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Splitting of ^{1}H NMR Signal of Long Methylene Chain with Various Terminal Substituent in Aromatic Solvent

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The splitting of the methylene peaks in ^{1}H NMR spectra was studied for alkyl compounds with various substituents in 1-chloronaphthalene solutions. The solvent shifts for the higher field split methylene peak and the α-methylene peak varied with a dependence on the magnitude of the electric group moment of the terminal substituent; those for the lower- and middle-field split methylene peaks and the terminal methyl peak remained constant. It was found that the different behaviors of the solvent shifts of the methylene signals could be ascribed to the origin of the peak splitting observed for long alkyl compounds.

For long-chain alkanes (number of carbons $n_c>16$) it was known that the methylene ^{1}H NMR peak was observed to split into a doublet in 1-chloronaphthalene.[1] After the discovery for *n*-alkanes, similar phenomena have been observed for long alkyl compounds with a terminal substituent, such as *N*-alkylmaleimides[2] and alkyl 11-maleimidoundecanoates.[3] On the other hand, methylene-peak splittings were observed for the long alkyls of surfactant molecules in water upon the addition of an aromatic solubilizate;[4–9] these phenomena have been discussed regarding the solubilization site of aromatics in surfactant micelles.

The first theoretical investigation of such splittig phenomena of the methylene peak was carried out by Ando and Nishioka.[10–12] They performed a chemical shift calculation and concluded that the splitting of peaks in an aromatic solvent arises from an increase in the number of gauche forms for long-chain hydrocarbons. On the other hand, Winnik et al. concluded that the splitting was due to a solvent effect associated with the chain end, and conclusively rejected the presence of slowly interconverting gauche and trans conformations for long alkyl chains.[13] Furthermore, several papers have been published which discuss the origin of these phenomena.[14,15]

The present authors studied the ^{1}H NMR spectra for the methyl alkanoates of various alkyl lengths in 1-chloronaphthalene and observed that the methylene peak splits into a doublet for a longer alkyl with $n_c\geq12$ and into a triplet for $n_c\geq20$.[16] We also studied aqueous dispersed systems of several surfactants of various chain lengths, and found that the methylene peaks of the ^{1}H spectra also split upon the addition of aromatic solubilizates, as similar manner in a homogeneous solution.[17] From those observations of the dependence of the chain length on the methylene ^{1}H NMR spectra for solutions and solubilizated dispersions, we speculated that the origin of the splitting phenomena can be ascribed to a solute-solvent interaction.

In this paper we will describe the relation between the solvent shifts in long alkyl compounds and the electric group dipole moment of their terminal substituent, the assignment of the methylene signal to 3 split peaks and, consequently, the origin of the splitting of the methylene peaks by aromatic solvents.

Experimental

Long-chain compounds with the following substituted groups were applied in this study: $-CH_3$, $-C_6H_5$, -SH, $-NH_2$, -OH, -Cl, -Br, $-COOCH_3$, -NCO, -COCl, $-COC_6H_5$, and -CN. These substances consist of long alkyl groups with carbon numbers of $n_c=12$ or 18. For compounds with a carbonyl function, the carbonyl carbon is included within the carbon number, n_c. The terminal group for nonsubstituted *n*-alkanes (dodecane and octadecane) could be represented by $-CH_3$. All the reagents used in this study were of commercially highest grade.

Samples were prepared in about a 0.5 mol dm^{-3} solution of chloroform-*d* or a mixed solvent of 90 vol% 1-chloronaphthalene/10 vol% benzene-d_6. (The latter benzene-d_6 was used to provide the deuteriumlock signal.)[15] Tetramethylsilane (TMS) was used as an internal standard. ^{1}H NMR spectra were observed using a JEOL FX-100 NMR spectrometer operated at 100 MHz at ambient temperature.

Results and Discussion

For the alkyl compounds with various terminal substituents, splittings of the methylene signal were observed in 1-chloronaphthalene, similar to that found for normal alkanes. For the compounds with the substituents, $-NH_2$, -OH, $-COOCH_3$, -NCO, -COCl, and -CN, the methylene signals (excluding of α- and β-methylenes) were observed to split into doublets for compounds of $n_c=12$ and into triplets for $n_c=18$. In the other compounds used in this study, i.e. $-CH_3$, $-C_6H_5$, -SH, -Cl, -Br, and $-COC_6H_5$ derivatives, the methylene signals did not split for $n_c=12$ but, rather, split into a doublet for $n_c=18$. Generally, the splitting for $n_c=12$ was observed for compounds with the terminal substituent of a larger electric dipole moment.

