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The Dynamical Structure of Normal Alcohols in Their Liquids as Determined by the Viscosity and Self-Diffusion Measurements

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The conformation of molecules of normal alcohols in their pure liquids is estimated through an analysis of their self-diffusion coefficients, viscosities, and molar volumes. The conformation of molecules of shorter chained alcohols (C_1-C_3) is approximately of sphere, while that for longer chains is of rodlike shape. In pure liquids of alcohols, rigid rod molecules whose free rotating motions along their rod axes seem to be restricted, are randomly orientated and entangled with one another. The self-diffusion of long-chain alcohols involves a longitudinal translation of rodlike molecules. Large apparent hydrodynamic radii suggest that the transport unit of normal alcohol is a dimer (on an average) of alcohol molecules.

A linear macromolecule in its solution is known to have many conformations such as a rod and a flexibly coiled shape[1] owing to interaction between solute and solvent molecules. However, the conformation of a small alcohol molecule in pure liquid state has scarcely been investigated probably because of theoretical and experimental difficulties. The present study has thus been made for estimating the rigidity and conformation of molecules of normal alcohol homologs (C_1—C_8) by use of data from viscosity, self-diffusion, and density experiments at 298 K.

Experimental

Materials. Purest grade samples (>99%) of methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, from Wako Pure Chemical Industries, Ltd., were used without further purification. The water used was triply distilled one. Deuterium oxide (99.75%) from E. Merck AG was used without further purification.

Viscosity. The viscosity of alcohol was measured with two Ostwald capillary viscometers (characterized by times 1 and 3 min required for a given volume of water to flow through their capillaries) in a thermostat with an accuracy of ±0.2 K. Pure water (0.8902 mPa s at 298.15 K)[2] was used for calibrating the viscosity.

Self-Diffusion Coefficient. The self-diffusion coefficient of alcohol was obtained by the pulsed-gradient FT-NMR method.[3,4,5] All measurements were made on protons at 99.6 MHz, with internal D_2O lock, at an ambient temperature of 298±0.5 K on a JEOL FX-100 Fourier transform NMR spectrometer.** A spin echo was produced by a $90°—\tau—180°$ pulse. The gradient was turned on before and after a 180° pulse. The magnitude of gradient, G, can be varied from 0 to about 0.5 T m^{-1}. The absolute magnitude of G was calibrated against the value of the diffusion coefficient of pure water at 298.15 K, 2.30×10^{-9} m^2 s^{-1}.[6]

The diffusional attenuation of a signal for the component i, at the time of echo, is given by[7]

$$\ln\frac{M(\mathrm{G})}{M(0)} = -\gamma^2G^2D_i\delta^2(\Delta-\delta/3), \tag{1}$$

where $M(\mathrm{G})/M(0)$ is the ratio of the echo amplitude in the presence of the gradient to that in its absence, γ the gyromagnetic ratio (2.675×10^{-8} T^{-1} s^{-1} for ^{1}H), δ the duration of each gradient pulse, and Δ the time between two gradient pulses. In our experiments, G was about 0.087 T m^{-1}. The value of Δ was kept constant at 50 ms and δ was varied from 4 to 12 ms. Each sample was placed in a 1 mm-dia. tube inserted in a 5 mm-dia. tube containing D_2O (for NMR lock) for avoiding the saturation of signal. All spectra were obtained with a high signal-to-noise ratio by one pulse sequence. Self-diffusion coefficients were obtained from gradients of $\ln M(\mathrm{G})/M(0)$ vs. $\delta^2(\Delta-\delta/3)$ plots.

Molar Volume. Molar volumes for normal alcohols were obtained from their densities.[8] Theoretical molar volumes were calculated by use of the CPK molecular model[9] and by assuming a hexagonal close-packed structure of rods rotating along the axis or pilelike packing of rectangular solids for longer chain alcohols (C_4—C_8) and a face-centered cubic packed structure of spheres for shorter ones (C_1—C_3).

Results and Discussion

Table 1 summarizes values of molar weight, density,[8] viscosity, and self-diffusion coefficient for normal alcohol homologs.

