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Solvation Effect on the Complex Formation between *o*-Quinones and Metal Chlorides in Nonaqueous Media

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The complex formation of *o*-quinones with metal chlorides was studied by means of spectrophotometry in CH_3NO_2 and CH_3CN, where the metal chloride behaved as a nonelectrolyte. The results obtained in both solutions showed that the complex formation was obviously affected by the solvation of CH_3CN to the metal chloride. The participation of CH_3CN in the *o*-quinone–$ZnCl_2$ complex was assumed as a result of comparing the $\Delta\nu_{max}$ values, and the results obtained by NMR and spectrophotometry proved the coordination of two molecules of CH_3CN to the complex. The values of K_c in CH_3NO_2 increased in the order of $BiCl_3 < ZnCl_2$, whereas those in CH_3CN were in the reverse order; this fact was ascribed to the number of the solvent molecules liberated in the complex formation. The conventional elimination of the solvation effect from the observed K_c was proposed in order to obtain a parameter of solvation-free K_c.

o-Quinones have been reported to form intensively colored complexes with various kinds of metal halides.[1,2] An extensive study of these complexes was first carried out by Crowley and Haendler.[2] However, there have been few reports on the equilibrium of the complex formation of *o*-quinones with metal halides in solution. The complex between *o*-quinones and some metal chlorides has already been examined in CH_3NO_2 by spectroscopy,[3] where the metal chloride behaved as a nonelectrolyte and a correlation was observed between the stability constants, K_c, and the complex shifts, $\Delta\nu_{max}$ ($=\nu_{max}$ of the free ligand$-\nu_{max}$ of its complex) or $\Delta\delta_{ML}$ ($=\delta_{ML}-\delta_L$), of the 1:1 complex. On the other hand, when CH_3CN is used as a solvent, the order of the increment of K_c's is not consistent with that in CH_3NO_2, particularly in the case of the *o*-quinone–$ZnCl_2$ complex. The coordination of CH_3CN is reasonable, since the donor strength of CH_3CN is larger than that of CH_3NO_2 (the donor numbers of CH_3CN and CH_3NO_2 are 14.1 and 2.7 respectively[4]). The purpose of this paper is to investigate the solvation for the *o*-quinone–$ZnCl_2$ complex in detail. In this work, cryptotanshinone and related compounds are used as the ligands, since some *o*-quinones having ether-type oxygen atoms form more stable complexes with metal chloride than does 1,2-naphthoquinone or 9,10-phenanthraquinone.[5]

Experimental

Materials. The cryptotanshinone(1,2,6,7,8,9-hexahydro-1,6,6-trimethylphenanthro[1,2-*b*]furan-10,11-dione) was isolated from the Chinese drug "Tan-shen" by the method of Takiura.[6] The 4,5-dimethoxy-1,2-benzoquinone and 4,5-diethoxy-1,2-benzoquinone were synthesized by the methods of Wanzlich and Jahnke.[7] Commercially available metal chlorides were purified by sublimation or distillation under reduced pressure. The CH_3CN was fractionally distilled from P_2O_5. The CH_3NO_2 and CH_2ClCH_2Cl were purified by distillation after drying on $CaCl_2$. The remaining water in the rectified solvents was checked by the measurement of the degree of the dissociation of the cryptotanshinone–$FeCl_3$ complex, which is liable to be decomposed by water;[5] the data were reproducible.

Procedures. In order to determine K_c, sample solutions containing a fixed overall concentration of the ligand and varying amounts of the metal chloride were prepared; stoppered cells were placed in a dry box under an N_2 atmosphere. The visible absorption spectra were measured on a Shimadzu UV-200 spectrophotometer at 25 or 34 °C. Changes in the absorbance by the complex formation were significant between 460 and 500 nm, and measurements of the absorbance were made at several wavelengths in this range. The K_c values of 1:1 complex formation were obtained by the curve-fitting method;[3] the root mean-square deviations of the absorbance were always within 0.003. The proton NMR spectra were measured in a Hitachi R-22 spectrometer (90 MHz) at 34 °C. The chemical shifts were determined by a frequency counter within an error of ±0.1 Hz, relative to the internal reference, TMS. The molar conductances ($\Lambda/\Omega^{-1}\,mol^{-1}\,cm^2$) of millimolar solutions of the metal chlorides, measured at room temperature on a Kyoto Denshi CM-07 conductivity meter, were as follows; $ZnCl_2=1.7$ and $BlCl_3=2.4$ in CH_3NO_2, and $ZnCl_2=2.2$ and $BiCl_3=1.2$ in CH_3CN. The values of the molar conductances of complexes prepared by adding an excess amount of cryptotanshinone to the above solutions were essentially invariable.

