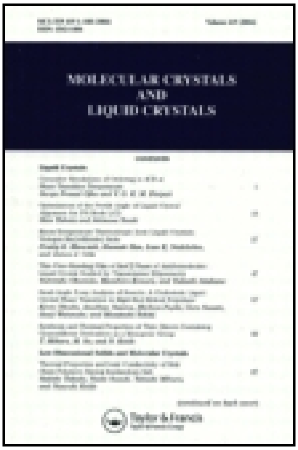

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Mesophase State of Amphoteric Surfactants of β-alanine Type and Their Temperature Dependence of ^{1}H-NMR and IR Spectra

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The condition of liquid crystal appearance for amphoteric surfactant molecules of N-dodecyl-β-alanine substituted by hydroxy groups was examined by the temperature dependence of ^{1}H-NMR and IR spectra. The half line-width of an active proton signal does not decrease in the liquid crystal state and the inter-molecular hydrogen bond between hydroxy groups attached to the 2-nd carbon atom in the dodecyl group begins to be broken just below the melting point. From these results, a liquid crystal model was proposed as following: a rod-like dimer is formed by a pair of strong hydrogen bonds $NH_2^+\text{---}^-O_2C$ between two molecules and the parallel orientation of these rod-like units are maintained by another type of hydrogen bonds between hydroxy group at the 2-nd carbon atom in dodecyl group on both sides of the central structure composed of $NH_2^+\text{---}^-O_2C$ hydrogen bonds. In addition, the information about the class of primary or secondary alcohols and the location of hydroxy groups was obtained by the analysis of time dependence of NMR spectra in the solvent of trifluoroacetic acid.

INTRODUCTION

As for the amphoteric surfactant molecules of β-alanine type substituted by hydroxy groups, a liquid crystal phase was formed for N-(2-hydroxydodecyl)-β-alanine (HD) and N-(2-hydroxydodecyl)-N-(2-hydroxyethyl)-β-alanine (HDHE), while no mesophase was observed for a parent molecule N-dodecyl-β-alanine (D) and also bis-N-(2-hydroxydodecyl)-β-alanine (BHD) by DSC measurements. In aromatic mesophase compounds $Y\cdot C_6H_4\cdot X\cdot C_6H_4\cdot Y$,[1] for example, the formation of liquid crystal is explained in the following way; a central group X is composed of rigid structure —CH=CH—, —N(→O)=N—, or —COOH$\cdots$HOOC—, and terminal groups Y are composed of alkyl chain, alkoxy chain, ester chain, or electrophilic substituents, at para position of two benzene rings on both sides of a central group, and they are built up into a long rod-like unit (molecule or associated dimer). Two conjugated benzene rings bring about weak attraction between these rod-like units on the basis of dipole interaction or π-electron interaction produced by the overlap of molecular planes. In order to examine our liquid crystal model for β-alanine amphiphiles, ^{1}H-NMR spectra for D, HD, and HDHE were investigated especially in regard to temperature dependence of an active proton signal, and infrared absorption spectra for these samples are also discussed.

EXPERIMENTAL

D was a commercial source obtained from Miyoshi Oil & Fat Co. Ltd. HD and BHD were obtained as follows: β-alanine was reacted with 1,2-epoxyalkane in ethanol aqueous solution (65 vol.%) at 80°C. HD and BHD were separated by the difference of solubility in acetone and further purified through gel permeation chromatography.[2] HDHE was synthesized by the addition of methyl acrylate to the adduct of 1,2-epoxydodecane and monoethanolamine.[3] They are all purified by the recrystallization from ethyl acetate or methanol-acetone (9:1) solution.

DSC curves were run on a Shimadzu DSC-20 differential scanning calorimeter. About three milligrams of each sample was sealed into an aluminum cell, and measured with reference to a few aluminum plates under a nitrogen atmosphere with a heating rate 10°C min^{-1} and range 5 mcal·s^{-1}.

