

The effect of hydrogen bonding on the diffusion of water in *n*-alkanes and *n*-alcohols measured with a novel single microdroplet method

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While the Stokes–Einstein (SE) equation predicts that the diffusion coefficient of a solute will be inversely proportional to the viscosity of the solvent, this relation is commonly known to fail for solutes, which are the same size or smaller than the solvent. Multiple researchers have reported that for small solutes, the diffusion coefficient is inversely proportional to the viscosity to a fractional power, and that solutes actually diffuse faster than SE predicts. For other solvent systems, attractive solute-solvent interactions, such as hydrogen bonding, are known to retard the diffusion of a solute. Some researchers have interpreted the slower diffusion due to hydrogen bonding as resulting from the effective diffusion of a larger complex of a solute and solvent molecules. We have developed and used a novel micropipette technique, which can form and hold a single microdroplet of water while it dissolves in a diffusion controlled environment into the solvent. This method has been used to examine the diffusion of water in both *n*-alkanes and *n*-alcohols. It was found that the polar solute water, diffusing in a solvent with which it cannot hydrogen bond, closely resembles small nonpolar solutes such as xenon and krypton diffusing in *n*-alkanes, with diffusion coefficients ranging from 12.5×10^{-5} cm²/s for water in *n*-pentane to 1.15×10^{-5} cm²/s for water in hexadecane. Diffusion coefficients were found to be inversely proportional to viscosity to a fractional power, and diffusion coefficients were faster than SE predicts. For water diffusing in a solvent (*n*-alcohols) with which it can hydrogen bond, diffusion coefficient values ranged from 1.75×10^{-5} cm²/s in *n*-methanol to 0.364×10^{-5} cm²/s in *n*-octanol, and diffusion was slower than an alkane of corresponding viscosity. We find no evidence for solute-solvent complex diffusion. Rather, it is possible that the small solute water may be retarded by relatively longer residence times (compared to non-H-bonding solvents) as it moves through the liquid. © 2010 American Institute of Physics. [doi:10.1063/1.3298857]

I. INTRODUCTION

Diffusion of a small solute in a solvent with which it can hydrogen bond is an important, yet poorly understood problem in liquids. According to the Einstein relation, the diffusion coefficient of a solute moving through a solvent is given by $D = k_B T / \zeta$, where ζ is a friction coefficient, k_B is the Boltzmann constant, and T is the temperature. This relation is often combined with the Stokes equation, which describes the friction force as the drag force on a sphere moving through a continuous solvent. The resulting equation, $D = k_B T / 6\pi R_{\text{solute}} \eta$ (in which η is the shear viscosity of the solvent and R_{solute} is the radius of the solute¹), the Stokes–Einstein equation, predicts that for a given particle radius, at known temperature, the diffusion coefficient is simply inversely proportional to the solvent viscosity. It is the most commonly used equation for estimation of the diffusion coefficient of a solute in a solvent.² However, for solutes smaller than the solvent, the Stokes–Einstein equation is of questionable validity, as the continuum assumption inherent in the Stokes drag equation no longer holds. In fact, experiments reveal that small solutes in a large solvent diffuse

more quickly than predicted by the Stokes–Einstein equation. Furthermore, any attractive solute-solvent interactions, such as hydrogen bonding, would also affect the friction coefficient, and hence retard the motion of the solute through the solvent, lowering the diffusion coefficient.^{3,4} In order to examine these effects in more detail and to test the SE in systems with and without hydrogen bonding, we have used a novel, micropipette technique and analysis to measure the diffusion of water in *n*-alcohols (with hydrogen bonding) and compared the results to that in *n*-alkanes (without hydrogen bonding).

As a water molecule is smaller than a molecule of *n*-alkane or *n*-alcohol, we can reasonably expect diffusion behavior for water in both solvents to deviate from that predicted by the Stokes–Einstein model. Some experiments on solute diffusion with hydrogen bonding have found that it retarded the motion of the solute as compared to a similarly sized and shaped solute incapable of hydrogen bonding. These data have been interpreted by some as the solute effectively diffusing as part of a solute-solvent complex.

One common experimental method of determining the diffusion coefficient of a liquid in another is the Taylor dispersion.² This method is based on laminar flow of the solvent, into which a pulse of immiscible solute is injected.

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The decay of this pulse is dependent on the diffusion of the solute in the solvent, and so, by measuring the shape of this pulse the diffusion coefficient of the solute in the solvent can be determined.

