



## Prediction of Density for Aromatic-Compounds from the Statistical-Thermodynamically Perturbation Theory Based Equation of State

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In this studies, an analytical equation of state proposed by Ihm-Song-Mason was employed to calculate the density of aromatic-compounds including: benzene, anisole, bromobenzene, ethylbenzene, heptylbenzene, toluene, diphenylmethane, tetralin, *m*-cresol, *o*-xylene, *m*-xylene, *p*-xylene, 2,4-dichlorotoluene and 1,2,3-trimethylbenzene. The best available values of the Lennard-Jones (12,6) parameters have been taken to evaluate the second virial coefficient for each compounds required by the equation of state. The second virial coefficient is not very sensitive to the feature of the intermolecular potential. The remaining parameters in the equation of state depend only on the repulsive part of the potential. Consequently, they are insensitive to the details of the interaction 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 aromatic-compounds. A comparison between the experimental values of density and the calculated values from Ihm-Song-Mason equation of state has been made. Agreement with experiment is very good for all of the compounds.

**Key Words:** Density, Statistical thermodynamic perturbation theory, Equation of state, Pair interaction potential.

### INTRODUCTION

The lack of various data on thermodynamic properties severely limits the ability of scientists and engineers to propose innovative solutions to old or new problems of designing. Scientists and engineers are using computer frequently to predict thermodynamic properties of fluids. Because of time and financial constraints the computer-calculation can be carried out very fast. These methods are more efficient and cost effective. The laboratory experiments require much more effort and cost to determine the thermodynamic properties. Thermodynamic properties of fluids are required to design heat transfer machinery and chemical processes. The quality and efficiency of chemical processing, including shrinking the time lines for industrial process scale-up and optimizing processes to maximize yields and maximize undesired wastes and by products, can be greatly enhanced through theoretical studies. The thermodynamic properties of fluids are essential for process design and control in the chemical, natural gas, aerospace, environmental and other related industries.

Moreover, all of the thermodynamic properties of a fluid are encapsulated in the mathematical relationship between the fluid's pressure, volume and temperature- which is commonly called its "equation of state"<sup>1</sup>. It is therefore hardly surprising

that an ability to predict accurately such equations of state and with a minimum of empiricism has been received conspicuous attentions in engineering applications<sup>2,3</sup>.

The thermophysical properties such as viscosity<sup>4</sup>; the molar volume or density<sup>5,6</sup> and common intersection point<sup>7</sup> are important quantities in both science and engineering.

Meanwhile, 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 varied diversity.

Indeed, an ability to understand equations of state on purely molecular level, using nothing more than information on intermolecular potentials and the tools of equilibrium statistical mechanics<sup>8</sup>, was a challenge posed of over a century ago by van der Waals<sup>1</sup>. It also signifies that one could claim some reasonable measure of understanding of at least the equilibrium properties of liquids and gases.

Consequently, equation of state's are widely used to predict the volumetric behaviour of fluids. Since van der Waals (vdW) proposed the first version of his celebrated equation of state more than a century ago, many modifications have been proposed in the literature to improve the predictions of volumetric properties. After the visionary work of van der Waals the importance of defining a suitable pair interaction in order

to understand the thermodynamic properties of fluids has become clear. Most of the equation of state of practical interest are based on the assumption that the structure of fluids is preliminary determined by short-range repulsive and long-range attractive intermolecular forces<sup>9-11</sup>. Henceforth, intermolecular forces are a fundamental ingredient of computer simulations<sup>12,13</sup>, generic van der Waals theory<sup>14</sup> and density-fluctuation theory of fluids state<sup>15</sup>.

Meanwhile, present 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 Ihm-Song-Mason (ISM) equation of state<sup>8</sup>. This is a versatile equation with physically sound parameters, *i.e.*, having explicitly significance in terms of intermolecular potential. The purpose of the present work is to re-examine the Ihm-Song-Mason equation of state<sup>5,16</sup> for the aromatic-compounds series for predicting their density.

## EXPERIMENTAL

There exists a simple analytical equation of state, based on statistical mechanical perturbation theory for fluids<sup>17,18</sup>. Knowledge of the intermolecular potential allows the complete specification of this equation of state. The Ihm-Song-Mason equation of state<sup>8</sup> 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  $P$ ,  $\rho$ ,  $k$  and  $T$  are pressure, density, Boltzmann's constant and temperature, respectively.  $\lambda$  is known as the characteristic adjustable (free) parameter of the Ihm-Song-Mason equation of state. 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 co-volume. The term  $\delta$  is a small correction and its value has been determined from experimental factors. For hard spheres  $\delta$  is zero, for noble gases  $\delta = 1$  and for molecular gases  $\delta \leq 0.01$ .  $\delta$  is proportional to  $\lambda$ ,  $\delta = 0.22 \lambda$ .

