Study on the Adsorption Behavior of Dispersants onto Pigment Using ^1H NMR Spin-Lattice Relaxation Time

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Abstract : In order to obtain information concerning the function of the polar group of polymeric dispersants generally used for pigment particles in a non-aqueous medium, alkylamine, alkylammonium salt, amide, and carboxylic acid were selected as the model dispersants and their adsorption behavior onto the phthalocyanine blue (PhB) pigment was studied by means of ^1H NMR spin-lattice relaxation time using a high-resolution magic angle spinning ^1H NMR probe. The amino group, particularly the primary amino group, was found to be the most effective as the adsorption site for the pigment among the functional groups examined in this study. The results obtained in this work suggest that the coordination of a lone electron pair on the nitrogen atom of an amino group to the Cu(II) of PhB is the driving force for the adsorption.

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1 Introduction

As an effective dispersant for pigment particles in a non-aqueous medium, so-called "polymeric dispersants" are successfully used instead of ionic dispersants, which are effective only in an aqueous medium. The polymeric dispersant molecule consists of many polar groups, which cumulatively interact with the particle surface, and many nonpolar chains which have high compatibility with the nonpolar medium. The adsorption mechanism of a polymeric dispersant onto the pigment is schematically shown in Fig. 1 (1).

The polymeric dispersants in practical use are prepared by reacting poly(ethyleneimine) with polyester containing a free carboxylic group, which is derived from 12-hydroxy stearic acid or ϵ -caprolactone. Its schematic structure is shown in Scheme 1 (2). In this compound, the polar part consists of primary, secondary, and tertiary amino groups, a carboxylic group, an amide group, and an ammonio group, while the nonpolar part consists of the hydrophobic

polyester chains. Looking into this molecular structure, we can naturally consider that all or some kinds of these polar groups should work as adsorption parts onto the pigment. However, no direct evidence has been reported for this consideration so far, though the clarification of the adsorption mechanism of this type of dispersant onto pigment would contribute to the development of more effective dispersants.

Since NMR spin-lattice relaxation time (T_1) is related to molecular mobility, there are many studies on this subject using T_1 (3-8), especially, the mobility of a molecule adsorbed on the solid surface using magic angle spinning (MAS) NMR, which can eliminate line-broadening to some extent (6-8).

Fig. 1 Adsorption mechanism of dispersant with multi-anchoring group on pigment.

R: polyester remainder excluding a carboxylic group

Scheme 1 Structure of representative dispersants.

Recently, a high-resolution MAS ¹H NMR probe called ¹H Nano-nmrTM Probe, which is useful for the measurement of heterogeneous samples, was developed (9). By using the *T₁* value for the ¹H nucleus instead of the ¹³C nucleus, the measurement time is greatly shortened because of the high ratio of the natural occurrence of the ¹H nucleus. Furthermore, it was expected that some valuable and direct information about adsorption would be obtained by this technique, when hydrogen atom is more related to the adsorption of a dispersant molecule than carbon atom, for example, in the case of hydrogen bonding and protonation.

From this point of view, we investigated, as the first example, the mobility of ethylenediammonium dioctanoate adsorbed onto the phthalocyanine blue (PhB) surface with ¹H NMR spin-lattice relaxation time by using the ¹H Nano-nmrTM Probe, and it was suggested that the reduction in the ¹H *T₁* value observed reflects adsorption of ethylenediammonium dioctanoate and the ammonio groups apparently function as the anchoring parts (10).

In order to obtain further information about the mechanism of adsorption of the polar group of a polymeric dispersant onto PhB, we studied adsorption behavior of several model dispersants (MD), such as alkylamine, alkylammonium salt, amide, and carboxylic acid, onto PhB in chloroform-*d* by using the above-mentioned ¹H NMR *T₁* method.

2 Experimental

2.1 Materials

Octylamine, *N,N*-dimethyloctylamine, ethylenediamine, diethylenetriamine, octanamide, and octanoic acid are of reagent grade from commercial sources. *N*-Methyloctylamine and *N*-octyltrimethylammonium chloride were prepared according to the

literature (11). PhB is of reagent grade and its specific surface area was measured to be 45.8 m²/g by the BET method.

2.2 Measurement of *T₁* Values of MD

¹H NMR measurement was conducted with a Varian Unity INOVA 600 spectrometer operating at 600 MHz, using a cell for the ¹H Nano-nmrTM Probe, in which 40 μL of well-shaken chloroform-*d* suspension of a mixture of PhB and MD was charged. On measuring the ¹H NMR *T₁*, the inversion recovery method (180°-τ-90°-FID) was used with delay time τ, varying between 0.125 ms and 16.38 s. All the measurements were carried out at 25°C.

