

Self-Association of *cis*-9-Octadecen-1-ol in the Pure Liquid State and in Decane Solutions As Observed by Viscosity, Self-Diffusion, Nuclear Magnetic Resonance, Electron Spin Resonance, and Near-Infrared Spectroscopic Measurements

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Received: July 5, 1994; In Final Form: October 24, 1994[®]

The self-association of *cis*-9-octadecen-1-ol in the pure liquid state and in decane solutions has been studied mainly through near-infrared spectroscopic observation over the temperature range 298.1–348.1 K. The analysis of the sharp band at 1410 nm (the first overtone band of OH-stretching vibration mode attributed to free OH-monomer and partly to OH-polymer) leads to a conclusion that the apparent degree of association, n , of the polymer of *cis*-9-octadecen-1-ol is 2.37–3.78 (average 2.95) both in the pure liquid state and in decane solutions; the n value has a tendency to decrease with an increase in temperature. The apparent association constant, K , which is relatively low, also decreases with an increase in temperature. The low K value, which means small portions of polymerized molecules, is most likely responsible for the high self-diffusion and the low viscosity of *cis*-9-octadecen-1-ol, compared with those of *cis*-9-octadecenoic acid, existing almost entirely as cyclic dimers.

Introduction

The absorption bands in the near-infrared (NIR) region are mainly due to overtones and combinations of the mid-IR fundamentals associated with the groups having a hydrogen atom, such as C–H, O–H, and N–H.^{1,2} Consequently, NIR spectroscopy is a powerful tool to investigate the hydrogen bondings of alcohols, fatty acids, water, and so on. In a previous paper³ we developed a quantitative method to obtain the degree of association and the thermodynamic properties such as the association enthalpy and entropy for octan-1-ol, which possesses a straight hydrocarbon chain in its molecule, in the pure liquid state and in decane solutions through NIR spectroscopic measurement. The association number n obtained for octan-1-ol was *ca.* four: *i.e.*, octan-1-ol molecules most likely exist as tetramers. On the other hand, the fatty acid molecules exist almost entirely as cyclic dimers in the liquid state and even in nonpolar solvents^{4–7} except at extremely low concentrations. Thus, the large association number for the normal alcohol, compared with that for the saturated fatty acid, in the liquid state is responsible for the higher viscosity^{3,8} and the lower self-diffusion coefficient³ of the alcohol than those of the fatty acid having the same number of carbon atoms.

As shown in Figures 1 and 2, however, *cis*-9-octadecen-1-ol (oleyl alcohol), possessing a *cis*-type double bond in its hydrocarbon chain, has a lower viscosity and a higher self-diffusion coefficient than *cis*-9-octadecenoic acid (oleic acid),

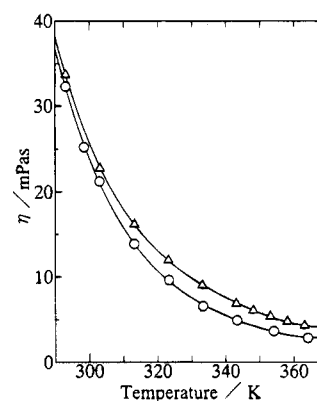


Figure 1. Temperature dependence of viscosity for *cis*-9-octadecen-1-ol (○) and *cis*-9-octadecenoic acid (Δ).

which consists mostly of cyclic dimers.^{6,7} This is opposite to the case for the normal alcohols and the saturated fatty acids. Namely, *cis*-9-octadecen-1-ol appears to have a smaller aggregation number and/or to abound more in free monomeric molecules than *cis*-9-octadecenoic acid.

In the present study, in order to know the effect of the molecular structure, especially of the aliphatic chain, on the hydrogen bonding of the alcohol, we carried out NIR spectroscopic measurement for *cis*-9-octadecen-1-ol in the pure liquid state and in decane solutions; we evaluated the extent of the self-association of the alcohol, employing a new analytical technique for the removal of the absorbance due to the alkyl group included in the alcohol itself. In addition, the dissociation of the aggregates of *cis*-9-octadecen-1-ol into its monomers with

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[®] Abstract published in *Advance ACS Abstracts*, February 15, 1995.

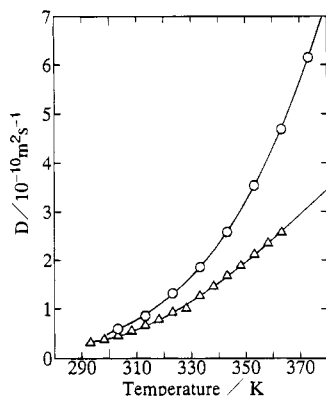


Figure 2. Temperature dependence of self-diffusion coefficient for *cis*-9-octadecen-1-ol (O) and *cis*-9-octadecenoic acid (Δ).

an increase in temperature was investigated through the measurements of ^{13}C NMR spin-lattice relaxation time and ESR order parameter.

