The Journal of Physical Chemistry A

VOLUME 103, NUMBER 7, FEBRUARY 18, 1999

LETTERS

Diffusion of Dioxygen in *n*-Alkanes

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Received: October 12, 1998; In Final Form: December 18, 1998

The translational diffusion constant, *D*, of dioxygen, O_2, has been measured in *n*-alkane solutions drawn through a microcapillary by reduced pressure. The passage of O_2 through the capillary has been monitored using its UV absorption at 190 nm. Data were taken in hexane, octane, decane, dodecane, tetradecane, and hexadecane. The diffusion constants decrease as the chain length increases and are not in agreement with the Stokes–Einstein relation. The data can be fitted to $D/T = A/\eta^p$ with $A = 1.27 \times 10^{-8}$ and $p = 0.562$ ($p = 1$ for the Stokes–Einstein relation); *T* is the absolute temperature, and η is the viscosity in *P*.

Introduction

The *n*-alkanes are an important series of homologous, nonpolar, organic solvents. They have often been used in studies of solute dynamics[1] because their physical properties as a function of chain length are well-known. The motion of O_2 in the *n*-alkanes is of interest because of the disparate size difference between the small solute and the progressively larger solvent molecules. Investigations of O_2 in the *n*-alkanes can also yield results relevant to certain biochemical systems; the interior of biological membranes contains acyl chains with 16–18 carbon atoms, and molecular dynamics calculations have shown that the fast dynamics of a pure dipalmitoyl phosphatidycholine bilayer and neat hexadecane are very similar.[1,2] The diffusion of O_2 through membranes is an active area of research;[3–5] data in *n*-alkanes would provide baseline information for the discussion of dioxygen's molecular motion in these environments.

In this Letter, we report the determination of the translational diffusion constant, *D*, of dioxygen in hexane, octane, decane, dodecane, tetradecane, and hexadecane. The method we have employed is based on Taylor–Aris[6,7] dispersion theory. Oxygenated *n*-alkanes are drawn through a microcapillary by reduced pressure; ultraviolet (UV) detection at 190 nm is used to determine the solute dispersion (elution profile) of O_2 as it moves through the capillary. The profile width and elution time for the maximum of the profile can be used to calculate *D*.

Our results show that the diffusion of O_2 is faster than predicted on the basis of macroscopic viscosity and the Stokes–Einstein relation[8]

$$D = k_B T/(f\pi\eta r) \qquad (1)$$

where k_B is Boltzmann's constant, *T* is the absolute temperature, η is the viscosity, and *r* is the solute's hydrodynamic radius; $f = 6$ or 4 for the stick and slip limits, respectively. The deviations from the Stokes–Einstein predictions become larger, i.e., the molecular "size" *r* from eq 1 becomes smaller, as the chain length increases. As a control, we found that *D* for toluene in hexane is in agreement with the literature value.[9]

Experimental Section

Gaseous oxygen and nitrogen were obtained from Acetylene Gas Co. and Gateway Airgas, respectively. The solvents hexane (Fisher), octane (Sigma), decane (Aldrich), dodecane (Aldrich), tetradecane (Aldrich), hexadecane (Aldrich), and toluene (Aldrich) were used as received. The solvent viscosities are from ref 10.

The elution profiles used to calculate *D* for O_2 were obtained by using reduced pressure to draw oxygenated and deoxygenated

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10.1021/jp984025k CCC: $18.00

