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Effect of Pressure on Self-Diffusion in Liquids

R. P. Chhabra[1]

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The pressure dependence of the self-diffusion in simple nonpolar liquids has been examined. It is shown that an equation based on Lamm's formalism provides an adequate representation of the variation of self-diffusion with pressure at constant temperature over wide ranges of pressure and temperature. Data on cyclohexane, *n*-hexane, benzene, tetramethylsilane, methylcyclohexane, and chlorotrifluoromethane conform to this behavior. The analysis presented herein provides a method for estimating self-diffusion coefficients at elevated pressure from a knowledge of the shear viscosity coefficient values under the same conditions without introducing any adjustable parameters.

KEY WORDS: high pressures; Lamm's equation; nonpolar liquids; self-diffusion.

1. INTRODUCTION

In spite of concentrated efforts, progress on the development of models for the liquid state has been rather slow. Consequently, a model for the liquid state which can rival the kinetic theory of gases is yet to emerge. Transport properties (viscosity and self-diffusion), together with thermodynamic and structural information, are often used to validate liquid state theories. Conversely, the utility of a specific model is judged by its ability to predict viscosity and self-diffusion for a given liquid as functions of pressure and temperature. It is well known that the self-diffusion coefficient is strongly influenced by both pressure and temperature. Admittedly, considerable progress has been made in elucidating the temperature dependence of the self-diffusion coefficient at atmospheric pressure. Informative and critical accounts of the theoretical as well as experimental developments in this area are available [1–3].

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[1] Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208016, India.

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On the other hand, very little is known about the variation of the self-diffusion coefficient of nonpolar substances at elevated pressure. There are two possible reasons for this. First, the experimental values of self-diffusion coefficients at elevated pressures have been reported only during the last 10 to 15 years. Second, most models which purport to describe the phenomenon of self-diffusion in liquids have an inherent weakness since they involve adjustable parameters of dubious physical value. This deficiency is indeed serious from a theoretical as well as from a practical standpoint, as neither can one ascribe a physical meaning to such adjustable parameters nor are these capable of providing a priori estimation (especially at elevated pressures).

In this paper, the pressure dependence of self-diffusion coefficients of various liquids is examined with the aid of a formulation already available in the literature. However, prior to presenting the new analysis, it is instructive to present a concise description of previous work in this area.

2. PREVIOUS WORK

As remarked earlier, high-pressure measurements of self-diffusion coefficients not only are limited but also are of recent vintage. In many instances, the experimental data have merely been reported without an attempt at explanation, while some investigators have provided some sort of interpretation. For instance, Doane and Drickamer [4] postulated that the pressure effects of self-diffusion in carbon tetrachloride and SnI_4 could be explained solely in terms of the orientation of molecules. Benedek and Purcell [5] reported a monotonic decrease in the values of the self-diffusion of water and methyl iodide with increasing pressures. An excellent review of the work in this area prior to 1963 has been given by Steele and Webb [6], who concluded that the ratio $D\mu/kT$ (where D is the coefficient of self-diffusion, μ is the shear viscosity, T is the absolute temperature, and k is the Boltzmann constant) is not pressure and temperture *invariant*. Recent years have witnessed a renewed interest in the phenomenon of self-diffusion in liquids at elevated pressures. McCool and Woolf [7] reported experimental values of the self-diffusion coefficient of cyclohexane over wide ranges of temperature and pressure and concluded that $\ln D$ varies linearly with pressure at a constant temperature. Not only is it difficult to explain this type of variations, but also it is not obeyed by other substances. A number of investigators [8–11] have reported departures from the linearity in $\ln D$–pressure plots. More recently, Easteal [12] has argued that $\ln D$ varies linearly with $P^{0.75}$ rather than with P, except at low pressures. However, his assertion is based on the results for only one substance, namely, *n*-hexane. Unfortunately when the results for other substances (for which the relevant data are available) are plotted in this manner, nonlinear behavior is observed. For instance, Figs. 1 and 2 show data for methylcyclohexane and chlorotrifluoromethane, respectively, plotted in a manner as suggested by Easteal, and one can clearly discern that a nonlinear relation between ln D and $P^{0.75}$ is present in these figures.