Experimental Section

Materials. The samples of *cis*-9-octadecen-1-ol, 1-bromo-*cis*-9-octadecene, and *cis*-9-octadecenoic acid of very high purity (greater than 99.9%) were supplied by Nippon Oil and Fats Co. Ltd. (Amagasaki, Japan) and used without further purification. Decane (with purity greater than 99%, Tokyo Kasei Kogyo Co. Ltd.) was dried over 5A molecular sieves and distilled. The distilled decane was refluxed over anhydrous calcium sulfate and distilled again. Carbon disulfide-free carbon tetrachloride (CCl_4 , its purity greater than 99.9%, Dojin Co. Ltd.) was also dried over 5A molecular sieves and distilled. The distilled CCl_4 was refluxed over P_2O_5 and distilled again. All the distillations were carried out under an atmosphere of dried nitrogen. The purity for the samples of the alcohol, the bromide, and the acid was confirmed by gas-liquid chromatography (Shimadzu GC-14A with a capillary column of SP-2560). The following ESR spin probes from Sigma Chemical Co. were used without further purification: 5-(*N*-oxy-4,4-dimethyl-3-oxazolidinyl)octadecanoic acid (5NS), 7-(*N*-oxy-4,4-dimethyl-3-oxazolidinyl)octadecanoic acid (7NS), 12-(*N*-oxy-4,4-dimethyl-3-oxazolidinyl)octadecanoic acid (12NS), and 16-(*N*-oxy-4,4-dimethyl-3-oxazolidinyl)octadecanoic acid (16NS). The samples for ESR and NMR measurements were prepared after being fully purged with argon gas.

Near-Infrared Absorption Spectrum Measurement. A Hitachi-330 spectrophotometer, connected to a personal computer (NEC Model PC-9801RX2), was used to obtain the absorption spectra. A rectangular quartz cell having 1 cm path length was used. A Hitachi temperature-regulated cell holder (No. 210-2111) was used to maintain the temperature of the sample within ± 0.05 K.

Density. The densities for the samples of *cis*-9-octadecen-1-ol, *cis*-9-octadecenoic acid, and decane and for the solutions of *cis*-9-octadecen-1-ol dissolved in decane in the temperature range $293.15\text{--}323.15 \pm 0.01$ K were measured on a twin-cell-type vibrational densimeter (Shibayama Kagaku Co., Model SS-200), and those in the temperature range $313.15\text{--}363.15 \pm 0.01$ K with a Gay-Lussac-type pycnometer.⁹ Degassed distilled water and mercury purified by distillation were used for calibrating the densimeter and the pycnometer, respectively.

Viscosity. The viscosities, η , for the samples of *cis*-9-octadecen-1-ol and *cis*-9-octadecenoic acid were measured with an Ostwald capillary viscometer in the temperature range $293.15\text{--}363.15$ K with an accuracy of ± 0.05 K. Distilled water was used for calibrating the viscometer.

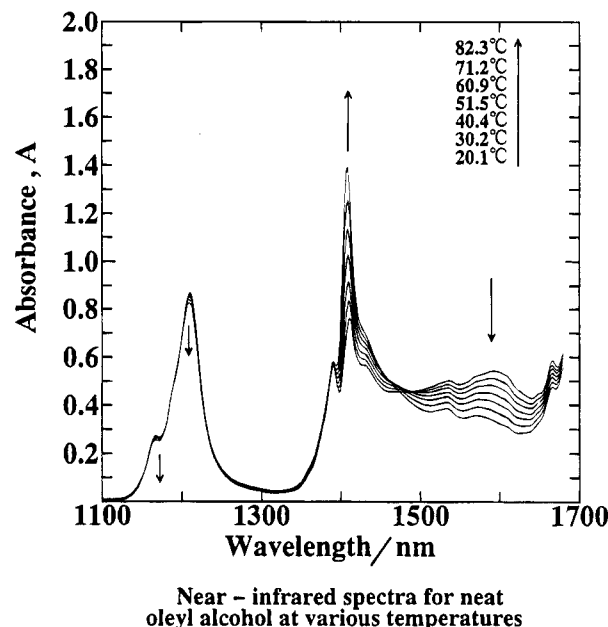


Figure 3. Effect of temperature on near-infrared spectrum (absorbance) for *cis*-9-octadecen-1-ol at (a) 293.2, (b) 303.3, (c) 315.3, (d) 324.6, (e) 334.0, (f) 344.3, and (g) 355.4 K.

Self-Diffusion Coefficient. The self-diffusion coefficient, D , for the samples of *cis*-9-octadecen-1-ol and *cis*-9-octadecenoic acid was obtained by the pulsed-gradient NMR method. All measurements were made on protons at 399.65 MHz in the temperature range $303.1\text{--}373.1 \pm 0.5$ K on an NMR spectrometer (JEOL EX-400).

