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Calculation of Molecular Radius of Pure Liquids using Sound Speed Data

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Abstract

Molecular radius of some pure liquids has been evaluated using various methods at varying conditions of temperatures. Sound speed and density data have been employed to compute the molecular radius and the liquids under consideration are n-hexane, n-heptane, n- dodecane, cyclohexane and toluene. A comparison has been made between the values obtained from acoustic methods and non-acoustic methods. The variation pattern of molecular radius using various methods has been studied and an attempt has been made to correlate the molecular radius with the relative merits of these methods.

Keywords: *Ultrasonic velocity; Density, Refractive index, Molecular radius, Face centered cubic structure.*

Introduction:

The molecular radius is useful for determining various physical and chemical properties of liquids and liquid mixtures **[2,6,11,12]**. It reflects not only the structural features of liquids and liquid mixtures but is also a useful parameter in the theories of liquids like collision factor theory (CFT), scaled particle theory **[10,13,14,16]**.

Atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of electrons. In simpler terms, it can be defined as something similar to the radius of a circle for the outermost orbital of electron. Determining the atomic radius is rather difficult in the position of the outermost electron as one does not know exactly where the electron is positioned. This phenomenon can be explained by the Heisenberg uncertainty principle. According to the Heisenberg uncertainty principle, it is not possible to measure the momentum and the position of the electron simultaneously. So, as the position of electron is not certain rather can be explained as an electron cloud around the nucleus, it is hard to measure the atomic radius accurately. There are different methods for calculating the radius by measuring the distance between two nuclei when an atom is bonded in a molecule **[1,2]**. Since the boundary is not a well-defined physical entity, there are various definitions of atomic radius. Three widely used definitions of atomic radius are van der Waals radius, ionic radius and covalent radius[15]. For several purposes, atoms can be modelled as spheres. This is only a crude approximation, but it can provide quantitative explanations and predictions for many phenomena such as the density of liquids and solids, the diffusion of fluids through molecular sieves and the size and shape of molecules **[17,18,19,20]**.

Various methods of determining the molecular radius of liquid mixtures have been utilized by several workers. Surface tension or viscosity have been employed to compute the molecular radius or

diameter by some workers **[5,8,9]**. Refractive index and density data can also be utilized to compute the molecular radius **[9]**.

Acoustic methods are considered as one of the most powerful tools for the structural and physico-chemical studies of liquids **[12]**. Ultrasonic velocity and density data have been utilized to estimate the molecular radius in pure liquids at varying temperatures. The liquids used for investigations are n-hexane, n-heptane, n-dodecane, cyclohexane and toluene and the temperature range is 293.15K to 333.15K. Various acoustic methods suggested by Schaaffs, Rao and Kittel have been used to estimate the molecular radius. The relation based upon the assumption that liquid system is made up of closely packed molecules with face centered cubic structures has also been employed **[7]**. Another method employing refractive index has been used to compute the values of molecular radius and the values obtained from other acoustic methods have been compared to these values. The results obtained from these acoustic methods are useful to compute various other parameters and can be related with velocity of sound in liquids.

Experimental:

Theoretical Formulation

Acoustic methods used for computation of molecular radius are as follows:

Schaaffs' method:

This method is based upon van der Waals equation of state-

$$r= (M/\rho N)^{1/3}\sqrt[3]{\left[\left(\frac{3}{16\pi}\right)\left[1-\gamma RT/Mu^2\left(\sqrt[2]{\{1+(Mu^2/3\,\gamma RT)\}}-1\right)\right]\right]} \quad (1)$$

Rao's method:

This relation is also based upon van der Waals equation of state-

$$r= (M/\rho N)^{1/3}\sqrt[3]{\left[\left(\frac{3}{16\pi}\right)\left[1-\gamma RT/Mu^2\left(\sqrt[2]{\{1+(Mu^2/\gamma RT)\}}-1\right)\right]\right]} \quad (2)$$

Kittel's method is based upon the assumption that the observed velocity of sound results from the propagation of sound waves inside the molecule and in the free space between them.

