

Extension of linear isotherm regularity to long chain primary, secondary and tertiary alcohols, ketones and 1-carboxylic acids by group contribution method

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Abstract

In this work, the group contribution approach has been used in combination with the linear isotherm regularity (LIR) equation of state to estimate pvT properties of primary, secondary and tertiary alcohols, ketones and 1-carboxylic acid. In addition, the isothermal compressibility and thermal expansion coefficient of these compounds have been predicted. We assume each of these organic compounds 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. Then, the LIR equation of state (EOS) has been extended to such a hypothetical mixture. 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 functional groups, such as: 1-pentanol for the contribution of $-\text{CH}_2\text{OH}$, 2-pentanol for the contribution of $>\text{CHOH}$, 2-methyl-2-propanol (*t*-BuOH) for the contribution of $-\text{C}(\text{OH})_3$, 2-pentanone for the contribution of $>\text{C}=\text{O}$ and 1-pentanoic acid for the contribution of $-\text{COOH}$ groups. The calculated EOS parameters along with the modified EOS are then used to calculate the density of different compounds at different pressures and temperatures with the average percentage error less than 1.2. Also, the thermal expansion coefficient at different temperatures and isothermal compressibility at different pressures are calculated for some hydrocarbons with absolute percent deviation less than 1.0.

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1. Introduction

The base for design and simulation of many chemical processing units is a set of physical and thermodynamic properties of compounds in a process that undergoes some forms of transformation. It is not always possible, however, to find experimental values of the properties for the compounds of interest in the literature. Since, it is not practical to measure them as the need arises, estimation methods are generally

employed in this and other similar situations. The group contribution theories seem to be the most promising fields of the practical application of the thermodynamic models to describe the real systems. The main idea 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, the physical property of a compound (gas, liquid, or solid) is a sum of that property for all basic functional groups. Therefore, the fundamental assumption is the additivity of these contributions. This concept may be adapted to a great variety of thermodynamic models.

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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 for the constituent chemical groups.

Therefore the contribution of a given group in a molecule is assumed to be the same as that for other molecules. Nevertheless the definition of constituent “group” is a very subjective matter.

In the last 3 decades, this method is used to obtain the parameters of a few equations of state. In 1974, Nitta et al. published the first group contribution EOS [1] 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-Jorgensen [4] developed a group contribution equation of state (GC-EOS) by employing a Carnahan-Starling–van der Waals equation. Majeed and Wagner [5] developed the parameters of the modified Flory–Huggins theory to account for the molecular size difference. Georgeton and Teja [6] developed a GC-EOS using a modified form for the perturbed hard chain equation of state. Pults et al. [7] developed chain-of-rotator group contribution equation of state. Also, a few group contribution hole models and their numerous versions have been appeared [8–10].

Recently, the extension of the linear isotherm regularity to long chain *n*-alkanes is reported via group contribution method [11]. The purpose of this work is to examine the extension of the LIR equation of state to other long chain organic compounds. The LIR equation of state was derived on the basis of the concept of the average effective pair potential (AEPP), the mathematical form of which is considered to be the Lennard-Jones (12, 6), the same as that for the isolated pair potential, except that the AEPP parameters for dense fluids ($\rho > \rho_B$, where ρ_B is the Boyle density) depend on temperature [12]. Since such interaction potential function is appropriate for the spherical-symmetrical molecules then nonspherical molecules, such as long chain organic compounds, show some deviation from the linearity predicted by the LIR. The deviation becomes more significant when the chain is longer [11]. Hence, using the group contribution method, the LIR was modified for long chain normal alkanes.

2. Linear isotherm regularity equation of state

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

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

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. The AEPP is considered to be the interaction of the nearest neighbor molecule in which all of the longer range interactions are added to it, and also the effect of the medium in the charge distributions of two neighbor molecules is included. On the basis of a simple model that mimics the linearity, the temperature dependencies of the LIR parameters were found as follows:

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

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

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 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 many experimentally known regularities for dense pure fluids [15] and its extension to fluid mixtures [16].

To investigate such linearity for different *n*-alkanes, we used the experimental pVT data for these fluids. We found that if one hydrogen atom of methane is replaced with alkyl group, the deviation from the linearity is introduced and the deviation increases with the chain length, see 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 more appropriate for the spherical-symmetrical molecules, then nonspherical molecules, such as chain organic compounds, show deviation from the linearity of the LIR. Hence, using the group contribution method, the LIR may be modified for such fluids.

3. Modified LIR equation of state for long chain alkanes

We considered each normal alkane fluid ($\text{CH}_3\text{--}(\text{CH}_2)_{n-2}\text{--CH}_3$) 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. Note that the potential includes both physical and chemical (bond) interactions. Then, according to the van der Waals

Table 1

Comparison of linear correlations (R^2) of the LIR and the MLIR for a given isotherm of some selected n -alkanes for given pressure and density ranges