NMR Spin-Lattice Relaxation Time. The ^{13}C NMR spin-lattice relaxation time, T_1 , for the sample of *cis*-9-octadecen-1-ol was obtained by the inversion-recovery method employing a $180^\circ\text{--}\tau\text{--}90^\circ$ pulse sequence, using a 400-MHz NMR spectrometer (JEOL EX-400) in the temperature range $303.1\text{--}363.1 \pm 0.5$ K.⁹

ESR Measurements. ESR spectra were recorded in the temperature range of $297\text{--}353$ K on an ESR spectrometer (Japan Electron Optics Laboratory Model JES-FE) with 100-kHz, 0.63-G modulation. The concentration of the spin probe was kept on the order of 10^{-4} mol dm^{-3} . The apparent order parameter, S , was established from the spectra.⁹

Results and Discussion

Figure 3 shows the temperature dependence of the NIR spectrum for the sample of *cis*-9-octadecen-1-ol in the pure liquid state. The sharp band at 1410 nm increases in peak height with increasing temperature, while the broad bands at lower frequencies (1500–1650 nm) decrease in intensity; the 1410-nm band was assigned to the first overtone of the OH-stretching mode of the monomeric alcohol, and the broad bands (1500–1650 nm) were assigned to the first overtone of the OH-stretching vibration in the hydrogen-bonded alcohol, respectively.³ Other absorption bands at 1170, 1210, 1390, and 1430 nm, which slightly decrease with increasing temperature, are assigned to CH vibrations.^{3,10,11} Unfortunately, the 1410-nm band and the broad bands (1500–1650 nm) also include the contribution from the CH vibrations of methyl and methylene groups.^{3,10,11}

In a previous study³ on octan-1-ol in the pure liquid state and in decane solutions, we used the peak height of the second overtone of the CH-stretching mode of decane as a reference for subtracting the contribution of the alkyl groups of octan-1-ol and decane used as solvent from the absorptions due mainly

to the OH groups. Namely, the bands of the methylene groups exist commonly in both spectra for octan-1-ol and decane, and the former has the same number of methylene groups in its molecule as the latter. Thus, the net spectra excluding the contribution of alkyl groups for monomeric OH and hydrogen-bonded OH were obtained: this cancellation method was successful for the octan-1-ol/decane system.

For the sample of *cis*-9-octadecen-1-ol in the pure liquid state and in decane solutions, the same cancellation method using decane was tried after the normalization of both spectra for decane and neat *cis*-9-octadecen-1-ol (or the *cis*-9-octadecen-1-ol/decane solution) using the 1210-nm band as the internal reference. The difference spectra obtained for the pure liquid and for the solutions also have an isosbestic point. However, the analysis of the sharp 1410-nm band (monomeric OH band) did not give any satisfactory association number, n , and association constant, K . The values obtained for n and K were significantly large and beyond the limit of the reasonable values. Thus, such a CH cancellation procedure using decane has failed for *cis*-9-octadecen-1-ol. This is probably because the band profile of the spectrum of the alkyl chain in the *cis*-9-octadecen-1-ol molecule possessing a *cis*-type double bond is clearly distinct from that of the alkyl chain in the decane molecule. Consequently, in order to get reasonable values for n and K , we used a new procedure using 1-bromo-*cis*-9-octadecene to analyze the spectrum results for *cis*-9-octadecen-1-ol.

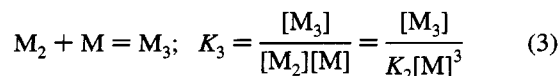
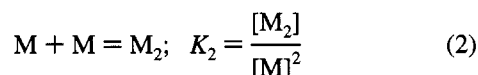
In the new analysis, first of all, the net absorbance at 1410 nm for the *cis*-9-octadecen-1-ol dissolved in decane was obtained through the subtraction of the absorbance attributed to the solvent (decane) from the total absorbance at 1410 nm for the solution of *cis*-9-octadecen-1-ol in decane. For neat *cis*-9-octadecen-1-ol, of course, such a subtraction is not necessary.

Namely,

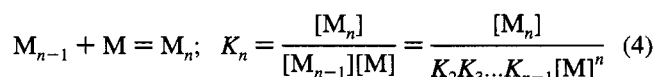
$$\begin{aligned} A_{\text{alc}}^{1410}(t) &= A_{\text{soln}}^{1410}(t) - A_{\text{dec}}^{1410}(t) \\ &= A_{\text{soln}}^{1410}(t) - C_{\text{dec}}(t)\epsilon_{\text{dec}}^{1410}L \end{aligned} \quad (1)$$

where $A_{\text{alc}}^{1410}(t)$, $A_{\text{soln}}^{1410}(t)$, and $A_{\text{dec}}^{1410}(t)$ are absorbances at 1410 nm for alcohol, solution, and decane at an arbitrary temperature t , respectively. $C_{\text{dec}}(t)$ is the concentration of decane at t , which was evaluated from weights of the alcohol and its solutions and the density for alcohol, decane, and the solutions at t because the $C_{\text{dec}}(t)$ value changes with a change of t . $\epsilon_{\text{dec}}^{1410}$ is the molar absorption coefficient of decane at 1410 nm, which was obtained as $0.107 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ from the absorbance vs concentration relationship for decane dissolved in CCl_4 . L is the light-path length.