Kittel's method:

$$r= (M/\rho N)^{1/3}\,(1/2)\,\sqrt[3]{\left[\{1-(\tfrac{1}{u})\sqrt[2]{(3\,\gamma RT/M)}\}\,\sqrt[2]{2}\,\right]} \quad (3)$$

where $\gamma = C_p / C_v = 17.1/ (T^{4/9}\,\rho^{1/3})$, R= 2 Cal K^{-1} mol^{-1}, N is Avogadro number,

refractive index $n= (u/u_o)^{1/4}$ and speed of sound in air, $u_o = 34500$ cms^{-1}

Molecular radius can also be obtained from another method based upon the system made up of closely packed molecules with face centered cubic structure [7]. Assuming that there is no space between the molecules, the following equation can be used -

$$r= (1/2)\,\sqrt[3]{\{(M\sqrt{2})/(\rho N)\}} \quad (4)$$

The values obtained from above relation must always be greater than the values obtained from any other method.

A non-acoustic method employing refractive index and molar volume has been utilized to compute the molecular radius

$$r= [(3/4\pi N)\{(n^2-1)/ (n^2+2)\} *V_m]^{(1/3)} \quad (5)$$

The values of density and sound speed at varying condition of temperatures for all the pure liquids have been reported in Table -1**[4]**.

Table 1: Speed of sound (u) and density (ρ) of pure liquids at 293.15K-333.15K.

	n-hexane		n-heptane		n-dodecane		cyclohexane		toluene	
Temp (K)	**u (cms^{-1})**	**ρ (gcm^{-3})**	**U (cms^{-1})**	**ρ (gcm^{-3})**	**u (cms^{1})**	**ρ ($g\ cm^{-3}$)**	**u (cms^{-1})**	**ρ ($g\ cm^{-3}$)**	**u (cms^{-1})**	**P ($g\ cm^{-3}$)**
293.15	107770	0.65941	114990	0.68369	130120	0.74875	129200	0.77853	132430	0.86684
298.15	105620	0.65489	112850	0.6796	128090	0.74518	125780	0.77387	130290	0.8622
313.15	992390	0.6411	106670	0.6667	122190	0.7344	116890	0.7597	123980	0.8482
333.15	90856	0.6221	98592	0.6491	114660	0.7199	107030	0.7404	115800	0.8292

Results and Discussion:

The molecular radii of the pure liquids have been computed using Schaaffs', Rao's, Kittel's approaches and the relations mentioned in Eqs. 4 and 5. The computed values of molecular radii have been reported in Table- 2.

Table 2: Values of molecular radii r ($*10^{-8}$ cm) obtained using different methods at varying temperatures for the liquids n-hexane, n- heptane, n-dodecane, cyclohexane and toluene.

n-hexane (T)	r (Schaaffs)	r (Rao)	r (Kittels)	r (fcc)	r (n)
293.15	2.348	2.348	3.372	3.372	2.19
298.15	2.354	2.354	3.38	3.381	2.19
313.15	2.371	2.371	3.404	3.404	2.16
333.15	2.394	2.394	3.438	3.438	2.11
n-heptane					
293.15	2.44	2.44	3.503	3.503	2.32
298.15	2.445	2.445	3.511	3.511	2.32
313.15	2.46	2.46	3.53	3.53	2.29
333.15	2.482	2.48	3.56	3.56	2.25
n-dodecane					
293.15	2.82	2.82	4.054	4.054	2.78
298.15	2.83	2.83	4.061	4.061	2.77
313.15	2.84	2.84	4.08	4.08	2.75
333.15	2.86	2.86	4.107	4.107	2.72

cyclohexane					
293.15	2.203	2.203	3.164	3.164	2.17
298.15	2.207	2.207	3.17	3.17	2.16
313.15	2.22	2.22	3.18	3.18	2.13
333.15	2.24	2.24	3.217	3.217	2.09
toluene					
293.15	2.191	2.191	3.146	3.146	2.17
298.15	2.195	2.195	3.152	3.152	2.16
313.15	2.207	2.207	3.169	3.169	2.15
333.15	2.223	2.223	3.193	3.193	2.12

The graphical representation of all the computed values of molecular radius for various pure liquid at different temperatures has been presented in Fig 1.

