BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1053—1056 (1970)

Solvent Effect on the Electronic Spectra of Bis(8-quinolinolato)-nickel(II) at 80°C[*1,*2]

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(Received June 11, 1969)

The visible absorption spectra were observed on bis(8-quinolinolato)nickel(II) in molten 8-quinolinol as well as in other solvent systems such as molten naphthalene, molten β-methoxynaphthalene or toluene containing various amounts of 8-quinolinol at 80°C. Little interaction was found between the solute and naphthalene or toluene. However, a weak interaction was observed between the solute and β-methoxynaphthalene or 8-quinolinol. The extent of interaction between the solute and 8-quinolinol in toluene was evaluated spectrophotometrically.

Concerning the zone-melting process of the systems containing metal chelates of 8-quinolinol,[1)] we are interested in the behavior of 8-quinolinolato metal chelates in molten 8-quinolinol or other solid solvents such as naphthalene or β-methoxynaphthalene. Bis(2,4-pentanedionato)nickel(II) exists as a hexa-coordinate trimeric form in a solid state, but exists as a solvated octahedral monomeric form in donating solvents and as a polymeric or a tetrahedral monomeric form in non-donating solvents.[2)] In this connection, it is of interest to study the interaction between the solute, bis(8-quinolinolato)nickel(II), and the solvents such as molten 8-quinolinol or other solvents.

The visible absorption spectra were observed on bis(8-quinolinolato)nickel(II) in molten 8-quinolinol as well as in other solvent systems such as molten naphthalene, molten β-methoxynaphthalene or toluene containing various amounts of 8-quinolinol at 80°C. The analysis of the spectra showed that there was definitely a weak interaction between the dissolved chelate and β-methoxynaphthalene or 8-quinolinol. As the observed absorption bands are due to d–π transition, and as the d–d band was too weak to be observed no significent discussion could be made on the coordinating structure of dissolved 8-quinolinolato metal chelate.

Experimental

Materials. 8-Quinolinol was purified by steam distillation and was dried over phosphorus pentoxide. Bis(8-quinolinolato)nickel(II) was obtained according to the standard procedure as dihydrate,[3)] which was then dehydrated by heating at 100°C for 6 hr in a vacuum over phosphorus pentoxide. The dehydrated sample was found to have a composition of $Ni(ox)_2 \cdot 1/2H_2O$. It was a brownish yellow powder relatively soluble in hot toluene or in pyridine at room temperature. Although we tried to obtain a completely dehydrated sample,[4)] further dehydration under severer conditions

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[*1] Contribution No. 172 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

[*2] Presented at the 18th Symposium on Coordination Chemistry sponsored by the Chemical Society of Japan, October, 1968, Kyoto University.

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1) H. Kaneko, H. Kanagawa, H. Kobayashi and K. Ueno, *Talanta*, **14**, 1411 (1967).

2) F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961).

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4) M. Borrel and R. Paris, *Anal. Chim. Acta*, **4**, 272 (1950).

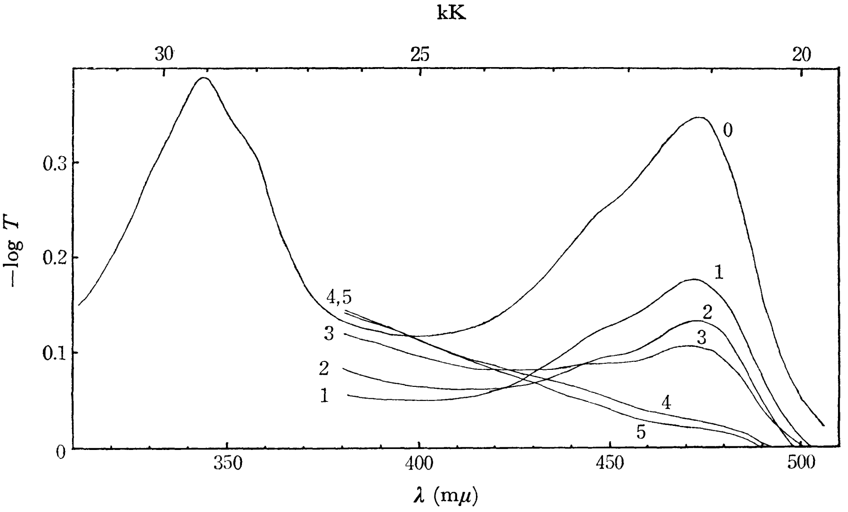

Fig. 1. Absorption spectra of bis(8-quinolinolato)nickel(II) in toluene containing various amounts of 8-quinolinol at 80°C. Concentration of nickel chelate 2.76×10^{-5}M. Concentration of 8-quinolinol increases from curve 0 to 5; zero, 1.95×10^{-4}M, 1.01×10^{-3}M, 1.95×10^{-3}M, 1.08×10^{-2}M and 1.95×10^{-2}M respectively.

resulted in the decomposition of the chelate.

Other solvents were purified and dried according to standard procedures.