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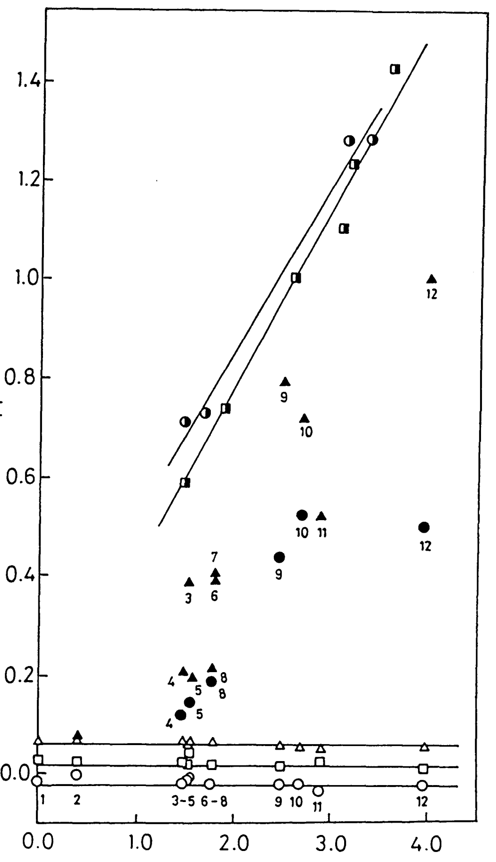

Fig. 1. Plots of the solvent shifts vs. dipole moment, for the compounds of n_c=18. ▲: α-methylene ●: higher △: middle □: lower field methylene ○: terminal methyl ◨,◑: methyl for CH_3-X compounds (Ref. from 18 and 19, respectively).
1: -CH_3 2: -C_6H_5 3: -SH 4: -NH_2 5: -OH 6: -Cl 7: -Br 8: -$COOCH_3$ 9: -NCO 10: -COCl 11: -COC_6H_5 12: -CN.

In Fig. 1 the values of the solvent shifts ($\Delta\delta = \delta(CDCl_3) - \delta$(1-chloronaphthalene)) of the signals are plotted against the electric dipole moment of the substituents, where δ are chemical shift of solute relative to TMS in $CDCl_3$ or 1-chloronaphthalene. The absolute magnitudes of these solvent shifts must be interpreted with caution since there were negative solvent shifts relative to the internal TMS standard. The observed solvent shifts are the difference in the specific interaction on the reference and the solute. Thus, the relative magnitude of the solvent shifts and their dependence on the terminal substituents are discussed. For low molecular weight compounds, the aromatic solvent-induced shift (ASIS) has been well studied. For example, ASIS for compounds of CH_3-X in benzene have been known to depend on its dipole moment or the group moment of substituent (X).[18,19] In Fig. 1 ASIS vs. the dipole moment (μ) of the CH_3-X compounds are also plotted. It should be noted that the aromatic and inert solvents used for CH_3-X were not the same as those used in this study.

We now discuss the relative solvent shifts of split methylene signals compared with those of small molecules. For the higher-field split methylene and α-methylene peaks, the solvent shifts depended on the electric dipole moment of the terminal substituent, as in CH_3-X compounds; however, no dependence was found for the other peaks, i.e. lower- and middle-field split methylene peaks and terminal methyl peaks. Thus, the higher-field split-methylene and α-methylene peaks behaved in a similar manner to ASIS for simple compounds, such as CH_3-X. Though the solvent shifts for the lower and middle methyene peaks and the terminal methyl peaks are different from that for CH_3-X regarding behavior, they are not affected by the choice of the terminal substituents.

Similarities in the solvent shifts for compounds of n_c=12 and 18 are as follows. For α-methylene and the higher-field split methylene peaks, solvent shifts depended on μ; for other peaks, however, they were independent. The dependence of the solvent shifts on μ for α- and higher-field methylene peaks did not vary for n_c=12 and n_c=18. In Fig. 2 the solvent shifts for α- and higher-field split methylene peaks of n_c=12 are plotted against those of n_c=18. It can be recognized that the ASIS for these peaks is not affected by the chain length, but is affected by the substituent. Figure 1 shows that the dependence of the solvent shifts on μ for n_c=18 is smaller than those for CH_3-X compounds; data are sometimes scattered. However, this phenomena is interpreted as having the same origin in both cases, i.e. an interaction between aromatics and substituent.

The difference in the splittings at n_c=12 and 18 was that the former splitting was observed to be dependent on the types of terminal substituents; the later splitting, however, into a triplet or doublet was always observed, irrespective of the substituents. (It may be noted that the splitting was observed exceptionally for longer alkyls than n_c=20 for some compounds.)

In the series of methyl alkanoates, the intensity of the higher-field split peak relative to that of lower-field split peak decreased with an increase in the total

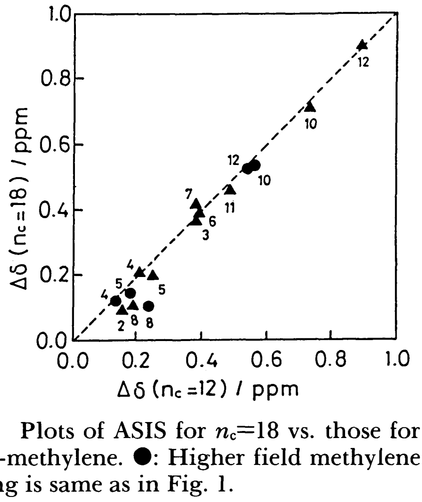

Fig. 2. Plots of ASIS for n_c=18 vs. those for n_c=12. ▲: α-methylene. ●: Higher field methylene. Numbering is same as in Fig. 1.

