2154 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 2154—2158 (1990) [Vol. 63, No. 8

Dynamical Structures of Normal Alkanes, Alcohols, and Fatty Acids in the Liquid State as Determined by Viscosity, Self-Diffusion Coefficient, Infrared Spectra, and ^{13}C NMR Spin-Lattice Relaxation Time Measurements

Makio Iwahashi,* Yoshimi Yamaguchi, Yoshio Ogura,†† and Masao Suzuki†
Department of Chemistry, School of Hygienic Sciences, Kitasato University, Sagamihara, Kanagawa-ken 228
†Nippon Oil and Fats Co. Ltd., Ohama, Amagasaki 660
(Received February 24, 1990)

The dynamical structures of molecules of normal alkanes (C_5—C_{14}) and normal fatty acids (C_8 and C_9) in the liquid state were estimated through analyses of their self-diffusion coefficients (D), viscosities (η), molar volumes, and ^{13}C NMR spin-lattice relaxation time (T_1). The apparent hydrodynamic radius evaluated from D and η for the alkanes was ca. 2.5×10^{-10} m and that for the fatty acids, ca. 3.1×10^{-10} m, irrespective of their hydrocarbon chain length: The former value is almost equal to that of the van der Waals radius (2.4×10^{-10} m) of the cross section of a hydrocarbon chain; the latter is in agreement with that of the normal alcohols reported in a previous paper. It is thus concluded that in the pure liquid of a rod-like compound such as normal alkane, alcohol, and fatty acid, the free rotational (end-over-end) as well as the transverse motion of the rod-like molecule is severely restricted due to the entanglements of the molecules; only a longitudinal translation is allowed. In addition, the infrared-spectrum results suggest that a unit in translational motion for a normal fatty acid is a dimer.

In a previous paper[1)] we reported that the apparent hydrodynamic radius for normal alcohol homologs (C_1—C_8), evaluated through the Stokes-Einstein formula under slip boundary conditions,[2,3)] was always constant (ca. 3.2×10^{-10} m), irrespective of the hydrocarbon chain length of the alcohol, except for methanol. The value, 3.2×10^{-10} m, is appreciably large compared with that of the van der Waals radius, 2.4×10^{-10} m, which was evaluated using a CPK molecular model for the cross section of a hydrocarbon chain. This large value could be elucidated by decreasing the self-diffusion coefficient caused by a longitudinal self-association of two alcohol molecules. It is likely that the self-diffusion coefficient for a doubly associated molecule is smaller than that for a monomer molecule, probably being $1/\sqrt{2}$ of that for a monomer molecule. Namely, the hypothetical value of the self-diffusion coefficient for the monomer alcohol is larger than the observed value by a factor of $\sqrt{2}$, and gives 2.25×10^{-10} m as the apparent hydrodynamic radius. This seems to be reasonable for the cross-section of the hydrocarbon chain. The constancy of the apparent radius for a normal alcohol molecule, irrespective of the number of carbon atoms, has also been ascribed only to the longitudinal motion of an extended rod-like dimer. Both the rotational and transverse (to the direction perpendicular to the rod axis) motions of a rod-like dimer are hindered by other rods in its vicinity.[1,4,5)]

If the above-mentioned concept for normal alcohols in the liquid state is completely valid, alkane molecules, which do not form any dimer, should have the same value for the radius as that of the van der Waals type of the cross section of a hydrocarbon chain; fatty acid molecules, which are expected to perfectly form a linearly combined dimer, should have the same value as that for normal alcohol.

In the present study we have measured the density, viscosity and self-diffusion coefficient for normal alkane homologs (C_5—C_{14}) and normal fatty acids (C_8 and C_9), the ^{13}C NMR spin-lattice relaxation time for the alkanes, and the infrared spectra for 1-octanol and octanoic acid; we also estimated the dynamical structures for their compounds and verified the concept[1)] for a normal alcohol in the liquid state.

Experimental

Materials. Gas-chromatographically pure samples of pentane (99.9%; Tokyo Kasei Industry Co.), hexane (99.8%; Wako Pure Chemical Industries Ltd.), heptane, octane (99.9%; Tokyo Kasei Industry Co.), nonane, decane (99.9%; Wako Pure Chemical Industries Ltd.), undecane, dodecane, tridecane, tetradecane (99.9%; Kanto Kagaku Co.), and octanoic and nonanoic acids (99.99%; Nippon Oil and Fats Co., Ltd.) were used without further purification. The purity for the above-mentioned samples was confirmed by gas-liquid chromatography (Hitachi 663-50 with a column of SE-30 for the alkanes and Shimazu GC-14A with a capillary column of SP-2560 for the acids). The water used was a triply distilled type. Deuterium oxide (99.95%) from E. Merck A.G. was used without further purification.