On the other hand, numerous workers [11, 13–17] have employed analytical expressions which can be regarded as direct descendants of the hard-sphere theory of Enskog. In particular, the modification of the hard-sphere theory by Dymond [18] has gained wide acceptance. Unfortunately, not only does this approach break down in the low-density region [14], but also its predictions are extremely sensitive to the values of the hard-sphere diameter. For instance, a variation of the order of 1–2% in the value of the hard-sphere diameter can result in a change of about 20% in the corresponding values of viscosity and self-diffusion [19].

It is clear from the above discussion that the nature of the pressure dependence of the coefficient of self-diffusion is not yet well understood, and a satisfactory method is yet to emerge. In this paper, it is demonstrated how an existing formulation (which has proved highly successful in depicting the *temperature* dependence of self-diffusion coefficients in ordinary liquids and molten metals) can also be used to elucidate the *pressure* dependence of self-diffusion coefficients.

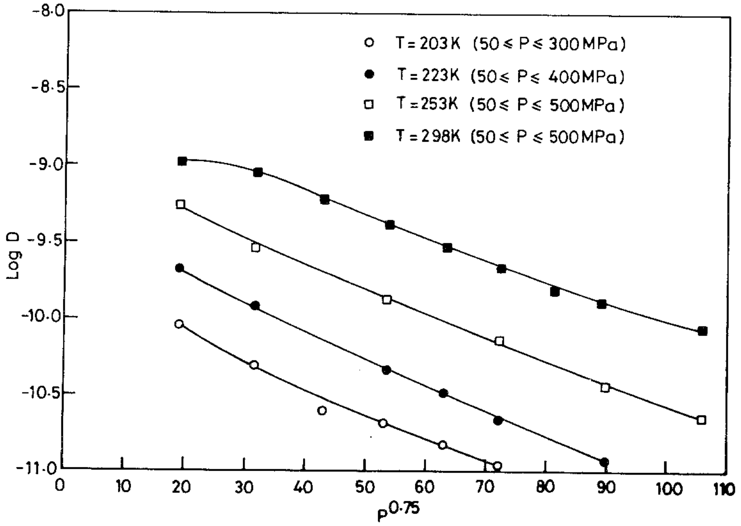

Fig. 1. Plot of ln D against $P^{0.75}$ for methylcyclohexane showing nonlinear behavior (data from Ref. 17). (The quantity D is in $m^2 \cdot s^{-1}$ and P is in MPa.)

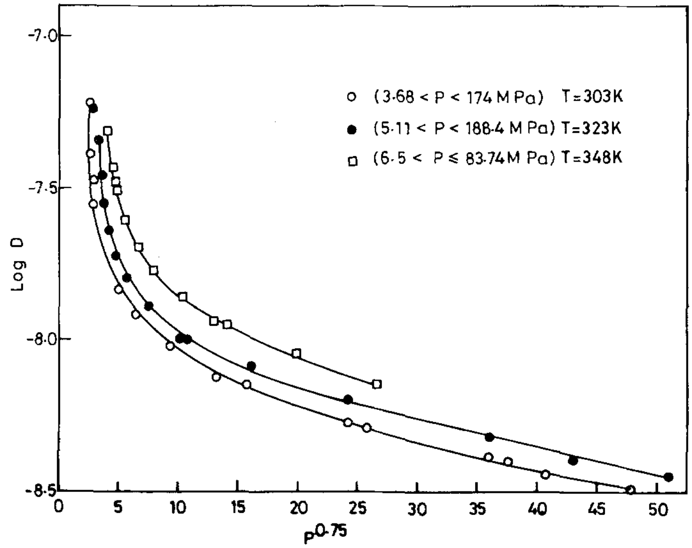

Fig. 2. Plot of $\ln D$ against $P^{0.75}$ for chlorotrifluoromethane showing nonlinear dependence (data from Ref. 13). (The quantity D is in $m^2 \cdot s^{-1}$ and P is in MPa.)

