The First Study on the Mobility of Surface-Adsorbed Molecules Using ^{1}H NMR Spin–Lattice Relaxation Time

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The function of alkanoic acid amine salt adsorbed onto the pigment surface was examined by means of ^{1}H NMR spin–lattice relaxation time using a high-resolution magic angle spinning (MAS) ^{1}H NMR probe called ^{1}H Nano·nmr™ Probe. The adsorption mechanism of the salt to the pigment was discussed on the bases of the results.

As NMR spin–lattice relaxation time (T_1) is related to molecular mobility, there are many studies on the mobility of a molecule using T_1,[1,2] especially, the molecule adsorbed on the solid surface using the T_1-value for the ^{13}C nucleus.[2] However, there is no report so far about the molecule adsorbed on the solid surface using the T_1-value for the ^{1}H nucleus, because a conventional probe usually used for a homogeneous sample brings about exceeding broadening of the line width.[3] It is reported that MAS NMR, which is widely applied for solid surface,[4,5] can eliminate line broadening in some extent for ^{1}H NMR.[3,6] However, there is no study on the mobility of a molecule using T_1-value with MAS ^{1}H NMR. Recently, a high-resolution MAS ^{1}H NMR probe called ^{1}H Nano·nmr™ Probe was developed by Varian NMR Instruments. It is so designed that even a heterogeneous system can also be measured by spinning samples at the magic angle to eliminate any line broadening caused by magnetic-susceptibility discontinuities either around or within the sample.[3] Furthermore, by using the T_1-value for the ^{1}H nucleus instead of the ^{13}C nucleus, measurement time is largely shortened because of the high ratio of the natural occurrence of the ^{1}H nucleus. Accordingly, we decided to investigate the molecule adsorbed onto the solid surface with ^{1}H NMR spin-lattice relaxation time by using the ^{1}H Nano·nmr™ Probe. As the first example, we chose a pigment-dispersant system as the research object. It was expected that some valuable information about adsorption would be obtained by using T_1 for the ^{1}H nucleus instead of that for the ^{13}C nucleus, because hydrogen bonding is thought to be an important driving force of the adsorption of a dispersant molecule onto the pigment particle surface.

Usually, a dispersant molecule consists of polar groups having high interaction with the particle surface and nonpolar groups having high compatibility with a nonpolar medium. For the purpose of increasing the interaction with the particle, dispersants with a multi-anchoring group were developed, whose function mechanism onto pigment is schematically shown in Figure 1.[7]

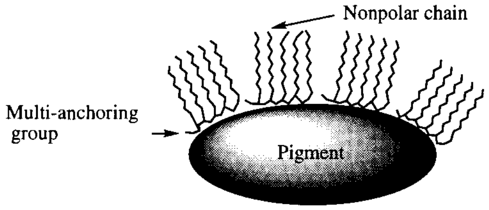

Figure 1. Function mechanism of dispersant with multi-anchoring group on pigment.

For simplicity, we used ethylenediammonium dioctanoate (EDADO), $(C_7H_{15}COO^-)_2\cdot H_3N^+C_2H_4N^+H_3$, as a model dispersant, which was prepared by mixing ethylenediamine with a stoichiometrically equivalent amount of octanoic acid, and commercially available phthalocyanine blue (PhB) as a model pigment, the specific surface area of which was measured to be 45.8 m^2/g by the BET method.

Measurement was conducted with a Varian Unity INOVA 600 spectrometer operating at 600 MHz, using a cell for the ^{1}H Nano·nmr™ Probe, in which 40 µL of well-shaken chloroform-*d* suspension of a mixture of PhB and EDADO was charged. The concentration of EDADO was fixed to be 15 mg/mL of $CDCl_3$.

Spectra of EDADO with and without PhB, obtained with a conventional 5mm-probe, are shown in Figure 2.[8] Even a small amount of PhB in the sample brought about remarkable broadening of the line width. However, satisfactory spectra were obtained by using the ^{1}H Nano·nmr™ Probe (Figure 3). When the PhB/EDADO ratio was small, all of the signals of EDADO were quite sharp. As the PhB/EDADO ratio became larger, the signals of the ammonio protons and the ethylene protons between the two ammonio groups broadened. The farther the proton was situated from the ionic parts in the molecule, the smaller the broadening rate of the line width became. Additionally, as the PhB/EDADO ratio became larger, the signal of the ammonio protons, which are considered to belong to the anchoring parts, shifted gradually to the upper field. This

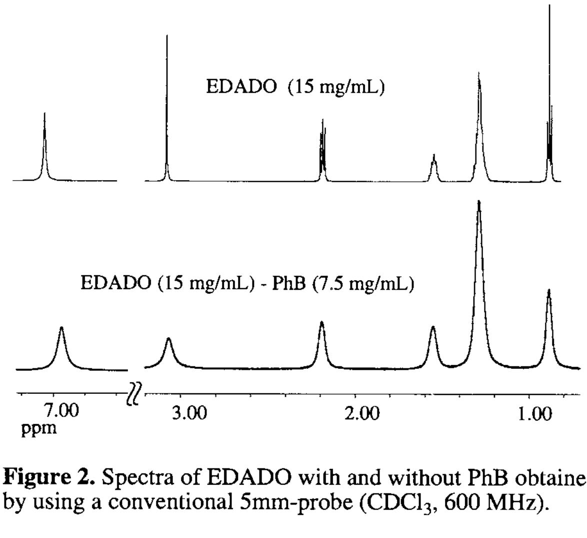

Figure 2. Spectra of EDADO with and without PhB obtained by using a conventional 5mm-probe ($CDCl_3$, 600 MHz).