Density. The densities of normal alkanes and normal fatty acids were obtained on a twin-cell-type vibrational densimeter (Shibayama Kagaku Co., Model SS-D-200), with reference to degassed pure water.

Viscosity. The viscosities of the alkanes and fatty acids were measured with Ostwald capillary viscometers. Pure water was used for calibrating the viscosity.

Self-Diffusion Coefficient. The self-diffusion coefficients of the alkanes and fatty acids were obtained by a pulsed-

---

†† Present address: Tokyo Ohka Kogyo Co., Samusawa, Kanagawa 253-01.

gradient FT-NMR method[6–8] All measurements were made on protons at 99.6 MHz, with an internal D_2O lock at the temperatures of 298 K and 323 K±0.5 K on a NMR spectrometer (JEOL FX-100). Each sample was placed in a 1 mm-dia. tube inserted in a 5 mm-dia. tube containing D_2O (for NMR lock).

^{13}C NMR Spin-Lattice Relaxation Time T_1. The ^{13}C NMR relaxation time (T_1) of the alkanes, which were fully deoxigened with bubling argon gas, was obtained by an inversion recovery method[8] on a 90 MHz-NMR spectrometer (JEOL FX-90Q). The sample was placed in a 5 mm-dia. tube with a 1 mm-dia. tube containing D_2O.

Infrared Spectrum. The infrared spectra of octanoic acid and 1-octanol were obtained on a Parkin-Elmer infrared spectrometer (Model 983) equipped with a heating device (Hitachi Model 1RH-2).

Molar Volume. The molar volumes of the normal alkane homologs were obtained from their densities. Theoretical molar volumes were calculated by the use of the CPK molecular.model, assuming a hexagonal close-packed structure of rods rotating along the axis, a face-centered cubic packed structure of spheres of randomly coiled alkane molecules, or pile-like packing structure of rectangular solids.

Results and Discussion

Table 1 summarizes the experimental values of the density (ρ), viscosity (η), and self-diffusion coefficient (D) for normal alkane homologs and for octanoic and nonanoic acids at 298.1 and 323.1 K. In the same table, literature data[9–15] are also tabulated. On the whole, our data are in agreement with the reference values. The apparent hydrodynamic radius (α) for the above samples was calculated by substituting our data for η and D into the following Stokes-Einstein equation under the slip boundary conditions:[2,3]

$$\alpha = \frac{kT}{4\pi\eta D}, \qquad (1)$$

where k is Boltzmann's constant and T the absolute temperature.

In Fig. 1 the apparent hydrodynamic radius (Stokes-Einstein radius) at 298.1 K of the normal alkanes (α; open circles) is plotted against their hydrocarbon-chain length, together with the hypothetical radius (α_0; closed circles) obtained by substituting the value of the density (ρ) at 298 K into

Table 1. Density ρ, Viscosity η, and Self-Diffusion Coefficient D for Normal Alkanes and Acids