Fluid	T (K)	Δp (MPa)	$\Delta \rho$ (mol L $^{-1}$)	R^2 for LIR	R^2 for MLIR	Ref.
CH ₄	160	2–30	21.08–24.34	1.0000	1.0000	[17]
C ₂ H ₆	300	16–40	13.58–15.37	0.9995	0.9999	[17]
C ₃ H ₈	300	1–100	11.10–13.70	0.9987	1.0000	[17]
C ₄ H ₁₀	300	1–70	9.84–11.04	0.9989	0.9999	[17]
C ₉ H ₂₀	303.15	20–620	5.70–6.98	0.9983	0.9996	[18]
C ₁₅ H ₃₂	323.15	0.1–149.55	3.53–3.87	0.9973	0.9997	[19]
C ₁₇ H ₃₆	323.15	0.1–139.60	3.16–3.44	0.9964	0.9996	[19]
C ₁₉ H ₄₀	353.15	0.1–149.55	2.78–3.07	0.9969	0.9996	[20]

one-fluid approximation, the LIR equation of state would be appropriate for such a mixture, but the new equation of state parameters depend 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

$$\frac{\left(\frac{p}{n\rho RT} - 1\right)}{n^2\rho^2} = A_m + B_m n^2 \rho^2 \Rightarrow \frac{\left(\frac{Z}{n} - 1\right)}{\rho^2} = A' + B' \rho^2 \quad (4)$$

which we shall refer to it as the modified linear isotherm regularity (MLIR) from now on. Like the LIR, the MLIR is expected to be valid for dense fluids only ($\rho > \rho_B$). Due to strong attractions (chemical bonds) among neighboring groups, Z/n appears instead of compressibility factor in Eq. (4). Such appearance is expected because of the fact that attraction force reduces p and Z . Such reduction increases with the number of chemical bond among chemical groups. Owing to the fact that the number of bonds is equal to $(n - 1)$ for linear molecules, then p and Z both reduce with n .

The A_m and B_m are the MLIR parameters per each carbonic group and

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

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

For all n -alkanes with $1 \leq n \leq 20$, we have 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, see Table 1 and also Table 1 in ref. [11]. 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 MLIR parameters. Also we found that the obtained values of A_m and B_m are linear with respect to $1/T$ just the same as those for the LIR parameters.

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

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

Then we predicted the MLIR parameters (A_m, B_m) for the linear alkanes using the group contribution method. To do so, we considered 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 attached to a methyl group (2), and $n - 4$ methylene groups at the middle of the chain (3). The contributions of two methyl (carbonic 1) and two terminal methylene groups (carbonic 2) in A_m and B_m parameters were obtained from two basic compounds, namely propane and n -butane. Since the dependencies of the LIR parameters to system composition have already been derived [14], 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:

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

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

where A_{11} and B_{11} are the contributions of methyle groups in A_m and B_m and A_{22} and B_{22} are those for the terminal methylene groups, respectively. The unlike parameters are taken as the mean geometric of the like parameters, i.e.

$$B_{12} = \sqrt{B_{11}B_{22}} \text{ and } \frac{A_{12}}{B_{12}} = \sqrt{\left(\frac{A_{11}}{B_{11}}\right)\left(\frac{A_{22}}{B_{22}}\right)}. \text{ Note that the}$$

2/3 and 1/3 coefficients in 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 (carbonic 3) in A_m and B_m parameters were related to those of CH₂ in cyclohexane. 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.

Table 2

The calculated values of a_1/R , a_2 , b_1/R and b_2 for propane, *n*-butane, cyclohexane, 1-pentanol, 2-pentanol, *t*-BuOH, 2-pentanone and 1-pentanoic acid

Basic compound	$\frac{b_1}{R} \times 10^4$ (L ⁴ mol ⁻⁴ K)	$b_2 \times 10^7$ (L ⁴ mol ⁻⁴)	$\frac{a_1}{R}$ (L ² mol ⁻² K)	$a_2 \times 10^4$ (L ² mol ⁻²)	Ref.
Propane	3.330	4.677	-0.982	6.057	[17]
<i>n</i> -Butane	2.830	1.810	-0.911	6.570	[17]
Cyclohexane	1.006	1.323	-0.532	0.2458	[21]
1-Pentanol	3.559	1.605	-1.139	4.759	[22]
2-Pentanol	4.914	-3.473	-1.582	21.24	[22]
<i>t</i> -BuOH	3.285	5.264	-1.098	2.289	[23]
2-Pentanone	3.549	-0.329	-1.207	10.624	[24]
1-Pentanoic acid	3.860	-0.0648	-1.191	8.182	[25]

At temperatures for which the experimental data for three basic compounds are available, we may use the experimental values of the A_m and B_m and at temperatures for which the experimental data for these 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. (7) and (8) to obtain values of the A_m and B_m at any temperature. As an example the contribution of different constituent groups, are summarized in Table 3 for 298.15 and 323.15 K. It is obvious that the values for other temperatures can be easily calculated via Eqs. (7) and (8) and those given for basic compounds like Eqs. (9) and (10).

Having the contributions of three constituent groups of the EOS parameters along with dependencies of the LIR parameters to system composition, the MLIR parameters for each *n*-alkane were predicted from the following expressions:

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

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

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:

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

Then using the calculated A_m and B_m parameters along with Eq. (4), the density of the normal alkanes and their

Table 3

The calculated values of $A_{ii} \times 10^3$ (L² mol⁻²) and $B_{ii} \times 10^6$ (L⁴ mol⁻⁴) ($i = 1, \dots, 8$) at 298.15 and 323.15 K

<i>i</i>	$A_{ii} \times 10^3$ (L ² mol ⁻²)		$B_{ii} \times 10^6$ (L ⁴ mol ⁻⁴)	
	$T = 298.15$ K	$T = 323.15$ K	$T = 298.15$ K	$T = 323.15$ K
1	2.276	2.524	2.716	2.409
2	0.887	1.201	0.228	0.323
3	1.764	1.622	0.468	0.444
4	6.580	4.627	6.462	4.657
5	8.544	4.368	2.140	1.381
6	0.293	0.693	0.031	0.098
7	6.247	3.471	1.286	0.850
8	5.754	3.693	5.788	3.901

binary mixtures at different pressures and temperatures was calculated with the average percentage error less than 1.5, see Tables 3–5 in ref. [11].