Another common method of experimental determination of diffusion coefficients is the diaphragm cell, which is comprised of two compartments of liquid of different concentrations separated by either a porous membrane or a glass frit.² The diffusion coefficient is measured by determining the concentration present in each compartment after a given length of time. Eastaie⁵ used the diaphragm cell to study the diffusion of water in a variety of organic liquids, but did not extend his work to *n*-alkanes of chain length longer than hexane. Previous work on water diffusion in alcohols has similarly been limited to the shorter chain alcohols (up to *n*-butanol), in which water is more soluble and for methanol and ethanol, is miscible. These values are important and give us a point of calibration for the longer alkanes and alcohols studied here.

The novel method and analyses described in this paper do not require any sort of flow, and our droplets are kept spherical by surface tension. Here, we present a novel technique for determining the diffusion coefficient of one liquid in another, where the two liquids form an interface. This method is based on the observation of the dissolution of a microdroplet on the end of a micropipette. Because small microdroplets can be manipulated this way, the shrinkage of the droplet due to dissolution of the organic into the water can be measured in seconds to minutes.

As will be further described, a micron-scale water droplet placed in an excess of pure *n*-alcohol or *n*-alkane solvent will lose mass because the water will dissolve completely into the solvent. This mass loss is visually observable in a light microscope as a reduction in the dimensions (diameter) of the droplet, and, assuming that mass transfer is governed only by diffusion, the time dependence of the mass loss is directly related to the concentration gradient of water at the boundary of the droplet. The gradient is, in turn, directly related to the solubility of water in the medium as well as the diffusion of water in that medium as it disperses in the medium away from the droplet interface. The relationship between diffusion, solubility, and the radius of the droplet forms the basis of the Epstein–Plesset equation initially developed to describe the *Stability of Gas Bubbles in Liquid-Gas Solutions*,⁶ but applied here for liquid-liquid systems.

As derived previously⁶ and used for gas microbubble and liquid in liquid droplet dissolution,⁷ the Epstein–Plesset equation used in this work is

$$\frac{dR}{dt} = -\frac{DC_s(1-f)}{\rho} \left\{ \frac{1}{R} + \frac{1}{\sqrt{\pi Dt}} \right\}. \quad (1)$$

It is thus, a relation for the radius versus time behavior of a water droplet in a dehydrating medium, where *f* is defined as C_i/C_s , the ratio of initial concentration to the saturation concentration, ρ is the density of the droplet material, and *R* is the radius of the liquid droplet.

The micropipette technique has been used in previous work by Duncan and Needham,⁷ which has shown that the Epstein–Plesset model accurately predicts the radius versus

time behavior of various two phase microsystems both for liquid-in-liquid⁷ and gas bubble-in-liquid systems⁸ from which mass is transferred purely through diffusion, and where the parameters of diffusion coefficients and solubility are known.

Because of the small size of our droplets (on the order of picoliters that can be suspended in hundreds of microliters of solvent), our method is ideal for the study of sparingly soluble solutes, such as in the case of water dissolving into longer chain *n*-alkanes, where typical solubilities are on the order of $10^{-8}M$. Our method bears conceptual resemblance to other methods of determining diffusion coefficient which are based on motion or decay of an interface.

In this paper we have used the diffusion of water in long chain alcohols and alkanes to examine the effect of hydrogen bonding on small solute diffusion. By using a homologous series of alcohols and alkanes, we are able to vary solvent viscosity while maintaining similar intermolecular interactions within each series. While dispersion (van der Waals) interactions are present in both, water will hydrogen bond with alcohols and not with alkanes. Thus, diffusion of water molecules through long chain *n*-alcohols and *n*-alkanes allows us to examine the effect of hydrogen bonding on diffusion behavior and quantify it. By using the same solute, we eliminate any effects on diffusion from changes in solute shape or solute polarity, and work with a more unifying system.

In the real world, the diffusion coefficient generally varies with solute concentration. Constant diffusion coefficient is an approximation, which is generally made at low solute concentration. The Epstein–Plesset equation assumes that shrinkage of the droplet is governed by diffusive mass transfer at the boundary of the droplet. At the boundary of the droplet, the concentration of the contents of the droplet is assumed to be the saturation concentration, and it is at this concentration that diffusion is being measured. The saturation concentration of water in *n*-alkanes is quite low, and hence closer to infinite dilution, but this is not necessarily the case for water in the *n*-alcohols. While this holds true for any method of measuring diffusion coefficient by observation of a moving interface, it is something that should be kept in mind.