Results and Discussion

Stability Constant and Complex Shift. The K_c and $\Delta\nu_{max}$ values on the complex formation between cryptotanshinone and $BiCl_3$ or $ZnCl_2$ in CH_3NO_2 and CH_3CN are listed in Table 1. The values of K_c in CH_3CN are smaller than those in CH_3NO_2; this is reasonable considering the donor strength of the two solvents. However, the order of K_c in CH_3CN differs from that in CH_3NO_2. A detailed discussion of this disagreement will be given below.

On the other hand, the values of $\Delta\nu_{max}$ are almost invariable with the solvent, but those of K_c are much

Table 1. The $\log K_c$ and $\Delta\nu_{max}$ values of the complex formation between cryptotanshinone and metal chlorides in two solvents at 25 °C

Solvent	MX_n	$\log(K_c/mol^{-1}\,dm^3)$	$\Delta\nu_{max}/10^3\,cm^{-1}$
CH_3NO_2	$ZnCl_2$	3.27 ± 0.03	3.68
	$BiCl_3$	2.63 ± 0.03	2.73
CH_3CN	$ZnCl_2$	0.83 ± 0.06	3.35
	$BiCl_3$	1.39 ± 0.03	3.00

ν_{max} of cryptotanshinone/$10^4\,cm^{-1}=2.273$ in CH_3NO_2, 2.304 in CH_3CN.

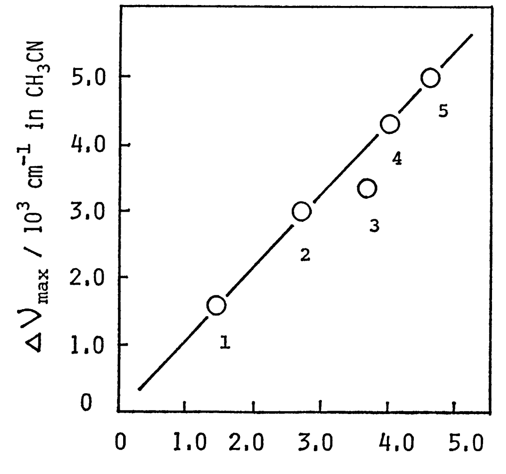

Fig. 1. Plot of $\Delta\nu_{max}$ of cryptotanshinone–MX_n complexes; CH_3CN *vs.* CH_3NO_2.
MX_n: 1; $HgCl_2$, 2; $BiCl_3$, 3; $ZnCl_2$, 4; $InCl_3$, 5; $SnCl_4$.

affected by the solvent. This fact suggests that $\Delta\nu_{max}$ does not depend on the donor strength of the solvent. A slope of *ca.* 1.0 was also given by plotting the values of $\Delta\nu_{max}$ in CH_3CN against those in CH_3NO_2, as shown in Fig. 1, where the plots of the $\Delta\nu_{max}$ values of other metal chlorides have been added. The value of the slope is consistent with the ratio of CH_3CN *vs.* CH_3NO_2 in the dielectric constant.

Participation of Solvent. The $\Delta\nu_{max}$ values of the cryptotanshinone–metal chloride complexes obtained in CH_3CN were of the same order as those obtained in CH_3NO_2. However, the plot of the $\Delta\nu_{max}$ values of the cryptotanshinone–$ZnCl_2$ complex deviated from the linear relation, as is shown in Fig. 1. This deviation should first be examined. Taking into account the complex formation of CH_3CN with $ZnCl_2$[8] or the reports[9,10] on the solvent participation in the complex, this deviation is probably to be ascribed to the coordination of the solvent molecules to the cryptotanshinone–$ZnCl_2$ complex in CH_3CN. The report on the Ni(II) complex[10] is cited as an example of the studies of the solvent participation, where the solvated species were estimated by the shift of the d-d transition band of the Ni(II) complex. In this work, however, the formation of the solvated species can not be confirmed by the method discribed above. Accordingly, the coordination of CH_3CN to the cryptotanshinone–$ZnCl_2$ complex was examined. In this work, CH_2ClCH_2Cl was used as a suitable solvent, since the cryptotanshinone–$ZnCl_2$ complex is sufficiently soluble in this solvent; in addition, the donor strength of CH_2ClCH_2Cl is very weak (*e.q.*, the donor number is 0[4]).

