Extension of Linear Isotherm Regularity to Long Chain Alkanes

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ABSTRACT: *In this work, we consider each normal alkane as a hypothetical mixture of methyl and methylene groups, in which the interaction potential of each pair is assumed to be the average effective pair potential. Then, the LIR equation of state (EOS) is extended for such a hypothetical mixture. Also, three basic compounds, namely, propane, n-butane and cyclohexane, are used to obtain the contribution of each carbonic group in the EOS parameters. Using the calculated EOS parameters along with the modified EOS, the density of n-alkanes and their mixtures at different pressures and temperatures are calculated. The average percentage error in density is found to be less than 1.5% for both the pure normal alkanes and their binary mixtures.*

KEY WORDS: *Equation of state, Group contribution method, Average effective pair potential*

INTRODUCTION

In the study of a chemical, biochemical and environmental system, knowledge of a variety of physical and chemical properties of pure compounds and mixtures under specified conditions is required. It is not always possible, however, to find reliable experimental values of these properties for the compounds of interest in the literature, nor is it practical to measure such properties as the need arises [1].

The method of group contribution has been a powerful tool for predicting the physical and thermodynamic properties from the chemical composition and state of matter. This method is easy, quick, and reliable method for predicting the physical and thermodynamic properties such as the critical parameters [1], acentric factor [2-3], heat of vaporization [4-6]. The main reason for making use of group contribution method is as follows: whereas there are thousands of chemical compounds of interest to science and technology, the number of structural and functional groups which constitute all these compounds are very much smaller. The basic assumption is made that the physical property of a material (gas, liquid, or solid) is a sum of contributions of that property for all basic

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functional groups. The fundamental assumption is the additivity of these contributions.

The development and use of the group contribution methods proceed in two stages:

1. The properties of some known materials are correlated with their chemical structure in order to identify the additive molar quantities (AMQ) of the basic groups.

2. The properties of new materials are estimated through direct addition of the AMQ of the constituent chemical groups.

Therefore the contribution of a given group in a molecule is assumed to be the same as that in another molecule. Nevertheless the definition of constituent "group" is a very subjective matter. Recently, this method is used to obtain the parameters of a few equations of state. Majeed and Wagner [7] developed the parameters of the modified Flory-Huggins theory to account for the molecular size difference. Skjold-Jorgensen [8] developed a group contribution equation of state (GC-EOS) by employing a Carnahan-Starling-van der Waals equation form. Georgeton and Teja [9] developed an GC-EOS using a modified form for the perturbed hard chain equation of state. Pults et al. [10] developed chain-of-rotator group contribution equation of state.

The purpose of this work is to extend the LIR equation of state to long chain organic compounds using the group contribution method (GCM). In the LIR equation of state which has been derived on the basis of the concept of the effective pair potential, the mathematical form of the average effective pair potential (AEPP) function is considered to be the Lennard-Jones (12,6), the same as that for the isolated pair potential, except that the effective pair potential parameters in dense fluid ($\rho > \rho_B$ where ρ_B is the Boyle density) depend on temperature [11-12]. Since this potential function is appropriate for the spherical-symmetrical molecules then nonspherical molecules, such as long chain organic compounds, show some deviation from the linear behaviour of the LIR.

Linear Isotherm Regularity (LIR) 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 dense fluids and considering only the nearest neighbor

interactions, linear isothermal regularity (LIR) was derived from the exact thermodynamic relations as [13]

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

where $Z = p/\rho RT$ is the compressibility factor and $\rho = 1/v$ is the molar density and A and B are the temperature dependent parameters. On the basis of a simple model that mimics the linearity, the temperature dependencies of the LIR parameters were found as follows

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

$$B = \frac{B_1}{RT} \tag{3}$$

where A_1 and B_1 are related to the attraction and repulsion terms of the average effective pair potential and A_2 is related to the nonideal thermal pressure. The LIR 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 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 [14]. Furthermore, the LIR has been used to predict much experimentally known regularities for dense pure fluids and fluid mixtures [15-16].