Now, if the values of  $\bar{\alpha}$ ,  $B_2$  and  $b$  are known, the free parameter  $\lambda$  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 follow:

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

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

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

Statistical thermodynamics provide 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 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<sup>17-19</sup>. 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 theory<sup>18</sup>, *viz.*

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

$$u^{(0)} = u(r) + \varepsilon \quad r < 2^{1/6} \sigma$$

$$u^{(0)} = 0 \quad r \geq 2^{1/6} \sigma \quad (6)$$

$$\text{and} \quad u^{(1)} = -\varepsilon \quad r < 2^{1/6} \sigma$$

$$u^{(1)}(r) = u(r) \quad r \geq 2^{1/6} \sigma \quad (7)$$

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

So, thermodynamic perturbation theory provides the properties of state on the basis of the intermolecular interaction. The Lennard-Jones (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, it 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-wise (*i.e.*, they only require pair separation as inputs), they are often in reality effective potentials which should not be confused with genuinely two-body potentials<sup>20,21</sup>.

The purpose of the present work is to predict P- $\rho$ -T surfaces for aromatic-compounds including: benzene, anisole, bromobenzene, ethylbenzene, heptylbenzene, toluene, *m*-cresol, *o*-xylene, *m*-xylene, *p*-xylene, 2,4-dichlorotoluene, 1,3,5-trimethylbenzene. To pursue this aim we have to find the second virial coefficients as well as the parameters  $\bar{\alpha}$  and  $b$  for aforesaid compound. Henceforth, the best values of the Lennard-Jones (12,6) potential parameters have been taken<sup>22</sup> to calculate the second virial coefficients as well as the parameters  $\bar{\alpha}$  and  $b$  for aforesaid compounds.

## RESULTS AND DISCUSSION

An analytical equation of state has been used for predicting pressure-density-temperature properties of aforesaid compounds. We used the Lennard-Jones (12,6) intermolecular potential as input to calculate the second virial coefficient of aforementioned compounds. Thanks to the procedure presented above, 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 aromatic-compounds are plotted in Figs. 1-14. It should also be mentioned that the second virial coefficient is not very sensitive to the form of the intermolecular potential<sup>23</sup>. It must also be notified that since  $\bar{\alpha}$  and  $b$ , which depend only on the repulsion (see eqns. 3-4), are rather insensitive to the details of the interaction potential, for most practical purposes can be calculated with reasonable accuracy from the Lennard-Jones (12,6) model potential.

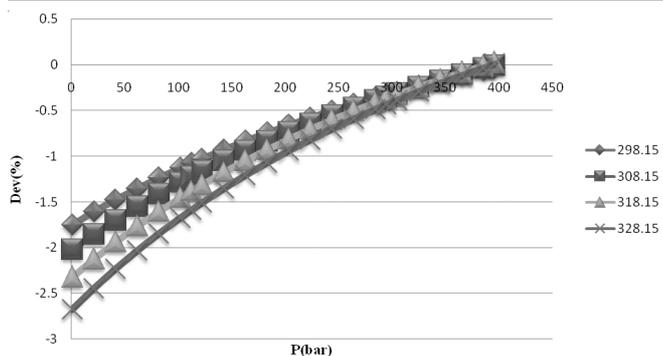


Fig. 1. Deviation between predicted and experimental values of density for benzene. The experimental values of density have taken from Ref. 24

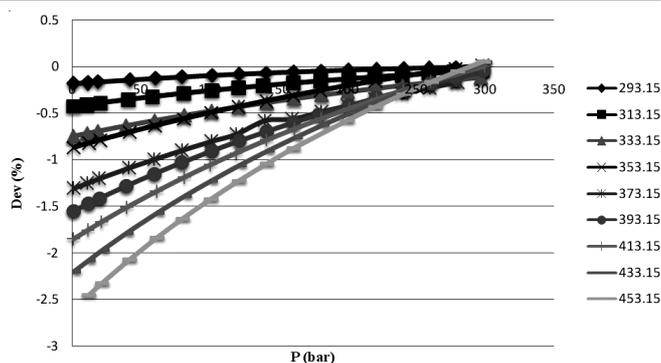


Fig. 5. Same as Fig. 1 for 2,4-dichlorotoluene. The experimental values of density have taken from Ref. 26

