Adsorption Mechanism of Poly(Ammonium Carboxylate) onto Phthalocyanine Blue Pigment Deduced by ^1H NMR Spin-Lattice Relaxation Time

Taizo MOHRI, Yoshio NAKAHARA, Wanbin ZHANG, Toshiyuki KIDA,
Yohji NAKATSUJI and Isao IKEDA

Department of Applied Chemistry, Faculty of Engineering, Osaka University
(2-1 Yamadaoka, Suita, Osaka 565-0871, JAPAN)

Edited by D. Kitamoto, AIST, Tsukuba, and accepted June 11, 2001 (received for review May 15, 2001)

Abstract : ^1H NMR spin-lattice relaxation time of ethylenediammonium dioctanoate (EDADO), a model dispersant (MD) for phthalocyanine blue (PhB) pigment, was examined with a high-resolution magic angle spinning (MAS) ^1H NMR probe (^1H Nano·nmrTM Probe). The adsorption mechanism of EDADO onto PhB was discussed on the basis of the spin-lattice relaxation time obtained by changing the polarity of the solvent and the temperature in the ^1H NMR measurement. In addition to the deduction shown in our previous report that the adsorption of the MD molecule onto the pigment is induced by the coordination of a lone electron pair of a nitrogen atom of the amino group onto Cu(II) of PhB, it became clear that equilibrium among a diammonium salt, a half-salt, and diamine (ethylenediamine, EDA) is an important factor in the adsorption behavior. A comparison of measurements in chloroform-*d* and in methanol-*d*₄ suggests that the complex of PhB and a half-salt composed of EDA and octanoic acid still has interaction with a carboxylic acid molecule through proton-transfer from the carboxylic acid to PhB (PhB of the complex and/or free PhB) and successive hydrogen bonding which may effect the dispersion of pigment in a nonpolar medium. The results obtained in this model system may afford a basis for explaining the good dispersing ability of poly(ammonium carboxylate), that is, polymeric dispersants in practical use.

J. Oleo Sci. 50, 857-863 (2001).

Key words : adsorption, coordination, pigment, ^1H NMR, spin-lattice relaxation time

1 Introduction

Dispersion technique plays an important role in a variety of technologies. A proper selection of the dispersant determines the successful preparation of a stable dispersion for specific systems. For example, the so-called "polymeric dispersants" are practically used at present as an effective dispersant for pigment particles in nonaqueous medium. This dispersant molecule consists of polar groups having high interaction with the pigment particle surface and nonpolar groups having high compatibility with a nonpolar medium. The structure of the representative polymeric dispersant in practical use is shown in Scheme 1(1).

The adsorption of the dispersant onto the pigment particle should be essential for creating a stable dispersion state. Accordingly, clarification of the adsorption mechanism of the dispersant onto the pigment would contribute to the development of more effective dispersants. As a method for examining the behavior of the

R: polyester remainder excluding a carboxylic group

Scheme 1 Structure of Representative Dispersants.

Corresponding author : Isao IKEDA

E-mail: ikeda@ap.chem.eng.osaka-u.ac.jp

molecule adsorbed on a solid, we focused on the ^1H NMR spin-lattice relaxation time (T_1), which has been used as an effective tool for elucidating the mobility of a molecule (2-7). Our study has been realized by the development of a high-resolution MAS ^1H NMR probe called ^1H Nano·nmrTM Probe, which is useful for the measurement of heterogeneous samples (8). As the first example of research of the mobility of a surface-adsorbed molecule using ^1H NMR T_1 , we chose ethylenediammonium dioctanoate (EDADO) and phthalocyanine blue (PhB) as the model for the polymeric dispersant in practical use (Scheme 1) and the pigment, respectively (9), and clarified that the reduction in the ^1H T_1 value observed reflected adsorption of EDADO onto PhB and that the ammonio group apparently functioned as the anchoring part.

