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Analytical Study of Effect of Temperature on Hard Sphere Diameter of Some Organic Liquids

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ABSTRACT

Here, we have used theoretical computation based upon Khasare formulation, using computer code developed in "C". Equation of State is applied to compute values of three model parameters hard sphere diameter (σ), reduced depth of potential ($\beta\varepsilon$) and temperature variation of depth of potential ($\delta(\beta\epsilon T)$) . These are used to estimate theoretical values of hard-sphere diameter to study the behaviour of the real liquids The Temperature is varied in equal steps of 5K from 298.16 K to 313.16 K. The hard-sphere diameter dependence upon temperature is studied. Hard-sphere diameter seems to be fairly invariable over the above temperature range.

Keywords: Khasare EOS, Depth of potential, Space filling ratio, Hard sphere
PACS: *51.30.+I Thermodynamic properties, equation of state*

INTRODUCTION

Over the years various models have been proposed by number of researchers for theoretical understanding of liquids and liquid mixtures. Most of them are based on the concept of hard-sphere. Hard spheres are widely used as model particles in the statistical mechanical theory of fluids. They are impenetrable spheres that cannot overlap in space. They mimic the extremely strong repulsion that atoms and spherical molecules experience at very close distances. Hard spheres systems are studied by analytical means, by molecular dynamics simulations [1-3], and by the experimental study of certain model systems.

Hard spheres of diameter σ are particles with the following pair wise interaction potential:

$$V(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} 0 & \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| \geq \sigma \\ \infty & \text{if} \quad |\mathbf{r}_1 - \mathbf{r}_2| < \sigma \end{cases}$$

where r_1 and r_2 are the positions of the two particles

The prediction of thermodynamic properties of the hard-sphere system has been broadly acknowledged as a problem of statistics, subject to constraints of geometry. The most direct theory in this respect is scaled particle theory (SPT). Other closely related approaches, based on structural geometry have appeared in recent literature. Hard-sphere system has been studied intensively for two main reasons. Firstly, hard-sphere potential accounts well for high density and wide temperature region of the fluid phase diagram of real fluids. Secondly, it gives plausibly accurate analytical expression for thermodynamic and structural properties. Hard-sphere fluids, with ease, are used as reference system in perturbation theories. As a preparatory supposition, scaled particle theory is used in many approaches for further development of theoretical background to get insight of molecular interactions and structural geometry of liquid phase, where, hard-sphere potential plays an imperative role. Khasare [4] using perturbation approach, presented an equation of state for liquid mixtures. This first EOS is used by many researchers [5-13].

Three model parameters, namely hard-sphere diameter, related to molecular hard-sphere volume ($\pi d^3/6$), depth of potential correspond to binding energy ($\beta\varepsilon$), and variation of depth of potential with temperature ($\delta(\beta\varepsilon T)$).

Hence estimate of hard-sphere diameter has great significance in the studies in liquids. The space filling factor (η) changes with temperature and composition of the mixture. The variation in the sound velocity for mixture reflects the variation of (η) . The study of properties of liquids finds direct applications in chemical and biochemical industries. Speed of sound is highly responsive to the structure and interaction present in the liquids, as it is fundamentally related to the binding forces between the components of the liquid medium. The measurement of speed of sound in liquids enables determination of some useful acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions in liquid mixtures. Ultrasonic study [14-22] is exhaustively used by large number of workers to grasp the molecular behaviour of liquids. Propagation of the ultrasonic waves in liquid mixtures depends upon molecular geometry and on intermolecular interactions.

Khasare Equation of State for Real Fluid Mixtures

Khasare formulation is applied to compute values of three model parameters (1) hard sphere diameter (σ), (2) reduced depth of potential ($\beta\varepsilon$) and (3) temperature variation of depth of potential ($\delta(\beta\epsilon T)$) . These are used to estimate theoretical values of Geometric packing fraction (η), reduced depth of potential ($\beta\epsilon T$), and ultrasonic wave velocity to predict the behaviour of the real liquids

Initially values for

$$\left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{\gamma R}\right)$$

(Where P-pressure, V-Volume, R- Universal gas constant, T-Temperature in Kelvin, u - Ultra sonic wave velocity, M -Molecular Weight, γ-specific heat ratio, α -volume expansion coefficient) are calculated for pure liquid from experimental data of nine real systems for ultrasonic velocities and densities. From these values three model parameters (σ, ($\beta\epsilon T$), ($\delta(\beta\epsilon T)$)) are predicted for pure liquids using computer code developed in "C" at different temperatures. The temperature variation used for computation is 293.16 K to 313.16 K in equal steps of 5K. Data for following nine pure real liquids is used.