Apparatus. Absorption spectra in a visible region were measured with a Hitachi Model 124 recording spectrophotometer, and the optical densities at controlled temperature were measured with a Hitachi-Perkin Elmer Model 139 spectrophotometer equipped with a constant temperature cell compartment which was heated by circulating silicone oil. The temperature fluctuation in the compartment was kept within ±1°C. The spectra were measured against the composite solvent which has exactly the same composition as the solution. However, no reliable specrta could be observed in a region shorter than 390 mμ where a strong absorption of 8-quinolinol was observed, since both solvent and solution contained relatively high concentration of 8-quinolinol.

The molecular weight of 8-quinolinol in toluene was determined by a Mechrolab Model 301A vapour pressure osmometer.

Result and Discussion

The absorption spectrum of bis(8-quinolinolato)-nickel(II) in toluene at 80°C is shown in Fig. 1. The spectrum is characterized by a peak at 473 mμ with an intensity of $\log \varepsilon \approx 4$, and is interpreted as a d-π transition band of the chelate.[5] Almost similar spectrum was observed for the nickel chelate in molten naphthalene at 83°C. Thus, this spectrum may represent the chelate species which is dissolved in non-donating solvents. On the other hand, when 8-quinolinol is added to the toluene solution of nickel chelate, the peak at 473 mμ diminishes with increasing concentration of 8-quinolinol as illustrated in Fig. 1. Further increase of 8-quinolinol concentration does not change the spectrum appreciably. The spectrum is almost the same as that of nickel chelate in molten 8-quinolinol at 82°C.

When the spectra of nickel chelate are observed in weak donating solvents such as β-methoxynaphthalene, dioxane, cyclohexanol or toluene-methanol, a similar diminution of the 473 mμ peak is noticed, but to a lesser extent than in the case of 8-quinolinol as illustrated in Fig. 2. When the spectra are observed in strong donating solvents, such as pyridine or benzylamine, the spectra changed completely and a new band appeared at 410 mμ. Thus, the absorption band of nickel chelate at 473 mμ was found to be rather sensitive against the donating solvents. The curve 5 in Fig. 1 may be assumed to represent the chelate species which is fully solvated with 8-quinolinol.

In order to estimate the extent of interaction between the nickel chelate and 8-quinolinol, an equilibrium constant of the reaction

$$\mathrm{Ni(ox)_2 \cdot \tfrac{1}{2}H_2O} + n\,\mathrm{Hox} \overset{K}{\rightleftharpoons} \mathrm{Ni(ox)_2 \cdot (Hox)_{\mathit{n}} \cdot \tfrac{1}{2}H_2O} \qquad (1)$$

was determined by means of a modified Benesi-Hildebrand method[6] using the spectrophotometric data of Fig. 1.

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[5] a) K. Sone, *J. Amer. Chem. Soc.*, **75**, 5208 (1953); b) A. S. Bailey, R. J. P. Williams and J. D. Wright, *J. Chem. Soc.*, **1965**, 2579; c) J. Szoke, *Acta Chim. Acad. Sci. Hung.*, **35**, 179 (1963); d) R. Yamaguchi, H. Takahashi and T. Asano, *The Annual Report of the Hoshi College of Pharmacy*, **11**, 9 (1962), *Chem. Abstr.*, **59**, 1195 g (1963).

[6] a) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949); b) Y. Oka, "Jikken Kagaku Koza" Supl. Vol. 7, ed. The Chem. Soc. of Japan, Maruzen, Tokyo (1966), p. 202.

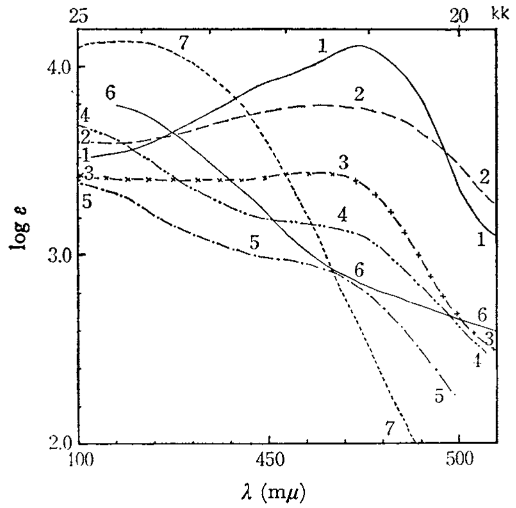

Fig. 2. Absorption spectra of bis(8-quinolinolato)-nickel(II) in various solvents.
Curve 1, in toluene at 80°C; Curve 2, in β-methoxynaphthalene at 77°C; Curve 3, in dioxane at 80°C; Curve 4, in toluene containing 0.5M methanol at 80°C; Curve 5, in cyclohexanol at 60°C; Curve 6, 8-quinolinol at 82°C, Curve 7, in pyridine at room temperature. The values of ε are approximate for the solution of β-methoxynaphthalene (curve 2) and of 8-quinolinol (curve 6), because no volume corrections were made for those solutions. However, these values are still meaningful for the sake of comparison with other solvent systems.

