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COBALT(II) CHLORO COMPLEXATION IN *N*-METHYLFORMAMIDE–*N*, *N*-DIMETHYLFORMAMIDE MIXTURES
Titration calorimetry and spectrophotometry

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Cobalt(II) chloro complexation has been studied by titration calorimetry and spectrophotometry in solvent mixtures of *N*-methylformamide (NMF) and *N*,*N*-dimethylformamide (DMF). It revealed that a series of mononuclear $CoCl_n^{(2-n)+}$ (n=1–4) complexes are formed in the mixtures of NMF mole fraction x_{NMF}=0.05 and 0.25, and the $CoCl^+$, $CoCl_3^-$ and $CoCl_4^{2-}$ complexes in the mixture of x_{NMF}=0.5, and their formation constants, enthalpies and entropies were obtained. As compared with DMF, the complexation is markedly suppressed in the mixtures, as well as in NMF. The decreasing formation constant of $CoCl^+$ with the NMF content is mainly ascribed to the decreasing formation entropy. DMF is aprotic and thus less-structured, whereas NMF is protic to form hydrogen-bonded clusters. In DMF-NMF mixtures, solvent clusters in neat NMF are ruptured to yield new clusters involving DMF, the structure of which depends on the solvent composition. The entropy of formation of $CoCl^+$ will be discussed in relation to the liquid structure of DMF, NMF and their mixtures.

Keywords: *cobalt(II) chloro complexation, liquid structure, N-methylformamide–N, N-dimethylformamide mixtures, titration calorimetry and spectrophotometry*

Introduction

N-Methylformamide (NMF), a protic amide, forms chain-like and ring structures through intermolecular –NH···O=C– hydrogen bonds in the liquid state [1–13]. On the other hand, aprotic *N*,*N*-dimethylformamide (DMF) is less-structured [14–21]. Metal-ion complexation depends on the solvent, as metal ions are solvated. So far, the metal–ion complexation has been discussed mainly in view of electron-pair donating and accepting abilities of solvent. However, liquid structure of solvent also plays an essential role. Indeed, the metal-halogeno complexation in water is much weaker than that in DMF, although the electron-pair donating ability of water is less than that of DMF [22].

Metal-halogeno complexation has been studied in DMF [23–25] and NMF [26]. Both solvents have high and similar electron-pair donating abilities, whereas the electron-pair accepting ability is much higher for NMF than DMF [27, 28]. It has been established that the complexation in NMF, as well as water, is significantly weaker than that in DMF. This is mainly ascribed to the smaller formation entropy in NMF than that in DMF, as the corresponding enthalpy is not significantly different. The metal ion is strongly solvated in these solvents almost to the same extent, and bound solvent molecules are thus strongly restricted, or the freedom motion is low. Solvent molecules bound to the metal ion are liberated upon complexation to obtain high freedom of motion, or the entropy increases, as is the case for the complexation in less-structured DMF. However, the liberated solvent molecules are accommodated in the bulk structure of solvent to lose again their freedom of motion, if the solvent is structured like NMF. The extent of entropy change thus depends on the extent of structuredness in the bulk.

The liquid structure of solvent mixtures, particularly protic and aprotic solvent mixtures, may be interesting from both thermodynamic and structural viewpoints. With aprotic DMF and protic NMF mixtures, according to thermo-chemical [29, 30] and ^{1}H-NMR [31] studies, the mixture is regarded as to be homogeneous over the whole range of solvent composition, implying that hydrogen-bonded chain-like and ring structures of NMF is ruptured to form other type of hydrogen-bonded clusters involving DMF molecules. Disruption and formation of hydrogen-bonded clusters may significantly affect on the meta-ion complexation in the mixtures. Therefore, to obtain further insight into the effect of liquid structure, in the present work, the complexation of cobalt(II) with chloride ions has been studied in NMF-DMF mixtures by titration calorimetry and spectrophotometry, and thermodynamic parameters will be discussed in relation to liquid structure in the mixtures.