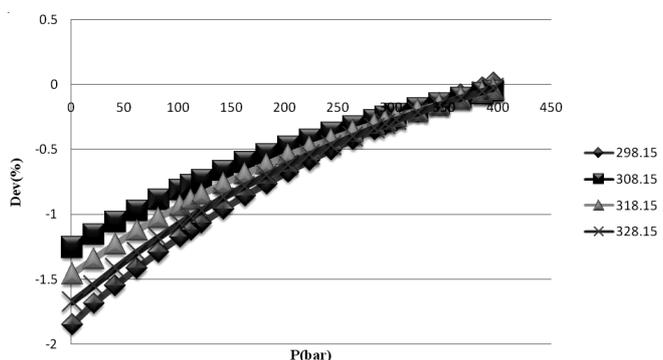


Fig. 2. Same as Fig. 1 for 1,3,5-trimethylbenzene. The experimental values of density have taken from Ref. 24

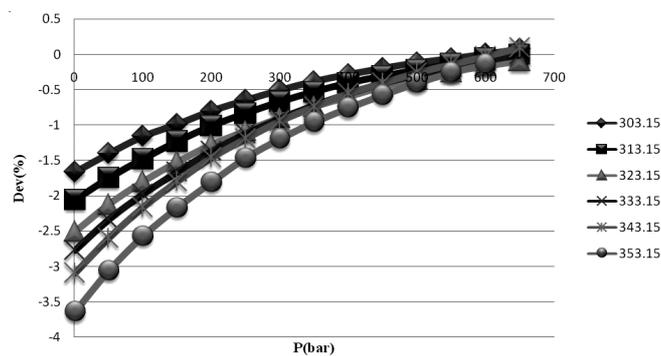


Fig. 6. Same as Fig. 1 for toluene. The experimental values of density have taken from Ref. 27

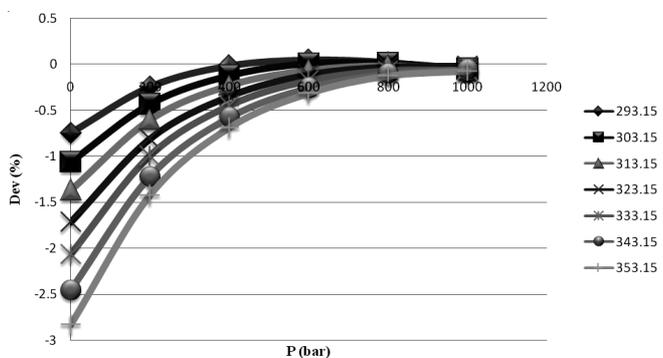


Fig. 3. Same as Fig. 1 for heptylbenzene. The experimental values of density have taken from Ref. 25

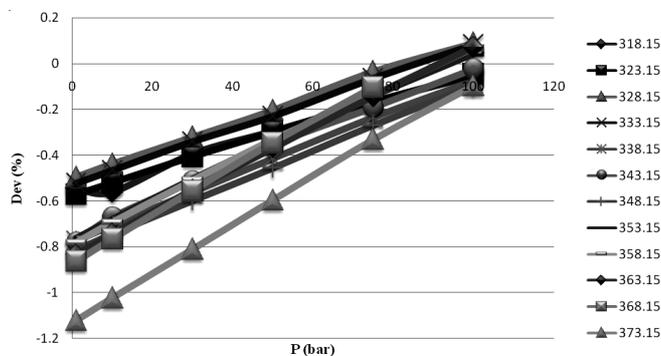


Fig. 7. Same as Fig. 1 for ethylbenzene. The experimental values of density have taken from Ref. 28

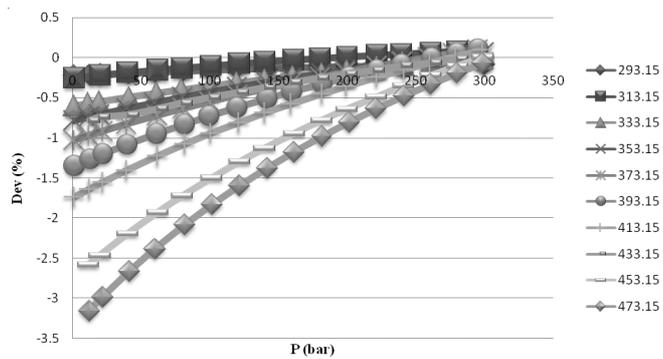


Fig. 4. Same as Fig. 1 for bromobenzene. The experimental values of density have taken from Ref. 26

