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Estimation of molecular radius of liquids and liquid mixtures from sound velocity

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Abstract

Various acoustic methods have been utilized to compute the molecular radius of pure liquids and liquid mixtures at varying conditions. The values thus obtained have been compared against the values obtained from a non-acoustic method, which uses refractive index data. These results have been utilized to study the relative merits of these various relations. An attempt to correlate the molecular radii of the liquids and liquid mixtures with other related properties of the liquid system has also been made. The applicability of an acoustic method like Schaaffs' method for the computation of the molecular radius in *liquid mixtures* has also been authenticated.

Keywords: Ultrasonic velocity; Refractive index; Face centered cubic structure

1. Introduction

The molecular radius is one of the parameters of pure liquids and liquid mixtures, which reflects their structural features. Liquids in their mixtures behave differently than they behave individually. Relative strength of A–B interaction is different in different mixtures. The molecular radius is thus not only related to the number of atoms involved but also to the nature of liquids. It is, directly or indirectly, an important parameter in the theories of liquids like Collision factor theory (CFT) [1,2] and Scaled particle theory [3,4]. Molecular radius has been utilized to evaluate some other important properties of liquids [5,6]. Surface tension or viscosity have been utilized for the computation of molecular diameter/radius by some workers [7–9].

Acoustic methods are the most powerful tools for the structural and physico-chemical studies of liquids [10]. Ultrasonic velocity and density data can be utilized to estimate the molecular radius in pure liquids and liquid mixtures. The effects of various parameters on molecular radius in pure liquids have been studied earlier [11], using various acoustic methods suggested by Schaaffs [1,12], Rao [13], Eyring [14,15] and Kittel [16]. Along with these acoustic methods, 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 [11]. The results obtained from these acoustic methods can be utilized to compute various other parameters and can be related with velocity of sound in liquids.

To the best of our knowledge, various methods of determining the molecular radius of *liquid mixtures* have not been analyzed by the previous workers. The studies on these relations, for pure liquids also, are not sufficient to provide an idea about the variation of molecular radius in a homologous series. In the present work, the acoustic methods for estimating the molecular radius have been employed in various organic liquids and liquid mixtures. The molecular radius can also be computed using refractive index and density data [17]. An attempt has also been made to compare the values obtained from the acoustic methods with the values obtained from the refractive index method. The values obtained from the refractive index method have been taken as the reference or experimental ones, the concept being used elsewhere [11] also. The contributing parameters have been correlated with molecular radius. The deviations in variation patterns of molecular radii with

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changing temperature and mole fraction of a particular type of the component of the mixture have also been studied.

2. Theory

A number of relations, Eqs. (1)–(4), can be employed to estimate the molecular radius of liquids using sound velocity and related data. Out of which, Schaaffs' and Rao's methods are based upon van der Waals equation of state. Kittel's and Eyring's methods are 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. These acoustic methods for the determination of molecular radius are summarized here.

Schaaffs' relation:

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

Rao's relation:

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

Eyring's relation:

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

Kittels's relation:

$$r=\sqrt[3]{\frac{M}{\rho N}}\ \frac{1}{2}\sqrt[3]{\left(1-\frac{1}{u}\sqrt{\frac{3\gamma RT}{M}}\right)\sqrt{2}}. \tag{4}$$

In all these relations, N = Avogadro's number; ρ = density; u = sound velocity; M = molecular mass; γ = specific heat ratio.

Besides acoustic methods, for a system made-up of spheres with mass M/N in a close-packed face-centered cubic structure (CP-FCC), molecular radius can also be obtained from the relation [11]

$$r=\frac{1}{2}\sqrt[3]{\frac{M\sqrt{2}}{\rho N}}. \tag{5}$$

This equation is based upon the assumption that there is no free space between the spheres (molecules). The values of molecular radius obtained from any other method must always be lower than the values obtained from this method. Refractive index data can be utilized in conjunction with molar volume to compute the molecular radius using the following relation [17]:

$$r=\left[\frac{3}{4\pi N}\frac{n^2-1}{n^2+2}V_m\right]^{\frac{1}{3}}. \tag{6}$$

This relation provides non-acoustic method for the estimation of molecular radius.

3. Results and discussion

The molecular radii of various organic liquids and liquid mixtures at various conditions of temperature and pressure have been computed using Eqs. (1)–(6). Sound velocity and related data required for the computation have been taken from the various sources [18–21]. The computed values of molecular radius for various pure liquids and liquid mixtures have been graphically displayed in Figs. 1–4. Eq. (6) has been considered as an experimental method for the determination of molecular radius and has been taken as reference.

