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Calorimetric study on complexation of copper(II) ion with some amide solvents in acetonitrile

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Abstract

Complexation of copper(II) ion with some amide solvents such as *N*-methylformamide (NMF), formamide (FA), *N*,*N*-dimethylacetamide (DMA) and *N*-methylacetamide (NMA) has been studied by titration calorimetry in acetonitrile containing 0.1 mol dm^{-3} $(C_2H_5)_4ClO_4$ as an ionic medium at 298 K. These amides coordinate to the metal ion to form a series of mononuclear complexes, and their formation constants, enthalpies and entropies have been obtained. Thermodynamic parameters of formation of $Cu(NMF)^{2+}$ and $Cu(FA)^{2+}$ are not significantly different from those of $Cu(DMF)^{2+}$ (DMF: *N*,*N*-dimethylformamide), implying that a strong hydrogen-bonded structure of liquid NMF and FA are practically ruptured in the acetonitrile solution examined. The formation of $Cu(DMA)^{2+}$ and $Cu(NMA)^{2+}$ are appreciably less exothermic than the respective formation of $Cu(DMF)^{2+}$ and $Cu(NMF)^{2+}$ complexes, implying that the presence of the acetyl group causes steric hindrance upon its coordination to the metal ion.

Keywords: Titration calorimetry; Complexation of copper(II) ion; Amides; Acetonitrile

1. Introduction

Solvent–solvent interaction, as well as solute–solvent interaction, play an essential role in metal-ion complexation in solution [1–8]. Indeed, halogeno complexation of metal ions in *N*-methylformamide (NMF) is significantly weaker than that in *N*,*N*-dimethylformamide (DMF), mainly due to a decreased formation entropy [4]. This is ascribed to the formation of a strong hydrogen-bonded structure in liquid NMF [9–24], unlike DMF [25–33]. The electron-pair accepting ability, or the ability to form hydrogen bonds, is much higher for protic NMF than aprotic DMF, while the electron-pair donating ability of these amides, or the ability to bind to the metal ion, is almost the same.

The electron-pair donating ability of NMF and FA is much higher than that of acetonitrile (AN). The metal ion is thus preferentially solvated by an amide solvent in amide–AN mixtures over a wide range of solvent composition. The metal-ion complexation in an amide–AN mixture may thus depend on the extent of preferential solvation of the metal ion and the extent of solvent–solvent interactions in the bulk. Complexation of copper(II) ions and DMF has been examined in AN [34]. As expected, DMF molecules exothermically solvate the copper(II) ion. In the AN–DMF mixtures, solvent–solvent interaction among DMF molecules is weak and practically negligible. On the other hand, NMF and FA form a chain-like hydrogen-bonded structure in the liquid state [35–38], and thus solvent–solvent interaction among amides may not be negligible even in AN-rich mixtures.

To elucidate effect of solvent–solvent interaction on preferential solvation of the metal ion, in the present work, complexation of copper(II) ion with NMF and FA has been

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investigated in AN, and the result was compared with that in the copper(II)–DMF system. We also examined complexation of copper(II) ion with *N*,*N*-dimethylacetamide (DMA) and *N*-methylacetamide (NMA) in AN. As these amides involve a bulky acetyl group in the vicinity of the coordinating oxygen atom, a solvation steric effect play an essential role in the complexation of the metal ion in these amide solvents [39,40].

2. Experimental

2.1. Materials

Nitrosyl perchlorate was prepared by passing nitrogen oxides, which was obtained by adding concentrated nitric acid to sodium nitrate, into 70% perchloric acid. Nitrosyl perchlorate crystals thus obtained was filtered, repeatedly washed with nitromethane and acetonitrile on a glass filter, and finally dried in a desiccator over P_2O_5 under a reduced pressure. The nitrosyl perchlorate was reacted with metallic copper according to the reaction, $Cu + 2NOClO_4 = Cu(ClO_4)_2 + 2NO$, in dry acetonitrile under a reduced pressure [41]. The metal-ion concentration was determined by an EDTA titration.