To investigate such linearity for different linear alkanes from C_2 to C_{20} we have used the experimental *pvT* data for these fluids. We have found that if one of hydrogen atom of methane is replaced with alkyl group, the deviation from the linearity is introduced and the deviation is increased with the chain length, see Fig. 1 and Table 1. Such a behavior is expected, because of the mathematical form of the AEPP function is assumed to be the LJ (12,6), the potential function which is appropriate for the spherical-symmetrical molecules, then 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.
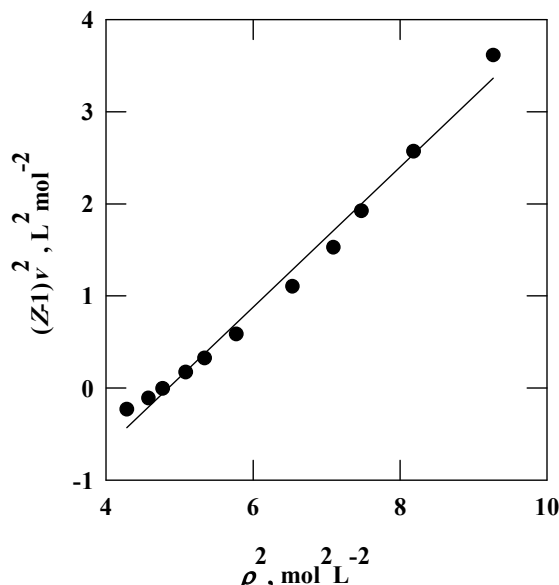
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Fig 1: The deviation from the linear behavior of the LIR for n-eicosane at 573.15 K [18].

Modified LIR Equation of State

We may consider a normal alkane fluid ($CH_3 - (CH_2)_{n-2} - CH_3$) as a hypothetical mixture of methyl and methylene groups, in which the interaction potential of each pair is assumed to be the average effective pair potential. Then, according to the van der Waals one-fluid approximation, the LIR equation of state will be appropriate for such a mixture, but the new equation of state parameters depends on the group compositions in the mixture (the length of the chain, for this case). Hence, if the molar density of the alkane 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 reduces to:

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

or

$$\left(\frac{p}{n\rho RT}-1\right)\Big/n^2\rho^2 = A_m + B_m n^2\rho^2 \qquad (4)$$

where A_m and B_m are the new EOS parameters per each carbonic group and

$$A' = A_m n^2 \qquad (5)$$

$$B' = B_m n^4 \qquad (6)$$

EXPERIMENTAL TESTS

First using the experimental *pvT* data for a linear alkane, accuracy of the new EOS may be investigated by plotting *(Z/n -1) v²* versus ρ^2 for any isotherm of that alkane. We have found a quite good linearity for each isotherm of all n-alkanes with $1 \leq n \leq 20$, in such a way that the correlation coefficient, R^2, is greater than or equal to 0.9994, results are summarized in Table 1. As shown in this table, the isotherm of Eq. (4) shows a better linearity than the original LIR, specially for the longer chains, compare the value of R^2 of LIR with that for Eq. (4) given in Table 1. The fact that the LJ (12, 6) potential is more appropriate for spherical molecules, such a result is expected. The line for each isotherm was used to determine A' (from the intercept) and B' (from the slope) to calculate A_m and B_m for that isotherm from Eqs. (5) and (6). Furthermore the calculated values of A_m and B_m were plotted versus *1/T* to obtain the temperature dependencies of the parameters for the new equation of state and found that the obtained values of A_m and B_m are linear with *1/T* as

$$A_m = \frac{a_1}{RT} + a_2 \qquad (7)$$

$$B_m = \frac{b_1}{RT} + b_2 \qquad (8)$$

just the same as the LIR parameters. The calculated values of a_1/R, a_2, b_1/R, and b_2 are given in Table 2 for each *n*-alkanes. Since with increase of the chain length, the contribution of the methyl group decreases, while that increases for the methylene group, we expect that a_1/R and b_1/R approach to limiting values when the chain length becomes large. This expectation is in accordance with the results given in Table 2.

