Addition Effect of NaF on the Deodorant Efficiency of an Iron Phthalocyanine Derivative

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Synopsis. A low temperature ESR spectrum shows that Fe(III) of an iron phthalocyanine derivative treated with NaF takes a high spin state. The deodorant efficiency of the derivative treated with NaF is three times higher than that without NaF treatment.

Hydrogen sulfide (H_2S) is one of "the eight bad smells",$^{1)}$ and many reports have appeared concerning the deodorant method for it.$^{2)}$ The reaction type deodorant materials containing copper(II) ion as an active substance were investigated for use in air conditioners with cleaner.$^{3)}$ The lifetime of the copper(II) deodorant materials are not long enough. Biomimetic deodorant materials containing iron phthalocyanine derivatives as an enzyme-like catalyst were then studied in view of their theoretically infinite lifetimes.$^{4)}$ The efficiency of these deodorant materials is not high enough for air conditioners. We improved the deodorant efficiency of a biomimetic deodorant material for H_2S by adding NaF to an iron phthalocyanine derivative. The relation between the deodorant efficiency and the high spin character of the iron phthalocyanine derivative is discussed.

Experimental

Iron(III)-4,5,4′,5′,4″,5″,4‴,5‴-octacarboxyphthalocyanine (FePc) was synthesized and purified by the method described in the literature.$^{5)}$ The untreated deodorant material (UTD) was prepared by dipping 10 g of cotton in a 10 mmol dm^{-3} FePc aqueous solution followed by rinsing with 0.1 mol dm^{-3} HCl and drying at 100 °C for 1 h. The NaF-treated deodorant material (FTD) was fabricated by dipping UTD in a 1% NaF aqueous solution and drying at 100 °C for 1 h.

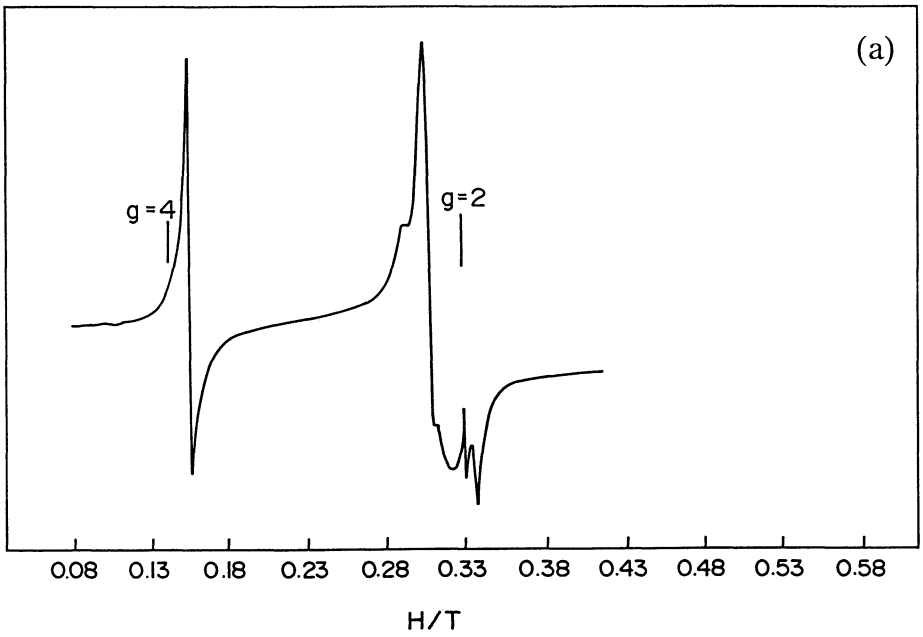
The deodorant efficiency, η (%) for H_2S was evaluated by the formula.$^{6)}$

$$\eta=(C_0-C)/C_0\times 100 \qquad (1)$$

Here C_0 (170 ppb) is the H_2S concentration in the absence of the deodorant material and C the concentration passing through the deodorant material. The flow rate of air was 5 ml min^{-1}. ESR measurements were done with a JEOL JES-FX2XG spectrometer equipped with a temperature controler.

Results and Discussion

Low-temperature ESR spectra of the deodorant materials UTD and FTD are shown in Fig. 1 (a) and (b), respectively. The intensity ratio of the g=4 peak to the g=2 peak was examined. The high-spin signal at g=4 indicates that the axial symmetry of FePC is distorted.$^{7)}$ Since the g value remained unchanged by addition of NaF, the symmetry arround the Fe(III) ion did not change by coordination of F^- ion to the 5th site of Fe. Because intensity ratio of the g=4 peak to g=2 peak was increased, NaF treatment may increase the ratio of the molecular number of Fe(III) in the high-spin state to that in the low-spin state. Here, g=2 peak is the overlapped signals between high spin state and low spin state.$^{7)}$ The intensity ratio is 0.96 for UTD and 1.27 for FTD. The superiority of the high-spin state fraction in the FTD sample is due to the addition of F^- to the 5th coordination site of Fe(III). This phenomenon