In the later study using some model dispersants such as alkylamine, alkylammonium halide, amide, and carboxylic acid (10), the coordination of a lone electron pair on the nitrogen atom of an amino group to Cu(II) of PhB was found to be the driving force for the adsorption. In this study, in order to obtain further information regarding the adsorption mechanism of the polymeric dispersant on the pigment, the adsorption behavior of EDADO onto PhB with the ^1H NMR T_1 by using the ^1H Nano·nmrTM Probe was examined in more detail.

2 Experimental

2.1 Materials and Method

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

Ethylenediammonium dioctanoate (EDADO), ($\text{C}_7\text{H}_{15}\text{COO}^-$)₂ · $\text{H}_3\text{N}^+\text{C}_2\text{H}_4\text{N}^+\text{H}_3$: Ethylenediamine (3.01 g, 0.05 mol) and octanoic acid (14.42 g, 0.10 mol) were dissolved in 20 mL of methanol, and the methanol was removed by evaporation. The resulting solid was dried under reduced pressure to afford a lightyellow powder. mp 89-91°C. ^1H NMR (600 MHz, chloroform-*d*), δ =7.03 (6H, s, $-\text{NH}_3^+$), 3.07 (4H, s, $-\text{CH}_2\text{CH}_2-$), 2.18 (4H, t, $J=7.8$ Hz, $-\text{OCOCH}_2-$), 1.54 (4H, m, $-\text{OCOCH}_2\text{CH}_2-$), 1.28 (16H, m, $-(\text{CH}_2)_4-$), 0.88 (6H, t, $J=7.2$ Hz, $-\text{CH}_3$). Anal. Found: C, 61.91; H, 11.51; N, 8.00%. Calcd. for $\text{C}_{18}\text{H}_{40}\text{N}_2\text{O}_4$: C, 62.00; H, 11.60; N, 8.00%.

2.2 Measurement of T_1 Values of EDADO

^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 a well-shaken suspension of a mixture of PhB and EDADO in chloroform-*d* or methanol-*d*₄ was charged. The concentration of EDADO was fixed at 15 mg/mL of chloroform-*d* or methanol-*d*₄. 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.

3 Results and Discussion

Satisfactory ^1H NMR spectra of EDADO with and without PhB were both obtained by using the ^1H Nano·nmrTM Probe. For the convenience of discussion concerning various factors responsible for the T_1 value variation, $T_{1\text{ sus}}/T_{1\text{ sol}}$, the ratio of the T_1 value of EDADO mixed with PhB ($T_{1\text{ sus}}$) to that without PhB ($T_{1\text{ sol}}$), was used. From Fig. 1, where $T_{1\text{ sus}}/T_{1\text{ sol}}$ obtained in chloroform-*d* are shown, it can be seen that, as the PhB/EDADO ratio increased, $T_{1\text{ sus}}/T_{1\text{ sol}}$ of all the protons of the EDADO molecule decreased. The closer a proton was situated to the ionic part in the molecule, the larger the decrement of $T_{1\text{ sus}}/T_{1\text{ sol}}$ became, and the ammonio protons, which are situated closest to the ionic part, showed the largest decrement of $T_{1\text{ sus}}/T_{1\text{ sol}}$.

It was estimated in a preliminary communication that the ammonio group of EDADO functions as the adsorption site for the pigment (PhB) (9). However, it was found later that the real adsorption site is the amino group, not the ammonio group (10). This result suggested to us that an equilibrium of the ammonium salt and the free amine should be considered for the case of EDADO in a solution. EDADO exists as an equilibrium mixture with ethylenediamine (EDA), octanoic acid, and the half-salt in a solvent (Scheme 2). In addition, this equilibrium should be largely affected by the presence of PhB because of the basicity of its nitrogen atoms and the Lewis acid property of Cu(II). It is well known that the equilibrium of the ammonium salt and the free amine and the degree of interaction of the cation and the counter anion in a solution, i.e., intimate ion pair, solvent separated ion pair, or dissociated ions, depend on the polarity of the solvent (11, 12). Usually, solvents of high dielectric constant are polar and good ionizing media (13). By choosing a highly polar solvent, it is expected that the equilibrium would shift to the right in Scheme 2 and, moreover, the counter anion would become more free from the binding onto PhB by forming a separated ion pair or dissociated ions. Thus, the

Fig.1 Changes in $T_{1\text{ sus}}/T_{1\text{ sol}}$ of EDADO Protons Affected by the Amount of PhB in Chloroform-*d* (*The value shows $T_{1\text{ sol}}$ of the corresponding proton).

