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Water diffusivity in a mixed phase binary system: Effective water diffusion coefficients in tetradecanol–eicosanol mixtures

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ABSTRACT

Fourier-transform infrared attenuated total reflection spectroscopy is used to measure the effective water diffusion coefficients in pure tetradecanol between 313 K and 338 K and in liquid and liquid–solid mixtures of tetradecanol ($C_{14}H_{29}OH$) and eicosanol ($C_{20}H_{41}OH$) at 313 K. The temperature dependent data in tetradecanol yields an activation energy for diffusion higher than that measured in pure alkanes. This is consistent with the critical role hydrogen bonds play in diffusion. Differential scanning calorimetry and infrared spectroscopy are used to construct the solid–liquid phase diagram for the tetradecanol–eicosanol system. Diffusion measurements in these mixtures are linked to the experimental phase diagram. Water diffusivity in liquid mixtures at low eicosanol concentrations (80 to 100 mol percent tetradecanol) suggests that the measured diffusion coefficient of water is independent of the mixture's bulk viscosity. We find a six-fold decrease in water diffusivity when the solid fraction of the equilibrium mixture increases from zero to thirty percent. The decrease in water diffusivity results from a longer diffusion path length caused by solid portions of the mixture acting as barriers to diffusion.

1. Introduction

In nature, long-chain alcohols mixtures exhibit a complex phase behavior that depends on the chain lengths of the component molecules. These mixtures along with fatty-acid mixtures limit water transport in a broad range of systems, including plant and insect cuticles and atmospheric aerosols [1–4]. Long-chain alcohols are significant industrially as materials for latent energy storage and are often found in pharmaceuticals, cosmetics, and various consumer products [5]. Fatty alcohols also serve as models for more complex amphiphilic molecules such as phospholipids. These relatively simple molecules have complex phase behavior [6]. The aim of this study is to use infrared spectroscopy and differential scanning calorimetry to investigate water diffusivity in mixed solid–liquid systems. We know of no other study that looks at water diffusion in a system where solid fraction varies with composition. We investigate the lesser studied wax mixture of two long-chain *n*-alcohols: tetradecanol ($C_{14}H_{29}OH$) and eicosanol ($C_{20}H_{41}OH$). Our interest in tetradecanol–eicosanol mixtures was motivated by experimental temperature constraints, the wealth of previous studies on tetradecanol mixtures, and the composition of natural barrier layers. For example, the leaf cuticle often contains alcohols with chain lengths between 20 and 30 carbons [7]. We found that 313 K was an optimal experimental temperature because the tetradecanol–eicosanol mixture possesses both fully liquid and solid–liquid regions, depending on the mixture composition. Although the phase diagrams for other mixtures of long chain alcohols have been well characterized, to our knowledge the phase diagram for tetradecanol and eicosanol has not been previously investigated [8,9].

Studies of solute diffusion in complex solvent systems help elucidate the role of solvent properties on solute transport [10–12]. Tracer diffusion studies provide information on solute–solvent interactions at very low solute concentrations. Methods that probe self-diffusion follow the dynamics of an isotopically labeled solute in system containing the non-labeled solute [13]. This work investigates the mutual diffusion of water into tetradecanol–eicosanol mixtures. We quantify water's diffusion rate using effective translational diffusion coefficients calculated from the time evolution of water's concentration profile in the mixtures [14]. The viscosity and hydrogen-bond dynamics of the liquid component of the long-chain alcohol mixtures influence the diffusive motion of individual water molecules. As the mole fraction of eicosanol increases, the mixtures contain solid domains in equilibrium with the liquid that present barriers to diffusion.

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The diffusivity of a large solute molecule in a liquid solvent of smaller molecules is generally predicted within 20% by the Stokes–Einstein equation, $D = k_BT/C\pi\eta r$ [13]. The diffusion coefficient (D) depends on the solute radius (r), solvent bulk viscosity (η), and temperature (T) as well as a stick ($C = 6$) or slip ($C = 4$) condition that accounts for solute–solvent interactions. For small solute molecules moving through large solvent molecules and for systems that have strong solute–solvent interactions, no one model predicts all observed diffusion coefficients. Small changes to the Stokes–Einstein equation extend the equation's ability to model experimentally determined diffusion coefficients [12,13,15–19]. For example, if water's hydrodynamic radius is varied to reflect whether the solvent is hydrophobic, polar, or capable of forming hydrogen bonds, the Stokes–Einstein equation models water diffusion in a range of organic solvents [20]. The Stokes–Einstein equation is also modified by raising the solvent viscosity to a fractional power. This reduced-viscosity approach gives $D = k_BT/C\pi\eta^{\alpha}r$ where $\alpha < 1$ accounts for a smaller bulk viscosity effect on the translational motion of small solutes [11,16,19].

Solutes diffuse more slowly through solvents in which solute–solvent association occurs [15,18,20–22]. For example, the diffusion coefficient of water is roughly three times smaller in an alcohol than in an alkane with the same viscosity due to hydrogen-bond interactions between the water and the hydroxyl group. Using the reduced-viscosity approach, Needham et al. used a single solute hydrodynamic radius (r) to fit water diffusivity data in a homologous series of straight chain alcohols ($n = 4$–8). The constant solute radius suggests that water molecules diffuse more slowly through alcohols not because they drag a partial solvation shell of alcohol molecules with them but because hydrogen-bond interactions cause water molecules to reside longer at each alcohol hydroxyl group [15].