The range of density and temperature over which the linearity of Eq. (4) is valid, is $\rho > \rho_B$ ($\rho_B \approx 1.8\rho_c$, where ρ_c is the critical density) and temperature less than critical temperature of propane (369.7 K), because of the fact that the linearity of A_m and B_m versus $1/T$ do not hold for propane (as basic compound) for temperatures higher than its critical temperature. Note that such a limitation has nothing to do with the group contribution approach presented in this work, based on van der Waals one-fluid approximation. It is merely due to the nonlinearity of A_m and B_m versus $1/T$ for dense supercritical isotherms of the chosen basic compound, i.e. propane. However, the temperature is so high that such limitation is not serious from application point of view for liquid density prediction.

4. Extension of LIR to long chain primary, secondary and tertiary alcohols

The main purpose in this section is to investigate the accuracy of the MLIR for different alcohols. To do so, we may use the experimental pvT data for the primary, secondary and tertiary alcohols, to plot $(Z/n - 1)v^2$ against ρ^2 for each isotherm. We have found that the linearity of each isotherm of Eq. (4) is better than that of the original LIR for different alcohols (Table 4).

The next step is to predict the MLIR parameters for different alcohols using the group contribution method. At first, we consider the primary alcohols (1-alkanol). Compare to a *n*-alkane, in a 1-alkanol ($\text{H}_3\text{C}-\text{CH}_2-(\text{CH}_2)_{n-4}-\text{CH}_2-\text{CH}_2\text{OH}$) one methyle group is replaced with a $-\text{CH}_2\text{OH}$ group. Hence, in 1-alkanols, we consider $-\text{CH}_2\text{OH}$ as a new functional group and use the values of A_m and B_m of 1-pentanol, to calculate the contribution of $-\text{CH}_2\text{OH}$ group (A_{44} , B_{44}) from the following expressions at temperature of interest:

$$(B_m)_{1\text{-pentanol}} = \left(\frac{1}{5} \sqrt{B_{11}} + \frac{2}{5} \sqrt{B_{22}} + \frac{1}{5} \sqrt{B_{33}} + \frac{1}{5} \sqrt{B_{44}} \right)^2 \quad (13)$$

Table 4

Comparison of linear correlations of the LIR and the MLIR for a given isotherm of different alcohols, ketones and 1-carboxylic acid for given pressure and density ranges

Fluid	T (K)	Δp (MPa)	$\Delta \rho$ (kg m ⁻³)	R^2 for LIR	R^2 for MLIR
1-Butanol ^a	298.15	0.1–205.9	805.5–897.3	0.9991	1.0000
1-Pentanol ^b	313.2	10–200	805.7–895.3	0.9989	0.9999
1-Hexanol ^c	298.15	0.1–40	815.7–839.4	0.9991	0.9999
1-Octanol ^c	323.15	0.1–40.18	804.6–829.5	0.9988	0.9998
1-Decanol ^c	323.15	0.1–40	809.4–833.2	0.9984	0.9997
1-Dodecanol ^c	323.15	0.1–40	812.9–836.1	0.9973	0.9996
1-Tetradecanol ^c	323.15	0.1–39.4	815.5–837.9	0.9964	0.9997
1-Hexadecanol ^c	348.15	0.1–40.1	800.2–824.9	0.9951	0.9995
2-Propanol ^a	298.15	0.1–173.4	781.9–871.4	0.9996	0.9999
2-Butanol ^a	298.15	0.1–206.5	802.4–896.9	0.9991	0.9999
2-Pentanol ^b	283.4	10–200	822.3–908.1	0.9989	0.9999
3-Pentanol ^b	283.6	10–200	836.6–919.0	0.9988	0.9999
<i>t</i> -BuOH ^a	323.15	0.1–68.4	754.1–808.5	0.9983	0.9997
2-Butanone ^d	298.15	2.69–281.66	787.6–915.3	0.9989	0.9999
2-Pentanone ^e	298.14	2.55–373.78	803.6–951.2	0.9973	0.9999
2-Hexanone ^e	298.14	2.55–323.42	809.0–938.7	0.9957	0.9998
1-Hexanoic acid ^f	298.15	0.1–25	921.2–941.2	0.9976	0.9997
1-Octanoic acid ^f	298.15	0.1–25	907.3–926.4	0.9951	0.9996
1-Decanoic acid ^g	353.15	0.1–9.0	853.9–861.1	0.9985	0.9994
1-Dodecanoic acid ^g	353.15	0.1–9.0	848.4–855.2	0.9981	0.9995

^a Ref [23].

^b Ref [22].

^c Ref [26].

^d Ref [27].

^e Ref [24].

^f Ref [25].

^g Ref [28].

$$\left(\frac{A_m}{B_m}\right)_{1\text{-pentanol}} = \left(\frac{1}{5}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5}\sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5}\sqrt{\frac{A_{33}}{B_{33}}} + \frac{1}{5}\sqrt{\frac{A_{44}}{B_{44}}}\right)^2 \quad (14)$$

Note that, mole fraction of the methyle, terminal methylene, middle methylene and $-\text{CH}_2\text{OH}$ groups in 1-pentanol is $\frac{1}{5}$, $\frac{2}{5}$, $\frac{1}{5}$, and $\frac{1}{5}$, respectively.