Acetonitrile was dried over molecular sieves 4 Å for several weeks and further dried with calcium hydride, and used after distillation under an atmospheric pressure. All amide solvents used were dried over molecular sieves 3 Å for several weeks and distilled under a reduced pressure. The dried solvents thus obtain were stored in a dark bottle with a P_2O_5 drying tube. Water contents were checked to be negligible by a Karl–Fisher titration. Tetraethylammonium perchlorate was dried at 373 K in a vacuum oven, and used without further purification. All test solutions were prepared in a grove box under an atmosphere of argon.

2.2. Measurements

Calorimetric measurements were carried out using an online controlled titration and data acquisition system in a thermostated room at 298 ± 0.5 K. All test solutions contained 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium. A 5–25 mmol dm^{-3} $Cu(ClO_4)_2$ acetonitrile solution was placed in a Teflon vessel, and the vessel was installed in an aluminum block kept at 298 ± 0.0001 K in an air-bath. The $Cu(ClO_4)_2$ solution was titrated with an amide acetonitrile solution by using an auto burette (Kyoto Electronics APB-510) under a dry argon atmosphere. The titrant contained 0.2 mol dm^{-3} FA, 0.2 mol dm^{-3} NMF, 0.5 mol dm^{-3} DMA or 0.3 mol dm^{-3} NMA. Measured heats of reaction were corrected for heats of dilution, which were determined in advance by separate experiments.

2.3. Data analyses

Complexation between copper(II) ion and an amide (L = NMF, FA, DMA or NMA) in acetonitrile can be represented according to

$$\mathrm{Cu}^{2+} + n\mathrm{L} = [\mathrm{CuL}_n]^{2+},$$
$$\beta_n = [\mathrm{CuL}_n{}^{2+}]/[\mathrm{Cu}^{2+}][\mathrm{L}]^n \quad (1)$$

where β_n denotes the formation constant of $\mathrm{CuL}_n{}^{2+}$. Total concentrations of copper(II) and amide, $C_{\mathrm{Cu},i}$ and $C_{\mathrm{L},i}$, at the *i*th titration point are given as

$$C_{\mathrm{Cu},i} = [\mathrm{Cu}^{2+}]_i + \sum \beta_n[\mathrm{Cu}^{2+}]_i[\mathrm{L}]_i{}^n \quad (2)$$

$$C_{\mathrm{L},i} = [\mathrm{L}]_i + \sum n\beta_n[\mathrm{Cu}^{2+}]_i[\mathrm{L}]_i{}^n \quad (3)$$

The heat q_i observed at the *i*th titration point can be represented as

$$q_i = -(V_i \sum \beta_n \Delta H^\circ_{\beta n}[\mathrm{Cu}^{2+}]_i[\mathrm{L}]_i{}^n - V_{i-1} \sum \beta_n \Delta H^\circ_{\beta n}[\mathrm{Cu}^{2+}]_{i-1}[\mathrm{L}]_{i-1}{}^n) \quad (4)$$

where $\Delta H^\circ_{\beta n}$ and V_i denote the overall formation enthalpy of $[\mathrm{CuL}_n]^{2+}$ and the volume of the test solution at the *i*th titration point, respectively. The formation constants and enthalpies were simultaneously determined by minimizing the error square sum, $U = \sum (q_{i,\mathrm{obs}} - q_{i,\mathrm{calc}})^2$.

3. Results and discussion

Calorimetric titration curves obtained for the Cu(II)–NMF system are shown in Fig. 1. In the figure, an apparent enthalpy value, $-q/[(\mathrm{d}v)C_{\mathrm{NMF,tit}}]$, is plotted against the ratio of total concentrations of NMF to the metal ion, $C_{\mathrm{NMF}}/C_{\mathrm{Cu}}$, where q, $\mathrm{d}v$ and $C_{\mathrm{NMF,tit}}$ denote the measured heat of reaction, the volume of an aliquot of the titrant added at each titration point, and the concentration of NMF in the titrant solution, respectively. As seen in Fig. 1, apparent enthalpy values are negative and increase monotonically with increasing $C_{\mathrm{NMF}}/C_{\mathrm{Cu}}$. The similar titration curves have been obtained also in other Cu(II)–amide systems examined.