^{1}H-NMR spectra were recorded at 90 MHz with a Hitachi R-22 spectrometer equipped with a Hitachi variable temperature assembly, whose temperature in all experimental measurements was calibrated by the difference of chemical shifts of ethylene glycol. A powder sample was put into a sample tube, heated and melted in an electric furnace at 150–200°C, bubbled by argon or nitrogen gas, and sealed for temperature variation after adding a few drops of hexamethyldisiloxane. At each temperature the adjustment of the magnetic homogeneity and sensitivity was repeated to get the same condition as possible, but a little fluctuation could not be avoided. In addition, NMR spectra for three samples (5%) dissolved in trifluoroacetic acid solution were observed immediately after preparation and at an interval of one or two hours and later at an interval of one or two days.

Infrared absorption spectra were measured using a Shimadzu IR 450-S spectrophotometer. Each pure solid sample dissolved in ethyl acetate was uniformly coated several times on a potassium bromide plate to make a thin film layer by evaporating the solvent. The cells for sample and reference were warmed by a string heater in the same manner and their temperature was detected by a couple of thermisters.

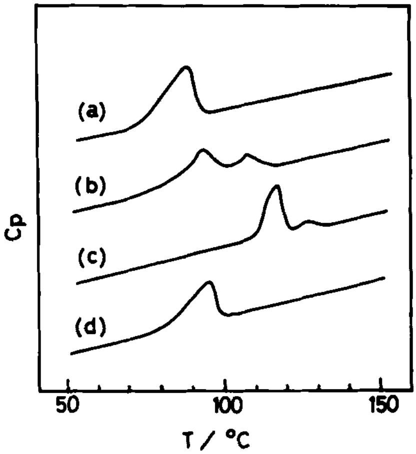

FIGURE 1 DSC curves for β-alanine type surfactants; (a) D, (b) HD, (c) HDHE, and (d) BHD.

RESULTS AND DISCUSSION

1. Observation of liquid crystal phase

DSC curves for D and BHD gave only one endothermic peak, while those for HD and HDHE two peaks. This was interpreted as an appearance of a mesophase as is seen in Figure 1. HDHE showed a broad complicate curve and no clear-cut peaks in the successive runs after the first scanning. It may suggest that this molecule takes easily a transparent glassy state once the mesophase is formed. Recrystallization from ethyl acetate solution was repeated several times, but sharp peaks could not be obtained for these samples. For convenience a peak position was assigned for the phase transition point and a transition-starting point is also shown in parenthesis to the right.

The melting points for D and BHD are 88° (74°C) and 95° (82°C), respectively. The S → LC transition point for HD is 93° (76°C) and its melting point 108° (100°C). The transition point for HDHE is 116° (102°C) and its melting point 126° (123°C).

2. Dependence of ^{1}H-NMR spectra on temperature

NMR spectra of pure substances were measured in the range of 35° to 150°C with temperature interval of 5 or 10 degrees. Most typical spectra for solid, liquid crystal, and isotropic liquid phase of D, HD, and HDHE are illustrated in Figure 2. Though the assignment of the spectra in trifluoroacetic acid solution is unequivocal as discussed in the Appendix, the spectra of pure substances are very complicated especially for HD and HDHE, in which broad or anomalous peaks appeared in the region of chemical shift $\delta = 1.5$ to 4.5 ppm. In the

