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Studies on the Complex Formation between *o*-Quinones and Metal Chlorides in Nitromethane Solution

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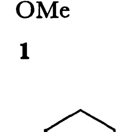
Complex formation between several kinds of metal chlorides and 4,5-dimethoxy-1,2-benzoquinone (**1**) or 4-methoxy-1,2-naphthoquinone (**2**) has been studied by means of NMR and spectrophotometry in CH_3NO_2. Stability constants of the 1 : 1 complex were found to decrease in the order of $SnCl_4 > InCl_3 > ZnCl_2 > BiCl_3 > SbCl_3 > HgCl_2$. $\Delta\delta_{ML}$ and $\Delta\nu_{max}$, which indicate the change in the chemical shift and the wavenumber on the formation of the 1 : 1 complex, were also arranged in the above order. The same order was reproduced from an electrostatic potential. Both $\Delta\delta_{ML}$ and $\Delta\nu_{max}$ were proved to be a convenient scale for the relative acceptor strength of metal chlorides. For the basicity of *o*-quinones, the order of **1**>**2** was obtained from the thermodynamic data and from the negative charge on the carbonyl oxygens. The solute-solvent interaction model was also found appliciable in this system.

o-Quinones have been reported to form intensively colored complexes with various kinds of metal chlorides.[1,2] An extensive study of these complexes was first carried out by Crowley and Haendler.[2] However, few reports have been published on the study of these complexes in solution, since they are liable to decompose in aqueous and/or polar solvents. Some *o*-quinones having ether type oxygen, such as cryptotanshinone (**3**), were observed to form complexes with $FeCl_3$ in nonaqueous media, and they are more stable than the similar complexes of 1,2-naphthoquinone or 9,10-phenanthraquinone.[3] In the previous work,[4] the complex formation between **3** and some metal chlorides in CH_3CN was examined by spectrophotometry, and the shift of wavenumber $\Delta\nu_{max}$ of the ligand absorption band due to complex formation was correlated to the stability constant K_c. In that work, however, a partial disagreement was observed between the order of $\Delta\nu_{max}$ and that of K_c; this was interpreted by the solvation effect of CH_3CN. In this work, CH_3NO_2 is chosen as a solvent, because it has a modest solubility for the metal chloride and a smaller donor strength than CH_3CN (*e.g.*, the donor numbers of CH_3CN and CH_3NO_2 are 14.1 and 2.7, respectively[5]). 4,5-Dimethoxy-1,2-benzoquinone (**1**) and 4-methoxy-1,2-naphthoquinone (**2**) are used as ligands. ^1H NMR signals of 3,6-H in **1** and 3-H in **2** and absorption bands between 400 and 600 nm are examined in detail.



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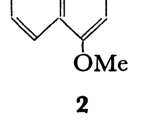

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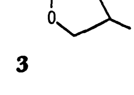

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Experimental

Materials. **1** and **2** were prepared by the methods of Wanzlik[6] and Fieser,[7] respectively. 1,2,6,7,8,9-Hexahydro-1,6,6-trimethylphenanthro[1,2*b*]furan-10,11-dione (**3**) was isolated from the Chinese drug "Tan-shen" by Takiura.[8] Commercially available metal chlorides ($SnCl_4$, $InCl_3$, $SbCl_3$, $BiCl_3$, $ZnCl_2$, and $HgCl_2$) were purified by sublimation or distillation under reduced pressure. Commercially available CH_3NO_2 was purified by distillation after drying over $CaCl_2$, and the remaining water was removed by azeotropic distillation. Residual water in the rectified solvent was checked by the measurement of the degree of dissociation of **3**-$FeCl_3$ complex, which is liable to be decomposed by water,[3] and the data were found to be reproducible.