Evaluation of Association Number and Association Constant. Polymers of *cis*-9-octadecen-1-ol would be formed through the following successive association process:



and for an n -mer, in general,



where $[M]$, $[M_2]$, $[M_3]$, and $[M_n]$ denote the concentration of

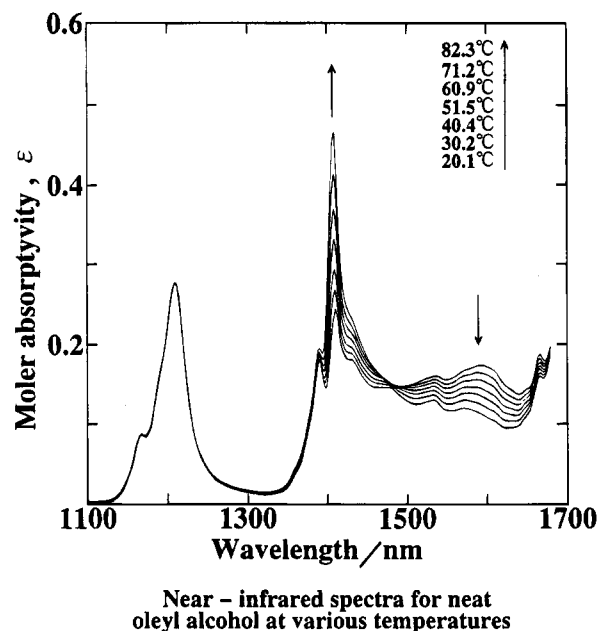


Figure 4. Effect of temperature on near-infrared spectrum (molar absorption coefficient) for *cis*-9-octadecen-1-ol. Temperatures as in Figure 3.

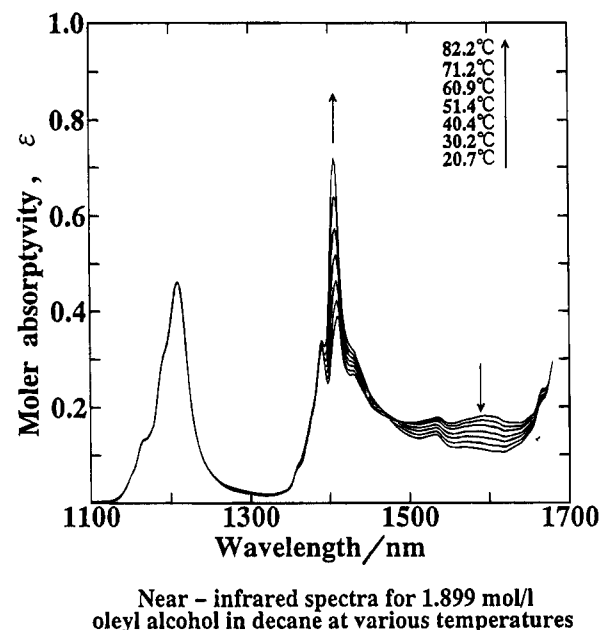


Figure 5. Effect of temperature on near-infrared spectrum for the 1.90 mol dm^{-3} solution of *cis*-9-octadecen-1-ol in decane at (a) 293.8, (b) 303.3, (c) 313.5, (d) 324.5, (e) 334.0, (f) 344.3, and (g) 355.3 K.

monomer, dimer, trimer, and n -mer molecules, respectively, and K_2 , K_3 , and K_n denote the association constants for the formation of the dimer, trimer, and n -mer, respectively.

In the spectra (Figure 4) presented by the apparent molar absorption coefficient, ϵ , for the sample of *cis*-9-octadecen-1-ol in the pure liquid state, an isosbestic point exists at 1470 nm. Such an isosbestic point was observed not only for the pure liquid but also for the decane solutions at various concentrations. A typical example is shown in Figure 5.

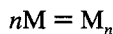
The existence of the isosbestic point suggests that the *cis*-9-octadecen-1-ol molecules in the pure liquid state and also in the decane solutions likely exist in two distinct forms: One form is a monomer, and the other is probably only one kind of polymer species. Thus, as a first approximation we assume that the n -mer is a major self-association species: *cis*-9-octadecen-

1-ol would exist as an equilibrium mixture of the monomeric and n -meric species.

Consequently, from eq 4, we obtain eq 5, expressing the overall association constant, K ,

$$K = \frac{[M_n]}{[M]^n} \quad (5)$$

where $K = K_2 K_3 \dots K_{n-1} K_n$. This equation corresponds to the following direct n -mer formation process:



If we define C as the total concentration of *cis*-9-octadecen-1-ol and x as the mole fraction (in the monomeric unit) of the n -mer molecules to the total concentration, $[M]$ and $[M_n]$ are represented as follows:

$$\begin{aligned} [M] &= C(1 - x) \\ [M_n] &= Cx/n \end{aligned} \quad (6)$$

Hence K is given by

$$K = \frac{x}{nC^{n-1}(1-x)^n} \quad (7)$$

The apparent molar absorption coefficient, ϵ , of the 1410-nm band partly superimposed by the absorption due to the hydrogen-bonded polymers, can be expressed by the following equation:

$$\epsilon = (1 - x)\epsilon_m + x\epsilon_n \quad (8)$$

where ϵ_m is the molar absorption coefficient at 1410 nm for monomer molecules and ϵ_n is the molar absorption coefficient per monomeric unit for the n -mer, respectively. Both ϵ_m and ϵ_n include the contribution from the CH vibrations of the alkyl groups (ϵ^{CH}). The contributions from the monomers and the n -mers change depending on temperature, but the total ϵ^{CH} value remains unchanged because ϵ^{CH} values for the monomers and the n -mers are the same: *i.e.*, $\epsilon^{\text{CH}} = \epsilon_m^{\text{(CH)}} = \epsilon_n^{\text{(CH)}}$.