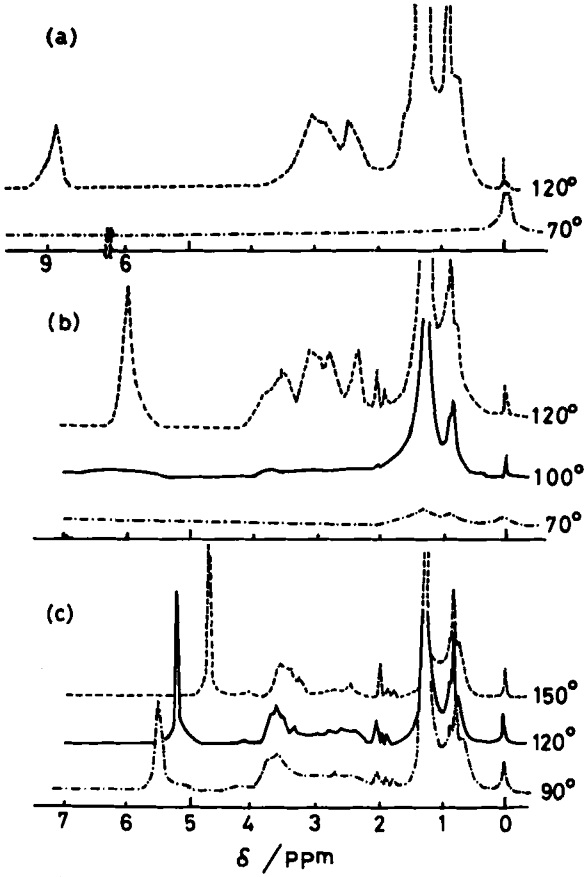

FIGURE 2 Typical ^{1}H-NMR spectra for (a) D, (b) HD, and (c) HDHE in the solid (····), liquid crystal (——), and isotropic liquid state (----). Temperature in experimental measurements is written on the right side of each curve.

case of HDHE, for example, we should have signals of one methylene at the 3-rd position in the dodecyl group, one methylene next to CO_2^-, three methylene attaching to NH^+, and one methylene and one methin containing OH downward the magnetic field, but the signals of three methylenes adjacent to NH^+ are broadened and obscured very much and the origin of three peaks near $\delta = 2$ ppm cannot be explained. Several peaks $\delta = 2.00, 2.52, 3.31$, and 4.11 ppm at 120°C were observed to shift to higher field by the order of 0.1 ppm with heating. In this region we have signals from a central part of a rigid structure and its binding part, which might be related to the anisotropic alignment of liquid crystal. In any way, two signals of methylene protons occupying hydrophobic part of the dodecyl group and of active protons averaged over by the rapid

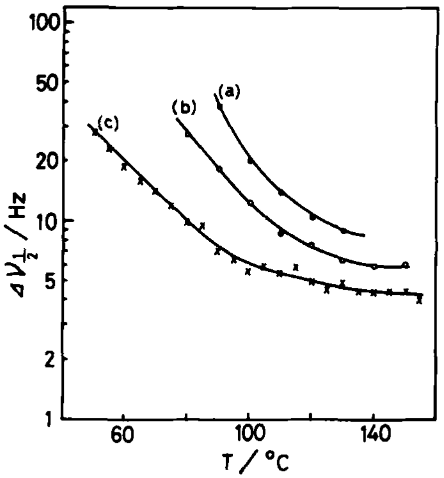

FIGURE 3 Dependence of half line-width for hydrophobic methylene proton signals in (a) D, (b) HD, and (c) HDHE on temperature.

exchange of NH^+ and two OH protons showed clear-cut peaks not disturbed from others.

High-resolution NMR spectra was obtained even in the solid and liquid crystal state for these samples, and so the temperature dependence of half line-widths and chemical shifts of active protons and hydrophobic methylene protons were examined. The dependence of half line-width on temperature for hydrophobic methylene protons and active protons is shown in Figures 3 and 4, respectively. As seen from these figures, the half line-width for D having no branched chain is large due to close packing, while the line-width for HDHE is considerably smaller because HDHE having a big branch is bulky and has many vacancies in the packing and thus it gains large mobility. The line-width of hydrophobic methylenes decrease continuously and smoothly for all three samples with increase in temperature, as is clear from Figure 3. On the other hand, the line-width of active protons remains nearly constant in the region of 95° to 110°C for HD and of 100° to 120°C for HDHE, while that for D decreased smoothly with increase in temperature. In general, the half line-width in NMR spectra around the melting point is considered to be inversely proportional to transverse relaxation time T_2, and to be proportional to correlation time τ_c.[4] As molecular orientation is more disturbed with increase in temperature and the correlation time of active protons with the same kind of surrounding protons decreases more, the line-width decreases more. The fact that this decrease in line-width was not observed only for active protons in the region of liquid crystal phase suggests the idea that the local inter-molecular motion near active protons varies very little in the liquid crystal state.

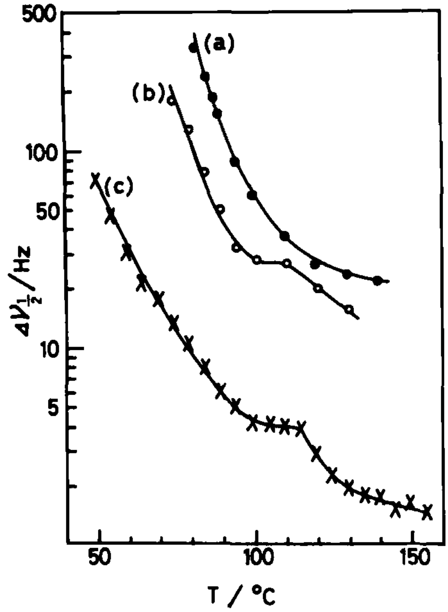

FIGURE 4 Dependence of half line-width for active proton signals in (a) D, (b) HD, and (c) HDHE on temperature.