Preparation of Samples. In order to determine the stoichiometry by the continuous variation method, both solutions of ligand and metal chloride were prepared at the same concentration, and mixed in various ratios. For the determination of K_c, the solutions containing a fixed overall concentration of the ligand and a varying amount of the metal chloride were prepared: In the case of NMR, the concentrations of **1** and **2** were held constant at *ca.* 0.01 and 0.02 M (1 M = 1 mol dm^{-3}), respectively, and the maximum concentration of the metal chloride was kept in the range of *ca.* 0.02 ($InCl_3$) to 0.13 M ($HgCl_2$). In the spectrophotometry, the concentrations of **1** and **2** were held constant at *ca.* 2.5×10^{-3} and 0.7×10^{-3} M, respectively, and the maximum concentration of the metal chloride was kept in the range of *ca.* 0.001 ($SnCl_4$) to 0.13 M ($HgCl_2$). The sample solutions were prepared by weight, and their final concentrations were calculated by taking the density of the solutions as equal to that of the pure solvent. These solutions were sealed in the NMR sample tubes or in the stoppered cells. All procedures described above were carried out in a dry box under N_2 atmosphere.

Measurements. Visible absorption spectra were measured on a Shimadzu UV-200 spectrophotometer at 34 °C. The change of absorbance due to complex formation was significant between 460 and 500 nm, and measurements were made at several wavelengths in this range. Proton NMR spectra were measured on a Hitachi R-22 spectrometer (90 MHz) at 34 °C. Chemical shifts of 3,6-H of **1** and 3-H of **2** were determined by a frequency counter within an error of ±0.1 Hz, relative to an internal reference TMS. Signals due to methoxyl groups were masked by the solvent peak. Variable temperature experiments of spectrophotometry were carried out by using a Tajiri Kikai ECW-108 electronic cooling circulator in the range of 10 to 55 °C. Molar conductances of millimolar solutions of the metal chlorides in CH_3NO_2 were measured at room temperature on a Kyoto Denshi CM-07 conductivity meter. $\Lambda/\Omega^{-1}\ mol^{-1}\ cm^2$: $HgCl_2$; 0, $ZnCl_2$; 1.7, $SbCl_3$; 2.6, $BiCl_3$; 2.4, $InCl_3$; 33.7, and $SnCl_4$; 21.8. The values of molar conductance of their complexes, which were prepared by adding an excess amount of the ligand to the solutions of the metal chlorides, were essentially unchanged from the above values.

Results and Discussion

Complex Formation between o-*Quinones and Metal Chlorides in* CH_3NO_2. *Change of Spectra*: **1** and **2** changed color from yellow to vermilion or red violet on addition of metal chloride in CH_3NO_2, suggesting formation of a complex. In the visible region, the absorption maxima of **1** and **2** due to the quinonoid π-π^* transition were observed at 407 and 400 nm, respectively. A typical example of the spectral change of **1** and **2** with metal chloride is shown in Fig. 1. The presence of isosbestic points in all systems except **2**+$InCl_3$ and **2**+$SnCl_4$ suggests the presence of only one kind of complex. It was found that the spectral change of **2** differed from that of **1** (*cf.* Fig. 1b). Existence of the absorption band in the neighborhood of 400 nm for the complex of **2** with $SnCl_4$ may be due to the red shift of the benzenoid π-π^* transition of **2**, since the latter transition is absent in **1**.[9)]