II. DIFFUSION OF SMALL SOLUTES

One way to view the diffusion of water in *n*-alcohols and *n*-alkanes is diffusion of a small solute in a solution of larger molecules. The Stokes–Einstein equation [Eq. (2)] is commonly used to describe diffusion,

$$D = \frac{k_B T}{f} = \frac{k_B T}{C \pi \eta R_{\text{solute}}}, \quad (2)$$

where k_B is the Boltzmann constant, *T* is the temperature, η is the shear viscosity of the solvent, *C* is a constant, which is dependent on the boundary condition (slip or stick), and R_{solute} is the radius of the solute.¹ However, since the equation was originally derived for a relatively large solute in a continuum solvent, it is not applicable to the case we wanted to test, where the solute is smaller than the solvent (as in our

case of water in the homologous series of alcohols and alkanes).⁹

One modification to the Stokes–Einstein equation for small solutes is based on a reduced viscosity assumption,¹ which states that $D \propto \eta^{-\alpha}$, where α lies between 2/3 and 1.^{10,11} Kowert³ examined the diffusion of O₂, biphenyl, anthracene, diphenylacetylene, diphenylbutadiyne, pyrene, perylene, coronene, and rubrene and found that α may increase with solute size, approaching the Stokes–Einstein limit ($\alpha=1$) as the solute size becomes large as compared to the solvent. This relationship has been tested by molecular dynamics simulation as well, for example by Harris,¹¹ who showed that the molecular dynamics simulations of Meier *et al.*¹² of a Lennard-Jones fluid resulted in a self-diffusion value of 0.921 ± 0.003 for α .

Zwanzig and Harrison¹³ argued that it is more accurate to describe this deviation from Stokes–Einstein diffusion in terms of an effective hydrodynamic radius reflective of the strength of solute-solvent interactions. They examined the data of Pollack and Enyeart¹⁴ for Xe (131 g/mol) diffusion in alkanes (72.15–226.44 g/mol) and argued that while the data for a small solute diffusing in a solvent of larger molecules fit an equation of the form of viscosity to some power very well, the viscosity itself is also related to other physical parameters, which might affect diffusion.

III. HYDROGEN BONDING AND DIFFUSION

A water molecule is composed of a single, comparatively large, oxygen atom covalently bonded to a pair of smaller hydrogen atoms, with an angle between the two O–H bonds of 104.52°. Water is both a hydrogen bond donor and a hydrogen bond acceptor. Because of the geometry of the water molecule, it is highly polar, having a permanent dipole moment of 6.17×10^{-30} C m (=1.85 D), due to a partial negative charge on the oxygen, and a partial positive charge near the hydrogen atoms.¹⁵

N-alcohols have a hydrophobic aliphatic group attached to a hydrogen bond-capable OH group [dipole moment from 1.7 (*n*-pentanol) to 2.0 D (*n*-octanol)¹⁶]. Thus, both water and alcohols can hydrogen bond, making the water-alcohol system ideal for studying the effect of this bonding on diffusion. *N*-alkanes on the other hand have zero dipole moment, no capacity to hydrogen bond, and so represent the control system of the same hydrocarbon composition but lacking the –OH of the homologous alcohols.

Solute-solvent interactions, such as hydrogen bonding, have been found to affect the diffusion of a solute in a solvent. Easteal and Woolf¹⁷ examined the diffusion of short chain alcohols in water under various pressures and attributed initial increase in diffusion coefficient under increasing pressure as being due to the disruption of hydrogen bonded networks, allowing a solute to move while breaking fewer bonds. Tominaga *et al.*¹⁸ examined the diffusion of cyclohexane and cyclohexanol in ethanol, methanol, and 1-hexanol, and similarly found the diffusion of cyclohexanol to be slower in alcohols as compared to that in cyclohexane, sig-

nifying that when a solute can hydrogen bond with the solvent, its progress through the solvent, by diffusion, is retarded.

Chen and Chan¹⁹ used Taylor dispersion to measure the diffusion of various solutes in ethanol. They found that the solutes that were capable of hydrogen bonding diffused more slowly than nonassociated solutes, and concluded that the retardation was equivalent to an increase in the equivalent van der Waals volume of a hydrogen bonding solute. They also compared this increase in van der Waals volume with the van der Waals volume of the ethanol monomer and attributed this difference to solute-associated ethanol monomers. They calculated, using the Stokes–Einstein equation, that phenols, on average, diffused with approximately 2.5 ethanol molecules, and that all aromatic amines diffused with approximately one ethanol molecule. This would suggest that a solute larger than the solvent molecules with which it is surrounded can effectively pick up the smaller solvent molecules and diffuse as a complex. In the same year, (1997), Chan *et al.*²⁰ examined the diffusion of various pseudoplanar solutes in acetone and, using similar assumptions, concluded that all phenols on average diffused with approximately one acetone molecule and that all aromatic amines diffused with approximately 0.6 molecules of acetone, on average.

This slowing of diffusion due to hydrogen bonding has been used to investigate hydrogen bonding in dilute solutions, for example, by Lu *et al.*²¹ This is also supported by molecular dynamics simulations, which predict a slower diffusion coefficient for a solute that interacts attractively with the solvent, and a faster diffusion coefficient for a solute, which interacts repulsively with the solvent,²² when compared to a model which had no interaction between solute and solvent.