TABLE 1: Diffusion Constants and Hydrodynamic Radii for O_2 in *n*-Alkanes and H_2O

solvent (day)	T, K	10^5D, cm^2 s^{-1}	η, cP[10]	r_{stick}, Å	r_{slip}, Å
C_6H_{14} (1)	296.2	9.96	0.306	0.712	1.07
C_6H_{14} (2)	295.7	10.3	0.307	0.681	1.02
C_6H_{14} (3)	295.2	9.45	0.309	0.740	1.11
C_6H_{14} (4)	296.2	9.93	0.306	0.714	1.07
C_8H_{18} (1)	296.2	6.89	0.520	0.605	0.908
C_8H_{18} (2)	296.2	7.21	0.520	0.578	0.868
C_8H_{18} (3)	298.2	7.04	0.508	0.611	0.916
C_8H_{18} (4)[a]	295.7	6.94	0.523	0.596	0.894
C_8H_{18} (5)[a]	295.2	7.04	0.527	0.583	0.875
$C_{10}H_{22}$ (1)	299.2	5.52	0.825	0.481	0.722
$C_{10}H_{22}$ (2)	297.2	5.57	0.856	0.456	0.684
$C_{12}H_{26}$ (1)	294.7	4.11	1.47	0.357	0.535
$C_{14}H_{30}$ (1)	295.7	3.40	2.21	0.289	0.434
$C_{14}H_{30}$ (2)	294.2	3.20	2.28	0.296	0.444
$C_{16}H_{34}$ (1)	298.7	2.59	3.00	0.282	0.422
$C_{16}H_{34}$ (2)	298.7	2.73	3.00	0.267	0.400
H_2O	298.2	2.31[19]	0.892	1.06	1.59

[a] Obtained using the sintered-glass disk as N_2 bubbling agent.

n-alkanes through a microcapillary (Polymicro Technology, 77 mm i.d.); the reduced pressure, ~50 Torr less than atmospheric pressure, was obtained using an aspirator and controlled by a Garst regulator. After the deoxygenated *n*-alkane (the preparation of which is described below) had been pulled through the microcapillary for at least 1 h, the reduced pressure was broken and the capillary was placed in a beaker of the same solvent through which O_2 had been bubbled for at least 1 h; a siphon effect pulled the oxygenated solution into the capillary. After a measured length of time, t (the load time), the capillary was returned to the O_2-free solution and the data acquisition was started as the reduced pressure was reset. Profiles were taken for several different load times in each solvent; the load times were solvent-dependent and varied from 2 to 30 s; at least five profiles were taken for each load time.

The deoxygenated solvents were prepared by bubbling N_2 through the *n*-alkanes; this method of O_2 removal has been used in electron spin resonance (ESR)[11] and electrochemical[12,13] studies. All of our profiles (with the exception of two control experiments) were taken after the N_2 was bubbled through the *n*-alkane for at least 1 h using a Pasteur pipet with a 1 mm i.d. tip; for the two control experiments, the N_2 was bubbled through *n*-octane for 45 and 60 min, respectively, using a glass tube with a sintered-glass disk (8 mm diameter). We found, as reported previously,[12] that the O_2 is removed more quickly using the sintered-glass disk but that diffusion constants obtained using the two bubbling methods were in agreement (see Table 1). The efficiency of the O_2 removal from an electrochemical cell using an 18 mm i.d. sintered-glass disk was studied by Laitinen and Burdett;[13] measurements of the O_2 diffusion current showed "essentially all the oxygen was removed by passing gas" for 30 s through 50 mL of a 0.1 N air-saturated aqueous KCl solution.

The progress of the oxygenated solution through the capillary was followed using UV detection. The O_2 absorption near 200 nm in liquid hydrocarbons has been known since Evans compared spectra taken before and after deoxygenation;[14] this absorption has been studied and discussed in a wide range of solvents.[15,16] All of the oxygenated *n*-alkanes showed appreciable absorption relative to the deoxygenated "blanks" at 190 nm (the lower limit for our Thermo Separation Products model SC100 detector); this wavelength was used for all of our profiles. The maxima of elution profiles taken as a function of wavelength were used to obtain the absorption spectrum of O_2 in octane shown in Figure 1; a single profile was taken at each wavelength (other than 190 nm). A detection wavelength of 260 nm was used for toluene in hexane. Other aspects of the instrumentation and data gathering are described in ref 17.