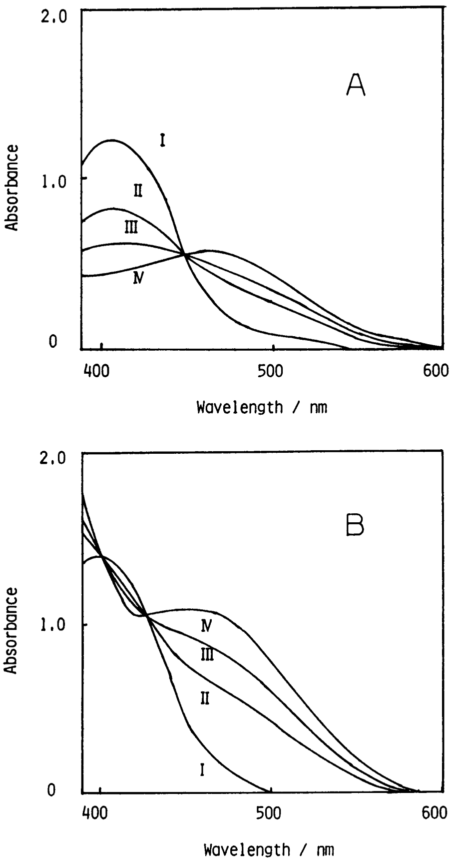

Fig. 1a. Spectral change of *o*-quinones with $ZnCl_2$ in CH_3NO_2. A: Concn of 4,5-dimethoxy-1,2-benzoquinone is maintained at 2.0×10^{-3} M, and concn of $ZnCl_2$ is varied as follows, I; 0, II; 2.0×10^{-3}, III; 3.8×10^{-3}, and IV; 1.0×10^{-2} M. B: Concn of 4-methoxy-1,2-naphthoquinone is maintained at 7.2×10^{-4} M, and concn of $ZnCl_2$ is varied as follows, I; 0, II; 3.6×10^{-3}, III; 5.9×10^{-3}, and IV; 1.0×10^{-2} M.

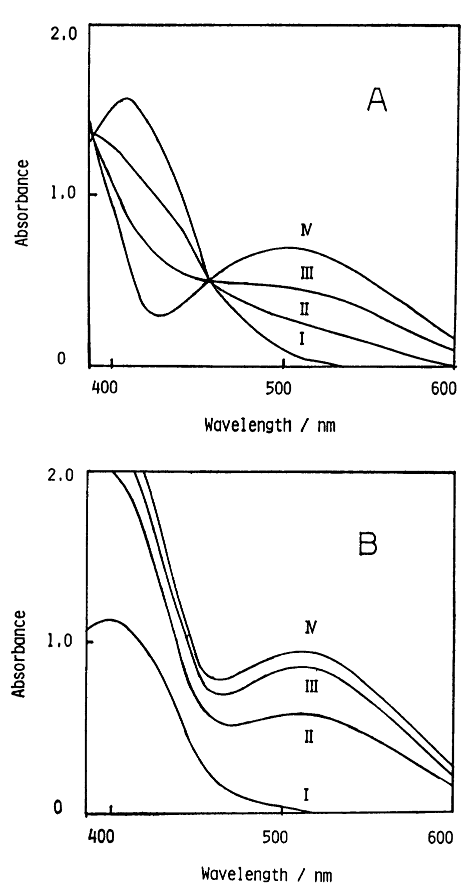

Fig. 1b. Spectral change of *o*-quinones with $SnCl_4$ in CH_3NO_2. A: Concn of 4,5-dimethoxy-1,2-benzoquinone is maintained at 2.6×10^{-3} M, and concn of $SnCl_4$ is varied as follows, I; 0, II; 6.4×10^{-4}, III; 1.8×10^{-3}, and IV$=3.0\times10^{-3}$ M. B: Concn of 4-methoxy-1,2-naphthoquinone is maintained at 5.7×10^{-4} M, and concn of $SnCl_4$ is varied as follows, I=0, II; 3.7×10^{-4}, III; 7.2×10^{-4}, and IV; 1.0×10^{-3} M.

In the ^1H NMR spectra, chemical shifts of 3,6-H of **1** and 3-H of **2** were observed at 5.76 and 5.99 ppm, respectively. When metal chloride was added to the solution of the *o*-quinone, the signal of the *o*-quinones was displaced to the downfield site, since the signals of free and complexed species were averaged; the downfield shift means an electron withdrawal by the metal chloride.