Molecular dynamic simulations have further verified that hydrogen bonds play a significant role in determining water diffusivity. Water self-diffusion values in aqueous solutions of glycerol, ethylene glycol, or methanol correlate with long hydrogen-bond lifetimes [23]. Hydrogen bonds formed between water and glycerol molecules in dilute aqueous glycerol solutions lead to slower glycerol diffusive motions, greatly affecting the overall water diffusion rate [24]. Molecular dynamic simulations also demonstrate that water diffusion rates decrease in hydrogel polymer systems when hydrogen-bond dynamics are slower [25].

Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectroscopy is a robust technique for quantifying the diffusivity of water and other small solutes in thin-film polymeric systems [26–30]. The diffusion coefficients determined by this method match values measured by a variety of other experimental methods [31]. The principle advantages of this technique include the capacity to measure the diffusivity of more than one solute at a time (as long as each solute has independent absorption bands in the infrared spectrum), the ability to monitor changes in polymer characteristics due to the permeation of the solute in to the polymer matrix, and the capability to investigate solute–solvent interactions [26,32]. FTIR-ATR has been used to investigate solute diffusion in a wide range of systems, including rubbery, glassy, or crystalline polymers, copolymers, polymer blends, polymer-clay composites, asphalt binders, and porous TiO_2 films [26,33–36]. To our knowledge this technique has not been extended to the highly viscous liquid or mixed solid–liquid systems that are studied here. We utilize the ability of FTIR-ATR to provide information on both the solute and solvent to characterize water diffusivity into fully liquid and solid–liquid tetradecanol–eicosanol mixtures.

The complex phase behavior of mixtures of long-chain alcohols has been examined in detail by several research teams. Long-chain alcohols exhibit two distinct ordered solid phases. In addition, long chain alcohols exhibit several distinct minimally disordered rotator phases just below the melting temperature [5,37]. The rotator phase is characterized by rotational disorder around the length of the carbon chain. These rotator phases are most distinctly seen on cooling due to a hysteresis of the rotator-crystal transition [37]. Differential scanning calorimety (DSC) and X-ray diffraction studies of binary mixtures of eicosanol ($C_{20}H_{41}OH$) with octadecanol ($C_{18}H_{37}OH$) or nonadecanol ($C_{19}H_{39}OH$) reveal a rich solid–liquid phase behavior for both mixtures [5,9,38,39]. Separate DSC studies of the solid–liquid phase behavior of five long-chain alcohol mixtures with the components differing in their carbon chain length by either four or six carbons demonstrate a eutectic composition rich in the shorter chain alcohol. The previously studied mixture closest to the tetradecanol–eicosanol system is a 1-dodecanol ($C_{12}H_{25}OH$) and 1-octadecanol ($C_{18}H_{37}OH$) mixture. This mixture as well as the others exhibited additional solid–solid transitions that hint at the rich phase behavior of these long-chain alcohols due to the stability of both a solid rotator phase and a solid crystalline phase [8].

Separate studies have compared the bulk and surface thermodynamics of dry and hydrated *n*-alcohols and alcohol mixtures with chain lengths from 12 to 26 carbons [6,37]. For a dry mixture of tetradecanol and octadecanol, the thermodynamics of the bulk depend on the stability of four separate regions of the phase diagram: the liquid phase, the solid rotator phase, the crystalline solid phase, and a mixed phase containing both rotator and crystalline solids [6]. Additionally, kinetic effects cause supercooling to occur during the formation of each bulk solid phase in dry mixtures but not in hydrated mixtures. Hydration increases both the surface and bulk freezing temperatures and the temperature range over which the rotator phase is stable.

Using tetradecanol and eicosanol mixtures at 313 K, we show that the FTIR-ATR technique can be used to measure the diffusivity of water in a viscous liquid and a mixed solid–liquid system. We quantify the decrease in water diffusivity as the solid fraction of the mixture increases. By increasing the eicosanol mole fraction, we are able to investigate systems with varying amounts of solid at a single temperature. We are able to monitor any phase change that occurs in our system as a result of water diffusion, and we can link the measured effective diffusion coefficients to the relative solid fraction observed in each mixture.

2. Experimental methods

2.1. Waxes

1-Tetradecanol (99+%, Acros Organics) and 1-eicosanol (98%, Acros Organics), were melted in a nitrogen atmosphere and dried using activated molecular sieve type 3A (Fluka). The sieve was activated prior to each use by heating to 473 K for at least 4 h under vacuum [40]. To avoid water absorption from the atmosphere during mixing, the waxes were melted and mixed under nitrogen. The mixtures were stirred in a fully liquid state for at least 45 min prior to cooling and solidification under nitrogen. Octanol (99%, Acros Organics) was dried over activated molecular sieve prior to use.

2.2. Differential scanning calorimetry

A Thermal Analysis Tzero *Q20* differential scanning calorimeter calibrated using indium was used to record thermograms of the pure wax and wax mixtures. Thermograms were used to determine the temperature-composition phase diagram for the bulk tetradecanol–eicosanol system. Mixtures were made as described above and thoroughly ground using a mortar and pestle prior to sampling. The sample cell was purged with nitrogen during each