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Diffusion of spherical solutes: A fractional molecular-hydrodynamic study of solvent dependence

T.C. Chan *, K.Y. Li, H.T. Li

Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

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ABSTRACT

Diffusivities of tetramethyltin, tetraethyltin, tetraethyllead, and 2,2-dichloropropane in methanol as well as tetraethyltin and tetraethyllead in ethanol were measured and combined with other literature data of spherical solutes in various solvents to study the effects of solvent on diffusivity. A new fractional molecular-hydrodynamic relation is found to well represent the solvent dependence for the diffusivities of carbon tetrachloride, tetramethyltin, tetraethyltin, tetrapropyltin, and tetrabutyltin at diverse temperatures. The relation consists of two components: one is a function of the hydrodynamic viscosity and the other associated with the molecular properties of solvent. Each has a fractional exponent dependent on solute size. The results here indicate that the relative importance of the viscosity component consistently increases with solute size, but that the trend for the molecular component is reversed. Comparison with other diffusion relations reveals that the newly developed model is more applicable and accurate for expressing the effects of solvent on diffusivity.

1. Introduction

Diffusion of molecules in solutions is of immense importance in many chemical reactions, biological systems, and industrial processes. Notwithstanding the intensive research efforts devoted to this subject in the past, our knowledge regarding diffusion in dense fluids is nevertheless rudimentary. One of the areas that have not yet been completely understood is the diffusion behavior of solute molecules that are either smaller than or comparable in size to the solvent molecules. In particular, it appears that solvent dependence of diffusivity of such solutes in liquid solutions is still controversial in the literature. However, non-macromolecular solutes commonly occur in chemical and biological systems, and solvent plays an essential role in diffusion. Hence, the effects of solvents and solutes on diffusion in liquids warrant further investigations.

For diffusion of a solute at infinite dilution in a particular solvent, the diffusivity of that solute can be significantly affected by motions of the solvent molecules. Details of the molecular dynamics in real systems of liquid solutions are extremely complicated, however, making the use of first principles to describe diffusion impractical in spite of the very advanced computing technology available today. Thus, phenomenological description in terms of viscosity (a hydrodynamic variable) of solvent's collective dynamics is traditionally used to study the effects of solvent on diffusivity, although molecular dynamic simulations and kinetic molecular theory can also provide insights into the diffusive process. The utilization of viscosity for relating solvent dependence of diffusion is known to originate from the hydrodynamic theory (HT) typified by the Stokes–Einstein–Sutherland equation (also known as the Stokes–Einstein (SE) relation). For diffusion at trace concentration of solute, the SE relation is commonly expressed by

$$D_{12} = \frac{k_B T}{6\pi r_1 \eta} \tag{1}$$

where D_{12} is the diffusion coefficient of solute 1 at infinite dilution in solvent 2, T is the temperature, k_B represents the Boltzmann constant, 6 denotes a numerical value for the 'stick' boundary condition [1], η refers to the viscosity of the pure solvent, and r_1 is the radius of the solute molecule. In fact, the SE relation can interpret the diffusion of vast or macromolecule-sized spherical solutes quite well. For non-macromolecular solutes, however, many studies [2–8] have found this hydrodynamic relation to be invalid. Detailed reviews of SE have been given by Cussler [9] and by Tyrrell and Harris [1].

A different approach in the study of diffusion in dense fluids is adopted in the kinetic theory (KT), another well-established diffusion theory in the literature. This approach takes binary molecular collisions into consideration during the diffusive process, in a fashion that is distinct from the hydrodynamic approach. In this theory, diffusion in the liquid state is normally described by temperature,

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* Corresponding author.
E-mail address: tcc.chan@polyu.edu.hk (T.C. Chan).

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number density, masses and sizes of molecules, radial distribution function, translation-rotation coupling, free volume, and other microscopic contributions, though different KT models such as the free volume and the rough-hard-sphere models may have different functions for relating diffusivity data. A review of previous models of KT has also been provided by Tyrrell and Harris [1]. A well-recognized weakness of KT is that the effects of molecular mass on diffusivity is often overestimated by the theory [10,11]. It also appears in the literature that relatively few kinetic models of diffusion have demonstrated good validation by a wide range of experimental diffusivities measured under various conditions.

The two major diffusion theories cited above are actually quite different in terms of their fundamental concept. Whereas HT considers solvent to be a continuum, KT perceives it as an aggregation of discrete molecules. It appears, however, that none of these theories alone could be indisputably regarded as very successful in providing accurate numerical representation for a broad range of experimental diffusivities of non-macromolecular solute molecules. In an effort to mend the gap between experiment and theory, we previously presented a relation [12] for correlating the tracer diffusivities of nonassociated pseudoplanar solutes. The relation developed in that study, which combines various molecular effects with the hydrodynamic viscosity of solvent, can be given as follows:

$$D_{12} = \frac{T}{(bV_1 + c)\left(\eta^{2/3} M_2^{1/4} \rho_2^{1/3} \bar{V}_m / \bar{V}_f\right)} \tag{2}$$

where b and c are constants, V_1 represents the van der Waals (VDW) volume of the solute molecule, M_2 is the mass of the solvent molecule, ρ_2 denotes solvent's molar number density, and $\bar{V}_m/\bar{V}_f$ is the reciprocal of solvent's free volume fraction. Such fraction of solvent is given [12] by the expression:

$$\bar{V}_f/\bar{V}_m = \frac{\bar{V}_m - N_A V_2}{\bar{V}_m} \tag{3}$$

where N_A refers to the Avogadro constant, V_2 is the VDW volume of the solvent molecule, and $\bar{V}_m$ represents solvent's molar volume. This dimensionless quantity is actually equivalent to the average fraction of free space available to each solvent molecule in the liquid. The establishment of Eq. (2) is based on the framework of the SE relation but uses two functions to replace the Stokes law (i.e. $6\pi r_1 \eta$) in the relation. However, similar to the Stokes law, one function in the relation depends on the solute and the other depends on the solvent. In Eq. (2), the function for the solute can be represented by the expression ($bV_1 + c$), which originates from the rough-hard-sphere model [13–15] of the kinetic theory with a simplification for the diffusion of solutes of similar shape at infinite dilution [12,16]. The function depending on various solvent properties is due to available theoretical expressions and explanations (see Section 3.2). Details of the development of Eq. (2) have been given in Ref. [12]. It is remarkable that Eq. (2), with only two constants ($b = 0.800$ and $c = 53.9$), has been shown to be able to correlate 176 diffusivity data of pseudoplanar solute molecules for a wide range of temperatures and solvents to an average absolute deviation (AAD) within 2.8% [12].

Recently we have further demonstrated [17] that the solvent dependence of diffusion in Eq. (2), i.e.

$$D_{12}/T = \frac{a_4(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3} M_2^{1/4} \eta^{2/3}} \tag{4}$$

is also applicable to the spherical solute carbon tetrachloride (CCl_4). In Eq. (4), a_4 is a solute-dependent constant. In that study, it was also found that diffusivity of a solute is weakly dependent on the dielectric constant of the solvent by the relation

$$D_{12}/T = \frac{a_5\left(\varepsilon_r^{1/48}\right)(\bar{V}_f/\bar{V}_m)}{\rho_2^{1/3} M_2^{1/4} \eta^{2/3}} \tag{5}$$

In Eq. (5), a_5 denotes a constant that is dependent on the solute and ε_r represents solvent's relative permittivity or dielectric constant. With a single proportional constant a_5 for each solute, Eq. (5) has been demonstrated to be capable of relating the diffusion coefficients of spherical CCl_4 and of five disc-like aromatic solutes in various solvents at different temperatures to within an AAD of 3.2% and 2.4%, respectively [17]. The success of Eqs. (4), (5) can be attributed to the coupling of the hydrodynamic viscosity with various molecular contributions of solvent. It also indicates that the approach considering solvent as having both the properties of discrete particles and of continuum medium is useful and realistic for interpreting the effects of solvent on diffusivity of solutes that are not huge in molecular size. Although Eq. (5) is applicable for representing the dependence of diffusion on solvent for both the spherical and disc-shaped solutes studied in Ref. [17], the range of solute sizes considered in the previous work is not very wide. In particular, carbon tetrachloride is the only spherical solute in that study. Additionally, it is commonly known that the diffusivity of a very large solute with a spherical shape can be well described by SE, i.e. its value is dependent on the viscosity of the solvent as follows:

$$D_{12}/T = a_1 \eta^{-1} \tag{6}$$

where a_1 is a constant dependent on solute. Eq. (6) actually represents the solvent dependence of diffusivity for the SE relation, in which microscopic effects of solvent molecules are not considered. This implies that Eq. (5), which includes the molecular properties of solvent, is likely valid for the small CCl_4 molecule but is invalid for macromolecule-sized spherical solutes. It should be pointed out that unlike thin disc-shaped and other non-spherical solute molecules, whose diffusion in dense fluids is generally anisotropic and dependent on the translation-rotation coupling [18,19], the diffusion of spherical solutes is isotropic, and their translational motions should be uniquely different from those of non-spherical solutes. In view of these facts, it is necessary to further investigate the effect of solute size on the solvent dependence of diffusion using molecular modifications of hydrodynamics for spherical solutes with sizes below the Stokes–Einstein limit where SE is inapplicable. The results, together with those for the pseudoplanar solutes, should also provide useful information concerning the effect of solute shape on diffusion, another area that has not yet been well understood.

In this work, we report limiting mutual diffusion coefficients of some spherical solutes which are incapable of forming strong intermolecular associations (e.g. hydrogen bonding) with solvent molecules. These newly measured diffusivities are combined with other literature data to study the effects of solvent on diffusion for a large number of solvents, temperatures, and solute sizes. The objective is to obtain a more generally applicable and accurate relation that can mend the inadequacies of the traditional relations in the literature for representing the diffusivities of nonassociated spherical solutes, in particular those of relatively small sizes. It is also our aim to find out the role that solute size plays on solvent dependence of diffusion. We use basically the molecular-hydrodynamic coupling approach developed in our previous studies [12,17]. Modifications that are required for the spherical solutes in the present investigation are given in Section 3.

2. Experimental

Mutual diffusion coefficients at infinite dilution of tetramethyltin (Me_4Sn), tetraethyltin (Et_4Sn), tetraethyllead (Et_4Pb), and