Therefore having the values of the parameters given in Table 2 and using Eqs. (7) and (8), the values of A_m and B_m of a chain may be calculated at any temperature. Then having the calculated A_m and B_m parameters for an *n*-alkanes and using Eqs. (5) and (6) along with Eq. (4), the density of that alkane at different pressures and temperatures can be calculated.

The next step is to predict the new EOS parameters for the alkanes using the GCM. To do so, we have assumed that each normal alkane fluid as a hypothetical mixture of three carbonic groups: two methyl groups at the ends of the chain (1), two methylene groups each

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Table 1: Comparison of linear correlations of the LIR and the New EOS, eq. 4, for an isotherm of

n-alkane for given pressure and density ranges.

fluid	T, K	Δp, MPa	$\Delta\rho$, mol L^{-1}	R^2 for LIR	R^2 for eq (4)	Ref.
CH_4	160	2-30	21.08-24.34	1.0000	1.0000	[19]
C_2H_6	300	16-40	13.58-15.37	0.9995	0.9999	[19]
C_3H_8	300	1-100	11.10-13.70	0.9987	1.0000	[19]
C_4H_{10}	300	1-70	9.84-11.04	0.9989	0.9999	[19]
C_5H_{12}	303.15	0.1-251.6	8.56-10.45	0.9988	0.9998	[20]
C_6H_{14}	298.15	0.1-533.8	7.62-9.75	0.9976	0.9998	[21]
C_7H_{16}	303.15	0.1-240.98	6.75-7.88	0.9989	0.9997	[22]
C_8H_{18}	298.03	0.1-479.5	6.13-7.55	0.9979	0.9995	[23]
C_9H_{20}	303.15	20-620	5.70-6.98	0.9983	0.9996	[17]
$C_{10}H_{22}$	303.15	0.1-238.8	5.09-5.82	0.9984	0.9997	[20]
$C_{11}H_{24}$	373.15	5-300	4.36-5.55	0.9941	0.9994	[18]
$C_{12}H_{26}$	348.16	0.1-441.9	4.17-5.11	0.9981	0.9996	[23]
$C_{13}H_{28}$	373.15	0.1-500	3.80-4.77	0.9943	0.9994	[18]
$C_{15}H_{32}$	352.55	0.1-275.6	3.43-3.97	0.9986	0.9994	[24]
$C_{16}H_{34}$	348.15	0.1-290	3.26-3.78	0.9971	0.9996	[21]
$C_{17}H_{36}$	473.15	5-500	2.71-3.63	0.9922	0.9995	[18]
$C_{18}H_{38}$	343.15	0.1-149.55	2.95-3.24	0.9988	0.9996	[25]
$C_{19}H_{40}$	353.15	0.1-149.55	2.78-3.07	0.9969	0.9996	[25]
$C_{20}H_{42}$	373.15	5-500	2.61-3.19	0.9953	0.9996	[18]
C_6H_{12}	323.15	0.1-80.1	8.93-9.62	0.9986	0.9998	[26]

Table 2: The calculated values of a_1/R , a_2, b_1/R, and b_2 for linear alkanes and cyclohexane.