	Number of carbon atom	$\rho/10^3$ kg m^{-3}		$\eta/10^{-3}$ Pa s			$D/10^{-9}$ m^2 s^{-1}		
298.1 K	5	0.6210	0.62139[a] 0.6210[f]	0.225	0.225[a] 0.215[f]	0.22[b]	5.96	5.45[b]	5.535[f]
	6	0.6556	0.65481[a] 0.655[g]	0.309	0.2985[a] 0.2937[g]	0.29[b]	4.44	4.21[b]	
Alkanes	7	0.6793	0.67951[a] 0.6795[g]	0.393	0.3967[a] 0.386[g]	0.38[b]	3.32	3.12[b]	3.13[c]
	8	0.6983	0.69849[a] 0.698[g]	0.515	0.5151[a] 0.5082[g]	0.51[b]	2.55	2.25[b]	
	9	0.7137	0.71381[a] 0.71328[g]	0.648	0.6696[a] 0.6621[g]	0.67[b]	1.96	1.70[b]	1.72[c]
	10	0.7265	0.72625[a] 0.72643[g]	0.833	0.8614[a] 0.8527[g]	0.85[b]	1.48	1.31[b]	1.38[c]
	11	0.7363		1.159			1.17		
	12	0.7455	0.74516[a]	1.324	1.378[a]		0.93		0.86[c]
	13	0.7528		1.649			0.75		
	14	0.7590		2.028			0.60		0.58[c]
Acids	8	0.9060	0.9064[d]	5.105	5.16[d]		0.221		
	9	0.9008		6.754			0.156		
323.1 K	6	0.6325		0.251			5.96		
	7	0.6577	0.6582[e]	0.315	0.3100[e]		4.47	4.2[b,β]	4.24[c]
Alkanes	8	0.6779	0.6782[e]	0.388	0.3928[e]		3.50	3.1[b,β]	
	9	0.6941	0.6942[e]	0.486	0.4968[e]		2.75	2.6[b,β]	2.49[c]
	10	0.7074		0.603			2.17	2.1[b,β]	2.06[c]
	11	0.7177	0.7180[e]	0.736	0.7609[e]		1.72		
	12	0.7269		0.891			1.44		1.32[c]
	13	0.7349	0.7349[e]	1.075	1.1177[e]		1.15		
	14	0.7413		1.290			0.92		0.92[c]
Acids	8	0.8860		2.839	2.62[e]		0.421		
	9	0.8807		3.595	3.79[e]		0.316		

a): Riddick and Bunger,[9] b): Douglass and McCall,[10] c): Erth and Dullien,[11] d): Jones et al.,[12] e): Doolittle and Peterson,[13] f): Fisher,[14] g): Timmermans,[15] and β): Interpolated value of the data by Douglass and McCall.[10]

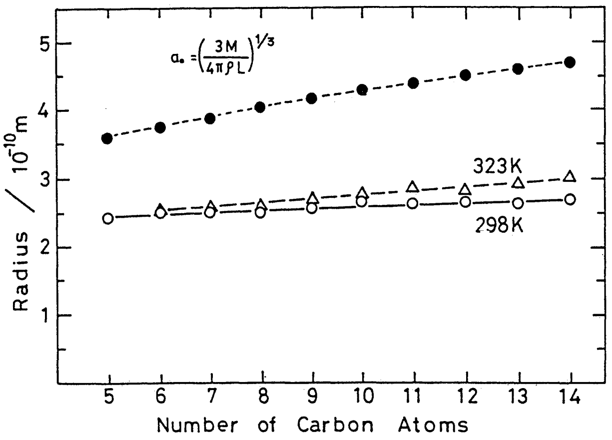

Fig. 1. Molecular radius of normal alkane against the number of carbon atoms. Open circles indicate the apparent hydrodynamic radius (the Stokes-Einstein radius) at 298 K and open triangles, at 323 K; filled circles being calculated from the densities of the normal alkane homologs at 298 K according to Eq. 2.

$$\alpha_0 = \left(\frac{3M}{4\pi\rho L}\right)^{1/3}, \tag{2}$$

where M is the molar weight of alkane, and L Avogadro's number.

The latter radius increases monotonously with an increase in the chain length, whereas the former is almost constant (ca. 2.5×10^{-10} m in average, although a slight increment from 2.4 to 2.7×10^{-10} m being observed). The constant value is comparable to the van der Waals radius of the cross section of the hydrocarbon chain (2.4×10^{-10} m).

To confirm the validity of the value 2.5×10^{-10} m, we compared the experimental molar volumes based on the density data for the normal alkanes with those estimated from the CPK molecular model. Figure 2 shows the effects of the number of carbon atoms in a alkane molecule on its molar volume based on various calculations. The experimental values (open circles) are in fair agreement with the theoretical values calculated by assuming a hexagonal close-packing of the rotating rods, the radii of which are commonly 2.5×10^{-10} m; they differ significantly from those obtained by assuming a face-centered cubic packing of a sphere of randomly coiled normal alkanes as well as from those based on the pile-like packed model (open rectangles) with a value of $3.6\times4.0\times10^{-20}$ m^2 for the cross-sectional area of a rectangular rod.