1) Carbon tetrachloride 2) Tetrahydrofuran 3) 1-4 Dioxane
4) MethylCyclohexane 5) Cyclohexanol 6) Benzene
7) Cyclohexane 8) Methyl alcohol 9) Tetrahydropyrrole

For a fluid of hard sphere molecules each of diameter d, compressibility factor Z, is defined as

$$Z(be) = \frac{\beta P}{\rho};\ \beta = \frac{1}{(K_B T)};\ \eta = \frac{\pi \rho d^3}{6} \tag{1}$$

where P is pressure, ρ is density, $K_B T$ is Boltzman Constant and T is temperature.

The factor $\left(\frac{\pi}{6}\right) d^3$ is the volume of hard sphere

Khasare Equation of State for real binary fluid mixture is expressed as

$$\frac{PV}{RT} = \frac{1}{(1-\eta)} + \frac{3e\eta}{(1-\eta^2)} + \frac{3f\eta^2}{(1-\eta)^3} + \frac{7\beta\epsilon\left(\eta + log(1-\eta)\right)}{\eta} \tag{2}$$

$$\theta_a = \frac{1}{(1-\eta)} + \frac{3e\eta}{(1-\eta^2)} + \frac{3f\eta^2}{(1-\eta)^3} \tag{3}$$

$$\theta_b = \frac{7\beta\epsilon\left(\eta + log(1-\eta)\right)}{\eta} \tag{4}$$

Hence equation (2) can be rearranged as

$$\frac{PV}{RT} = \theta_a + 7\beta\epsilon\theta_b \tag{5}$$

The related thermodynamic relations are obtained as

$$\frac{Mu^2}{\gamma RT} = \frac{1}{(1-\eta)^2} + \frac{6e\eta}{(1-\eta)^3} + \frac{9f\eta^2}{(1-\eta)^4} - \frac{7\beta\epsilon\eta}{(1-\eta)} \tag{6}$$

We define

$$\theta_c = \frac{1}{(1-\eta)^2} + \frac{6e\eta}{(1-\eta)^3} + \frac{9f\eta^2}{(1-\eta)^4} \tag{7}$$

And

$$\theta_d = \frac{\eta}{(1-\eta)} \tag{8}$$

So equation (6) takes the form

$$\frac{Mu^2}{\gamma RT} = \theta_c - 7\beta\epsilon\theta_d \tag{9}$$

Where M = is molecular weight, u = ultrasonic velocity, γ = ratio of specific heat.

Computational Aspect

Experimental data for ultrasonic wave velocity (at 2MHz) and density of liquids at fixed temperature is taken from literature. For pure liquids, we have e=f=1.0. The numerical value of η (a space filling ratio) for each liquid component is found out by finding the root of the equation (10) by computer code.

$$\frac{Mu^2}{\gamma RT} = \theta_c - \frac{\left(\frac{PV}{RT} - \theta_a\right)\theta_d}{\theta_b} \tag{10}$$

Mean radius of curvature (σ /2), reduced depth of potential and its temperature dependence worked out as

$$\left(\frac{\sigma}{2}\right)^3 = \frac{3\eta v}{4\pi N_A} \tag{11}$$

$$(\beta\epsilon) = \theta_c - \frac{\left(\frac{PV}{RT} - \theta_a\right)\theta_d}{7\theta_b} \tag{12}$$

$$\delta(\beta\epsilon T) = \frac{\left(\frac{Mu^2\alpha}{R}\right)\theta_a}{7\theta_b} \tag{13}$$

As a result the temperature variation for depth of potential can be stated as

$$\epsilon(T) = (\beta\varepsilon)K_B T(14) \tag{14}$$

The general scheme for developing model parameters is given here for pure liquid.

$$\left(\frac{PV}{RT}, \frac{Mu^2}{\gamma RT}, \frac{Mu^2\alpha}{R}\right)_{pure} \dashrightarrow [\sigma, \beta\epsilon, \delta(\beta\epsilon T)]_{pure} \tag{15}$$

Thus Hard sphere diameter is obtained using above formulation.