Similarly, in a *sec*-alcohol we consider >CHOH as a new functional group and use the values of A_m and B_m of 2-pentanol to calculate the contribution of >CHOH group (A_{55} , B_{55}) in the MLIR parameters at each temperature from the following expressions:

$$(B_m)_{2\text{-pentanol}} = \left(\frac{2}{5}\sqrt{B_{11}} + \frac{2}{5}\sqrt{B_{22}} + \frac{1}{5}\sqrt{B_{55}}\right)^2 \quad (15)$$

$$\left(\frac{A_m}{B_m}\right)_{2\text{-pentanol}} = \left(\frac{2}{5}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5}\sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5}\sqrt{\frac{A_{55}}{B_{55}}}\right)^2 \quad (16)$$

where the mole fractions of the methyle, terminal methylene and >CHOH groups in 2-pentanol are $\frac{2}{5}$, $\frac{2}{5}$, and $\frac{1}{5}$, respectively.

In a *ter*-alcohol, we consider $-\overset{|}{\text{C}}\text{OH}$ as a functional group and use the values of A_m and B_m of *t*-BuOH. Therefore, the contribution of $-\overset{|}{\text{C}}\text{OH}$ group (A_{66} , B_{66}) in the MLIR parameters at each temperature may be calculated from the following expressions:

$$(B_m)_{t\text{-BuOH}} = \left(\frac{3}{4}\sqrt{B_{11}} + \frac{1}{4}\sqrt{B_{66}}\right)^2 \quad (17)$$

$$\left(\frac{A_m}{B_m}\right)_{t\text{-BuOH}} = \left(\frac{3}{4}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{1}{4}\sqrt{\frac{A_{66}}{B_{66}}}\right)^2 \quad (18)$$

where the coefficients show the mole fractions of two different groups of *t*-BuOH.

We may use the values a_1/R , a_2 , b_1/R and b_2 for these basic compounds given in Table 2 along with Eqs. (7) and (8) to obtain values of the A_m and B_m at any temperature. We have calculated the contribution of three carbonic groups and the alcoholic functional groups at different temperatures: at 303.15 and 323.15 K for which no experimental pvT data is reported for propane, *n*-butane and cyclohexane and also at 298.15 and 348.15 K for which experimental pvT data is reported for propane, *n*-butane, cyclohexane and *t*-BuOH only. The contribution of different constituent groups is calculated and given in Table 3 for given temperatures. Having the contributions of the constituent groups in the MLIR

parameters along with dependencies of the LIR parameters to system composition, the values of A_m and B_m for each alcohols may be calculated from the following expressions:

$$(B_m)_{\text{alcohol}} = \left(x_1\sqrt{B_{11}} + x_2\sqrt{B_{22}} + x_3\sqrt{B_{33}} + x_4\sqrt{B_{44}} + x_5\sqrt{B_{55}} + x_6\sqrt{B_{66}} \right)^2 \quad (19)$$

$$\left(\frac{A_m}{B_m} \right)_{\text{alcohol}} = \left(x_1\sqrt{\frac{A_{11}}{B_{11}}} + x_2\sqrt{\frac{A_{22}}{B_{22}}} + x_3\sqrt{\frac{A_{33}}{B_{33}}} + x_4\sqrt{\frac{A_{44}}{B_{44}}} + x_5\sqrt{\frac{A_{55}}{B_{55}}} + x_6\sqrt{\frac{A_{66}}{B_{66}}} \right)^2 \quad (20)$$

where

$$x_i = \frac{\text{number of group } i}{\text{total number of groups}(n)} \quad (21)$$

Then we may use the calculated values of A_m and B_m parameters at temperature of interest along with Eq. (4) for a given alcohol, to obtain its density at different pressures. Some of the calculated results are given in Table 5. The average percentage error and its maximum value for density were found to be lower than 0.86 and 1.2, respectively.

5. Extension of LIR to long chain ketones

In this section, we investigate the accuracy of the MLIR for ketones by using experimental pVT data. We have again found a better linearity for $(Z/n - 1)v^2$ versus ρ^2 than $(Z - 1)v^2$ against ρ^2 for each isotherm of ketones, see Table 4.

The next step is to predict the MLIR parameters for the ketones using the GCM. This may be done similar to that for alcohol, but $>C=O$ is the new functional group rather than alcohol group. We have used the values of A_m and B_m of 2-pentanol, as a basic compound, to obtain the contribution of such a group (A_{77} , B_{77}) in the MLIR parameters at any

Table 5

Average absolute percent deviation of the calculated density for some alcohols, ketones and 1-carboxylic acids at given temperatures and for the given pressure range (Δp), using the calculated values of A_m and B_m parameters along with Eq. (4)