Consequently, the value of 2.5×10^{-10} m is adequately correct for normal alkanes at 298 K. The slight deviation from the van der Waals radius (2.4×10^{-10} m) is mainly attributable to vigorous, segmental motions in the hydrocarbon chain. In fact, as shown in Fig. 1, the radii for the alkanes at 323 K (triangles) are always larger than those at 298 K (open circles). The segmental motion becomes large as the

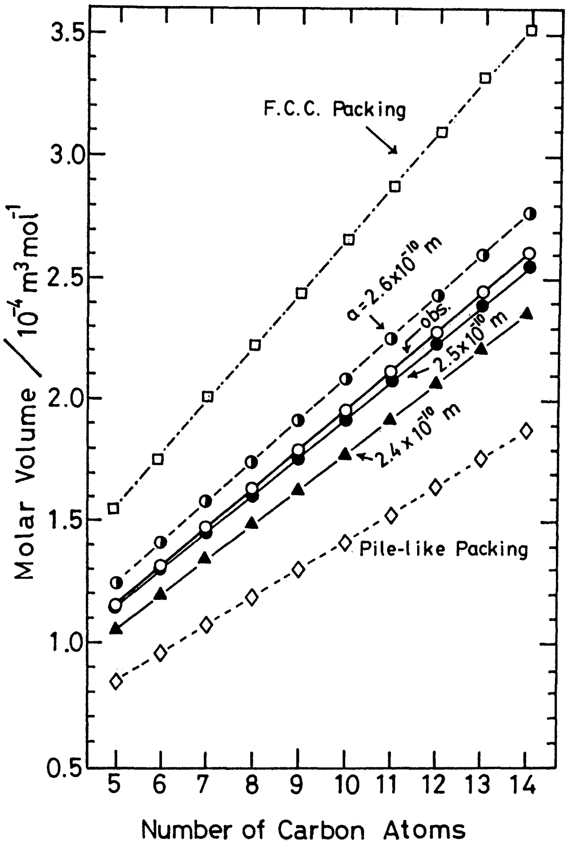

Fig. 2. Effects of the number of carbon atoms in the normal alkane molecule upon the molar volumes based on the density data (○), and on the CPK model with assumptions of the hexagonal close packing of the rotating rods with a radius of 2.6×10^{-10} m (◑), 2.5×10^{-10} m (●), 2.4×10^{-10} m (▲), the face-centered cubic packing of the sphere (□), and the pile-like packing of rectangular rods with a cross sectional area of $3.6\times4.0\times10^{-20}$ m^2 (◇).

Table 2. Relaxation in Normal Alkanes. T_1 (sec) as a Function of Carbon Number

	C1	C2	C3	C4	$(CH_2)_n$
308 K					
C_6H_{14}	16.49	19.08	18.19		
C_7H_{16}	9.91	11.59	11.26	10.95	
C_8H_{18}	9.14	11.00	9.52	10.22	
C_9H_{20}	7.40	8.58	6.98	7.17	6.09
$C_{10}H_{22}$	7.39	7.47	6.48	5.85	5.62
$C_{11}H_{24}$	6.23	5.64	5.13	4.24	3.98
$C_{12}H_{26}$	5.81	5.29	4.06	3.92	2.92
$C_{13}H_{28}$	5.51	4.51	4.05	3.01	2.46
$C_{14}H_{30}$	5.02	4.67	3.31	3.07	1.96
323 K					
C_6H_{14}	20.32	20.78	20.43		
C_7H_{16}	15.06	17.54	17.01	15.83	
C_8H_{18}	11.64	13.72	12.56	11.97	
C_9H_{20}	9.37	10.72	9.43	8.31	7.88
$C_{10}H_{22}$	8.79	9.76	8.09	7.75	5.80
$C_{11}H_{24}$	8.29	7.91	6.13	5.71	5.46
$C_{12}H_{26}$	7.92	6.91	5.63	5.14	3.91
$C_{13}H_{28}$	7.68	6.30	4.95	4.14	3.24
$C_{14}H_{30}$	6.57	6.13	4.41	3.88	2.63

temperature is increased. This is further supported by the fact that the ^{13}C NMR spin-lattice relaxation time (T_1) for each segment in the alkane molecule at 323 K is always larger than that at 308 K, as tabulated in Table 2.

A comparison of the T_1 values of the carbon atoms located at the same position, counted from the methyl group for the alkanes at each constant temperature, indicates that the T_1 value at the same position decreases with increasing the molecular weight of the alkanes. In spite of a decrease in the segmental motion with increasing chain length, the hydrodynamic radius for the alkane increases slightly from 2.4 to 2.7×10^{-10} at 298 K or from 2.5 to 3.0×10^{-10} m at 323 K. This is probably due to an increase in the gauche structure in the hydrocarbon chain with increasing the chain length.[16]

Erth and Dullien[10] evaluated the apparent molecular diameter (d) for normal alkane homologs using

$$d = 2.24\sqrt{\frac{\eta VD}{RT}}\,, \tag{3}$$

where V is the molar volume of the alkane, and R the gas constant. However, the obtained d values (6.5—7.65×10^{-10} m for C_5H_{12}, C_6H_{14}, C_7H_{18}, C_9H_{20}, and $C_{10}H_{22}$) at their melting points are too large to satisfy the molar volumes of the alkanes obtained from their density data.