For a moving spherical particle almost equal in size to surrounding solvent molecules under the slip boundary condition, Stokes' equation for frictional coefficient,[5,10,11] f, is given by

$$f = 4\pi\eta a, \tag{2}$$

where π is the ratio of the circular constants, η the viscosity of the solvent, and a the radius of the spherical particle.

Let us apply this equation to a flow of a pure normal alcohol. By assuming a hypothetical sphere with an equivalent radius a_0 for a linear alcohol molecule, the a_0 is expressed as

$$a_0 = \left[\frac{3M}{4\pi\rho N}\right]^{1/3}, \tag{3}$$

where M is the molar weight of the alcohol, ρ the density of the alcohol at 298.15 K, and N the Avogadro number. By substituting a_0 in Eq. 3 for a in Eq. 2, the

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**PGNMR measurements were carried out at the Instrument Center of Institute for Molecular Science.

Table 1. Molar Weight (M), Density (ρ), Viscosity (η), and Self-diffusion Coefficient (D) for Normal Alcohol Homologs

	$M/10^{-3}$ kg	$\rho/10^{-9}$ kg m^{-3}	$\eta/10^{-3}$ N s m^{-2}	$D/10^{-10}$ m^2 s^{-1}
Methanol	32.04	0.78664[8]	0.5573 0.5445[8]	23.2[18]
Ethanol	46.07	0.78504[8]	1.056 1.078[8]	10.1[18]
1-Propanol	60.10	0.79975[8]	1.887	5.52[19]
1-Butanol	74.12	0.8060[8]	2.479	4.16 4.26[19]
1-Pentanol	88.15	0.8115[8]	3.519 3.347[8]	2.96
1-Hexanol	102.18	0.8159[8]	4.551 4.592[8]	2.18
1-Heptanol	116.21	0.8189[8]	5.897	1.72
1-Octanol	130.23	0.8221[8]	7.450	1.42 1.38[19]

frictional coefficient, f_0, for the hypothetical sphere is given by

$$f_o = 4\pi\eta\left[\frac{3M}{4\pi\rho N}\right]^{1/3}. \tag{4}$$

On the other hand, from Einstein's equation for diffusion, the frictional coefficient is expressed by

$$f = kT/D, \tag{5}$$

where k is the Boltzmann constant, T the absolute temperature, and D the diffusion coefficient.

Combining Eqs. 4 and 5, we obtain

$$f/f_o = kT/[4\pi\eta D(3M/4\pi\rho N)^{1/3}]. \tag{6}$$

The ratio f/f_0 should be unity when the actual molecule is a sphere. For most rod-shaped or prolate macromolecules including proteins in an organic solvent or in an aqueous solution, the frictional ratio is in general greater than unity.[12]

Figure 1 shows a plot of the ratio against the number of carbon atoms for normal alcohols. The ratios for the short-chained alcohols (C_1—C_3) are almost unity, while, for those with longer chains, they decrease with increasing hydrocarbon chain. This suggests that the molecule of a short-chain alcohol (C_1—C_3) can be regarded as a sphere and that a molecule with a longer chain is deformed more from a spherical shape.

Let us estimate the shape of a long-chained molecule in its pure liquid. By combining Eqs. 2 and 5, the apparent hydrodynamic radius, a, is given by

$$a = kT/(4\pi\eta D). \tag{7}$$

This is the Stokes-Einstein formula under the slip boundary condition.[5,10,11]

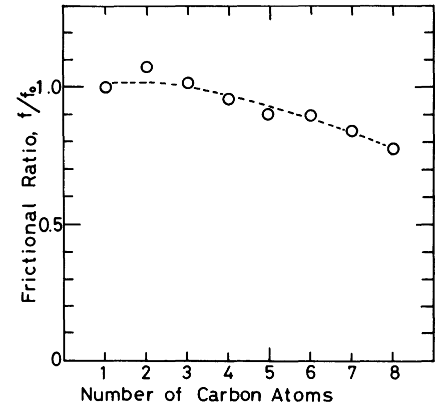

Fig. 1. Frictional ratio, f/f_o, of n-alcohol against the number of carbon atoms at 298.15 K.