As far as molecular radii data obtained from Eq. (6) are considered, molecular radii are not found to change remarkably with changing temperature (Fig. 1). Though results from Rao's method show a regular trend of change in molecular radius with changing temperature (Fig. 1), there is a bit high departure in values from the experimental values. This departure can be explained in terms of difference of only one term in the relation given by Shaaffs and Rao, Eqs. (1) and (2). The values of molecular radius obtained from Eyring's and Kittel's relations have not been found to be in agreement with the experimental values (Figs. 1, 3 and 4). These results show that the assumptions of free space made by these relations have to be reconsidered. These relations need modifications in the present cases. The values of molecular radius obtained from Eq. (5) are always found to be higher than the values obtained from any other method (Figs. 1–4). These results are obvious, as this equation is based upon the assumption that there is no free space between the spheres. The application of this equation for any liquid system should only be limited to estimate the maximum possible values of molecular radius. Schaaffs' method has been found to give the best results as compared with the experimental results (Figs. 1, 3 and 4). The benefit of using Schaaffs' method is not only its applicability but also the need of a minimum of easily measurable data like ultrasonic velocity, density and specific heat ratio. In the case where specific heat ratio is not available, the equation can be simplified by neglecting the γ term without significant differences [5,6]. There is a regular increase of molecular radius in the case of the members of homologous series of alkanes. This fact seems to be obvious and has a regular trend also (Fig. 1). It is also

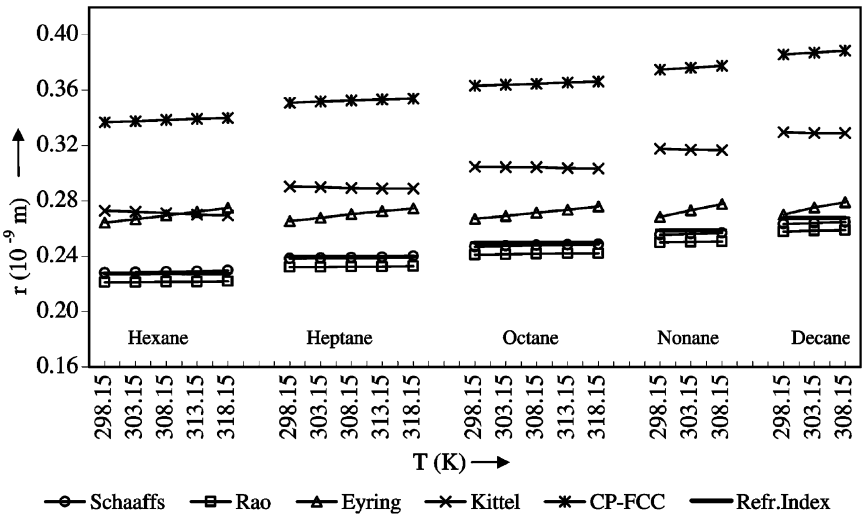

Fig. 1. Molecular radius (r) of alkanes at varying temperatures.

interesting to note that, though Schaaffs' method gives slight deviations from experimental results in case of higher members, the deviation pattern is constant and not tangible.

Figs. 1, 3 and 4 show the applicability of Schaaffs' method for the computation of molecular radius of binary liquid mixtures. The values of molecular radius obtained in the case of liquid mixtures show that Schaaffs' method provides best results in these cases. The regular decrease in molecular radius with increasing mole fraction of ethyl ethanoate (Fig. 3) also seems to be obvious as ethyl ethanoate has a lower molecular radius than cyclohexane. Similar obvious results have been obtained in the binary liquid mixture of cyclohexane + benzene. The applicability of these relations has also been verified for the computation of internal pressure in liquid mixtures.

4. Conclusion

The acoustic methods for the determination of molecular radius are found to be very suitable for *pure liquids* as well as for *liquid mixtures*. The increase in molecular radius in the higher homologues is found to be very convincing and logical. The variation pattern of molecular radius with the change in various parameters of liquids and liquid mixtures seems to be very convincing. Schaaffs' method seems to be applicable for *pure liquids* as well as for *liquid mixtures*. This relation can, thus,

