Dissolution of Phthalocyanines in Dense Carbon Dioxide and Its Solvatochromic Behavior under Pressureized Conditions

Hajime Kawanami, Yutaka Ikushima, and Nagao Kobayashi*[†]
Supercritical Fluid Research Center, National Institute of Advanced Science and Technology, and CREST,
Japan Science and Technology, 4-2-1, Nigatake, Miyagino-ku, Sendai 981-3214
[†]*Department of Chemistry, Graduate of Science, Tohoku University, Sendai 980-8578*

(Received March 18, 2004; CL-040305)

Metallophthalocyanines having alkoxy groups have been found to dissolve in dense carbon dioxide in the presence of small amount of cosolvent such as methanol or pyridine. The pressure dependence of the absorption maximum of these phthalocyanines can be used as an indicator for measuring solvent polarity.

Phthalocyanines (Pcs) and their related macrocyclic π-delocalized molecules such as naphthalocyanines continue to attract considerable attention because of their potential usefulness for dyes and pigments, catalysts for removing sulfur from crude oil, molecular devices, electrical conductors, nonlinear optical materials, deodorants, charge generation materials in photocopiers, and so forth.[1] More than fifty thousand tons per year of these materials are produced world wide.

Dense CO_2 (such as supercritical CO_2 ($scCO_2$)), on the other hand, has been noted as an environmentally friendly solvent because it is nontoxic, nonflammable, accessible, and an inexpensive medium for extraction, precipitation, and reaction.[2] Furthermore, it is possible to tune solubilities, mass transfer, and reaction kinetics of reacting species simply by manipulating the pressure and temperature under $scCO_2$ conditions.[3] Although both Pcs and dense CO_2 have been studied in many fields and have shown numerous chemical advantages, no reports have appeared as yet, on the application of Pcs to dense CO_2 such as the $scCO_2$ system. In order to initiate and develop the chemistry of Pcs under such supercritical states, it is fundamentally necessary to know whether or not these compounds are soluble in dense CO_2 or $scCO_2$, and to investigate the pressure dependence of the spectra of Pcs under CO_2 conditions. In this communication, we report for the first time that some Pcs can be dissolved in CO_2 under high-pressure conditions, the extent of which is strongly influenced by the central metal and substituents. Moreover, we show that the soluble Pc exhibits solvatochromic behavior under pressurized conditions, which can be used as an indicator for embodying solvent polarity of $scCO_2$.

As peripherally substituted Pcs, we have attempted to dissolve zinc, silicone with two hydroxy axial ligands, nickel, copper and cobalt complexes of tetra-15-crown-5-ed, tetranitro-, tetra-*tert*-butyl-, and tetrabutoxy-, octabuoxy-substituted Pcs, and iron and cobalt tetracarboxy Pcs into $scCO_2$, but they are only slightly soluble.[4] In addition, tri-*tert*-butyl subphthalocyanine (SubPc) with a hydroxy axial ligand, and iron and cobalt tetrapyrazinoporphyrazines[4] have also been examined; however, the latter two could not be dissolved.[4] On the other hand, *tert*-butylated Pcs and SubPc and octabutoxy-substituted Pcs dissolved easily in high-pressure CO_2, suggesting that $scCO_2$ is essentially hydrophobic (otherwise more polar Pcs such as 15-crown-5-ed Pc would be expected to dissolve). When pyridine was used as cosolvent (ca. 10 vol % of $scCO_2$), the solubility generally increased, but was found to decrease in the order of zinc, nickel, and copper. If 10 volumetric percent of methanol was used, silicon Pcs were the most soluble, suggesting that the coordination of solvent molecules to the central metal or the presence of two axial (hydroxy) ligands affects the solubility.

Figure 1 shows the absorption spectra of 1,4,8,11,15,18,22,25-octabutoxyphthalocyaninato nickel (OBNiPc) at various pressures and the photograph in $scCO_2$ at the pressure of 15 MPa.[5] At pressures higher than 7 MPa, this compound dissolved in a similar manner as in normal organic solvents, producing a characteristic green color. The absorption spectrum in the Q-band region (Figure 1) indicates that the compound is in almost completely monomeric state. In addition, the curve in Figure 1 shows that the Q band is strongest at around 7 MPa (near-critical condition), and that at further higher pressures (near and supercritical region) it shifts to shorter wavelength with concomitant decrease in absorbance (as shown below, this may be due to the solvatochromism of Pc).

