Copper(II) Chelates of Cyclam and Dicyclohexylcyclam as Solvatochromic Indicators for an Easy Prediction of Solvent Parameters

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Various scales for such solvent parameters as DC , DN , AN , Z , π^* , α , β , Et and B , etc. have been derived and defined by means of various physicochemical and spectroscopic measurements using various indicator compounds.¹⁻⁶ Especially, three parameters, dielectric constant, DC , donor number, DN , and acceptor number, AN serve as fundamental and extensive set for applications. However, it is not easy to directly derive these parameters by means of the original measurement method. It is expected that they can be predicted by easy means such as a UV/Vis spectroscopic measurement. UV/Vis spectroscopic measurements using solvatochromic chelate compounds, such as diamine- β -diketone Cu(II) and 1,4,8,11-tetramethylcyclam Ni(II), are used to derive some solvent parameters based on a correlation between the solvent-solute interaction and the solvent polarity.^{7,8} In a previous report, we discussed the complexations and solvatochromic behaviors of macrocyclic Cu(II) chelates of 1,4,8,11-tetraazacyclotetradecane (cyclam, **1**) and 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-

continuously depending on the solvent characters from D_{4h} to axial-elongated D_{4h} by a solvent-solute interaction without any essential change from square-planar to octahedral or square-pyramidal geometry, as observed in Ni(II) chelates.¹⁰

In this work, by applying the Cu(II) chelates of **1**, **2** and **3** as the solvatochromic indicators for the easy prediction of solvent parameters, we tried to collect a set of three fundamental parameters for some organic solvents with one or two unknowns among them.

Experimental

The Cu(II) chelates of cyclam (**1**) and dicyclohexylcyclam (**2**, **3**) were prepared as the perchlorate, $[Cu(L)](ClO_4)_2$, in the same manner as previous reports.^{9,10} These chelates are hereinafter described as chelates **1**, **2** and **3**. Commercial GR-grade, Dotite Spectro-sol and Wako GR reagents were used for organic solvents without any further purification. The UV-Vis spectra were measured with a Hitachi U-2000 double-beam spectrophotometer at 25°C.

Results and Discussion

The solvatochromic shifts of the Cu(II) chelates of **1**, **2** and **3** are assumed to be caused by a perturbation of an axially-elongated ligand field through an axial approach of the solvent to the cyclam ring with D_{4h} symmetry.¹⁰ This is well known to be a pentaammine effect.^{12,13} The stronger is the axial interaction between the chelate and the solvent, the lower are the maximum absorption wave number (*i.e.* red-shift). The interaction effect is closely correlated with the three most basic solvent parameters, DC , DN and AN .

When the maximum absorption wavenumbers of chelates **1**, **2** and **3** in the organic solvents are given by a multiparameter equation, Eq. (1), correlated with DC and DN , a linear equation, Eq. (2), is given by a modification of Eq. (1):

$$\nu(S)_{\max} = \alpha_1 DN(S) + \beta_1 (1/DC(S)) \quad (1)$$

$$\nu(S)_{\max} DC(S) = \alpha_1 DN(S) DC(S) + \beta_1 \quad (2)$$

where, $\nu_{\max}(S)$, $DN(S)$ and $DC(S)$ are the maximum absorption wavenumber, the donor number and the dielectric constant for

docosahydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine (dicyclohexylcyclam P and N, **2**, **3**) as shown in Formula. Their solvatochromic shifts on the visible absorption spectra were measured in water and some typical organic solvents, namely propylenecarbonate (PC), acetone (AC), methanol (MeOH), formamide (FA), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetonitrile (AcCN). Their maximum absorption wavenumbers for the solvatochromic spectra shift depended on three fundamental solvent parameters, such as DC , AN and DN .⁹⁻¹¹

Their solvatochromic shifts change moderately and

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Fig. 1 Linear relationship expressed by Eq. (2) in the text. 1, water; 2, propylenecarbonate; 3, acetone; 4, methanol; 5, formamide; 6, *N,N*-dimethylformamide; 7, dimethylsulfoxide; 8, acetonitrile.

Fig. 2 Linear relationship expressed by Eq. (4) in the text. 1, water; 2, propylenecarbonate; 3, acetone; 4, methanol; 5, formamide; 6, *N,N*-dimethylformamide; 7, dimethylsulfoxide; 8, acetonitrile.

solvent S, respectively; constants α_1 and β_1 are the contribution factors to D_N and D_C , respectively.

As shown in Fig. 1, two split straight lines, which are expressed by Eq. (2), have been obtained for chelate 1. The upper line is followed by solvents with higher dielectric constant ($D_C > 50$, e.g. H₂O, PC, FA). Equation (2) for chelates 2 and 3 also gives two similar split straight lines in Fig. 1.

In a similar manner as above, when the maximum absorption wavenumbers, $\nu_{\max}$, of chelates 1, 2 and 3 in the organic solvents are given by a multiparameter equation, Eq. (3), correlated with D_N and A_N , a linear equation, Eq. (4), is given by a modification of Eq. (3):

$$\nu_{\max}(S) = \alpha_2 D_N(S) + \beta_2 A_N(S) \quad (3)$$

$$\nu_{\max}(S)/A_N(S) = \alpha_2 D_N(S)/A_N(S) + \beta_2 \quad (4)$$

where $A_N(S)$ is an acceptor number for solvent S, and constants α_2 and β_2 are contribution factors to D_N and A_N , respectively.