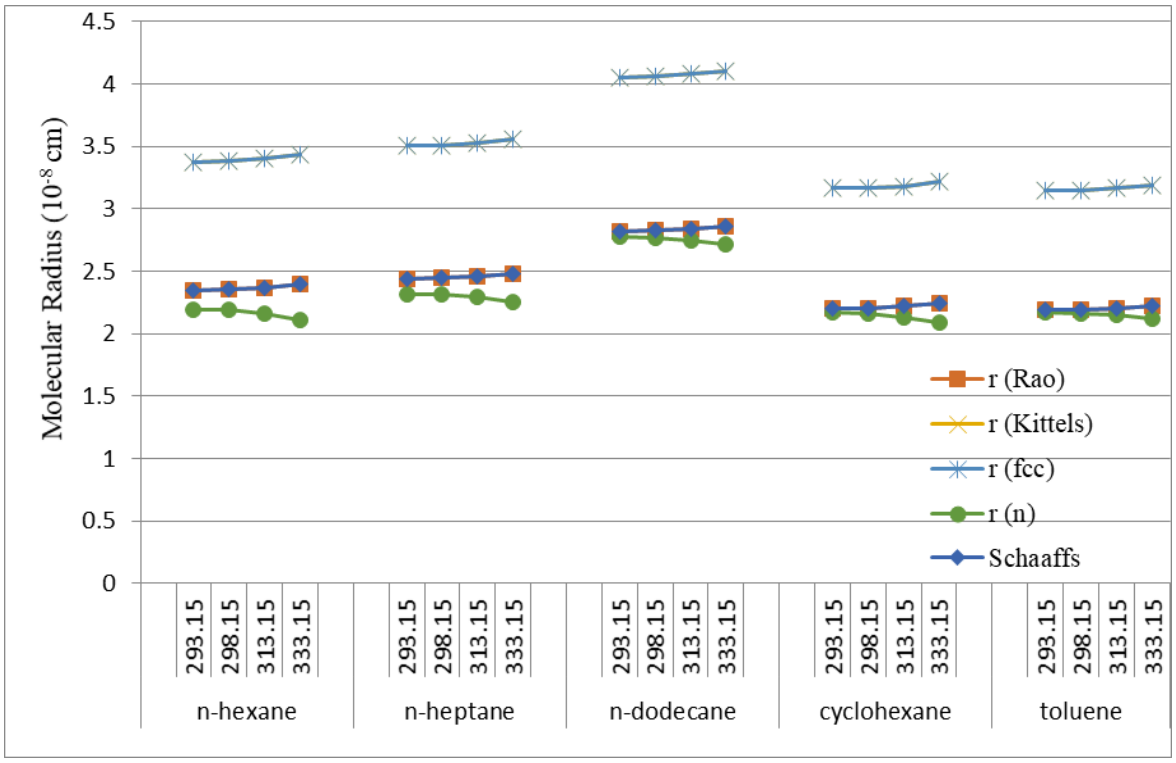

Fig.1. Molecular radius (r) of pure liquids at varying temperatures(K).

The refractive index method has been considered as an experimental method for the computation of molecular radius and has been taken as reference. The values obtained using Rao's, Schaaffs', Kittels approaches, refractive index relation and face centered cubic (FCC) assumption is not found to change remarkably with change in temperature. All the approaches have been found to give the best results as compared with the experimental results. There is found a bit high departure in obtained values using the method based upon assumption of FCC structure and Kittel's method from the experimental values. The values obtained using Kittel's method are almost equal to the values obtained from FCC based assumption. The statement [3] that the values obtained from the method based upon the assumption that

there is no free space between the spheres must always be higher than the values obtained from any other method is not true for Kittel's method. This result shows that the assumption of free space has to be reconsidered in present case.

The data like ultrasonic velocity, density and specific heat ratio are easily measurable and can be utilized in Schaaffs' and Rao's methods to compute the molecular radius of liquids. The application of the method FCC and Kittel's method given in Eqs.4 and 5 for these liquids should only be limited to estimate the maximum possible values of molecular radius.

Conclusion:

The present study shows that the acoustic relations used for computing molecular radius are very suitable for pure liquids. Schaaffs' method and Rao's method seems more convincing and applicable for pure liquids. These methods can be employed to estimate the various parameters and can be related with velocity of sounds in liquids.

Conflict of Interest:

The authors declared that they have no conflict of interest.

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