Scheme 2 EDADO in Solvent.

solvent for the NMR measurement was changed from chloroform-*d* to more polar methanol-*d*₄ (14), which should give some important information concerning the adsorption phenomenon.

The values $T_{1\text{ sus}}/T_{1\text{ sol}}$ obtained using methanol-*d*₄ are shown in Fig. 2. As the PhB/EDADO ratio increased, $T_{1\text{ sus}}/T_{1\text{ sol}}$ of the methylene protons of EDA decreased as largely as in chloroform-*d*. On the other hand, $T_{1\text{ sus}}/T_{1\text{ sol}}$ of the protons of the octanoyl moiety increased, which is quite different from the case in chloroform-*d* (Fig. 1). The closer a proton was situated to the carboxyl group in the molecule, the larger the increment of $T_{1\text{ sus}}/T_{1\text{ sol}}$ became. All these results may indicate that one of the carboxylate ions of EDADO which is bound to an ammonium ion site would be set free formally as a carboxylic acid on addition of PhB in methanol-*d*₄ different from the case in chloroform-*d*, while the ethylenediammonium moiety is kept bound to PhB forming a complex with the half-salt.

In the range larger than 0.25 (g/g), the higher the

PhB/EDADO value became, the smaller the increment of $T_{1\text{ sus}}/T_{1\text{ sol}}$ of all the protons of octanoyl moiety became, the reason for which is not clear at present.

Another intriguing method effective for shifting the equilibrium is a change in the temperature, and so ¹H NMR was measured by changing the temperature using chloroform-*d* as the solvent.

For the convenience of discussion of the various factors dominating the T_1 value reduction, $T_{1\text{ meas}}/T_{1\text{ 25}^\circ\text{C}}$, the ratio of the T_1 value of EDADO mixed with PhB at some specific temperature ($T_{1\text{ meas}}$) to that at 25°C ($T_{1\text{ 25}^\circ\text{C}}$), was used. The dependence of $T_{1\text{ meas}}/T_{1\text{ 25}^\circ\text{C}}$ of all the protons of EDADO on the temperature in chloroform-*d* is shown in Fig. 3. The higher the temperature became, the lower the $T_{1\text{ meas}}/T_{1\text{ 25}^\circ\text{C}}$ of all the protons of the ethylenediammonium moiety became and, on the contrary, the higher the $T_{1\text{ meas}}/T_{1\text{ 25}^\circ\text{C}}$ of protons of the octanoyl moiety became except for that of the α -methylene protons which remained unchanged. The closer a proton was situated to the carboxylate

Fig.3 Changes in $T_{1\text{ meas}}/T_{1\text{ }25^\circ\text{C}}$ of EDADO Protons Affected by ^1H NMR Measurement Temperature in Chloroform- d (PhB/EDADO=1/1 (g/g)) ($T_{1\text{ meas}}$: T_1 at measurement temperature, $T_{1\text{ }25^\circ\text{C}}$: T_1 at 25°C . *The value shows $T_{1\text{ }25^\circ\text{C}}$ of the corresponding proton).

Fig.4 Changes in $T_{1\text{ meas}}/T_{1\text{ }25^\circ\text{C}}$ Ratio of Octanoic Acid Protons Affected by ^1H NMR Measurement Temperature in Chloroform- d (PhB free) ($T_{1\text{ meas}}$: T_1 at measurement temperature, $T_{1\text{ }25^\circ\text{C}}$: T_1 at 25°C . *The value shows $T_{1\text{ }25^\circ\text{C}}$ of the corresponding proton).