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Experimental

Reagents

DMF solvates of cobalt(II) perchlorate were prepared by dissolving their hydrates in DMF, followed by repeated recrystallization from DMF. DMF solvate crystals thus obtained were dried in a vacuum oven at 327 K and kept in a desiccator over P_2O_5. The number of DMF bound to the metal ion was 6.0 according to EDTA titration. Tetra-*n*-butylammonium perchlorate and tetra-*n*-butylammonium chloride were dried in vacuo at 303 K, and used without further purification. NMF was dried over molecular sieves 3 Å (Kishida) for several weeks, and further dried by fresh BaO for one day. NMF thus treated was distilled at 328 K under reduced pressure (400 Pa) and stored in a dark bottle with a P_2O_5 drying-tube. DMF was dried over molecular sieves 4 Å for several weeks and distilled at 303 K under reduced pressure. The water content was checked to be negligible by a Karl-Fisher titration. All materials and solutions were treated and stored in a glove box under an atmosphere of argon.

Measurements

Calorimetric measurements were carried out in a thermostated room at 298±0.5 K using an on-line titration and data acquisition system developed in our laboratory [32–34]. A 7–20 mmol dm^{-3} $Co(ClO_4)_2$ solution was placed in a Teflon vessel, and installed in an aluminum block at 298±0.0001 K in an air-bath. The metal solutions (20 cm^3) were titrated with 0.1 mol dm^{-3} (x_{NMF}=0.05, 0.1 and 0.25) or 0.4 mol dm^{-3} (x_{NMF}=0.5) $(n\text{-}C_4H_9)_4NCl$ by using an auto-burette (Kyoto Electronics APB-510) under a dry argon atmosphere. Ionic medium was kept constant by using $(n\text{-}C_4H_9)_4NClO_4$ throughout titration. Measured heats of reaction were corrected for heats of dilution, which have been determined in advance by separate experiments.

Spectrophotometric measurements were carried out using an on-line titration and data-acquisition system with a spectrophotometer (Hitachi U-3500). A flow cell with a light-path length of 0.5 cm was connected to a titration vessel through Teflon tube and a pump. A 7–20 mmol dm^{-3} $Co(ClO_4)_2$ solution was placed in a vessel under a dry argon atmosphere, and titrated with 0.1 or 0.4 mol dm^{-3} $(n\text{-}C_4H_9)_4NCl$. At each titration point, an electronic spectrum was recorded every 1 nm over the range 450–750 nm.

Data analyses

Overall formation of $CoCl_n^{(2-n)+}$ with formation constant β_n can be represented as

$$Co^{2+} + nCl^- = CoCl_n^{(2-n)+} \qquad (1)$$

$$\beta_n = [CoCl_n^{(2-n)+}]/[Co^{2+}][Cl^-]^n \qquad (2)$$

and total concentrations of cobalt(II) and chloride ions, $C_{Co,i}$ and $C_{Cl,i}$, at the ith titration point are given as

$$C_{Co,i} = [Co^{2+}]_i + \sum\beta_n[Co^{2+}]_i[Cl^-]_i^n \qquad (3)$$

$$C_{Cl,i} = [Cl^-]_i + \sum n\beta_n[Co^{2+}]_i[Cl^-]_i^n \qquad (4)$$

The heat qi at the ith titration point is represented using formation constants β_n and overall formation enthalpies $\Delta H_{\beta n^\circ}$ of $CoCl_n^{(2-n)+}$ as

$$q_{i,calc} = -(V_i\sum\beta_n\Delta H_{\beta n}^\circ\,[M^{2+}]_i[Cl^-]_i^n - V_{i-1}\sum\beta_n\Delta H_{\beta n}^\circ[M^{2+}]_{i-1}[Cl^-]_{i-1}^n) \qquad (5)$$

where V_i denotes volume of test solution at the ith titration point. Formation constants and enthalpies were simultaneously determined by minimizing the error square sum, $U = \sum(q_{i,obs}-q_{i,calc})^2$.