Combination of eqs 7 and 8 yields

$$\log[C(1 - \epsilon/\epsilon_m)] = n \log[C(\epsilon - \epsilon_n)/\epsilon_m] + \log(BK) \quad (9)$$

where

$$B = n \left(\frac{\epsilon_m - \epsilon_n}{\epsilon_m} \right)^{1-n} \quad (10)$$

In these equations the ϵ_m for the alcohol monomer can be obtained from the absorbance vs concentration ($A - C$) relationship at low concentrations where most alcohol molecules exist predominantly as monomers. The $A - C$ relationship for *cis*-9-octadecen-1-ol in CCl_4 at 296.7 K gave a straight line at $C < 6.0 \times 10^{-2} \text{ mol dm}^{-3}$, giving $1.64 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ as the ϵ_m value. Another experiment showed that the ϵ_m value was almost independent of temperature.

As mentioned before, the ϵ_n includes the contribution of the CH vibrations and can be described as follows:

$$\epsilon_n = \epsilon_n^{\text{(CH)}} + \epsilon_n^{\text{(OH)}} \quad (11)$$

where $\epsilon_n^{\text{(OH)}}$ denotes the molar absorption coefficients at 1410 nm attributable to the OH vibrations of the polymeric alcohol.

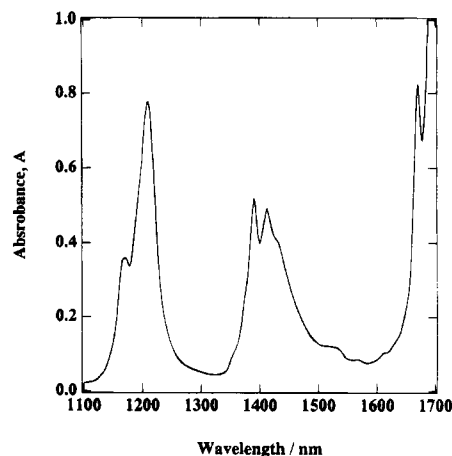


Figure 6. Near-infrared spectrum for 1-bromo-*cis*-9-octadecene at 293.2 K. From the spectrum, the molar absorption coefficient of CH vibration at 1410 nm was estimated to be $0.17 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

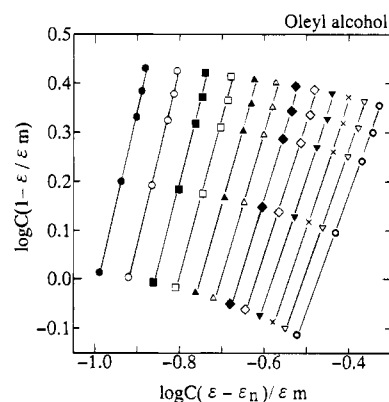


Figure 7. $\log[C(1 - \epsilon/\epsilon_m)]$ vs $\log[C(\epsilon - \epsilon_n)/\epsilon_m]$ plots at various temperatures: ●, 293.1 K; ○, 298.1 K; ■, 303.1 K; □, 308.1 K; ▲, 313.1 K; △, 318.1 K; ◆, 323.1 K; ◇, 328.1 K; ▼, 333.1 K; ×, 338.1 K; ▽, 343.1 K; ○, 348.1 K.

The spectrum of 1-bromo-*cis*-9-octadecene, which does not contain the OH moiety, should give an $\epsilon_m^{\text{(CH)}}$ value because there are no n -mers in this sample. The $\epsilon_m^{\text{(CH)}}$ value, which is the same as the $\epsilon_n^{\text{(CH)}}$ value, was determined to be $0.17 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ from the spectrum (Figure 6) of 1-bromo-*cis*-9-octadecene in the pure liquid state. *cis*-9-Octadecenoic acid, whose OH vibration exists far from the position at 1410 nm, also gave the same $\epsilon_n^{\text{(CH)}}$ value at 1410 nm.

In the previous paper,³ the $\epsilon_n^{\text{(OH)}}$ value for octan-1-ol was estimated to be 10^{-3} to $10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, which is negligibly small compared with the $\epsilon_n^{\text{(CH)}}$ value.

Thus, the ϵ_n in eq 11 becomes

$$\epsilon_n \cong \epsilon_n^{\text{(CH)}} = 0.17 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

Next, the ϵ values at various concentrations at a constant temperature were obtained from interpolation of the $\epsilon - T$ relationships obtained at various concentrations. The values of ϵ and C (corrected for the density change) of *cis*-9-octadecen-1-ol at various temperatures are tabulated in Table 1.