The metal chlorides in nonaqueous media are usually treated as nonelectrolytes, arguing from the conductance data.[10)] In the present work also, the molar conductance of the metal chloride measured in CH_3NO_2 suggests the lack of dissociation. The relatively large values of the molar conductance found in the cases of $InCl_3$ and $SbCl_4$ are attributed to the hydrolysis of the metal chloride by the residual water in CH_3NO_2. When the ligand was added to the solution of metal chloride, the value of molar conductance remains essentially constant. In this experiment, a large excess amount of the

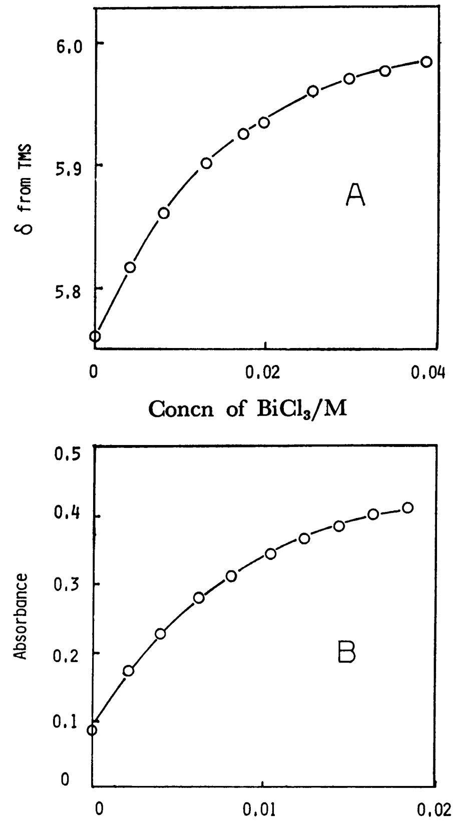

Fig. 2. Concentration dependence of the observed chemical shifts and absorbances. A: NMR method; ○: experimental point, —— : calculated curve with $K_c=98.1\ \mathrm{M}^{-1}$, $\delta_{ML}=6.057$ ppm, $\delta_L=5.760$ ppm, and concn of ligand$=8.30\times10^{-3}$ M. B: Spectrophotometric method; ○: experimental point, ——: calculated curve with $K_c=115\ \mathrm{M}^{-1}$, $\varepsilon_{ML}=369$, $\varepsilon_L=77$ and concn of ligand$=1.56\times10^{-3}$ M.

ligand was added, in the case of the metal chloride, giving a small value of K_c. From these results, the metal chloride and its complexes are treated as nonelectrolytes in this work.

Stability Constant and Complex Shift: The continuous variation method supported the formation of a 1 : 1 complex in all cases. To determine K_c, both absorbances and chemical shifts of solutions containing fixed amounts of ligand and varying amounts of metal chloride were measured. The results of the **1**+BiCl$_3$ system are shown in Fig. 2 as an example. The K_c values are calculated as follows. For an equilibrium of the formation of 1 : 1 complex, K_c is expressed as follows:

$$\mathrm{MX_n} + \mathrm{L} \overset{K_c}{\rightleftharpoons} \mathrm{MX_nL}$$

$$K_c = [\mathrm{MX_nL}]/[\mathrm{MX_n}][\mathrm{L}] = C_{ML}/(C_M^\circ - C_{ML})(C_L^\circ - C_{ML}), \tag{1}$$

where MX$_n$, L, and MX$_n$L mean metal chloride, ligand, and complex, C_{ML}, C_M° and C_L° are the equilibrium concentration of MX$_n$L, and the initial concentrations of MX$_n$ and L, respectively. In an equilibrium state, Eqs. 2 and 2′ are appliciable:

$$A_{cal} = \varepsilon_{ML}C_{ML} + \varepsilon_L(C_L^\circ - C_{ML}), \tag{2}$$

$$\delta_{cal} = \delta_{ML}C_{ML}/C_L^\circ + \delta_L(C_L^\circ - C_{ML})/C_L^\circ, \tag{2'}$$

where A_{cal}, ε_{ML}, and ε_L are the calculated absorbance and the molar absorption coefficients of MX$_n$L and L, and δ_{cal}, δ_{ML}, and δ_L are the calculated chemical shift and the chemical shifts of MX$_n$L and L, respectively. Equations 3 and 3′ are derived from Eqs. 1 and 2 or 2′.