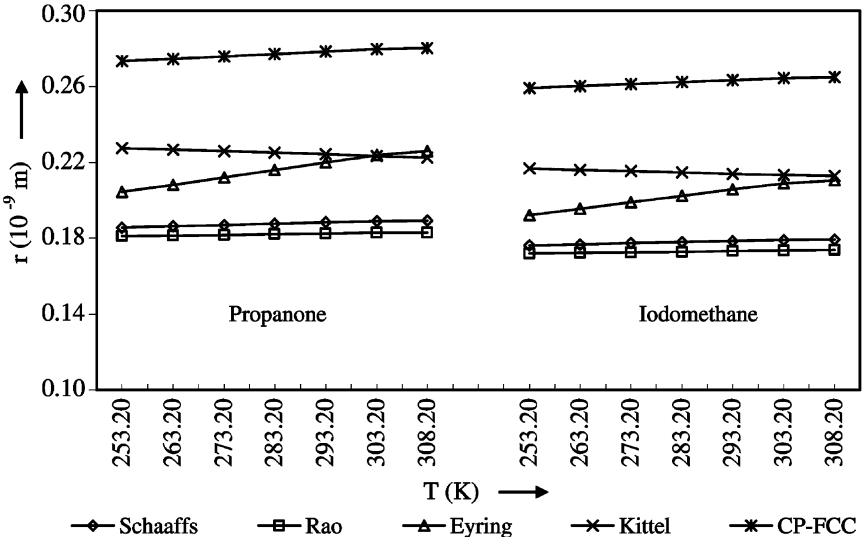

Fig. 2. Molecular radius (r) of propanone and iodomethane.

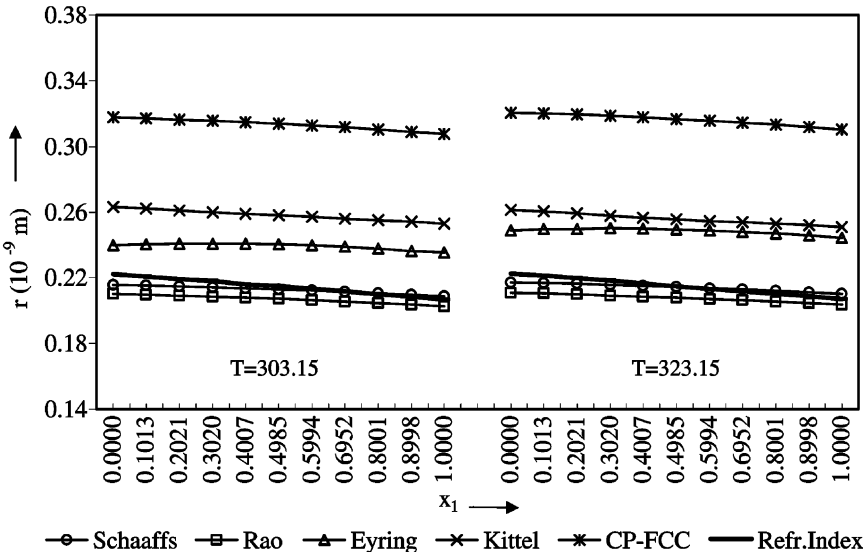

Fig. 3. Molecular radius (r) of binary liquid mixture: ethyl ethanoate (1) + cyclohexane.

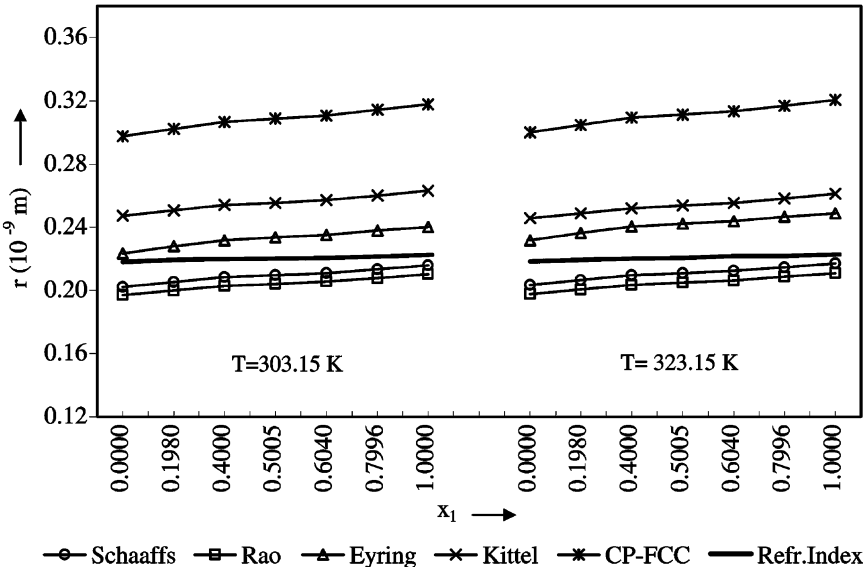

Fig. 4. Molecular radius (r) of binary liquid mixture: cyclohexane(1) + benzene

be utilized to estimate the variety of other parameters of liquids and liquid mixtures.

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