Figure 7 shows the $\log[C(1 - \epsilon/\epsilon_m)]$ vs $\log[C(\epsilon - \epsilon_n)/\epsilon_m]$ relationship at various temperatures, which give very good straight lines. The slope for each line gives the association number, n , and the intercept on the ordinate also gives the apparent association constant, K ; the n and K values obtained are tabulated in Table 2.

As shown in Figure 8, the n value is always less than four (average 2.95) and decreases gradually with a rise in temper-

TABLE 1

T/K	C/mol dm ⁻³	ϵ/dm^3 mol ⁻¹ cm ⁻¹	T/K	C/mol dm ⁻³	ϵ/dm^3 mol ⁻¹ cm ⁻¹
293.1	1.27	0.303	323.1	1.23	0.449
	1.90	0.270		1.85	0.391
	2.53	0.251		2.47	0.354
	2.85	0.244		2.78	0.342
	3.16	0.238		3.10	0.328
298.1	1.26	0.326	328.1	1.22	0.475
	1.89	0.288		1.84	0.413
	2.52	0.267		2.46	0.374
	2.84	0.259		2.77	0.361
	3.15	0.251		3.09	0.345
303.1	1.25	0.350	333.1	1.22	0.501
	1.88	0.308		1.83	0.435
	2.51	0.283		2.45	0.394
	2.83	0.274		2.76	0.380
	3.14	0.265		3.08	0.363
308.1	1.25	0.374	338.1	1.21	0.528
	1.87	0.328		1.82	0.458
	2.50	0.300		2.44	0.415
	2.82	0.290		2.75	0.400
	3.13	0.280		3.07	0.382
313.1	1.24	0.399	343.1	1.20	0.554
	1.87	0.348		1.81	0.482
	2.49	0.317		2.43	0.437
	2.81	0.307		2.74	0.421
	3.12	0.295		3.06	0.402
318.1	1.23	0.424	348.1	1.20	0.582
	1.87	0.369		1.81	0.506
	2.48	0.336		2.42	0.459
	2.80	0.324		2.73	0.442
	3.11	0.311		3.05	0.423

TABLE 2: Aggregation Number and Association Constant for *cis*-9-Octadecen-1-ol and *cis*-9-Octadecenoic Acid

<i>cis</i> -9-octadecen-1-ol			<i>cis</i> -9-octadecenoic acid	
T/K	<i>n</i>	$K/\text{mol}^{-n} (\text{dm}^3)^n$	<i>n</i>	$K/\text{mol}^{-1} \text{dm}^3$
293.1	3.78	1097	2	1.95×10^5
298.1	3.58	414	2	6.99×10^4 (297.7 K)
303.1	3.40	185	2	2.52×10^4
308.1	3.22	93.3	2	1.37×10^4
313.1	3.07	52.5	2	5380
318.1	2.93	31.7	2	3830
323.1	2.81	21.0	2	2330
328.1	2.70	14.4	2	1470
333.1	2.61	10.5	2	926
338.1	2.51	7.83	2	667
343.1	2.43	6.06	2	474
348.1	2.37	4.80	2	357

ature. At a low temperature range tetramers seem to be the main associated species for *cis*-9-octadecen-1-ol as well as for octan-1-ol;³ at a high temperature range dimers seem to be the main associated species. Namely, different types of polymers seem to coexist with monomers in the neat and decane solutions; the population of the polymers would change depending on temperature.

Our first assumption was that the *cis*-9-octadecen-1-ol molecules exist as an equilibrium mixture of the monomer and one kind of polymer molecules. Thus, the first assumption seems to have a discrepancy with the obtained results. However, even if the different types of polymers coexist, they would have almost a comparable molar absorption coefficient with each other regardless of the association number of the polymers. In fact, as shown in Figure 4, the isosbestic point obtained seems to be somewhat obscure in comparison with the case of octan-1-ol.³

Judging from the *n* - *T* relationship in Figure 8, large polymers seem to dissociate into small species and finally into monomers. In the figure, there exists a break point at around 320 K.

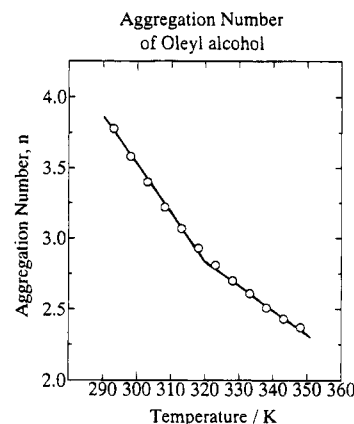
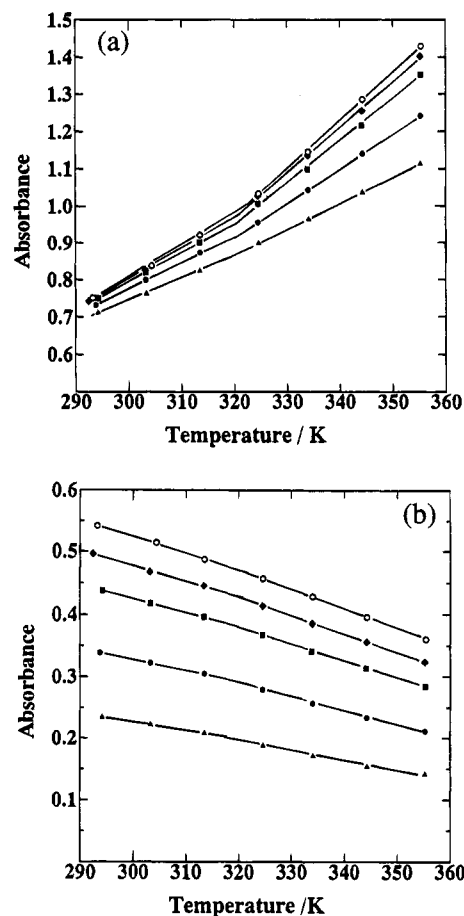
Figure 8. Apparent aggregation number *n* vs *T* relationship.