$$A_{cal} = \varepsilon_L C_L^\circ + (\varepsilon_{ML}-\varepsilon_L)\{1+K_cC_M^\circ+K_cC_L^\circ - \sqrt{(1+K_cC_M^\circ+K_cC_L^\circ)^2-4K_c^2C_M^\circ C_L^\circ}\}/2K_c, \tag{3}$$

$$\delta_{cal} = \delta_L + (\delta_{ML}-\delta_L)\{1+K_cC_M^\circ+K_cC_L^\circ - \sqrt{(1+K_cC_M^\circ+K_cC_L^\circ)^2-4K_c^2C_M^\circ C_L^\circ}\}/2K_cC_L^\circ. \tag{3'}$$

The root mean square deviations of the calculated and observed shifts were minimized by the curve fitting method. The results are listed in Table 1; the root mean square deviations of NMR and spectrophotometry were always<0.3 Hz and 0.003, respectively. In the case

Table 1. Stability constants and spectral data of complex formation between *o*-quinones and metal chlorides in CH$_3$NO$_2$ at 34 °C by NMR and spectrophotometry

L	MX$_n$	NMR		Spectrophotometry		
		log (K_c/M^{-1})	δ	log (K_c/M^{-1})	λ_{max}/nm	log ε_{max}
(1)	Free		5.76		407	2.78
	SnCl$_4$	Large	6.57	Large	503	2.45
	InCl$_3$	Large	6.39	Large	480	2.40
	ZnCl$_2$	2.62±0.06	6.35	2.61±0.06	471	2.49
	BiCl$_3$	1.99±0.01	6.06	2.06±0.01	455	2.67
	SbCl$_3$	0.68±0.05	6.04	0.96±0.09	460	2.75
	HgCl$_2$	0.63±0.03	6.00	0.64±0.02	440	2.63
(2)	Free		5.99		400	3.30
	SnCl$_4$	Large	6.76	4.75±0.03	509	3.23
	InCl$_3$	Large	6.71	4.28±0.10	485	3.26
	ZnCl$_2$	—	—	2.07±0.06	470	3.35
	BiCl$_3$	1.69±0.05	6.31	1.75±0.03	439	3.40
	SbCl$_3$	0.60±0.12	6.31	0.63±0.10	435	3.40
	HgCl$_2$	0.46±0.04	6.22	0.49±0.03	435	3.37

(1): 4,5-Dimethoxy-1,2-benzoquinone; (2): 4-methoxy-1,2-naphthoquinone.

of **2**+$ZnCl_2$, measurement of NMR spectra was unsuccessful, since the complex precipitated. The term "large" written in Table 1 means that the K_c value is too large to determine from the concentration dependence of the observed shift. However, approximate values of δ_{ML}, λ_{max}, and ε_{max} were obtained directly from the observed data, because the spectra were measured under the conditions where almost all ligands were transformed into the complex due to large K_c. In the case of smaller K_c, the visible absorption spectra were constructed as the sum of absorption bands of free and complexed species; accordingly, the ε_{ML} value at each wavelength of the spectra was calculated from Eq. 3, when C°_M and C°_L were known and the value of K_c was estimated. λ_{max} and ε_{max} of the complex were determined from the calculated spectra given by the calculated ε_{ML}.

The values of K_c determined by NMR and spectrophotometry were comparable with each other, as follows:

$$\log K_c(\text{NMR}) = 1.02 \log K_c(\text{spectrophotometry}) - 0.09 \quad (r=0.993). \tag{4}$$

The linear relation between $\Delta\delta_{ML}$ and $\Delta\nu_{max}$ is obvious as shown in Fig. 3. Furthermore, the other of the above parameters agree with those of K_c.

