



Density Estimation Assessment in Fluid State Based on Statistical Thermodynamics Perturbation Theory for Cyclo-Compounds

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In this paper, Ihm-Song-Mason (ISM) analytical equation of state (EoS) was employed to calculate the density of cyclo-compounds of cyclohexane, methyl cyclohexane, propyl cyclohexane, heptyl cyclohexane, *cis*-decalin, *trans*-decalin, cyclo pentane in fluid states. The best two available characteristic parameters of the Lennard-Jones (LJ) (12,6) potential were utilized to evaluate the second virial coefficients for each compounds required by the equation of state. As we know, the second virial coefficient is not very sensitive to the feature of the intermolecular potential so choosing the Lennard-Jones potential (12,6) for this propose is logical. Our previous results showed that the remaining parameters in the equation of state depend only on the repulsive part of the potential. The calculated second virial coefficients in conjunction to the other temperature-dependent parameters of the equation of state were employed to predict the density of cyclo-compounds. A comparison between the experimental values of density and the calculated values from Ihm-Song-Mason equation of state has been made. We found out that the agreement with experimental results is fairly good for all of the pertinent compounds.

Key Words: Density, Statistical thermodynamic perturbation theory, Equation of state, Cyclo-compounds, Pair interaction potential, Lennard-Jones potential.

INTRODUCTION

The lack of various data on thermodynamic properties severely limits the ability of scientists and engineers to propose innovative solutions to resolve designing problems. For rapid estimation of thermodynamic properties of fluids, calculations are prominent^{1,2}. These methods are more efficient and cost effective than the laboratory experiments. Thermodynamic properties of fluids are required to design heat transfer machinery and chemical processes. Theoretical studies contribute greatly to the quality and efficiency of chemical processing, including shrinking the time lines for industrial process scale-up, optimizing processes to maximize yields and minimizing undesired wastes and by products. The thermodynamic properties of fluids are essential for process design and control in the chemical, natural gas, aerospace, environmental and other related industries.

The thermophysical properties such as viscosity³⁻⁵; Joule-Thomson inversion curve⁶ and the molar volume or density^{7,8} are important quantities in both science and engineering. Anyhow, volumetric properties are ubiquitous in chemical processes

and form the building blocks of process designing. The importance of the volumetric properties of fluid in technology is maintained across the industrial diversities.

Meanwhile, our knowledge of the thermodynamic properties, however, can be simplified when a connection is made with the intermolecular potential. Hence, for predicting purposes, it may be preferable to use a derived-from-statistical thermodynamics, such as Song-Mason (SM) equation of state (EoS)^{9,10}. This is a versatile equation with physically sound parameters, *i.e.*, having explicitly significance in terms of intermolecular potential. It should also be mentioned that the modified Song-Mason equation of state by Ihm was named as Ihm-Song-Mason (ISM) EoS^{11,12}. The purpose of the present work is to re-examine the ISM EoS for the cyclo compounds series for predicting their densities.

EXPERIMENTAL

There exists a simple analytical EoS, based on statistical mechanical perturbation theory for fluids. Knowledge of the intermolecular potential allows us to implement the EoS for

predicting thermodynamic properties of fluid states of aforesaid compounds. The ISM EoS¹¹ is given as:

$$P/\rho k_B T = 1 + \frac{\bar{\alpha}\rho}{1 - \lambda b\rho} - \frac{(\bar{\alpha} - B_2)\rho}{1 + \delta b\rho} \quad (1)$$

where P , ρ , k and T are pressure, density, Boltzmann's constant and temperature respectively. λ is known as the characteristic adjustable (free) parameter of the ISM EoS. These parameters varies slightly with temperature and can be calculated from P-V-T experimental data. $\bar{\alpha}$ is the correction factor of the repulsive forces to the second virial coefficient (B_2), b is a temperature-dependent parameter analogous to the van der Waals (vdW) co-volume. The term δ is a small correction and its value has been determined from experimental factors. For hard spheres δ is zero, for noble gases $\delta = 1$ and for molecular gases $\delta < 0.1$. δ is directly proportional to λ , so $\delta = 0.22\lambda$.