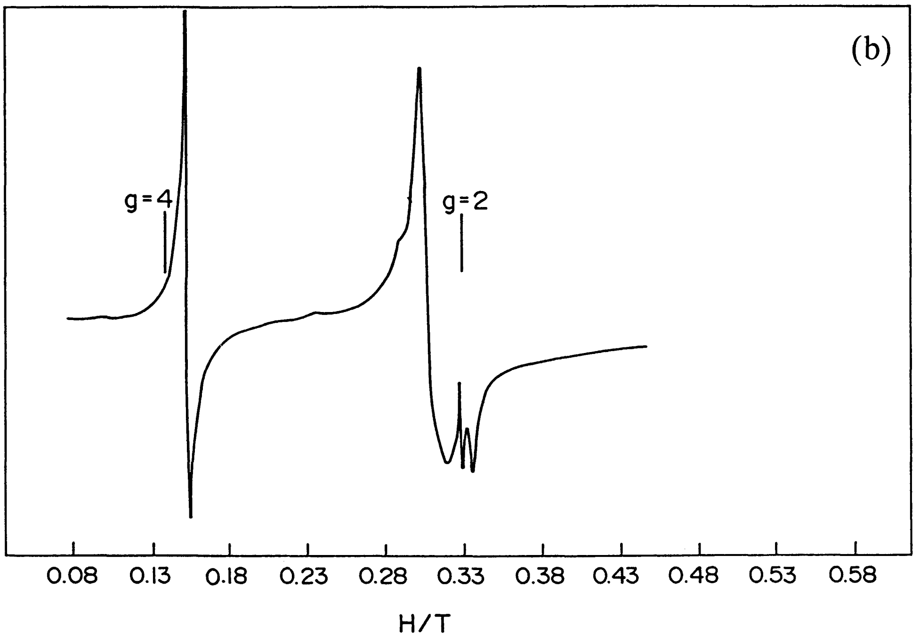


Fig. 1. (a) ESR spectrum of FePc held on cotton. (b) ESR spectrum of FePc treated with NaF and held on cotton. Temp: −143 °C, RF: 1 mW, 9.2 GHz, Field: 0.3287±0.25 T, Mod: 100 kHz, 0.63 mT, Amp: 5×10.

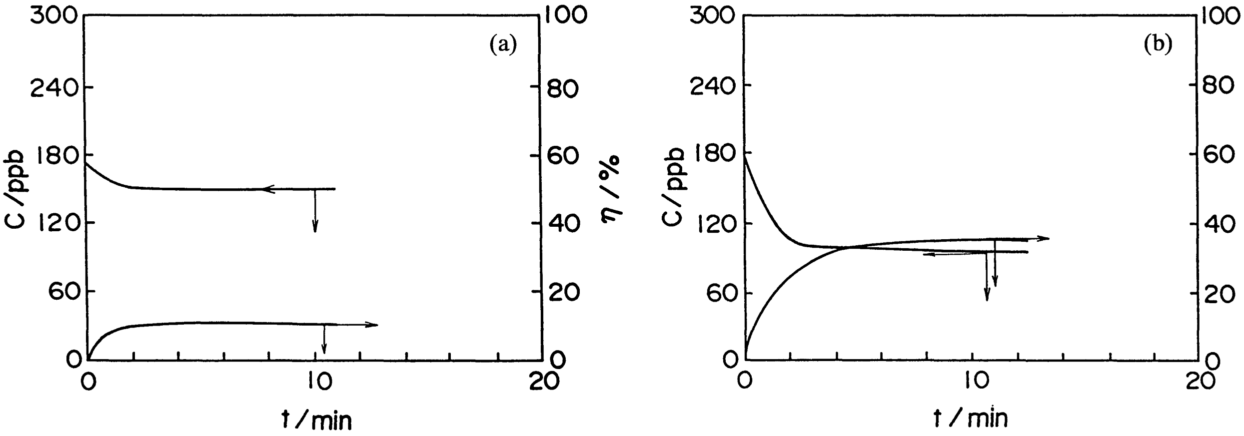


Fig. 2. (a) Time dependent deodorant efficiency of untreated deodorant material. (b) Time dependent deodorant efficiency of NaF treated deodorant material. Initial H_2S concentration, 170 ppb; Flow rate, 5 ml min^{-1}.

is related to the fact that the Bohr magnetic number of methemoglobin, whose 6th coordination site is occupied with F^-, was 5.92.[8]

The small and sharp peak at g=2.0023 originates most probable from the superoxide radical, in view of the generation of superoxide radical in the FePc systems.[4] Comparison of the peak height at g=4.0023 between UTD and FTD shows that the superoxide radical is more abundant in FTD than in UTD.

Fe(III) ion of FePc in the high-spin state has a larger reaction rate of oxidation than that in the low-spin state.[4] The results of deodorant efficiency measurements for UTD and FTD are shown in Fig. 2 (a) and (b), respectively. The efficiency of FTD was three times higher than that of UTD. This could be related to coordination of F^- to the 5th site of Fe in FePc. Details of the reaction mechanism are left for a future study.

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