3. ANALYSIS AND DISCUSSION

Based on Lamm's theory [20, 21], Dullien [22] evaluated a molar average friction coefficient. Further, making use of the fact that the molar average friction coefficient and viscosity are two different ways of averaging friction coefficients, he derived the following analytical expression for the self-diffusion.

$$\delta = \left[\frac{2\mu V D}{RT} \right]^{1/2} \tag{1}$$

In the above equation, μ is the shear viscosity, V is the molar volume, D is the self-diffusion coefficient, T is the absolute temperature, R is the universal gas constant, and δ is the average momentum transfer distance, which bears a constant ratio with the molecular diameter for various simple liquids [23] and with the atomic diameter for molten metals [24].

Equation (1) is not based on any particular model of the liquid state, but it is consistent with the elementary kinetic theory. Although it has been shown elsewhere [23–25] that Eq. (1) describes the temperature dependence of self-diffusion coefficients in simple liquids and molten

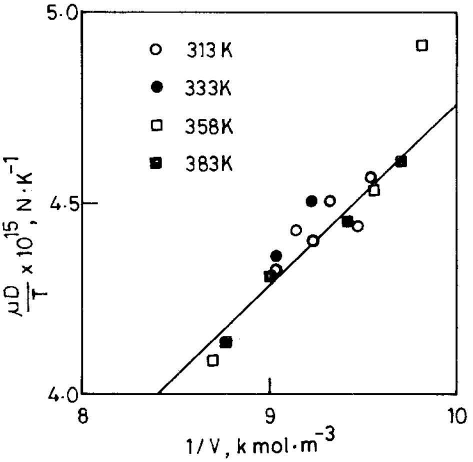

Fig. 3. Plot of ($\mu D/T$) versus ($1/V$) for cyclohexane in accordance with Eq. (2) (data from Ref. 26). [The line represents the predictions of Eq. (2).]

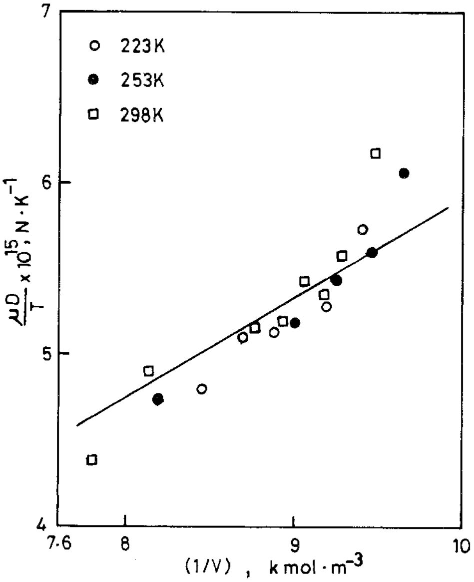

Fig. 4. Plot of ($\mu D/T$) versus ($1/V$) for methylcyclohexane in accordance with Eq. (2) (data from Ref. 17). [The line represents the predictions of Eq. (2).]

metallic systems remarkably well, its applicability to high-pressure data has not been examined to date. Equation (1) can be rearranged as

$$\frac{\mu D}{T}=\frac{\delta^2 R}{2V} \tag{2}$$

The left-hand side of Eq. (2) is the well-known Stokes–Einstein ratio, whereas the right-hand side is a function of both temperature and pressure. However, it is not immediately obvious to specify a priori whether the pressure and temperature dependence of the right-hand side, as asserted by Steele and Webb [6], is due solely to V or due to δ or due to both.

In order to establish the applicability of Eq. (2) to the phenomenon of self-diffusion (D), the molecular volume (V) or density (ρ), and the

Table I. Values of Average Momentum-Transfer Distance, δ, for Cyclohexane Calculated from Corresponding Individual Measurements of μ, V, D (Data from Ref. 7)

Temp. (K)	Pressure (10^5 Pa)	δ (10^{-10} m)
288.2	1.01	3.383
	39	3.387
	42	3.374
298.2	1.01	3.390
	114	3.423
	177	3.342
	273	3.293
	331	3.358
313.2	1.01	3.403
	210	3.371
	358	3.428
	468	3.404
328.2	1.01	3.447
	163	3.362
	269	3.343
	496	3.341
	659	3.460
	661	3.443
	821	3.544

Mean value 3.393 + 4.2 %[a]
−3.1 %[a]