Now, if the values of $\bar{\alpha}$, B_2 and b are known, the free parameter λ will be determined from high-density P-V-T experimental data such as liquid density. Hence, the major problem now is to find the parameters $\bar{\alpha}$, B_2 and b . The statistical thermodynamic expressions of $\bar{\alpha}$, B_2 and b are as follows:

$$B_2(T) = 2\pi \int_0^\infty (1 - e^{-u(r)/k_B T}) r^2 dr \quad (2)$$

$$\bar{\alpha}(T) = 2\pi \int_0^{r_m} (1 - e^{-u^0(r)/k_B T}) r^2 dr \quad (3)$$

$$b(T) = 2\pi \int_0^{r_m} (1 - [1 + u^0(r)/k_B T] e^{-u^0(r)/k_B T}) r^2 dr \quad (4)$$

Statistical thermodynamics provides the properties of state on the basis of the intermolecular potential. The calculation of the thermodynamic functions of state is possible by many statistical thermodynamic theories. One of the most successful formulations is the thermodynamic perturbation theory. Several approaches have been proposed for the thermodynamic perturbation theory. The details of various kinds of thermodynamic perturbation theory are given elsewhere^{13,14}. With the terminology of the thermodynamic perturbation theory, the intermolecular potential is defined by $u(r)$, whereas the repulsive part, $u^{(0)}(r)$, has its usual meaning of decomposition of $u(r)$ according to the Chandler, Weeks, Andersen (CWA) formulation of the thermodynamic perturbation theory¹⁵, *viz.*

$$u(r) = u^{(0)}(r) + u^{(1)}(r) \quad (5)$$

$$\begin{aligned} u^{(0)} &= u(r) + \epsilon & r < 2^{1/6} \sigma \\ u^{(0)} &= 0 & r \geq 2^{1/6} \sigma \end{aligned} \quad (6)$$

and

$$\begin{aligned} u^{(1)} &= -\epsilon & r < 2^{1/6} \sigma \\ u^{(1)}(r) &= u(r) & r \geq 2^{1/6} \sigma \end{aligned} \quad (7)$$

where $-\epsilon$ is the depth of the potential and σ is the corresponding value of r , where $u(\sigma) = 0$. $u^{(0)}(r)$ is the interaction potential of reference model (a repulsive part) and $u^{(1)}(r)$ is the perturbation potential (an attractive part).

So, thermodynamic perturbation theory provides the properties of state on the basis of the intermolecular interaction. The Lennard-Jones (LJ) (12,6) potential is undoubtedly the most widely used intermolecular potential in statistical thermodynamics. It is a simple continuous potential that provides adequate description of intermolecular interactions for various applications. Albeit, it is treated as a pair-wise potential and is more accurately described as an effective potential. It is important to make the distinction between effective and true two-body potentials. Even though many potentials are functionally pair-wised (*i.e.*, they only require a separation pair as inputs), they are often in reality effective potentials, which should not be confused with genuinely two-body potentials¹⁶.

The purpose of the present work was to predict P- ρ -T surfaces for cyclo compounds including cyclohexane, methyl cyclohexane, propyl cyclohexane, heptyl cyclohexane, cyc-decalin, *trans*-decalin and cyclo pentane. To pursue this aim we have to find the second virial coefficients as well as the parameters $\bar{\alpha}$ and b for aforesaid compounds. In order to calculate the aforesaid parameters, we need to know scaling parameters σ and ϵ for each system. From computer simulation the critical parameters of a single-component LJ fluid are¹⁷:

$$v_c/\sigma^3 = 3.29 \pm 0.07 \quad (8)$$

and the values of v_c were calculated using the foregoing equation¹⁷:

$$k_B T_c/\epsilon = 1.316 \pm 0.006 \quad (9)$$

Henceforth, the best values of the LJ (12,6) potential parameters have been taken¹⁸ to calculate the second virial coefficients as well as the parameters $\bar{\alpha}$ and b for mentioned compounds.