Absorbance A_{ij} at a given wavelength λ_j in a solution i is represented as

$$A_{ij,calc}=\sum\varepsilon_n(\lambda_j)\beta_n[Co^{2+}]_i[Cl^-]_i^n + +\varepsilon_{Co}(\lambda_j)[Co^{2+}]_i+\varepsilon_{Cl}(\lambda_j)[Cl^-]_i \qquad (6)$$

where $\varepsilon(\lambda_j)$ denotes molar extinction coefficient of species at λ_j. Formation constants and molar extinction coefficients at given 50 wavelengths were simultaneously obtained by minimizing the error-square sum, $U=\sum\sum(A_{ij,obs}-A_{ij,calc})^2$.

Nonlinear least-square programs MQCAL and MQSPEC were used for calorimetric and spectrophotometric data analyses throughout [35].

Results and discussion

Complexation of cobalt(II) and chloride Ions

Electronic spectra of cobalt(II) chloride solutions observed in NMF-DMF mixtures are shown in Fig. 1, together with those in pure DMF and NMF. These were analyzed by assuming various sets of complexes. Among sets of complexes examined, set assuming the formation of $CoCl_n^{(2-n)+}$ (n=1–4) gave relatively small Hamilton R-factors of 0.00488, 0.0037 and 0.0039 in the mixtures, x_{NMF}=0.05, 0.1 and 0.25, respectively. Although formation of the di-chloro complex is concluded, it is rather suppressed in the mixtures, as well as DMF. In the mixture x_{NMF}=0.5, the formation constant of the di-chloro complex involves a relatively large uncertainty, implying that formation of the complex is very weak. Indeed, the R-factor was sufficiently small (0.0048), even if formation of the di-chloro complex is neglected. We thus finally pro-