n	$(b_1/R)\times10^4$ (L^4 mol^{-4} K)	$b_2\times10^7$ (L^4 mol^{-4})	a_1/R (L^2 mol^{-2} K)	$a_2\times10^4$ (L^2 mol^{-2})	Ref.
2	4.580	9.353	-1.152	1.021	[19]
3	3.330	4.677	-0.982	6.057	[19]
4	2.830	1.810	-0.911	6.570	[19]
5	2.326	2.093	-0.803	3.098	[20]
6	2.403	1.675	-0.802	1.930	[21]
7	2.186	1.258	-0.798	2.870	[22]
8	2.051	1.402	-0.804	2.730	[23]
9	2.030	1.093	-0.764	1.686	[17]
10	1.483	2.345	-0.654	-1.034	[20]
11	1.395	2.035	-0.588	-1.988	[18]
12	1.364	2.345	-0.626	-1.795	[23]
13	1.361	1.875	-0.561	-2.950	[18]
15	1.367	2.077	-0.642	-1.395	[24]
16	1.347	1.839	-0.626	-1.267	[21]
17	1.364	1.552	-0.546	-2.700	[18]
18	1.389	1.449	-0.638	-0.471	[25]
19	1.386	1.406	-0.623	-0.873	[25]
20	1.355	1.289	-0.552	-2.540	[18]
C_6H_{12}	1.006	1.323	-0.532	0.2458	[26]

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attached to a methyl group (2), and *n*-4 methylene groups at the middle of the chain (3). Using three basic compounds, namely, propane, *n*-butane, and cyclohexane we have found the contributions of these carbonic groups in the new EOS parameters.

Carbonic Group Contributions in A_m and B_m Parameters

First we consider the temperatures at which the experimental data for three basic compounds are available. The contribution of two methyl (carbonic 1) and two terminal methylene groups (carbonic 2) in A_m and B_m parameters are obtained from two basic compounds, propane and *n*-butane. Since the dependencies of the LIR parameters to system composition have already been derived [13], by assuming the random distribution and using the experimental values of A_m and B_m for propane and *n*-butane, the contributions of the methyl and terminal methylene groups may be obtained from the following expressions

$$\begin{cases} (B_m)_{\text{Propane}} = \left(\frac{2}{3}\sqrt{B_{11}} + \frac{1}{3}\sqrt{B_{22}}\right)^2 \\ (B_m)_{\text{n-Butane}} = \left(\frac{2}{4}\sqrt{B_{11}} + \frac{2}{4}\sqrt{B_{22}}\right)^2 \end{cases} \quad (9)$$

$$\begin{cases} \left(\frac{A_m}{B_m}\right)_{\text{Propane}} = \left(\frac{2}{3}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{1}{3}\sqrt{\frac{A_{22}}{B_{22}}}\right)^2 \\ \left(\frac{A_m}{B_m}\right)_{\text{n-Butane}} = \left(\frac{2}{4}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{4}\sqrt{\frac{A_{22}}{B_{22}}}\right)^2 \end{cases} \quad (10)$$

where A_{11} and B_{11} are the contribution of methyle groups in A_m and B_m and A_{22} and B_{22} are those for the terminal methylene groups, respectively. Note that the 2/3 and 1/3 coefficients in former expressions are the fraction of carbonic groups (1) and (2) respectively in propane, and the 2/4 in the others are for *n*-butane. The contributions of a middle methylene group (carbonic 3) in A_m and B_m parameters may be related to those of CH_2 in cyclohexane. Since a methylene group in cyclohexane and a middle methylene group in a linear alkane is expected to have a similar interactions with their neighboring carbonic groups (both have two covalence bonds with two CH_2 groups), we may assumed that their contributions in A_m and B_m are the same. Therefore, using the experimental *pvT* data for cyclohexane [26] we have plotted $(Z/n - 1)\,v^2$ against ρ^2 at temperature of

interest to obtain the A_m and B_m parameters at that temperature, using Eqs. (5) and (6). If A_{33} and B_{33} are the contributions of the middle methylene groups (carbonic 3) in the A_m and B_m, then the values of A_m and B_m of cyclohexane are the same as A_{33} and B_{33} for the linear alkanes.