Attempts have been made to modify the Stokes–Einstein equation to make the equation applicable to polar solute diffusion in alcohols and alkanes. Because a polar solute will have a different interaction with an alkane as compared to an alcohol, it becomes necessary to change the equation's boundary equation from the slip ($C=6$) to the stick condition ($C=4$) to reflect this interaction.²³ Wakai and Nakahara,²⁴ however, studying molecular diffusion using H-Fourier-transform pulsed field-gradient spin-echo NMR, found that this boundary condition change overestimated the friction ζ when the Einstein relation was applied to the diffusion coefficients of water in carbon tetrachloride, benzene, chloroform, dichloromethane, acetonitrile, and acetone.

Wakai and Nakahara²⁴ also examined the diffusion of different solutes in a variety of solvents, varying solute size, solute-solvent interaction, and solute polarity. They found that water molecules diffusing in organic solvents had an irregular dependence on viscosity, with, for example, a higher diffusion coefficient of water in acetonitrile as compared to acetone, despite acetonitrile's higher viscosity.

With this previous work in mind, we examined the diffusion of water in a more complete homologous series of *n*-alcohols and *n*-alkanes than has been previously performed. Previous experimental studies of small solute diffusion with hydrogen bonding have either focused on a single solvent with a variety of solutes or a variety of unrelated

solvents with a single solute. Our investigation concentrates on a single solute (water), diffusing in a series of homologous solvents, which differ only in chain length and presence or absence of an –OH group. Thus, we can isolate the effect of hydrogen bonding on diffusion for the case of water. The relative simplicity of the technique and its analyses means that it is applicable to other solvent-solute systems for quantification of diffusion.

IV. MATERIALS AND METHODS

A. Materials

The materials used were *n*-butanol (EMD Biosciences), *n*-pentanol (Sigma Aldrich), *n*-hexanol (Acros Organics), *n*-heptanol (Sigma Aldrich), *n*-octanol (Sigma Aldrich), *n*-pentane (Burdick & Jackson), *n*-hexane (Sigma Aldrich), *n*-heptane (Sigma Aldrich), *n*-octane (Sigma Aldrich), *n*-decane (TCI America), *n*-undecane (Sigma Aldrich), *n*-tetradecane (Sigma Aldrich), *n*-hexadecane (Sigma Aldrich), and de-ionized water. All solvents were dried of any dissolved water prior to experimentation using type 3A molecular sieves (EM Science) by placing 40 beads of sieve into the bottom of a 20 ml scintillation vial, which were then covered with 15 ml of the solvent and sealed with a tight screw cap.

B. Methods

Individual microdroplets were formed, manipulated, and observed using a micropipette manipulation system. The micropipette technique for liquid microdroplets has been explained in a previous paper by Duncan.⁷ Briefly, micropipettes are formed from glass capillary tubes, which were then microforged to provide a flat tip of about 8–10 μm internal diameter. These pipettes were then treated with hexamethyldisilazane to make them hydrophobic. The micropipette is then used to blow 50 μm droplets of water into aniline, and aniline into water. Through observation of the radius of the droplet as the droplet dissolves into the surrounding solvent, the mass flow from the droplet is measured and found to be well modeled by the Epstein–Plesset equation.⁷

All solubility values of water in the various *n*-alcohols were found in the literature.²⁵ Solubility of water in the *n*-alkanes was calculated using an empirical equation obtained by Tsonopoulos for alkanes from C_2 to C_{16} .²⁶

$$\ln x_w = \frac{-79.6677 - 6.6547\text{CN}}{9.5470 + \text{CN}}, \quad (3)$$

where CN is the carbon numbers of a hydrocarbon and x_w was the mole fraction of water. The values obtained from the Tsonopoulos equation were compared to those values for water solubility in pentane, hexane, heptane, and octane available from literature,²⁷ and found to correspond well.

As mentioned above, the task is to form a single picoliter scale water droplet on the end of the pipet immersed in a microchamber of the organic solvent. Simply filling a pipet with water and trying to expel a single droplet proved very difficult because even though the pipet was treated to be hydrophobic on the outside, it did not have sufficient wetting

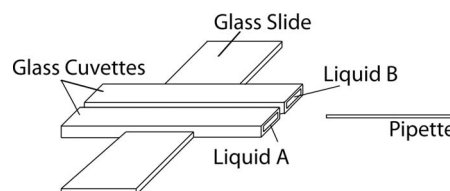


FIG. 1. Two-cuvette system for micropipette based technique. This system allows us to control the amount of liquid A that we draw into our micropipette. We can then blow a droplet of liquid A into liquid B.