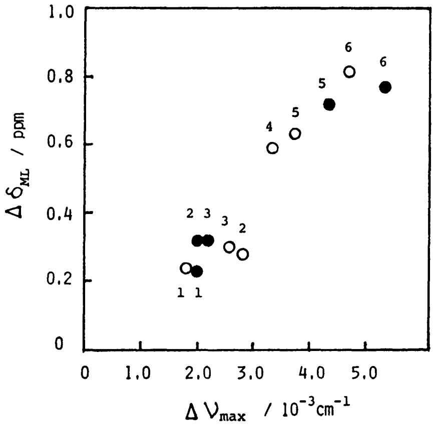

Fig. 3. Relationship between $\Delta\delta_{ML}$ and $\Delta\nu_{max}$.
○: 4,5-Dimethoxy-1,2-benzoquinone, ●: 4-methoxy-1,2-naphthoquinone, 1: $HgCl_2$, 2: $SbCl_3$, 3: $BiCl_3$, 4: $ZnCl_2$, 5: $InCl_3$, and 6: $SnCl_4$.

Electrostatic Model: The relative acceptor strengths of metal chloride toward *o*-quinones decrease in the order of $SnCl_4 > InCl_3 > ZnCl_2 > BiCl_3 > SbCl_3 > HgCl_2$. Parameters of the metal ions are unable to explain the above order; this should be ascribed to the molecular (*i.e.*, non-ionic) property of the metal chloride. When the partial charge q on the metal atom of metal chloride was calculated by the method of Sanderson,[11] the electrostatic potential q/r (r means the distance between metal and chlorine) could be estimated. As shown in Fig. 4, the plots of log K_c against q/r are linear. This result suggests that the complex formation of this type is electrostatic in nature, and also supports the assumption that the metal chloride in CH_3NO_2 behaves as a nonelectrolyte.

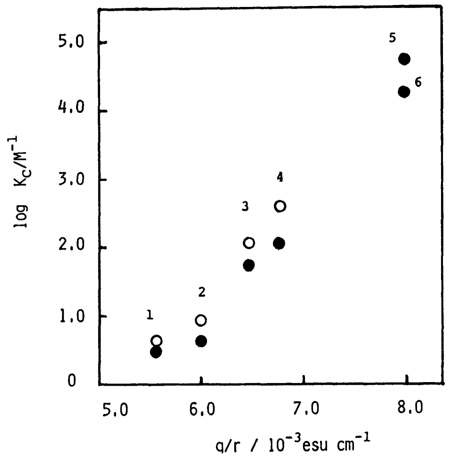

Fig. 4. Plots of log K_c against electrostatic potential (q/r) for metal chloride.
1: $HgCl_2$, 2: $SbCl_3$, 3:$BiCl_3$, 4: $ZnCl_2$, 5: $SnCl_4$, and 6: $InCl_3$.

Basicity of o-*Quinones*: In respect of the electronic structure of *o*-quinones, the negative charge on the carbonyl oxygen was reported to increase slightly in the order of 1,2-benzoquinone<1,2-naphthoquinone.[12] However, the values of K_c obtained in this work increased in the order of **2**<**1**. This disagreement is probably ascribable either to an inversion of the negative charge on the carbonyl oxygen or to an entropy effect due to the steric effect of aromatic moiety of **2**.

TABLE 2. π-ELECTRON CHARGE DENSITIES OF THE TWO CARBONYL OXYGEN ATOMS OF *o*-QUINONES CALCULATED BY HMO METHOD

o-Quinones	π-Electron density of oxygen atoms	
1,2-BQ	1.463	1.463
1,2-NQ	1.496	1.549
4-MeO-1,2-NQ	1.503	1.607
4,5-(MeO)$_2$-1,2-BQ	1.530	1.530
Cryptotanshinone	1.531	1.647

BQ: Benzoquinone; NQ: naphthoquinone.