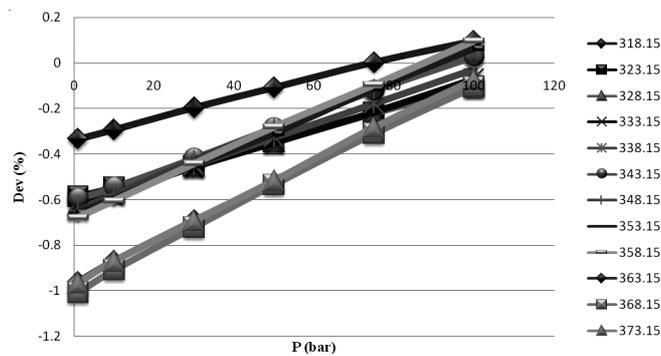


Fig. 8. Same as Fig. 1 for *o*-xylene. The experimental values of density have taken from Ref. 28

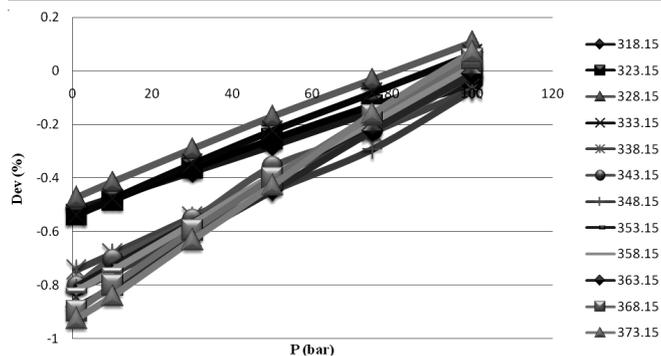


Fig. 9. Same as Fig. 1 for *m*-xylene. The experimental values of density have taken from Ref. 28

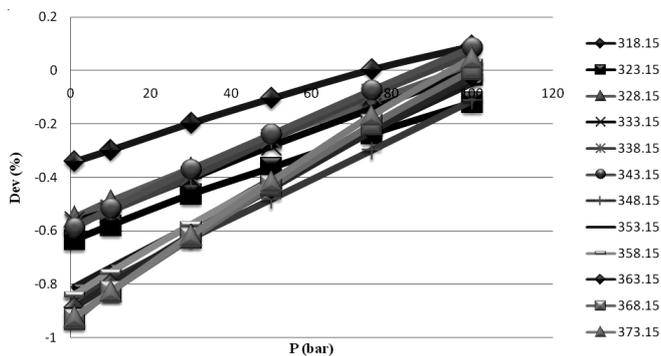


Fig. 10. Same as Fig. 1 for *p*-xylene. The experimental values of density have taken from Ref. 28

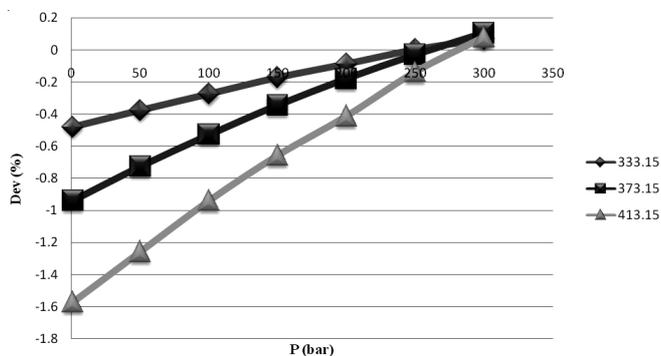


Fig. 11. Same as Fig. 1 for *m*-cresol. The experimental values of density have taken from Ref. 29

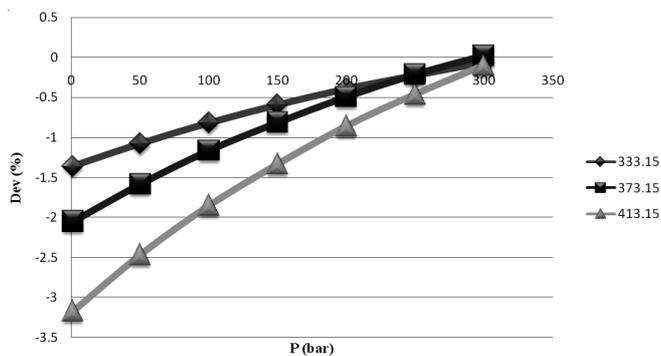


Fig. 12. Same as Fig. 1 for diphenylmethane. The experimental values of density have taken from Ref. 29