3 Results and Discussion

3.1 Alkylamine

First, the *T₁* values of all protons of octylamine were determined. For comparing the adsorption effects of different types of MDs, the relative ratio of *T₁* values (*T_{1 sus}*/*T_{1 sol}*) was used as a function of PhB(g)/MD(equiv.), where *T_{1 sus}* and *T_{1 sol}* are the *T₁* values of the MD protons with and without PhB, respectively, and MD(equiv.) is defined as a quotient resulted from division of weight (g) of the added MD by the molecular weight of MD per one nitrogen atom. The relative ratios of *T₁* values against PhB(g)/MD(equiv.) are shown in Fig. 2 together with the *T_{1 sol}* values. As the PhB/MD ratio increased, the relative ratios of *T₁* values of all the protons of the octylamine molecule decreased. The closer a proton was situated to the amino group in the molecule, the larger the rate of decrease in the relative ratios of *T₁* value became. These results suggest that the octylamine molecule adsorbs onto the PhB particle surface *via* the amino group, and the farther segment from the amino group in the molecule maintains mobility to greater extent.

The relative ratios of *T₁* values of *N*-methyloctylamine are shown in Fig. 3. Comparison of these relative ratios of *T₁* values with those of octylamine shows that the secondary amine does not adsorb on the pigment so effectively as the primary amine.

Little reduction in the relative ratios of *T₁* value of *N,N*-dimethyloctylamine (Fig. 4) was observed even when a large amount of PhB was added.

Thus, the order of reduction in the relative ratios of *T₁* value of amines on adding PhB is: primary amine > secondary amine >> tertiary amine, suggesting that the adsorption of alkylamines on PhB is largely

Fig. 2 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of octylamine protons affected by mixing PhB (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

Fig. 3 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of *N*-methyloctylamine protons affected by mixing PhB (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

affected by their steric effect.

3.2 The Effect of Cu(II) in PhB Molecule

The interaction between octylamine and phthalocyanine (Ph), which does not contain Cu(II), was also investigated. In this case, obvious reduction in the relative ratios of T_1 value was not observed (Fig. 5), indicating the presence of Cu(II) in the PhB molecule

is essential for the adsorption of alkylamine onto PhB. Judging from the fact that the adsorption depends both on the presence of Cu(II) and on the steric effect of alkylamines, the adsorption onto PhB appears to be induced by coordination of a lone electron pair of the nitrogen atom to Cu(II).

When the Cu(II) ion in the PhB molecule was replaced by other metal ions such as Pb(II), Mg(II),

Fig. 4 Changes in $T_{1 \text{ sus}}/T_{1 \text{ sol}}$ ratio of *N,N*-dimethyloctylamine protons affected by mixing PhB (^aThe value shows $T_{1 \text{ sol}}$ of the corresponding proton).

Fig. 5 Changes in $T_{1 \text{ sus}}/T_{1 \text{ sol}}$ ratio of octylamine protons affected by mixing Ph (^aThe value shows $T_{1 \text{ sol}}$ of the corresponding proton).

and Zn(II), reduction of the relative ratios of T_1 value was not observed at all (**Fig. 6**). On the other hand, in the cases of Co(II) and Fe(II), reduction of the relative ratios of T_1 value was observed similarly to the case of Cu(II). This result may show that paramagnetic relaxation by Co(II) and Fe(II) as well as Cu(II) plays an important role in the relaxation process. It is difficult to distinguish the decrement of T_1 value by the reduction of segmental mobility due to adsorption of

MD onto the pigment from that by paramagnetic relaxation. However, as the paramagnetic relaxation rate depends on the distance between the metal ion and the proton, the T_1 value reduction of each proton of the octylamine, for example, which is continuously diminishing from amino protons to the end methyl protons, also shows that the octylamine is adsorbed onto PhB by part of the amino group.