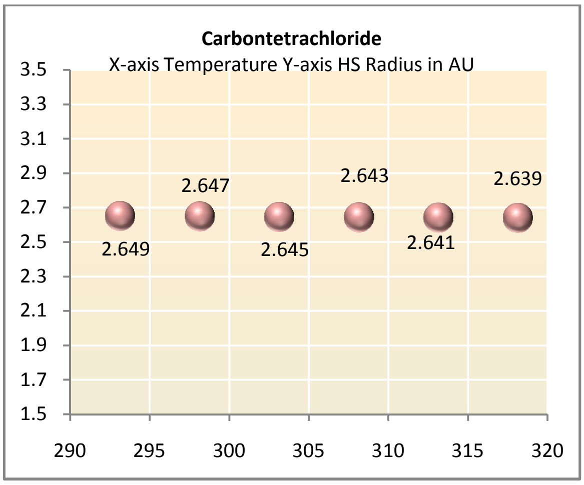
RESULTS

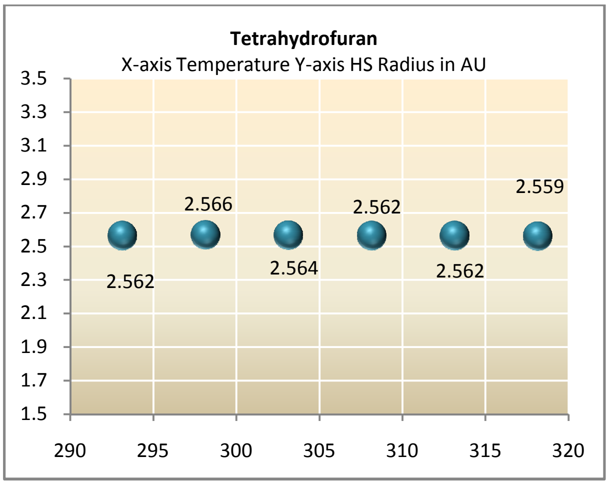
The values of hard-sphere diameter for different organic liquids are presented in the tabular form.

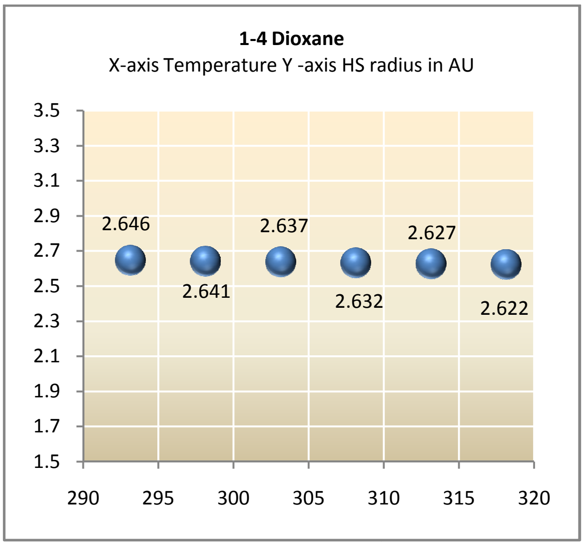
Table for Hard-sphere (in AU) radius vs Temperature

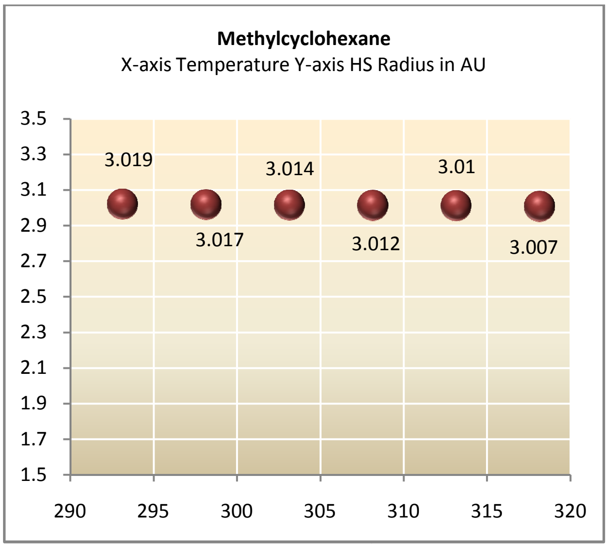
Temp in K	Carbontetracloride	Tetrahydrofuran	1-4 Dioxane
293.16	2.649	2.568	2.646
298.16	2.647	2.566	2.641
303.16	2.645	2.564	2.637
308.16	2.643	2.562	2.632
313.16	2.641	2.562	2.627
318.16	2.639	2.559	2.622
	MethylCyclohexane	Cyclohexanol	Benzene
293.16	3.019	2.893	2.654
298.16	3.017	2.889	2.653
303.16	3.014	2.885	2.651
308.16	3.012	2.880	2.649
313.16	3.010	2.875	2.647
318.16	3.007	2.870	2.645
	Cyclohexane	Methyl alcohol	Tetrahydropyrrole
293.16	2.848	1.919	2.600
298.16	2.846	1.918	2.598
303.16	2.843	1.917	2.596
308.16	2.841	1.915	2.594
313.16	2.838	1.914	2.592
318.16	2.835	1.912	2.590