No dependence of chemical shifts on temperature was observed for hydrophobic methylene signals, but the remarkable change of shift for active proton signals was observed as shown in Figure 5. As seen also in Figure 2, an active proton signal for D appears at the lowest magnetic field reflecting the strongest hydrogen bond of NH_2^+---^-O_2C, and that for HD appears at higher field due to the addition of a weaker hydrogen bond of OH---O between CHOH groups, and that for HDHE appears at the highest field as an averaged peak over NH^+ of NH^+---^-O_2C and two OH's of OH---O between CHOH groups and between CH_2OH groups. Three slopes for HDHE correspond to three processes in which three kinds of hydrogen bonds of active protons are broken down in the order of strength. In the region of lower temperature OH hydrogen bond of hydroxyethyl group, which is thought to be not necessary for maintaining mesophase, is broken at first, and next above 120°C the hydrogen bond of OH in the dodecyl group, which combines rod-like units, begins to be broken and HDHE melts to the liquid after serious break. At last above 145°C the strongest hydrogen bond of NH^+---^-O_2C is broken down. With respect to HD an active proton signal has also three slopes as for HDHE, and hydrogen bonds are not broken in the solid state, and OH hydrogen bond attached to dodecyl chain is broken above 110°C, and the hydrogen bond of NH_2^+---^-O_2C is broken down above 140°C. D has no mesophase and only two slopes, and it is almost

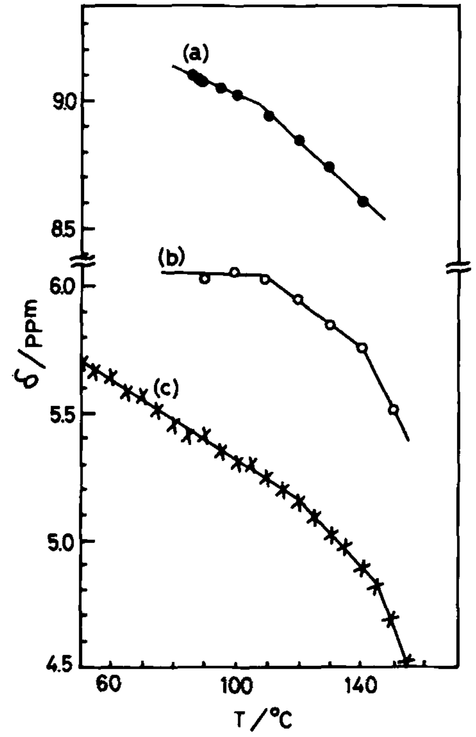

FIGURE 5 Dependence of chemical shifts for active proton signals in (a) D, (b) HD, and (c) HDHE on temperature.

in the liquid state as for the temperature range for peaks to be detected. Two slopes may suggest two kinds of breaking of hydrogen bond between NH_2^+ and CO_2^-; partial breaking from higher polymers to lower polymers and complete breaking from dimers to monomers.

3. Infrared absorption spectra and strength of hydrogen bonds

The dependence of infrared spectra on temperature was measured for D, HD and HDHE in the range of 20° to 140°C, using a sample coated on KBr window plate. Spectra at room temperature and about 120°C are shown in Figure 6. As for D which showed considerable temperature dependence, the band near 1570 cm^{-1} at room temperature, which is assigned to CO_2^- anti-symmetric stretching vibration[5] overlapped by NH_2^+ deformation vibrations, becomes much broader and is shifted to higher frequency by 20 cm^{-1} with increase in temperature. The band near 1395 cm^{-1}, assigned to CO_2^- symmetric stretching mode, appears at lower frequency by 30 cm^{-1} with increasing temperature. With respect to HD, only one band of CO_2^- anti-symmetric stretching vibration