Fluid	T (K)	Δp (MPa)	100 ($ \Delta\rho /\rho$) _{av} ^a	Ref.
1-Propanol	298.15	0.1–206.9	0.76 (1.2)	[23]
1-Butanol	323.15	0.1–204.7	0.34 (0.70)	[23]
1-Hexanol	323.15	0.1–38.90	0.19 (0.21)	[26]
1-Heptanol	323.15	0.1–10	0.51 (0.68)	[29]
1-Octanol	323.15	0.1–40.18	0.85 (0.92)	[26]
1-Nonanol	323.15	0.1–10	0.83 (0.85)	[29]
1-Decanol	323.15	0.1–40	0.86 (0.99)	[26]
1-Dodecanol	323.15	0.1–40	0.79 (1.0)	[26]
1-Tetradecanol	323.15	0.1–39.40	0.80 (1.0)	[26]
1-Hexadecanol	348.15	0.1–40.1	0.74 (1.1)	[26]
2-Propanol	298.15	0.1–173.4	0.71 (1.2)	[23]
2-Butanol	298.15	0.1–206.5	0.53 (0.95)	[23]
3-Pentanol	313.2	10–200	0.69 (0.95)	[22]
1,2-Propanediol	298.15	0.1–60	0.85 (1.1)	[30]
1,2-Butanediol	298.15	0.1–60	0.47 (0.52)	[30]
1,3-Butanediol	303.15	0.1–274.4	0.34 (0.96)	[31]
1,5-Pentanediol	303.15	0.1–274.4	0.58 (1.0)	[31]
2-Methyl-2,4-pentanediol	303.15	0.1–274.4	0.55 (0.70)	[31]
2-Octanol	298.15	0.1–400	0.82 (1.28)	[32]
3-Octanol	298.15	0.1–400	0.82 (1.1)	[32]
2-Propanone	298.15	2.55–389.82	1.1 (1.5)	[33]
2-Butanone	298.15	2.69–281.66	0.23 (0.65)	[27]
2-Butanone	323.15	2.61–282.25	0.77 (1.0)	[27]
3-Pentanone	298.15	2.73–280.18	0.65 (0.99)	[34]
3-Pentanone	323.15	2.55–381.06	0.62 (0.83)	[34]
2-Hexanone	298.15	2.55–323.42	0.18 (0.29)	[24]
2-Hexanone	323.15	2.55–371.12	0.27 (0.45)	[24]
Cyclopentanone	303.15	0.1–400	0.47 (1.1)	[35]
1-Butanoic acid	323.15	0.1–25	0.89 (1.0)	[25]
1-Hexanoic acid	323.15	0.1–25	0.18 (0.30)	[25]
1-Heptanoic acid	323.15	0.1–25	0.65 (0.79)	[25]
1-Octanoic acid	323.15	0.1–25	0.56 (0.70)	[25]
1-Decanoic acid	353.15	0.1–9	0.33 (0.41)	[28]
1-Dodecanoic acid	353.15	0.1–9	0.30 (0.44)	[28]
1-Tetradecanoic acid	353.15	0.1–9	0.62 (0.69)	[28]
1-Hexadecanoic acid	353.15	0.1–9	0.82 (0.85)	[28]

^a Maximum deviations are given in parentheses.

given temperature. The contribution of $>C=O$ group may be calculated from the following expressions:

$$(B_m)_{2\text{-pentanone}} = \left(\frac{2}{5}\sqrt{B_{11}} + \frac{2}{5}\sqrt{B_{22}} + \frac{1}{5}\sqrt{B_{77}} \right)^2 \quad (22)$$

$$\left(\frac{A_m}{B_m} \right)_{2\text{-pentanone}} = \left(\frac{2}{5}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5}\sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5}\sqrt{\frac{A_{77}}{B_{77}}} \right)^2 \quad (23)$$

where the coefficients show the mole fractions of three different groups of 2-pentanone. The values for A_{ii} and B_{ii} are given in Table 3 for 298.15 and 323.15 K isotherms ($i = 1, \dots, 8$).

We have calculated the contribution of three carbonic and the $>C=O$ functional group at two different temperatures: specifically at 298.15 K for which experimental pvT data are reported for propane, *n*-butane, cyclohexane and 2-pentanone and also at 323.15 K for which experimental pvT data are not reported for propane, *n*-butane and cyclohexane (see Table 3). Such values for the constituent groups were used, along with

$$(B_m)_{\text{ketone}} = \left(x_1\sqrt{B_{11}} + x_2\sqrt{B_{22}} + x_3\sqrt{B_{33}} + x_7\sqrt{B_{77}} \right)^2 \quad (24)$$

$$\left(\frac{A_m}{B_m} \right)_{\text{ketone}} = \left(x_1\sqrt{\frac{A_{11}}{B_{11}}} + x_2\sqrt{\frac{A_{22}}{B_{22}}} + x_3\sqrt{\frac{A_{33}}{B_{33}}} + x_7\sqrt{\frac{A_{77}}{B_{77}}} \right)^2 \quad (25)$$

to calculate the MLIR parameters. We may then use the calculated values of A_m and B_m parameters along with Eq. (4) at 298.15 and 323.15 K for any ketone to calculate its density at any pressure. Some of the results are given in Table 5. The average percentage error and its maximum values in density are found to be less than 1.1 and 1.5, respectively.

6. Extension of LIR to straight chain 1-carboxylic acids

Similar investigation may be done to predict the MLIR parameters for the 1-carboxylic acids, using the group contribution method. In this case, we consider $-COOH$ as a new functional group and use the values of A_m and B_m of 1-pentanoic acid to obtain the contribution of $-COOH$ group (A_{88} , B_{88}) which may be calculated from the following expressions

$$(B_m)_{1\text{-pentanoic acid}} = \left(\frac{1}{5}\sqrt{B_{11}} + \frac{2}{5}\sqrt{B_{22}} + \frac{1}{5}\sqrt{B_{33}} + \frac{1}{5}\sqrt{B_{88}} \right)^2 \quad (26)$$

$$\left(\frac{A_m}{B_m} \right)_{1\text{-pentanoic acid}} = \left(\frac{1}{5}\sqrt{\frac{A_{11}}{B_{11}}} + \frac{2}{5}\sqrt{\frac{A_{22}}{B_{22}}} + \frac{1}{5}\sqrt{\frac{A_{33}}{B_{33}}} + \frac{1}{5}\sqrt{\frac{A_{88}}{B_{88}}} \right)^2 \quad (27)$$

where the mole fractions of the methyle, terminal methylene, middle methylene and $-COOH$ groups in 1-pentanoic acid are $\frac{1}{5}$, $\frac{2}{5}$, $\frac{1}{5}$ and $\frac{1}{5}$, respectively.