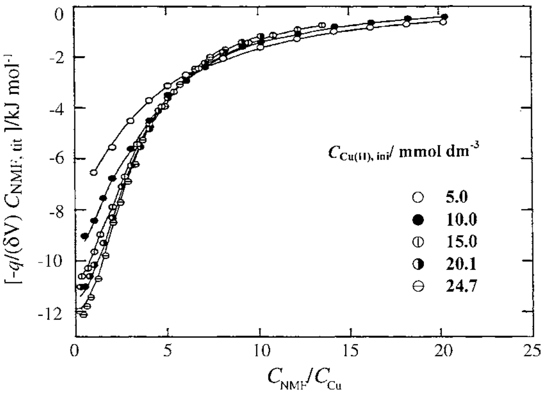

Fig. 1. Calorimetric titration curves for the Cu(II)–NMF system obtained in acetonitrile containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 298 K. The solid lines are the curves calculated using the optimized constants.

Table 1
Stepwise thermodynamic parameters, $\log(K_n)$ ($\mathrm{mol^{-1}\,dm^3}$), ΔH_n° ($\mathrm{kJ\,mol^{-1}}$) and ΔS_n° ($\mathrm{J\,K^{-1}\,mol^{-1}}$), for the formation of $\mathrm{CuL}_n{}^{2+}$ in acetonitrile at 298 K[a]

	DMF[b]	NMF	FA	DMA	NMA
$\log K_1$	2.64	2.25 (0.05)	1.99 (0.09)	1.84 (0.07)	1.78 (0.07)
$\log K_2$	1.82	1.70 (0.08)	1.0 (0.1)	1.66 (0.07)	1.65 (0.08)
$\log K_3$	1.66	1.07 (0.09)	–	0.86 (0.03)	0.80 (0.03)
$\log K_4$	1.09			–	–
ΔH_1°	−15.8	−15.9 (0.5)	−14 (2)	−13 (1)	−10 (1)
ΔS_1°	−2	−11 (2)	−11 (5)	−6 (4)	−0.4 (5)

[a] Values in parentheses refer to a standard deviation.

[b] Ref. [34].

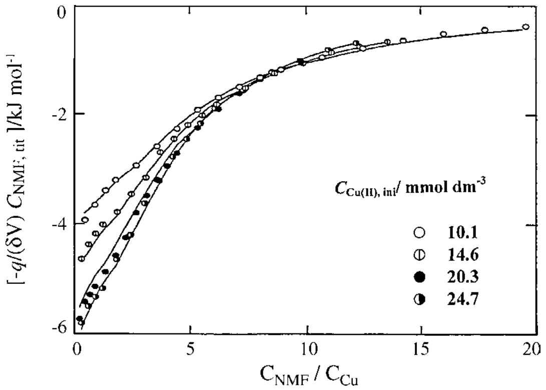

Fig. 2. Calorimetric titration curves for the Cu(II)–NMA system obtained in acetonitrile containing 0.1 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ at 298 K. The solid lines are the curves calculated using the optimized constants.