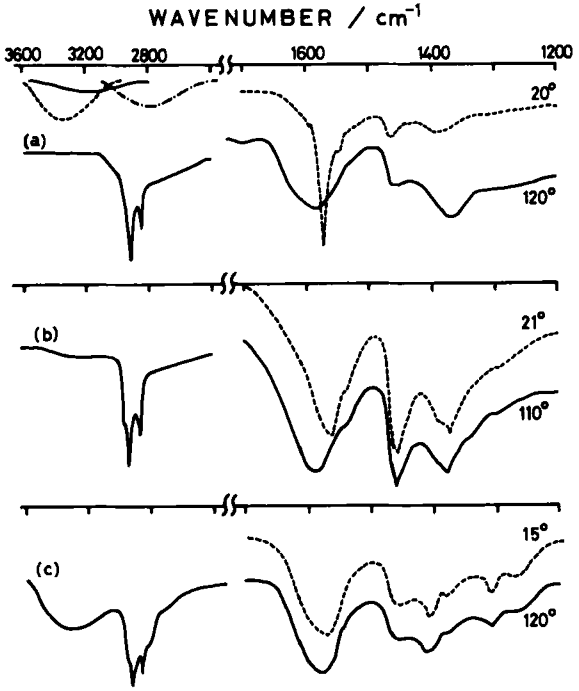

FIGURE 6 IR spectra for (a) D, (b) HD, and (c) HDHE in the region of active hydrogen stretching vibrations and of carboxylate stretching vibrations at high temperature (——) and at room temperature (----). Temperature in experimental measurements is written on the right side of each curve. Three upper curves on the high-frequency side are schematically represented in order to show separately three contributions from hydrogen stretching vibrations corresponding to CH_2OH---O (-----), CHOH---O (——) and NH_3^+---^-O_2C hydrogen bond (·-·-), respectively.

depends on temperature to some extent. But these bands for HDHE do not change any more, and another band of OH stretching vibration near 3300 cm^{-1} shifts to higher frequency by more than 50 cm^{-1}. Temperature dependence of wavenumber of these bands is shown in Figure 7. Both HD and HDHE seem to take transparent glassy state very often, but the dependence of wavenumber shift on temperature, also it is not so drastic, has a tendency of reflecting a phase transition in each curve. It was illustrated from these figures that amphiphiles of β-alanine type keep a form of zwitterion of CO_2^- and NH_3^+ even at high temperature of 140°C as at room temperature. Infrared spectra in the region of stretching vibrations of active protons making hydrogen bond are given on the left side of Figure 6. D showed one broad band whose center is 2770 cm^{-1}. The band is assigned to NH_3^+ stretching vibration suggesting the strongest hydrogen bond between NH_3^+ and CO_2^-. HD has another broad band around 3200 cm^{-1} superposed on the former band, and the second band is assigned to the stretching vibration of hydroxy group in the dodecyl chain com-

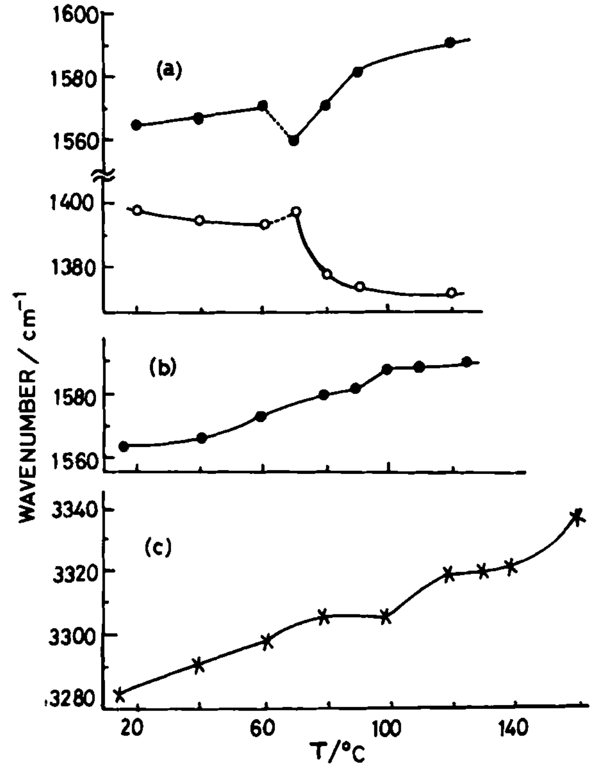

FIGURE 7 Dependence of IR band frequencies on temperature for (a) D, (b) HD, and (c) HDHE with respect to the modes of CO_2^- anti-symmetric stretching vibration (●), CO_2^- symmetric stretching vibration (O), and OH stretching vibration (x).

bining rod-like units at two sites by hydrogen bond. HDHE has the third rather strong band around 3350 cm^{-1}, which reflects a weaker OH hydrogen bond of hydroxyethyl group.