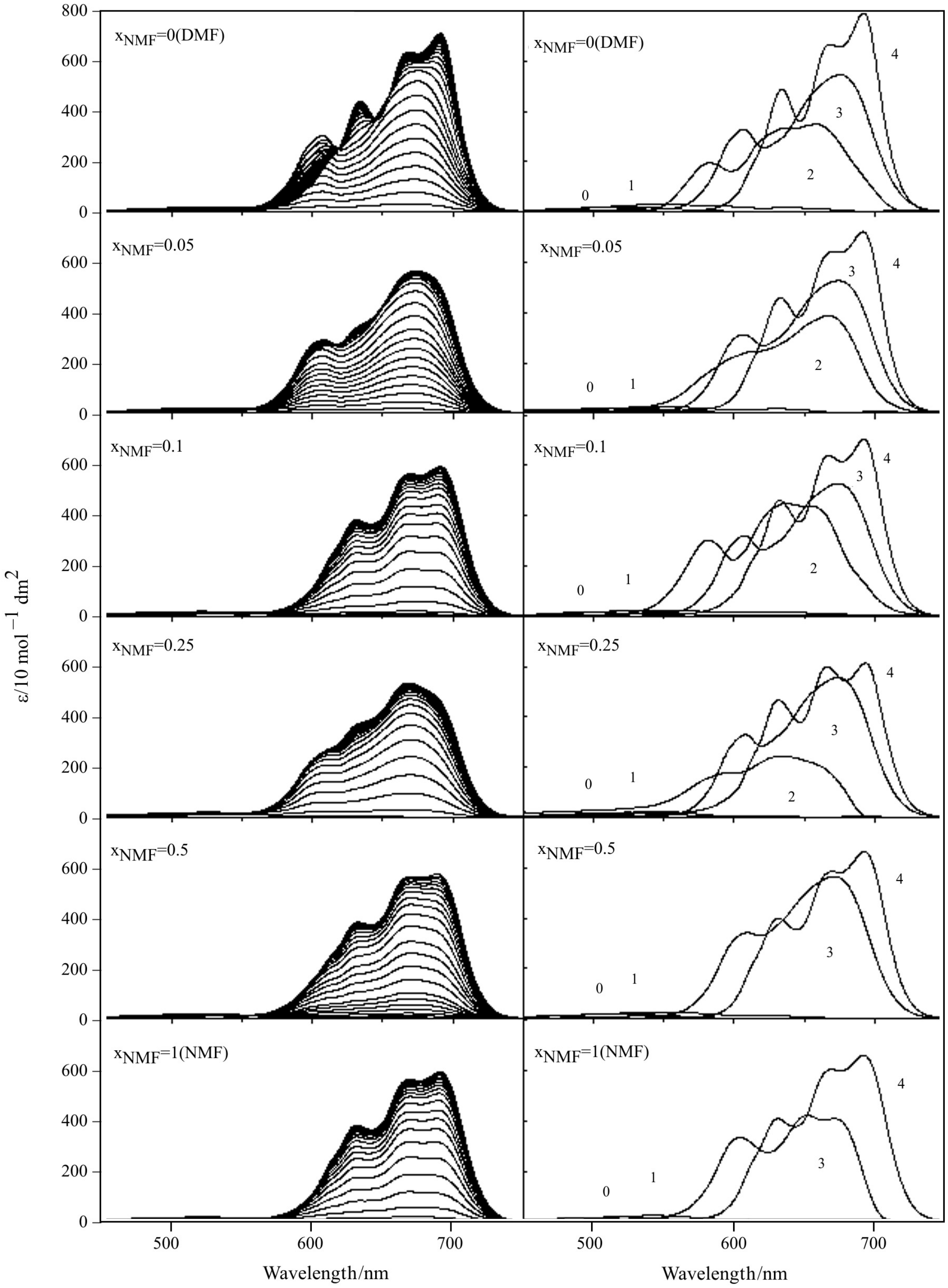

Fig. 1 Measured and extracted spectra of cobalt(II) chloro complexes in NMF-DMF mixtures of varying C_{Cl}/C_{Co} ratio at 298 K. The number represents *n* within $CoCl_n^{(2-n)+}$

pose the formation of $CoCl_n^{(2-n)+}$ (n=1, 3 and 4) in the mixture x_{NMF}=0.5. Formation constants thus obtained are summarized in Table 1. Species distribution in the cobalt(II)-chloride systems in DMF and NMF and their mixtures examined is depicted in Fig. 2. Evidently, the tri- and tetra-chloro complexes are extensively formed in the mixture over the whole range of solvent composition, although the formation of the tri-chloro complex is suppressed at high x_{NMF}. Though minor, the mono-chloro complex is appreciably formed over the whole range of solvent composition, as well. Extracted individual electronic spectra of $CoCl_n^{(2-n)+}$ (n=0–4) are also shown in Fig. 1. Co^{2+} and $CoCl^+$ show weak bands in the range 450–600 nm, typical for six-coordination of the cobalt(II) ion, and $CoCl_2$, $CoCl_3^-$ and $CoCl_4^{2-}$ show strong absorption bands in the wavelength range 600–700 nm, typical for four coordination.

Table 1 Overall formation constants, $\log(\beta_n/\mathrm{mol}^{-n}\ \mathrm{dm}^{3n})$ for the formation of $\mathrm{CoCl}_n^{(2-n)+}$ in NMF-DMF mixtures at 298 K by spectrophotometry[a]

	x_{NMF}			
	0.05	0.1	0.25	0.5
$\log\beta_1$	2.99(0.05)	2.53(0.02)	1.73(0.03)	1.05(0.07)
$\log\beta_2$	5.8(0.2)	4.6(0.2)	3.4(0.1)	–
$\log\beta_3$	9.93(0.05)	8.66(0.01)	6.19(0.02)	3.90(0.02)
$\log\beta_4$	11.52(0.08)	10.02(0.02)	7.31(0.04)	5.08(0.03)
R	0.0049	0.0037	0.039	0.0048