We have calculated the contributions of three carbonic groups and $-COOH$ functional group at two different temperatures: at 323.15 K for which experimental pvT data is only reported for 1-pentanoic acid and at 353.15 K for which no experimental pvT data are reported for propane, *n*-butane, cyclohexane and 1-pentanoic acid. Again, having the contributions of the constituent groups of the MLIR parameters along with dependencies of the LIR parameters to system composition, the values of A_m and B_m for each 1-carboxylic acid may be predicted from the following expressions:

$$(B_m)_{1\text{-carboxylic acid}} = \left(x_1\sqrt{B_{11}} + x_2\sqrt{B_{22}} + x_3\sqrt{B_{33}} + x_8\sqrt{B_{88}} \right)^2 \quad (28)$$

$$\left(\frac{A_m}{B_m} \right)_{1\text{-carboxylic acid}} = \left(x_1\sqrt{\frac{A_{11}}{B_{11}}} + x_2\sqrt{\frac{A_{22}}{B_{22}}} + x_3\sqrt{\frac{A_{33}}{B_{33}}} + x_8\sqrt{\frac{A_{88}}{B_{88}}} \right)^2 \quad (29)$$

Then, using the calculated values of A_m and B_m parameters at 323.15 and 353.15 K along with Eq. (4), the density of any 1-carboxylic acid may be calculated at different pressures. Some of the results are given in Table 5. The average percentage error and its maximum value for density were found to be lower than 0.89 and 1.0, respectively.

7. Extension to mixture

The main purpose in this section is to investigate the accuracy of the MLIR for mixtures of the mentioned compounds. To do so, we may use the experimental pvT data for binary mixture, to plot $(Z/n - 1)v^2$ against ρ^2 for each isotherm. Again, we have found that the linearity for a mixture is as good as those for its pure compounds. Note that, the average value of n for a mixture may be defined as

$$n_{\text{mix}} = \sum_{\text{number of component}} x_i n_i \quad (30)$$

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

We may use the GCM to predict the MLIR parameters for mixtures. The contributions of different groups at the

Table 6

Same as Table 4 for binary mixture of (a) x_1 n -C₆H₁₄ + x_2 1-hexanol, (b) x_1 n -C₆H₁₂ + x_2 n -C₈H₁₈, (c) x_1 n -C₆H₁₂ + x_2 n -C₁₂H₂₆ and (d) x_1 n -C₆H₁₂ + x_2 n -C₁₆H₃₄ at given temperatures and mole fractions

Mixture	x_1	T (K)	Δp (MPa)	$100(\Delta\rho/\rho)_{av}^a$	Ref.		
(a) x_1 n -C ₆ H ₁₄ + x_2 1-hexanol	0.25	303.15	0.09–49.91	0.11 (0.20)	[36]		
		323.15	0.1–50.32	0.11 (0.17)			
		353.15	0.49–49.85	0.69 (0.80)			
	0.599	303.15	0.27–49.69	0.38 (0.56)			
		323.15	0.51–50.36	0.66 (1.0)			
		353.15	0.53–50.15	0.61 (1.1)			
(b) x_1 n -C ₆ H ₁₂ + x_2 n -C ₈ H ₁₈	0.4	298.15	0.1–152.6	0.84 (1.1)	[21]		
		348.15	0.1–163	0.18 (0.37)			
	0.8	298.15	0.1–79.3	0.82 (0.93)			
		348.15	0.1–160.7	0.53 (0.74)			
	(c) x_1 n -C ₆ H ₁₂ + x_2 n -C ₁₂ H ₂₆	0.4	298.15	0.1–100.8		0.35 (0.72)	[21]
			348.15	0.1–159.9		0.81 (1.1)	
0.8		298.15	0.1–48.15	0.68 (0.82)			
		348.15	0.1–179.6	0.41 (0.81)			
(d) x_1 n -C ₆ H ₁₂ + x_2 n -C ₁₆ H ₃₄		0.4	298.15	0.1–50.3	0.96 (1.2)	[21]	
			348.15	0.1–180.8	0.77 (1.2)		
	0.8	298.15	0.1–40.6	0.24 (0.37)			
		348.15	0.1–150.4	0.52 (1.1)			

^a Maximum deviations are given in parentheses.

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:

$$(B_m)_{\text{mixture}} = \left(\sum_{j=1}^8 X_j \sqrt{B_{jj}} \right)^2 \quad (31)$$

$$\left(\frac{A_m}{B_m} \right)_{\text{mixture}} = \left(\sum_{j=1}^8 X_j \sqrt{\frac{A_{jj}}{B_{jj}}} \right)^2 \quad (32)$$

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:

$$X_j = \frac{\text{total number of component}}{\sum_{i=1}^{\text{total number of component}} x_i \times \frac{n_j}{n_i}} \quad (33)$$

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 Eq. (4), 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 -hexane with 1-hexanol and binary mixtures of cyclohexane with n -C₈H₁₈, n -C₁₂H₂₆ and n -C₁₆H₃₄ at different pressures, temperatures and mole fractions. Some of

the results are given in Table 6. The average percentage error and its maximum values for density were found to be lower than 0.96 and 1.2, respectively.