The chemical shifts of aromatic protons of the cryptotanshinone–$ZnCl_2$ complex, prepared by dissolving equimolar amounts of cryptotanshinone and $ZnCl_2$ in CH_2ClCH_2Cl, are concentration-independent in the range from 0.1 to 0.01 mol dm^{-3} of the complex. This suggests that cryptotanshinone and $ZnCl_2$ were almost transformed into the complex. It can therefore, be expected that the values of K_c of the cryptotanshinone–$ZnCl_2$ complex in CH_2ClCH_2Cl are very large. In order to obtain the number of CH_3CN coordinated, the continuous-variation method was performed by the NMR method. As is shown in Fig. 2, the results suggest that two molecules of CH_3CN take part in this equilibrium. In spite of the small displacement of the observed shift, the data were well reproduced. In addition, the molar conductance indicates that $ZnCl_2$ and the cryptotanshinone–$ZnCl_2$ complex in CH_3CN behave as nonelectrolytes. Accordingly, the above results lead to the following two equilibria, the addition type (Eq. 1) and the replacement type (Eq. 2):

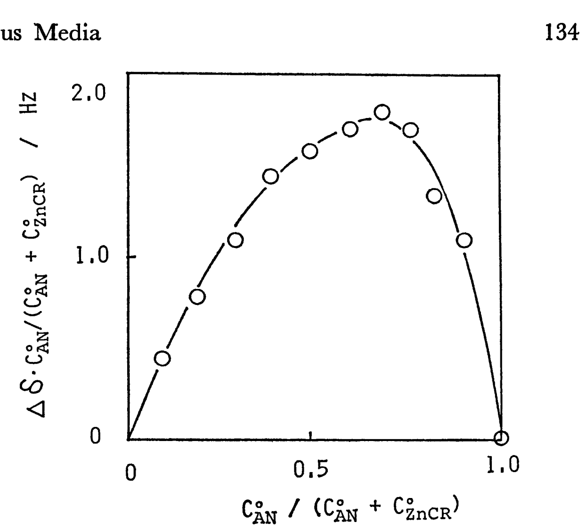

Fig. 2. Continuous variation method of cryptotanshinone–$ZnCl_2$+CH_3CN in 1,2-dichloroethane by NMR.
C°_{AN}: concn of CH_3CN, C°_{ZnCR}: concn of cryptotanshinone–$ZnCl_2$, $C^\circ_{AN}+C^\circ_{ZnCR}=0.13$ mol dm^{-3}, $\Delta\delta=\delta_{obsd}-\delta_{CH_3CN}$.

$$\text{CR-ZnCl}_2 + 2\text{CH}_3\text{CN} \rightleftharpoons \text{CR-ZnCl}_2\text{-2CH}_3\text{CN}, \quad (1)$$

$$\text{CR-ZnCl}_2 + 2\text{CH}_3\text{CN} \rightleftharpoons \text{CR} + \text{ZnCl}_2\text{-2CH}_3\text{CN}, \quad (2)$$

where CR denotes cryptotanshinone. The possibility of Eq. 1 is a matter of concern in the present work, though the possibility of Eq. 2 will be estimated by considering the value of K_c of the cryptotanshinone–$ZnCl_2$ complex in CH_3CN.

The formation of solvated species was further examined by means of spectrophotometry. The change in the spectra of cryptotanshinone with $ZnCl_2$ in CH_2ClCH_2Cl having isosbestic points is shown in Fig. 3. When the concentration of CH_3CN increases gradually while the concentrations of cryptotanshinone and $ZnCl_2$ are held constant (*cf.* Fig. 3 IV), the absorption curves deviate from the isosbestic point, as is shown in Fig. 3 C. This fact suggests that the species containing cryptotanshinone, other than free cryptotanshinone and the cryptotanshinone–$ZnCl_2$ complex, are formed by the addition of CH_3CN. This result supports the priority of Eq. 1. In the case of the complex formation in CH_3CN, therefore, the cryptotanshinone–$ZnCl_2$ complex is almost completely transformed into the solvated species cryptotanshinone–$ZnCl_2$–$2CH_3CN$. On the other hand, the cryptotanshinone–$ZnCl_2$ complex is inert to CH_3NO_2.