RESULTS AND DISCUSSION

An analytical equation of state has been used for predicting pressure-density-temperature properties of present compounds. We set the LJ (12,6) intermolecular potential as input to calculate the second virial coefficients. The values of the parameters $\bar{\alpha}$, b and B_2 , which derived from eqns. (2)- (4) are directly inserted to eqn. (1). The calculated values of the density for pure cyclo compounds are shown in Fig. 1-7. Knowing that the second virial coefficient is insensitive to the form of the intermolecular potential¹⁹ and $\bar{\alpha}$ and b are rather unaffected to the details of the interaction potential, for most practical purposes can be estimated with reasonable accuracy from the LJ (12, 6) model potential.

The remaining problem is to find λ which appears in eqn. (1). We have followed the method of Ihm *et al.*,¹¹ for obtaining the λ -parameter empirically from P- ρ -T data of dense pure compounds. Now, by knowing the temperature-dependent parameters, second virial coefficient, $\bar{\alpha}$, b , along with the values of λ , the ISM EoS is employed to predict P- ρ -T surfaces of aforesaid compounds. The values of adjustable parameter λ are given in Table-1.

TABLE-1 THE VALUES OF ADJUSTABLE PARAMETER, λ .	
Compound	λ
Cyclohexane (C ₆ H ₁₂)	0.481
Methyl cyclohexane (C ₇ H ₁₄)	0.446
Propyl cyclohexane (C ₉ H ₁₈)	0.447
Heptyl cyclohexane (C ₁₃ H ₂₆)	0.415
<i>cis</i> -Decalin (C ₁₀ H ₁₈)	0.441
<i>trans</i> -Decalin (C ₁₀ H ₁₈)	0.408
Cyclopentane (C ₅ H ₁₀)	0.434

As we know, one of the advantages of the present EoS is that if there is any uncertainty or an error in one of the parameters $\bar{\alpha}$, b and B_2 , then the free parameter, λ , will adjust itself, so that it could compensate for uncertainty in the afore-said parameters¹¹. Additional benefit of the ISM EoS is that thermodynamic properties of fluids are directly related to the intermolecular forces.

We selected cyclo-compounds. By assuming that they obey the LJ (12,6) model potential. Using our calculations, the values of deviation of density *versus* pressures at different temperatures were depicted for cyclohexane, methyl cyclohexane, propyl cyclohexane, heptyl cyclohexane, *cis*-decalin, *trans*-decalin, cyclopentane in their fluid states, respectively (Fig. 1-7). The values of deviation of density *versus* pressures at different temperatures were: -3.5-0.0 % for cyclohexane, -4.0-0.0 % for methyl cyclohexane, -7.0-0.0 % for propyl cyclohexane, -3.0-0.0 % for heptyl cyclohexane, -2.25-0.0 % for *cis*-decalin, -2.0-0.0 % for *trans*-decalin, -1.5-0.0 % for cyclopentane in their fluid states. As it is clear from Figs. 1-7 the overall agreement between our predicted values and the experimental values of density is quite good and the deviation between predicted and the experimental values are commensurate to the usual measurements. By overseeing the above-mentioned figures it is obvious that the accuracy of the ISM EoS was better at high pressures, henceforth we believe that the compensation effects of the second and third terms in the R.H.S. of eqn. (1) predominates at adequately high pressures (≈ 200 bar or greater than that). Thus, finding the temperature dependencies of ISM EoS parameters, $\bar{\alpha}$, b and B_2 , explicitly from their analytical forms combined to the LJ (12,6) model potential requires no estimation of their values from correlation equations²⁰. Hence, calculations can be performed more convenient in shorter times.