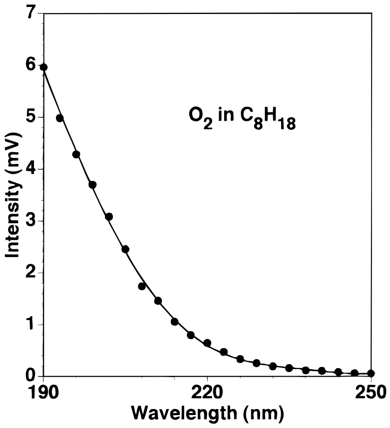

Figure 1. Intensities of the profiles for O_2 in octane as a function of wavelength. The intensities are the difference (in mV) between the maximum and baseline for a given profile. The smooth curve is a fit to a sixth-order polynomial.

As discussed in ref 17, D can be calculated from the Taylor–Aris dispersion theory using

$$D = 0.2310R^2t_R/(W_{1/2})^2 \qquad (2)$$

where R is the capillary radius, t_R is the elution (retention) time for the maximum of the profile, and $W_{1/2}$ is the full width of the profile at half-height. The dependence of D on the load time is given by $D^{-1}(t) = D^{-1}(0) + bt^2$;[7] plots of $D^{-1}(t)$ vs t^2 were used to determine the "zero load time" values of $D^{-1}(0)$ (which correspond to a "δ function" plug of oxygenated solution). The reciprocals of $D^{-1}(0)$ are shown in Table 1. The average of the uncertainties in the $D(t)$ for all of the load times for all of the solvents was (3.9 ± 2.1)%.

Direct temperature control of our solutions, capillary, and detector was not possible. We did, however, measure room temperature while each elution profile was being obtained and found that the temperature was either constant or varied by no more than 1 °C during the 2–4 h needed to acquire the O_2 profiles for a given solvent on a given day. In Table 1, the temperature shown is either the constant or average temperature (± 0.5 °C) for that day. Here and in Table 1, "day" refers to a set of profiles taken as a function of load time for the only solvent studied on that day. The determinations for each solvent were completed before moving on to the next.

Results and Discussions

The D values for O_2 in the alkanes are shown in Table 1. Also given are the r values calculated from eq 1 for the stick and slip limits. The r values decrease from 0.712 (stick) and 1.07 Å (slip) in hexane to 0.275 (stick) and 0.411 Å (slip) in hexadecane. These r values, the averages for the multiple determinations in a given solvent, are small compared to the van der Waals radius of O (1.50 Å)[18] and the r values calculated from D for O_2 in H_2O[19] (1.06 Å for stick and 1.59 Å for slip). This decrease in r as the chain length increases indicates that the diffusion of O_2 in the *n*-alkanes is progressively faster than predicted by a constant solute "size" and is not in agreement with the Stokes–Einstein relation. The *n*-alkanes clearly become more "slippery" as the chain length increases. Molecular dynamics simulations of hexadecane[2] have shown an end-to-end distance of 14.5 Å, indicating that the chains are, on average,

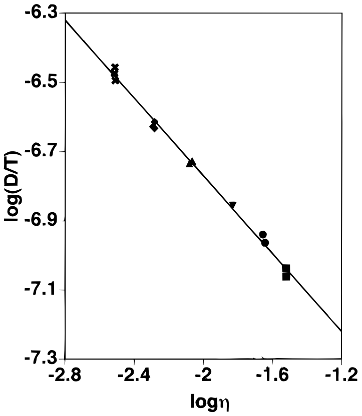

Figure 2. Fit of the diffusion constants for O_2 in *n*-alkanes to $D/T = A/\eta^p$. The slope and intercept of the line give $p = 0.562$ and $A = 1.27 \times 10^{-8}$, respectively. The *n*-alkanes are hexane (×), octane (◆), decane (▲), dodecane (▼), tetradecane (●), and hexadecane (■).

relatively extended. A possible explanation is that as the *n*-alkanes increase in length, they provide regions of increasing length in which the interactions between O_2 and the hydrocarbon are relatively weak and through which diffusion is relatively rapid.