Having the contributions of three constituting groups in the EOS parameters along with dependencies of the LIR parameters to system composition, the new EOS parameters for each *n*-alkane may be predicted from the following expressions

$$(B_m)_{\text{Alkane}} = \left(x_1\sqrt{B_{11}} + x_2\sqrt{B_{22}} + x_3\sqrt{B_{33}}\right)^2 \quad (11)$$

$$\left(\frac{A_m}{B_m}\right)_{\text{Alkane}} = \left(x_1\sqrt{\frac{A_{11}}{B_{11}}} + x_2\sqrt{\frac{A_{22}}{B_{22}}} + x_3\sqrt{\frac{A_{33}}{B_{33}}}\right)^2 \quad (12)$$

where x_1, x_2, and x_3 are the mole fraction of carbonic group (1), (2), and (3) respectively, which may be obtained from the following expressions

$$x_1 = \frac{2}{n} \qquad\qquad x_2 = \frac{2}{n} \qquad\qquad x_3 = \frac{n-4}{n}$$

Using the calculated equation of state parameters along with Eq. (4), the density of normal alkane at any pressure and temperature of interest may be calculated. We have calculated the contribution of three carbonic groups (1), (2), and (3) at 300 K (in which the experimental *pvT* data for three basic compounds are available) as follows

$$\begin{cases} B_{11} = 2.716 \times 10^{-6}\ \text{L}^4\text{mol}^{-4} \\ B_{22} = 2.228 \times 10^{-7}\ \text{L}^4\text{mol}^{-4} \end{cases}$$

$$\begin{cases} \dfrac{A_{11}}{B_{11}} = 838.1\,\text{mol}^2\text{L}^{-2} \\ \dfrac{A_{22}}{B_{22}} = 3981.6\,\text{mol}^2\text{L}^{-2} \end{cases}$$

$$\begin{cases} \dfrac{A_m}{B_m} = \dfrac{A_{33}}{B_{33}} = 3772.5\,\text{mol}^2\text{L}^{-2} \\ B_m = 4.676 \times 10^{-7}\ \text{L}^4\text{mol}^{-4} \end{cases}$$

Having the contributions of three constituent groups in the EOS parameters along with Eqs. (11) and (12), the A_m and B_m parameters for each *n*-alkanes were calculated. Then using the calculated A_m and B_m parameters along with Eq. (4), the density of the normal alkanes at different pressures and 300 K has been calculated, for *n*-pentane up to *n*-tridecane, see Table 3. The average percentage error in density was obtained to be lower than 1.5%.

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Table 3: The experimental pvT data for three basic compounds, namely propane, normale butane, and cyclohexane at 300 K
were used to calculate the density of other normal alkanes at the same temperature for given pressure range (Δp).

fluid	$(A_m)_{cal} \times 10^3$, $L^2 mol^{-2}$	$(B_m)_{cal} \times 10^7$, $L^4 mol^{-4}$	Δp, MPa	$100\left(\left|\Delta\rho\right|/\rho\right)_{av}^a$	Ref.
n-C_5H_{12}	-2.338	9.698	0.1-251.30	0.49(0.66)	[20]
n-C_6H_{14}	-2.286	8.735	0.1-533.8	0.54(0.82)	[2]
n-C_7H_{16}	-2.237	8.078	0.1-240.98	0.38(0.60)	[22]
n-C_8H_{18}	-2.194	7.602	0.1-479.50	0.82(1.66)	[23]
n-C_9H_{20}	-2.157	7.242	20-620	0.57(1.38)	[17]
n-$C_{10}H_{22}$	-2.126	6.961	0.1-238.79	1.50(2.18)	[20]
n-$C_{11}H_{24}$	-2.098	6.734	5-500	1.03(1.55)	[18]
n-$C_{12}H_{26}$	-2.075	6.548	0.1-163.50	1.21(1.92)	[23]
n-$C_{13}H_{28}$	-2.054	6.393	5-500	0.93(1.52)	[18]

(a) Maximum deviations are given in parentheses.