8. 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, bulk modulus and thermal expansion coefficient via the GCM. We may use the calculated values of A_m and B_m parameters along with an appropriate derivative of pressure

$$p = n\rho RT + n^3 \rho^3 RTA_m + n^5 \rho^5 RTB_m \quad (34)$$

to obtain other properties at any thermodynamic state. For instance, the isothermal compressibility (κ_T) or bulk modulus ($B = 1/\kappa_T$) may be calculated from the following expressions:

$$\kappa_T = \frac{1}{n\rho R + 3n^3 \rho^3 RTA_m + 5n^5 \rho^5 RTB_m} \quad (35)$$

$$B = \frac{1}{\kappa_T} = n\rho RT + 3n^3 \rho^3 RTA_m + 5n^5 \rho^5 RTB_m \quad (36)$$

and the thermal expansivity (α_p), may be calculated from the following expression:

$$\alpha_p = \frac{n\rho R + n^3 \rho^3 R(A_m + A'_m T) + n^5 \rho^5 R(B_m + B'_m T)}{n\rho RT + 3n^3 \rho^3 RTA_m + 5n^5 \rho^5 RTB_m} \quad (37)$$

Table 7

Average absolute percent deviation of the calculated isothermal compressibility of some *n*-alkanes at given temperatures and for given pressure range (Δp), using the calculated values of A_m and B_m parameters along with Eq. (35)

Fluid	T (K)	Δp (MPa)	$100(\Delta\kappa /\kappa)_{av}^a$	Ref.
<i>n</i> -C ₁₅ H ₃₂	323.15	0.1–149.55	0.82 (1.2)	[19]
<i>n</i> -C ₁₇ H ₃₆	323.15	0.1–139.60	0.85 (1.3)	[19]
<i>n</i> -C ₁₈ H ₃₈	323.15	0.1–89.80	0.95 (1.4)	[20]
<i>n</i> -C ₁₉ H ₄₀	323.15	0.1–79.85	0.99 (1.4)	[20]
<i>n</i> -C ₂₃ H ₄₈	353.15	0.1–149.55	1.0 (1.4)	[37]
<i>n</i> -C ₂₄ H ₅₀	353.15	0.1–129.65	1.1 (1.6)	[37]
<i>n</i> -C ₂₈ H ₅₈	353.15	0.1–79.85	1.2 (1.6)	[38]

^a Maximum deviations are given in parentheses.

where

$$A'_m = \frac{dA_m}{dT} = \frac{-a_1}{RT^2} \quad (38)$$

$$B'_m = \frac{dB_m}{dT} = \frac{-b_1}{RT^2} \quad (39)$$

We have calculated A_m and B_m parameters for *n*-C₁₅H₃₂, *n*-C₁₇H₃₆, *n*-C₁₈H₃₈ and *n*-C₁₉H₄₀ at 323.15 K and for *n*-C₂₃H₄₈, *n*-C₂₄H₅₀ and *n*-C₂₈H₅₈ at 353.15 K as explained before, along with Eq. (35), to calculate κ_T for these compounds at different pressures, see Table 7. The average percentage error and its maximum value for κ_T were found to be less than 1.2 and 1.6, respectively.

Table 8

The calculated values of α_p for some *n*-alkanes at 298.15 K, 323.15 K, and 348.15 K for atmospheric pressure, using the calculated values of A_m and B_m parameters along with Eq. (37)

Fluid	T (K)	$\alpha_p \times 10^3$ (K ⁻¹)	
		This work	Literature
<i>n</i> -Hexane	298.15	1.386	1.385 ^a , 1.391 ^b
	323.15	1.520	1.507 ^a , 1.513 ^b
	348.15	1.666	1.676 ^a , 1.650 ^b
<i>n</i> -Heptane	298.15	1.246	1.253 ^b
	323.15	1.329	1.321 ^b
	348.15	1.437	1.424 ^b
<i>n</i> -Octane	298.15	1.160	1.159 ^a , 1.165 ^b
	323.15	1.225	1.227 ^a , 1.232 ^b
	348.15	1.294	1.311 ^a , 1.303 ^b
<i>n</i> -Deane	298.15	1.056	1.050 ^c
	323.15	1.089	1.082 ^c
	348.15	1.142	1.132 ^c
<i>n</i> -Dodecane	298.15	0.9890	0.9800 ^c
	323.15	1.018	1.011 ^c
	348.15	1.044	1.047 ^c
<i>n</i> -Hexadecane	298.15	0.8857	0.9010 ^a , 0.8840 ^c
	323.15	0.9215	0.9190 ^a , 0.9160 ^c
	348.15	0.9589	0.9440 ^a , 0.9500 ^c
<i>n</i> -Eicosane	298.15	0.8311	0.8300 ^c
	323.15	0.8660	0.8590 ^c

^a Ref [39].

^b Ref [40].

^c Ref [41].

Also, we have used the calculated values of A_m and B_m parameters for *n*-alkanes at 298.15, 323.15 and 348.15 K along with Eq. (37), to calculate the thermal expansivity (α_p) of these compounds at atmospheric pressure, for which the results are given in Table 8. The calculated results are compared with those given in literature.