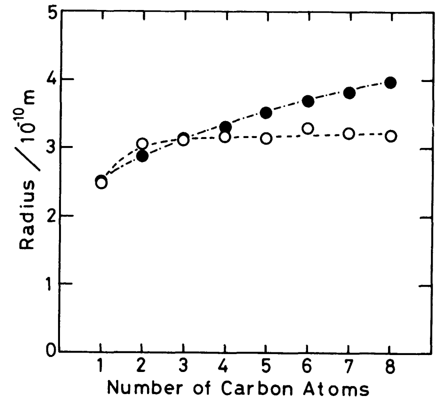

Fig. 2. Molecular radius of normal alcohol against the number of carbon atoms at 298.15 K. Open circles indicate the apparent hydrodynamic radius (the Stokes-Einstein radius), while filled ones were obtained from the density of the normal alcohol according to Eq. 3.

In Fig. 2, the Stokes-Einstein radii, a, of the normal alcohols (open circles) are plotted against the hydrocarbon chainlengths, together with the hypothetical radii (filled ones) obtained by substituting the value of the density of normal alcohol into Eq. 3. The latter radii increase monotonously with increase in the chainlength, whereas the former increase up to 1-propanol and saturate at 1-butanol giving a constant value of ca. 3.2×10^{-10} m., which suggests a sphere for the molecules of the short-chained alcohols and a rod with a

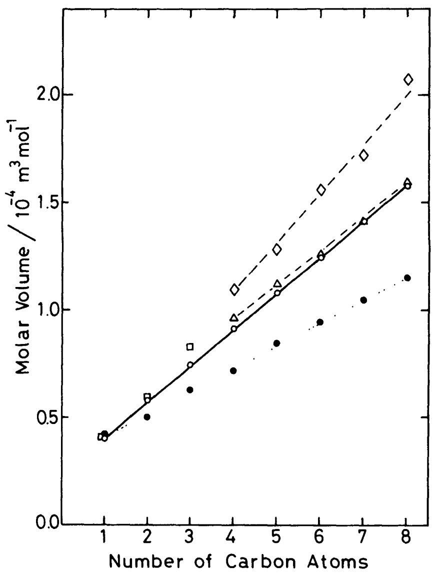

Fig. 3. Effects of the number of carbon atoms in the normal alcohol molecule upon the molar volumes based on the density data,[8] ○, and on the CPK model with assumptions of the hexagonal close packing of the rotating rods with a radius of 3.2×10^{-10} m, ◇, the hexagonal close-packing of the rotating rods with a radius of 2.4×10^{-10} m, △, the face-centered cubic packing of the sphere with radii of 2.4×10^{-10} m (methanol), 2.63×10^{-10} m (ethanol) and 2.96×10^{-10} m (1-propanol), □, and the pile-like packing of rectangular rods with a corss sectional area of $3.6\times4.0\times10^{-20}$ m^2, ●.

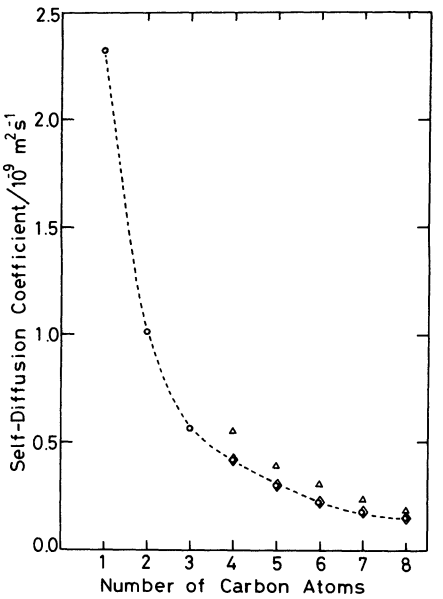

Fig. 4. Self-diffusion coefficient of normal alcohol against the number of carbon atoms at 298.15 K. ○, experimental results; △ and ◇, calculated by Eq. 7 using the hydrodynamic radii of 2.4×10^{-10} m, and 3.2×10^{-10} m, respectively.

constant crosssection for the alcohol molecules having longer hydrocarbon chains than 1-butanol.