[a]Values in parentheses refer to three standard deviations

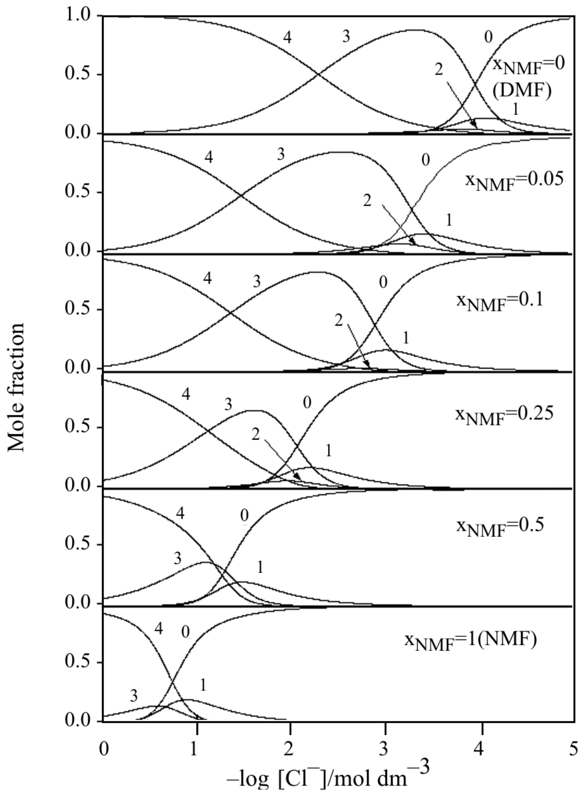

Fig. 2 Species distribution of $\mathrm{CoCl}_n^{(2-n)+}$ (*n*=0–4) in NMF-DMF mixtures. The numbers represent *n* within $\mathrm{CoCl}_n^{(2-n)+}$

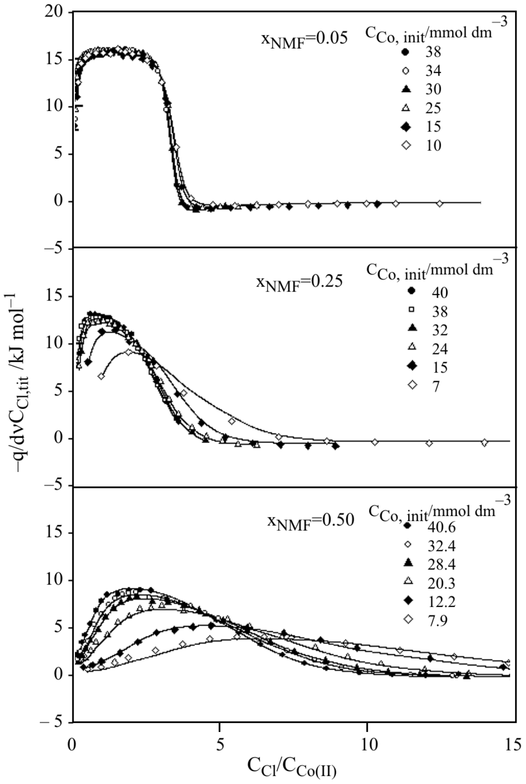

Fig. 3 Calorimetric titration curves in the cobalt(II) chloride system obtained in NMF-DMF mixtures of NMF content x_{NMF} = 0.05, 0.25 and 0.5 at 298 K. The solid lines are the curves calculated by using constants in Table 2