Table 1. Spin-lattice relaxation time of protons of EDADO suspended with PhB in $CDCl_3$[a]

PhB/EDADO (g/g)	T_1 / s					
	$-NH_3^+$	$-CH_2CH_2-$	$^-OCOCH_2-$	$^-OCOCH_2CH_2-$	$-(CH_2)_4-$	$-CH_3$
0	0.266	0.397	0.613	0.771	1.157	1.787
0.125	0.112	0.147	0.426	0.592	1.048	1.687
0.25	0.084	0.109	0.370	0.525	0.953	1.588
0.5	0.033	0.067	0.289	0.422	0.853	1.515
1.0	0.017	0.033	0.220	0.320	0.712	1.437
2.0	0.009	0.017	0.141	0.209	0.542	1.248
4.0	0.005	0.009	0.082	0.124	0.367	0.973

[a]Inversion recovery method (180°-τ-90°-FID).

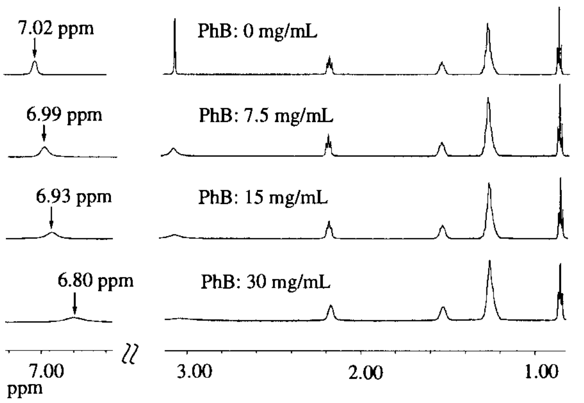

Figure 3. Spectra of EDADO (15 mg/mL) - PhB mixture obtained by using a ^1H Nano•nmr™ Probe ($CDCl_3$, 600 MHz, MAS: 1800 Hz).

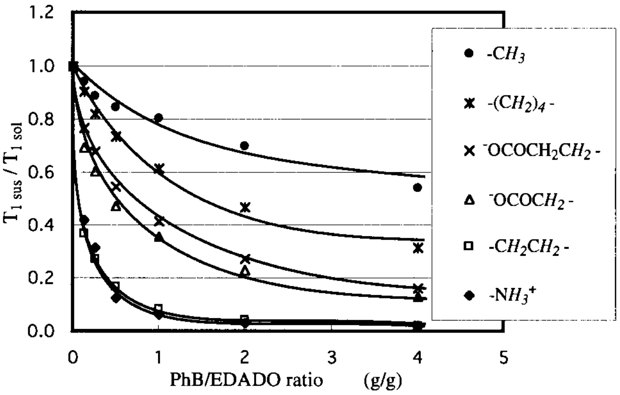

Figure 4. $T_{1\ sus}$ / $T_{1\ sol}$ ratio changes of EDADO protons affected by mixing PhB ($T_{1\ sus}$: T_1-value of a sample with PhB, $T_{1\ sol}$: T_1-value of a sample without PhB).

fact may suggest the existence of an equilibrium between free and adsorbed EDADO molecules.

On measuring the ^1H NMR T_1, the inversion recovery method (180°-τ-90°-FID) was used with delay time, τ, varying between 0.125 ms and 16.38 s. The repetition time was 17.5 s. All measurements were carried out at 25 °C. The T_1-value for each proton of the dispersant molecule thus determined is shown in Table 1. Concerning the protons of the EDADO molecule, T_1-values in the case of a sample mixed with PhB ($T_{1\ sus}$) were evaluated by comparison with T_1-values of that without PhB ($T_{1\ sol}$). The relative values ($T_{1\ sus}$ / $T_{1\ sol}$) are shown in Figure 4.

It can be seen from Figure 4 that, as the PhB/EDADO (g/g) ratio increased, the relative values of all the protons of the dispersant molecule decreased; especially, those of the six ammonio protons and the four ethylene protons between the two ammonio groups decreased largely. The farther the proton was situated from the ionic parts in the molecule, the smaller the decreasing rate became, and the methyl protons, which are situated in the other end, showed the smallest change in relative value.

All the facts suggest that the ammonio groups function as the anchoring parts. These results support the conventional polar group anchoring mechanism of this type of dispersant onto pigment.[7]

In conclusion, information regarding the function mechanism of EDADO adsorbed onto PhB was obtained from the ^1H NMR spin–lattice relaxation time. Further study is in progress in our laboratory.

References and Notes

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8 The ^1H NMR data of EDADO without PhB: ^1H NMR (600 MHz, $CDCl_3$), δ 7.03 (6H, s, $-NH_3^+$), 3.07 (4H, s, $-CH_2CH_2-$), 2.18 (4H, t, J=7.8 Hz, $^-OCOCH_2-$), 1.54 (4H, m, $^-OCOCH_2CH_2-$), 1.28 (16H, m, $-(CH_2)_4-$), 0.88 (6H, t, J=7.2 Hz, $-CH_3$).