Figure 2 shows details of the pressure dependence of the Q-band absorption of OBNiPc (726.0 nm) at a fixed temperature. The absorbance suddenly increases above 6.8 MPa, reaching a maximum at the near-critical pressure of 7.0 MPa, then decreasing with increasing pressure and finally leveling off. The behavior is contrary to the conventional knowledge that the absorbance of a solute should increase with the density of $scCO_2$.[2a] As a possible cause of this phenomenon, molecular aggregation of solute molecules may be taken into consideration, which is characteristic of the near-critical region of $scCO_2$ i.e., the local concentration of OBNiPc may be high in the limited pressure

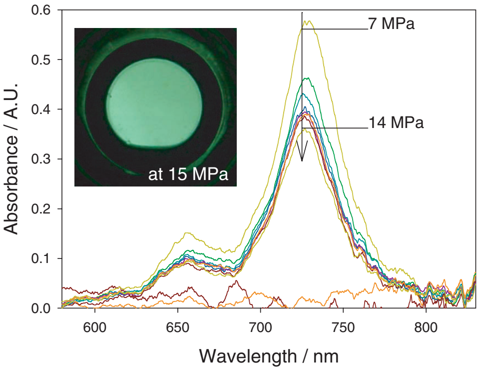

Figure 1. The photograph of OBNiPc in $scCO_2$ containing ca. 10 vol % of pyridine at 15 MPa and the variation of absorption spectra with increasing pressure up to 25 MPa.

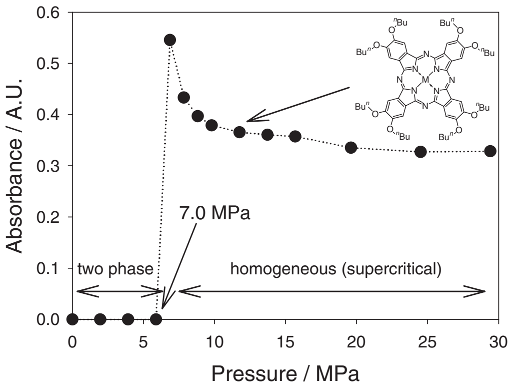

Figure 2. Pressure dependence of absorbance of OBNiPc at 50 °C with 10 vol % of pyridine under pressurized conditions.

ranges around the critical pressure, leading to marked increases in absorbance. At higher pressures, microscopic observation indicated that the OBNiPc molecules appeared to have dispersed homogeneously, so that monomeric spectra were recorded in $scCO_2$. The higher tendency of OBNiPc for aggregation in nonpolar $scCO_2$ may therefore be ascribed to the presence of eight polar oxygen atoms. The type of central metal and substituents on the Pc molecules thus seems to influence the molecular behavior in $scCO_2$.

Figure 3 shows how the Q-band position of OBNiPc (●) depends on pressure at a constant temperature of 50 °C. At the supercritical condition, with increasing pressure, the Q band shifts nonlinearly from 726.3 nm at 9 MPa to 725.0 nm at 18–30 MPa. This solvatochromism of OBNiPc in the supercritical region can be ascribed to a change of polarity of the supercritical phase from a polar state of $scCO_2$ containing pyridine to a less polar state, which is derived from decreasing mole fraction of pyridine with increasing pressure. To explain in more detail the hypsochromic shift of the absorption maximum, we introduce the $E_T(30)$ parameter (solvatochromic parameter of solvent)[6] using the λ_{max} values of OBNiPc at each pressure to evaluate the polarity of the supercritical phase, since Pcs are intensely colored chromophores. The $E_T(30)$ values (□) were found to be obtained from Eq 1 and are shown in Figure 3.[7]

$$E_T(30)\ \text{kcal/mol} = 0.6419 * \lambda - 434.779 \qquad (1)$$

The maximum and minimum $E_T(30)$ are 31.4 kcal mol^{-1} at 9.8 MPa and 30.5 kcal mol^{-1} at 24.5 MPa, which correspond to those of *cis*-decalin (31.9 kcal mol^{-1}) and tetramethylsilane (30.7 kcal mol^{-1}), respectively, and are almost comparable to those in a previous report.[8] Thus, although the shift of the Q band on pressure is not particularly large, OBNiPc is important to estimate the polarity of solvents under supercritical conditions such as high pressure and temperature, which usual chromophores can not stand.[9,10]