As shown in Fig. 2, two split straight lines, which are expressed by Eq. (4), have been obtained for chelate 1. The

Table 1 Contribution factors of solvent parameters in Eqs. (1) and (3)

	$\alpha_1(\times 10^{-2})$		$\beta_1(\times 10^{-4})$	
	u_1	l_1	u_1	l_1
Chelate 1	5.06	2.40	82.5	53.6
Chelate 2	4.95	4.25	82.9	31.1
Chelate 3	5.00	4.45	83.1	30.5

	$\alpha_2(\times 10^{-2})$		$\beta_2(\times 10^{-4})$	
	u_2	l_2	u_2	l_2
Chelate 1	9.50	5.86	3.26	1.73
Chelate 2	9.44	5.78	3.26	1.73
Chelate 3	9.41	5.93	3.33	1.70

u_1 and l_1 show the upper and lower lines in Fig. 1, respectively.

u_2 and l_2 show the upper and lower lines in Fig. 2, respectively.

Chelate 1, Cu(II)-cyclam; chelate 2, Cu(II)-dicyclohexylcyclam P; chelate 3, Cu(II)-dicyclohexylcyclam N.

upper line is followed by solvents with a small difference in the numerical value between D_N and A_N ($|D_N - A_N| < 5$, e.g. PC, AC, AcCN).

Equation (4) for chelates 2 and 3 also gives two similar split straight lines in Fig. 2. The contribution factors α_1 , β_1 , α_2 and β_2 , which are shown in Table 1, were obtained from the slope and the intercept of the straight lines on Figs. 1 and 2. Each difference for the factors between chelates 1, 2 and 3 is small, except for α_1 and β_1 for the lower line in Fig. 1. For the lower line, the value of α_1 for chelate 1 is almost half that of chelates 2 and 3; and on the other hand, the value of β_1 is about two-times larger than that of chelates 2 and 3. The effects of D_N and D_C on the solvatochromic shift of chelate 1 are smaller and larger than each effect on chelates 2 and 3, respectively. In the same solvent with medium D_C , why the effect of the donor character on chelate 1 is smaller may be related to the higher basicity of ligand 1.¹⁰ For a lower basicity of the solute and a higher donor character of the solvent, the interaction between the solute and the solvent becomes stronger causing a larger solvatochromic shift.

We have tried to apply Eqs. (1) and (3) for roughly predicting unknown solvent parameters to three cases of solvents as follows: 1) For a solvent such that one of three parameters is unknown, the unknown parameter is predictable from Eq. (1) or (3) by means of a measurement of $\nu_{\max}(S)$ for chelate 1 or 2 in solvent S. This case has been applied to predict acceptor numbers to acetonitrile (AcCN), propionitrile (PrCN), butyronitrile (BuCN) and benzonitrile (BzCN). 2) For a solvent such that two of the three are unknown, the two unknown parameters are in principle predictable from a set of simultaneous equation for Eq. (1) or (3) by means of measurements of $\nu_{\max}(S)$ for two complementary indicators, chelates 1 and 2 in the same solvent S. This case has been applied for predicting D_N and A_N to cyclohexanone (CyhCO). 3) For a solvent such that D_C is known, two unknown parameters are predictable from Eqs. (1) and (3) by means of a measuring $\nu_{\max}(S)$ for chelate 1 or 2. This case has been applied for predicting D_N and A_N to *N*-methylformamide (NMF). These results are listed in Table 2.

By compiling the solvent parameters of various solvents, Schmidt has proposed linear equations which can be represented by relations between D_N and Lewis basicity parameter B , and between A_N and Dimroth-Reichardt value E_T .¹⁶ Although the

Table 2 Prediction of unknown parameters of some solvents using Eq. (1) or/and (3)

Indicator	Maximum absorption wavenumber in solvent $\nu_{\max} (\times 10^{-4} \text{ cm}^{-1})$					
	AcCN	PrCN	BuCN	BzCN	CyhCO	NMF
Chelate 1	1.986	2.005	2.005	1.988	2.024	1.930
Chelate 2	1.965	1.982	1.976	1.845	2.012	
D_C	(35.95)	(27.2)	(20.3)	(25.2)	(18.3)	(182.4)
D_N	(14.1)	(16.1)	(16.6)	(11.9)	13	29
					((18.7))	
A_N	20	15	13	26	23	13
	((18.9))	((16.0))		((13.8))	((13.2))	((29.4))

AcCN, acetonitrile; PrCN, propionitrile; BuCN, butyronitrile; BzCN, benzonitrile; CyhCO, cyclohexanone; NMF, *N*-methylformamide.

() used reference value^{14,15} for prediction of unknown parameters by Eqs. (1) and (3).

(()) estimated value by Schmidt proposed equation.¹⁶

A_N values for AcCN and PrCN by Schmidt's equation are almost equivalent to those obtained by Eq. (3), the values for BzCN are fairly small, and the value for NMF is fairly large. The application of case 2 to predictions of D_N and A_N for CyhCO gives a value near to that for D_N and a fairly large value for A_N . The A_N for NMF by Schmidt's equation seems to be overestimated compared with that for a similar solvent, DMF (16.0). One of the causes of these discrepancies is assumed to be that Schmidt's equation applies the parameter, E_T derived from solvatochromic shift by π - π^* transition for betaine compounds; on the other hand, Eqs. (1) and (3) in this report apply $\nu_{\max}(S)$ derived from a solvatochromic shift by the d-d transition for metal chelate compounds.

The Cu(II) chelates of **1**, **2** and **3** are expected to be applied to predicting solvent parameters for wide-coverage solvents from the following viewpoints: 1) extended solubility for organic solvents by substitution effect of cyclohexyl and 2) extended application for the complementary indicator. By a checking on various other solvents, their applications as solvatochromic indicator are expected to be more useful for easily predicting the most basic three solvent parameters, D_C , D_N and A_N , and for assigning their relative order among some solvents.

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