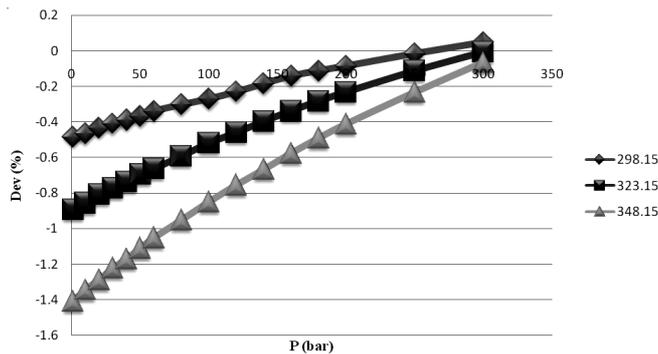


Fig. 13. Same as Fig. 1 for tetralin. The experimental values of density have taken from Ref. 30

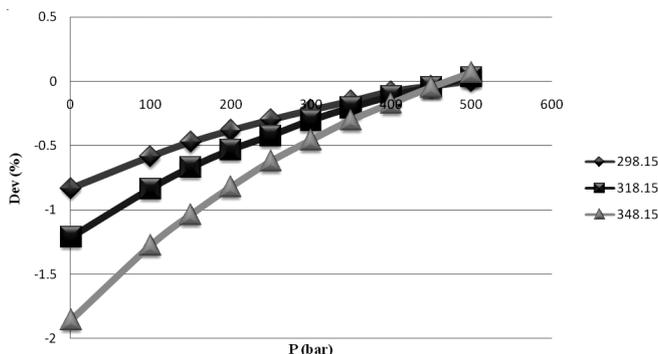


Fig. 14. Same as Fig. 1 for anisole. The experimental values of density have taken from Ref. 31

The last problem is to find  $\lambda$  which appears in eqn. 1. We have followed the reported method<sup>5,16</sup> for obtaining the  $\lambda$ -parameter empirically from P- $\rho$ -T data of dense pure compounds. Now, by knowing the temperature-dependent parameters, second virial coefficient,  $\bar{\alpha}$ ,  $b$ , along with the values of  $\lambda$ , the Ihm-Song-Mason equation of state is employed to predict P- $\rho$ -T surfaces of aforesaid compounds. The values of adjustable parameter  $\lambda$  are given in Table-1. As it is clear from Figs. 1-14 the overall agreement between our predicted values and the experimental values of density is quite good because the deviation between predicted and the experimental values are commensurate to the best measurements.

TABLE-1  
VALUES OF ADJUSTABLE PARAMETER,  $\lambda$

Compound	$\lambda$
Benzene (C <sub>6</sub> H <sub>6</sub> )	0.481
Anisole (C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub> )	0.415
Bromobenzene (C <sub>6</sub> H <sub>5</sub> Br)	0.427
Ethylbenzene (C <sub>8</sub> H <sub>10</sub> )	0.417
Heptylbenzene (C <sub>13</sub> H <sub>20</sub> )	0.412
Toluene (C <sub>7</sub> H <sub>8</sub> )	0.485
Diphenylmethane (C <sub>13</sub> H <sub>12</sub> )	0.411
Tetralin (C <sub>10</sub> H <sub>12</sub> )	0.465
<i>m</i> -Cresol (C <sub>7</sub> H <sub>8</sub> O)	0.477
<i>o</i> -Xylene (C <sub>8</sub> H <sub>10</sub> )	0.418
<i>m</i> -Xylene	0.411
<i>p</i> -Xylene	0.409
2,4-Dichlorotoluene (C <sub>7</sub> H <sub>6</sub> Cl <sub>2</sub> )	0.404
1,3,5-Trimethylbenzene (C <sub>9</sub> H <sub>12</sub> )	0.408

## Conclusion

Nowadays, the problem of deriving an analytical equation of state for real fluids has been remained as an important problem in the area of fluids thermodynamics. Consequently, obtaining the more explicit relations for the thermodynamic variables in terms of relevant molecular features have been partially attained by the Ihm-Song-Mason equation of state. The used effective potential 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.

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