Fig. 6 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of MD protons affected by mixing PhX (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

Fig. 7 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of ethylenediamine protons affected by mixing PhB (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

3.3 Polyamine

The relative ratios of T_1 values of the amino protons and α -methylene protons of ethylenediamine decreased depending on the amount of PhB added (Fig. 7), but those rates of decrease were smaller compared to those of the corresponding protons of octylamine (Fig. 2). The decreasing curve for the α -methylene protons of ethylenediamine lies apparently in the

region between the curves for the α -methylene and β -methylene protons of octylamine. This result does not show that ethylenediamine adsorbed less effectively onto PhB than octylamine but that the ethylenediamine molecule adsorbs onto PhB with only one of two amino groups. The distance between the terminal amino groups of ethylenediamine is not long enough for both amino groups to coordinate simultaneously to

Fig. 8 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of diethylenetriamine protons affected by mixing PhB (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

Fig. 9 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of octyltrimethylammonium chloride protons affected by mixing PhB (^aThe value shows $T_{1\text{ sol}}$ of the corresponding proton).

each Cu(II) in adjacent PhB molecules.

The decrease rates of the relative ratios of T_1 values of diethylenetriamine were almost equal to those of the corresponding ethylenediamine protons (Fig. 8). This result is also explained by the above assumption that two or all of three amino groups in the molecule

can not participate in simultaneous coordination to Cu(II).

3.4 Ammonium Halide

The relative ratios of T_1 values of octyltrimethylammonium chloride increased by the addition of PhB

Fig. 10 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of octylammonium chloride protons affected by mixing PhB (*The value shows $T_{1\text{ sol}}$ of the corresponding proton).

Fig. 11 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ ratio of octylammonium bromide protons affected by mixing PhB (*The value shows $T_{1\text{ sol}}$ of the corresponding proton).

(Fig. 9), contrary to the cases of primary, secondary, and tertiary amines. This phenomenon is reasonably explained by considering that the coordination of the chloride ion to Cu(II) weakens the electrostatic interaction between the octyltrimethylammonium cation and the chloride anion, which enhances the segmental mobility of the ammonium cation in chloroform-*d*. Octylammonium chloride showed the

same tendency as octyltrimethylammonium chloride possibly for the same reason (Fig. 10). On the other hand, the relative ratios of T_1 values of octylammonium bromide were little affected by the addition of PhB (Fig. 11). Furthermore, in the case of octylammonium iodide, the relative ratios of T_1 values decreased albeit only minimally (Fig. 12). These results may reflect the order of the coordination ability

Fig. 12 Changes in $T_{1 \text{ SMS}}/T_{1 \text{ sol}}$ ratio of octylammonium iodide protons affected by mixing PhB (^aThe value shows $T_{1 \text{ sol}}$ of the corresponding proton).

Fig. 13 Changes in $T_{1 \text{ SMS}}/T_{1 \text{ sol}}$ ratio of octanamide protons affected by mixing PhB (^aThe value shows $T_{1 \text{ sol}}$ of the corresponding proton).

of the halide ion toward Cu(II), that is, $\text{Cl}^- > \text{Br}^- > \text{I}^-$.

3.5 Amide and Carboxylic Acid

The results of amide and carboxylic acid are shown in Figs. 13 and 14, respectively. In the case of carboxylic acid, MD(equiv.) is defined as a quotient resulted by division of weight (g) of added MD by the molecular weight of MD per one carboxylic group. No

obvious reduction in the relative ratios of T_1 value of the protons of the octanamide molecule was observed by adding PhB. For octanoic acid, a large reduction in the relative ratios of T_1 value was observed only in the carboxylic proton; the decrement of T_1 values of protons of the alkyl part was small. It is likely that the basic part of PhB captured the acidic proton to make it stiffer, but the alkyl part remains in rather easy motion

Fig. 14 Changes in $T_{1 \text{ SMS}}/T_{1 \text{ sol}}$ ratio of octanoic acid protons affected by mixing PhB (*The value shows $T_{1 \text{ sol}}$ of the corresponding proton).

due to weak electrostatic interaction between the carboxylate ion and the protonated PhB, where the positive charge is delocalized in the molecule.

4 Conclusion

Studied was the adsorption of several model compounds for polymeric dispersants, such as alkylamine, alkylammonium salt, amide, and carboxylic acid onto PhB in chloroform-*d* by examining changes in the T_1 values of protons of these molecules on the addition of PhB. It became clear that primary amine is the most effective for the adsorption on PhB among amines and quaternary ammonium salt. Polyamines, such as ethylenediamine and diethylenetriamine, are also strongly adsorbed on PhB. No obvious adsorption was observed for octanamide. For octanoic acid, the acidic proton is captured by PhB, while the alkyl part remains rather free. Therefore, it may be suggested that the adsorption of the polymeric dispersant onto PhB is largely ascribed to the adsorption of the amino groups, particularly the primary amino group. The detailed adsorption mode of the amino groups onto PhB is not evident at present, but coordination of the amino group to Cu(II) in PhB is assumed to induce the adsorption.

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