[a] The percentage error is defined as 100 {[mean value − minimum (or maximum) value]/minimum (or maximum) value}.

viscosity (μ) are needed as functions of pressure (P) and temperature (T). Indeed, measurements of this kind are very limited and are available only for six substances. Figures 3 and 4 show plots of $\mu D/T$ versus $(1/V)$ for cyclohexane and methylcyclohexane, respectively, at a range of pressures and temperatures. An examination of Figs. 3 and 4 reveals that the formulation of Dullien [Eq. (2)] is indeed applicable even at high pressures. The behavior of the remaining four substances (not shown here) also conforms to Eq. (2). Furthermore, the fact that the data points pertaining to different values of pressure and temperature fall on a single curve suggests that the average momentum transfer distance (δ) is virtually pressure and temperature independent. This is established unequivocally in Table I, where the values of δ for cyclohexane, calculated from individual measurements, are presented. An examination of the data in Table I shows that the value of δ varies only about $\pm 4\%$ from its mean value for a range of pressure and temperature conditions encompassed by the measurements. Similar results are obtained for the remaining five substances, and a summary of results is presented in Table II along with the sources of data used in this study. In particular, attention is drawn to the case of cyclohexane for which experimental measurements are available from two independent studies. The agreement between the two values of δ is excellent. Bearing in mind the experimental uncertainty associated with

Table II. Values of Mean Momentum Transfer Distance (δ)

System	T range (K)	P range (10^5 Pa)	δ (10^{-10} m)	Source of data
Cyclohexane	288.2–328.2	1.01–821	$3.393 + 4.2\%$ $- 3.1\%$	ρ, μ, D—Ref. 7
	313–383	1–2140	$3.383 + 4.9\%$ $- 3.4\%$	ρ, μ, D—Ref. 26
n-Hexane	273.15–333.15	1.01–392.4	$3.56 + 3.3\%$ $- 6.2\%$	ρ, D—Ref. 28 μ—Ref. 27
Tetramethyl silane	298–373	45–4500	$3.046 + 6.3\%$ $- 7.0\%$	ρ, μ, D—Ref. 11
Benzene	303–433	1–4000	$3.011 + 4.3\%$ $- 5.0\%$	ρ, μ, D—Ref. 11
Methylcyclohexane	223–298	1–5000	$3.78 \pm 5\%$ $- 6.8\%$	ρ, μ, D—Ref. 17
Chlorotrifluoromethane	303–348	50–700	$2.68 + 6\%$ $- 7\%$	ρ, μ, D—Ref. 13

high-pressure work, it is safe to conclude that the mean momentum transfer distance (δ) is independent of pressure and temperature for the six substances studied here. General conclusions regarding the invariance of δ should await more experimental work. Although the extent of experimental uncertainty associated with the measurements of self-diffusion coefficients is somewhat temperature and pressure dependent, it is believed to be of the order of 5–10% [16]. Notwithstanding this fact, the average value of the mean momentum–transfer distance (δ) seems to bear a near-constant ratio (0.63–0.65) with the corresponding molecular diameter as originally postulated by Dullien [22]. Therefore, the dependence of $\mu D/T$ on pressure and temperature can be explained in terms of the variation of molar volume with pressure and temperature. Finally, since the present approach is concerned with the group $\mu D/T$ and not the diffusion and viscosity coefficient individually, the values of self-diffusion coefficient calculated as outlined herein are not as sensitive to the value of the molecular diameter as in the formulation of Dymond [18].

4. CONCLUDING REMARKS

In this work, it has been demonstrated that the formulation of Dullien can also be used to depict the pressure dependence of self-diffusion over wide ranges of temperature and pressure without any adjustable parameters. The mean momentum transfer distance appears to be independent of pressure and temperature for the systems studied herein, and it bears a near-constant ratio with molecular diameter. However, data for more substances over a wide range of pressure and temperature are needed to generalize this observation. The interpretation presented herein provides another vantage point for studying the transport properties of liquids. Finally, unlike the hard-sphere theories which attempt to represent the density dependence of individual transport properties, the present method allows the value of the self-diffusion coefficient at elevated pressures to be calculated simply from a knowledge of the value of the shear viscosity coefficient under the same conditions.

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