Calorimetric data were analyzed by assuming various sets of mononuclear complexes. In the Cu(II)–NMF system, set (1) which takes into account the formation of sole $\mathrm{Cu(NMF)^{2+}}$ gave a large Hamilton *R*-factor of 0.134 ($R\text{-factor} = (\sum(q_{\mathrm{obs}} - q_{\mathrm{calc}})^2/\sum(q_{\mathrm{obs}}^2))^{1/2}$). The value was significantly reduced to 0.0510 by assuming the formation of both $\mathrm{Cu(NMF)^{2+}}$ and $\mathrm{Cu(NMF)_2{}^{2+}}$, set (1, 2). The *R*-factor was further reduced to 0.0230 and 0.0167 by taking into account an additional formation of $\mathrm{Cu(NMF)_3{}^{2+}}$, set (1–3), and $\mathrm{Cu(NMF)_4{}^{2+}}$, set (1–4), respectively. However, the formation of the $\mathrm{Cu(NMF)_4{}^{2+}}$ complex is not conclusive at the present stage, because the decrease of the *R*-factor is not large, and the β_3 and $\Delta H_{\beta 3}^\circ$ values change largely by introducing the $\mathrm{Cu(NMF)_4{}^{2+}}$ complex. On the other hand, the β_n and $\Delta H_{\beta n}^\circ$ ($n = 1$ and 2) values are kept practically unchanged in sets (1, 2), (1–3) and (1–4). We thus conclude the formation of $\mathrm{Cu(NMF)}_n{}^{2+}$ ($n = 1$–3) in acetonitrile, and their formation constants and enthalpies were obtained. The same procedure of analyses was applied to the Cu(II)–FA system. The *R*-factor values are 0.0692, 0.0349 and 0.0342 for set (1), set (1, 2) and set (1–3), respectively, indicating that the formation of $\mathrm{Cu(FA)^{2+}}$ and $\mathrm{Cu(FA)_2{}^{2+}}$ is plausible. Stepwise formation constants, enthalpies and entropies were calculated form the β_n and $\Delta H_{\beta n}^\circ$ values thus obtained, and are summarized in Table 1. As compared with enthalpy and entropy values at the first step, the corresponding values at the later consecutive steps involve larger uncertainties due to weak formation of the complexes. We thus concentrate our discussion on the complex that forms at the first step as a main species.

Although less, the formation constant decreases appreciably in the order $\mathrm{Cu(DMF)^{2+}} > \mathrm{Cu(NMF)^{2+}} > \mathrm{Cu(FA)^{2+}}$, the order of increasing electron-pair accepting ability of amides. These imply that NMF and FA are aggregated even in such a diluted solution as they can be regarded as ligands in acetonitrile, as NMF and FA involve the –NH group that has an ability to form hydrogen bonds, unlike aprotic DMF. However, note that aggregation may not be extensive, as formation enthalpy and entropy values of $\mathrm{Cu(NMF)^{2+}}$ and $\mathrm{Cu(FA)^{2+}}$ are not significantly different from the corresponding values of $\mathrm{Cu(DMF)^{2+}}$ within experimental uncertainties.

Calorimetric titration curves obtained for the Cu(II)–NMA system are shown in Fig. 2. Apparent enthalpies observed for DMA are almost to the same extent as those for NMA. As seen, the values in the Cu(II)–NMA system are significantly less negative than the values in the Cu(II)–NMF system. By analyzing these data according to the procedure as mentioned above, it was found that set (1–3) is plausible and gives the small *R*-factors of 0.0169 and 0.0240 in the Cu(II)–DMA and Cu(II)–NMA systems, respectively. Thermodynamic parameters thus obtained involve relatively large uncertainties, however. Although the $\log \beta_1$ values are less reliable, the value (1.84) of $\mathrm{Cu(DMA)^{2+}}$ is appreciably smaller than that (2.64) of $\mathrm{Cu(DMF)^{2+}}$. The same is also found for $\mathrm{Cu(NMA)^{2+}}$ (1.78) and $\mathrm{Cu(NMF)^{2+}}$ (2.25). This is ascribed mainly to an enthalpy term, i.e., the ΔH_1° value of $\mathrm{CuL_A{}^{2+}}$ ($\mathrm{L_A}$ = DMA, NMA) is appreciably less negative than that of the corresponding $\mathrm{CuL_F{}^{2+}}$ ($\mathrm{L_F}$ = DMF, NMF). This is unexpected because the electron-pair donating ability of DMA (the donor number DN = 27.8) is even higher than that of DMF (DN = 26.6). It has been established that solvation of DMA, which have a bulky acetyl group in the vicinity of the coordinating oxygen atom, suffers from a steric hindrance among solvent molecules simultaneously bound to the metal ion (*solvation steric effect*), and solvation enthalpy usually decreases when metal-ion solvation is sterically hindered. We thus suppose that DMA coordinates to the copper(II) ion to form the distorted octahedral $\mathrm{[Cu(DMA)(AN)_5]^{2+}}$ complex, in which DMA is sterically hindered, and the Cu–DMA bond is thus weaker than the Cu–DMF bond in the $\mathrm{[Cu(DMF)(AN)_5]^{2+}}$.

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