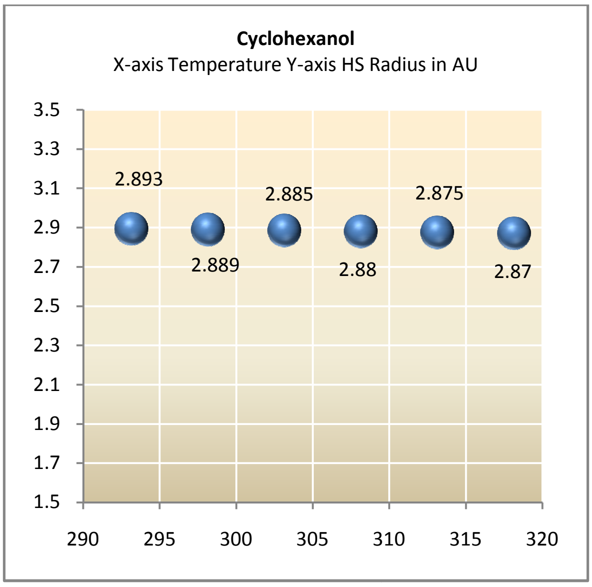
Graphs for Hard sphere radius vs Temperature

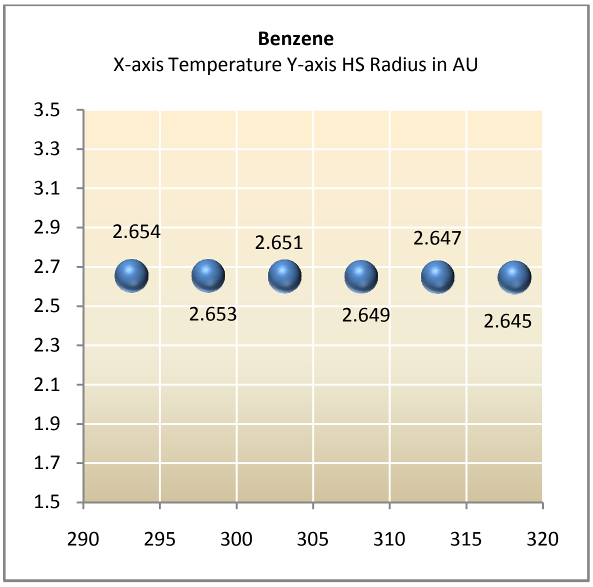


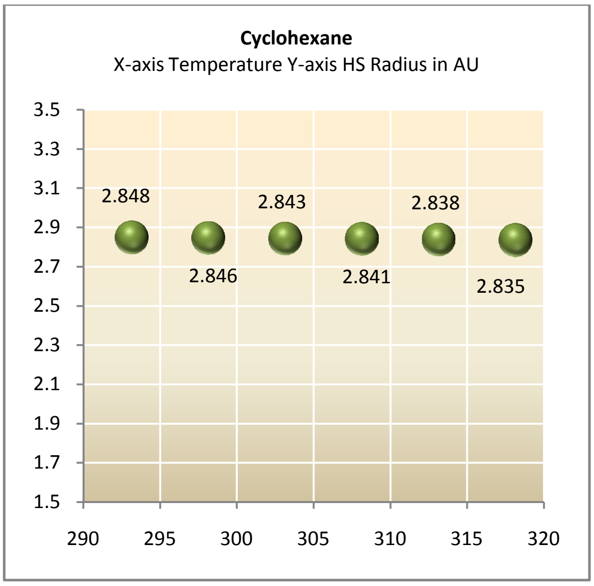


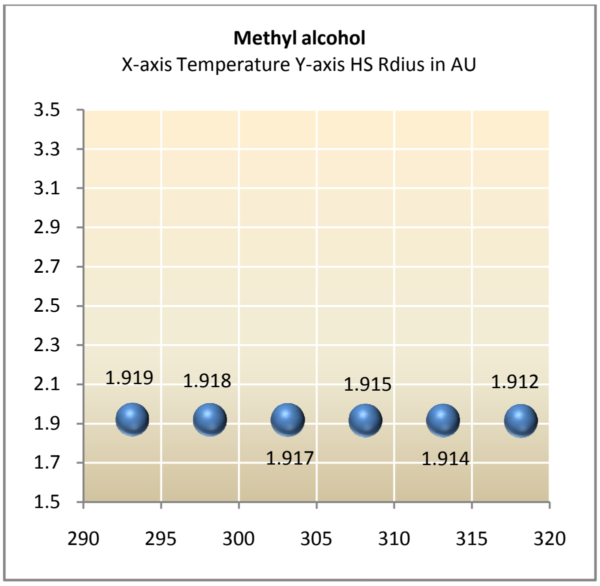


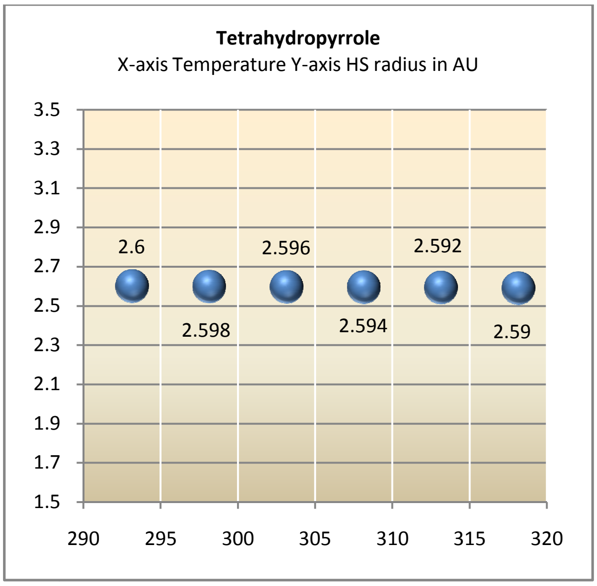



Cyclohexanol
X-axis Temperature Y-axis HS Radius in AU
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
290
295
300
305
310
315
320
2.893
2.889
2.885
2.88
2.875
2.87


Benzene
X-axis Temperature Y-axis HS Radius in AU
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
290
295
300
305
310
315
320
2.654
2.653
2.651
2.649
2.647
2.645


Cyclohexane
X-axis Temperature Y-axis HS Radius in AU
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
290
295
300
305
310
315
320
2.848
2.846
2.843
2.841
2.838
2.835


Methyl alcohol
X-axis Temperature Y-axis HS Rdius in AU
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
290
295
300
305
310
315
320
1.919
1.918
1.917
1.915
1.914
1.912


Tetrahydropyrrole
X-axis Temperature Y-axis HS radius in AU
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
290
295
300
305
310
315
320
2.6
2.598
2.596
2.594
2.592
2.59

DISCUSSION

Here, we have used theoretical computation based upon Khasare formulation, using computer code developed in "C". First Khasare Equation of State is applied to compute values of three model parameters: hard sphere diameter (σ), reduced depth of potential (βε) and temperature variation of depth of potential (δ(βϵT)) . These are used to estimate theoretical values of hard-sphere diameter to study the behaviour of the real liquids. The Temperature is varied in equal steps of 5K from 298.16 K to 313.16 K.

Temperature variation plays an important role in the study of liquids. A change in temperature produces change in the space filling factor. This change in space filling factor is indicative of the intermolecular interactions and change in structural geometry. These parameters are vital in deciding the volume of a liquid. Any small change in space filling factor induces significant change in the velocity of ultrasonic waves in liquid. Intermolecular interactions and structural geometry decides the volume of a liquid. Thus geometry of molecules plays important role in determining volume of a liquid and hence hard-sphere diameter has special significance in the liquid studies.

CONCLUSION

The hard-sphere diameter dependence upon temperature is studied. Hard-sphere diameter form graphs seem to be fairly invariable over the above temperature range.

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