Figure 9. (a) Temperature dependence of absorbance at 1410 nm for the monomeric OH band: \blacktriangle , 1.26 mol dm⁻³; \bullet , 1.90 mol dm⁻³; \blacksquare , 2.53 mol dm⁻³; \blacklozenge , 2.85 mol dm⁻³; \circ , 3.16 mol dm⁻³. (b) Temperature dependence of absorbance at 1580 nm for the polymeric OH band: \blacktriangle , 1.26 mol dm⁻³; \bullet , 1.90 mol dm⁻³; \blacksquare , 2.53 mol dm⁻³; \blacklozenge , 2.85 mol dm⁻³; \circ , 3.16 mol dm⁻³.

As shown in Figure 9, the break points also exist at around 320 K in the curves of the temperature dependence of the absorbance at 1410 nm (monomer band) and at 1589 nm (polymer band) for *cis*-9-octadecen-1-ol in the pure liquid state and in the decane solutions. The absorbance of the monomer band (Figure 9a) increases relatively steeply with an increase in temperature above *ca.* 320 K, while that of the polymer band (Figure 9b) also decreases relatively steeply above that temperature. The temperature at the break point in both parts a and b of Figure 9 decreases slightly with decreasing concentration of the alcohol. This suggests that the polymers of *cis*-9-octadecen-1-ol tend to dissociate more easily in the dilute

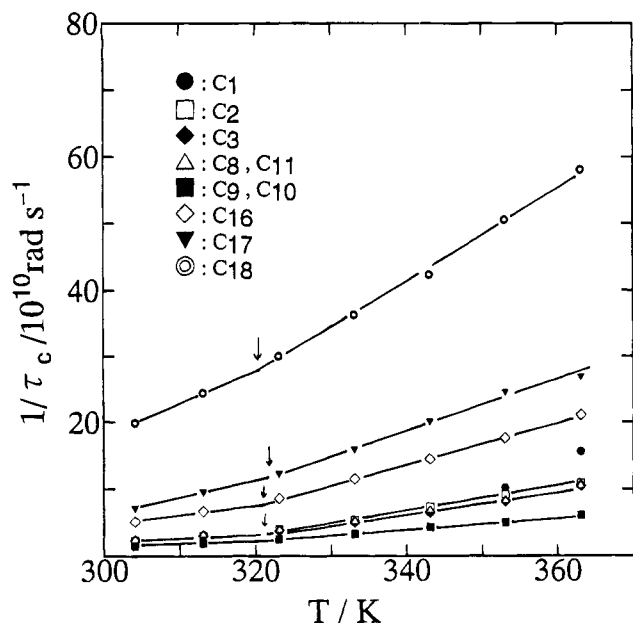


Figure 10. Temperature dependence of the reciprocal of effective correlation time τ_c , which is evaluated from the ^{13}C NMR spin-lattice relaxation time for *cis*-9-octadecen-1-ol. The symbols denote the carbon position: ●, 1; □, 2; ◆, 3; △, 8 or 11; ■, 9 or 10; ◇, 16; ▼, 17; ○, 18.

solution than in the pure liquid state. In addition, the depression in the slope of the curve above *ca.* 320 K in the $n - T$ relationship suggests that dimers dissociate preferentially into monomers: Dissociation of dimers would not decrease so steeply the n value but would increase extensively the number of monomeric molecules (see Figure 9a).

The dissociation of the alcohol polymers into monomer molecules with increasing temperature was confirmed by the measurement of the ^{13}C NMR spin-lattice relaxation time, T_1 , and ESR order parameter, S , for the sample of *cis*-9-octadecen-1-ol in the pure liquid state.

Figure 10 shows the temperature dependence of the reciprocal of the effective correlation time, $1/\tau_c$,⁷ which is evaluated from T_1 for the rotational movement of the segments in the *cis*-9-octadecen-1-ol molecule. The $1/\tau_c$ value, which indicates the magnitude of the fragmental movement, for the carbon at a different position increases with a rise in temperature; furthermore, the rotational movement of each segment seems to increase somewhat steeply above around 320 K. At any temperature the rotational movements for the segments at the C(9) and C(10) positions, the double-bond positions, are considerably restricted, while those for other fragments increase toward the end of the hydrocarbon chain. The methyl group positioned at the end of the alcohol molecule moves around most vigorously.