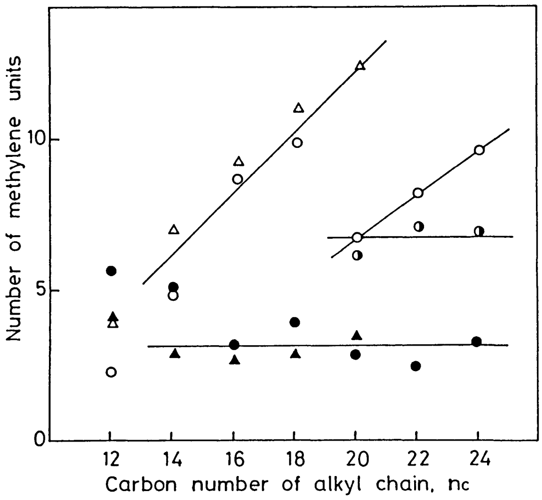

Fig. 3. Plots of methylene units assigned to higher (●), middle (◑) and lower field (○) split peaks vs. carbon numbers of alkyl chain, n_c. ○: in 1-chloronaphthalene, △: in benzene.

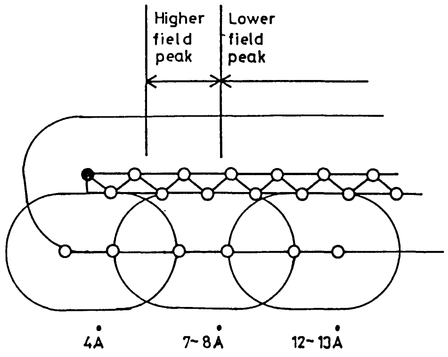

Fig. 4. Model for long alkyl compounds.

chain length. The region of the alkyl chain which experiences the solvent shifts varies with X, and is considered to consist of a definite number of methylene units. Since the solvent shifts for higher-field split peaks behaved in the same manner as those for α-methylene peaks, a definite number of methylene units neighboring the substituent are considered to be shielded by an aromatic solvent. In order to estimate the number of methylene units of the alkyl chain affected by the magnetic anisotropy of the aromatic solvent, the authors tried to assign the methylene signal to three peaks for the series of methyl alkanoates of various chain lengths from an estimation of the intensities of the split signals. The numbers of methylene units estimated for split peaks are plotted against the total carbon numbers of the alkyl chain, n_c, in Fig. 3. The contribution of the higher-field split peaks, which is affected by an aromatic solvent, was about 3 methylene units and almost constant regardless of the chain length. The contribution of the lower-field split peaks increased with n_c. This contribution increased linearly with the carbon numbers of alkyls, n_c, while the contribution of the middle peak was about 7 methylene units and almost constant. Thus, the shielded region by aromatic molecules next to the substituent consists of about 5 methylene units, in which α and β methylenes are included.

Since the behavior of solvent shifts for alkyl compounds with various substituent (X) is similar to that for CH_3-X compounds and the shielded region of alkyl chains consists of a definite number of methylene units, the solvent shifts for such long alkyl compounds can be interpreted as having the same origin as that for small molecules such as CH_3-X compounds. In the ASIS phenomena for small molecules, the association of the solute and the solvent is considered to be favorite in the so-called "solvation sphere". For long alkyl containing molecules, the corresponding solvation sphere would be restricted to local areas of the polar end of the alkyl chain.

Based on the time-averaged cluster model for ASIS,[20,21] the associated states between a long-size solute and a small solvent is considered to involve a variety of orientations of aromatic molecules and their interaction energies. However, some distinct orientations which shield about 5 methylene units are favorite around the polar end of the alkyl chain. These orientations of aromatic molecules are remarkable regarding the first neighbors, just around the polar groups. The aromatic molecules around alkyl chains far from the polar site are randomly oriented around the alkyl methylene units.

The distinct energy difference of the orientation between the first and second neighbors produces a splitting of the methylene signals. In the case of a small energy difference, for example in the substituent of -Cl and -Br, there was observed only a broadening of the methylene signals, but no splitting, was observed.

A schematic representation of the solvent effect for long alkyls is shown in Fig. 4 using Kihara's core model.[22] A distance of 70 to 80 nm from the substituent corresponds to the size of the aromatic molecule in the first neighbors and include approximately 5 methylene units.

In conclusion, observations on the peak splitting of methylene proton signals in terminal substituted alkyl compounds indicated a larger aromatic solvent shift of the terminal end methylenes than the methylene envelopes. These different behaviors of the solvent shifts between the methylenes neighboring of the polar end group and those distant from it in a long alkyl compound are concluded to be the origin of the peak splitting of the methylene signals in long alkyl compounds in aromatic solvents. A schematic molecular model for the aromatic solvent effect on a long alkyl compounds has been proposed as the result of the assignment of split methylene signals for methyl alkanoates.

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