Calorimetric titration curves in the mixtures x_{NMF}=0.05, 0.25 and 0.5 are shown in Fig. 3. In the figure, apparent enthalpies $\Delta H°=-q/(\mathrm{d}v\ C_{\mathrm{Cl,tit}})$ are plotted *vs.* $C_{\mathrm{Cl}}/C_{\mathrm{Co}}$, where q, dv, C_{Cl} and C_{Co} denote the measured heat of reaction, the volume of an aliquot of the titrant added and total concentrations of chloride and metal ions, respectively, at each titration point, and $C_{\mathrm{Cl,tit}}$ denotes concentration of chloride ions in the titrant solution. Calorimetric data were analyzed using formation constants determined by spectrophotometry (Table 1), and formation enthalpies and entropies were obtained. Stepwise formation constants, $\log(K_n/\mathrm{mol}^{-1}\ \mathrm{dm}^3)$, enthalpies, $\Delta H_n°/\mathrm{kJ\ mol}^{-1}$, and entropies, $\Delta S_n°/\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$, for the cobalt(II) chloro complexes in the solvents x_{NMF}=0, 0.05, 0.25, 0.5 and 1 are summarized in Table 2. The solid lines in Fig. 3 are calculated using formation constants and enthalpies in Table 2, which reproduce well all-experimental points.

Coordination structure change

According to individual electronic spectra in Fig. 1, Co^{2+} and CoCl^+ show weak bands in the range 450–600 nm, typical for six-coordination of the cobalt(II) ion, and CoCl_2, CoCl_3^- and CoCl_4^{2-} show strong absorption bands in the wavelength range

Table 2 Stepwise thermodynamic parameters, log K_n/mol^{-1} dm^3, ΔH_n°/kJ mol^{-1} and ΔS_n°/J K^{-1} mol^{-1}, for the formation of $CoCl_n^{(2-n)+}$ in NMF-DMF mixtures at 298 K[a,b]

	x_{NMF}				
	0 (DMF)[c]	0.05	0.25	0.5	1 (NMF)[c]
log K_1	3.64	2.99	1.73	1.05	0.44
log K_2	3.52	2.84	1.65	–	–
log K_3	4.92	4.10	2.81	–	–
log K_2K_3	8.44	6.94	4.46	2.85	1.34
log K_4	2.06	1.59	1.12	1.18	1.20
ΔH_1°	8.5	10.6(0.7)	12(1.3)	7.8(0.7)	7.3
ΔH_2°	27.9	27(4)	2(11)	–	–
ΔH_3°	–2.5	10(3)	43(11)	–	–
ΔH_2°+ΔH_3°	25.4	37	45	52(1)	29
ΔH_4°	–6.3	–5.1(0.4)	–35(3)	–16(1)	14
ΔS_1°	87	93(2)	72(4)	46(2)	33
ΔS_2°	241	146(12)	37(36)	–	–
ΔS_3°	12	112(11)	196(36)	–	–
ΔS_2°+ΔS_3°	253	258	233	230(4)	122
ΔS_4°	23	13(2)	–96(11)	–33(4)	71
log β_4	14.1	11.52	7.31	5.08	2.98
$\Delta H_{\beta 4}$°	28	42.8(0.4)	21(3)	43.8(0.6)	23
$\Delta S_{\beta 4}$°	363	364(2)	210(10)	244(2)	226
R		0.027	0.028	0.027	

[a]Values in parentheses refer to three standard deviations; [b]Formation constants are fixed to those obtained by spectrophotometry; [c]Ref. 26

600–700 nm, typical for four coordination. If the coordination number of the metal ion, six- and four-coordinated for the $CoCl^+$ and $CoCl_3^-$, respectively, is taken into account, the coordination number decreases upon reaction, $CoCl^+ + 2Cl^- \rightarrow CoCl_3^-$, and four solvent molecules simultaneously desolvate the metal ion. Here, note that the metal ion may be solvated with both DMF and NMF in the mixtures, as these solvents have almost the same coordinating ability to the metal ion. Indeed, in all mixtures examined, the ΔH_2°+ΔH_3° and ΔS_2°+ΔS_3° values are large and positive, indicating that a large number of solvent molecules bound to the cobalt(II) ion are extensively liberated.