In Fig. 3 the Stokes-Einstein radii for octanoic and nonanoic acids (closed rectangles) at 298.1 K are also plotted against the hydrocarbon chain length, together with those for normal alcohols[1] (circles). The radius for the each acid is apparently equal to that for the alcohols. Thus, the acids seem to be in similar molecular conformation to the alcohols.

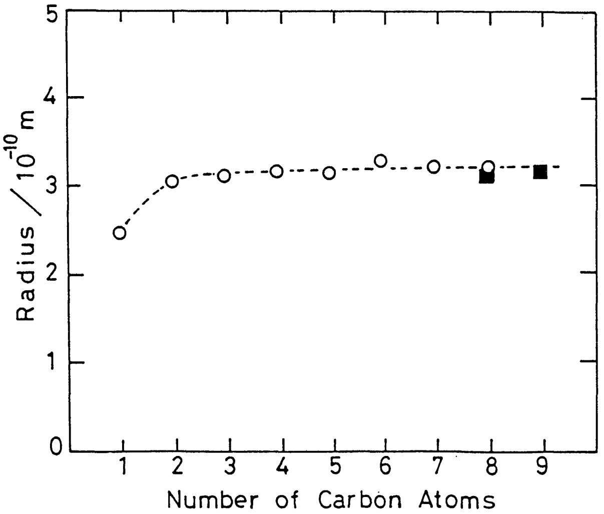

Fig. 3. Molecular radius of normal fatty acids (C_8 and C_9) and normal alcohols (C_1—C_8) against the number of carbon atoms at 298 K. Open circles indicate the apparent hydrodynamic radius for the alcohols[1] and filled rectangles, for the acids.

The IR spectra of octanoic acid in its liquid state in the temperature range 296—346 K indicated that the acid molecules were always linearly self-associated to be cyclic dimers by the hydrogen bonds of their carboxyl groups. Namely, the strong absorption band at 1710 cm^{-1} due to the C=O streaching vibration and the relatively broad band at 920 cm^{-1} due to the OH out-of-plane bending vibration of the carboxyl group (assigned to the cyclicly hydrogen-bonded dimer) remained completely unaltered throughout the temperature range.

Longsworth[14] designated, from the magnitude of the mutual diffusion coefficient and its concentration dependence, that the carboxylic acids in carbon tetrachloride at 298 K were present almost entirely as dimers and gave no indication of further association.

The IR spectra of 1-octanol in its liquid state in the same temperature range also indicated that the alcohol molecules were always self-associated by hydrogen bonds of their OH groups, although the peak due to the hydrogen-bonded OH-streching vibration was too broad to be assigned to a dimer or a higher polymer.

It can consequently be concluded that the unit, at least in the translational motion for alcohol molecules, is a linearly self-associated dimer as well as that for acid molecules. The large apparent hydrodynamic radii for the alcohols or for fatty acids, compared with those for alkanes, are also attributed to the lower self-diffusion coefficients for their dimers than those for their monomers (as predicted in a previous paper[1]). Namely, the self-diffusion coefficient of such a dimer is assumed to be inversely proportional to the root of the mass for two monomers. In fact, the mutual diffusion coefficient reported for alcohols in carbon tetrachloride is high at low concentrations, decrease steeply with increasing concentration, and finally becomes almost equal to that for a dimerlzed fatty acid possessing the same number of carbon atoms.[17] Thus, the hypothetical value of the self-diffusion coefficient for the monomeric alcohol or acid gives 2.25×10^{-10} m or 2.20×10^{-10} m as the apparent hydrodynamic radius, which seems to be reasonable for the cross-section of the hydrocarbon chain.

In general, the Stokes-Einstein formula under the slip boundary conditions is applicable for only a spherically shaped molecule having a similar size to that for the surrounding-solvent molecules.[18] Judging from the results for rod-like compounds such as normal alkanes, alcohols, and acids, however, we can conclude that the formula is sufficiently applicable, even to rod-like molecules having a relatively long-hydrocarbon chain.