It is well known that the partial charge on the metal

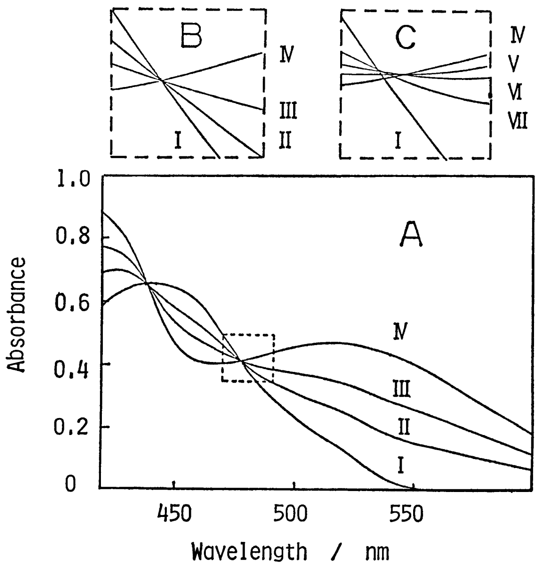

Fig. 3. Spectral change of cryptotanshinone with $ZnCl_2$ in 1,2-dichloroethane and the effect of CH_3CN. Concn of cryptotanshinone/mol dm^{-3}; 0.001 constant, concn of $ZnCl_2$/mol dm^{-3}: I; 0, II; 0.0003, III; 0.0006, IV—VII; 0.0009, concn of CH_3CN/mol dm^{-3}: I—IV; 0, V; 0.09, VI; 0.14, VII; 0.28. B and C are in the wavelength region surrounded by the dotted line in A.

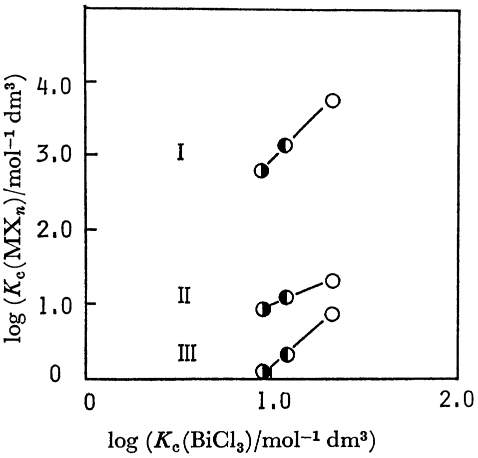

Fig. 4. Plots of $\log K_c$ of the complex formation of *o*-quinones with MX_n against that with $BiCl_3$ in CH_3CN.
MX_n: I; $InCl_3$, II; $BiCl_3$, III; $ZnCl_2$. *o*-Quinones: ○; cryptotanshinone, ◐; 4,5-diethoxy-1,2-benzoquinone, ◑; 4,5-dimethoxy-1,2-benzoquinone.

atom of metal chloride is one of the factors controlling the complex formation.[3] The partial charges in the Zn of $ZnCl_2$ and $ZnCl_2$–$2CH_3CN$, as calculated by the method of Sanderson,[11] were 0.36 and 0.32 respectively. The decrease in the partial charge on the addition of CH_3CN (0.36→0.32) is consistent with the deviation of the plot of $\Delta\nu_{max}$ in the cryptotanshinone–$ZnCl_2$ complex (*cf.* Fig. 1). This fact also supports the presence of the solvated cryptotanshinone–$ZnCl_2$ complex in CH_3CN.

Number of Solvent Molecules Liberated in Complex Formation. In general, the complex formation in donor solvents is a replacement reaction, as is expressed by Eq. 3:

$$MS_m + L \overset{K_{obsd}}{\rightleftharpoons} MS_{m-n}L + nS, \tag{3}$$

where M, L, and S are the metal, the ligand, and the solvent, respectively. When $m=n$, K_{obsd} (the K_c of the complex formation is expressed by Eq. 3; *i.e.*, the K_c given in Table 1 corresponds to K_{obsd}) can be approximately expressed by Eq. 4, where K_{ML} and K_{MS} are the K_c's of the complex formation between M and L and between M and S in the inert solvents:

$$\log K_{obsd} = \log K_{ML} - \log K_{MS}. \tag{4}$$

In the complex formation of a given ligand with a series of metals, if $\log K_{MS} \ll \log K_{ML}$, or if the n's are constant in this series, K_{obsd} will be proportional to K_{ML}. That is, the increasing order of K_{obsd} agrees with that of K_{ML}. On the other hand, if the relative values of K_{MS} can not be ignored, and if the n's are variable between metals, the order of K_{obsd} probably disagrees with that of K_{ML}. In this work, the values of K_c in CH_3NO_2 increased in the order of $BiCl_3 < ZnCl_2$, whereas those in CH_3CN were in the reverse order. This disagreement in the order seems to be responsible for the difference of n. Accordingly, the values of n in the complex formation of cryptotanshinone with $ZnCl_2$ and $BiCl_3$ were examined.