The stepwise ΔH_2° and ΔS_2° values are also large and positive, indicating that solvent molecules bound to the cobalt(II) ion are extensively liberated upon reaction $CoCl^+ + Cl^- \rightarrow CoCl_2$ in neat DMF. In contrast, the ΔH_3° and ΔS_3° values are much less than the respective ΔH_2° and ΔS_2° values, indicating that the coordination structure changes from six- to four-coordination at the second consecutive step according to the reaction, $[CoCl(DMF)_5]^+ + Cl^- \rightarrow [CoCl_2(DMF)_2] + 3DMF$. The similar applies also for the ΔH_2° and ΔS_2° values in the mixture x_{NMF}=0.05. However, both ΔH_3° and ΔS_3° values in the mixture x_{NMF}=0.05 are markedly larger than the corresponding values in neat DMF. This is even more enhanced in the mixture x_{NMF}=0.25. This implies that the six-coordinated di-chloro complex is also formed, together with the four-coordinated di-chloro complex, and geometry equilibrium is established in the mixtures. Thus, the coordination structure change upon complexation may shift gradually from the second consecutive step in neat DMF to the third consecutive step in the mixtures. The chloro complexes may be solvated also in the second coordination sphere through the chloride ion and NMF bound to the metal ion in the mixtures, unlike in neat DMF. This might prevent the structure change of the di-chloro complex from six- to four-coordination in the mixtures.

Effect of liquid structure on the complexation

The Gibbs energy, enthalpy and entropy of formation of the mono-chloro complex, ΔG_1°, ΔH_1° and ΔS_1°, are plotted *vs.* x_{NMF} in Fig. 4. As seen, the ΔG_1° value increases, or the formation constant K_1 decreases, monotonically with increasing x_{NMF}. The corresponding $\Delta H_1°$ is almost kept unchanged over the whole range of solvent composition, indicating that the $\Delta S_1°$ decrease plays a role in decreasing K_1.

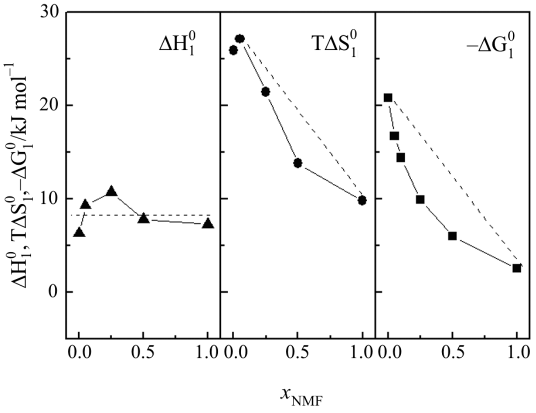

Fig. 4 The $\Delta G_1°$, $\Delta H_1°$ and $\Delta S_1°$ for the formation of $\mathrm{CoCl^+}$ in NMF-DMF mixtures

The cobalt(II) ion is six-coordinated in both DMF and NMF [24–26]. The metal ion in the $\mathrm{CoCl^+}$ complex is also six-coordinated in both DMF and NMF, according to its individual electronic spectra in the solvents. The same coordination number may apply also for the metal ion in their mixtures, although solvent composition in the coordination sphere varies depending on the composition in the bulk. According to our previous work [36], the metal ion is not strongly preferentially solvated in the mixture, as expected from the electron-pair donating ability of DMF and NMF, which is almost to the same extent. Formation equilibrium is thus described as

$$[\mathrm{Co(solvent)_6}]^{2+}+\mathrm{Cl^-}=[\mathrm{CoCl(solvent)_5}]^{+}+\mathrm{solvent} \quad (7)$$