Table 4: The same as Table 3 at 348 K, for which no experimental pvT data is reported for three basic compounds.

fluid	$(A_m)_{cal} \times 10^3$, $L^2 mol^{-2}$	$(B_m)_{cal} \times 10^7$, $L^4 mol^{-4}$	Δp, MPa	$100\left(\left|\Delta\rho\right|/\rho\right)_{av}^a$	Ref.
n-C_6H_{14}	-2.022	8.221	0.1-564.00	0.35(0.62)	[2]
n-C_7H_{16}	-1.969	7.558	0.2-248.88	1.17(1.70)	[22]
n-C_8H_{18}	-1.925	7.084	0.1-460.00	1.22(2.01)	[23]
n-$C_{10}H_{22}$	-1.856	6.446	0.24-254.37	0.99(1.93)	[20]
n-$C_{12}H_{26}$	-1.805	6.038	0.1-163.50	0.74(1.32)	[23]

(a) Maximum deviations are given in parentheses.

Contributions of Carbonic Groups in A_m and B_m at Other Temperatures

At temperatures for which the experimental data for three basic compounds are not available, we may use the values a_1/R, a_2, b_1/R, and b_2 for the basic compounds given in Table 2 along with Eqs. (5) and (6) to obtain A_m and B_m at any temperature. Having the values of A_m and B_m, the properties of the alkane chains can be calculated as explained before. We have calculated the contributions of three carbonic groups at 348 K at which the experimental pvT data for the basic compounds are not reported. Having the contributions of the constituent groups in the EOS parameters along with Eqs. (11) and (12), the values of A_m and B_m for each n-alkanes can be calculated. Then using the calculated values of A_m and B_m parameters along with Eq. (4), the density of normal alkanes at different pressures and 348 K has been calculated for n-hexane up to n-dodecane, see Table 4. The average percentage error in density was found to be lower than 1.3%.

Normal Alkane Binary Mixtures

The main purpose in this section is to investigate the accuracy of the new EOS for normal alkane binary mixtures. To do so, we may use the experimental pvT data for the linear alkane mixtures, to plot $(Z/n - 1)$ v^2 against ρ^2 for each isotherm. In fact we have found that the linearity is as good as that for the pure alkanes. Note that, an average value for the parameter n of a mixture may be defined as,

$$n_{mix} = \sum x_i n_i \qquad (13)$$

We may use the GCM to predict the new EOS parameters for linear alkane mixtures. The contributions of methyl (1), terminal methylene (2), and middle methylen (3) groups at the temperature of interest may be calculated from the same procedure explained in the previous section. Having the contributions of three constituent groups in the EOS parameters along with the dependencies of the LIR parameters to system

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composition, the new EOS parameters for a mixture may be calculated from the following expressions

$$\left(B_\text{m}\right)_\text{mixture} = \left(x_1\sqrt{B_{11}} + x_2\sqrt{B_{22}} + x_3\sqrt{B_{33}}\right)^2 \qquad (14)$$

$$\left(\frac{A_\text{m}}{B_\text{m}}\right)_\text{mixture} = \left(x_1\sqrt{\frac{A_{11}}{B_{11}}} + x_2\sqrt{\frac{A_{22}}{B_{22}}} + x_3\sqrt{\frac{A_{33}}{B_{33}}}\right)^2 \qquad (15)$$

where x_1, x_2, and x_3 are the mole fraction of carbonic group (1), (2), and (3) respectively. Of course the mole fraction of carbonic groups in a hypothetical mixture may be calculated from the following expressions

$$x_1 = \sum x_\text{i} \times \frac{2}{n_\text{i}} \qquad (16)$$

$$x_2 = \sum x_\text{i} \times \frac{2}{n_\text{i}} \qquad (17)$$

$$x_3 = \sum x_\text{i} \times \frac{n_\text{i} - 4}{n_\text{i}} \qquad (18)$$

Using the calculated values of A_m and B_m parameters along with Eq. (4), the density of mixtures at any pressure, temperature, and mole fraction can be calculated. We have used this approach to calculate the density of n-hexane+n-hexadecane at different pressures, temperatures, and mole fractions, see Table 5 .The average percentage error in density was obtained to be lower than 1.5%.