The strength of three hydrogen bonds of CH_2OH---O, CHOH---O, and NH_2^+ ---^-O_2C increases in this order, which is well corresponding to the result of temperature dependence for active proton chemical shifts in ^{1}H-NMR spectra as described before.

CONCLUSION

Our liquid crystal model is illustrated in Figure 8. With respect to the amphoteric surfactants of β-alanine type a rod-like dimer is formed by a pair of strong hydrogen bonds of NH_2^+---^-O_2C. The dimer is superposed on one another in parallel to make an oligomer or crystal. With increase in temperature, weak

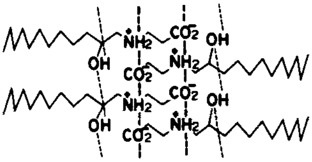

FIGURE 8 Schematic illustration of our liquid crystal model for HD.

van der Waals' bonds are broken at first, and terminal methyl and hydrophobic methylene groups begin to move around.[6] The most stable form of CCCC axis in *n*-alkyl chain is well known to be a trans form, but the probability to take gauche forms increase with increase in temperature, and the dodecyl group may turn at some carbon atoms in this chain. Therefore the chain is illustrated to spread more to the terminal. D and BHD melt directly from solid to the isotropic liquid because D has no hydroxy groups attached to the dodecyl group and BHD cannot form a rod-like unit due to two long alkyl chains. In the case of HD and HDHE which have a hydroxy group at the 2-nd carbon of dodecyl group, the parallel orientation of rod-like units is maintained by OH---O hydrogen bonds which combine two units at two sites outside a central part and thus it brings about a mesophase. The hydrogen bond of a hydroxy group in hydroxyethyl group for HDHE is weak, leaves space in the packing and does not contribute much to mesophase formation. With further rising in temperature, OH hydrogen bonds associated with the dodecyl group are completely broken, and then strong hydrogen bonds between NH_2^+ and CO_2^- are finally broken and many oligomers in the liquid state gradually decompose to monomer molecules.

APPENDIX

Time dependence of ^{1}H-NMR spectra in the solvent of trifluoroacetic acid and their assignment

It is more convenient to measure NMR spectra for *β*-alanine type surfactants in solution in order to make sure of the assignment. However, hydrophilic property of these three samples depends on the number of substituted OH groups, and it was very difficult to solubilize all of them in the order of several percents in common solvent like D_2O or $CDCl_3$. It is well known in the literature[7,8] that trifluoroacetic acid is a miscible solvent for amino acids and shifts NMR signals of the group neighbored by proton acceptor to the lower magnetic field by less than 1 ppm on the basis of a weak hydrogen bond. But it also acts as an acetylating agent to change a substance having a hydroxy group to a derivative of trifluoroacetate ester.[9] Therefore, in some cases the result might be interpreted erroneously. In the solvent of trifluoroacetic acid, NMR spectrum of D did not change for several days, while the spectrum for HD changed drastically in two days after the preparation and spectrum for HDHE changed *via* two steps in ten hours and in two days after the preparation. As listed in Table I, signals of HDHE having changed remarkably in ten hours are e″, f′ and g, which tells us the acetylation of hydroxyethyl group to $CH_2CH_2O \cdot C = O \cdot CF_3$. Perturbed signals after standing for two days in HD and HDHE are c, e, f, and g, in which step CH(OH) in the dodecyl group is interpreted to be esterified to $CH(O \cdot C = O \cdot CF_3)$. Acetylation rates for primary and secondary alcohols are obviously different; the acetylation of a primary alcohol terminated in several hours and of secondary alcohol in a few days at the temperature of 35°C. Even for unresolved signals immediately after the preparation of a solution, intrinsic chemical shifts of a sample in this solvent after the preparation could be evaluated from the analysis of time dependence of NMR spectrum. Spectra in trifluoroacetic acid solution have been referred to be