In the first place, π-electron density of the carbonyl oxygen was calculated by the HMO method. As shown in Table 2, the contribution of the electron release from the methoxyl group is obvious, but an adequate elucidation of this disagreement is not given by this result alone.

TABLE 3. THERMODYNAMIC DATA OF COMPLEX FORMATION OF *o*-QUINONES WITH $BiCl_3$ AND $HgCl_2$ IN CH_3NO_2
(1 cal=4.184 J)

MX_n	Ligand	$-\Delta H$[a] kcal/mol	$-\Delta S$[b] e.u.
$HgCl_2$	4-MeO-1,2-NQ	1.8	3.4
	4,5-(MeO)$_2$-1,2-BQ	2.1	3.6
	Cryptotanshinone	2.8	4.9
$BiCl_3$	4-MeO-1,2-NQ	3.4	3.3
	4,5-(MeO)$_2$-1,2-BQ	4.2	4.1
	Cryptotanshinone	5.3	5.6

BQ: Benzoquinone; NQ: naphthoquinone. a) Error; ±10%. b) Error; ±20%.

Subsequently, thermodynamic data were determined from the temperature dependence of the K_c. These results are summarized in Table 3, where additional data for **3** are listed in order to test the steric contribution on the complex formation. The values of $-\Delta H$ in the complex formation of *o*-quinones with $BiCl_3$ or $HgCl_2$ increase in the same order as K_c. The values of ΔS are proportional to those of ΔH; this finding suggests that the steric contribution is not evident. Therefore, it is concluded that the contribution of the steric effect of aromatic moiety is negligible, and the number of the methoxyl groups influences the order of K_c.

Solute-Solvent Interaction Model. Formerly, the solute-solvent interaction model was established for the study of the weak association by NMR;[13] the solvent molecules play a much larger role in solution than the two solutes. A modified Benesi-Hildebrand type equation (*cf.* Eq. 5) derived from this model was introduced for the estimation of 1 : 1 bound chemical shift $\Delta\delta_{AD}$ and the free energy of the complex formation ΔG_{AD}.[13]

$$1/\Delta\delta_{\text{obsd}} = C_S/k\Delta\delta_{AD}\cdot 1/C^\circ_A x + 1/\Delta\delta_{AD}, \tag{5}$$

where C_S and C°_A are the molarity of solvent and the initial concentration of acceptor, respectively, k is the Boltzmann factor $(=\exp(-\Delta G_{AD}/RT))$, and x is C°_A/C°_D when $C^\circ_A < C^\circ_D$, which is approximated to 1.0 when $C^\circ_A > C^\circ_D$. Equation 5 was modified to Eq. 6 in order to use spectrophotometry:

$$1/\Delta\varepsilon_{\text{obsd}} = C_S/k\Delta\varepsilon_{AD}\cdot 1/C^\circ_A x + 1/\Delta\varepsilon_{AD}. \tag{6}$$

As both NMR and spectrophotometry are employed in this work, so proof of this model must be evaluated by the comparison of the results obtained from this model with those of the previous section. ΔG_{AD} and $\Delta\delta_{AD}$ or $\Delta\varepsilon_{AD}$ were estimated from the linear relations between $1/C^\circ_A x$ and $1/\Delta\delta_{\text{obsd}}$ or $1/\Delta\varepsilon_{\text{obsd}}$. For $\Delta\delta$ and $\Delta\varepsilon$, the linear relations illustrated in Figs. 5 and 6 were formulated by Eqs. 7 and 8:

$$\Delta\delta_{AD} = 0.95\cdot\Delta\delta_{ML} + 0.025 \quad (r=0.974), \tag{7}$$

$$\Delta\varepsilon_{AD} = 1.10\cdot\Delta\varepsilon_{ML} + 2.03 \quad (r=0.996). \tag{8}$$

The results of NMR and spectrophotometry for ΔG are expressed in Eqs. 9 and 10, respectively. These results support the assertion that this model is reliable for the estimation of the thermodynamic parameter.