Fig.5 Adsorption Mechanism of EDADO onto PhB in Chloroform-*d*.

chloroform-*d* is speculated as follows: On addition of PhB, a lone electron pair on an amino nitrogen atom in EDA or the half-salt which exists in equilibrium with EDADO coordinates to Cu(II), and the T_1 value of the diamine protons decreased in both solvents, regardless of the polarity of the solvent. The acidic proton of the carboxylic acid liberated is adsorbed preferentially onto a nitrogen atom of the PhB molecule coordinated with an amino group of EDA. And the resulting carboxylate anion binds to an amino group being cationic due to coordination to Cu(II) or a protonated nitrogen atom of the PhB molecule through hydrogen bonding in chloroform-*d* (Fig. 5). Simultaneous hydrogen bonding to these two cationic hydrogens by a carboxylate anion may not be likely for structural reasons; however, this intimate interaction between the carboxylate ion and the cationic part shown in the model system may afford a basis for the good dispersing ability of polymeric dispersants in practical use in nonaqueous medium, as a moiety miscible with a nonpolar solvent is bonded to the PhB particle through hydrogen bonding as well as adsorption of the amino group.

4 Conclusion

The adsorption mechanism of EDADO onto PhB was deduced using ^1H NMR spin-lattice relaxation time, and in addition to the fact that the adsorption site onto PhB is the amino group of EDA as already shown in our previous report, it became clear that the complex of PhB

and a half-salt of EDA still has interaction with the carboxylate moiety, which is liberated as carboxylic acid on complexation of EDADO onto Cu(II) of PhB and successive deprotonation by PhB, through hydrogen bonding in a nonpolar solvent. The results obtained in this model system may afford a basis for explaining the good dispersing ability of polymeric dispersants.

References

1. Hutter, G. F. (1983) *US Pat.*, 4,415,705.
2. Bacaloglu, R., Blasko, A., Bunton, C. A., Cerichelli, G. & Shirazi, A. (1991) *Langmuir*, 7, 1107-1111.
3. Spera, S., Po, R. & Abis, L. (1996) *Polymer*, 37, 729-735.
4. Alsten, J. V. & Ovenall, D. W. (1991) *Polym. Commun.*, 32, 549-550.
5. White, J. L., Beck, L. W. & Haw, J. F. (1992) *J. Am. Chem. Soc.*, 114, 6182-6189.
6. Xu, T., Kob, N., Drago, S., Nicholas, J. B. & Haw, J. F. (1997) *J. Am. Chem. Soc.*, 119, 12231-12239.
7. Schwark, U. & Michel, D. (1996) *Colloids Surfaces A: Physicochem. Eng. Aspects*, 115, 267-276.
8. Keifer, P. A., Baltusis, L. D., Rice, M. A., Tymiak, A. & Shoolery, J. N. (1996) *J. Magn. Reson. Series A*, 119, 65-75.
9. Mohri, T., Nakahara, Y., Zhang, W., Nakatsuji, Y., Muneishi, T., Miyaji, Y. & Ikeda, I. (2000) *Chem. Lett.*, 9, 988-989.
10. Mohri, T., Nakahara, Y., Zhang, W., Kida, T., Nakatsuji, Y. & Ikeda, I. (2001) *J. Oleo Sci.*, 50, 623-631.

11. Remic, A. (1940) *Electronic Interpretation of Organic Chemistry*, John Wiley & Sons, Inc., New York, p.198.
 12. Winstein, S., Klinedinst Jr., P. E. & Robinson, G. C. (1961) *J. Am. Chem. Soc.*, 83, 885-895.
 13. Riddick, J. A. & Bunger, W. B. (1970) *Organic Solvents*, 3rd edn, John Wiley & Sons, Inc., New York, p. 57.
 14. Dielectric constant (ϵ): methanol, 32.70 (25°C); chloroform, 4.81 (20°C); cited from Riddick, J. A. & Bunger, W. B. (1970) *Organic Solvents*, 3rd edn, John Wiley & Sons, Inc., New York, p.146 and 350.
 15. Gurney, R. W. (1953) *Ionic processes in solution*, Dover, New York, p.32.
-