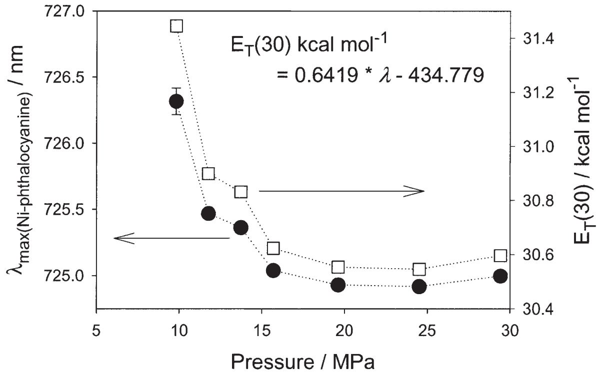

Figure 3. Pressure dependence of λ_{max} of Q band of OBNiPc at 50 °C. $E_T(30)$ values are obtained using Eq 1.

In conclusion, we have succeeded for the first time in finding soluble Pcs in $scCO_2$ (with a small amount of pyridine or methanol as cosolvent), and showed that the Pc would be used as an indicator of solvent polarity. To our knowledge, this is the first example of the dissolution of phthalocyanine in $scCO_2$.

This work was supported in part by CREST from Japan Science and Technology Corporation, Industrial Technology Research Grant Program in '03 from NEDO of Japan, and the Ministry of Education, Culture, Sports, Science and Technology, a Grant-in-Aid for the COE Project, Grant Molecules and Complex Systems, 2004, and Young Scientists (B), 16760619, 2004.

References and Notes

1 Some representative reviews and books on Pcs: in a) "Phthalocyanines: Properties and Applications," ed. by C. C. Leznoff and A. B. P Lever, VCH, New York (1989, 1992, 1993, 1996), Vol. 1–4. b) "Phthalocyanine Materials: Synthesis, Structure and Function," ed. by N. B. McKeown, Cambridge University Press, Cambridge (1998). c) "Phthalocyanines: Chemistry and Functions," ed. by H. Shirai and N. Kobayashi, IPC, Tokyo (1997).

2 Some representative reviews and books on $scCO_2$: a) "Chemical Synthesis Using Supercritical Fluids," ed. by P. G. Jessop and W. Leitner, Wiley-VCH, Weinheim (1999). b) "High Pressure Chemistry," ed. by R. van Eldik and F.-G. Klärner, Wiley-VCH, Weinheim (2002).

3 The recent example papers are follows: a) K. Matusi, H. Kawanami, Y. Ikushima, and H. Hayashi, *Chem. Commun.*, **2003**, 2502. b) H. Kawanami, A. Sasaki, K. Matsui, and Y. Ikushima, *Chem. Commun.*, **2003**, 896. c) K. Matusi, H. Kawanami, and H. Hayashi, *Stud. Surf. Sci. Catal.*, in press.

4 a) N. Kobayashi, in "The Porphyrine Hand Book," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2003), Vol. 14, Chap. 100. b) N. Kobayashi, *Bull. Chem. Soc. Jpn.*, **75**, 1 (2002). c) N. Kobayashi and A. B. P. Levere, *J. Am. Chem. Soc.*, **109**, 7433 (1987). d) N. Kobayashi, in Ref. 1a, Vol. 2, Chap. 3.

5 The typical experimental procedure was as follows: a pyridine solution of Pc (0.17 mL) was put into a high pressure UV cell, then CO_2 was introduced by liquid pump to desired pressure. Pressure control was achieved by a back pressure regulator from 0 to 50 MPa. After stirring for 1 h to be in a steady state, the spectrum is measured from 900 nm to 200 nm by using a JASCO UV-550 spectrometer.

6 K. Dimroh, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963).

7 The parameters were obtained by measuring the Q-band position of OBNiPc in various solvents. The detail is shown in supplentary data.

8 Y. Ikushima, N. Saito, and M. Arai, *J. Phys. Chem.*, **96**, 2293 (1992).

9 a) T. W. Randolph, D. S. Clark, H. W. Blanch, and J. M. Prausnitz, *Science*, **239**, 387 (1988). b) S. Kim and K. P. Johnston, *AIChE J.*, **33**, 1603 (1987).

10 a) Y. Ikushima, N. Saito, M. Arai, and H. W. Blanch, *J. Phys. Chem.*, **99**, 8941 (1995). b) Y. Ikushima, N. Saito, M. Arai, and K. Arai, *Bull. Chem. Soc. Jpn.*, **64**, 2224 (1991). c) Y. Ikushima, N. Saito, and M. Arai, *Bull. Chem. Soc. Jpn.*, **66**, 1817 (1993).

Published on the web (Advance View) June 7, 2004; DOI 10.1246/cl.2004.820