Here, solvent composition in the first coordination sphere is almost the same as that in the bulk, i.e., $y_{\mathrm{NMF}}\approx 6x_{\mathrm{NMF}}$ and $y_{\mathrm{DMF}}\approx 6(1-x_{\mathrm{NMF}})$, where y_{solvent} denotes the individual solvation number of a given solvent ($y_{\mathrm{NMF}}+y_{\mathrm{DMF}}=6$). On the other hand, the hydrogen-bonding ability is quite different between aprotic DMF and protic NMF, i.e., NMF strongly solvates the chloride ion. Indeed, the enthalpy of transfer of the chloride ion from DMF to NMF is –14.2 kJ mol^{-1} [37]. The $[\mathrm{Co(NMF)_6}]^{2+}$ and $[\mathrm{CoCl(NMF)_5}]^{+}$ are thus strongly solvated in NMF in the second coordination sphere through the chloride ion and NMF ligating to the metal ion. In contrast, the $[\mathrm{Co(DMF)_6}]^{2+}$ and $[\mathrm{CoCl(DMF)_5}]^{+}$ are hardly solvated in DMF in the second coordination sphere. The formation enthalpy difference is represented as

$$\Delta \mathrm{H}_1°(\mathrm{NMF})-\Delta_t H_1°(\mathrm{DMF})= \\ =\Delta_t H°(\mathrm{CoCl^+})-\Delta_t H°(\mathrm{Co^{2+}})-\Delta_t H°(\mathrm{Cl^-}) \quad (8)$$

where, $\Delta_t H°(i)$ denotes the enthalpy of transfer of species *i* from DMF to NMF. Formation enthalpies of $\mathrm{CoCl^+}$ in DMF and NMF are not appreciably different. We thus lead to the relationship, $\Delta_t H°(\mathrm{CoCl^+})-\Delta_t H°(\mathrm{Co^{2+}})=\Delta_t H°(\mathrm{Cl^-})$, implying that the chloride ion bound to the metal ion is solvated almost to the same extent as the free chloride ion. The similar applies also for the reaction, $\mathrm{Co^{2+}+4Cl^-=CoCl_4^{2-}}$. The corresponding enthalpy difference is –5 kJ mol^{-1}, i.e., the $\Delta_t H°(\mathrm{CoCl_4^{2-}})-\Delta_t H°(\mathrm{Co^{2+}})$ value is largely negative as much as $4\Delta_t H°(\mathrm{Cl^-})$ (–57 kJ mol^{-1}). On the other hand, the formation entropy is large in DMF, whereas it is significantly small in NMF. Note that liquid structure of solvent is weak in aprotic DMF, whereas it is strong in protic NMF. The smaller $\Delta S_1°$ value in NMF than that in DMF is thus expected, if we take into account that solvent molecules liberated the metal ion upon complexation gain high freedom of motion in DMF, but less freedom of motion in NMF. It is thus proposed that the solvent structure in the bulk plays a significant role in the complexation through the reaction entropy.

It has been established that solvent molecules are homogeneously mixed in the DMF-NMF mixture [29–31]. According to low-frequency Raman spectroscopic measurements in our recent study [36], NMF are hydrogen-bonded with DMF, and excess DMF is weakly self-aggregated in the DMF-rich mixture, and the extent of solvent structuredness increases with increasing NMF content x_{NMF}. On the other hand, practically no solvent molecule is hydrogen-bonded free, and thus the solvent is highly structured in the NMF-rich mixture. Indeed, as seen in Fig. 4, the $\Delta S_1°$ value decreases monotonically with increasing x_{NMF}, particularly, in the DMF rich mixture. Though small, the $\Delta H_1°$ value in the DMF-rich mixtures is appreciably larger than the value in NMF. We suppose that the chloride ion is strongly preferentially solvated with NMF in the DMF-rich mixture, although no experimental evidence is obtained at the present stage. The increase in the $\Delta H_1°$ value is appreciable, but not so marked, and thus the increase in the $\Delta G_1°$ value is mainly ascribed to the decreasing $\Delta S_1°$ with increasing x_{NMF}. Therefore, we conclude that the liquid structure of solvent plays a decisive role in the metal-ion complexation, i.e., we can control the metal-ion complexation by changing liquid structure in the solvent mixtures.

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