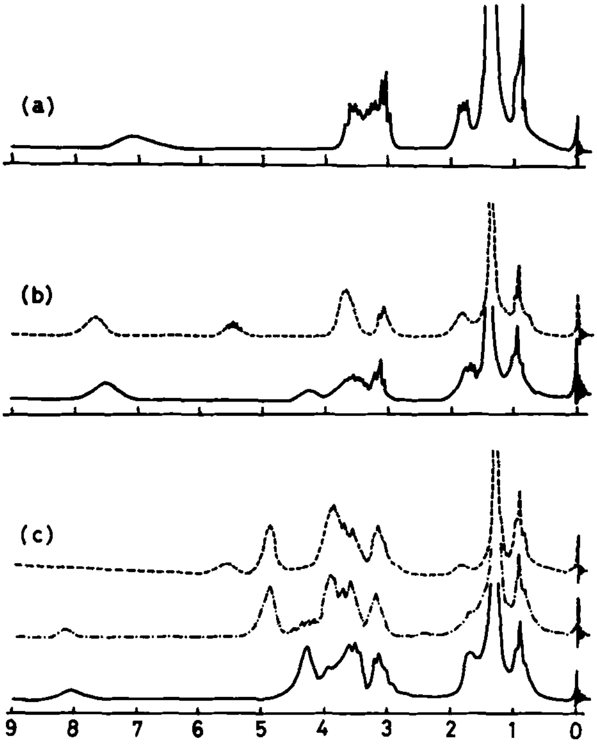

FIGURE 9 ^{1}H-NMR spectra for (a) D, (b) HD, and (c) HDHE in trifluoroacetic acid solution immediately (——), in ten hours (·–·–), and in two days (----) after the preparation.

TABLE I

Assignment of ^{1}H-NMR spectra of β-alanine type surfactants in trifluoroacetic acid solution.

Molecules[a]	δ/ppm									
	a	b	c	d	e	e′	e″	f	f′	g
D; $CH_3(CH_2)_9CH_2CH_2\overset{+}{N}H_2CH_2CH_2CO_2^-$ a b c e g e′ d	0.90	1.35	1.83	3.06	3.28	3.56				7.09
HD; $CH_3(CH_2)_8CH_2CH(OH)CH_2\overset{+}{N}H_2CH_2CH_2CO_2^-$ a b c f g e g e′ d	0.92	1.35	1.70	3.09	3.39	3.57		4.25		7.49
HD″ ; CH(OH) → CH(OC=OCF$_3$)	0.90	1.34	1.86	3.08	3.74	3.62		5.47		7.68
HDHE; $CH_3(CH_2)_8CH_2CH(OH)CH_2\overset{+}{N}H(CH_2CH_2OH)CH_2CH_2CO_2^-$ a b c f g e g e″ f′ g e′ d	0.90	1.35	1.68	3.16	3.50	3.73	3.57	4.31	4.28	7.97
HDHE′; CH$_2$OH → CH$_2$OC=OCF$_3$	0.91	1.36	1.70	3.17	3.59	3.73	3.91	4.28	4.88	8.13
HDHE″; CH(OH) → CH(OC=OCF$_3$) CH$_2$OH → CH$_2$OC=OCF$_3$	0.91	1.37	1.87	3.15	3.83	3.72	3.91	5.53	4.87	8.5[b]

[a] Chemical shifts for D, HD, and HDHE are the values recorded immediately after the preparation. Those for HDHE′ are in ten hours and those for HD″ and for HDHE″ are in two days after the preparation. Signals which changed obviously after standing for ten hours and for two days are shown under shift values by 〰 and —, respectively. Overlapped signals are shown as ⌐¬ on shift values.

[b] This signal is very broad and overlapped with a strong signal of the solvent.

improper for molecules possessing hydroxy groups due to their degeneration, but it turned out to be true that they are very useful for the identification of molecules and the assignment of chemical shifts from their time dependence on an acetylation rate of primary, secondary or tertiary alcohol. In regard to the identification of alcohols, this line of research will be continued for the factors about time, temperature and applicable samples in comparison with the established method using trichloroacetylisocyanate.[10]

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