In order to confirm the validity of the value 3.2×10^{-10} m, which is larger than expected for the crosssection of a hydrocarbon chain in its solid state,[13] the experimental molar volumes based on the density data[8] for the normal alcohols were compared with those based on the CPK molecular model.[9] In Fig. 3 are shown effects of the number of carbon atoms in the normal alcohol molecules on the molar volumes based on various calculations. The sphere molecule model (open rectangles) for the short-chained alcohols, except 1-propanol, gives a molar volume almost equal to that based on the density data[8] (open circles). The molecules of methanol and ethanol can therefore be perfectly spherical in their shape, while the 1-propanol molecule deviates more or less from the spherical shape. For the alcohols having longer carbon chains than 1-propanol, the molar volume values (open circles) are always larger than those based on the pilelike packed model (filled circles) with a value of $3.6\times4.0\times10^{-20}$ m^2*** for the crosssectional area of a rectangular rod, and also too small to be compared with those based on the hexagonal close-packed model (open diamonds) with a value of 3.2×10^{-10} m for the radius of the helically coiled hydrocarbon chain. For the rotating rods whose radii are commonly 2.4×10^{-10} m (a half of the diagonal length for the above rectangular rod), the calculated values (open triangles) are almost comparable with those based on the density data.

If, however, the pure liquid of the normal alcohol consists of the above rotating rods orientated in the hexagonal close-packed structure, optical anisotropy should be observed for the pure liquid of the normal alcohol as if it were a liquid crystal. However, no optical anisotropies such as streaming birefringence have ever been observed for pure liquids of short-chained normal alcohols. The alcohol molecules would therefore be randomly orientated and the free rotating motion along the rodaxis should be restricted, which conditions are in support of the experimental molar volumes. The gradual decrease in the self-diffusion coefficients (open circles in Fig. 4) from 1-butanol to 1-octanol may support the above argument; the straight rodlike molecules entangle with one another and the rotational (end-over-end), as well as transverse,[14] motion of each rod may be severely restricted. The self-diffusion of the long-chained alcohols, therefore, must involve the longitudinal rather than transverse motion of the rodlike molecules.[14]

In Fig. 4 are compared the experimental values of self-diffusion coefficient with the theoretical ones calculated by Eq. 7 with a value of 2.4×10^{-10} m (open triangles) or 3.2×10^{-10} m (open diamonds) for the hydrodynamic radius a. The open diamonds agree exactly with the experimental values. The value of the

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***The theoretical cross section of hydrocarbon chain in solid state was obtained by use of the CPK molecular model. The value is in fair agreement with the reference value by X-ray diffraction measurement.[13]

radius (3.2×10^{-10} m), however, does not satisfy the molar volume based on the density data as mentioned above. This discrepancy may be reconciled in terms of dimerization of alcohol molecules through hydrogen bonding of their hydroxyl groups.[15,16] Consequently, the self-diffusion coefficient of such a dimer becomes inversely proportional to the root of the mass for two molecules of monomeric alcohol, when one assumes a hard sphere model[12,17] for the self-diffusion of the alcoholic systems. Thus the hypothetical value of the self-diffusion coefficient for the monomer alcohol gives 2.25×10^{-10} m as the apparent hydrodynamic radius, which seems reasonable for the cross-section of hydrocarbon chain.[13] The values of the apparent hydrodynamic radii of methanol, ethanol, and 1-propanol have been similarly calculated as 1.77×10^{-10}, 2.15×10^{-10}, and 2.20×10^{-10} m, respectively. The significantly small value of methanol results from the extremely large value of its experimental self-diffusion coefficient as compared with those of the other alcohols (see Fig. 4); dimers of methanol molecules seem to be too short to entangle with one another and can translate not only longitudinally but also transversely.

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