characteristics for the water column in the pipet to pinch off and isolate the droplet. In the Duncan and Needham experiment, droplets were simply “tapped” off and, because of their neutral buoyancy, were readily recaptured. However, in these solvents the buoyancy difference prevented this delicate maneuver. Therefore, in a new micropipet method, developed specifically for this kind of study, two standard optical glass cuvettes with a 2 mm path length (Nova Biotech, G-126) were arranged as shown in Fig. 1. Approximate dimensions are $40 \times 10 \times 2 \text{ mm}^3$ for a volume of about 0.8 ml. The temperature was controlled by the ambient air temperature and was nearly constant at $22 \pm 1^\circ\text{C}$ in all experiments. (It should be noted that because temperature is controlled by ambient air temperature, localized temperature changes may occur for two liquids, which have a very high heat of mixing. This is offset by the fact that our droplets are very small and the volume they are in is very large.) One cuvette was filled with water, the other with the organic solvent of interest. The fluid in the microchambers was held intact at the one open interface by surface tension. The advantage of the two-chamber approach is that the size of the droplet can be accurately controlled by how much water is drawn into the pipette and that is then expelled into the solvent in the other microchamber.

In order to form a water droplet, the micropipette was first inserted into the water containing chamber. The desired amount of water ($\sim 0.5 \text{ nl}$) was drawn into the micropipette by slightly reducing the suction pressure, (micro to milliatmospheres negative pressure), rezeroing the pressure, and withdrawing the micropipette and inserting it into the solvent-containing cuvette. A droplet was then blown out and held on the pipette tip with a small suction pressure, well below the pressure required to overcome its surface tension²⁸ and cause it to flow into the pipette. The droplet was then allowed to dissolve in the organic solvent and this reduction in diameter was then recorded on video tape for subsequent analysis. To preserve the anhydrous nature of the solvent medium, a new cuvette full of freshly anhydrous solvent was used for each microdroplet experiment.

Examining the geometry of the pipette and droplet shown in Fig. 2, it is clear that, while holding the droplet on the end of the pipette is a prerequisite for maintaining a diffusion limited process and for visual observation and recording of droplet dimensions as it dissolves into the surrounding medium, there is the possibility for water to also transfer out of the droplet through the water/air interface into the shaft of the pipette. Even though water vapor saturates

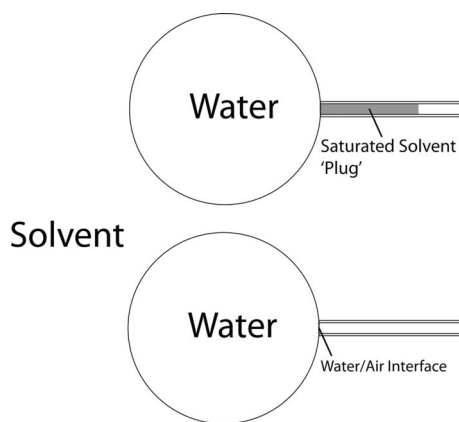


FIG. 2. A droplet suspended on the end of a micropipette, both with (top) and without (bottom) a saturated plug. Without the presence of a saturated plug, water leaves our droplet both through the solvent and through the air behind it in the pipette. Since the volume of the air behind the droplet is quite small, the concentration of water in the air is high; hence, the rate of transfer of water through the water/air interface is quite low. We can calculate this rate using certain geometrical assumptions.

the air space within the air-filled pipette, this transfer was found to be a source of error for the more slowly dissolving systems.

To eliminate this effect, a small amount of water-saturated *n*-tetradecane was drawn into the pipette prior to pulling water into the pipette. Because the tetradecane “plug” behind the water droplet was saturated with water, water did not diffuse into the tetradecane, and hence left the droplet solely by diffusion into the anhydrous solvent.

For the case of a droplet which transfers water both at the water/solvent interface and through an interface at the pipette, we can split the mass flux into two parts (for our saturated plug, J_{pipette} is, of course, zero),

$$J_{\text{total}} = J_{\text{water/solvent}} + J_{\text{pipette}}. \quad (4)$$

The surface area of a spherical cap of height h of a sphere with radius R and cap radius a is (see Fig. 2)

$$S_{\text{cap}} = 2\pi R(R - \sqrt{R^2 - a^2}). \quad (5)$$

We now assumed that mass leaving the spherical droplet into the solvent exited through a spherical surface area reduced by this amount. We can now modify the Epstein–Plesset equation to obtain

$$\frac{dR}{dt} = \frac{2\pi R(R + \sqrt{R^2 - a^2})Dc_s(1-f)\left(\frac{1}{R} + \frac{1}{\sqrt{\pi Dt}}\right)}{4\rho\pi R^2}. \quad (6)$$

This modified equation, along with the water-saturated plug, now allows us to obtain a more accurate curve fit for droplet radius versus time, eliminating error due to transfer of water into air in the pipette. The liquid droplets were formed and held by the same micropipette in the center of the chamber, similar to the previous experiment by Duncan and Needham⁷ and their diameters were measured versus time by using a calibrated video caliper system.