Formerly, a procedure for the determination of the number of solvent molecules liberated in the complex formation, utilizing the solubility equation and the solubility parameter,[13] was proposed by Tanaka.[12] In his work, $\log K_c$ is expressed in terms of the solubility parameter (δ) and the molar volume (V) as follows:

$$\begin{aligned}\log K_c = {} & 0.43(V_M + V_L - V_{ML})\delta_S^2/RT \\ & + 0.86(V_M\delta_M + V_L\delta_L - V_{ML}\delta_{ML})\delta_S/RT \\ & + \text{constant}.\end{aligned} \tag{5}$$

Equation 5 is modified to Eq. 6, providing $V_M + V_L - V_{ML} = nV_S$ and $\delta_{ML} = (V_M\delta_M + V_L\delta_L)/V_{ML}$:

$$\log K_c = 0.43\, nV_S\delta_S^2/RT + \text{constant}, \tag{6}$$

where n is the number of solvent molecules liberated in the complex formation. As two solvents were used in this work, n is given by solving two simultaneous equations for CH_3CN and CH_3NO_2; the values of δ_s are 11.9 and 12.6, while those of V_s are 52.9 and 54.0, respectively.[13] For $ZnCl_2$ and $BiCl_3$, the n values were 3.1 and 1.6 respectively. The calculated values of n are not integral: however, it is important that the value of n for $ZnCl_2$ is about twice that for $BiCl_3$.

In the case of the complex formation in CH_3NO_2, K_{MS} is negligible because of the weak donor strength of CH_3NO_2. It can be considered that there is no effect of the number of the liberated solvent molecule against the order of K_{obsd}. However, the donor strength of CH_3CN is strong, so K_{MS} could not be neglected. Therefore, it is estimated that the disagreement of the order of K_c among two solvents results from the difference in the number of the solvent molecule liberated in the complex formation.

Elimination of Solvation Effect. As was described in the previous section, it is evident that the order

Table 2. The $\log K_c$ and $\Delta\log K_c$ values of the complex formation between o-quinones and metal chlorides in CH_3CN at 34 °C

	$\log (K_c/\text{mol}^{-1}\,\text{dm}^3)$		$\Delta\log K_c$
	(a)	(b)	
$InCl_3$	3.15±0.04	2.81±0.04	0.34
$ZnCl_2$	0.34±0.04	0.08±0.04	0.26
$BiCl_3$	1.18±0.04	0.95±0.04	0.13

(a); 4,5-Diethoxy-1,2-benzoquinone, (b); 4,5-dimethoxy-1,2-benzoquinone, $\Delta\log K_c = \log K_c$ of (a) $-\log K_c$ of (b).

of K_c is very much affected by solvation, so information about solvation-free K_c is necessary in order to examine the acidity of metal chloride. However, the solubility of metal chloride inevitably requires donor solvents. As for the procedure for eliminating the term of solvation from an enthalpy of complex formation in donor solvents, ESP (Elimination of Solvation Procedure) has been proposed by Drago *et al.*[14] In ESP, the solvation term is cancelled by using a replacement reaction: A basic solvent is used to compare the donor strength of a series of bases, whereas an acidic solvent is used to compare the acceptor strength of a series of acids. In this work, a basic solvent is employed in order to compare the acceptor strength of a series of metal chlorides. ESP is not applicable as an intact whole, but the essentials of ESP are extended in this work. That is, the information of solvation-free K_c should be obtained from a comparison with $\Delta\log K_c$, given by subtracting the log K_c of ML′ from that of ML, where L and L′ are ligands with the same coordination geometry. On the other hand, to promote the quantitative accuracy, the slope a defined in Eq. 7 must be evaluated:

$$\log K_c \text{ of ML} = a \log K_c \text{ of M}'\text{L} + b. \tag{7}$$

The slope a indicates the relative value of the acidity of M to M′; it is given by the plots of log K_c of the complex formation of M and M′ with a series of ligands.

At first, the evaluation of a was attempted in CH_3CN. When M′ is $BiCl_3$, the a values of $InCl_3$, $ZnCl_2$, and $BiCl_3$ are 2.4, 2.0, and 1.0, respectively, as is shown in Fig. 4. This order of a was consistent with both the order of K_c in CH_3NO_2 and that of $\Delta\nu_{max}$ in the two solvents. For the sake of convenience, the values of $\Delta\log K_c$ can subsequently be compared with each other. The values of $\Delta\log K_c$ increased in the order of $BiCl_3 < ZnCl_2 < InCl_3$, as is shown in Table 2; this fact also supports the above results. Therefore, either $\Delta\log K_c$ or a is valid as a parameter of K_c without solvation.

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