As derived by Stokes, the frictional coefficient (f_0) is given by $f_0 = 6\pi\eta\alpha$: a spherical object of radius α, moving in a fluid continuum, is carried along with no slipage of the fluid layer in contact with it. Its movement of the object is impeled by a force due to the pressure built up in front of it ($=4\pi\eta\alpha$) and a frictional force parallel to its surface ($=2\pi\eta\alpha$); these two forces add up to the value given for the above frictional coefficient (f_0).

Even though the fluid does not stick to the surface of the spherical object (the slip boundary conditions), some fluid in front of the object must be displaced when the object moves.[19] There is some viscous dissipation of energy, and motion of the object is retarded. On the other hand, the side surface of the object undergoes a translational motion as well as a rotational type, and does not displace any fluid since the frictional force parallel to the surface of the spherical object is very small. Thus, the overall frictional force (f_0) becomes $4\pi\eta\alpha$.

In the case of a rod-like molecule in its pure liquid, the free rotational (end-over-end), as well as transverse, motion of the rod-like molecule is severely restricted[4,5] owing to entanglements of the molecules, even with slip between the molecules; this is because the liquid has very little space for motion, as assumed by the fact that only ca. 10% increases in volume at a solid-melt transition for a long-chained fatty acid.[20] Thus, the object molecule must displace many other molelcules in its transversal motion or end-over-end rotation.

On the other hand, in the longitudinal motion of a rod-like molelcule, although the object molecule should displace some other molecules in front of its head, its side surface may slightly displace a few molecules surrounding the object molecule. Thus, only a longitudinal translation is allowed and the resistant force comes to be only $4\pi\eta\alpha$. Douglass and McCall[10] also suggested that the elementary diffusion process for normal alkanes involves the translation of an extended molecule parallel to its chain axis, based on the fact that the activation energies of self-diffusion increase with increasing molecular weight of the alkanes.

The authors wish to express our thanks to Professor Hiroshi Kobayashi for his valuable discussions, to Professor Tadashi Kato, Tokyo Metropolitan University, for his help with the self-diffusion measurement, and to Professor Hideyo Hasumi, Faculty of Medicine, Kitasato University, for his help with the density measurement.

References

1) M. Iwahashi, Y. Ohbu, T. Kato, Y. Suzuki, K. Yamauchi, Y. Yamaguchi, and M. Muramatsu, *Bull. Chem. Soc. Jpn.*, **59**, 3771 (1986).

2) J. C. M. Li and P. Chang, *J. Chem. Phys.*, **23**, 518 (1955).

3) P. J. Espinosa and J. G. de la Torre, *J. Phys. Chem.*, **91**, 3612 (1987).

4) M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. 2*, **74**, 560 (1978).

5) O. Teraoka and R. Hayakawa, *J. Chem. Phys.*, **89**, 6989 (1988).

6) E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965).

7) E. O. Stejskal, *J. Chem. Phys.*, **49**, 1768 (1968).

8) T. C. Farrar and E. D. Becher, "Pulse and Fourier Transform NMR," Academic Press, New York (1971), Chap. 2.

9) J. A. Riddick and W. B. Bunger, "Organic Solvents," John-Wiely & Sons, Inc. New York (1970).

10) D. C. Douglass and D. W. McCall, *J. Phys. Chem.*, **62**, 1102 (1958).

11) H. Erth and F. A. L. Dullien, *AIChE J.* **19**, 1215 (1973).

12) W. J. Jones, S. T. Bowden, W. W. Yarnold, and W. H. Jones, *J. Phys. Coll. Chem.*, **52**, 753 (1948).

13) A. K. Doolittle and R. H. Peterson, *J. Am. Chem. Soc.*, **73**, 2145 (1951); A. K. Doolittle, *J. Applied Phys.*, **22**, 1031 (1951).

14) E. Fisher, *J. Phys. Chem.*, **57**, 4691 (1955).

15) J. Timmermans, "Physico-Chemical Constants of Binary Systems in Concurrent Solutions," Interscience, New York and London (1959).

16) T. Shimanouchi, "Intramolecular Rotation," Iwanami Co. Tokyo (1956), p.54.

17) L. G. Longsworth, *J. Colloid Interface Sci.*, **22**, 3 (1966).

18) J. T. Edward, *J. Chem. Education*, **47**, 261 (1970).

19) C. -M. Hu and R. Zwanzig, *J. Chem. Phys.*, **60**, 4354 (1974).

20) A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley & Sons, Inc., New York (1948), p. 351.