Constant diffusion coefficient is, of course, an approximation, as diffusion coefficients are generally expected to be concentration dependent. As the diffusion coefficient is re-

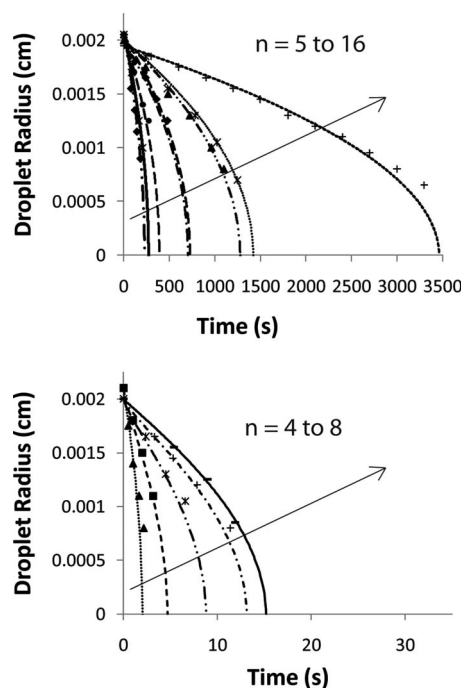


FIG. 3. Example radius vs time plots of water droplets in *n*-alkanes and *n*-alcohols, fit to the Epstein–Plesset equation [Eq. (1)]. The arrows point in the direction of increasing carbon number. Increasing chain length results in a longer dissolution time within a series of homologous alkanes or alcohols.

flected by the transfer of mass at the solute/solvent interface, the concentration at this interface is, strictly speaking, the concentration at which the diffusion coefficient is being measured. This concentration is, according to the Epstein–Plesset model, the saturation concentration of the solute in the surrounding solvent.

V. RESULTS AND DISCUSSION

A. Radius versus time for a dissolving water droplet in solvent

The radius versus time behavior of a water droplet dissolving in a surrounding solvent is shown in Fig. 3. The radius versus time curve was also fit to the Epstein–Plesset (EP) model. Having already shown that the EP model accurately defined the dissolution of water into aniline where both solubilities and diffusion coefficients are known,¹¹ and since the solubility of water in the various alcohols and alkanes was already known,²⁵ it was possible, using this simple data, to vary diffusion coefficients of a plotted Epstein–Plesset curve until a satisfactory fit was achieved. As Fig. 3 shows, dissolution times for a 40 μm diameter droplet are ten times slower for alkanes than the corresponding chain length alcohol.

In order to test our method against already measured values from the literature, 13 droplets of water were formed into a butyl alcohol solvent, in which the solubility and diffusion of water were already known,² and their dissolution time recorded. Analysis of the data for the droplet resulted in an experimental value of $4.36 \pm 0.57 \times 10^{-6} \text{ cm}^2/\text{s}$. By comparison, a literature value for water in butyl alcohol² was found to be $5.6 \times 10^{-6} \text{ cm}^2/\text{s}$. Our experimental value for

TABLE I. Diffusion coefficient of water in *n*-alcohols and *n*-alkanes. The diffusion coefficients of water in various *n*-alcohols and *n*-alkanes were obtained through use of the Epstein–Plesset equation.

Alkanes	Diffusion coefficients (cm ² /s)	Alcohols	Diffusion coefficients (cm ² /s)
<i>n</i> -pentane	$12.5 \pm 0.58 \times 10^{-5}$	<i>n</i> -methanol ^a	1.75×10^{-5}
<i>n</i> -hexane	$8.97 \pm 0.76 \times 10^{-5}$	<i>n</i> -ethanol ^a	1.22×10^{-5}
<i>n</i> -heptane	$7.42 \pm 0.75 \times 10^{-5}$	<i>n</i> -propanol ^a	0.61×10^{-5}
<i>n</i> -octane	$5.38 \pm 0.43 \times 10^{-5}$	<i>n</i> -butanol ^a	0.56×10^{-5}
<i>n</i> -decane	$4.06 \pm 0.43 \times 10^{-5}$	<i>n</i> -butanol	$0.44 \pm 0.06 \times 10^{-5}$
<i>n</i> -undecane	$3.17 \pm 0.27 \times 10^{-5}$	<i>n</i> -pentanol	$0.52 \pm 0.08 \times 10^{-5}$
<i>n</i> -tetradecane	$1.88 \pm 0.21 \times 10^{-5}$	<i>n</i> -hexanol	$0.35 \pm 0.03 \times 10^{-5}$
<i>n</i> -hexadecane	$1.15 \pm 0.13 \times 10^{-5}$	<i>n</i> -heptanol	$0.31 \pm 0.02 \times 10^{-5}$
		<i>n</i> -octanol	$0.20 \pm 0.05 \times 10^{-5}$

^aValues for diffusion coefficient of water in lower *n*-alcohols are obtained from Ref. 29.

the diffusion of water in hexane, 8.97×10^{-5} cm²/s, was also found to be quite close to the value obtained by Easta⁵ of 9.5×10^{-5} cm²/s.