Similar results were found by Pollack et al.[8] for the diffusion of ^{133}Xe in octane, decane, and tetradecane; their data (taken between 10 and 40 °C) also show that r decreases with increasing chain length at constant T. The lack of agreement with the Stokes−Einstein relation for O_2 and ^{133}Xe is not surprising since they are small probes diffusing in much larger solvent molecules (the reverse of the conditions for which the Stokes−Einstein relation is expected to hold). In related work, Subczynski and Hyde[20] used ESR to study the spin exchange between O_2 and nitroxide spin probes. Their results also indicate that dioxygen diffuses more rapidly in hydrocarbons than predicted from the macroscopic viscosity (although numerical values of D for O_2 were not given); the solvents considered were *sec*-butylbenzene, olive oil, and paraffin oil. The literature dealing with the diffusion of dioxygen has been discussed in several review articles.[21,22]

As seen in Figure 2, our results can be fitted to the relation obtained by Evans, Tominaga, and Chan[23]

$$D/T = A/\eta^p \tag{3}$$

where p and A are constants for O_2 in the *n*-alkanes. A plot of $\log(D/T)$ vs $\log \eta$ has $A = 1.27 \times 10^{-8}$ and $p = 0.562$ (compared to $p = 1$ for the Stokes−Einstein relation); the units for D/T and η are cm^2 s^{-1} K^{-1} and P, respectively. Pollack et al. also applied eq 3 to their ^{133}Xe data[8,24] as well as similar data obtained by Evans and co-workers.[25] Our value of p is smaller than the value for ^{133}Xe (0.708), i.e., we see a weaker dependence on viscosity and a faster rate of diffusion for the smaller O_2 molecule. Pollack's[8] results can be combined with ours to obtain $D(O_2)/D(^{133}\mathrm{Xe}) = 3.38\ \eta^{0.146}$ (η in P), which gives $D(O_2)/D(^{133}\mathrm{Xe}) \geq 1$ for $\eta \geq 2.37 \times 10^{-4}$ P. This is much smaller than η for our solvents and temperatures; hexane at 60 °C (bp 69 °C) has $\eta = 2.21 \times 10^{-3}$ P. More detailed comparisons of our data with motional models in terms of the properties of O_2[26,27] and the properties of the hydrocarbon environment in which it is diffusing[28,29] will be the subject of future work.

As a check of our method, we measured $D = 4.12 \times 10^{-5}$ cm^2 s^{-1} for toluene in hexane at 22 °C. If the factor T/η from the Stokes−Einstein relation is used to adjust this result to 25 °C (which seems reasonable for a larger molecule such as toluene), one has $D = 4.29 \times 10^{-5}$ cm^2 s^{-1}, in excellent agreement with the literature value of $D = 4.21 \times 10^{-5}$ cm^2 s^{-1}.[9]

Conclusions

The translational diffusion constant, D, for dioxygen has been measured in the *n*-alkanes hexane, octane, decane, dodecane, tetradecane, and hexadecane; O_2 is diffusing faster than predicted by the Stokes−Einstein relation and the viscosity of the *n*-alkanes. The D values have been determined by drawing the oxygenated *n*-alkane solutions through a microcapillary using reduced pressure; O_2 was monitored using its UV absorption at 190 nm. The method appears to be a useful means of determining diffusion data for dioxygen in liquids; the UV absorption of O_2 has been studied in a wide variety of solvents.[14−16] The study of other solutes may also be a possibility, e.g., nitric oxide, NO, has a UV absorption in methyl alcohol similar to that for O_2.[16]

Acknowledgment. This research has been supported by the Department of Chemistry, Saint Louis University. The computer and detector used to obtain the elution profiles were purchased with grants to Dr. Barry Hogan from Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. Dana Spence for supplying the capillary used in these studies.

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