9. Conclusions

In this work the MLIR equation of state is extended to long chain organic compounds by group contribution method. In the LIR equation of state which was derived on the basis of the concept of the effective pair potential, the mathematical form of the potential function is the same as that for the isolated pair, namely the LJ (12, 6), with the exception that the potential parameters in dense region ($\rho > \rho_B$, where ρ_B is the Boyle density) depend on temperature. Since this potential function is appropriate for spherical-symmetric species, then, nonsymmetric molecules such as long chain organic compounds show some deviations from the LIR linearity. However, we have considered that an organic compound as a hypothetical mixture of their constituent groups, in which the interaction potential among any two groups is assumed to be the AEPP. In such a hypothetical mixture both chemical (covalent bond) and physical (van der Waals) interactions among constituent groups are taken into account. Therefore, because of the strong covalent bonding compared to the van der Waals interactions, we may expect that the average interaction between two constituent groups are large, compare to that in a real fluid in which the van der Waals interactions exists only. Based on the van der Waals one-fluid approximation, the LIR equation of state is used for such a hypothetical mixture, but the new equation of state parameters depend on group composition of the mixture. In our previous work [11], the MLIR was successfully applied for long chain normal alkanes and their binary mixtures, according to which $(Z/n - 1)v^2$ is linear against ρ^2 for each isotherm of the dense fluid. Also, the temperature dependencies of the intercept and slope parameters were determined. In this work, the linearity of $(Z/n - 1)v^2$ against ρ^2 has been investigated for other long chain compounds, namely alcohols, ketones, carboxylic acids. Experimental pVT data of different chain compounds were used to check the linearity of $(Z/n - 1)v^2$ against ρ^2 for different isotherms (Table 4). As shown in this table the linearity holds quite well, with the correlation coefficient, $R^2 \geq 0.9994$, for all chains.

In order to predict the MLIR parameters for the primary, secondary and tertiary alcohols, ketones and 1-carboxylic acids via the group contribution method, we should use appropriate compounds to obtain the contribution of different functional groups in the MLIR parameters. The compounds used for this purpose are 1-pentanol, 2-pentanol, *t*-BuOH, 2-pentanone and 1-pentanoic acid to obtain the contribution of $-\text{CH}_2\text{OH}$, $>\text{CHOH}$, $-\overset{|}{\underset{|}{\text{C}}}\text{OH}$, $>\text{C}=\text{O}$, and $-\text{COOH}$ groups

in the MLIR parameters, respectively. Also, three basic compounds, namely propane, *n*-butane and cyclohexane had been used to obtain the contribution of methyl and methylene groups. All basic compounds used to calculate the contributions of different functional groups are given in Table 2, for which the parameters of Eqs. (7) and (8) are given. Having the contribution of constituent groups in 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 density of these series of compounds are calculated at different pressures and temperatures, with the average percentage error less than 1.1 (Table 5). Furthermore, we have used the GCM to predict the MLIR parameters for mixtures (Eqs. (31) and (32)). 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 may be calculated with the average percentage error less than 0.69 (Table 6). Using the parameters of Eqs. (7) and (8) in Table 2, we may calculate the density of pure or mixed fluids even for temperatures for which experimental data of basic compounds are not available.

Having an accurate EOS, i.e. the MLIR, we may use it to calculate other fluid properties such as isothermal compressibility, bulk modulus and thermal expansion coefficient from the GCM. We may use the calculated values of A_m and B_m parameters along with an appropriate pressure derivative (Eqs. (35) and (37)), to obtain other properties at any thermodynamic state. The thermal expansion coefficient at different temperatures and isothermal compressibility at different pressures were calculated for different hydrocarbons and compared with the literature values (Tables 7 and 8).

We may also use the EOS to calculate other fluid properties which are related to EOS. For instance, the thermal pressure coefficient, density dependencies of internal energy and constant-volume heat capacity are related to EOS as follows:

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\alpha}{\kappa_T} = n\rho R + n^3\rho^3 R(A_m + A'_m T) + n^5\rho^5 R(B_m + B'_m T) \quad (40)$$

where A'_m and B'_m may be calculated from the Eqs. (38) and (39),

$$C_v = T \int \left(\frac{\partial^2 p}{\partial T^2}\right)_v dv + \text{constant} \quad (41)$$

$$E = T \int \left(\frac{\partial p}{\partial T}\right)_v dv - \int p dv + \text{constant (for an isotherm)} \quad (42)$$

List of symbols

A, B parameters of the LIR
 A_m, B_m parameters of the MLIR
 A_{11}, B_{11} contributions of methyle groups in A_m and B_m

A_{22}, B_{22} contributions of the terminal methylene groups in A_m and B_m
 A_{33}, B_{33} contributions of the middle methylene groups in A_m and B_m
 A_{44}, B_{44} contributions of $-\text{CH}_2\text{OH}$ group in A_m and B_m
 A_{55}, B_{55} contributions of $>\text{CHOH}$ group in A_m and B_m
 A_{66}, B_{66} contributions of $-\overset{|}{\underset{|}{\text{C}}}\text{OH}$ group in A_m and B_m
 A_{77}, B_{77} contributions of $>\text{C}=\text{O}$ group in A_m and B_m
 A_{88}, B_{88} contributions of $-\text{COOH}$ group in A_m and B_m
 C_v constant-volume heat capacity
 E internal energy
 n number of carbonic groups of the molecule
 p pressure
 R universal gas constant
 T absolute temperature
 V reduced volume
 x_i $\frac{\text{number of group } i}{\text{total number of groups}(n)}$
 X_j mole fraction of group j in a mixture
 Z compressibility factor

Greek letters

ρ number density
 κ_T isothermal compressibility
 α_p thermal expansion coefficient

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