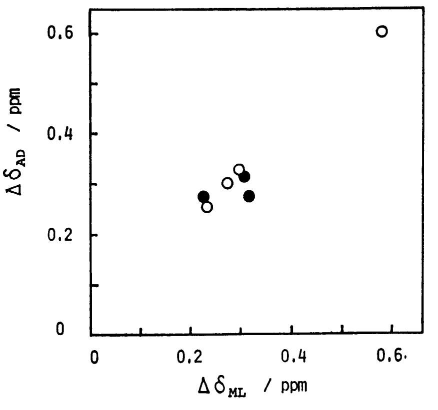

Fig. 5. Correlation between $\Delta\delta_{AD}$ and $\Delta\delta_{ML}$ in CH_3NO_2.
○: 4,5-Dimethoxy-1,2-benzoquinone+MX_c system,
●: 4-methoxy-1,2-naphthoquinone+MX_c system.

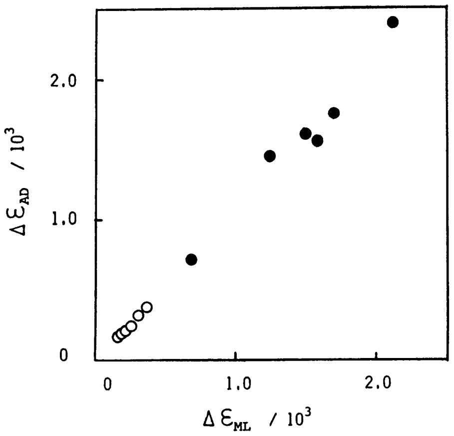

Fig. 6. Correlation between $\Delta\varepsilon_{AD}$ and $\Delta\varepsilon_{ML}$ at 490 nm in CH_3NO_2.
○: 4,5-Dimethoxy-1,2-benzoquinone+MX_n system,
●: 4-methoxy-1,2-naphthoquinone+MX_n system.

$$\Delta G_{AD} = 0.91\cdot\Delta G_{ML} + 1.77 \quad (r=0.996). \tag{9}$$

$$\Delta G_{AD} = 0.82\cdot\Delta G_{ML} + 2.05 \quad (r=0.994). \tag{10}$$

Lewis Acidity. Generally, Lewis acidity is evaluated by the change of the free energy or enthalpy of the complex formation. However, in the case of the complex formation between metal halide and Lewis base, the determination of the thermodynamic parameters is difficult for the wide range of metal halides. Therefore, several empirical scales have been presented to determine the relative acceptor strength of metal halides toward Lewis bases.[14] If these scales really represent a relative acceptor strength of metal halides, a correlation between them must occur. However, they are only qualitative.

In this work, the correlation between the values of K_c, $\Delta\nu_{\max}$, and $\Delta\delta_{ML}$ is acknowledged. This result supports that $\Delta\nu_{\max}$ and $\Delta\delta_{ML}$ are valid as a relative acidity scale. Formerly, in the study of the complex formation between benzamide and metal chloride in ether, Satchell *et al.*[15] concluded that the chemical shift was unlikely to represent the relative acidity. Unfortunately, they failed to account for the contribution of the solvation to K_c, since the donor strength of ether is evident. The effect of solvation on the order of K_c is ascertained in CH_3CN and CH_3NO_2; *i.e.*, the order of $ZnCl_2 > BiCl_3$ was obtained in the latter, whereas the reverse order was obtained in the former;[4] the contribution of the solvation is considered to be much less for CH_3NO_2. The determination of $\Delta\nu_{\max}$ and $\Delta\delta_{ML}$ is usually not so difficult as that of K_c, because the rigorous and quantitative experimental conditions are sometimes unnecessary for the former measurements. Therefore, these two parameters appear to offer a convenient scale for the Lewis acidity of metal halides.

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