As we did not succeed in obtaining the completely dehydrated nickel chelate, we could not confirm whether the 8-quinolinol adduct still holds water ($\mathrm{Ni(ox)_2 \cdot (Hox)_n 1/2H_2O}$) or the chelate releases water when the adduct is formed ($\mathrm{Ni(ox)_2 \cdot (Hox)_n}$). Thus, the equilibrium constant under discussion is merely an apparent one. However, it may still be useful to estimate the extent of interaction between the nickel chelate and 8-quinolinol.

The equilibrium constant, K, for Eq. (1) is defined by

$$K = \frac{x}{(a-x)(b-nx)^n}, \qquad (2)$$

where a and b are the initial molar concentrations of nickel chelate and 8-quinolinol, respectively, and x is the molar concentration of nickel chelate-8-quinolinol adduct in the equilibrium solution. Eq. (2) may be simplified to

$$K = \frac{x}{(a-x)b^n}, \qquad (3)$$

under the conditions, $b \gg a$ and $b \gg x$.

On the other hand, the optical density of the above system at the given wave length, A_s, can be expressed by

$$A_s = (a-x)\varepsilon_1 + (b-nx)\varepsilon_2 + x\varepsilon_3, \qquad (4)$$

where ε_1, ε_2, and ε_3 are the molar absorption coefficients of nickel chelate, 8-quinolinol and the adduct, respectively.

Thus, we have

$$\frac{a}{(A_s - A_{s_1} - A_{s_2})} = \frac{1}{(\varepsilon_3 - \varepsilon_1 - n\varepsilon_2)} + \frac{1}{(\varepsilon_3 - \varepsilon_1 - n\varepsilon_2)K} \cdot \frac{1}{b^n} \qquad (5)$$

by eliminating x from Eqs. (3) and (4), where, $A_{s_1} = a\varepsilon_1$ and $A_{s_2} = b\varepsilon_2$.

Equation (5) can be written as follows, because the molar absorption coefficient of 8-quinolinol, ε_2, at 476 mμ in toluene solution is assumed to be zero.

$$\frac{a}{(A_s - A_{s_1})} = \frac{1}{(\varepsilon_3 - \varepsilon_1)} + \frac{1}{(\varepsilon_3 - \varepsilon_1)K} \cdot \frac{1}{b^n} \qquad (6)$$

As illustrated in Fig. 3, the plot of $a/(A_s - A_{s_1})$ *vs.* $1/b^n$ becomes a straight line when n is assumed to be 0.5. From the slope of the line, the apparent equilibrium constant is obtained as 5.0 which is comparable to that of hydrogen bond formation in systems such as phenol-dioxane-iso-octane.[7]

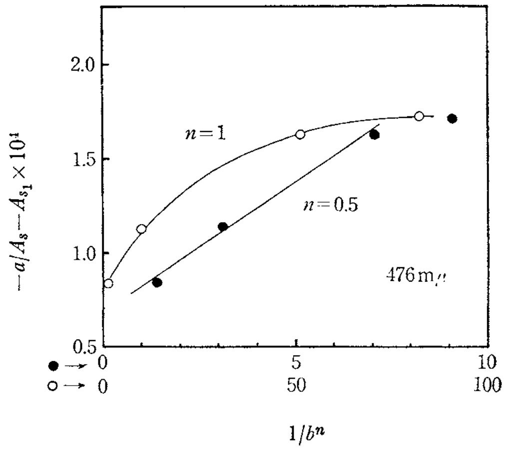

Fig. 3. Determination of equilibrium constant by the modified Benesi-Hildebrand plots.

The combining ratio of 0.5 suggests that one half mole of dimeric 8-quinolinol in toluene interacts with one mole nickel chelate. However, this was denied by the fact that 8-quinolinol exists as monomeric species in toluene as proved by the molecular weight determination.

Formation of 8-quinolinol adducts with 8-quinolinolato metal chelate was reported for several metals, and the equilibrium constant for the reaction

$$\mathrm{Zn(ox)_2 + Hox \rightleftharpoons Zn(ox)_2 \cdot (Hox)} \qquad (7)$$

in water-chloroform system, was studied by means

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[7] S. Nagakura and H. Baba, *J. Amer. Chem. Soc.*, **74**, 5693 (1952).

of the solvent extraction technique, and was found to be larger than $10^{2.6}$ at 25°C.[8] The value we obtained is much lower.

Thus, it may be concluded that the extent of interaction of bis(8-quinolinolato)nickel(II) and 8-quinolinol in toluene at 80°C is an order of hydrogen bond formation if the entropy effect is small enough to be neglected.

The authors wish to thank the Ministry of Education, Japanese Government, for financial support of this work. They are also grateful to Miss A. Itoh for the molecular weight determination.

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8) Fa-Chu Chou, Q. Fernando and H. Freiser, *Anal. Chem.*, **37**, 361 (1965).