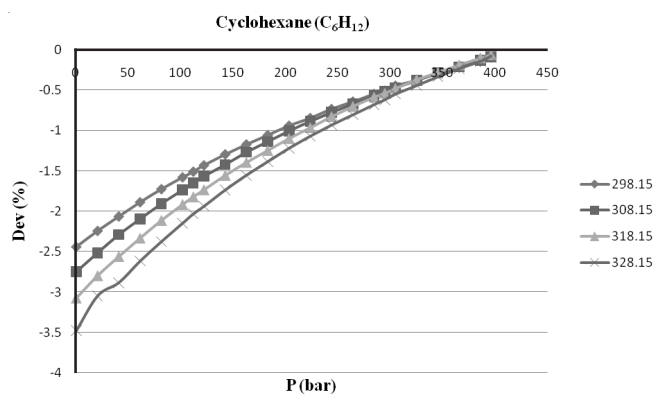


Fig. 1. The deviation between predicted and experimental values of density for cyclohexane. The experimental values of density have adopted from²¹

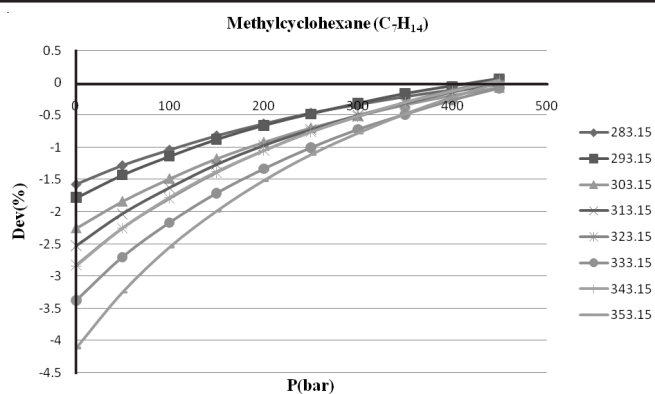


Fig. 2. Same as fig. 1. for methylcyclohexane. The experimental values of density have adopted from the work of Zeberg-Mikkelsen *et al.*²²

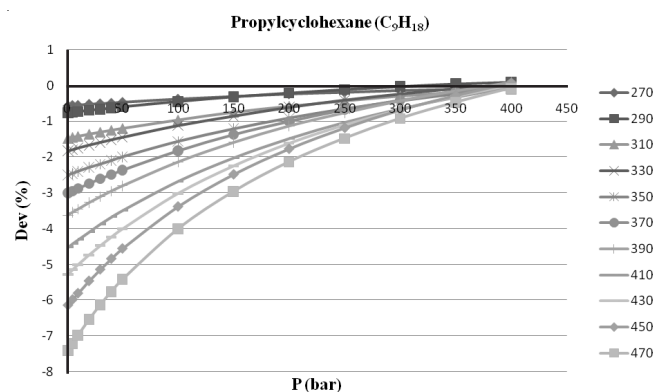


Fig. 3. Same as fig. 1. for propylcyclohexane. The experimental values of density have adopted from the work of Laesecke *et al.*²³

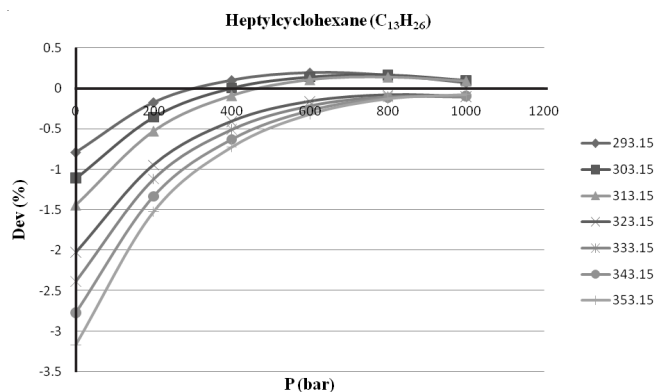


Fig. 4. Same as fig. 1. for heptylcyclohexane. The experimental values of density have adopted from the work of Baylaucq *et al.*²⁴

