1-butylamine (2), in a pressure range from 0.1 to 33.9 MPa and different mole fractions using the calculated values of A_m and B_m parameters along with (3) at 298.15 K.

Binary mixture	x_1	ADD	D_{max}
(a) Ethanol (1) + 1-butylamine (2)	0.1973	1.81	3.06
	0.4013	1.97	3.19
	0.6102	2.09	3.32
	0.7996	2.27	3.45
(b) 1-Propanol (1) + 1-butylamine (2)	0.2096	1.51	2.09
	0.4001	1.79	2.26
	0.5980	1.87	2.55
	0.7977	1.93	2.71
(c) 1-Butanol (1) + 1-butylamine (2)	0.2011	1.45	1.79
	0.3957	1.61	1.91
	0.5986	1.79	2.13
	0.7975	1.85	2.27

the hydroxyl and the amine groups) is an important factor influencing the predicted density deviation of these mixtures. The deviation is remarkable for the mixture with ethanol and decreases, as the chain length of the alkanol molecule increases. This result corresponds to heats of mixing study in these systems. Measured heats of mixing values at 298.15 K are -2915 , -2870 , and -2705 J·mol $^{-1}$ for the mixtures of *n*-butylamine with ethanol, 1-propanol, and 1-butanol, respectively [24].

3.4. Calculation of Other Properties. Having an accurate EOS, the MLIR for different chemicals, we may expect to make use of it to calculate other properties such as isothermal compressibility (κ_T) and thermal expansion coefficient (α_p) via the GCM. We may use the calculated values of A_m and B_m parameters along with an appropriate derivative of pressure to obtain these properties at any thermodynamic state. For instance, the isothermal compressibility may be calculated using the following expression:

$$\kappa_T = \frac{1}{n\rho R + 3n^3\rho^3RTA_m + 5n^5\rho^5RTB_m}. \quad (16)$$

We have calculated A_m and B_m parameters for pentylamine, hexylamine, heptylamine, 2-aminobutane and 2-aminooctane, at different temperatures: 303.15, 323.15, and 343.15 K as explained before along with (16) to calculate κ_T for these compounds at different pressures, see Table 5. The average percentage error for κ_T was found to be less than 2.11.

4. Conclusions

In this work the MLIR equation of state is extended to primary alkylamines by group contribution method. To do so, the linearity of $(Z/n-1)v^2$ against ρ^2 was investigated for aliphatic esters. Experimental pVT data for different aliphatic esters were used to check the linearity of $(Z/n-1)v^2$ against ρ^2 for different isotherms (Figure 1). As shown in this figure, the

TABLE 5: AAD and D_{\max} of the calculated isothermal compressibility of different alkylamines at given temperatures and in a pressure range from 0.1 to 140 MPa using the calculated values of A_m and B_m parameters along with (16).

fluid	T , K	AAD	D_{\max}
1-Hexylamine	303.15	1.95	3.02
	323.15	1.89	2.86
	343.15	1.71	2.56
1-Heptylamine	303.15	1.87	2.82
	323.15	1.66	2.58
	343.15	1.59	2.31
2-Aminooctane	303.15	2.11	3.45
	323.15	1.98	3.26
	343.15	1.89	2.98

linearity holds quite well with the correlation coefficient, $R^2 \geq 0.9994$, for these fluids over a wide range of temperatures and pressures. The temperature dependencies of the intercept and slope parameters of MLIR-EOS were also determined for these fluids.

In order to predict the MLIR parameters for primary alkylamines via the group contribution method, we had to use appropriate compounds to obtain the contribution of primary alkylamine functional groups in the MLIR parameters. Three basic compounds, namely, propane, *n*-butane, and cyclohexane were used to obtain the contribution of methyl and methylene groups and 1-pentylamine and 2-aminopentane for contribution of $-\text{CH}_2\text{NH}_2$, >CHNH_2 groups in the MLIR parameters. Having the contribution of constituent groups to the EOS parameters along with dependencies of the LIR parameters to system composition, the MLIR parameters for each compound were calculated. Using the calculated EOS parameters along with the MLIR, the densities of these series of compounds were calculated at different pressures and temperatures, with the average percentage error less than 1.54 (Table 3). Furthermore, we have used the group contribution method to predict the MLIR parameters for mixtures (14). Using the calculated values of A_m and B_m parameters along with (3), the density of mixtures at any pressure, temperature, and mole fraction may be calculated (Table 4). Thus, using the parameters of (5) for the basic compounds, we may calculate the density of pure or mixed fluids even for temperatures for which experimental data of basic compounds are not available.

We may use the calculated values of A_m and B_m parameters along with an appropriate pressure derivative, in order to obtain other properties at any thermodynamic state. The isothermal compressibility at different pressures was calculated for different alkylamines and compared with the literature values (Table 5).

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