Thus, we used the Epstein–Plesset equation to obtain values for the diffusion coefficient of water in C₅–C₁₆ *n*-alkanes and C₄–C₈ *n*-alcohols, i.e., the solubility limit of the droplet material in the surrounding medium was known, and the radius versus time behavior of the droplet was measured, and so we could deduce the diffusion coefficient of one material in the other. The results are shown in Table I. All values in this table were measured by the micropipette technique except for the miscible pairs of water in methanol, ethanol, and *n*-propanol. These values were obtained from the paper by Lusi and Ratcliff.²⁹

As listed in Table I and shown in Fig. 4, the diffusion coefficients of water in *n*-alcohols were generally an order of magnitude lower than the corresponding coefficient in *n*-alkanes of similar chain length despite the higher solubility of water in the alcohols. This difference in diffusion coefficient was most likely due to hydrogen bonding—alcohols are capable of hydrogen bonding to one another and water, while

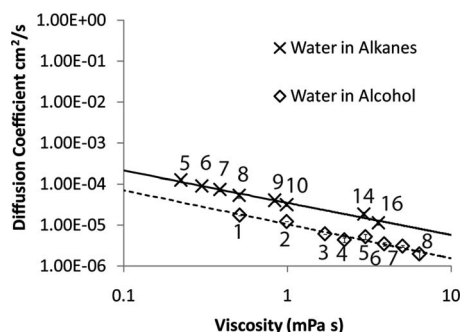


FIG. 4. Diffusion coefficients for water in alkanes and alcohols derived from our droplet dissolution experiments. The number of carbons in each solvent is next to the data point. Diffusion coefficients for water in *n*-alkanes are always higher than for the corresponding chain length *n*-alcohol. The diffusion coefficient of water in an *n*-alkane is also higher than in an *n*-alcohol of similar viscosity. Also, in accordance with Refs. 14–16, we found diffusion coefficient to be proportional to a fractional power of viscosity: $D \sim \eta^{-\alpha}$. For water diffusing in the *n*-alcohols $\alpha=0.83$ (dashed line). For water diffusing in the *n*-alkanes, our value was $\alpha=0.78$ (solid line). The error bars represent one standard deviation.

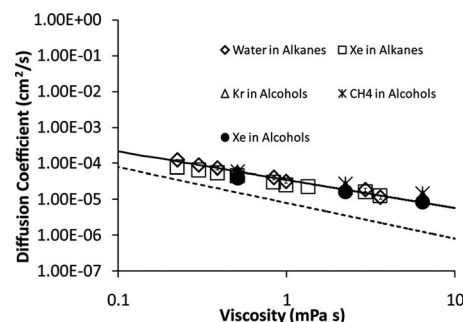


FIG. 5. Diffusion of water in alkanes compared to the diffusion of other small nonpolar solutes (Xe, Kr, CH₄) in polar (alcohol) and nonpolar (alkane) solvents. The power law is shown as a solid line. The Stokes–Einstein prediction for water in the *n*-alkanes is included as well (dotted line). Data for Xe diffusion in *n*-alkanes are taken from Pollack and Enyeart (Ref. 14). Data for Xe diffusion in three *n*-alcohols are taken from Chen *et al.* (Ref. 19).

alkanes cannot form these bonds. This was in accordance with the results of studies, which also found a decrease in diffusion coefficient due to the possibility of hydrogen bonding between a diffusing solute and the surrounding solvent.^{18,20,21,24,29,30}

Interestingly, plotting the diffusion coefficients of water in the various alkanes and alcohols (Fig. 4) did reveal a fractional power viscosity dependence as expected for the diffusion of a small solute: $D \sim \eta^{-\alpha}$. For water diffusing in the *n*-alcohols, we found a value of $\alpha=0.83$. For water diffusing in the *n*-alkanes, our value was $\alpha=0.78$. Relatively speaking each series does follow a reduced viscosity assumption.

B. Small solute diffusion without hydrogen bonding: Comparison to other systems

If we compare the diffusion of water in *n*-alkanes to the diffusion of other small solutes in those same alkanes, we find that their diffusion behavior is quite similar. Pollack and Enyeart¹⁴ examined the diffusion of xenon (Xe) through the *n*-alkanes (*n*-pentane to *n*-hexadecane) at 20 °C. Xe is an inert gas incapable of hydrogen bonding. Pollack and Enyeart modeled Xe as a sphere of diameter of about 4.5 Å, while water molecules are generally modeled as having a diameter of 2.75 Å.