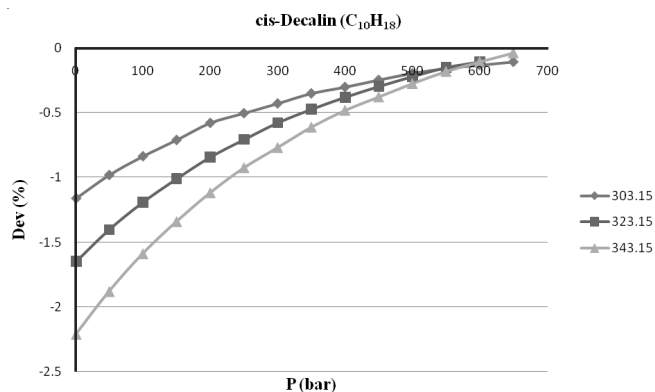


Fig. 5. Same as fig. 1. for *cis*-decalin. The experimental values of density have adopted from the work of Miyake *et al.*²⁵

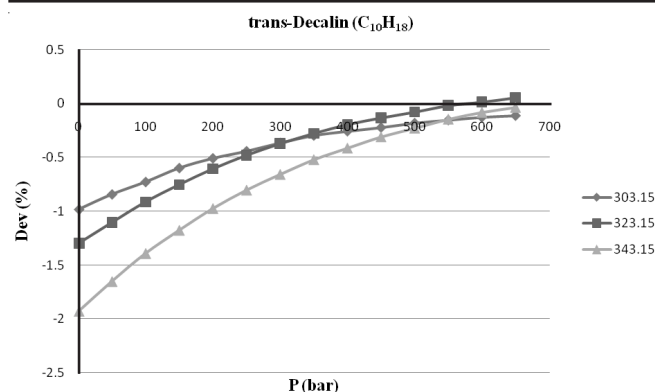


Fig. 6. Same as fig. 1. for *trans*-decalin. The experimental values of density have adopted from the work of Miyake *et al.*²⁵

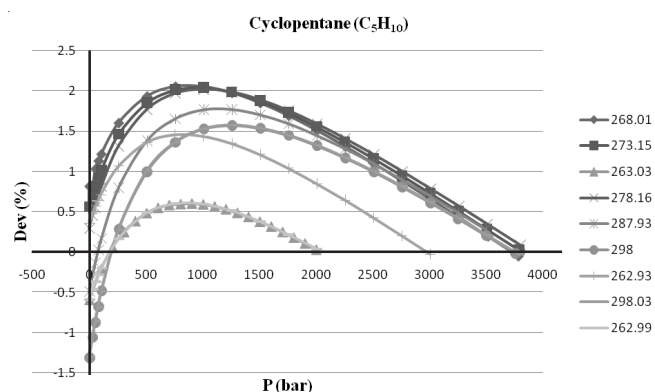


Fig. 7. Same as fig. 1. for cyclopentane. The experimental values of density have adopted from the work of Harris *et al.*²⁶

Conclusion

Nowadays, the problem of deriving an analytical equation of state for real fluids has been remained as an important problem in the field of interest for fluid's thermodynamics. A precise relations for the thermodynamic variables in terms of relevant molecular features have been partially attained by the Ihm-Song-Mason equation of state. Our used effective potential model in conjunction to the Ihm-Song-Mason equation of state signifies the importance of using the limited knowledge of properties of a substance in terms of its molecular features and makes feasible to carry out computation of the thermodynamic properties, especially density with complete theoretical expressions of Ihm-Song-Mason equation of state.

Nevertheless, the combination of the easiness of the calculation of the Ihm-Song-Mason equation of state parameters, which has been proposed by us is more successful than finding the temperature dependencies of them by direct prediction in laboratory or using the experimental expressions described by others.

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