RESULTS AND DISCUSSION

The purpose of this work is to extend the LIR equation of state to long chain organic compounds by group contribution method. In the LIR equation of state which has been derived on the basis of the concept of the effective pair potential, the mathematical form of the average effective pair potential function is the same as that for the isolated pair as LJ (12, 6), with the exception that of the effective pair potential parameters in dense region ($\rho > \rho_\text{B}$ where ρ_B is Boyle density) depend on temperature. Since this potential function is appropriate for spherical-symmetric particles, then, nonsymmetric molecules such as long chain organic compounds show some deviations from the linear behavior of the LIR equation of state, see Table 1. But if we assume each organic compound as a hypothetical mixture of their constituent groups, in which the interaction potential of each pair of these groups is the AEPP. However, in such a hypothetical mixture both the covalent and van der

Waals interactions are exist, but we assume that such interactions are as the AEPP. Therefore, because of the strong covalent bonding in comparison with the LJ (6, 12), we expect that the average methyle-methyle and methylene-methylene interactions are large, compare to those in a real fluid in which only the van der Waals interactions are exist. According to the van der Waals one- fluid approximation, LIR equation of state will be appropriate for such a mixture, but new equation of state parameters depends on group composition of the hypothetical mixture. The linearity of (Z/n -1) v^2 vs ρ^2 has been checked with experimental data (Table 1) and the temperature dependencies of the intercept and slope parameters have been determined (Table 2). Also we have shown that (Z/n -1) v^2 varies linearly with ρ^2 for mixtures.

Then we have predicted the new EOS parameters for the linear alkanes using the group contribution method. To do so, we have been considered each normal alkane fluid as a hypothetical mixture of three carbonic groups (1), (2), and (3). Using three basic compounds, namely, propane, n-butane, and cyclohexane we have found the contributions of three carbonic groups in the new EOS parameters. Having the contribution of three constituent groups in the EOS parameters along with dependencies of the LIR parameters to system composition, the new EOS parameters for each alkane chain have been predicted from Eqs. (11) and (12). Using the calculated EOS parameters along with the new EOS, the density of n-alkanes and their mixtures at different pressures and temperatures are calculated (Tables 3, 4, and 5). The average percentage error in density was obtained to be lower than 1.5% for normal alkanes and alkane mixtures. The range of density and temperature over which the linearity of Eq. (4) is valid, is for $\rho > \rho_\text{B}$ ($\rho_\text{B} \approx 1.8\rho_C$, where ρ_C is the critical density) and temperature less than critical temperature of propane, because of the fact that the linearity of (Z/n -1) v^2 vs ρ^2 does not hold for propane as a basic compound, for temperatures higher that its critical temperature.

Finally, we expect that the linearity of (Z/n -1) v^2 vs ρ^2 to be held for other nonassociative compounds as well. The reason for such an expectation is the fact that the random distribution of molecules is reasonable, for such compounds.

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Table 5: The same as Table 3 for binary mixture of x n-C$_{16}$H$_{34}$ + (1-x) n-C$_6$H$_{14}$ at given temperatures and mole fractions [2].

x	T, K	$(A_m)_{cal} \times 10^3$, L^{2}mol^{-2}	$(B_m)_{cal} \times 10^7$, L^{4}mol^{-4}	Δp, MPa	$100 \left(|\Delta\rho| / \rho \right)_{av}^a$
0.2	300	-2.24	8.16	20.2-143.4	1.12(1.95)
0.8	300	-2.08	6.55	0.1-46.0	1.08(1.87)
0.2	323	-2.21	8.03	0.1-301.3	1.17(1.81)
0.4	323	-2.14	7.45	0.1-202.0	1.38(1.89)
0.8	323	-1.99	6.36	40.7-158.3	1.03(1.68)
0.2	348	-1.98	7.65	48.4-490.8	1.14(1.97)
0.4	348	-1.93	7.10	51.8-352.1	1.41(2.48)
0.8	348	-1.81	6.06	0.1-304.3	073(2.99)

(a) Maximum deviations are given in parentheses.

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