It should be noted that the slope of the curve for the C(1)-positioned carbon more dominantly increases with a rise in temperature than that for the C(2)-carbon. This apparently indicates the rupture of the hydrogen bonding and the subsequent dissociation of the polymer molecules. Namely, under the low-temperature conditions the fragmental movement at the C(1)-position is restricted by the hydrogen bonding between the alcohol molecules making a polymer, since the C(1)-positioned carbon is close to the center of gravity for the polymer. With an increase in temperature the alcohol polymers gradually dissociate into free monomer molecules, whose center of gravity probably exists in the middle of the molecule. Thus the fragmental movement at the C(1)-position would become larger than that at the C(2)-position.

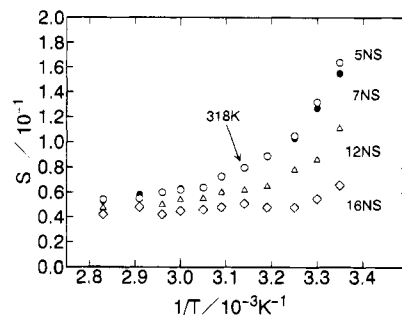


Figure 11. Relationship between ESR order parameters and the reciprocal of absolute temperature: ○, 5NS; ●, 7NS; △, 12NS; ◇, 16NS.

Figure 11 shows the relationship between the ESR order parameter, S ,¹² and a reciprocal temperature, $1/T$, for the octadecanoic acid-typed samples spin-labeled with a doxyl radical group at various positions. The movement of the doxyl radical part of the spin-labeled acid is more restricted at the position closer to its carboxyl group which would be linked by a hydrogen bond to the hydroxy groups of the surrounding alcohol molecules. Regardless of its position labeled with a doxyl radical, each curve also shows a break point at a temperature near 320 K. Namely, the steep lowering of the local viscosity with an increase in temperature comes to an end at this temperature; the subsequent, gradual lowering of the viscosity would mean the existence of a large number of monomer molecules. The break point temperatures also correspond to those for the $n - T$ (Figure 8) and the $A - T$ (Figure 9) relationships. Consequently, the NMR and ESR results suggest that the number of monomer molecules increases more steeply above this temperature.

As mentioned before, the $\eta - T$ and $D - T$ relationships shown in Figures 1 and 2 proposed that *cis*-9-octadecen-1-ol should have a lower association number, n , than *cis*-9-octadecenoic acid. However, the n value obtained for *cis*-9-octadecen-1-ol is more than two, *i.e.*, always larger than that for *cis*-9-octadecenoic acid, although less than that for the normal alcohol.³

The activation energies obtained from the Arrhenius plot (a relatively straight line) of the viscosities for *cis*-9-octadecen-1-ol and *cis*-9-octadecenoic acid are *ca.* 31.7 and 25.0 kJ/mol, at around 300–360 K, respectively; those of the self-diffusion coefficient are also *ca.* 31.2 and 25.3 kJ/mol, respectively, in the same temperature range. Namely, both the activation energies for *cis*-9-octadecen-1-ol are always higher than those for *cis*-9-octadecenoic acid. The high activation energies for *cis*-9-octadecen-1-ol, compared with those for *cis*-9-octadecenoic acid, obviously include the dissociation energy of the alcohol polymer. This is because of the weak hydrogen bondings between the alcohol molecules. On the other hand, because of the strong interaction between acid molecules, the dimer of the acid molecules is mostly the unit for the molecular movement such as the translational movement.

This is also applicable for the octan-1-ol and octanoic acid systems.³ Octan-1-ol has higher activation energies than octanoic acid, although the former has a higher viscosity and lower self-diffusion coefficient, compared with the latter. Namely, in the translational movement, alcohols, including *cis*-9-octadecen-1-ol, are energetically more restricted and should always show higher viscosities and lower self-diffusion coefficients than acids. In truth, however, *cis*-9-octadecen-1-ol has a lower viscosity and a higher self-diffusion coefficient than *cis*-9-octadecenoic acid. How can we explain the curious profile for the viscosities

and self-diffusion coefficients for *cis*-9-octadecen-1-ol and *cis*-9-octadecenoic acid?

The association constant, tabulated in the fifth column of Table 2, is for the dimer formation of *cis*-9-octadecenoic acid in the liquid state, which is evaluated from the degree of dissociation of the acid dimer into monomer molecules.¹² As can be seen by comparison of the third and fifth columns of Table 2, the numerical value of the apparent association constant for *cis*-9-octadecen-1-ol is extremely less than that for *cis*-9-octadecenoic acid. Thus, the low viscosity and high self-diffusion coefficient for *cis*-9-octadecen-1-ol, compared with those for *cis*-9-octadecenoic acid, seem to be attributable not to the aggregation number of the polymer but to the amount of the polymers.

Acknowledgment. The authors express their thanks to Professor Hiroshi Kobayashi, Dean of the School of Science, Kitasato University, for helpful discussions and to Miss Nami Taniguchi for her assistance with the NIR experiments. The present work was supported in part by a Grant-in-Aid for Scientific Research (No. 04640457) from the Ministry of Education, Science and Culture of Japan.

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JP941676H