If we plot the diffusion coefficients of water in the alkanes versus viscosity, and compare our values with those for diffusion coefficients of Xe in the same alkanes (Fig. 5), we find that the two are quite similar. This is to be expected because neither Xe nor water can hydrogen bond with the *n*-alkanes, and each solute molecule is considerably smaller than the solvent molecules.

Chen *et al.*¹⁹ examined the diffusion of Xe in the *n*-alcohols. Xe is not capable of hydrogen bonding, so we would expect the diffusion behavior of Xe in an *n*-alcohol of similar viscosity to be similar to that of Xe in an *n*-alkane (unlike what we find for the diffusion of water in *n*-alkanes versus *n*-alcohols). This is, indeed, the case.

The diffusion of other, similarly sized nonhydrogen bonding molecules in *n*-alcohols is also similar to the diffusion of water in alkanes. The diffusion of krypton (Kr) in

n-alcohols is similar to the diffusion of water in the *n*-alkanes. The diffusion of methane (CH₄) in *n*-alcohols is also similar to the diffusion of water in the *n*-alkanes (Fig. 5).

Interestingly then, each of these systems deviates from the Stokes–Einstein prediction in agreement with the reduced viscosity model of small solute diffusion. Pollack and Enyeart found $\alpha=0.686$ for Xe in the *n*-alkanes.

C. Small solute diffusion and the inclusion of hydrogen bonding

In contrast to the above, when water diffuses through an *n*-alcohol, its diffusion behavior shows a power law with viscosity, but the absolute rate of diffusion is significantly smaller than its diffusion in the same chain-length *n*-alkanes. Thus, we find that in line with the findings of Skipp and Tyrrell,³¹ Easteal and Woolf,¹⁷ and Tominaga *et al.*,¹⁸ solute-solvent interactions, such as hydrogen bonding, do reduce the diffusion of a hydrogen bonding solute in a solvent. We could interpret this as an increased residence time, as the water molecule binds briefly to the OH on the larger alcohol, or we could view this as possibly being due to the diffusion of a hydrogen bonded solute-solvent complex, diffusing as one species.

If we compare our data for the smaller water molecule [molecular volume of 30 Å³ (Ref. 32)] with that of the nonhydrogen bonding but larger organotins (molecular volume of 114.9 Å³ for tetramethyltin³³) in the same alcohols, we find that the diffusion of water in *n*-alcohols closely resembles that of several of the organotins in *n*-alcohols. This is notable because the organotins, being a single atom of tin surrounded by four alkanes, are much larger molecules than water. Thus water molecules diffuse in alcohols at the same rate for the same viscosity as a larger nonhydrogen bonding solute. This could imply that water molecules do indeed pick up a solvent molecule or two and carry it, thus slowing its diffusion. If this were the case, then we might expect to see an increasingly slower diffusion for water in the larger alcohols as compared to a same size nonhydrogen bonding solute moving through the same *n*-alcohols, since we have considered a series of *n*-alcohols, which differ by only a single CH₂ group, and addition of a single CH₂ group to an *n*-alcohol results in an increase in the van der Waals volume of a solvent by approximately 10.23 cm³/mol.³⁴ This is, however, not what we observe. The effective hydrodynamic radius of water diffusing in *n*-alcohols is not observed to increase with increasing solvent chain length, as might be expected if temporary association with solvent molecules occurred, and the same power law fits for all systems.

VI. CONCLUSION

The diffusion of water in both alkanes and alcohols shows deviations from the classical Stokes–Einstein model for a solute diffusing in a solvent, and follows a power law dependence on solvent viscosity (water in alkanes $\alpha=0.78$, and water in alcohols $\alpha=0.83$) that closely matches the reduced viscosity assumption. This power law dependence on viscosity of water in alkanes was similar to other nonhydro-

gen bonding solutes such as Xe in the same alkane series. However, for a hydrogen bonding system such as water in alcohols, water diffusion (at the same viscosity) was slowed reflecting a possible retardation of water diffusing in alcohols because of hydrogen bonding between the water and the OH group. Since water diffusion in alcohols is as slow as that for a larger (but nonhydrogen bonding) organotin, this slower diffusion could be interpreted as an increase in hydrodynamic radius where hydrogen bonding allows the smaller solvent to carry with it one or more solvent molecules. However, the fact that the effective hydrodynamic radius of water did not increase with increasing solvent chain length leads us to conclude that the slower diffusion of water in alcohols compared to alkanes is simply due to a longer residence time for water at the alcohol OH group.

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